

THE ACYLATION AND ALKYLATION OF
CYCLOPROPANES WITH AN APPENDIX ON
THE ROLE OF STYRENE IN THE RACEMIZATION
OF (1-CHLOROETHYL) BENZENE

Thesis for the Degree of Ph. D.
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George Levitt
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THE ACYLATION AND ALKYLATION OF CYCLOPROPANES
WITH AN APPENDIX ON
THE ROLE OF STEREOIS IN THE RACEMIZATION
OF (1-CHLOROCYCLOHEXYL)BENZENE

By

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A THESIS

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He is also indebted to his parents for their financial assistance.

* * * * *

To Julia

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$S_0 = \{A, B, C, D, E, F, G, H, I, J, K, L, M, N, O, P, Q, R, S, T, U, V, W, X, Y, Z\}$

1. *Journal of the American Medical Association*, 2000; 283: 2686-2692.

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Figure 1. The number of cases of COVID-19 in the United States by state and the number of deaths. The number of cases is shown in blue and the number of deaths is shown in red. The data is as of April 1, 2020.

Figure 1. The effect of the number of trials on the number of correct responses. The number of correct responses was significantly higher than the number of incorrect responses for all groups. The number of correct responses was significantly higher than the number of incorrect responses for all groups. The number of correct responses was significantly higher than the number of incorrect responses for all groups.

1. *Journal of the American Medical Association*, 1997; 278: 1039-1044.

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1. *Journal of the American Medical Association*, 2000; 283: 2689-2693.

1. *Journal of the American Medical Association*, 1997; 277: 1033-1038.

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1. *Journal of the American Medical Association*, 1997; 277: 1033-1038.

1. *Journal of the American Medical Association*, 2000; 284: 2689-2695.

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QUESTION 1

1

100%

Q.1. The following table shows the number of students who achieved different grades in a mathematics examination. The total number of students who took the examination is 120.

Grade	Number of Students
A	15
B	25
C	35
D	20
E	10
F	5

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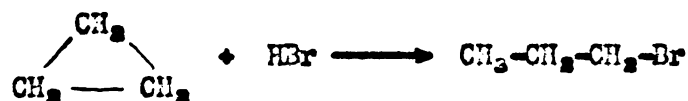
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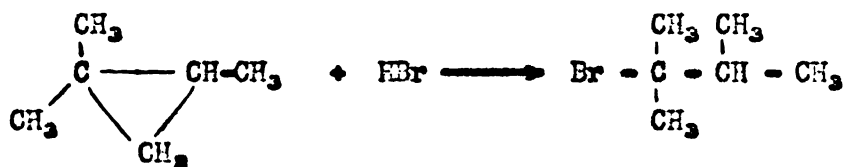
INTRODUCTION

Among the saturated cyclic hydrocarbons, cyclopropane represents the most unusual as well as the smallest ring. In fact, the cyclopropane ring behaves chemically and physically more like an olefinic double bond than like the larger saturated rings (1). Physical measurements, especially spectral data, have supplied much significant information concerning the unsaturated character of cyclopropyl compounds. Ultraviolet absorption spectra show that there is conjugation between a cyclopropane ring and an adjacent double bond (2-4). The bathochromic shift is less, however, in the cyclopropyl conjugated systems than in unsaturated ones. Recently it was demonstrated that a chain of conjugation is probably not transmitted through a cyclopropane ring (5). Infrared spectra, mainly of cyclopropyl ketones, also indicate that the conjugative effect of the cyclopropyl group is less pronounced than that of an ethylenic bond (6). In addition it is significant that cyclopropyl compounds exhibit C-H stretching frequencies at 3010 cm^{-1} and 3090 cm^{-1} , since olefins also absorb in this region (6,7). Other physical measurements such as molecular refraction (8), dipole moment (3), and electron diffraction (9) have also supplied important data relating to the π -bonded character of the cyclopropane ring.

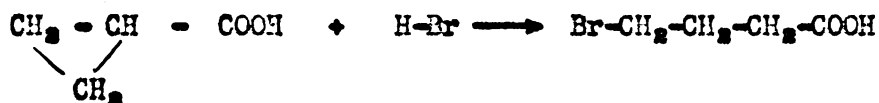
Typical of the reactions which occur with cyclopropane paralleling those of the olefinic double bond is the addition of hydrogen halides to form n-alkyl halides (10). Similarly,



organic acids in the presence of boron trifluoride produce n-propyl esters (11). Indeed Markownikoff's rule is obeyed, since in the addition of a hydrogen halide to an alkyl substituted cyclopropane one obtains predominantly product in which the halogen is bound to the carbon atom holding the largest number of alkyl groups and the hydrogen has added to the least substituted carbon (12). This is illustrated in the following example:



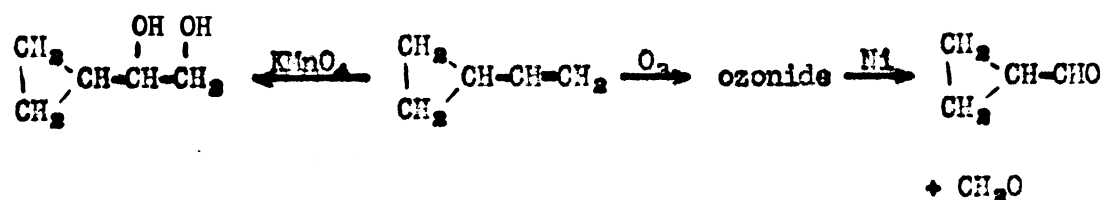
The studies of Kohler and Conant (12) have also shown that a system consisting of a three-membered ring attached to a carbonyl group is similar to α,β -unsaturated carbonyl compounds. Thus cyclopropanecarboxylic acid adds hydrogen bromide as shown.



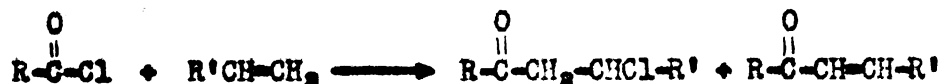
Cyclopropane also adds hydrogen, bromine and iodine in a manner analogous to olefinic compounds. Hence the ring may be hydrogenated to propane (13) and the addition of bromine or iodine yields the corresponding 1,3-dihalogenopropane (14). Chlorine reacts mainly by substitution to form cyclopropyl chloride (15). Cyclopropane also forms molecular or

charge-transfer complexes in a manner similar to ethylene. Thus cyclopropane forms complexes with platinum II (16), tetranitromethane (17) and iodine (18).

The most striking chemical difference between cyclopropane and the olefinic double bond is the resistance of cyclopropane toward oxidizing agents. Ozonolysis of vinylcyclopropane yields cyclopropanecarboxaldehyde and formaldehyde (19), and with cold aqueous potassium permanganate (20) vinylcyclopropane is oxidized to cyclopropyl-1,2-ethanediol.



The Friedel Crafts reaction of acyl halides with olefins to give unsaturated ketones and/or β -haloketones has been discussed in detail by Thomas (21). The products obtained from this reaction are those which would be predicted on the basis that the adding groups are $\text{R}-\text{C}=\text{O}$ and Cl^- .



The analogous reaction of acetyl chloride with cyclopropane was reported by Krapivin (22) to yield a ketone, $\text{C}_5\text{H}_8\text{O}$, which was not characterized further. More recently, in an attempt to prepare a series of γ -chloropropyl ketones, Hart and Curtis (23,24) treated a chloroform solution of the 1:1 complex of an acid chloride and aluminum chloride with cyclopropane. The reaction was found to proceed smoothly at

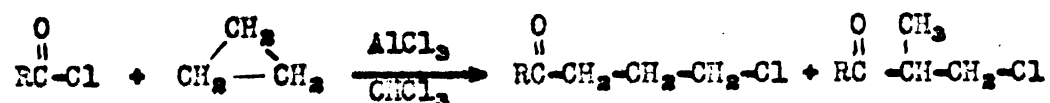
1. The first part of the paper is devoted to the study of the properties of the function $f(x)$ defined by the equation $f(x) = \sum_{n=0}^{\infty} \frac{f_n(x)}{n!}$, where $f_n(x)$ are the solutions of the system of differential equations $f_n'(x) = -f_n(x) + f_{n-1}(x)$, $f_0(x) = 1$. It is shown that the function $f(x)$ is analytic and that its Taylor series converges uniformly on any compact interval. The second part of the paper is devoted to the study of the properties of the function $g(x)$ defined by the equation $g(x) = \sum_{n=0}^{\infty} \frac{g_n(x)}{n!}$, where $g_n(x)$ are the solutions of the system of differential equations $g_n'(x) = -g_n(x) + g_{n-1}(x)$, $g_0(x) = 1$. It is shown that the function $g(x)$ is analytic and that its Taylor series converges uniformly on any compact interval.

$$\sum_{n=0}^{\infty} \frac{f_n(x)}{n!} = \sum_{n=0}^{\infty} \frac{g_n(x)}{n!}$$

2. The third part of the paper is devoted to the study of the properties of the function $h(x)$ defined by the equation $h(x) = \sum_{n=0}^{\infty} \frac{h_n(x)}{n!}$, where $h_n(x)$ are the solutions of the system of differential equations $h_n'(x) = -h_n(x) + h_{n-1}(x)$, $h_0(x) = 1$. It is shown that the function $h(x)$ is analytic and that its Taylor series converges uniformly on any compact interval. The fourth part of the paper is devoted to the study of the properties of the function $k(x)$ defined by the equation $k(x) = \sum_{n=0}^{\infty} \frac{k_n(x)}{n!}$, where $k_n(x)$ are the solutions of the system of differential equations $k_n'(x) = -k_n(x) + k_{n-1}(x)$, $k_0(x) = 1$. It is shown that the function $k(x)$ is analytic and that its Taylor series converges uniformly on any compact interval.

3. The fifth part of the paper is devoted to the study of the properties of the function $l(x)$ defined by the equation $l(x) = \sum_{n=0}^{\infty} \frac{l_n(x)}{n!}$, where $l_n(x)$ are the solutions of the system of differential equations $l_n'(x) = -l_n(x) + l_{n-1}(x)$, $l_0(x) = 1$. It is shown that the function $l(x)$ is analytic and that its Taylor series converges uniformly on any compact interval. The sixth part of the paper is devoted to the study of the properties of the function $m(x)$ defined by the equation $m(x) = \sum_{n=0}^{\infty} \frac{m_n(x)}{n!}$, where $m_n(x)$ are the solutions of the system of differential equations $m_n'(x) = -m_n(x) + m_{n-1}(x)$, $m_0(x) = 1$. It is shown that the function $m(x)$ is analytic and that its Taylor series converges uniformly on any compact interval.

temperatures from -40° to 0° to furnish 60-80% yields of chloroketones. Instead of obtaining the desired γ -chloropropylketones as the sole products, however, there were also obtained, as the predominant products, the unexpected β -chloroisopropyl ketones.



The only other reference to a Friedel-Crafts type of reaction between cyclopropane and a halogen-containing compound is a patent issued to Simons (10) in which he disclosed the reaction of cyclopropane with alkyl halides in the presence of aluminum chloride; no experimental detail or indication of the nature of the product was given.

It was the purpose of the present investigation to examine the scope of the acylation and alkylation of cyclopropane. In particular, the influence of selected substituents in the cyclopropane ring and in the acylating or alkylating agent in determining the course of the reaction was examined. It was hoped that in this way (for example, by studying the direction of ring-opening of a substituted cyclopropane) some clues would be obtained to the mechanism of the unusual rearrangement discovered by Curtis (24).

EXPERIMENTAL

I. Experiments Dealing with the Mechanism of the Reaction

A. The Reaction of Acetyl Chloride with Cyclopropane

The following reaction was carried out according to the procedure described by Curtis (24). This experiment was repeated several times in order to determine the average yield. In a two-liter three-necked flask, equipped with an addition funnel, thermometer, blow-out manometer and Teflon stirrer, there was placed 133 g. (1 mole) of aluminum chloride and 1000 ml. of chloroform. The mixture was cooled to 0-5° in an ice bath, and 78 g. (1 mole) of acetyl chloride was added during fifteen minutes. The mixture was stirred until all of the aluminum chloride dissolved. The addition funnel was replaced with a fritted-tip gas delivery tube and 45 g. (1.1 moles) of cyclopropane was slowly passed into the solution at such a rate that the pressure in the reaction vessel remained below 800 mm. mercury and the temperature remained below 20°. After all of the cyclopropane had been added the solution was stirred for one hour, then poured into a mixture of 750 g. of cracked ice and 150 ml. of concentrated hydrochloric acid. The chloroform layer was separated, washed once with 500 ml. of water, once with 500 ml. of 10% sodium bicarbonate, and again with 500 ml. of water. The chloroform solution was then dried over calcium chloride at 0°. The solvent was removed in vacuo, the pot temperature being kept below 40°. There was

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1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020, 2021, 2022, 2023, 2024, 2025, 2026, 2027, 2028, 2029, 2030, 2031, 2032, 2033, 2034, 2035, 2036, 2037, 2038, 2039, 2040, 2041, 2042, 2043, 2044, 2045, 2046, 2047, 2048, 2049, 2050, 2051, 2052, 2053, 2054, 2055, 2056, 2057, 2058, 2059, 2060, 2061, 2062, 2063, 2064, 2065, 2066, 2067, 2068, 2069, 2070, 2071, 2072, 2073, 2074, 2075, 2076, 2077, 2078, 2079, 2080, 2081, 2082, 2083, 2084, 2085, 2086, 2087, 2088, 2089, 2090, 2091, 2092, 2093, 2094, 2095, 2096, 2097, 2098, 2099, 2100, 2101, 2102, 2103, 2104, 2105, 2106, 2107, 2108, 2109, 2110, 2111, 2112, 2113, 2114, 2115, 2116, 2117, 2118, 2119, 2120, 2121, 2122, 2123, 2124, 2125, 2126, 2127, 2128, 2129, 2130, 2131, 2132, 2133, 2134, 2135, 2136, 2137, 2138, 2139, 2140, 2141, 2142, 2143, 2144, 2145, 2146, 2147, 2148, 2149, 2150, 2151, 2152, 2153, 2154, 2155, 2156, 2157, 2158, 2159, 2160, 2161, 2162, 2163, 2164, 2165, 2166, 2167, 2168, 2169, 2170, 2171, 2172, 2173, 2174, 2175, 2176, 2177, 2178, 2179, 2180, 2181, 2182, 2183, 2184, 2185, 2186, 2187, 2188, 2189, 2190, 2191, 2192, 2193, 2194, 2195, 2196, 2197, 2198, 2199, 2200, 2201, 2202, 2203, 2204, 2205, 2206, 2207, 2208, 2209, 2210, 2211, 2212, 2213, 2214, 2215, 2216, 2217, 2218, 2219, 2220, 2221, 2222, 2223, 2224, 2225, 2226, 2227, 2228, 2229, 2230, 2231, 2232, 2233, 2234, 2235, 2236, 2237, 2238, 2239, 2240, 2241, 2242, 2243, 2244, 2245, 2246, 2247, 2248, 2249, 2250, 2251, 2252, 2253, 2254, 2255, 2256, 2257, 2258, 2259, 2260, 2261, 2262, 2263, 2264, 2265, 2266, 2267, 2268, 2269, 2270, 2271, 2272, 2273, 2274, 2275, 2276, 2277, 2278, 2279, 2280, 2281, 2282, 2283, 2284, 2285, 2286, 2287, 2288, 2289, 2290, 2291, 2292, 2293, 2294, 2295, 2296, 2297, 2298, 2299, 2300, 2301, 2302, 2303, 2304, 2305, 2306, 2307, 2308, 2309, 2310, 2311, 2312, 2313, 2314, 2315, 2316, 2317, 2318, 2319, 2320, 2321, 2322, 2323, 2324, 2325, 2326, 2327, 2328, 2329, 2330, 2331, 2332, 2333, 2334, 2335, 2336, 2337, 2338, 2339, 2340, 2341, 2342, 2343, 2344, 2345, 2346, 2347, 2348, 2349, 2350, 2351, 2352, 2353, 2354, 2355, 2356, 2357, 2358, 2359, 2360, 2361, 2362, 2363, 2364, 2365, 2366, 2367, 2368, 2369, 2370, 2371, 2372, 2373, 2374, 2375, 2376, 2377, 2378, 2379, 2380, 2381, 2382, 2383, 2384, 2385, 2386, 2387, 2388, 2389, 2390, 2391, 2392, 2393, 2394, 2395, 2396, 2397, 2398, 2399, 2400, 2401, 2402, 2403, 2404, 2405, 2406, 2407, 2408, 2409, 2410, 2411, 2412, 2413, 2414, 2415, 2416, 2417, 2418, 2419, 2420, 2421, 2422, 2423, 2424, 2425, 2426, 2427, 2428, 2429, 2430, 2431, 2432, 2433, 2434, 2435, 2436, 2437, 2438, 2439, 2440, 2441, 2442, 2443, 2444, 2445, 2446, 2447, 2448, 2449, 2450, 2451, 2452, 2453, 2454, 2455, 2456, 2457, 2458, 2459, 2460, 2461, 2462, 2463, 2464, 2465, 2466, 2467, 2468, 2469, 2470, 2471, 2472, 2473, 2474, 2475, 2476, 2477, 2478, 2479, 2480, 2481, 2482, 2483, 2484, 2485, 2486, 2487, 2488, 2489, 2490, 2491, 2492, 2493, 2494, 2495, 2496, 2497, 2498, 2499, 2500, 2501, 2502, 2503, 2504, 2505, 2506, 2507, 2508, 2509, 2510, 2511, 2512, 2513, 2514, 2515, 2516, 2517, 2518, 2519, 2520, 2521, 2522, 2523, 2524, 2525, 2526, 2527, 2528, 2529, 2530, 2531, 2532, 2533, 2534, 2535, 2536, 2537, 2538, 2539, 2540, 2541, 2542, 2543, 2544, 2545, 2546, 2547, 2548, 2549, 2550, 2551, 2552, 2553, 2554, 2555, 2556, 2557, 2558, 2559, 2560, 2561, 2562, 2563, 2564, 2565, 2566, 2567, 2568, 2569, 2570, 2571, 2572, 2573, 2574, 2575, 2576, 2577, 2578, 2579, 2580, 2581, 2582, 2583, 2584, 2585, 2586, 2587, 2588, 2589, 2590, 2591, 2592, 2593, 2594, 2595, 2596, 2597, 2598, 2599, 2600, 2601, 2602, 2603, 2604, 2605, 2606, 2607, 2608, 2609, 2610, 2611, 2612, 2613, 2614, 2615, 2616, 2617, 2618, 2619, 2620, 2621, 2622, 2623, 2624, 2625, 2626, 2627, 2628, 2629, 2630, 2631, 2632, 2633, 2634, 2635, 2636, 2637, 2638, 2639, 2640, 2641, 2642, 2643, 2644, 2645, 2646, 2647, 2648, 2649, 2650, 2651, 2652, 2653, 2654, 2655, 2656, 2657, 2658, 2659, 2660, 2661, 2662, 2663, 2664, 2665, 2666, 2667, 2668, 2669, 2670, 2671, 2672, 2673, 2674, 2675, 2676, 2677, 2678, 26

the 1990s, the number of people in the world who are illiterate has increased from 1.2 billion to 1.5 billion. The number of illiterate people in the world is projected to reach 1.7 billion by the year 2015. The number of illiterate people in the world is projected to reach 1.7 billion by the year 2015.

obtained 30-33 g. (25-28%) of 5-chloro-2-pentanone b.p.₂₂ 65-75°, n_D^{20} 1.4365-1.4374 (lit. values, b.p.₂₂ 70-72°, n_D^{20} 1.4371 (24)). The material collected in the dry ice trap in the preceding distillation was dried over potassium carbonate. One gram of hydroquinone was added and there was distilled 25-27 g. (31-33%) of 3-methyl-3-buten-2-one, b.p._{1 atm.} 96-100°, n_D^{20} 1.4225 (lit. values, b.p.₇₆₀ 98°, n_D^{25} 1.4229 (24)).

B. Acetyl Chloride and Aluminum Chloride with 5-Chloro-2-pentanone

Thirty grams (0.25 mole) of 5-chloro-2-pentanone was added to a chloroform solution containing 78 g. (1 mole) of acetyl chloride and 67 g. (1 mole) of aluminum chloride prepared as described in the preceding experiment. The solution was stirred for one hour at 0-10° and worked up as previously described. After removal of the chloroform solvent there was recovered 24 g. (80%) of 5-chloro-2-pentanone, b.p.₂₂ 68-72°. No 3-methyl-3-buten-2-one was obtained.

C. The Reaction of Acetyl Chloride with Cyclopropane in the Presence of Added 5-Chloro-2-pentanone

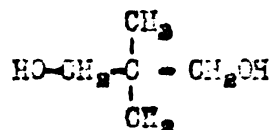
The acylation was carried out exactly as previously described, except that 46 g. (0.38 mole) or 38 g. (0.31 mole) of 5-chloro-2-pentanone was added just prior to passing in the cyclopropane. There was obtained 24-27 g. (31-33%) of 3-methyl-3-buten-2-one, b.p._{1 atm.} 96-100°. The total amount of 5-chloro-2-pentanone obtained was 70 g. in the first experiment and 56 g. in the second. Assuming an 80% recovery of the added 5-chloro-2-pentanone, the yields of this compound were 33 g. and 26 g. respectively.

II. The Acylation of Substituted Cyclopropanes

A. Acetylation of 1,1-Dimethylcyclopropane

1. 1,1-Dimethylcyclopropane

a. 2,2-Dimethyl-1,3-propanediol



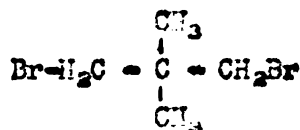
This compound was prepared by the procedure described by Whitmore *et al.* (25) as modified by Shortridge *et al.* (26).

In a three-liter flask fitted with a reflux condenser, stirrer and a one-liter dropping funnel, there was placed a solution of 150 g. (3.5 moles) of sodium hydroxide in 750 ml. of 95% ethanol. A solution was prepared from 500 ml. of 36% formaldehyde, 100 g. (2.5 moles) of isobutyraldehyde, and enough ethanol to give a homogeneous solution. The latter solution was added dropwise to the ethanolic alkali with stirring. The solution was warmed to reflux for 24 hours and then warmed on a steam bath, at water aspirator pressure of about 20 mm. of mercury, to remove the lower boiling components. The residue was extracted with eight 150-ml. portions of ether, the ether extracts combined and after removal of solvent there was distilled 146 g. (56%) of 2,2-dimethyl-1,3-propanediol, b.p._{1 atm.} 180-200° (lit value, b.p.₇₆₀ 200°). In several runs it was found advantageous to distil at reduced pressure, b.p.₃ 105-110°. After recrystallization from a benzene-petroleum ether

mixture the product melted at 123-130° (lit value, 130° (26)).

During the course of this investigation this compound was made available commercially by the Tennessee Eastman Company in a grade of 96% purity. Both synthetic and commercial material was used in the preparation described below.

b. 2,2-Dimethyl-1,3-dibromopropane



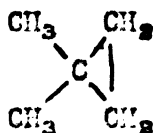
This compound was prepared by the method of Whitmore et al. (25) as modified by Shortridge et al. (26).

Four hundred and sixteen grams (4.0 moles) of 2,2-dimethyl-1,3-propanediol was placed in a two-liter three-necked flask equipped with a reflux condenser, a one-liter addition funnel, a stirrer with a large Teflon paddle and a thermometer. A variable speed stirring motor capable of stirring a heavy mass was used. The flask and contents were heated to 70° and 1084 g. (4.0 moles) of phosphorous tribromide was added at such a rate as to maintain the temperature at 70°. As soon as the mixture became mobile stirring was commenced. When all of the bromide had been added the mixture was warmed to 140-150° and maintained at that temperature for thirty hours. After six hours a bright crimson precipitate formed which gradually became quite tarry and heavy, making the mixture difficult to stir. The mixture was hydrolyzed by a slow dropwise addition of water and subjected to steam distillation until the distillate came over clear. The layers of the distillate were separated; the

water layer washed with ether and the combined organic layers dried over calcium chloride. After removal of the ether, 330 g. (36%) of 2,2-dimethyl-1,3-dibromopropane was distilled, b.p._o 68-70°, n_D^{20} 1.5040-1.5050 (lit. values, b.p._o 68°, n_D^{20} 1.5050 (25)).

The desired product was not obtained in several attempts under different conditions. Thus when the reaction mixture was allowed to stand for six days without heating, and worked up in the same manner as described above there was obtained from 104 g. of the diol 55 g. of a product b.p._o 75-76°, n_D^{20} 1.4750. This product was similar to that obtained when the reaction was quenched after the addition of the reagents at 70°. Shortridge (26) states the reaction is immediate at 70°. The addition of bromine to a mixture of phosphorous and the diol, at 70°, followed by thirty hours at 140-150°, did not produce a steam distillable product.

c. 1,1-Dimethylcyclopropane



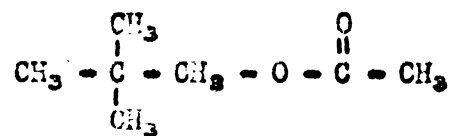
This compound was prepared by the procedure described by Shortridge et al. for obtaining a product of high purity (26).

In a one-liter three-necked flask equipped with an addition funnel, Teflon stirrer and reflux condenser connected to a dry ice trap, were placed 450 ml. of 95% ethanol, 95 ml. of distilled water and 314 g. (48 moles) of zinc dust. The mixture was stirred vigorously to prevent

the zinc from forming lumps and heat was applied to cause a gentle reflux. Two hundred and fifty grams (1.1 moles) of 2,2-diethyl-1,3-dibromopropane was added dropwise at this temperature. The heating and stirring were maintained for 24 hours. After 24 hours the water was drained from the condenser jacket and the mixture was kept warm for 30 minutes in order to drive over any remaining hydrocarbon. The crude product was washed with ice water and dried over calcium chloride. The product (70 g., 91%) was distilled below 23° , n_D^{20} 1.3676 (lit. values, b.p.-780 20.63, n_D^{20} 1.3668 (26)).

In an attempt to prepare 1,1-dimethylcyclopropane by another procedure, neopentyl acetate (the preparation of which is given immediately below) was pyrolyzed by distillation through a Vycor tube packed with Pyrex helices and maintained at temperatures from 450° to 700° . In all cases the neopentyl acetate was recovered unchanged.

2. Neopentyl Acetate



This ester was prepared from neopentyl alcohol (prepared by the method of Conant, Webb and Mondra (27)) and acetyl chloride. To 31 g. (0.35 mole) of neopentyl alcohol was added dropwise, at 0° , 27.5 g. (0.35 mole) of acetyl chloride. The mixture was allowed to warm to room temperature with occasional stirring and warmed to 50° for one-half hour. Twenty milliliters of 10% sodium bicarbonate was added dropwise to

hydrolyze any unused acetyl chloride. The layers were separated and the water layer washed with several small portions (25 to 50 ml.) of ether. The organic layers were combined, dried and distilled through an 8" Vigreux column to yield 25 g. (55%) of the desired ester, b.p._{1 atm.} 124-125°, n_D^{20} 1.3936-1.3942 (lit. values, b.p.₇₆₀ 125-126°, n_D^{20} 1.3893 (28)).

3. The Reaction of 1,1-Dimethylcyclopropane with Aluminum Chloride

To a suspension of 26.6 g. (0.2 mole) of aluminum chloride in 100 ml. of chloroform at 0° was added dropwise 10 g. (0.142 mole) of 1,1-dimethylcyclopropane. The reaction mixture quickly became yellow and then turned light green. After one hour the mixture was hydrolyzed by the dropwise addition of water. The system was connected to a water aspirator through a dry ice trap and some material was distilled into the trap in vacuo. Distillation of the material in the trap indicated the absence of starting material or any product boiling below 59°. The chloroform layer in the flask was separated and dried over calcium chloride. After removal of the solvent there remained a residue of 9 g. of polymerized material which could not be distilled, even at 3 mm. mercury, without decomposition. This material was not investigated further.

4. The Reaction of 1,1-Dimethylcyclopropane with Acetyl Chloride and Aluminum Chloride

In a one-liter three-necked flask equipped with a Trubore stirrer, thermometer, dry ice reflux condenser and addition funnel were placed

256 g. (2 moles) of aluminum chloride and 1000 ml. of chloroform. The mixture was cooled to $0-5^{\circ}$ and 156 g. (2 moles) of acetyl chloride was added slowly with stirring. The mixture was allowed to stand for two hours, then filtered with suction into a two-liter flask equipped like the first flask and cooled to zero.

To the chloroform solution there was added 100 g. (1.43 moles) of 1,1-dimethylcyclopropane at such a rate that the temperature remained below 10° . Some hydrogen chloride was evolved during the addition, but this diminished after the addition was completed. The reaction mixture was allowed to stand for one hour, and then hydrolyzed by pouring into a slurry of 1500 g. of ice and 300 ml. of concentrated hydrochloric acid. The chloroform layer was separated, washed successively with 500 ml. of water, 500 ml. of 10% sodium bicarbonate and 500 ml. of water, and dried over calcium chloride. The chloroform was removed by distilling in vacuo and 108 g. of crude product b.p.₃ $40-70^{\circ}$ was obtained. This was redistilled, using a 25 cm. column packed with glass helices to yield 91 g. (49%) of 4-chloro-3,4-dimethyl-2-pentanone b.p.₄ $44-49^{\circ}$, n_D^{20} 1.4398-1.4408 (lit. values, b.p.₁₄ $60-64^{\circ}$, n_D^{16} 1.4440 (29)). The first fractions had some unsaturated product present as indicated by a weak absorption at 1615 cm^{-1} in the infrared (fig. I).

Anal. Calc'd for $C_7H_{13}OCl$: Cl, 23.8.

Found: Cl, 22.8, 23.0, 22.6.

The 2,4-dinitrophenylhydrazone was prepared according to the method of Johnson (30) and after recrystallization from methanol melted at $130.5-131^{\circ}$.

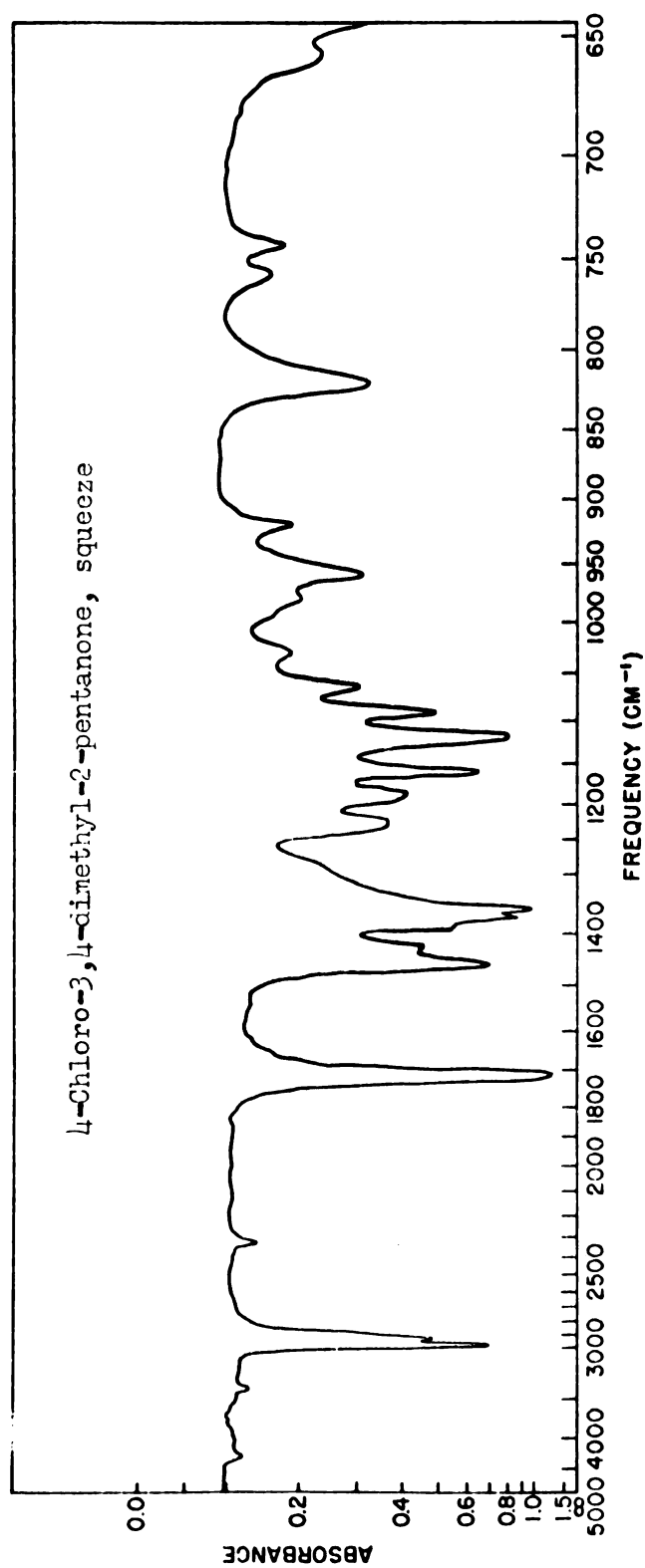


Figure I

Anal. Calc'd. for $C_{13}H_{17}O_4N_4Cl$: C, 47.50; H, 5.22, N, 17.03.

Found: C, 47.50; H, 5.27; N, 17.21.

Several attempts to prepare the semicarbazone, using the procedure of Shriner and Fuson (31), failed to give a solid derivative.

In addition to the distillable ketone there was obtained 33 g. of a polymeric material not unlike that obtained from 1,1-dimethylcyclopropane and aluminum chloride in chloroform. When the reaction was carried out at -50° and -15° the yield of the desired ketone was considerably reduced (5% and 20%) and more of the polymeric material was obtained. Attempts to recover unreacted 1,1-dimethylcyclopropane or any low boiling rearrangement product were made by reducing the pressure in the system through a dry ice trap to a water aspirator. These experiments showed that all of the 1,1-dimethylcyclopropane was converted to either the desired product, or the previously mentioned polymeric material.

5. Structure Proof of 4-Chloro-3,4-dimethyl-2-pentanone

a. Dehalogenation with zinc in acetic acid

To a vigorously stirred suspension of 15 g. (0.23 mole) of zinc in 60 ml. of acetic acid and 30 ml. of water there was added 12 g. (0.031 mole) of 4-chloro-3,4-dimethyl-2-pentanone. The mixture was warmed to gentle reflux for three hours, after which time the liquid was poured into 50 g. of ice and extracted with three 25-ml. portions of ethyl ether. The combined ether extract was neutralized by stirring with a potassium carbonate solution to which additional solid potassium carbonate was added until evolution of carbon dioxide ceased. The ether was decanted

and dried over potassium carbonate. After removal of the ether there was obtained 6.3 g. (63%) of 3,4-dimethyl-2-pentanone, b.p._{1 atm.} 135-140°, n_D^{20} 1.4198 (lit. values, b.p.₇₆₀ 135-136°, n_D^{14} 1.4129 (29)). The infrared absorption spectrum of this material is shown in figure II.

The semicarbazone was prepared according to the method of Shriner and Fuson (31) and after recrystallization from 50% ethanol melted at 113-114° (lit. value, 113-114° (29)).

b. Dehydrohalogenation with Sodium Hydroxide

Fifteen grams (0.1 mole) of 4-chloro-3,4-dimethyl-2-pentanone was added dropwise to an efficiently stirred solution of 78 ml. of 10% sodium hydroxide at reflux. The mixture was refluxed with stirring for one hour and then cooled in an ice bath. The mixture was extracted with ether, the organic layers combined and dried over magnesium sulfate. After removal of solvent, 5.6 g. (49%) of 3,4-dimethyl-3-penten-2-one was obtained, b.p._{1 atm.} 145-149°, n_D^{20} 1.4462-1.4474 (lit. values b.p.₇₆₀ 146-147°, n_D^{14} 1.4506 (29)). The infrared absorption spectrum (fig. III) showed peaks at 1690 cm^{-1} and 1620 cm^{-1} indicating an α,β -unsaturated ketone (32). In addition a sharp peak was also observed at 1780 cm^{-1} . Cyclobutanone absorbs in this region (31) and the formation of such a product might arise via hydrogen chloride elimination involving a hydrogen on the number one carbon of the parent compound (33).

The semicarbazone derivative was prepared and melted initially at 176-180°. When recrystallized in small amounts the derivative melted

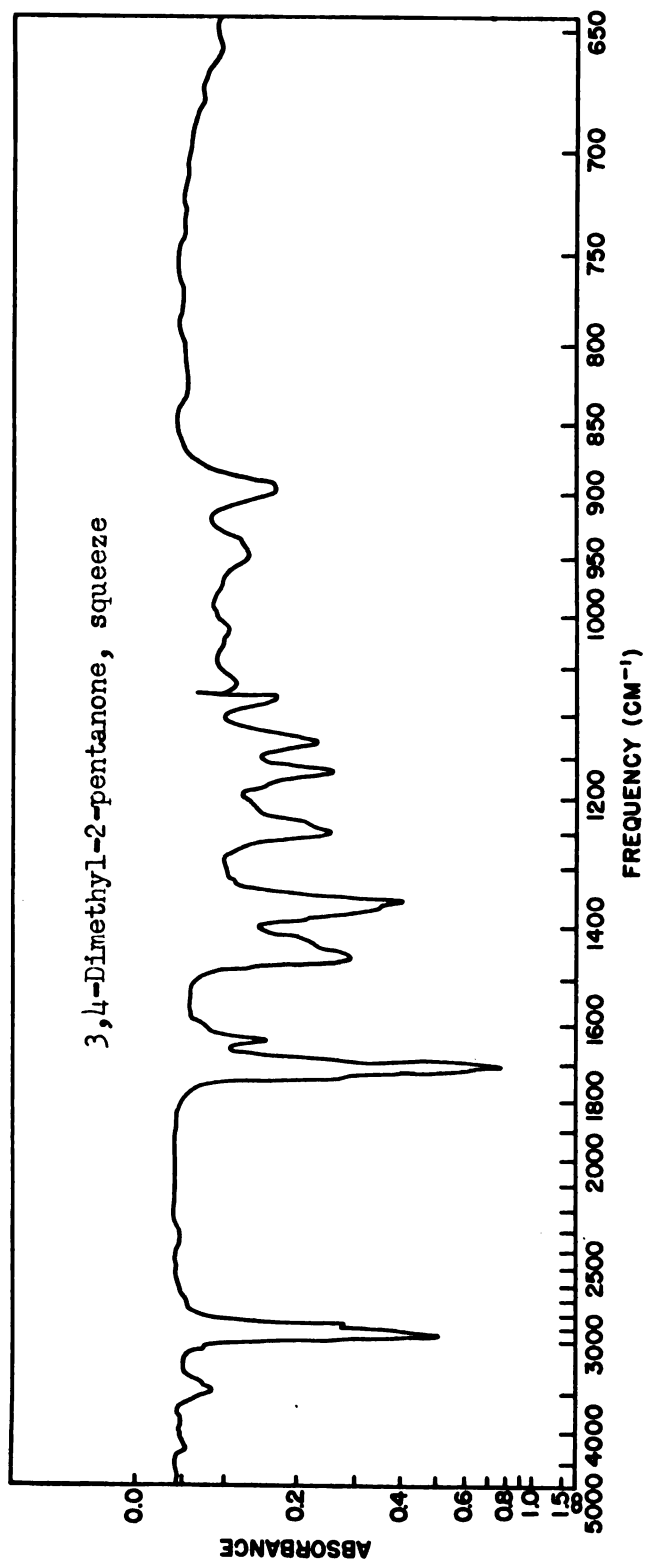


Figure II

at 179-180°; however, a large sample (2 g.) was prepared and after several recrystallizations from 50% ethanol melted at 191-192°.

All of these melting points have been recorded in the literature (22,34,35,36) and were attributed to the presence of small amounts of 3,4-dimethyl-4-penten-2-one (22) rather than a cyclobutanone derivative.

c. Dehydrohalogenation with Sodium Carbonate

Thirteen grams (0.037 mole) of 4-chloro-3,4-dimethyl-2-pentanone was refluxed with 200 ml. of 10% sodium carbonate for two hours. The product, 3,4-dimethyl-4-penten-2-one, b.p.: 1 atm. 145-149°, n_D^{20} 1.4442-1.4456, was isolated using the same procedure as described in the preceding experiment. The infrared absorption spectrum (fig. IV) of the product obtained from this reaction was identical to that of the product from the preceding reaction except for the absence of the strong peak at 1780 cm^{-1} and a weaker peak 1037 cm^{-1} . A cyclobutanone product is less likely to be formed here due to the decreased activity of the base used.

The semicarbazone derivative was prepared and after several recrystallizations from 50% ethanol melted at 191-192°. This product did not depress the melting point of the semicarbazone from the preceding experiment.

d. Preparation of 4-Chloro-3,4-dimethyl-2-pentanone by the Reaction of Acetyl Chloride with 2-Methyl-2-butene

A chloroform solution of aluminum chloride and acetyl chloride was prepared in the same manner as that used previously, except that one mole

THE HISTORY OF THE UNITED STATES

The history of the United States is a story of growth and development. It begins with the first settlers who came to the New World in search of a better life. They found a land of opportunity, but also a land of hardship. The early years were marked by struggle and sacrifice, but the spirit of the pioneers was unyielding. They built a nation that would stand the test of time.

THE FOUNDING OF THE NATION

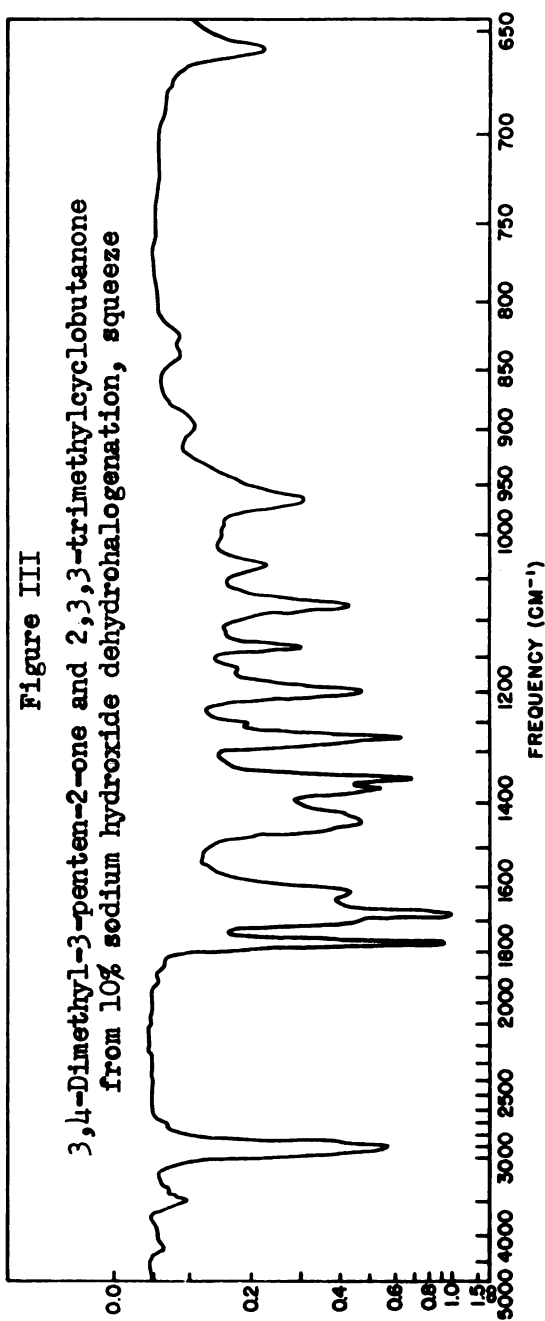
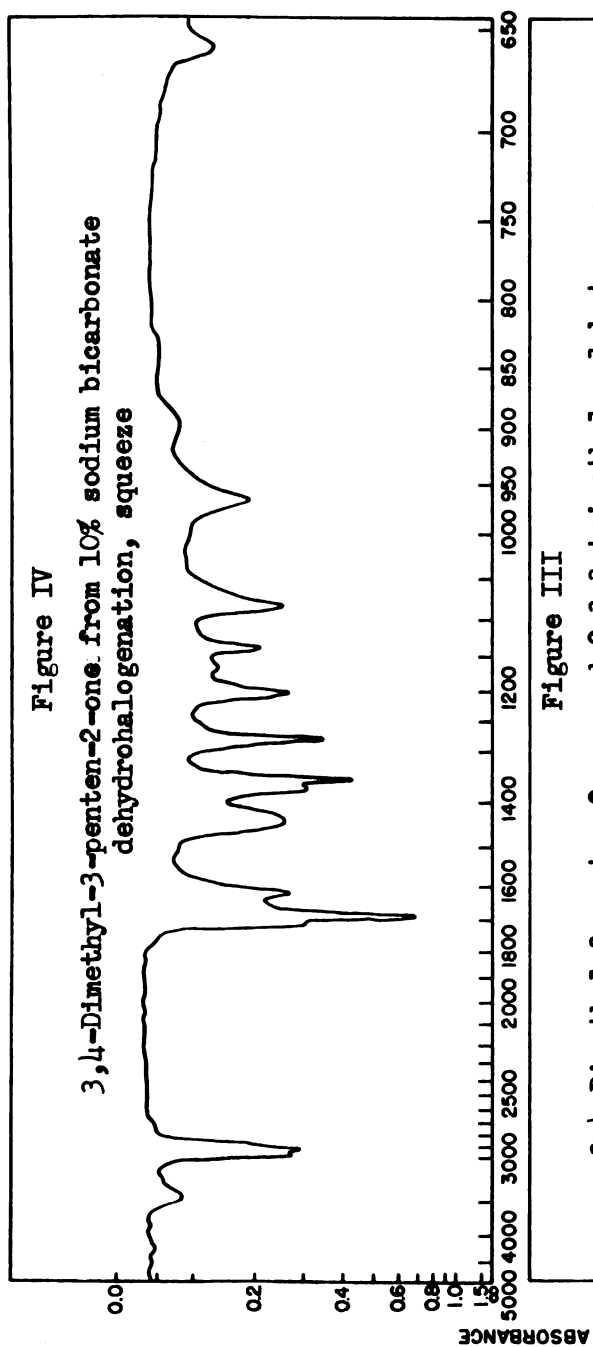
The story of the United States begins with the first settlers who came to the New World in search of a better life. They found a land of opportunity, but also a land of hardship. The early years were marked by struggle and sacrifice, but the spirit of the pioneers was unyielding. They built a nation that would stand the test of time. The Founding Fathers, men of vision and courage, laid the foundation for a new nation. They fought for freedom and justice, and their legacy lives on in the hearts of the American people. The United States has come a long way since those early days, but the principles of liberty and democracy remain its guiding light.

THE GROWTH OF THE NATION

The growth of the United States has been a remarkable journey. From a small colony of settlers to a vast nation spanning two continents, the United States has achieved incredible feats. The spirit of innovation and progress has driven the nation forward, and its influence is felt around the world. The challenges it has faced have only made it stronger, and its future is bright.

THE CHALLENGES OF THE FUTURE

As the United States looks to the future, it faces many challenges. The world is changing rapidly, and the nation must adapt to new circumstances. The challenges of the future are great, but the American people have the strength and resilience to overcome them. The United States will continue to be a beacon of hope and a leader in the world.



of each reagent was used in 500 ml. of chloroform. To the solution cooled to -20° there was added dropwise 70 g. (1.0 mole) of 2-methyl-2-butene, (Phillips Tech. grade (95% min.)) which had been fractionated through a 100-cm. column containing glass helices, b.p._{1 mm.} $38-39^{\circ}$ (lit. value, b.p.₇₆₀ 38.1°). The reaction mixture was stirred at -30 to -40° for one hour and then decomposed by pouring into a slurry of 750 g. of ice and 150 ml. concentrated hydrochloric acid. The organic layer was washed successively with 500 ml. of water, 500 ml. of 10% sodium bicarbonate and 500 ml. of water, dried over calcium chloride and the solvent stripped in vacuo. The product, 90 g. (52%), was distilled, b.p., $46-49^{\circ}$, n_D^{20} 1.4400. The residue was a polymeric material similar to that obtained from the analogous reaction with 1,1-dimethylcyclopropane.

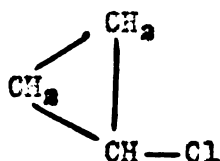
The infrared absorption spectrum was the same as that of the 4-chloro-3,4-dimethyl-2-pentanone from 1,1-dimethylcyclopropane and acetyl chloride.

The 2,4-dinitrophenylhydrazone derivative was prepared and after several recrystallizations from methanol melted at $130-131^{\circ}$. A mixed melting point determination with the same derivative as previously prepared from the reaction product of 1,1-dimethylcyclopropane and acetyl chloride gave no depression. The chloroketone obtained from this experiment, when dehydrohalogenated as previously described, gave a 2,4-dinitrophenylhydrazone and a semicarbazone which were identical to those obtained from the same procedure with the acetylation product of 1,1-dimethylcyclopropane as shown by mixed melting point determination.

The chloroketone was also reduced by zinc and acetic acid to yield a product which gave a semicarbazone identical to that described earlier as shown by a mixed melting point determination.

B. Acetylation of Cyclopropyl Chloride

1. Cyclopropyl chloride



This compound was prepared by the method described by Roberts and Dirstine (37) as modified by Slabey (38). Cyclopropane and chlorine were mixed and passed through a grid which was irradiated by two Ken-Rad E. S. 275 sun lamps. Three hundred and seventy grams (8.8 moles) of cyclopropane was consumed during eight hours of photolysis to yield 267 g. (40%) of cyclopropylchloride, b.p._{1 atm.} 43.5°, n_D^{25} 1.4080 (lit. values, b.p.₇₆₀ 43.5°, n_D^{25} 1.4079) (38). The apparatus and detailed procedure used for this preparation were described by J. M. Sandri (39).

2. The Reaction of Acetyl Chloride with Cyclopropyl Chloride

A solution of two liters of chloroform, 266 g. (2 moles) of aluminum chloride and 200 g. (2.2 moles) of acetyl chloride was prepared as previously described for the reaction of acetyl chloride with cyclopropane. The solution was filtered with suction into a three-liter three-necked flask, which was then equipped with a stirrer, reflux condenser and

addition funnel. One hundred and fifty-two grams (2 moles) of cyclopropyl chloride was added dropwise at room temperature. The temperature gradually rose to 35° after one to two hours. The solution was stirred for eighteen hours, and then poured into 1500 g. of ice.

The chloroform layer was separated from the amber aqueous layer and the water was extracted with five 100-ml. portions of chloroform. Even so, the water remained dark amber. The chloroform extracts were combined, washed successively with 500 ml. of water and dried over calcium chloride. After removal of the chloroform in vacuo an attempt was made to distill the product (202 g.) at 3 mm. mercury but decomposition appeared to take place. The product was therefore added to 500 ml. of 10% sodium bicarbonate and refluxed with vigorous stirring for two hours. The mixture was cooled and the organic layer separated from the brown aqueous layer. The aqueous layer was extracted with ether and the ether portions combined with the organic layer. The water solution was evaporated and the residue digested with isopropyl alcohol. Some of the colored material was taken up in the alcohol, but when the alcohol was decanted and distilled only a negligible amount of tarry residue remained.

The ether extract was dried over magnesium sulfate and after removal of the ether there was distilled 63 g. (23%) of 4-chloro-3-methyl-3-buten-2-one, b.p., $32-36^{\circ}$, $n_D^{25} 1.4694-1.4704$. The assignment of the above structure was based on elemental analysis, ultraviolet absorption spectrum, the infrared absorption spectrum and the nature of the products from several reactions of the compound.

[illegible]

Anal. Calc'd. for C_8H_7OCl : Cl, 29.9

Found: Cl, 29.1, 29.8.

The ultraviolet absorption spectrum (fig. V) of this compound showed a λ_{max} at 234 m μ , ϵ 1790 which is characteristic of α,β -substituted α,β -unsaturated ketones (40). The infrared absorption spectrum (fig. VI) showed strong peaks at 1687 cm^{-1} and 1615 cm^{-1} , characteristic of α,β -unsaturated ketones and a strong peak at 822 cm^{-1} , in the region characteristic of trisubstituted ethylenes (32). The 2,4-dinitrophenylhydrazones was prepared and after recrystallization from ethyl acetate melted at 204-205°.

Anal. Calc'd. for $C_{11}H_{11}O_4N_4Cl$: C, 44.23; H, 3.72; Cl, 11.87;

N, 18.73.

Found: C, 44.18; H, 3.78; Cl, 11.95; N, 18.50.

The semicarbazone was prepared and after recrystallization from 50% ethanol melted at 181-181.5°.

Anal. Calc'd. for $C_8H_{10}O_2N_3O$: C, 41.04; H, 5.74; N, 23.93.

Found: C, 40.72; H, 5.90; N, 24.64.

There was also obtained 9.2 g. of additional material b.p., 62-65°, n_D^{25} 1.4760. The infrared absorption spectrum (fig. VII) of this material showed peaks at 1615 cm^{-1} and 1605 cm^{-1} , indicating the presence of an α,β -unsaturated ketone, and 1630 cm^{-1} and 1725 cm^{-1} which could be due to the presence of a non-conjugated, unsaturated ketone (32). The mixture could not be separated by distillation through a 25-cm. column packed with glass helices. Prolonged heating caused some decomposition of this material.

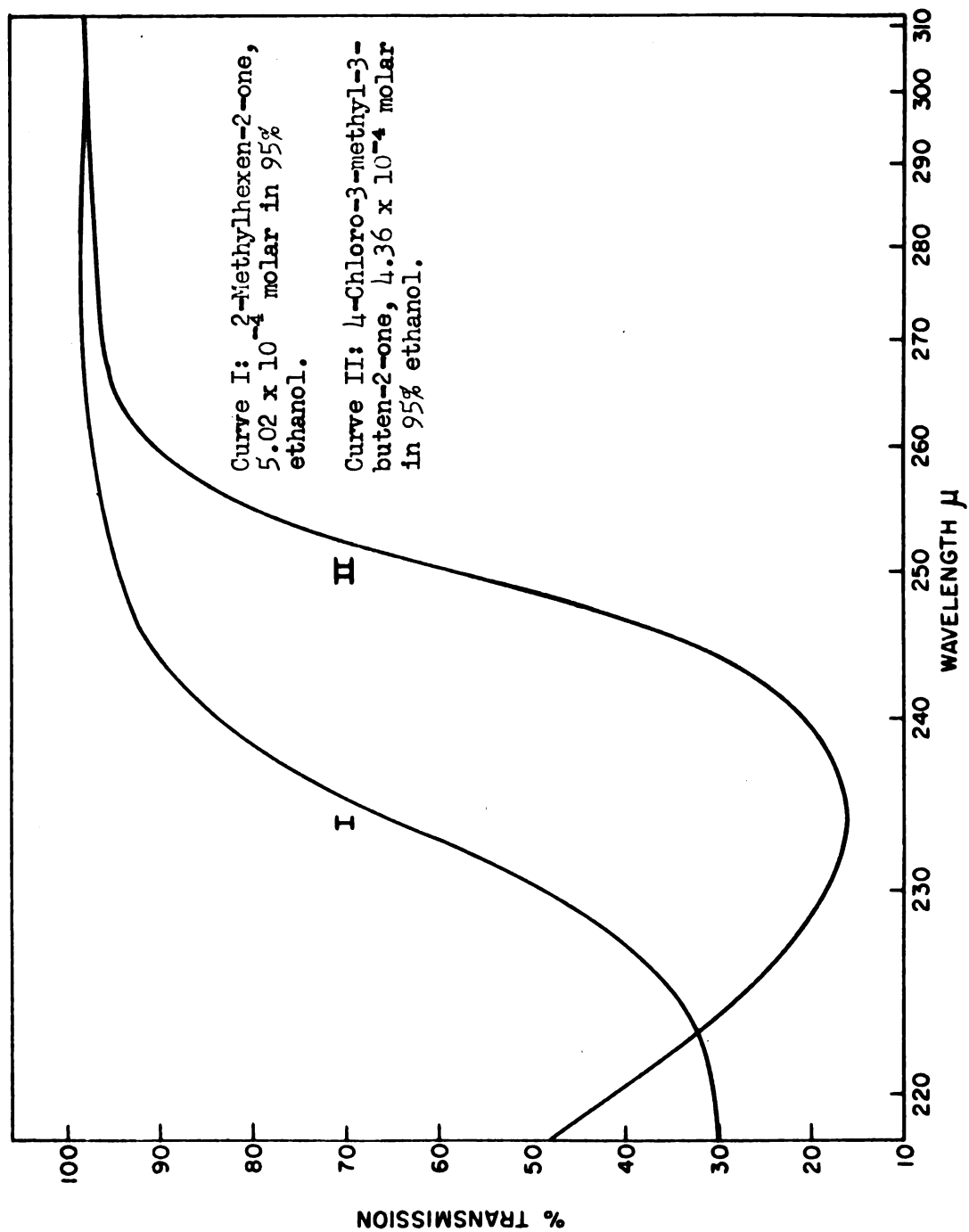


Figure V

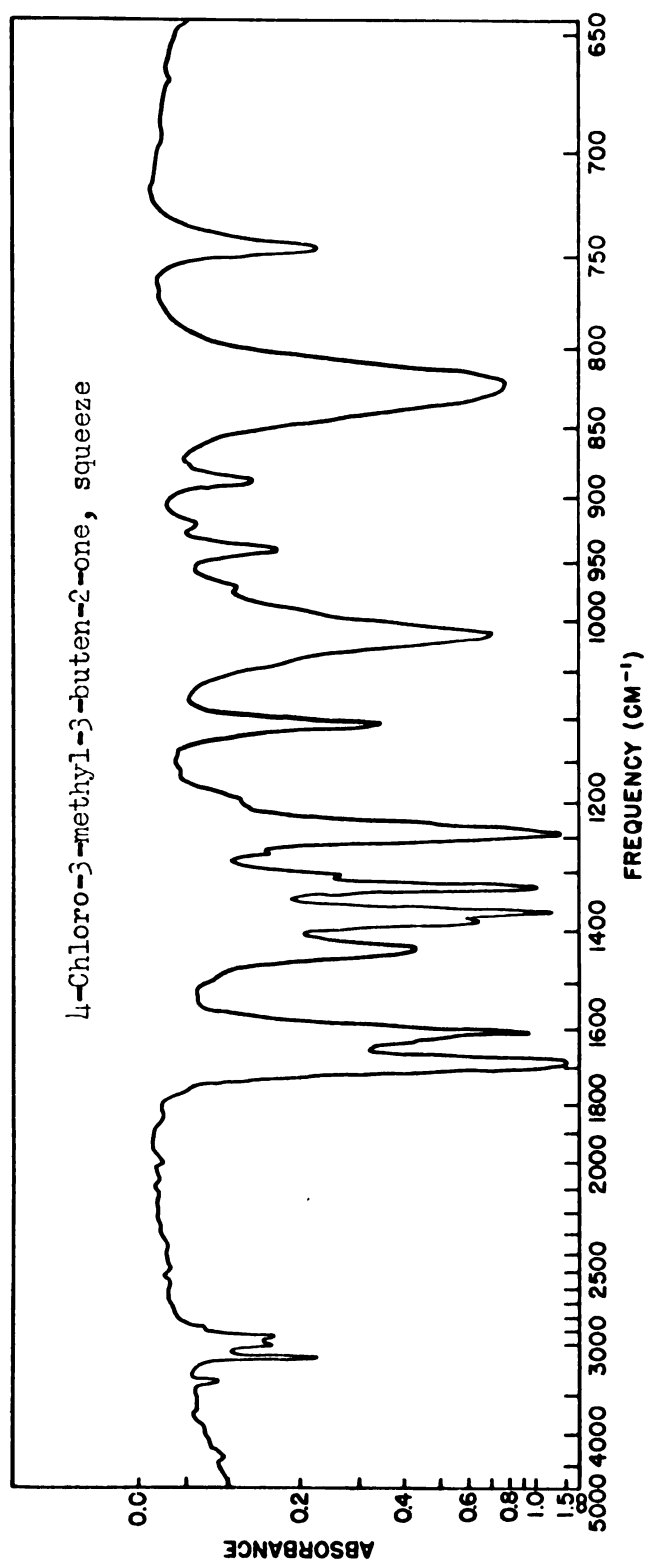


Figure VI

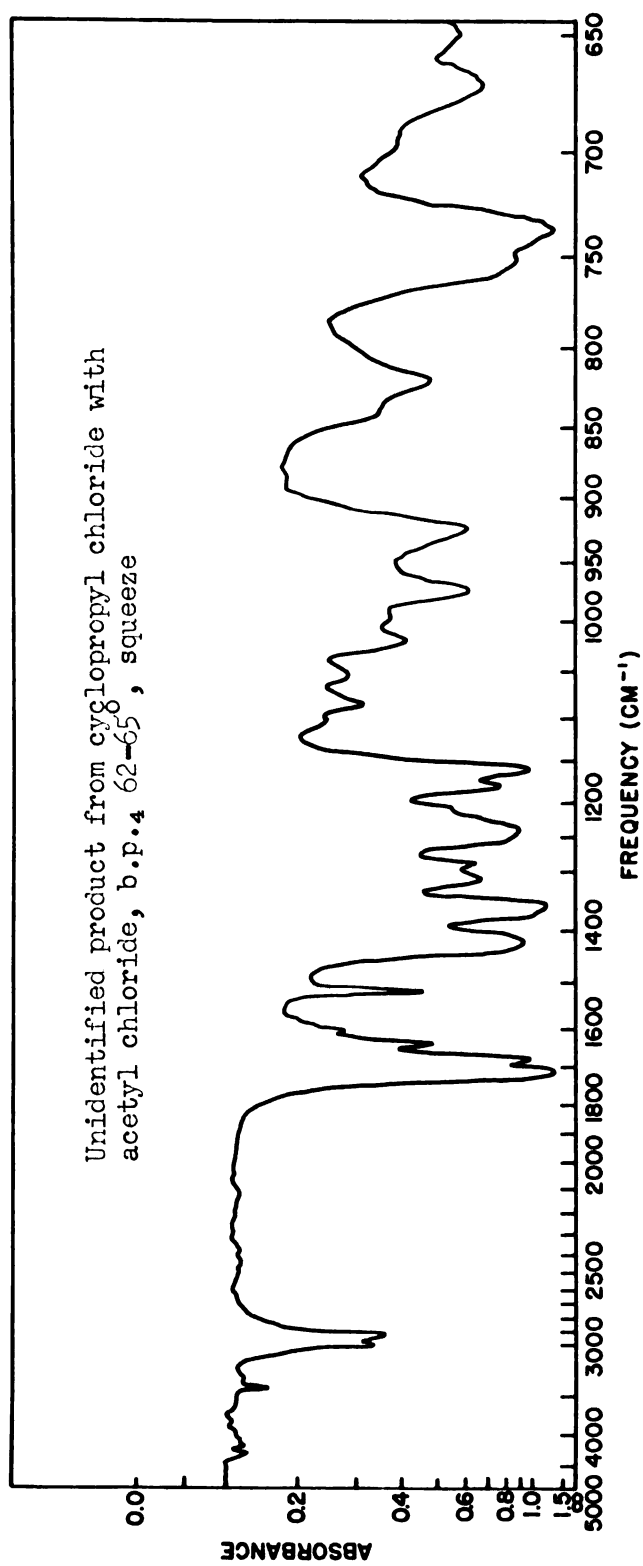


Figure VII

In one run the reaction mixture was added dropwise to 1500 g. of ice water in a five-liter three-necked flask equipped with one-liter addition funnel, stirrer, and a dry ice trap. The pressure was reduced in the system and some liquid was distilled into the trap. The trap was found to contain only chloroform and water and no unreacted cyclopropyl chloride.

3. Structure Proof of 4-Chloro-3-methyl-3-buten-2-one

a. Reduction with Lithium Aluminum Hydride

To a stirred suspension of 3.8 g. (0.1 mole) of lithium aluminum hydride in 50 ml. of anhydrous ether was added 10 g. (0.035 mole) of 4-chloro-3-methyl-3-buten-2-one. The mixture was stirred for four hours and then hydrolyzed in the usual manner. The ether was decanted and dried over magnesium sulfate. After removal of the solvent there was distilled 9.2 g. (90%) of 4-chloro-3-methyl-3-buten-2-one, b.p.₃ 65°, n_D^{25} 1.4670.

Anal. Calc'd. for C_5H_7Cl : C, 49.92; H, 7.52; Cl, 29.5.

Found: C, 49.73; H, 7.73; Cl, 29.6, 29.6.

The infrared absorption spectrum (fig. VIII) showed a strong peak at 814 cm.^{-1} the presence of which indicated a trisubstituted olefin (32).

One ml. of this compound was placed in 50 ml. of 30% ethanol containing 5% silver nitrate. No precipitate of silver chloride was observed. However, when one ml. of allyl chloride was treated in a like manner a precipitate formed indicating that the former compound probably did not contain an allylic chloride function.

1. The first part of the paper is devoted to the study of the

properties of the function $f(x)$ defined by the equation $f(x) = \int_0^x f(t) dt$. It is shown that $f(x)$ is a constant function, and the value of this constant is determined. The second part of the paper is devoted to the study of the properties of the function $g(x)$ defined by the equation $g(x) = \int_0^x g(t) dt$. It is shown that $g(x)$ is a constant function, and the value of this constant is determined. The third part of the paper is devoted to the study of the properties of the function $h(x)$ defined by the equation $h(x) = \int_0^x h(t) dt$. It is shown that $h(x)$ is a constant function, and the value of this constant is determined.

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It is shown that $i(x)$ is a constant function, and the value of this constant is determined. The fifth part of the paper is devoted to the study of the properties of the function $j(x)$ defined by the equation $j(x) = \int_0^x j(t) dt$. It is shown that $j(x)$ is a constant function, and the value of this constant is determined. The sixth part of the paper is devoted to the study of the properties of the function $k(x)$ defined by the equation $k(x) = \int_0^x k(t) dt$. It is shown that $k(x)$ is a constant function, and the value of this constant is determined.

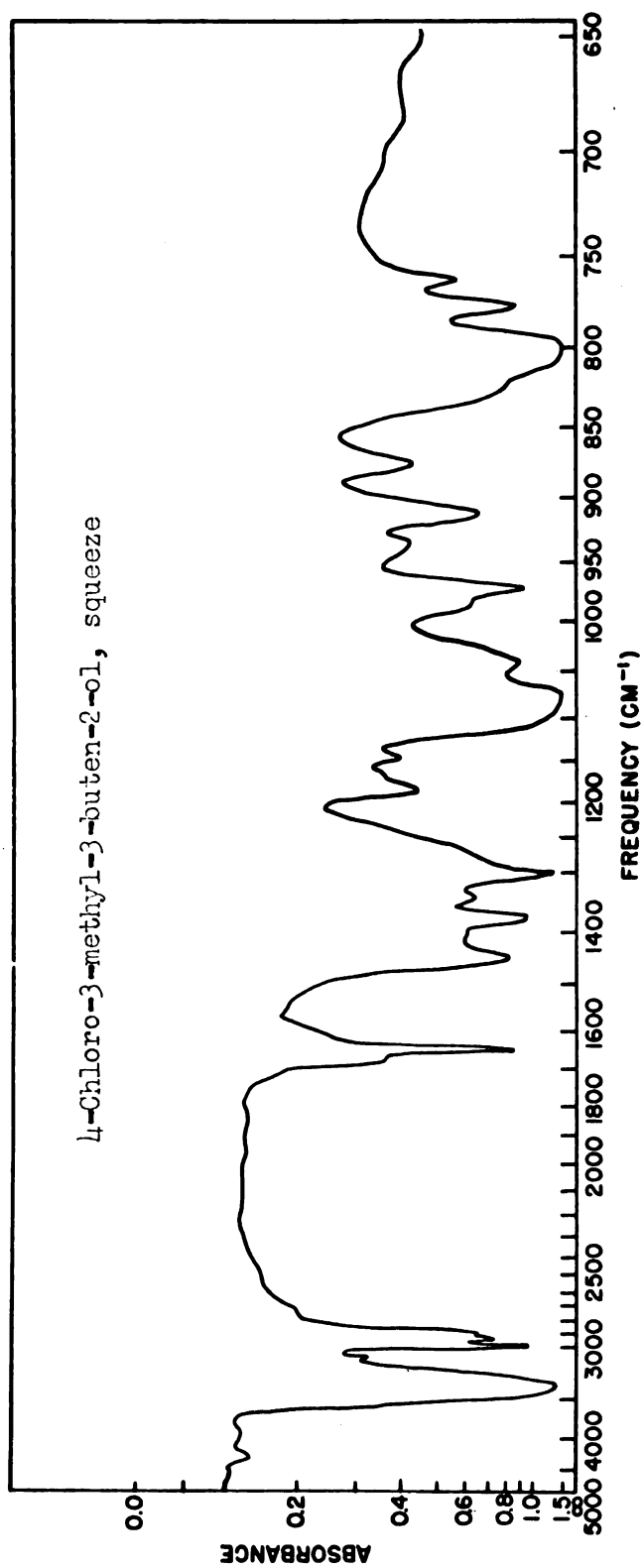


Figure VIII

The 1-naphthylurethan derivative was prepared and after recrystallization from petroleum ether melted at 97-98°.

Anal. Calc'd. for $C_{16}H_{13}NO_2$: C, 66.31; H, 5.56; N, 4.84;
Cl, 12.22.

Found: C, 66.43; H, 5.63; N, 5.11; Cl, 12.20.

b. Hydrogenation of 4-chloro-3-methyl-3-buten-2-one

Five grams (0.042 mole) of 4-chloro-3-methyl-3-buten-2-one was placed in 25 ml. of anhydrous ether and reduced with hydrogen (50 p.s.i.) over platinum oxide (0.2 g.) catalyst. After one-half hour 0.25 mole of hydrogen was absorbed, after which there was no further uptake of hydrogen. The solution was filtered and there was distilled 2.4 g. (65%) of 3-methyl-2-butanol, b.p._{1 atm.} 106-110°, n_D^{25} 1.3942 (lit. values, b.p.₇₆₀ 110-112°, n_D^{20} 1.3973) (41). The product contained a trace of chlorine which could not be removed by simple distillation.

The phenylurethan and 1-naphthylurethan were prepared and after recrystallization from petroleum ether melted at 65-67° and 107-108° respectively (lit. values, 63° and 112°) (31). Mixed melting point determinations with samples prepared from Eastman "white label," 3-methyl-2-butanol showed no depression.

c. The Reaction of Acetyl Chloride with Allyl Chloride

A solution containing 133 g. (1 mole) of aluminum chloride, 120 g. (1.5 moles) of acetyl chloride and 800 ml. of chloroform was prepared in the usual manner at 5°. Allyl chloride (74 g., 1.0 mole) was added dropwise, with stirring. The bright red solution thus formed was decomposed

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 2. 在 1950 年 10 月 1 日以前， H_2O 和 CO_2 的
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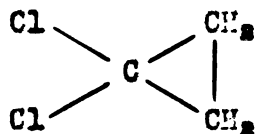
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and washed in the usual manner. After being dried over calcium chloride the chloroform was distilled in vacuo. Some decomposition was detected when distillation of the product at 3 mm. mercury was attempted. The product was, therefore, added to 300 ml. of 20% sodium bicarbonate and refluxed, with vigorous stirring for one hour. The solution was cooled down, separated, and the aqueous layer was extracted with ether. The organic layers were combined and dried over magnesium sulfate. After evaporation of the ether there was obtained a product which did not distill, without decomposition, below 60° at 3 mm. mercury. The product, which was quite viscous, was not investigated further.

C. Acetylation of 1,1-Dichlorocyclopropane

1. 1,1-Dichlorocyclopropane



This compound was obtained as a by-product from the preparation of cyclopropyl chloride. The by-products were fractionated and the material boiling at $75-75.5^{\circ}$, n_D^{25} 1.4373, (lit. values, b.p. 75.5° , n_D^{25} 1.4377) (38) was used in the following reaction.

2. The reaction of 1,1-dichlorocyclopropane with acetyl chloride

To a solution of acetyl chloride (22 g., 0.275 mole) and aluminum chloride (33 g., 0.25 mole) in 300 ml. of chloroform, prepared as previously described, was added 28 g. (0.25 mole) of 1,1-dichlorocyclopropane. The stirred solution was warmed to reflux for five hours after

The first part of the paper is devoted to the study of the properties of the function $f(x)$ defined by the equation $f(x) = \sum_{n=0}^{\infty} \frac{1}{2^n} f\left(\frac{x}{2^n}\right)$. It is shown that this function is continuous and satisfies the functional equation $f(x) = 2f\left(\frac{x}{2}\right)$. The second part of the paper is devoted to the study of the properties of the function $g(x)$ defined by the equation $g(x) = \sum_{n=0}^{\infty} \frac{1}{2^n} g\left(\frac{x}{2^n}\right)$. It is shown that this function is continuous and satisfies the functional equation $g(x) = 2g\left(\frac{x}{2}\right)$. The third part of the paper is devoted to the study of the properties of the function $h(x)$ defined by the equation $h(x) = \sum_{n=0}^{\infty} \frac{1}{2^n} h\left(\frac{x}{2^n}\right)$. It is shown that this function is continuous and satisfies the functional equation $h(x) = 2h\left(\frac{x}{2}\right)$.



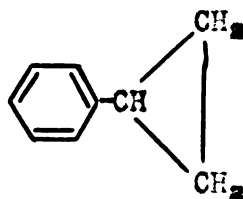
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which it was poured into 500 g. of ice and 100 ml. of concentrated hydrochloric acid. The hydrolysis mixture formed a viscous emulsion which was finally broken by the addition of 500 ml. of concentrated hydrochloric acid. The chloroform layer was then washed in the usual manner and dried over calcium chloride. After removal of the solvent and unreacted 1,1-dichlorocyclopropane in vacuo there was distilled at 70-80° and 3 mm. mercury, 5 g. of an unstable product. The infrared absorption spectrum (fig. IX) of this material showed peaks at 1611 cm.^{-1} , 1725 cm.^{-1} , indicating the presence of unsaturation and a carbonyl group in the product (32). This material was not investigated further. Nineteen grams (67%) of the 1,1-dichlorocyclopropane was recovered unchanged when the reaction mixture was allowed to stand for one hour at 50° after the addition of the reagents.

D. Acetylation of Phenylcyclopropane

1. Preparation of Phenylcyclopropane

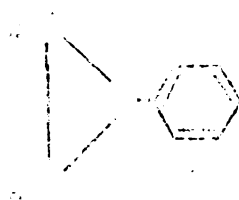


This compound was prepared by the procedure of Kizhner (42), except that the intermediate pyrazoline was not isolated, nor was any catalyst added to the pyrolysis mixture. In a two-liter three-necked flask equipped with an addition funnel, stirrer, and a reflux condenser were

the first two cases, the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is trivial, and the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is non-trivial. In the first case, the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is trivial, and the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is non-trivial. In the second case, the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is trivial, and the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is non-trivial. In the third case, the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is trivial, and the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is non-trivial. In the fourth case, the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is trivial, and the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is non-trivial. In the fifth case, the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is trivial, and the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is non-trivial. In the sixth case, the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is trivial, and the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is non-trivial. In the seventh case, the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is trivial, and the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is non-trivial. In the eighth case, the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is trivial, and the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is non-trivial. In the ninth case, the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is trivial, and the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is non-trivial. In the tenth case, the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is trivial, and the \mathbb{Z}_2 -action on the space of points of \mathbb{P}^1 is non-trivial.

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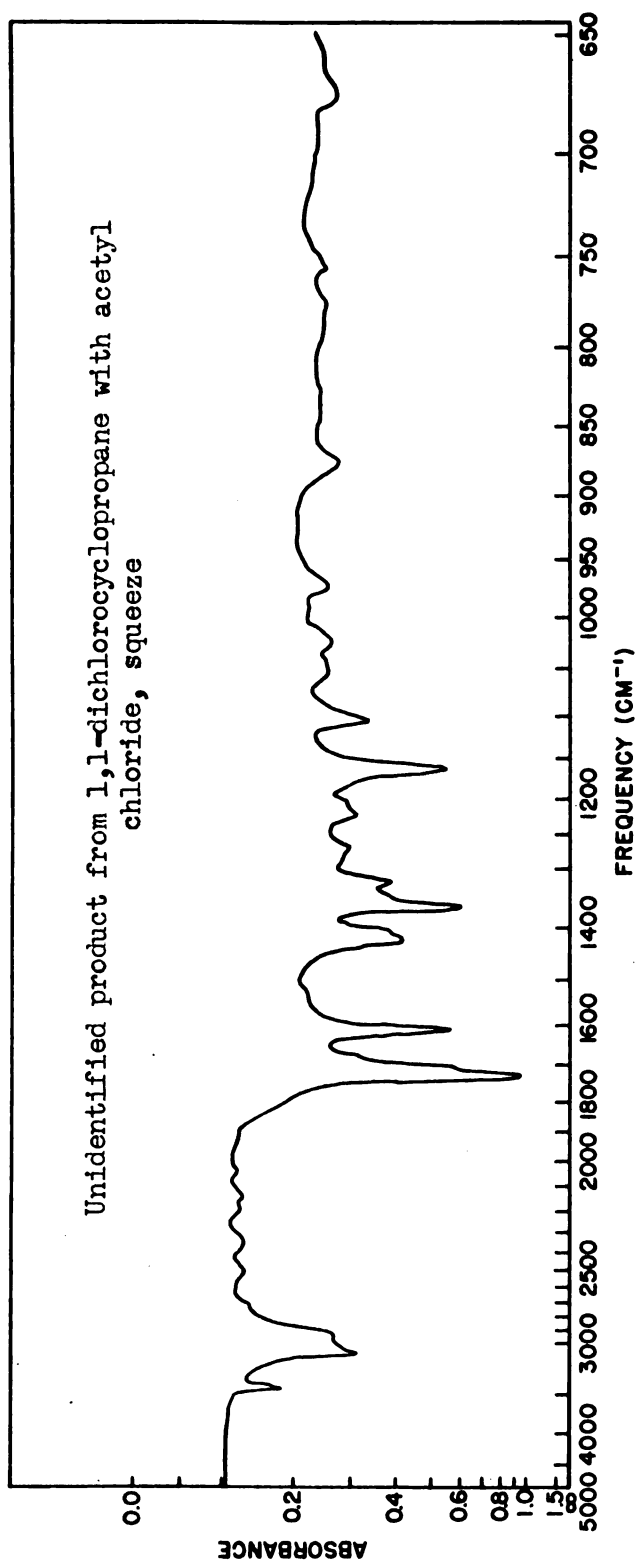


Figure IX

placed 590 g. (10 moles) of 85% hydrazine hydrate solution and 500 ml. of methanol. One kilogram (7.5 moles) of cinnamaldehyde was added dropwise with stirring. The mixture was refluxed for three hours and allowed to stand overnight at room temperature. The mixture was distilled at atmospheric pressure and the material boiling from 160-170° was collected. The oil thus obtained was washed with 200 g. of ice and 500 ml. of 1% potassium permanganate, dried and distilled, b.p.₃₀ 77° (lit. value, b.p.₃₀ 77.5°) (3). The wash and distillation were repeated until a constant refractive index, n_D^{22} 1.5308-1.5310 was obtained, (lit. values, n_D^{21} 1.5311, (43)). A yield of 304 g. (36%) was thus obtained.

2. The Reaction of Phenylcyclopropane with Acetyl Chloride

The acetylation mixture was prepared as previously described for the reaction 1,1-dimethylcyclopropane except that the reagents were added in one mole quantities to 750 ml. of chloroform. Phenylcyclopropane (118 g., 1.0 mole) was added dropwise to the mixture at 4°. After several milliliters had been added the temperature rose gradually and hydrogen chloride evolution was detected. The mixture was cooled down to -25° ± 5° and the addition continued, and was accompanied by a slow hydrogen chloride evolution. The mixture was stirred for one hour after the addition was completed and then poured into 750 g. ice and 200 ml. concentrated hydrochloric acid. The organic layer was separated, washed successively with 500 ml. of water, 500 ml. of 15% sodium bicarbonate, and 500 ml. of water, and dried over calcium chloride. The solvent was removed in vacuo and 104 g. of product was distilled, b.p.₂₋₄ 120-130°. The residue did not

distill below 165° at 2 mm. and after standing at 0° for several days, gave off some hydrogen chloride. Attempts to crystallize this tarry substance were without success, nor did refluxing with 10% potassium carbonate change the nature of this material. Fractionation of the distillate yielded 78 g. (46%) of *p*-cyclopropylacetophenone, b.p._{2.5-2.9} $114-119^{\circ}$, m.p. $35-36^{\circ}$. This compound was recrystallized from ethanol or petroleum ether by cooling to 0° .

Anal. Calc'd. for $C_{11}H_{12}O$: C, 82.47; H, 7.55.

Found: C, 82.27; H, 7.56.

The infrared absorption spectrum (fig. X) was studied to determine the nature of the product. The carbonyl peak at 1630 cm.^{-1} was the basis for believing that acetylation took place on the phenyl ring.

The 2,4-dinitrophenylhydrazone was prepared and after recrystallization from ethyl acetate melted at $219-220^{\circ}$. The compound was dissolved only after prolonged refluxing.

Anal. Calc'd. for $C_{17}H_{12}N_4O_4$: C, 59.98; H, 4.73; N, 16.46.

Found: C, 59.88; H, 4.90; N, 16.25.

The ultraviolet absorption spectrum (fig. XI) in 95% ethanol showed a λ_{max} at 265 m μ , ϵ 16,000. This was compared with the ultraviolet absorption spectrum of a freshly distilled sample of Eastman, "white label," acetophenone, λ_{max} 242 m μ , ϵ 16,000 (lit. values., λ_{max} 240 m μ , ϵ 13,000) (45).

There was also obtained 9.5 g. of material b.p._{2.5} $125-131^{\circ}$, n_D^{20} 1.5668-1.5532. This material gave a positive Beilstein test. Its infrared absorption spectrum (fig. XII) was very similar to that of

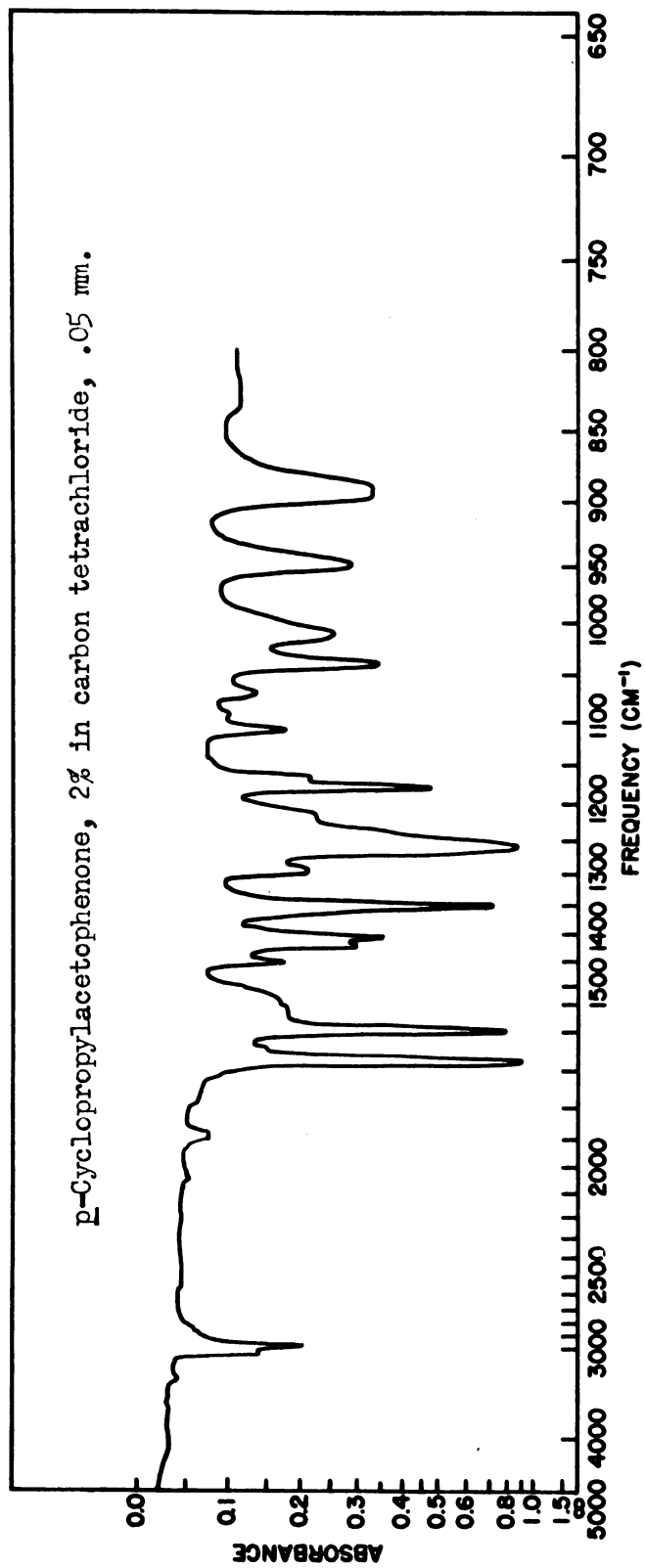


Figure X

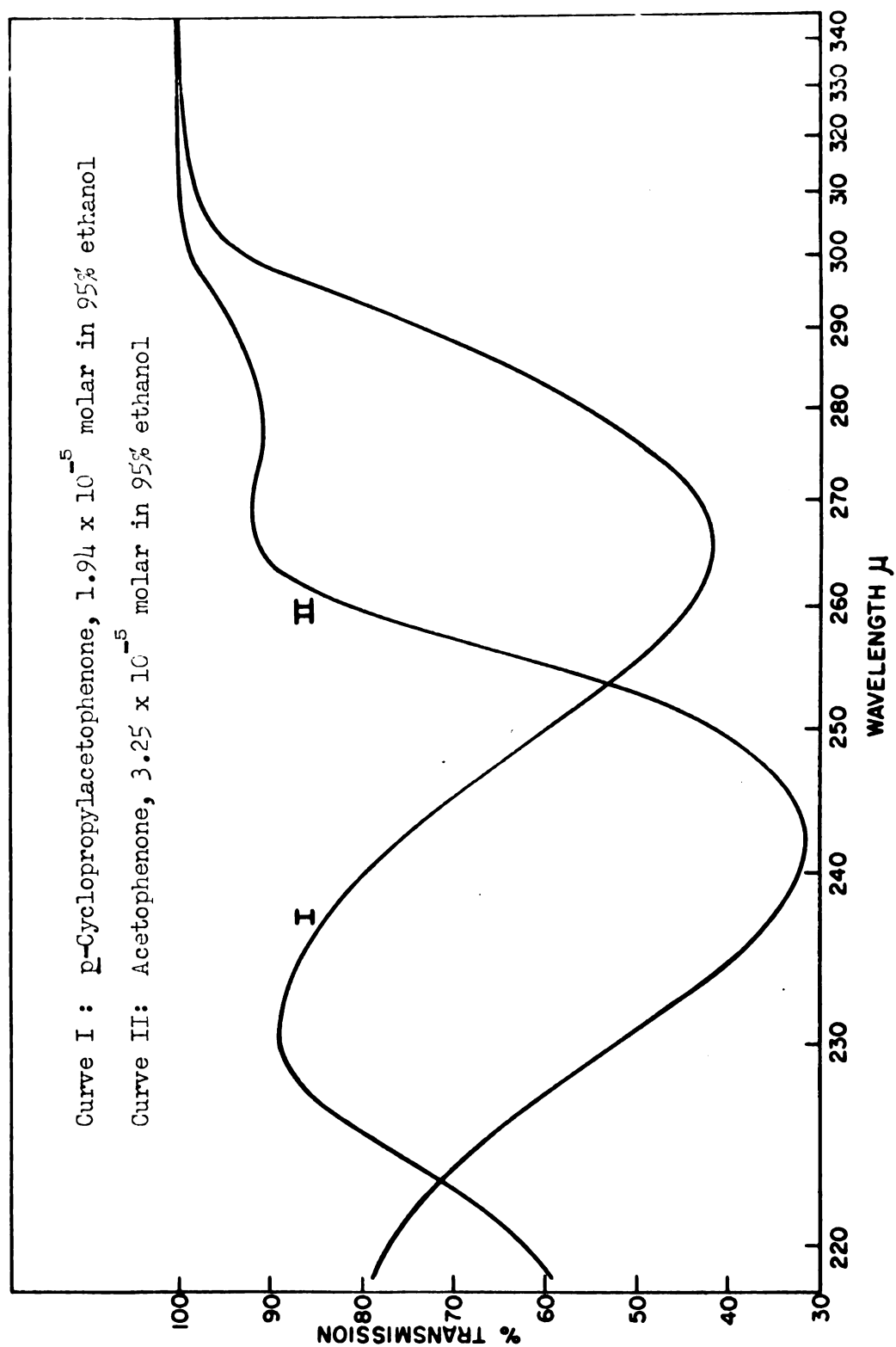


Figure XI

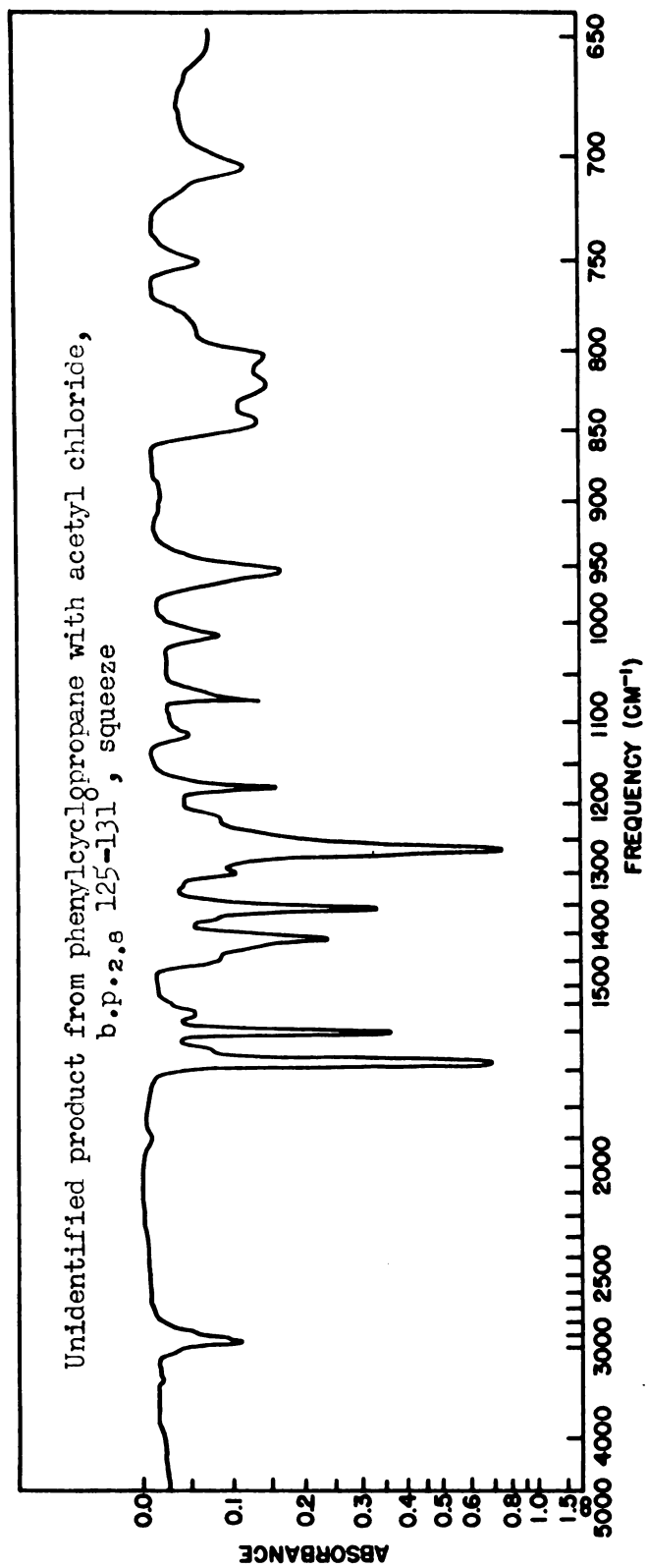


Figure XII

p-cyclopropylacetophenone. This fraction did not crystallize when cooled to -78° , but instead formed a glass. Seeding with p-cyclopropylacetophenone did not induce any crystallization. This product was not investigated further.

3. Structure Proof of p-Cyclopropylacetophenone

a. Oxidation to p-cyclopropylbenzoic Acid

One gram (0.006 mole) of p-cyclopropylacetophenone was added to a solution containing 20 ml. of water, 20 ml. of dioxane, 12 g. (0.3 mole) of sodium hydroxide and 9 g. (0.11 mole) of bromine. The mixture was stirred at room temperature for five hours, after which the dioxane was extracted with ether. The water layer was acidified with hydrochloric acid, decolorized with sodium bisulfite and the mixture was filtered with suction to yield 0.9 gram (80%) of p-cyclopropylbenzoic acid. After recrystallization from ethanol and water mixture the product melted at $157-158^{\circ}$ (reported value, m.p. $157-158^{\circ}$) (45).

Neutral. equiv. Calc'd. for $C_{10}H_{10}O_2$: 162.2.

Found: 164, 164.

Anal. Calc'd. for $C_{10}H_{10}O_2$: C, 74.03; H, 6.21.

Found: C, 73.82; H, 6.36.

b. Oxidation with Chromic Oxide

Six grams (0.0375 mole) of p-cyclopropylacetophenone was added to a solution of 33 g. (0.33 mole) of chromic oxide in 100 ml. of 50% acetic acid and the mixture was refluxed for eight hours. The mixture was then

poured into 100 g. of ice and filtered with suction. The precipitate was washed with water and warmed with 20 ml. of ethanol on a steam bath for one-half hour, filtered, and the precipitate washed with ether. There was obtained, in this manner, 3.8 g. (61%) of terephthalic acid, subl. $280-300^{\circ}$ (lit. value subl. below 300°) (46).

Neutral. equiv. Calc'd for $C_6H_4(COOH)_2$: 83.

Found: 85, 86.

Anal. Calc'd. for $C_8H_6O_4$: C, 57.85; H, 3.64.

Found: C, 58.35; H, 3.70.

The dimethyl ester was prepared according to the procedure of Smith (47) and after recrystallization from methanol melted at 141° (lit. m.p. 141°) (47). A mixed melting point with the ester prepared from an authentic sample of terephthalic acid gave no depression.

III. Reactions of Cyclopropane With Several Types of Chlorides

A. Chloroacetyl Chloride

1. Chloroacetyl Chloride

This compound was prepared by the procedure described by H. C. Brown (47). To a one-liter flask fitted with a 25-cm. heated column packed with glass helices was added 634.5 g. (4.5 moles) of benzoyl chloride and 293.5 g. (3 moles) of chloroacetic acid. The desired acid chloride was distilled from the mixture and collected from 95 to 103° . When redistilled, 217 g. (64%) of product, b.p._{1 atm.} $103-105^{\circ}$, n_D^{20} 1.4550 (lit. values, b.p.₇₆₀ 105° , n_D^{20} 1.4541) (48) was obtained.

The first part of the paper discusses the importance of the
 research and the objectives of the study. It also outlines the
 methodology used in the study and the results of the research.
 The second part of the paper discusses the results of the research
 and the conclusions drawn from the study. It also discusses the
 implications of the research and the future research needed in this
 area.

The third part of the paper discusses the results of the research
 and the conclusions drawn from the study. It also discusses the
 implications of the research and the future research needed in this
 area. The fourth part of the paper discusses the results of the
 research and the conclusions drawn from the study. It also
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 needed in this area.

The fifth part of the paper discusses the results of the research
 and the conclusions drawn from the study. It also discusses the
 implications of the research and the future research needed in this
 area. The sixth part of the paper discusses the results of the
 research and the conclusions drawn from the study. It also
 discusses the implications of the research and the future research
 needed in this area.

2. The reaction of chloroacetyl chloride and cyclopropane

The procedure was essentially the same as that described in detail for the reaction of acetyl chloride with cyclopropane. From 246 g. (2 moles) of chloroacetyl chloride, 266 g. (2 moles) of aluminum chloride and 90 g. (2.2 moles) of cyclopropane in 800 ml. of chloroform there was obtained 247.5 g. (69%) of a mixture of chloroketones, b.p., 70-90°. The resultant mixture of chloroketones could not be fractionated at 3 mm. of mercury without decomposition. To selectively dehydrohalogenate any β -haloketones, the chloroketone mixture was added to 500 ml. of 20% sodium bicarbonate solution and refluxed with vigorous stirring for one hour. The mixture was cooled, the lower layer removed and the aqueous layer extracted with ether. The organic layers were combined and dried over magnesium sulfate. After removal of the ether there was obtained, by distillation through a 25-cm. column packed with 1/8" glass helices, 55 g. (16.5%) of 1-chloro-3-methyl-3-buten-2-one, b.p., 56-57°, n_D^{25} 1.4692-1.4700.

Anal. Calc'd for C_5H_7OCl : Cl 29.9.

Found: Cl, 29.9, 29.6.

The infrared absorption spectrum (fig. XIII) showed peaks at 1700 cm^{-1} and 1630 cm^{-1} which are characteristic of α,β -unsaturated ketones (32). The compound also gave a positive iodoform test. The 2,4-dinitrophenylhydrazone was prepared according to the procedure of Johnson (30) and after recrystallization from methanol, melted at 121-122°.

Anal. Calc'd for $C_{11}H_{11}O_4N_4Cl$: C, 44.23; H, 3.72; N, 18.76;

Cl, 11.87.

Found: C, 44.03; H, 3.94; N, 18.53; Cl, 11.84.

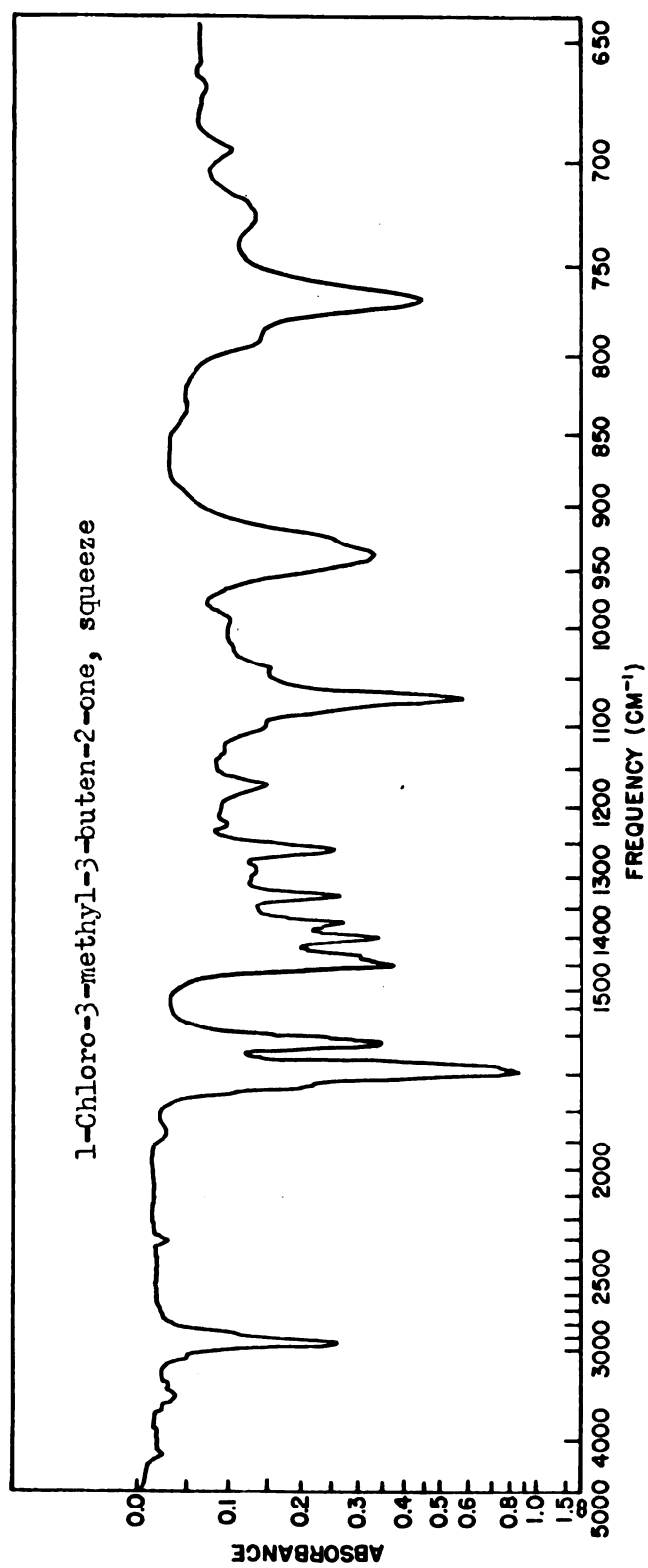


Figure XIII

There was also obtained 52 g. (14%) of 1,5-dichloro-2-pentanone, b.p.₃ 76-79°, n_D^{25} 1.476(-1.4770).

Anal. Calc'd for $C_5H_8OCl_2$: Cl, 45.8.

Found: Cl, 44.9, 44.7, 42.4.

The 2,4-dinitrophenylhydrazone was prepared and after recrystallization from methanol melted at 105-105.5°. A mixed melting point determination with the same derivative obtained from an independent synthesis gave no depression.

Anal. Calc'd. for $C_{11}H_{12}O_4N_4Cl_2$: C, 39.43; H, 3.61; N, 16.72;

Cl, 21.16.

Found: C, 39.47; H, 3.66; N, 16.87; Cl, 21.10.

Attempts to prepare solid semicarbazones of the two chloroketones, using the method described by Shriner and Fuson (31) were unsuccessful. The infrared absorption spectrum of this product (fig. XIV) was identical to that (fig. IV) obtained for the compound when synthesized from 4-chlorobutyryl chloride and diazomethane, except for a small peak at 1685 $cm.^{-1}$ in the latter which was probably due to the presence of γ -butyrolactone which absorbs strongly at that wave number.

3. Proof of structure for 1-chloro-3-methyl-3-buten-2-one

a. Hydrogenation

Six grams (0.05 mole) of 1-chloro-3-methyl-3-buten-2-one was reduced by hydrogen, at fifty p.s.i. and room temperature, using Raney nickel as the catalyst. In forty minutes, 0.03-0.1 mole of hydrogen was absorbed

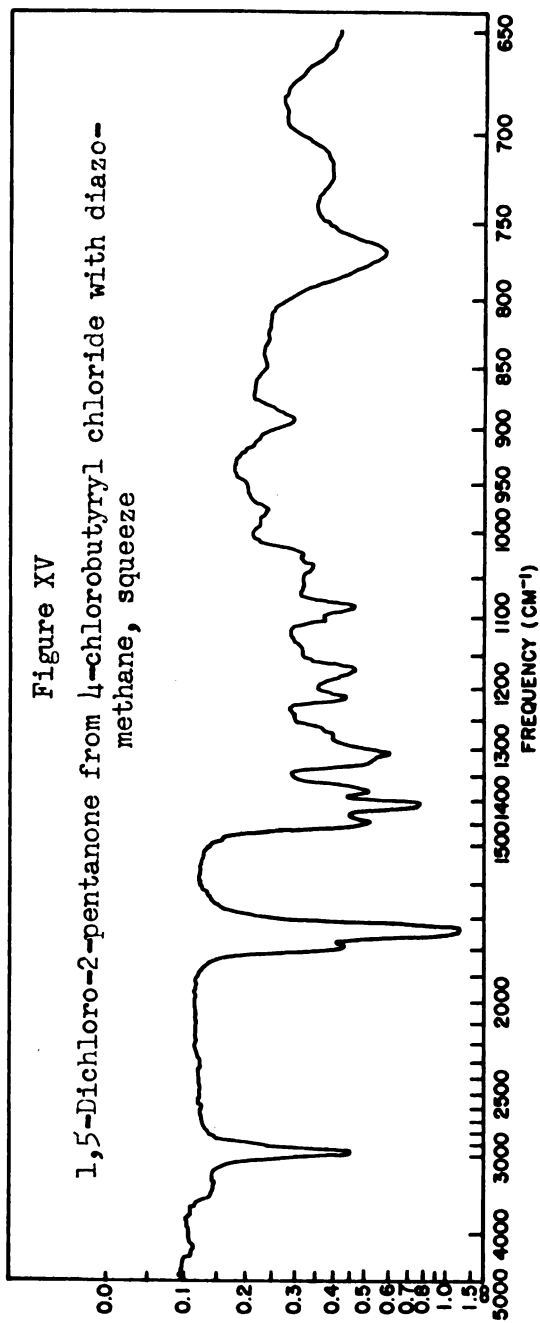
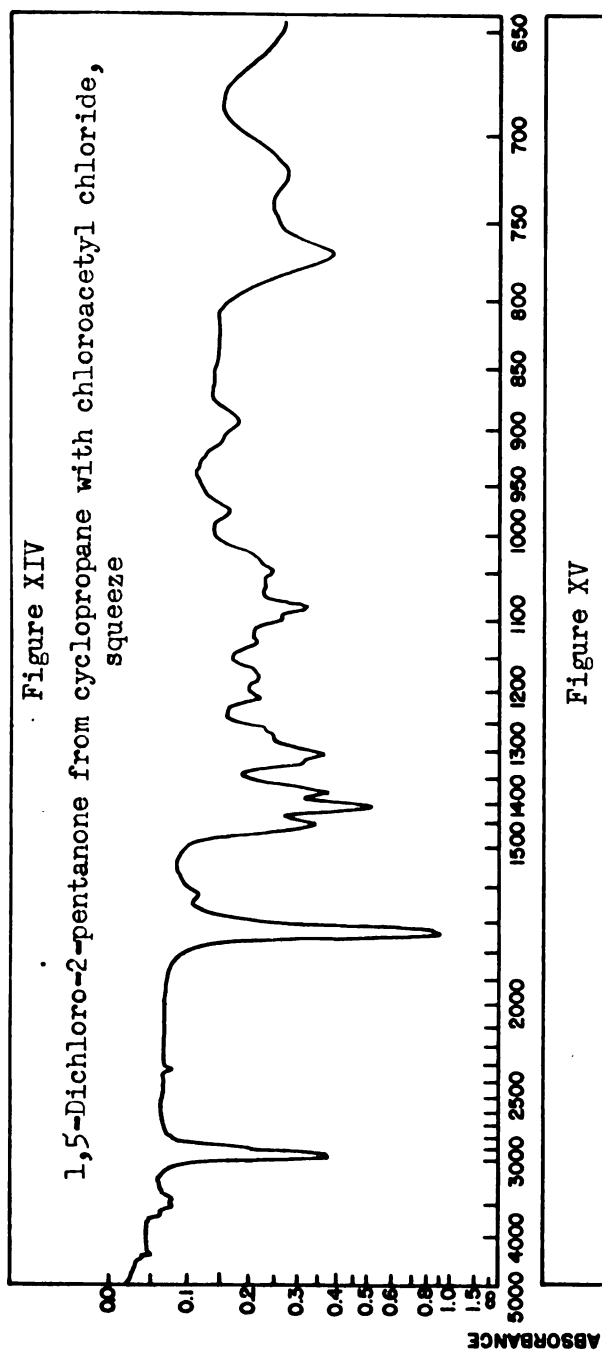
1. 1941年12月，日本帝国主义侵略军占领香港，香港同胞被迫开始了长达三年零八个月的沦陷生活。在日寇铁蹄蹂躏下，香港同胞在极其艰苦的条件下，坚持了英勇不屈的斗争，为祖国的抗战事业作出了巨大的贡献。

1998, 1999, 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020, 2021, 2022, 2023, 2024, 2025, 2026, 2027, 2028, 2029, 2030, 2031, 2032, 2033, 2034, 2035, 2036, 2037, 2038, 2039, 2040, 2041, 2042, 2043, 2044, 2045, 2046, 2047, 2048, 2049, 2050, 2051, 2052, 2053, 2054, 2055, 2056, 2057, 2058, 2059, 2060, 2061, 2062, 2063, 2064, 2065, 2066, 2067, 2068, 2069, 2070, 2071, 2072, 2073, 2074, 2075, 2076, 2077, 2078, 2079, 2080, 2081, 2082, 2083, 2084, 2085, 2086, 2087, 2088, 2089, 2090, 2091, 2092, 2093, 2094, 2095, 2096, 2097, 2098, 2099, 2100, 2101, 2102, 2103, 2104, 2105, 2106, 2107, 2108, 2109, 2110, 2111, 2112, 2113, 2114, 2115, 2116, 2117, 2118, 2119, 2120, 2121, 2122, 2123, 2124, 2125, 2126, 2127, 2128, 2129, 2130, 2131, 2132, 2133, 2134, 2135, 2136, 2137, 2138, 2139, 2140, 2141, 2142, 2143, 2144, 2145, 2146, 2147, 2148, 2149, 2150, 2151, 2152, 2153, 2154, 2155, 2156, 2157, 2158, 2159, 2160, 2161, 2162, 2163, 2164, 2165, 2166, 2167, 2168, 2169, 2170, 2171, 2172, 2173, 2174, 2175, 2176, 2177, 2178, 2179, 2180, 2181, 2182, 2183, 2184, 2185, 2186, 2187, 2188, 2189, 2190, 2191, 2192, 2193, 2194, 2195, 2196, 2197, 2198, 2199, 2200, 2201, 2202, 2203, 2204, 2205, 2206, 2207, 2208, 2209, 2210, 2211, 2212, 2213, 2214, 2215, 2216, 2217, 2218, 2219, 2220, 2221, 2222, 2223, 2224, 2225, 2226, 2227, 2228, 2229, 2230, 2231, 2232, 2233, 2234, 2235, 2236, 2237, 2238, 2239, 2240, 2241, 2242, 2243, 2244, 2245, 2246, 2247, 2248, 2249, 2250, 2251, 2252, 2253, 2254, 2255, 2256, 2257, 2258, 2259, 2260, 2261, 2262, 2263, 2264, 2265, 2266, 2267, 2268, 2269, 2270, 2271, 2272, 2273, 2274, 2275, 2276, 2277, 2278, 2279, 2280, 2281, 2282, 2283, 2284, 2285, 2286, 2287, 2288, 2289, 2290, 2291, 2292, 2293, 2294, 2295, 2296, 2297, 2298, 2299, 2300, 2301, 2302, 2303, 2304, 2305, 2306, 2307, 2308, 2309, 2310, 2311, 2312, 2313, 2314, 2315, 2316, 2317, 2318, 2319, 2320, 2321, 2322, 2323, 2324, 2325, 2326, 2327, 2328, 2329, 2330, 2331, 2332, 2333, 2334, 2335, 2336, 2337, 2338, 2339, 2340, 2341, 2342, 2343, 2344, 2345, 2346, 2347, 2348, 2349, 2350, 2351, 2352, 2353, 2354, 2355, 2356, 2357, 2358, 2359, 2360, 2361, 2362, 2363, 2364, 2365, 2366, 2367, 2368, 2369, 2370, 2371, 2372, 2373, 2374, 2375, 2376, 2377, 2378, 2379, 2380, 2381, 2382, 2383, 2384, 2385, 2386, 2387, 2388, 2389, 2390, 2391, 2392, 2393, 2394, 2395, 2396, 2397, 2398, 2399, 2400, 2401, 2402, 2403, 2404, 2405, 2406, 2407, 2408, 2409, 2410, 2411, 2412, 2413, 2414, 2415, 2416, 2417, 2418, 2419, 2420, 2421, 2422, 2423, 2424, 2425, 2426, 2427, 2428, 2429, 2430, 2431, 2432, 2433, 2434, 2435, 2436, 2437, 2438, 2439, 2440, 2441, 2442, 2443, 2444, 2445, 2446, 2447, 2448, 2449, 2450, 2451, 2452, 2453, 2454, 2455, 2456, 2457, 2458, 2459, 2460, 2461, 2462, 2463, 2464, 2465, 2466, 2467, 2468, 2469, 2470, 2471, 2472, 2473, 2474, 2475, 2476, 2477, 2478, 2479, 2480, 2481, 2482, 2483, 2484, 2485, 2486, 2487, 2488, 2489, 2490, 2491, 2492, 2493, 2494, 2495, 2496, 2497, 2498, 2499, 2500, 2501, 2502, 2503, 2504, 2505, 2506, 2507, 2508, 2509, 2510, 2511, 2512, 2513, 2514, 2515, 2516, 2517, 2518, 2519, 2520, 2521, 2522, 2523, 2524, 2525, 2526, 2527, 2528, 2529, 2530, 2531, 2532, 2533, 2534, 2535, 2536, 2537, 2538, 2539, 2540, 2541, 2542, 2543, 2544, 2545, 2546, 2547, 2548, 2549, 2550, 2551, 2552, 2553, 2554, 2555, 2556, 2557, 2558, 2559, 2560, 2561, 2562, 2563, 2564, 2565, 2566, 2567, 2568, 2569, 2570, 2571, 2572, 2573, 2574, 2575, 2576, 2577, 2578, 2579, 2580, 2581, 2582, 2583, 2584, 2585, 2586, 2587, 2588, 2589, 2590, 2591, 2592, 2593, 2594, 2595, 2596, 2597, 2598, 2599, 2600, 2601, 2602, 2603, 2604, 2605, 2606, 2607, 2608, 2609, 2610, 2611, 2612, 2613, 2614, 2615, 2616, 2617, 2618, 2619, 2620, 2621, 2622, 2623, 2624, 2625, 2626, 2627, 2628, 2629, 2630, 2631, 2632, 2633, 2634, 2635, 2636, 2637, 2638, 2639, 2640, 2641, 2642, 2643, 2644, 2645, 2646, 2647, 2648, 2649, 2650, 2651, 2652, 2653, 2654, 2655, 2656, 2657, 2658, 2659, 2660, 2661, 2662, 2663, 2664, 2665, 2666, 2667, 2668, 2669, 2670, 2671, 2672, 2673, 2674, 2675, 2676, 2677, 2678, 2679, 26

1. The following information was obtained from the records of the FBI, New York Office, dated 1/10/68:

2. The following information was obtained from the records of the FBI, New York Office, dated 1/10/68:

3. The following information was obtained from the records of the FBI, New York Office, dated 1/10/68:



and there was no further uptake of hydrogen. The solution was filtered and distilled to yield 2.2 g. (51%) of 3-methyl-2-butanone, b.p._{1 atm.} 94-97°, n_D^{25} 1.4204. The 2,4-dinitrophenylhydrazone melted at 117-118° (lit. value 117°) (31) after recrystallization from 95% ethanol, and did not depress the melting point of an authentic sample prepared from freshly distilled Eastman "white label" (methyl isopropyl ketone) 3-methyl-2-butanone.

b. Reduction with Zinc

Eleven grams (0.09 mole) of the chloroketone was added slowly to a vigorously stirred mixture of 20 g. of zinc and 50 ml. of 50% acetic acid. The mixture was stirred for one hour and then filtered with suction. The filtrate was extracted with three 25-ml. portions of ether. The combined ether extract was neutralized by the addition of solid sodium bicarbonate to a stirred mixture of the ether solution and water. The ether layer was decanted and dried over potassium carbonate. After removal of the solvent, 5 g. (65%) of 3-methyl-3-buten-2-ol was obtained, b.p._{1 atm.} 111-114°, n_D^{25} 1.4225 (lit. values, b.p.₇₆₀ 112-113°, n_D^{21} 1.4290) (49). The infrared absorption spectrum (fig. XVI) of this product is identical to that of 3-methyl-3-butene-2-ol obtained by the reduction of 3-methyl-3-buten-2-one with lithium aluminum hydride.

The phenylurethan and the 1-naphthylurethan of the 3-methyl-3-buten-2-ol obtained from this reaction were prepared according to the procedures described by Shriner and Fuson (31). After recrystallization from petroleum ether the derivatives melted at 66-66.5° and 97-98° respectively.

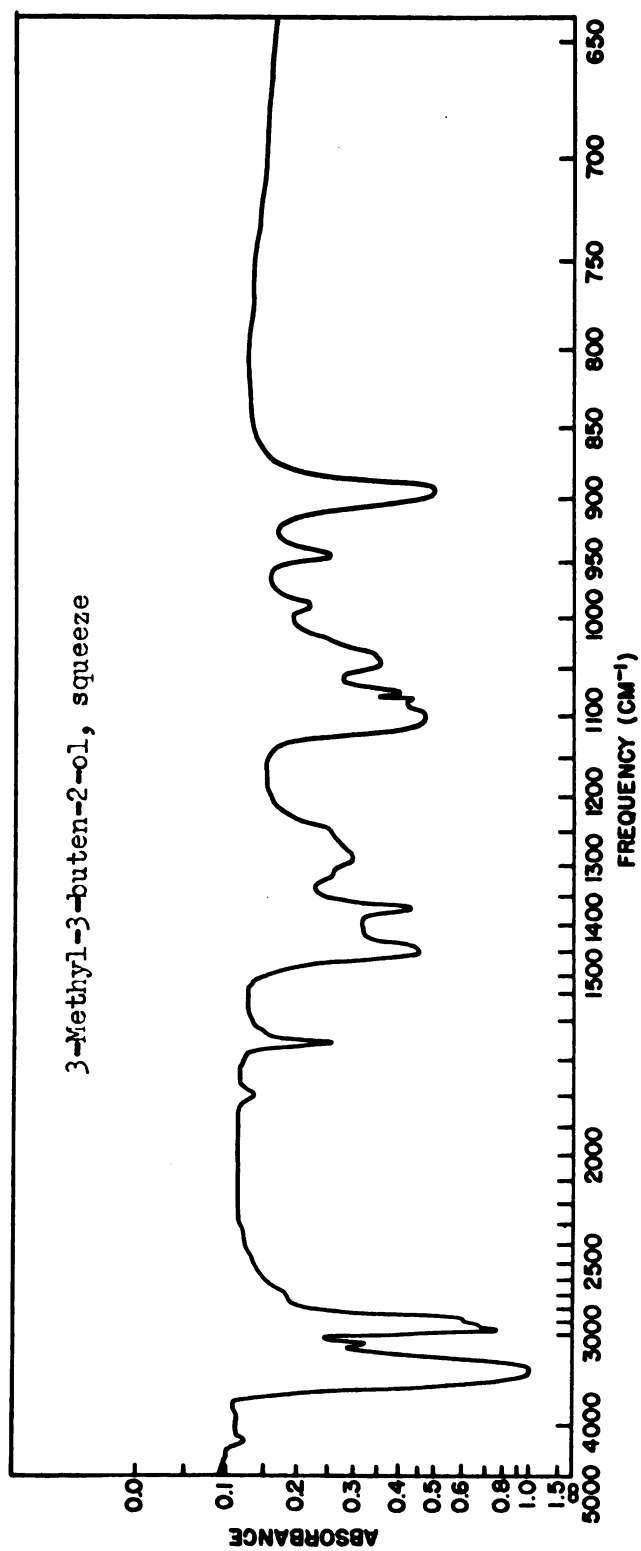


Figure XVI

The same derivatives prepared from the alcohol obtained from the reduction of 3-methyl-3-buten-2-one with zinc did not depress these melting points.

3-methyl-3-buten-2-ol phenylurethan

Anal. Calc'd for $C_{12}H_{15}O_2N$: C, 70.23; H, 7.36; N, 6.83.

Found: C, 70.00; H, 7.30; N, 7.52.

3-methyl-3-buten-2-ol (1-naphthyl)urethan

Anal. Calc'd for $C_{16}H_{17}O_2N$: C, 75.28; H, 6.71; N, 5.49.

Found: C, 75.40; H, 6.67; N, 5.63.

c. Preparation of 3-methyl-3-buten-2-one from butanone

The procedure used was that described by Landau and Irany (26). A mixture of 700 g. (10 moles) of butanone, 60 g. (2 moles) of paraformaldehyde and 5 ml. of 5 N potassium hydroxide was stirred at a temperature between 35° and 45° for two hours. The solution was neutralized with acetic acid and the excess butanone removed by distillation. Five milliliters of 85% phosphoric acid, 0.5 g. of copper powder and 0.5 g. of hydroquinone were added and the residue distilled at a pot temperature of $120-130^{\circ}$, under nitrogen. The distillate was washed with 5% potassium carbonate and dried over potassium carbonate. There was obtained 60 g. of 3-methyl-3-buten-2-one, b.p._{1 atm.} $96-100^{\circ}$, n_D^{25} 1.4192 (lit. values, b.p.₇₆₀ 98° , n_D^{25} 1.4163) (50).

d. Reduction of 3-Methyl-3-buten-2-one with Zinc

From fifteen grams (0.18 mole) of 3-methyl-2-buten-2-one, reduced by the same procedure as previously described for the reduction of

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1-chloro-3-methyl-3-butan-2-one, there was distilled 7 g. (67%) of 3-methyl-3-butan-2-ol, b.p._{1 atm.} 114-115°, n_D^{25} 1.4232.

e. Attempted synthesis of 1,4-dichloro-3-methyl-2-butanone

1) The preparation of α -chloroisobutyryl chloride. This compound was prepared using the procedure described by Kharasch and Brown (51). In a 250-ml. round-bottomed flask wrapped with black paper and equipped with a reflux condenser, was placed 53 g. (0.5 mole) of isobutyryl chloride, 54 g. (0.4 mole) of sulfuryl chloride and 0.5 g. of benzoyl peroxide. The mixture was warmed to gentle reflux until the hydrogen chloride evolution subsided. The products were separated by fractional distillation to yield 11.5 g. (16%) of the α -chloroisobutyryl chloride, b.p.₄₀ 39-40°, n_D^{25} 1.4340, (lit. values b.p.₄₀ 39-40° (52), n_D^{20} 1.4369 (51), and 16 g. (22%) of β -chloroisobutyryl chloride b.p.₄₀ 69-70°, n_D^{25} 1.4523, (lit. values, b.p.₄₀ 69-70° (52), n_D^{20} 1.4542 (51). This reaction was repeated several times in order to obtain a sufficient amount of material for the following reaction.

2) The reaction of β -chloroisobutyryl chloride with diazomethane.

An anhydrous ether solution of diazomethane was prepared from 82 g. of N-nitrosomethylurea, following the procedure described by Arndt (53). The ethereal solution of diazomethane was distilled into a two-liter, three-necked flask equipped with a stirrer and reflux condenser. When the ether residue became colorless the distillation was discontinued and an addition funnel was put in place of the distillation apparatus. β -Chloroisobutyryl chloride (47.0 g. 0.33 mole) in 50 ml. of ether was

added dropwise to the solution at 0°. The reaction mixture was stirred for an additional hour during which time a flocculant precipitate formed. The solution was then saturated with anhydrous hydrogen chloride and stirred for an additional half hour. Water was added slowly to the ether solution and the precipitate, which was water soluble, was separated by decanting the ether from the water layer. The ether layer was washed with 10% sodium bicarbonate solution and dried over magnesium sulfate. After removal of the solvent four fractions were distilled. The two lower boiling fractions were combined to give 8 g. of "A", b.p.₃ 55-75°, n_D^{25} 1.4470-1.4480 and the two higher boiling portions combined to give 8 g. of "B", b.p.₃ 75-85°, n_D^{25} 1.4640-1.4650.

Anal. Calc'd. for $C_5H_9Cl_2O$; Cl, 45.6.

Found: A: 38.2, 38.4

B: 41.0, 41.0

The infrared absorption spectra showed absorption at 1790 $cm.^{-1}$ for "A" (fig. XVII) and 1740 $cm.^{-1}$ for "A" and "B", (fig. XVIII) indicating the possible presence of both a lactone and a ketone in "A" and a ketone in "B".

The previously mentioned water soluble product was insoluble in organic solvents. Neutralization of the water solution with sodium bicarbonate caused the material to become soluble in petroleum ether indicating that it was a weak base and therefore possibly the product of a side reaction of the diazoketone involving the 2-chloro group. This product was not investigated further.

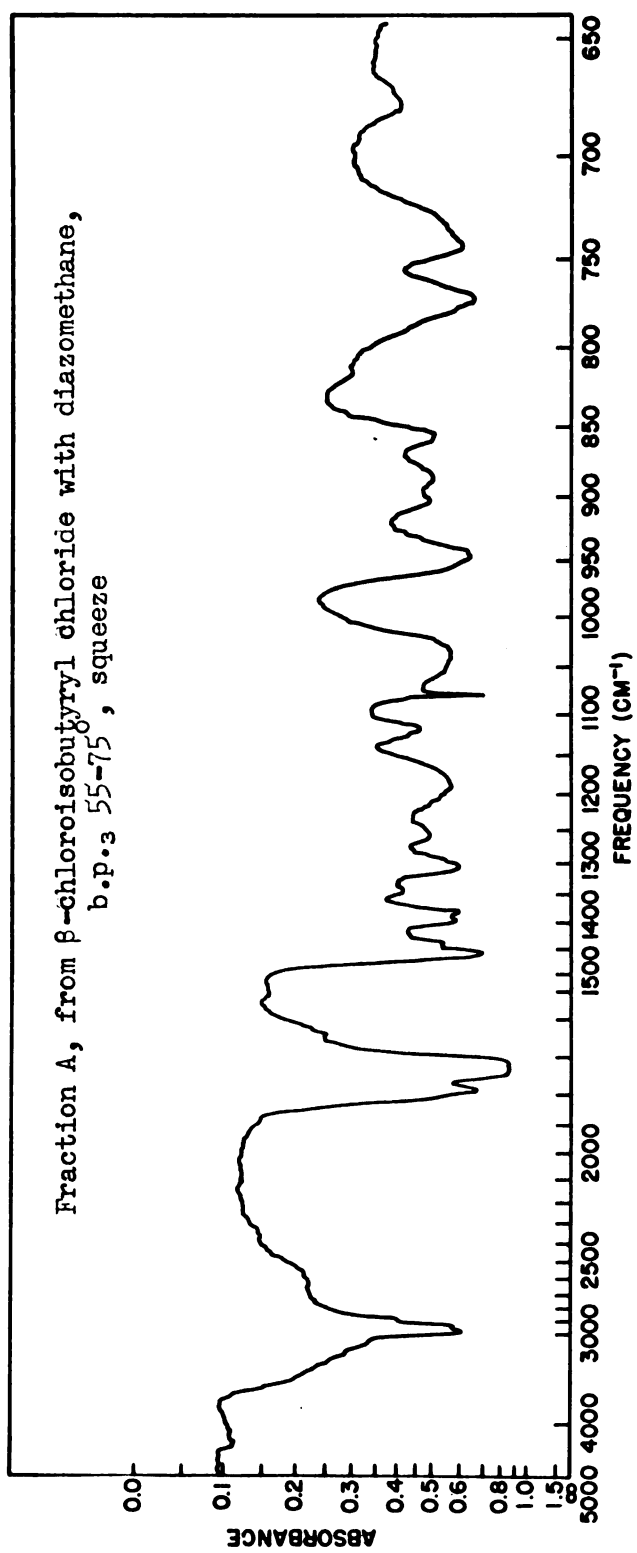


Figure XVII

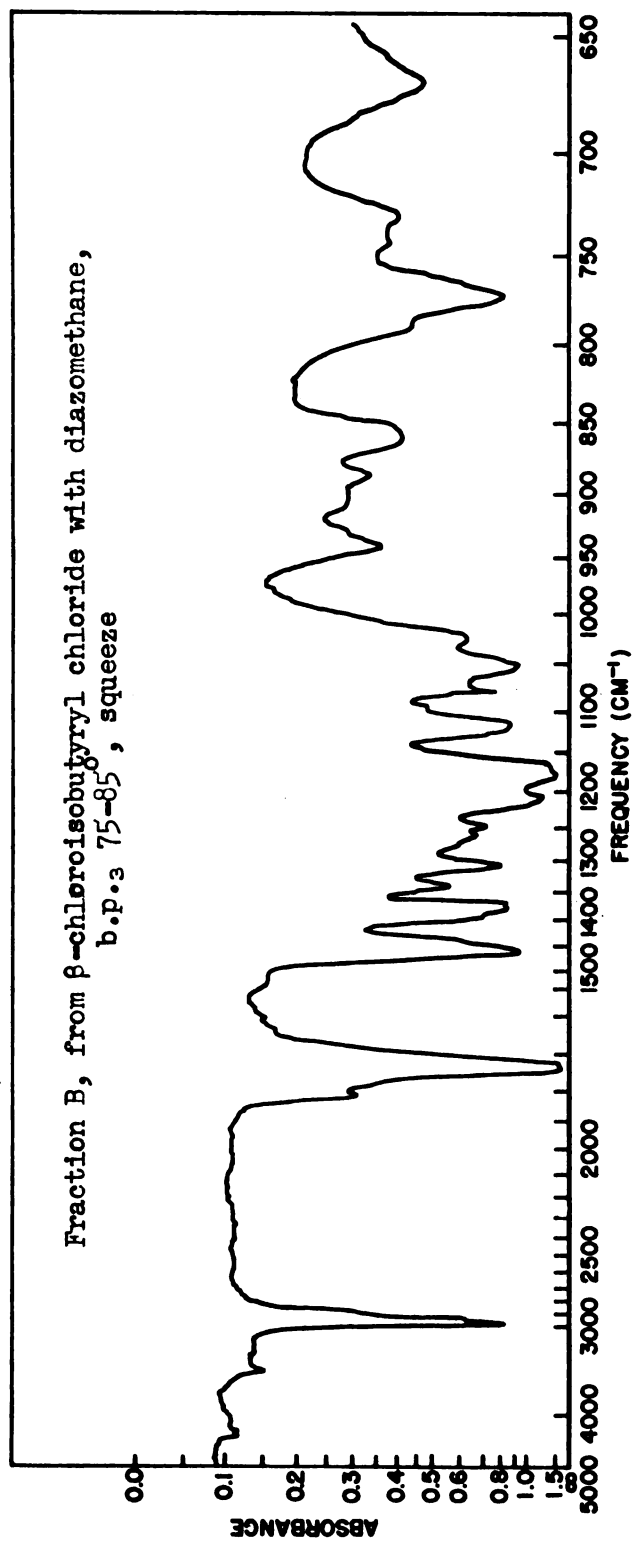


Figure XVIII

A mixture of ten grams of "A" and "B" was added to 100 ml. of 15% sodium bicarbonate and refluxed for one hour with efficient stirring in an attempt to dehydrohalogenate any β -chloro ketone present. The solution was allowed to cool and was extracted with three 25-ml. portions of ether. The ether extracts were combined and dried over magnesium sulfate. There was obtained 3 g. of a product b.p.₃ 40°. This material had a characteristic ester odor, and gave a positive Beilstein test. The infra-red spectrum (fig. XIX) showed two carbonyl peaks at 1740 cm.⁻¹ and 1710 cm.⁻¹ and only a small peak at 1640 cm.⁻¹ for carbon to carbon double bond. This spectrum was unlike that obtained for 1-chloro-3-methylbutane-2-one from chloroacetyl chloride and cyclopropanes. In view of the lack of clear-cut results this method for proof of structure was not investigated further.

4. The Synthesis of 1,5-Dichloro-2-pentanone

a. The preparation of 4-chlorobutyryl chloride from butyrolactone

Eighty-six grams (10 mole) of γ -butyrolactone was placed in a 500 ml. flask fitted with a reflux condenser and solid addition flask. There was added 220 g. (1 mole) of phosphorous pentachloride portionwise from the addition flask at such a rate that the exothermic reaction did not become too vigorous. The reaction mixture was then heated to 120° and a distillate collected, b.p.₁ atm. 75-105°. When this distillation subsided the pressure in the system was reduced to 15 mm. and 68 g. (50%) of 4-chlorobutyryl chloride, b.p.₁₅ 67-69°, n_D^{20} 1.4640 (lit. values, b.p.₁₅ 63°, n_D^{20} 1.4631) (49) was distilled.

the same time, the fact that the *Journal of the American Medical Association* (JAMA) has been the most influential journal in the field of medicine for over a century, and that it has been the primary source of information for the medical profession, is a testament to its long history and its commitment to the highest standards of medical research and practice. The JAMA's long history of publishing high-quality research and clinical studies, as well as its commitment to the highest standards of medical ethics and professional conduct, has made it the most respected and influential journal in the field of medicine. The JAMA's long history of publishing high-quality research and clinical studies, as well as its commitment to the highest standards of medical ethics and professional conduct, has made it the most respected and influential journal in the field of medicine.

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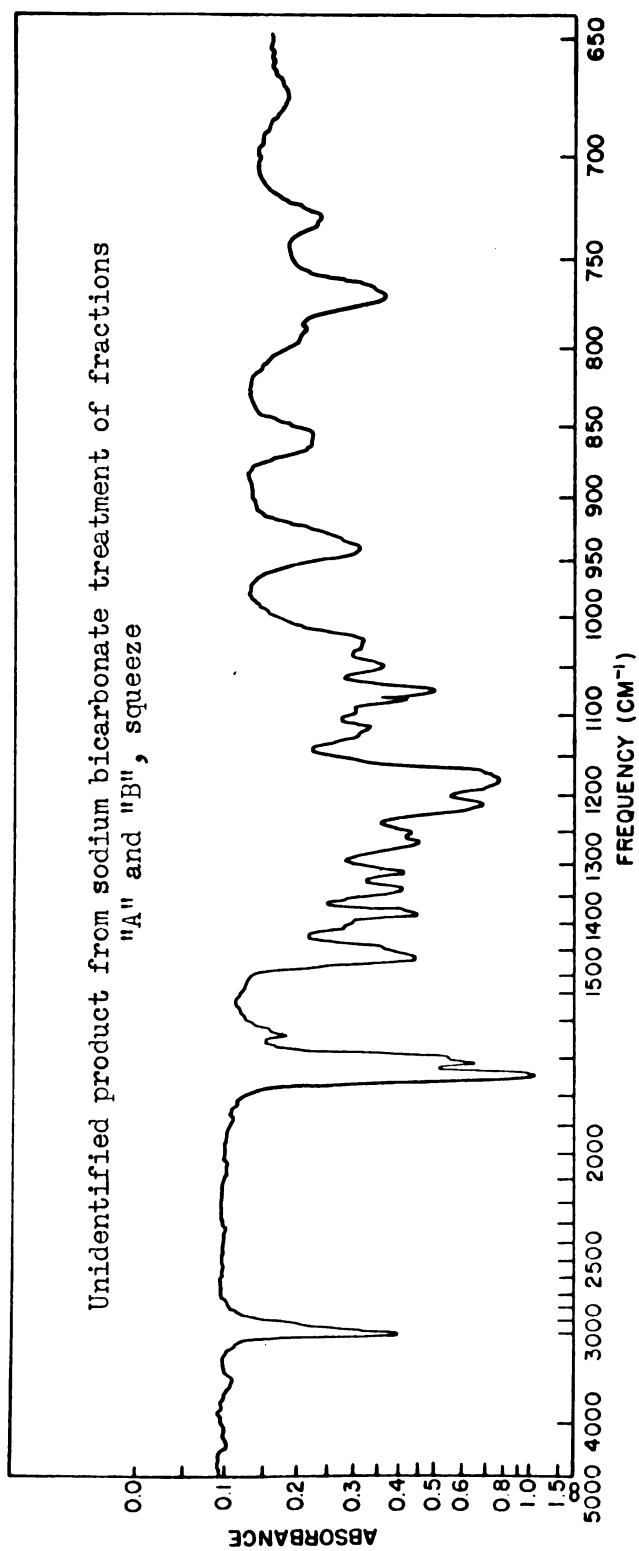


Figure XIX

b. The preparation of 1,5-dichloro-2-pentanone from 4-chlorobutyryl chloride and diazomethane

An anhydrous ethereal solution containing approximately 16.8 g. (0.4 mole) (based on lit. yield of 63%) was prepared from 61 g. of N-nitrosomethylurea as described by Armit (54). Twenty-one grams (0.15 mole) of 4-chlorobutyryl chloride in 10 ml. of ether was added dropwise to the solution at such a rate as to maintain a slow reflux. The mixture was allowed to stand for two hours and then cooled to 0°. Anhydrous hydrogen chloride was passed in for 25 minutes, during which time the yellow solution became colorless. The solution was allowed to stand for one hour, then hydrolyzed by the slow addition of water. The ether layer was decanted and washed with 100 ml. of 10% sodium bicarbonate followed with 50 ml. of water. There was obtained 16 g. (69%) of 1,5-dichloro-2-pentanone, b.p.₃ 80-85°, n_D^{25} 1.4766-1.4772. The infrared absorption spectrum (fig. XV) of this product was compared with 1,5-dichloro-2-pentanone obtained from chloroacetyl chloride and cyclopropane.

Anal. Calc'd. for $C_5H_8Cl_2O$: Cl, 45.8.

Found: Cl, 45.6, 46.2.

The 2,4-dinitrophenylhydrazone was prepared for comparison also and after recrystallization from methanol melted at 105-105.5°.

B. t-Butyl Chloride

The procedure used for this reaction was analogous to that described by Schmerling (54) for the reaction of an alkyl halide with olefins.

There is a significant positive correlation between the two variables.

The correlation coefficient is 0.85, which is statistically significant.

The correlation is significant at the 0.05 level (2-tailed).

The correlation is significant at the 0.01 level (2-tailed).

The correlation is significant at the 0.001 level (2-tailed).

The correlation is significant at the 0.0001 level (2-tailed).

The correlation is significant at the 0.00001 level (2-tailed).

The correlation is significant at the 0.000001 level (2-tailed).

The correlation is significant at the 0.0000001 level (2-tailed).

The correlation is significant at the 0.00000001 level (2-tailed).

The correlation is significant at the 0.000000001 level (2-tailed).

The correlation is significant at the 0.0000000001 level (2-tailed).

The correlation is significant at the 0.00000000001 level (2-tailed).

The correlation is significant at the 0.000000000001 level (2-tailed).

The correlation is significant at the 0.0000000000001 level (2-tailed).

The correlation is significant at the 0.00000000000001 level (2-tailed).

The correlation is significant at the 0.000000000000001 level (2-tailed).

The correlation is significant at the 0.0000000000000001 level (2-tailed).

The correlation is significant at the 0.00000000000000001 level (2-tailed).

The correlation is significant at the 0.000000000000000001 level (2-tailed).

The correlation is significant at the 0.0000000000000000001 level (2-tailed).

The correlation is significant at the 0.00000000000000000001 level (2-tailed).

The correlation is significant at the 0.000000000000000000001 level (2-tailed).

In a one-liter three-necked flask equipped with a dry ice condenser, stirrer, and thermometer was placed 212 g. (2 moles) of *t*-butyl chloride and 100 ml. of chloroform. The mixture was cooled to -50° in a dry ice-isopropyl alcohol bath. The thermometer was then replaced with a gas delivery tube and 90 g. (2.2 moles) cyclopropane was passed in. The delivery tube was replaced with a thermometer and seven grams (0.053 moles) of aluminum chloride was added. After ten minutes the aluminum chloride was completely dissolved and the reaction mixture became yellow, finally turning amber. The mixture was stirred for two hours during which time the temperature in the flask was allowed to rise to 0° . Twenty-five ml. of 50% methanol was then added to the mixture to hydrolyze the aluminum chloride. The chloroform layer was separated from the aqueous layer, washed with 100 ml. of water and dried over potassium carbonate. After the unreacted *t*-butyl chloride and chloroform were removed the product was distilled to yield 19 fractions as shown in Table I.

Anal. Calc'd for: $C_7H_{15}Cl$: C, 62.47; H, 11.24; Cl, 26.4

Pounds	Fraction	C	H	Avg. Cl	Total
	5	61.32	11.13	27.25	99.70
	8	62.90	11.29	25.6	100.4
	14	63.36	11.28	25.85	100.24

The plots of temperature (fig. IX) and refractive index (fig. XII) versus grams of product distilled show flat portions between 17-35 g. and 25-45 g. respectively. The fractions common to both of these areas are numbers 12-14; however, analysis of one of these, 14, was not satisfactory for $C_7H_{15}Cl$. The 49.83 g. of mixed product obtained from this

TABLE I

DESTILLATION OF PRODUCT FROM REACTION OF CYCLOPROPANE WITH *t*-BUTYL
CHLORIDE THROUGH A 75-cm. COLUMN OF 1" DIAMETER
PACKED WITH 1/8" GLASS BEADS

Fraction	T°	P(mm. Hg.)	Grams	n_D^{20}	%Cl
1	40-43	93	1.1	1.4178	
2	45-48	90	1.70	1.4161	
3	48-49	90	1.80	1.4170	
4	49-50	90	1.48	1.4178	27.9, 23.7
5	53-55	92	1.73	1.4181	27.2, 27.3
6	55-65	92	2.35	1.4191	
7	65-65	92	1.1	1.4208	
8	67-70	92	3.24	1.4230	25.8, 25.9
9	70-71	92	3.0	1.4253	
10	72-72	92	1.9	1.4278	
11	73-73	92	2.0	1.4298	26.0, 26.2
12	73-74	92	4.3	1.4294	
13	74-74	92	4.63	1.4300	
14	74-74	92	4.15	1.4301	25.2, 25.6, 25.6
15	76-82	92	4.0	1.4301	
16	86-92	92	3.6	1.4303	
17	93-95	92	3.0	1.4301	
18	97-103	92	2.45	1.4314	
19	100-110	92	2.3	1.4340	

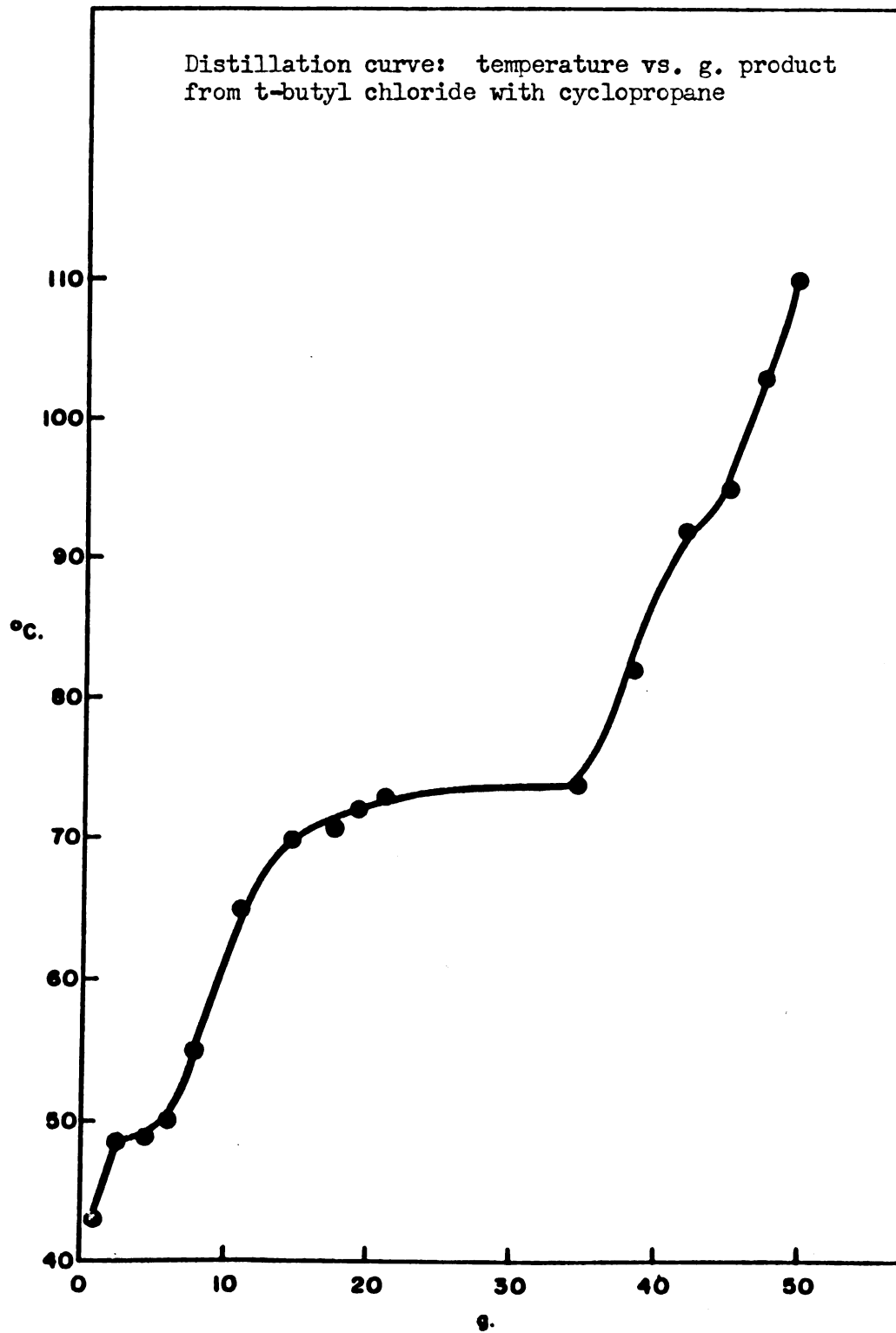


Figure XX

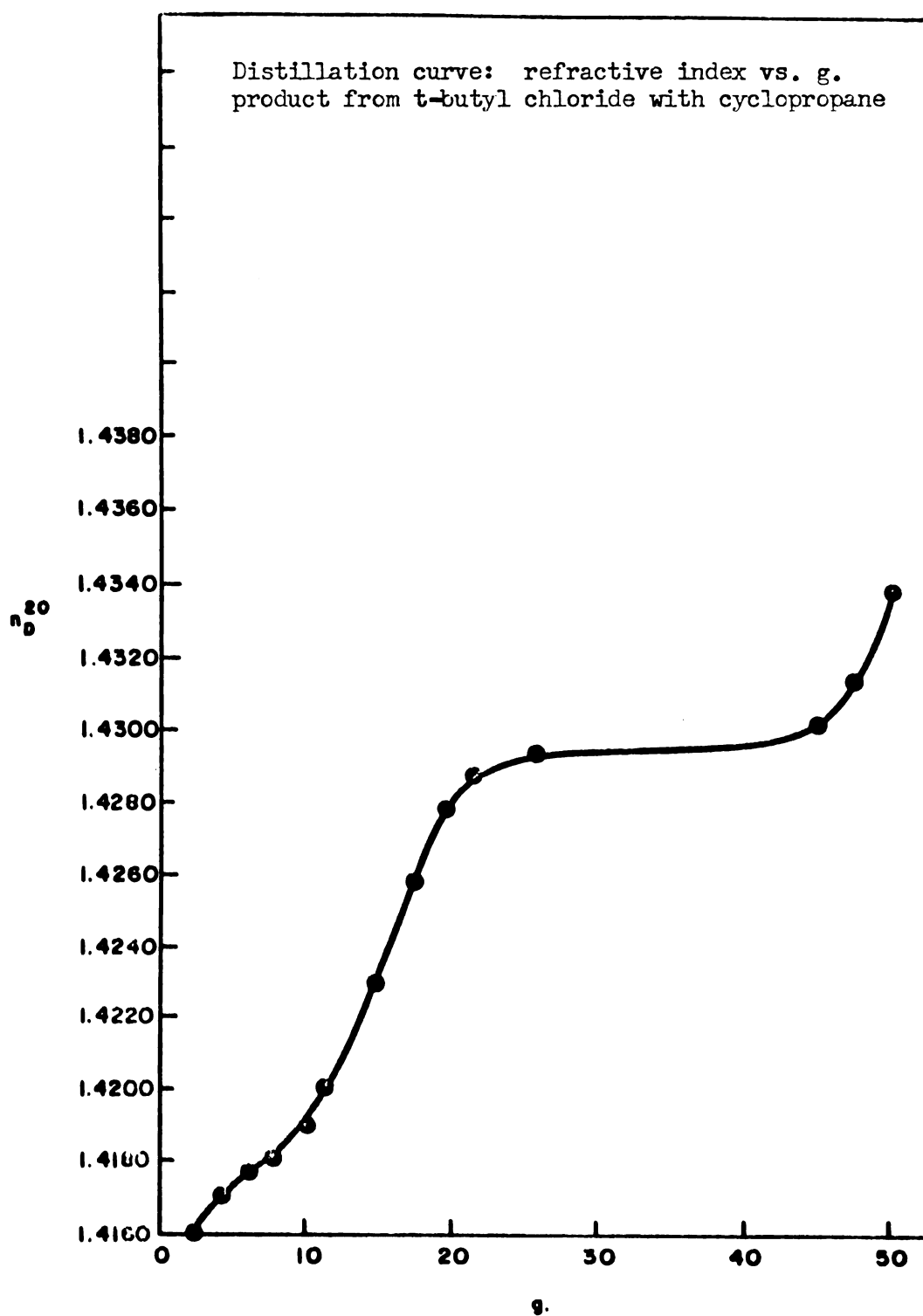


Figure XXI

reaction is considerably less than the theoretical yield of 302 g. Several attempts to identify the carbon skeleton by reduction of the chloride to an alkane, via the formation of a Grignard reagent and hydrolysis of this product or by reduction with zinc and acetic acid, did not yield a distillable hydrocarbon free of halogen. An infrared absorption spectrum (fig. XIII) of redistilled lower boiling fractions 1-6 showed characteristic alkane absorption peaks.

C. Sulfonyl Chlorides with Cyclopropane

A solution containing 54.3 g. (0.5 mole) of methanesulfonyl chloride, 67 g. (0.5 mole) of aluminum chloride and 500 ml. of chloroform was prepared in the usual manner. Twenty-five grams (0.6 mole) of cyclopropane was passed into the solution at 0°. The solution was maintained at 0° for one hour and then stirred at room temperature for twelve hours. The mixture was poured into 400 g. of ice and 100 ml. of concentrated hydrochloric acid. The chloroform solution was treated in the usual manner to yield only unchanged sulfonyl chloride and less than 1 g. of a material which boiled between 120-150° at 3 mm. This material decolorized bromine in carbon tetrachloride and gave a negative test for sulfur when a sodium fusion analysis was made.

Ethanesulfonyl chloride, butanesulfonyl chloride and p-toluenesulfonyl chloride were all treated in a similar manner but failed to yield any significant amount of product.

1. What is the main purpose of the document?

The main purpose of the document is to provide a comprehensive overview of the current state of the global economy and its impact on various sectors. It aims to identify key trends, challenges, and opportunities for growth. The document also seeks to inform policymakers and business leaders about the latest developments in the market, enabling them to make informed decisions and strategize effectively for the future.

Global Economic Outlook

The global economy has experienced significant volatility in recent years, characterized by rapid technological advancements, shifting consumer preferences, and geopolitical tensions. The COVID-19 pandemic has further exacerbated these challenges, leading to a global recession and a sharp decline in economic activity. However, as the world begins to recover, there are several key factors that will shape the future of the global economy. These include the continued growth of emerging markets, the increasing importance of digital technology, and the growing emphasis on sustainable and inclusive growth. Policymakers and business leaders must stay abreast of these trends and adapt their strategies accordingly to ensure long-term success in a rapidly changing environment.

In conclusion, the global economic outlook is complex and uncertain, but there are also many opportunities for growth and innovation. By staying informed and adaptable, stakeholders can navigate the challenges ahead and seize the opportunities that lie ahead.

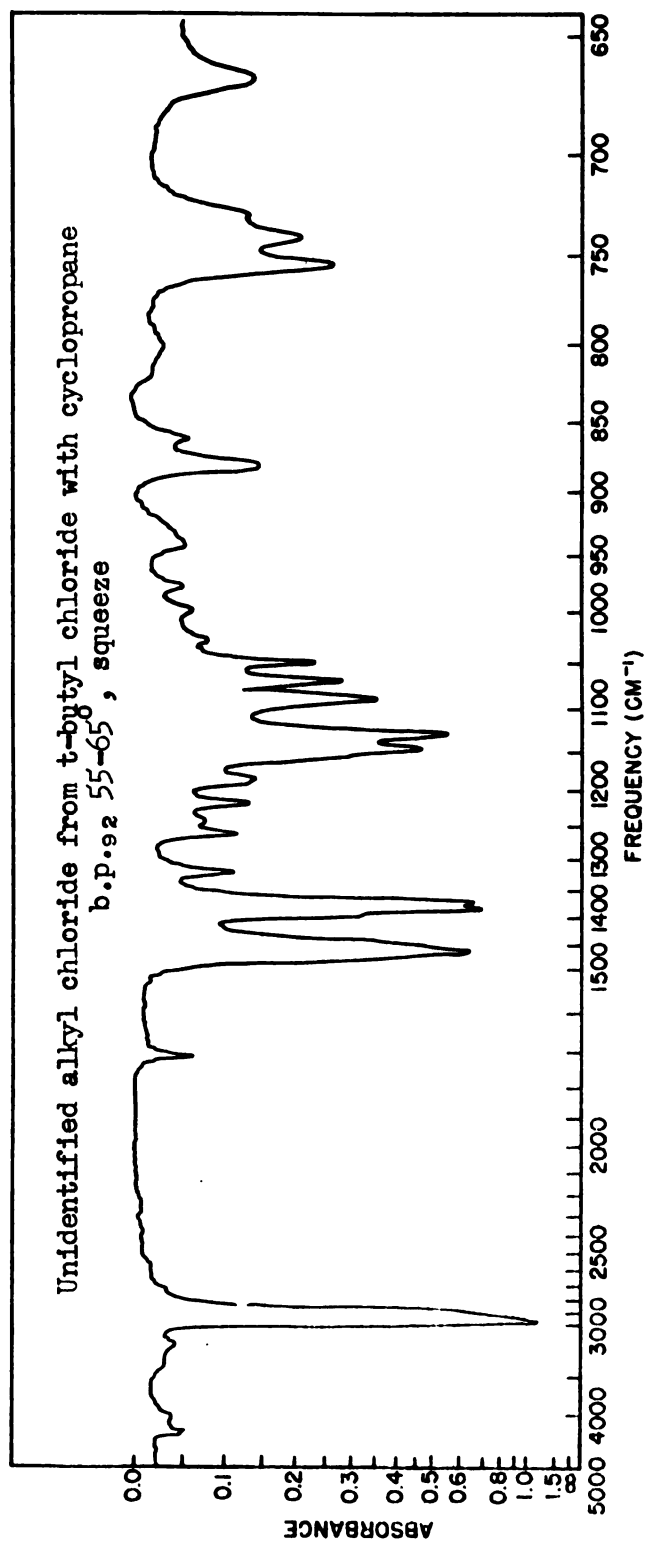


Figure XXII

D. Acetyl Perchlorate

1. Acetyl Perchlorate with Cyclopropane

The procedure used in this experiment to prepare the acetyl perchlorate was that described by Burton and Praill (55). Ten and a half grams (0.05 mole) of silver perchlorate, which was dried overnight over phosphorus pentoxide in a vacuum desiccator, was placed in 125 ml. of freshly distilled nitromethane. Six grams (0.076 mole) of acetyl chloride was added dropwise to the solution at 0°. The mixture was allowed to stand for one hour and then filtered, under nitrogen, into a three-necked flask. Five grams (0.12 mole) of cyclopropane was passed in. After one hour the solution was poured onto 300 g. of ice and 20 g. of sodium bicarbonate. The water layer was extracted with three 50-ml. portions of ether, and the ether layers were combined. The ether extract was washed with five 50-ml. portions of 10% sodium hydroxide. The ether was dried over magnesium sulfate. No residue remained after removal of the ether.

2. Acetyl Perchlorate with 1,1-Dimethylcyclopropane

A solution of acetyl perchlorate was prepared from 41 g. (0.2 mole) of silver perchlorate, 200 ml. of nitromethane and 17.2 g. (0.22 mole) of acetyl chloride as described in the preceding experiment. 1,1-Dimethylcyclopropane (14.4 g., 0.2 mole) was added to the solution, with stirring, at 0°. The mixture was allowed to stand for one hour and then poured into 200 ml. of 5% sodium bicarbonate. The water solution was extracted with five 50-ml. portions of ether. The ether extracts were combined

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and dried over magnesium sulfate. When distilled, the ether extracts did not yield any product which boiled above 100° (Nitromethane, b.p. 100°). The last portion of distillate did, however, yield a derivative with 2,4-dinitrophenylhydrazine which melted at $129-130^{\circ}$ and a mixed melting point determination with the 2,4-dinitrophenylhydrazones of 3,4-dimethyl-3-pentan-2-one as prepared previously gave no depression.

Analyses, Melting Points and Spectra

The method of Umhoefer (56) was used for the chlorine analyses of the liquid products. Two grams of sodium, cut into four or five pieces, was placed in a 250-ml. Soxhlet flask containing 35 ml. of 99% isopropyl alcohol. A sample of 0.10-0.30 g. of the compound being analyzed was added and the solution was refluxed for two to four hours. The excess sodium was decomposed by cautiously adding water through the condenser. Fifty milliliters of water was added, and the solution neutralized to congo red paper with 6 N nitric acid. The chloride ion was titrated by the Volhard method.

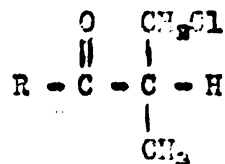
The other elemental analyses were done by Goller Microanalytical Laboratories, Hackensack, New Jersey, or Micro-Tech. Laboratories, Skokie, Illinois.

Melting points were determined in a capillary in an efficiently stirred, electrically heated, oil bath using a thermometer calibrated against a Bureau of Standards thermometer. Stem corrections were not made.

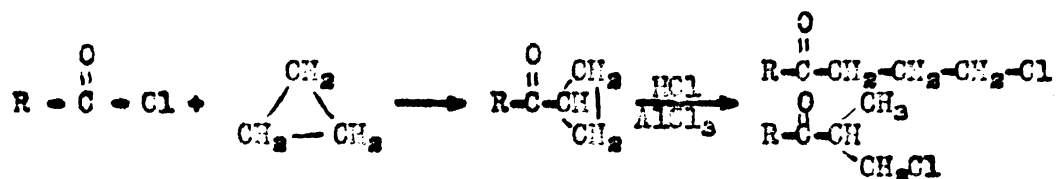
Infrared absorption spectra were run using a Perkin-Elmer, Model 21 spectrophotometer. The ultraviolet spectra were taken using a Beckman, Model DK recording spectrophotometer.

DISCUSSION

Several experiments were performed to determine whether the β -chloroketones



are formed directly in the acylation of cyclopropane, or whether they are formed by some indirect path. One of these possibilities had already been tested by Curtis (23). For example, it is conceivable that cyclopropane could be acylated directly to an alkyl cyclopropyl ketone, which, on subsequent reaction with hydrogen chloride (in the presence of aluminum chloride) might lead to the observed β - and γ -chloroketone mixture. Although ring opening to the β - (rather than γ -) chloroketone is an unlikely prospect, it was nevertheless investigated by Curtis, who



treated *n*-propyl cyclopropyl ketone with aluminum chloride and hydrogen chloride in chloroform solution for two hours at 0°. The ketone was recovered in greater than 80% yield and there was no evidence for the formation of any chloroketones. Thus, under the conditions of the acylation reaction alkyl cyclopropyl ketones are stable; they therefore cannot be intermediates in the formation of the chloroketones.

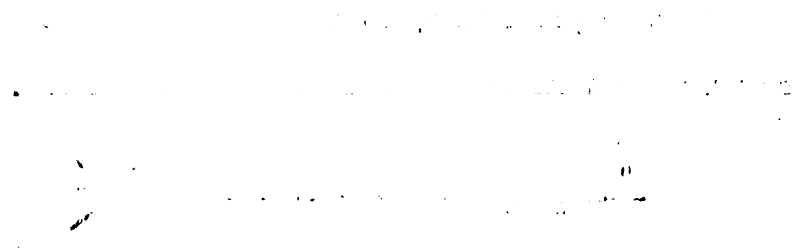
Another possibility is that the β -chloroketones are formed by some rearrangement during the course of the acylation.



Two experiments described in this thesis indicate that this postulate for the mode of formation of the β -chloroketones is also incorrect. When 5-chloro-2-pentanone (the γ -chloroketone from acetyl chloride and cyclopropane) was stirred, in chloroform solution at 0-10° for one hour, with a 4-fold excess of an equimolar mixture of acetyl chloride and aluminum chloride (thus reproducing all of the acylation conditions, except for the cyclopropane) it was recovered unchanged in 80% yield. There was no evidence for the formation of 4-chloro-3-methyl-2-butanone (the β -chloroketone) or 3-methyl-3-buten-2-one, its dehydrohalogenation product. Under these conditions, then, the γ -chloroketones do not rearrange to the β -isomers.

On the premise that perhaps during the acylation (with cyclopropane present) some circumstances are generated which allow this rearrangement to occur, the acylation was carried out in the presence of a rather large quantity of initially added γ -chloroketone. The yield of β -chloroketone (or its dehydrohalogenation product) was unaffected, and the amount of γ -chloroketone recovered corresponded closely to the sum of the initially added plus that expected to be formed from the acylation.

It is felt, therefore, that it is safe to conclude that the β -chloroketones are not formed by rearrangement of the γ -chloroketones, nor from



The graph shows a linear relationship between the number of people and the number of people. The x-axis represents the number of people, and the y-axis represents the number of people. The line starts at the origin (0,0) and extends to the point (10,10). This indicates that for every person, there is one person.

The graph is a straight line with a positive slope. The slope of the line is 1, which means that for every unit increase in the number of people on the x-axis, there is a corresponding unit increase in the number of people on the y-axis.

The equation of the line is $y = x$. This equation represents the relationship between the number of people on the x-axis and the number of people on the y-axis.

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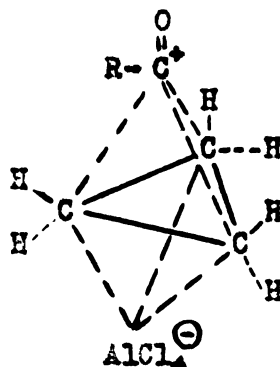
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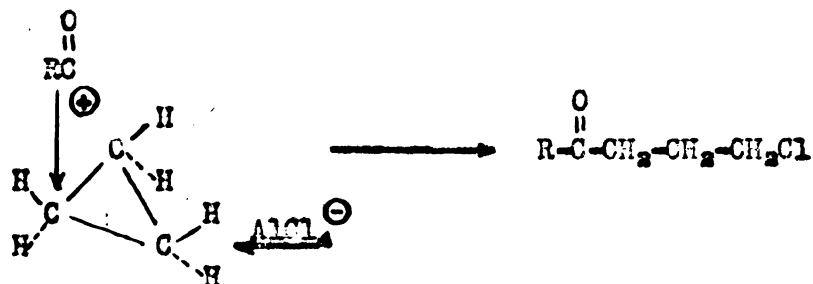
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the allyl cyclopropyl ketones and hydrogen chloride, but are probably produced by some more direct process from the reactants. One can speculate about the possible nature of this process. For example, a complex may form which could subsequently break down by either of two paths to yield either the β - or the γ -chloroketone. One may propose an intermediate such as a sandwich type aggregate consisting of a cyclopropane ring between the ions of the acylchloride-aluminum chloride complex.

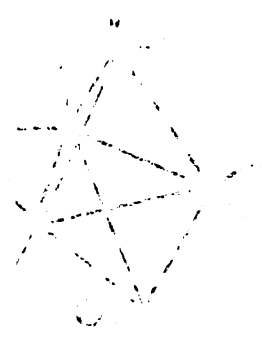


Rupture of a carbon-carbon bond in the cyclopropane ring with addition of the ions to the site of the cleavage would lead to the γ -chloroketone.

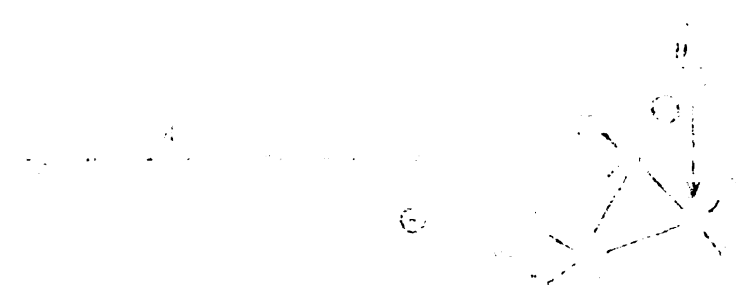


However, if rupture of a carbon-hydrogen bond rather than a carbon-carbon bond occurred (such a situation could presumably arise if the carbon-hydrogen bonding electrons were located more suitably for

The first part of the paper discusses the general theory of the problem. It is shown that the problem is equivalent to finding a minimum spanning tree in a graph. The graph is constructed as follows: the vertices are the nodes of the network, and the edges are the branches. The weight of an edge is the cost of the branch. The minimum spanning tree is found by the following algorithm: start with a tree consisting of a single vertex, and repeatedly add the edge with the minimum weight that does not create a cycle.

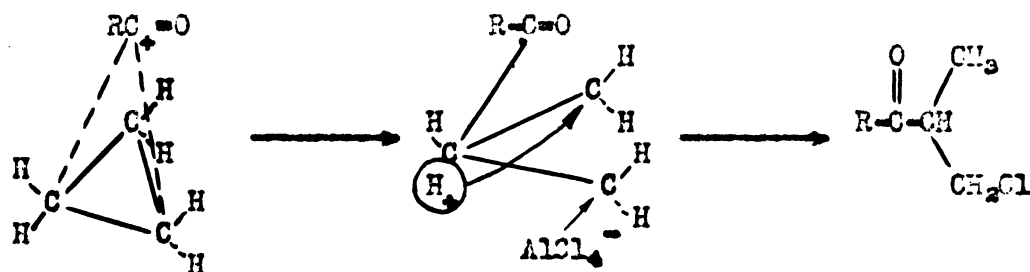


The second part of the paper discusses the application of the theory to a specific problem. It is shown that the problem can be solved by the following algorithm: start with a tree consisting of a single vertex, and repeatedly add the edge with the minimum weight that does not create a cycle.



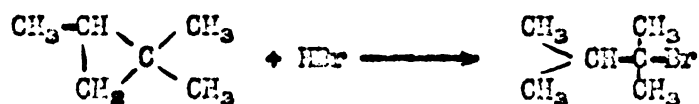
The third part of the paper discusses the application of the theory to a specific problem. It is shown that the problem can be solved by the following algorithm: start with a tree consisting of a single vertex, and repeatedly add the edge with the minimum weight that does not create a cycle.

interaction with the attacking acylium ion) followed by a concerted attack of the displaced proton and the aluminum tetrachloride ion, the β -chloroketone could be accounted for.

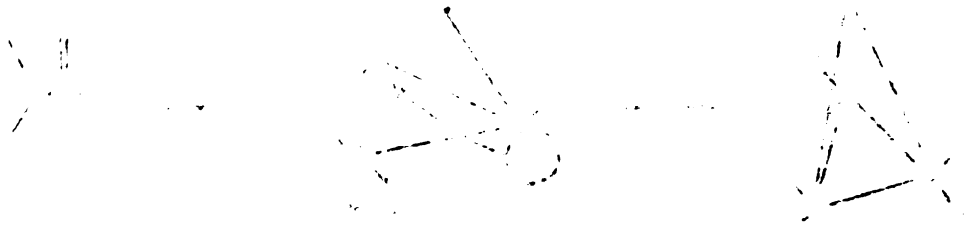


Such a mechanism, however, is difficult to accept because of the sequence requiring that the proton displaced by the acylium ion take part in the rupture of a bond which was stable toward the acylating agent. At the present writing, the mechanism of formation of the β -chloroketone is not yet clear.

In order to both determine the direction of ring opening in the acylation reaction and to further explore the scope of the reaction, the acylation of several substituted cyclopropanes was studied. Ordinarily, additions to substituted cyclopropanes follow Markownikoff's rule. For example, the reaction of 1,1,2-trimethylcyclopropane with hydrogen bromide yields 2-bromo-2,3-dimethylbutane (57).



Under certain circumstances, unusual steric requirements may cause non-Markownikoff ring opening. Thus, mauliane was transformed to an olefin,



The first diagram shows a star-like shape with several lines radiating from a central point. The middle diagram shows a more complex shape with multiple lines and a central point. The third diagram on the right shows a triangle with internal lines connecting vertices to a central point.

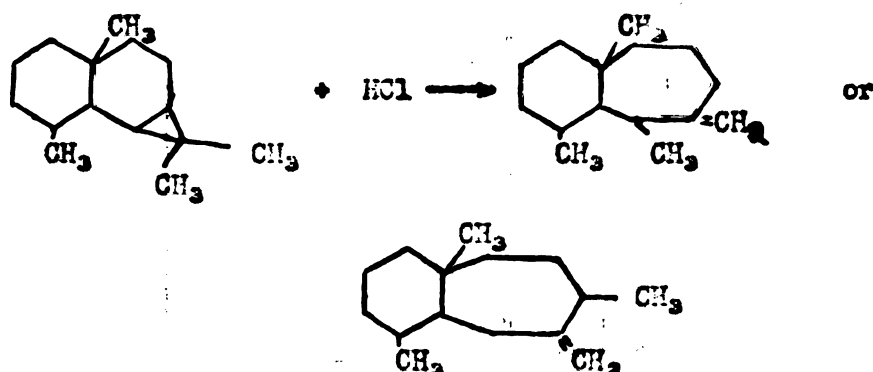
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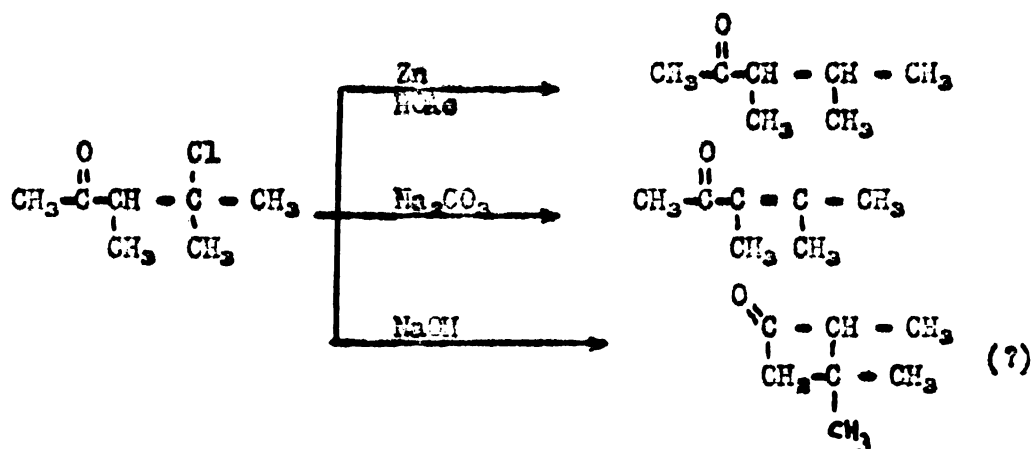


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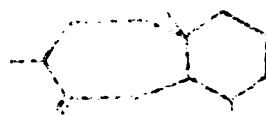
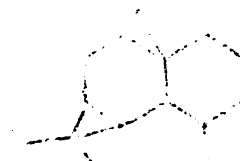
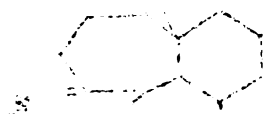
the structure of which indicated that the least substituted bond was broken, followed by Wagner-Meerwein rearrangement (58).



1,1-Diethylcyclopropane, prepared by methods described in the literature, reacted smoothly with the 1:1 complex of acetyl chloride and aluminum chloride in chloroform at -10 to 0° . A 59% yield of what appeared to be a single chloroketone was obtained. Dehalogenation of this product with zinc in glacial acetic acid gave 3,4-dimethyl-2-pentanone. Dehydrohalogenation, by 10% sodium carbonate gave 3,4-dimethyl-3-penten-2-one. Dehydrohalogenation with 10% sodium hydroxide gave the same α,β -unsaturated ketone plus a cyclobutanone derivative (probably 2,3,3-trimethyl cyclobutanone). The structure was thus shown to be 4-chloro-3,4-dimethyl-2-pentanone.

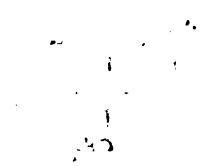
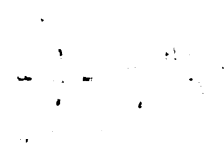
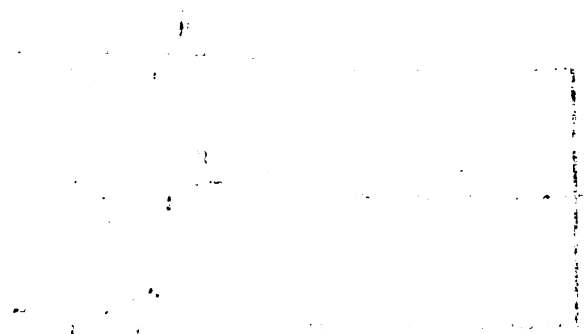


1. 1,2,3,4-tetrahydronaphthalene
 2. 1,2,3,4-tetrahydronaphthalene

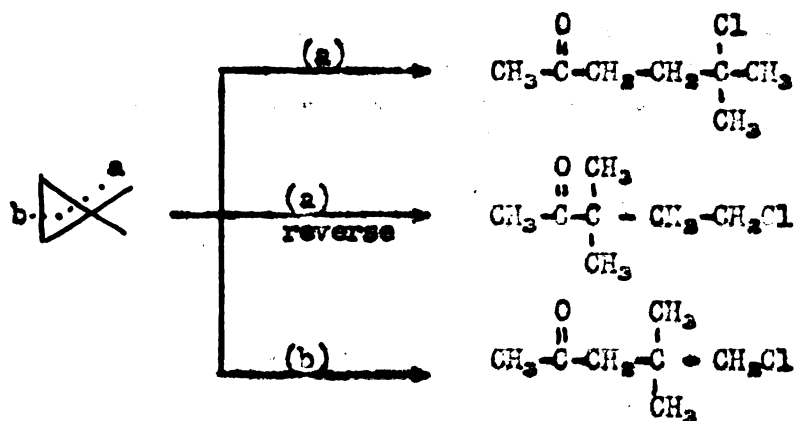


1,2,3,4-tetrahydronaphthalene

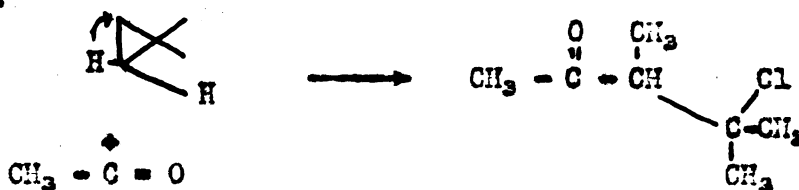
The first two structures are 1,2,3,4-tetrahydronaphthalene (tetralin) with a methyl group at position 1. The third structure is 1,2,3,4-tetrahydronaphthalene (tetralin) with a methyl group at position 1. The fourth structure is 1,2,3,4-tetrahydronaphthalene (tetralin) with a methyl group at position 1. The fifth structure is 1,2,3,4-tetrahydronaphthalene (tetralin) with a methyl group at position 1. The sixth structure is 1,2,3,4-tetrahydronaphthalene (tetralin) with a methyl group at position 1. The seventh structure is 1,2,3,4-tetrahydronaphthalene (tetralin) with a methyl group at position 1. The eighth structure is 1,2,3,4-tetrahydronaphthalene (tetralin) with a methyl group at position 1. The ninth structure is 1,2,3,4-tetrahydronaphthalene (tetralin) with a methyl group at position 1. The tenth structure is 1,2,3,4-tetrahydronaphthalene (tetralin) with a methyl group at position 1.



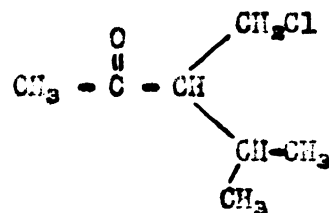
This structure does not correspond to any of the possible γ -chloro-ketones expected from 1,1-dimethylcyclopropane:



Of the β -chloroketones which might be expected (in view of the products obtained from cyclopropane itself) the most likely one is that which was observed as the major reaction product. It corresponds to attack by acyl at one of the methylene groups, with transfer of hydrogen to the other methylene:

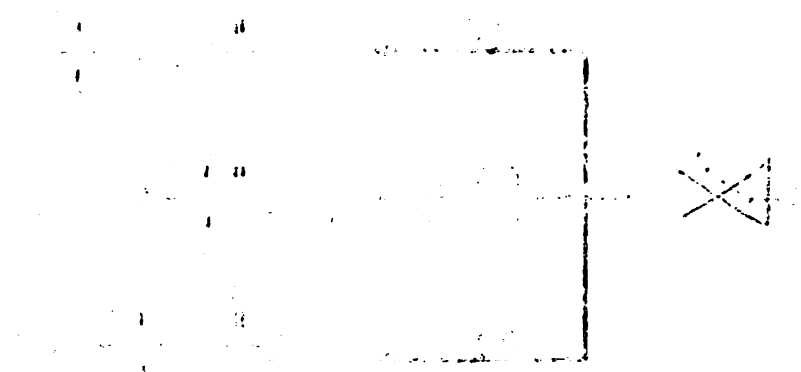


Transfer of the hydrogen to the more substituted position would give

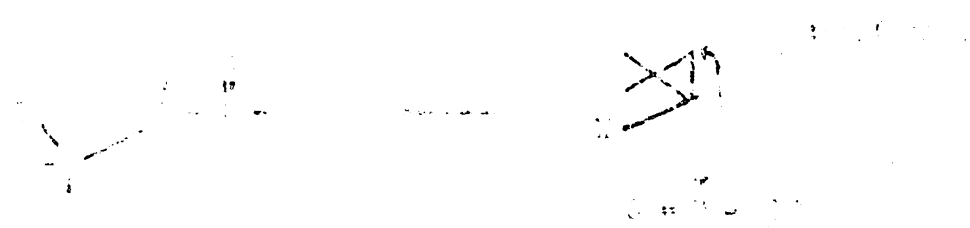


which is not rigorously excluded by the observed reactions of chloroketone obtained (since prototropic rearrangement of the double bond might occur

2. The first part of the problem is to find the value of x in the following figure.



The first part of the problem is to find the value of x in the following figure. The figure shows a rectangle with a diagonal line segment. The diagonal is labeled x . The rectangle is divided into two right-angled triangles. The top triangle has a vertical side of 3 and a horizontal side of 4. The bottom triangle has a vertical side of 4 and a horizontal side of 3. The diagonal is the hypotenuse of both triangles.



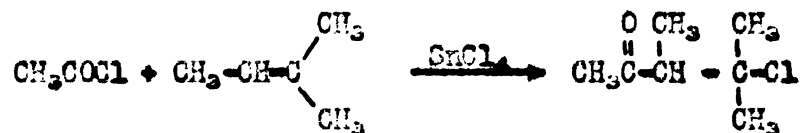
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upon dehydrohalogenation). The structure of the product was established as the former β -chloroketone by synthesis.

The reaction of 2-methyl-2-butene with acetyl chloride has been reported to yield the same product (29).



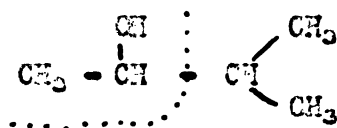
Repetition of this synthesis gave a product whose infrared spectrum was identical with that of the product from 1,1-dimethylcyclopropane. This conclusively proves the structure of the product, but also suggests an alternative method by which it might be formed; that is, the 1,1-dimethylcyclopropane might isomerize to 2-methyl-2-butene prior to acylation. This path was distinctly ruled out for cyclopropane itself, but cannot be excluded here. An increase in refractive index of 1,1,2-trimethylcyclopropane over aluminum chloride has been attributed to both an isomerization and polymerization (59). Other workers (60) report very rapid and complete polymerization of 1,1-dimethylcyclopropane in the presence of aluminum bromide even at -50° , the reaction being complete within a few minutes.

Several experiments were performed with the hope of gaining some insight regarding the mechanism of this reaction. 1,1-Dimethylcyclopropane was placed in chloroform containing aluminum chloride at 0° for one hour. Neither the cyclopropyl compound nor an isomerization product were recovered. Instead the cyclopropane was converted to a polymeric oil. When the acylation was carried out in the presence of excess

1,1-dimethylcyclopropane none of the excess was recovered, but appeared to be converted to the polymeric material. The acylation was also carried out at -50° and by inverse addition (the acylation solution is added to a chloroform solution of the cyclopropane). In both cases the yield of ketone was reduced (5%) while the amount of polymeric product increased. These experiments indicate that the acylation of 1,1-dimethylcyclopropane is accompanied by a competing reaction which produces the polymer. Perhaps milder conditions (e.g. a weaker Lewis acid catalyst) would produce a higher yield of ketone. The use of sulfur dioxide as solvent with a Lewis acid such as stannic chloride could possibly provide an ideal system for this reaction. Sulfur dioxide has been shown to be an excellent solvent for this type of reaction (51).

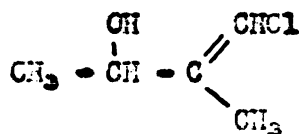
The next substituted cyclopropane whose acylation was investigated was cyclopropyl chloride, prepared by the irradiation of a mixture of cyclopropane and chlorine. It gave a slightly exothermic reaction with a 1:1 complex of acetyl chloride-aluminum chloride. Attempts to purify the product from this reaction by distillation at 3 mm. mercury gave decomposition. The structure of the initial product was therefore not established, but treatment with 10% sodium bicarbonate converted it to its dehydrohalogenation product, a distillable chloroketone, in an overall yield of 23%. The ultraviolet and infrared absorption spectra of this product were consistent with an α,β -disubstituted- α,β -unsaturated ketone. Reduction with hydrogen over platinum gave 3-methyl-2-butanol. This establishes the carbon skeleton

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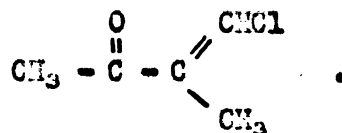


and further, shows that the product did not result from normal addition of acetyl chloride to the cyclopropane ring, which would have given n-propyl, rather than isopropyl-ethylcarbinol.

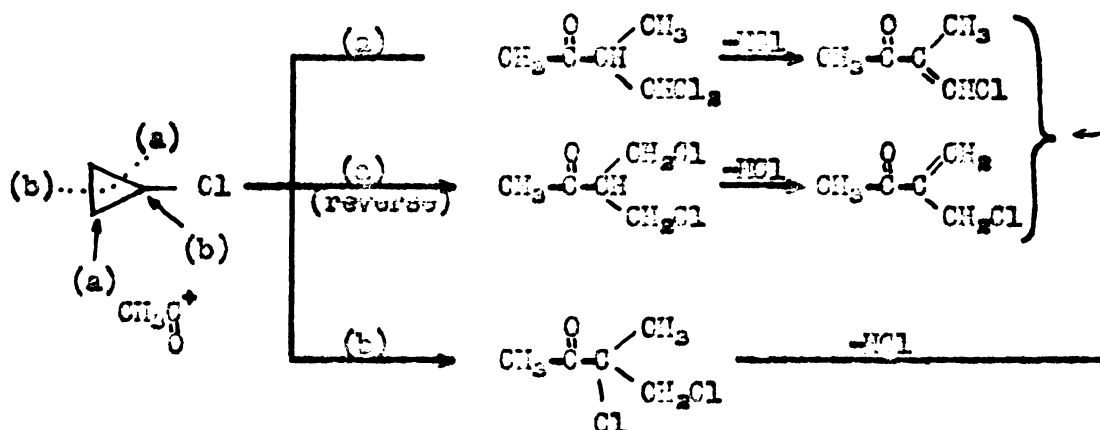
Lithium aluminum hydride reduced the ketone to a chlorine-containing unsaturated alcohol, the chlorine of which gave no precipitate with 5% alcoholic silver nitrate. Allyl chloride, under similar conditions, gave an immediate precipitate of silver chloride. These facts establish the alcohol as



and the ketone as

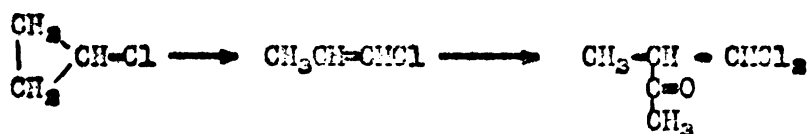


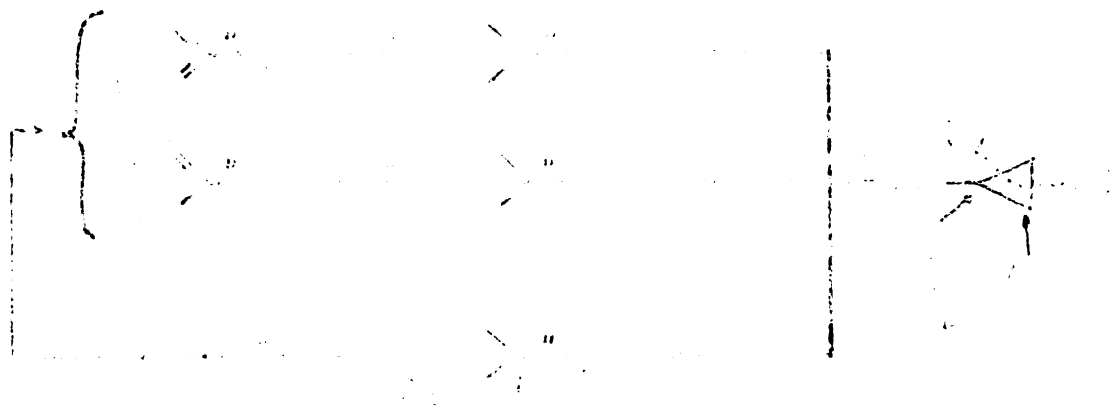
The possible products of the original acylation, again examining only those possibilities which would give the rearrangement product (i.e., β-chloroketones), are shown in the scheme:



The only path leading exclusively to the observed product is (a) which, like the 1,1-dimethylcyclopropane reaction, involves attack at the methylene and migration of the hydrogen to the least substituted of the remaining carbon atoms. Path (b), although expected to lead to two unsaturated ketones, one of which has an allylic chlorine, is not however rigorously excluded, for one of the two dehydrohalogenation products might predominate.

Prior rearrangement of cyclopropyl chloride to allyl chloride cannot lead to the observed product. Rearrangement to the vinyl chloride, followed by addition of acetyl chloride as shown, might be an alternative, though unlikely, path to the observed product.



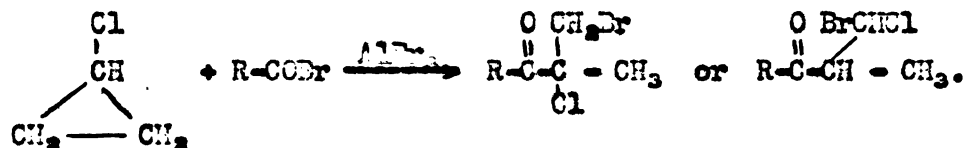


The first part of the document describes the general principles of the system. It outlines the main components and their functions, as well as the overall architecture. The text is written in a formal, technical style, typical of engineering documentation.

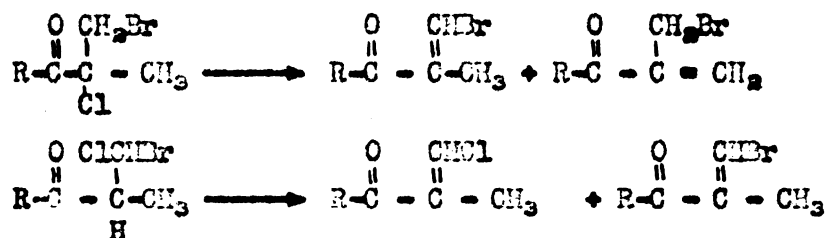
The second part of the document provides a detailed description of the system's operation. It explains how the various components interact and how the system as a whole functions. This section includes several diagrams and figures to illustrate the concepts discussed.



One possible way to decide between the alternative structures for the initial acylation product would be to study the reaction of cyclopropyl chloride with acetyl bromide; the dihaloketone product would be either a β -bromo- α -chloroketone or a β -bromo- β -chloroketone.



Dehydrohalogenation of the former would give α,β -unsaturated ketones containing bromine but free of chlorine, whereas the latter would yield a mixture of ketones containing bromine and chlorine.



The reaction of cyclopropyl chloride with acetyl chloride lead to an additional unidentified product, b.p. 62-65°, (approximately 5% yield). The infrared absorption spectrum of this material showed two carbonyl peaks. Attempts to separate the constituents by distillation were not successful.

1,1-Dichlorocyclopropane, obtained as a by-product from the preparation of cyclopropyl chloride, was acylated only with difficulty. In order to cause a reaction it was necessary to heat the chloroform solution to reflux for five to six hours. The unstable product, which was obtained

in small yield, gave an infrared absorption spectrum which indicated the presence of an unsaturated ketone. This material was not investigated further. The recovery of 67% of unreacted dichlorocyclopropane after one hour at 50° further testifies to slow reaction in this case. Such slow reaction with a highly negatively substituted cyclopropane suggests that the rate is determined by electrophilic attack (presumably by acyl carbonium ion).

In order to determine the effect of an aromatic substituent on the cyclopropane ring, the acylation of phenylcyclopropane was carried out. Phenylcyclopropane was prepared by distillation of the reaction mixture from cinnamaldehyde and hydrazine hydrate. This product was readily acylated at 0° to yield 48% of a product free of chlorine. The infrared absorption spectrum of this material was consistent with that for a disubstituted benzene ring. Oxidation with chromic acid gave terephthalic acid. The haloform reaction with bromine in 30% sodium hydroxide lead to p-cyclopropylbenzoic acid. It was thus shown that the product was p-cyclopropylacetophenone.



The formation of this product indicates that the phenyl ring is attacked in preference to the cyclopropane ring; presumably the cyclopropane ring acts as an electron donor activating the benzene ring, whereas the -I effect of the phenyl group deactivates the cyclopropane ring.

function $f(x)$ defined by the equation $f(x) = \int_0^x f(t) dt$. It is shown that $f(x)$ is a constant function. The second part of the paper is devoted to the study of the properties of the function $f(x)$ defined by the equation $f(x) = \int_0^x f(t) dt$. It is shown that $f(x)$ is a constant function. The third part of the paper is devoted to the study of the properties of the function $f(x)$ defined by the equation $f(x) = \int_0^x f(t) dt$. It is shown that $f(x)$ is a constant function.

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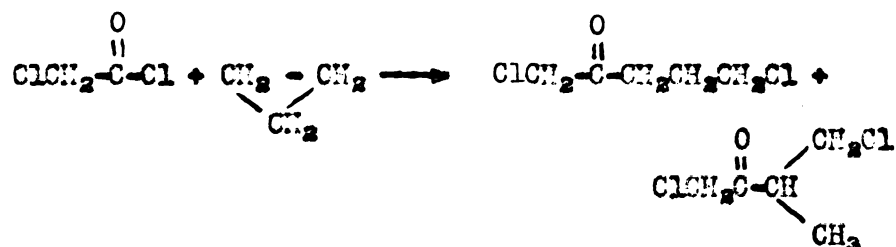
The ninth part of the paper is devoted to the study of the properties of the function $f(x)$ defined by the equation $f(x) = \int_0^x f(t) dt$. It is shown that $f(x)$ is a constant function. The tenth part of the paper is devoted to the study of the properties of the function $f(x)$ defined by the equation $f(x) = \int_0^x f(t) dt$. It is shown that $f(x)$ is a constant function. The eleventh part of the paper is devoted to the study of the properties of the function $f(x)$ defined by the equation $f(x) = \int_0^x f(t) dt$. It is shown that $f(x)$ is a constant function.

A small amount (10%) of the product obtained was a higher boiling liquid which did not crystallize, but rather formed a glass when frozen. This material had an infrared absorption spectrum characteristic of an acetophenone. The refractive index indicated that the material was a mixture and attempts to isolate its components by distillation were unsuccessful.

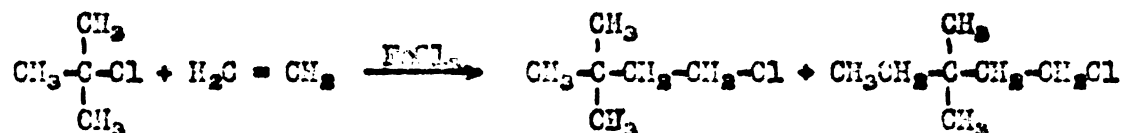
The study of this reaction by Curtis and Hart (23,24) was limited to the use of carboxylic acid chlorides containing only hydrocarbon substituents (e.g. benzoyl chloride, propionyl chloride, cyclopropanecarbonyl chloride). In order to further explore the scope and limitations of this reaction several experiments with compounds not in this category were studied.

Chloroacetyl chloride reacted readily with cyclopropane to yield 69% of a mixture of chloroketones. This material could not be fractionally distilled at 3 mm. of mercury pressure due to decomposition. It was therefore refluxed with 10% sodium bicarbonate to selectively dehydrohalogenate the β -chloroketone. The chloroketones obtained after this treatment were readily separated into two distinct fractions by distillation.

The lower-boiling product had the formula C_5H_7OCl and was reduced with hydrogen and Raney nickel to yield 3-methyl-2-butanone. Zinc and acetic acid reduced this product to 3-methyl-3-butan-2-ol, which was synthesized independently as shown in the scheme.



Two other types of compounds often used in Friedel-Crafts reactions are allyl and sulfonyl halides. Allyl halides are known to react with olefins to yield both an addition product and a product which appears to be the result of a disproportionation of the allyl chloride (55). Thus, the reaction of *t*-butyl chloride with ethylene is reported to yield 1-chloro-3,3-dimethylbutane as the principal product (55%) and 1-chloro-3,3-dimethylpentane as a by-product (6%).



The reaction of cyclopropane with *t*-butyl chloride (using the usual Friedel-Crafts alkylation conditions) gave a low yield (16%) of a mixture of alkyl halides. Analysis of several fractions showed an empirical formula of approximately $\text{C}_7\text{H}_{15}\text{Cl}$. Attempts to separate the mixture into its component parts by distillation were not successful. The boiling point rose steadily during the distillation without any clear-cut fractions.

Sulfonyl halides have been utilized only to a limited extent in Friedel-Crafts reactions and require carefully controlled conditions (62).

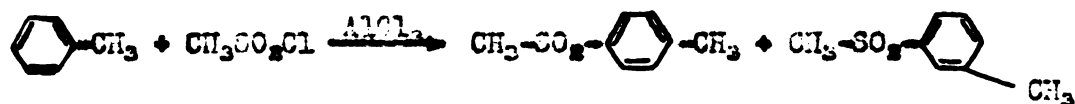


The first part of the paper discusses the importance of understanding the underlying structure of the data. This is particularly relevant in the context of machine learning, where the ability to identify patterns and relationships in the data is crucial for building accurate models. The second part of the paper focuses on the development of a new algorithm for solving the problem of finding the minimum variance unbiased estimator (MVUE) for the parameters of a normal distribution. This algorithm is based on the use of the Fisher information matrix and the Rao-Blackwell theorem. The third part of the paper discusses the application of this algorithm to the problem of finding the MVUE for the variance of a normal distribution. The fourth part of the paper discusses the application of this algorithm to the problem of finding the MVUE for the mean of a normal distribution. The fifth part of the paper discusses the application of this algorithm to the problem of finding the MVUE for the standard deviation of a normal distribution. The sixth part of the paper discusses the application of this algorithm to the problem of finding the MVUE for the standard error of the mean of a normal distribution. The seventh part of the paper discusses the application of this algorithm to the problem of finding the MVUE for the standard error of the variance of a normal distribution. The eighth part of the paper discusses the application of this algorithm to the problem of finding the MVUE for the standard error of the standard deviation of a normal distribution. The ninth part of the paper discusses the application of this algorithm to the problem of finding the MVUE for the standard error of the standard error of the mean of a normal distribution. The tenth part of the paper discusses the application of this algorithm to the problem of finding the MVUE for the standard error of the standard error of the variance of a normal distribution.

$$\frac{1}{n} \sum_{i=1}^n \frac{1}{x_i} = \frac{1}{n} \sum_{i=1}^n \frac{1}{x_i} \quad \text{and} \quad \frac{1}{n} \sum_{i=1}^n \frac{1}{x_i^2} = \frac{1}{n} \sum_{i=1}^n \frac{1}{x_i^2}$$

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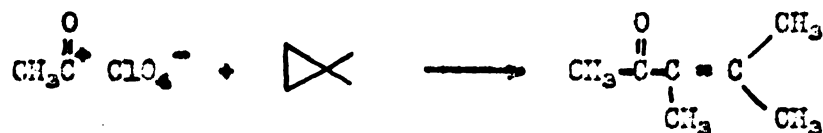
Thus toluene with methanesulfonyl chloride was reported to give methyl p-tolyl sulfone (36%) and methyl m-tolyl sulfone (15%).

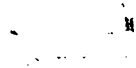
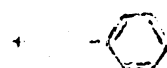


The reaction of olefins with sulfonyl halides under these conditions has not been studied.

Several experiments were performed in this work to investigate the action of sulfonyl halides with cyclopropane. Methane-, ethane-, butane- and benzenesulfonyl chlorides all failed to react.

Since the reaction of acyl halides with cyclopropanes seems to be initiated by attack of the acyl carbonium ion, it was of interest to examine this process more directly. Toward this end, acetyl perchlorate was prepared (54) from acetyl chloride and silver perchlorate in nitromethane. In this solvent, no reaction was observed with cyclopropane, but 1,1-dimethylcyclopropane gave a small amount of 3,4-dimethyl-3-penten-2-one, characterized as its 2,4-dinitrophenylhydrazone.





SUMMARY

1. The β -chloroketones from the reaction of acyl chlorides with cyclopropane are not the result of rearrangement of the γ -chloroketones, but rather appear to be direct reaction products. 5-Chloro-2-pentanone did not rearrange under acylation conditions, nor was the yield of 3-methyl-3-butanone-2-one affected by adding excess 5-chloro-2-pentanone to an acylation mixture of acetyl chloride and cyclopropane.

2. 1,1-Dimethylcyclopropane, with acetyl chloride, was shown to yield 4-chloro-3,4-dimethyl-2-pentanone, identical with the product from 2-methyl-2-butene and acetyl chloride.

3. The product from the reaction of cyclopropyl chloride with acetyl chloride was too unstable to be distilled; after dehydrohalogenation with sodium bicarbonate it gave 4-chloro-3-methyl-3-butanone-2-one. The original product was most likely 4,4-dichloro-3-methyl-2-butanone. A small amount of additional chloroketone was obtained but not identified. 1,1-Dichlorocyclopropane reacted slowly with acetyl chloride to yield a small amount of an unstable unsaturated chloroketone which was not identified.

4. Phenyl cyclopropane was acetylated to p-cyclopropyl acetophenone in good yield.

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5. Chloroacetyl chloride, with cyclopropane, gave both 1-chloro-3-methyl-3-buten-2-one and 1,5-dichloro-2-pentanone, corresponding to the rearranged and normal structures.

6. *t*-Butyl chloride reacted with cyclopropane to give a low yield of mixed alkyl halides which could not be separated. The main fractions corresponded to a molecular formula $C_7H_{15}Cl$.

7. Sulfonyl halides did not yield any significant amount of product with cyclopropane.

8. No product was isolated from the reaction of acetyl perchlorate with a cyclopropane in nitromethane, but 1,1-dimethylcyclopropane gave a small yield of 3,4-dimethyl-3-penten-2-one, isolated as its 2,4-dinitro-phenylhydrazone.

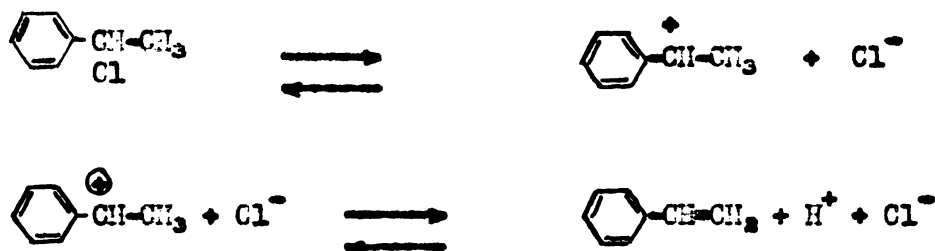
9. The mechanism of the acylation of cyclopropane has been discussed in the light of these results.

APPENDIX

The Role of Styrene in the Racemization of (1-Chloroethyl)benzene (C)

INTRODUCTION

The racemization of optically active (1-chloroethyl)benzene has been observed in polar solvents such as liquid sulfur dioxide (61) and formic acid (65) and in non-polar solvents such as carbon tetrachloride (66) or benzene (67) provided Lewis acids are present. Thus with phenol in benzene, the racemization was found to be first order with respect to phenol and first order with respect to the chloride (67). 2-(1-Chloroethyl)nositylone racemized unimolecularly even in acetone (68). Although it has been generally presumed that the racemization proceeds by a rate-determining ionization of the carbon-chloride bond, the importance of the possible equilibrium of the carbonium ion thus formed with styrene and a proton has not been evaluated, and earlier workers (69) ascribed the racemization to this equilibrium.



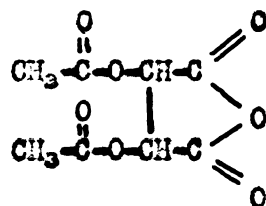
Heald and Williams (66) have shown that hydrogen chloride adds to styrene in carbon tetrachloride containing stannic chloride at a rate ($k = 123 \times 10^{-4} \text{ mol. l.}^{-1} \text{ min.}^{-1}$) which is comparable with the rate at which the chloride racemizes in the same medium ($k = 108 \times 10^{-4} \text{ mol. l.}^{-1} \text{ min.}^{-1}$). However, Böhme and Siering (70) have claimed that the rate of addition of

hydrogen chloride to styrene is too slow to explain the racemization.

In order to evaluate the importance of styrene in the racemization process, the exchange of (1-chloroethyl-2,2,2- d_3)benzene with phenol was studied. Thus, if the equilibrium involving styrene were important, the deuterium content of the chloride should decrease since the exchange between deuterium chloride and phenol is known to be rapid and extensive (71).

EXPERIMENTAL

Diacetyl Tartaric Anhydride



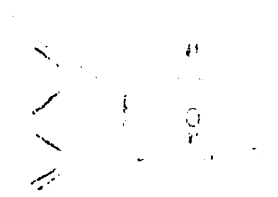
This compound was prepared by the method of Wohl and Osterlin (72). To a mixture of 220 ml. of acetic anhydride and 4 ml. of concentrated sulfuric acid was added 100 g. (0.56 mole) of tartaric acid portionwise with shaking. The mixture, which became warm during the addition, was allowed to stand for several minutes and then heated on a steam bath for one-half hour, after which time it was cooled in an ice bath. The crystals thus obtained were removed by filtration and washed with several small portions of cold benzene and dried. The product (200 g., 91%) melted at 135°. (lit. value, 135°) (72).

Preparation of Carbon Suboxide by the Pyrolysis of
Diacetyl Tartaric Anhydride



The procedure used was that described by Hurd and Pilgrim (73). A Pyrex combustion tube of one cm. inner diameter and sixty cm. length was sealed to the side arm of a 125 ml. distilling flask which was

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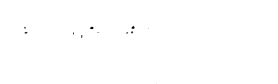


The first step in the synthesis of the compound is the reaction of the starting material with the reagent. This reaction is carried out in a round-bottom flask equipped with a magnetic stirrer and a reflux condenser. The reaction mixture is stirred at room temperature for 24 hours. The reaction is then quenched with water and the mixture is extracted with diethyl ether. The organic layer is washed with water and dried over anhydrous sodium sulfate. The solvent is removed under reduced pressure to give the intermediate compound.

The intermediate compound is then subjected to a series of reactions to yield the final product. The first reaction is a reduction of the carbonyl group using sodium borohydride. The reaction is carried out in a round-bottom flask equipped with a magnetic stirrer and a reflux condenser. The reaction mixture is stirred at room temperature for 24 hours. The reaction is then quenched with water and the mixture is extracted with diethyl ether. The organic layer is washed with water and dried over anhydrous sodium sulfate. The solvent is removed under reduced pressure to give the intermediate compound.

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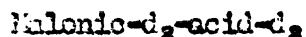
The final product is a substituted benzene ring with the following structure:



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equipped with a dropping funnel whose tip was drawn to a capillary. The combustion tube was connected to a "T-junction" so arranged that a flask was connected beneath it for collecting liquid by-products, and a water cooled condenser lead vertically from the "T". A series of two dry ice traps, which acted as receivers for the desired carbon suboxide were connected to the top of the condenser. Any gases not condensed were passed through a trap containing aniline and into the hood. The reaction tube was heated to 625-650°C. One hundred grams of diacetyl tartaric anhydride was placed in the flask and heated to 150° on an oil bath. Mercury was then added through the dropping funnel at a constant rate during 4 hours to float the liquified reagent into the pyrolysis tube. The procedure was repeated several times until a total of 30 g. of carbon suboxide was collected. The average yield of carbon suboxide was 7 to 9 g. per 100 g. of the material pyrolyzed. The carbon suboxide was stored at -73°C with a small amount of hydroquinone until a sufficient quantity was obtained for the succeeding reaction.



This compound was obtained using the procedure described by Halford and Anderson (74). Carbon suboxide (30 g., 0.44 moles) obtained in the previous step was distilled back and forth through an excess of deuterium oxide (Stuart Oxygen Co., San Francisco, Calif. 99.65%, D₂O) until all of the suboxide had reacted. A considerable amount of polymerization of

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the suboxide took place on the walls of the containers and especially at stopcocks. The excess deuterium oxide was removed by evaporation in vacuo at 30-70° and the malonic acid residue was pyrolyzed without purification.

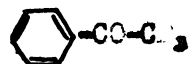
Acetic-d₃-acid-d



The method described by Halford and Andersen (74) was used. The deuterated malonic acid was thoroughly dried by heating to 100°/1 mm. in the first bulb of an apparatus consisting of two small Pyrex bulbs followed by a phosphorus pentoxide tube avoiding rubber connections. Immersion of the first bulb in an oil bath at 140-150° brought about the decomposition and the acetic-d₃-acid-d was collected in the second tube which was of the bubbler type, cooled to 0°. There was obtained 9 g. of acetic-d₃-acid-d, b.p._{1 atm.} 119-120°, a 32% yield based on the carbon suboxide used.

Acetyl-d₃-Chloride

Eight grams (0.172 equiv.) of phosphorus trichloride was added dropwise to 8.7 g. (0.136 mole) of acetic -d₃-acid-d. The mixture was warmed to 40-50° for one-half hour and the desired product, 8.6 g. (80%), was then distilled under atmospheric pressure at 51-52°.

Acetophenone- α,α,α - d_3 

To 44 g. of benzene mixed with 15 g. (0.11 mole) of anhydrous aluminum chloride was added dropwise a solution of 8.6 g. (0.106 mole) of acetyl- d_3 -chloride in 20 g. of benzene. After the addition was completed, the mixture was warmed to 50° for one hour and allowed to stand at room temperature for two hours. It was poured into 150 g. of ice and the organic layer washed with water until neutral to litmus. The benzene layer was dried over calcium chloride and decanted. After removal of the benzene at reduced pressure, 9.7 g. (76%) of the desired product, b.p. 1 atm. $193-203^\circ$, n_D^{20} 1.5350 (lit. value, n_D^{19} 1.5431), was obtained.

The product was analyzed by mass spectrograph.

Anal. Found: acetophenone- α,α,α - d_3 $90.9 \pm 0.5\%$

acetophenone- α,α,α - d_3 $9.1 \pm 0.5\%$

 α -Methyl- d_3 -benzyl alcohol

To 1.2 g. (0.0325 mole) of lithium aluminum hydride in 50 ml. of anhydrous ethyl ether, under a nitrogen atmosphere, a solution of 9.7 g. (0.031 mole) of acetophenone- α,α,α - d_3 in 20 ml. of anhydrous ether was added dropwise with stirring. The mixture was stirred for one-half hour after the addition was completed and then cooled to 0°C . Water was then added very slowly to form two layers. The ether layer was decanted and

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the water layer extracted with an additional 25 ml. of ether. The combined ethereal portions were dried over magnesium sulfate and decanted. After evaporation of the ether there was distilled 9 g. (91%) of α -methyl- d_3 -benzyl alcohol, b.p.₃ 75-80°, n_D^{25} 1.5241 (lit. value, n_D^{25} 1.5232 for the non-deuterated carbinol) (75).

(1-Chloroethyl-2,2,2- d_3)benzene



The procedure used was that described by Spliethoff (75). To 9.1 ml. (0.125 moles) of freshly distilled thionyl chloride in a 25 ml. round bottom flask was added dropwise 9 g. (0.075 mole) of α -methyl- d_3 -benzyl alcohol at room temperature. After one-half hour the excess thionyl chloride was stripped off under reduced pressure and 9.6 g. (83%) of (1-chloroethyl-2,2,2- d_3)benzene, b.p.₁₃ 75-76°, n_D^{25} 1.5248 was distilled.

(1-Chloroethyl-2,2,2- d_3)benzene with Phenol in Benzene

This experiment was carried out in the manner previously shown to racemize optically active chloride from an original rotation of -47.7° to a final rotation of -21.1° (75). Into a 4 x 1 glass-stoppered test tube equipped with a stopcock was placed 5 ml. of 4.32 M., triply distilled phenol in benzene solvent. The tube was cooled to -78° and 5 ml. of 3.5 M(1-chloroethyl-2,2,2- d_3)benzene in benzene was added. The test



the 1990s, the number of people in the world who are undernourished has declined from 1.1 billion to 800 million. The number of people who are malnourished has declined from 1.5 billion to 1 billion. The number of people who are obese has increased from 100 million to 300 million. The number of people who are overweight has increased from 100 million to 300 million. The number of people who are obese and overweight has increased from 100 million to 300 million. The number of people who are obese and overweight has increased from 100 million to 300 million.

tube was then degassed and placed in a thermostatted bath at $50^{\circ} \pm 0.5^{\circ}$. After two minutes the container was removed and shaken and then allowed to stand in the bath for a total of 34 minutes. The mixture was then poured into 25 ml. of 5 N sodium hydroxide and 25 ml. of benzene, shaken and extracted. The benzene layer was washed twice with 25-ml. portions of 3 N sodium hydroxide and 5 times with 10-ml. portions of water. The benzene solution was dried over sodium sulfate and after removal of the benzene, 1.3 g. (60% recovery) of chloride distilled, b.p.₁₂ 76° .

Mass spectrometric analyses of the deuterated compounds were carried out by Dr. C. E. Johnson and Mr. S. Meyerson of Standard Oil Company of Indiana according to a method reported by Mr. Meyerson (76).

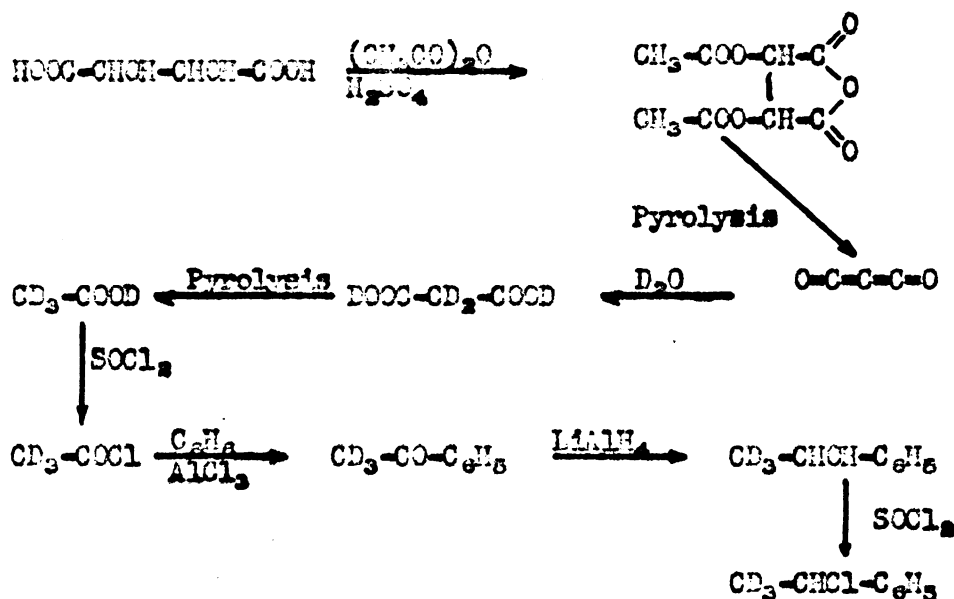
TABLE II

DISTRIBUTION EXCHANGE OF $C_3H_5CHClD_2$ (1.75 MOLAR) AND PHENOL (2.16 MOLAR)
IN BENZENE, 50°, 34 MINUTES

Species	Volume %	
	Before	After
$C_3H_5CHClD_2$	90.7 ± 0.5	90.5 ± 0.7
$C_3H_5CHClCH_2D$	9.0 ± 0.5	8.8 ± 0.7
$C_3H_5CHClCH_2D$	0.3 ± 0.1	0.7 ± 0.1
Total % of terminal hydrogens as deuterium	96.8	96.6

RESULTS

The deuterated chloride used in this study was prepared according to the following scheme:



The chloride thus obtained was allowed to go through one racemization half life. Using a deuterium isotope effect of 1.28 the time allowed was equivalent to that required for forty percent racemization for the deuterated compound. (Lewis and Coppinger (77) have shown that the k_H/k_D ratio for the acetolysis of *p*-(1-chloroethyl-2,2,2- d_3) toluene is 1.28.)

The results as shown in Table II indicate that under the conditions of these experiments, the formation of styrene as an intermediate is not important in the racemization.

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the 1990s, the number of people in the world who are undernourished has declined from 1.1 billion to 800 million. The number of people who are malnourished has declined from 1.5 billion to 1 billion. The number of people who are obese has increased from 100 million to 300 million. The number of people who are overweight has increased from 100 million to 300 million. The number of people who are obese and overweight has increased from 100 million to 300 million. The number of people who are obese and overweight has increased from 100 million to 300 million.

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...and the fact that the *Journal* is a journal of the American Psychological Association, the largest and most influential organization in the field of psychology, adds to the journal's prestige and makes it a must-read for all psychologists.

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1. *Journal of the American Medical Association*, 1990; 263: 1025-1026.

1. *Journal of the American Medical Association*, 1997; 277: 1039-1043.

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1. *Chlorophyll a* (Chl *a*)

• **Prevalence:** 10% of the population has a mental health condition.

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1. The first part of the document discusses the importance of maintaining accurate records of all transactions and activities. It emphasizes that proper record-keeping is essential for transparency and accountability, particularly in financial matters. The text outlines various methods for organizing and storing data, suggesting that digital tools can be highly effective for this purpose.

2. The second section focuses on the role of communication in project management. It argues that clear and consistent communication is the foundation of any successful team effort. The document provides several strategies for improving communication, such as holding regular meetings and using collaborative platforms. It also stresses the importance of active listening and being open to feedback.

3. The third part of the document addresses the challenges of time management. It notes that many professionals struggle to balance their workload with their personal lives, which can lead to burnout and decreased productivity. To overcome these challenges, the text recommends prioritizing tasks and creating a realistic schedule. It also suggests taking short breaks throughout the day to refresh the mind.

4. The fourth section discusses the importance of continuous learning and professional development. In a rapidly changing world, it is crucial to stay updated on the latest trends and technologies in your field. The document encourages individuals to invest in their education and skills, whether through formal courses or self-paced learning. It also highlights the value of networking and seeking mentorship from experienced professionals.

5. The final part of the document provides a summary of the key points discussed and offers some concluding thoughts. It reiterates that success is not achieved overnight and that a combination of hard work, effective communication, and a commitment to growth is necessary. The document ends with an encouraging message about the potential for a bright future ahead.

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