SOME DIARYL-ALKYL CARBINOLS AND THEIR BEHAVIOR TO THE ACTION OF ALUMINUM CHLORIDE

THESIS FOR THE DEGREE OF M. S.
Joseph R. Hradel
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A THESIS

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JOSEPH R. HRADEL

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-ACKNOWLEDGMENT-

To Dr. Ralph C. Huston the writer wishes to express his most sincere appreciation for the personal and professional counsel without which this work could not have been completed.

Joseph R. Hradel

-FOREWORD-

The fact that the aluminum chloride condensation was conceived by another and, in past years, has been the subject of many papers; also the possibility that, through oversight, credit has not been given where credit is due; the use of such an ideal abstraction as the term "I" has been omitted.

Joseph R. Hradel

-CONTENTS-

Historical:

Experimental:

-INTRODUCTION AND NOMENCLATURE-

INTRODUCTION

The subject of this paper is an outgrowth of the work of Wilsey (1), Erickson (2), and Walters (3) in this laboratory. Their attempts to prepare 1,1,1-triphenyl-alkyl hydrocarbons, the expected compounds on condensation of diphenyl-alkyl carbinols with benzene in the presence of aluminum chloride, failed.

Wilsey proved that the reaction gave an unsaturated diphenyl hydrocarbon which was identified and a small quantity of a saturated hydrocarbon which he failed to identify since it did not conform to the constants of the expected compound.

It is the subject of this paper to check the work; to further substantiate the results by condensation of carbinols identical in type but containing methyl substituted aryl substituent and carbinols containing a branched chain alkyl substituent; and if possible, to definately establish the course of the reaction since it does not fall in line with the expected.

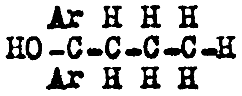
THE NOMENCLATURE

Throughout this paper the naming of compounds will be in accord with the Definitive Report of the Commission (4).

Carbinols:

$$\mathrm{HO{-}\underset{1}{C}{-}\underset{2}{C}{-}\underset{3}{C}{-}\underset{4}{C}{-}}$$

In the case of the presence of aryl groups, the name and numbering will be as in the following example:



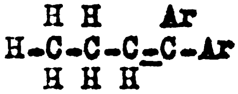
$$\begin{array}{ccccccccc} & & Ar & & H & & H & & H \\ HO & - & C & - & C & - & C & - & C-H \\ & & Ar & & H & & H & & H \end{array}$$

1,1-diaryl-butanol-1.

Unsaturated hydrocarbons:

$$\mathrm{-\underset{1}{C}{=}\underset{2}{C}{-}\underset{3}{C}{-}\underset{4}{C}{-}}$$

Hydrocarbons of this type with aryl groups will be named and numbered as follows:

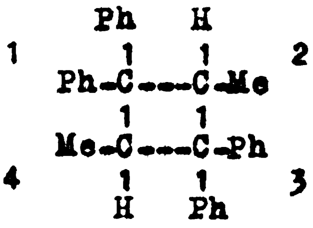


$$\begin{array}{ccccccccc} & & H & & H & & & & Ar \\ H & - & C & - & C & - & C & = & C-Ar \\ & & H & & H & & H & & \end{array}$$

1,1-diaryl-butene-1.

Cyclic hydrocarbons:

Substituted cyclic hydrocarbons containing aryl and alkyl groups, the numbering will start with the aryl as shown in the following example:



1,1,3,3-tetraphenyl-2,4-dimethyl-cyclobutane

-HISTORICAL-

Dehydration of Carbinols

It is found, on looking through the literature, that there are cases of intramolecular dehydration of carbinols by the use of heat and chemical agents. A detailed discussion of these would be too lengthy, hence they are only listed. Wagner (5), Sudborough (6), Tiffeneau (7), Schorigin (8), Masson (9), Hemilian (10), and Michael and Jeanpretre (11).

Condensation

Intermolecular dehydration has been found to take place mainly by the use of such dehydrating agents as zinc chloride: Fisher and Roser (12 and 13), Liebmann (14), and Kippenberg (15); Hydrochloric acid: Suais (16); Sulfuric acid: Bistrzycki and Flateau (17), Meyer and Wurster (18), Becker (19), Noelting (20), Gattermann and Koppert (21), Fritsch (22), and Bistrzycki and Simonis (23).

The most important agent of dehydration and the one most worked with is anhydrous aluminum chloride. It has been in use since 1882 and still holds its place as a dehydrating agent. Some of the earlier work that was carried out was by: Wass (24), Merz and Weith (25), Graebe (26 and 27), Jaubert (28), Shell and Seer (29), Frankfurter and Kritchevsky (30), Frankfurter and Kokatnur (31), and Schaarschmidt, Homann, and Szemo (32). The later and more extensive work of Huston and his Co-workers is taken up in references (33-44 inclusive).

Huston and Friedemann (33) condensed methyl phenyl carbinol with benzene in the presence of aluminum chloride to obtain 1,1-diphenylethane in a 30% yield. Also ethylphenyl carbinol was condensed to obtain 1,1-diphenylpropane in yields of 40%.

Huston (34) working with benzyl alcohol in an aluminum chloride dehydration with phenol obtained p-benzylphenol in yields of 45%. Similarly, condensation of the alcohol with anisole gave the methyl ether of p-benzylphenol and with phenetole a yield of 57% of ethyl ether of p-benzyl phenol was obtained.

Huston and Sager (35) obtained allyl-benzene in quantities of 16% in an aluminum chloride dehydration reaction between allyl alcohol and benzene.

Huston, Lewis, and Grotemut (36) condensed methylphenyl carbinol with phenol to obtain a 35% yield of p-hydroxy-1,1-diphenylethane. Ethylphenyl carbinol with phenol gave a 30% yield of p-hydroxy-1,1-diphenylpropane. Benzhydrol with phenol gave a 40% yield of p-hydroxy-triphenylmethane.

Huston, Swartout, and Wardwell (37) condensed o-cresol and benzyl alcohol to obtain three products: 4-benzyl-o-cresol, 2-benzyl-o-cresol, and 2,4-benzyl-o-cresol.

Huston and Strickler (41) condensed phenylpropyl carbinol with phenol to obtain a 20% yield of 4-(a-phenylbutyl)-phenol and a 6% yield of 2-(a-phenylbutyl)-phenol.

Huston and Houk (40) benzylated m-cresol to obtain two mono benzylated and one dibenzyl-m-cresol.

Huston and Fox (44) condensed tertiary butyl alcohol with benzene to obtain tertiary butyl-benzene in yields of 55-67%. Tertiary butyl-benzene was condensed with butyl alcohol to give 17-22% yields of p-ditertiarybutylbenzene. Tertary amyl alcohol was then condensed to give a yield of 61% tertaryamyl-benzene. Dimethyl-n-propyl carbinol with benzene gave a 44% yield of dimethyl-n-propyl-phenylmethane. Dimethyl-isopropyl carbinol with benzene gave 36% yield of dimethyl-isopropyl-phenylmethane.

-Summary-

Tertiary aliphatic alcohols, aromatic alcohols in which the hydroxyl is on the carbon adjacent to the phenyl group, and unsaturated alcohols with the double bond adjacent to the hydroxyl carbon are found to condense in the presence of aluminum chloride with benzene or, in many cases, with phenol.

-EXPERIMENTAL-

-Materials-

Benzophenone used was E.K. practical grade.

Benzoyl chloride, E.K., M.P. 0.5°.

Toluene, B.P. 109-110.5 dried over calcium chloride for a period of a week.

Benzene, (thiophene free) M.P. 5° dried over calcium chloride for one week.

Nitric acid, Red fuming, sp. gr. 158-1.6.

Ethyl bromide, E.K., practical grade but redistilled to fraction B.P. 38-40° and dried over calcium chloride.

Propyl bromide, prepared from n-propyl alcohol with sodium bromide and sulfuric acid. Fraction B.P. 70-71° was used.

Isopropyl bromide, prepared from isopropyl alcohol with sodium bromide and sulfuric acid. Fraction B.P. 59-61° was used.

Other materials used were magnesium ribbon and technical bromine.

All fractionations were carried out in a 250 x 20 mm modified Claisen column, used in standard as well as vacuo distillations.

-Carbinols-

In the preparation of carbinols of this type, considerable difficulty was experienced which made essential the modifiaction of procedure. The modification was found to work very well for all the carbinols prepared, so it may be considered as general.

PREPARATION OF 1,1-DIPHENYL-PROPANOL-1

Grignard reagent (8, 45, and 46);

A three liter three necked flask was fitted with a sealed mechanical stirrer, a reflux condenser with a drying tube of soda-lime, and a dropping funnel. The entire apparatus was then placed into a large cooling receptacle. Into the above setup were placed 25 gr. (1 mole) of cleaned magnesium ribbon, one liter of anhydrous ethyl ether, and a crystal of iodine. To the above was added, through a dropping funnel, slowly and with constant stirring, 110 gr. (1 mole) of anhydrous ethyl bromide 37-39° fraction. After the reaction had subsided, the mixture was allowed to stand for 2 to 4 hours.

Reaction with benzophenone: (47)

To the above Grignard reagent, at 10-15°, was introduced, slowly and with constant stirring, technical benzophenone dissolved in anhydrous ethyl ether until a colorless solution resulted (note 1). The mixture was allowed to stand for a period of one hour and then decomposed by slowly pouring into a four liter Erlenmeyer flask containing one Kg. of cracked ice and 100 cc of concentrated hydrochloric acid. The ether layer was then separated and allowed to evaporate spontaniously. The resulting crystalline substance was pressed free of oil on a porous plate, recrystallized three times from 95% ethyl alcohol, filtered, washed with 20 cc of ethyl ether at 0°, and dried over anhydrous magnesium sulfate in vacuo. The crystals of 1,1-diphenyl-propanol-1 were found to melt sharply at 94-94.5° and boil at 175-80°/17 mm (45 and 46), 149-151°/2 mm (note 2).

Notes

1. At the start of the addition of benzophenone, a very intense red color developed, this was lost after the addition of 150 gr. of the ketone resulting in a clear solution. The coloration is explained by Gomberg and others as due to Ketyl formation (47). It was found that reactions that gave this coloration, gave good yields of the carbinol. Those that did not give it resulted in precipitation, and on subsequent decomposition gave 100% recovery of the ketone. The coloration and increase in yield was found to be favored by a slight excess of magnesium in the Grignard reagent.

Contamination of the carbinols with ketone was found to be less if ketone addition was stopped on the disappearence of the coloration.

2. The carbinol distilled as a colorless liquid.

1,1-diphenyl-butanol-1

Was prepared in the same manner as 1,1-diphenyl-propanol-1 with the exception that 123 gr. (1 mole) of n-propyl bromide was used, B.P. 70-71°, in the preparation of the reagent. The fraction 160-65°/10 mm was found to be the carbinol (46). The carbinol was purified by crystallization from ligroin. Crystallization from alcohols resulted in the formation of compounds as a result of interation of the carbinol and the alcohol solvent, Huston and Macomber (48). The carbinol distilled as a colorless liquid 162-63°/10 mm and crystallized in white needles melting at 65°.

1,1-diphenyl-2,2-dimethyl-ethanol-1

1,1-diphenyl-isopropyl carbinol was prepared in an identical manner as the others except that 123 gr. (1 mole) of isopropyl bromide (49) fraction 59-61° was used. The reaction mixture after expulsion of the ether, was distilled resulting in the fraction 150-53°/3 mm as the carbinol.

1-phenyl-1-p-tolyl-propanol-1

In this case the ketone was phenyl-p-tolyl ketone prepared by method of Ador and Rilliet (50) M.P. 57°.

The carbinol prepared distilled as a brownish-yellow liquid at 175-80°/2 mm, 210-15°/20 mm (51).

Yields

Compound	Quant. used	% yield	gr. yield
1,1-diphenyl-propanol-1	Full	72	150.0
1,1-diphenyl-butanol-1	Full	72	163.0
1,1-diphenyl-2,2-dimethyl-ethanol-1	Full	80	180.0
1-phenyl-1-p-tolyl-propanol-1	Half	70	79.0

The yield and per cent based on runs made by the modified method.

-Condensations-

1,1-diphenyl-propanol-1 with benzene at 20°:

100 cc dry benzene was placed into a three necked 500 cc flask equipped with a mechanical stirrer and dropping funnel. To this was then added 27 gr. (1/5 mole) of aluminum chloride and allowed to stir for 15 minutes. 42.5 gr. (1/5 mole) of diphenyl ethyl carbinol were then dissolved in dry petrolium ether and introduced slowly and with constant stirring into the benzene-aluminum chloride mixture with the temperature maintained at 20°. The addition taking about an hour, stirring allowed for a period of five hours after the addition. During the addition of the carbinol much hydrochloric acid was given off and the reaction mixture was observed to change to a reddish-brown color. The reaction mixture was then poured slowly into a flask containing cracked ice and hydrochloric acid, the ether-benzene layer was separated off and dried over calcium chloride. At this point the mixture had a greenish color like that of cylinder oil. After a day of drying the mixture was distilled free of ether and benzene, the remainder fractionating into:

29 gr. ---140-45°/3 mm
5 gr. ---145-95°/3 mm
2 gr. ---195-200/3 mm
1 gr. ------------tar

The first fraction was found to be unsaturated and identified as 1,1-diphenyl-propene-1. It crystallized in five sided plates from 95% ethyl alcohol and melted at 48.5-49° sharp (45, 46, 52, 53, and 54).

The second and third fractions were combined and crystallized from hot 95% ethyl alcohol and found to be 1,1,3,3-tetraphenyl-2,4-dimethyl-cyclobutane (by analysis an molecular weight determination). The crystals are rhombic, white with a shiny luster, insoluble in petrolium and ethyl ether, slightly soluble in hot alcohol. When dissolved in cold benzene a very slight violet fluorescence results.

1,1-diphenyl-propanol-1 with benzene at 0°:

The technique of condensation was the same as used in the first condensation. Fractions obtained:

20 gr. ---140-45°/3 mm
4 gr. ---145-95°/3 mm
15 gr. ---195-200/3 mm
0 gr. ------------tar

The first fraction again being the 1,1-diphenyl-propene-1 and the second and third fractions resolving into the cyclo butane derivative.

1,1-diphenyl-propanol-1 in petrolium ether at 20°:

The condensation being the same as the others with the exception that benzene was left out. Resulted in the following:

20 gr. 1,1-diphenyl-propene-1

4 gr. 1,1,3,3-tetraphenyl-2,4-dimethyl-cyclobutane

6 gr. Tar

1,1-diphenyl-butanol-1 with benzene at 20^0:

Procedure as used before. 45 gr. carbinol, 100 cc benzene, and 27 gr. aluminum chloride. Fractions:

33 gr.---1,1-diphenyl-butene-1---155-60^0/14 mm

4 gr.---1,1,3,3-tetraphenyl-2,4-diethyl-cyclobutane
260-65^0/62 mm

5 gr.---Tar

Condensation at 0^0:

27 gr. ---155-60^0/14 mm

13 gr. ---260-65^0/62 mm

2 gr. -------------tar

1,1-diphenyl-2,2-dimethyl-ethanol-1 at 20^0

45 gr. carbinol, 100 cc benzene, and 27 gr. of aluminum chloride. Fractions:

31 gr. ---1,1-diphenyl-2-methyl-propene-1--170-75^0/3 mm

8.5 gr.---1,1,3,3-tetraphenyl-2,2,4,4-tetramethyl-
cyclobutane 215-17^0/3 mm

2 gr. ----tar

Condensation at 0^0:

23 gr. ---170-75^0/3 mm

17.5 gr.--215-17^0/3 mm

0.5 gr. ----------tar

1-phenyl-1-p-tolyl-propanol-1 at 20°:

35 gr. carbinol, 100 cc benzene, 27 gr. of aluminum chloride. Fractions:

1-phenyl-1-p-tolyl-propene-1 38 gr. ---175-80°/2 mm
1,3-diphenyl-1,3-di-p-tolyl-2,4-dimethyl-cyclobutane
3.5 gr. ---210-15°/2 mm
Tar-------------0.5 gr.

Condensation at 0°:

35.5 gr. ---175-80°/2 mm
5.8 gr. ---210-15°/2 mm
0.0 gr. -----------tar

The yields, constants and other information will be found in the tabulated data.

Yields

Condensations and Heat Effect

Unsaturated Hydrocarbons:

Compound	Condensation		Heat	
	0°	20°	Temp.	yield
1,1-diphenyl-propene-1	51.0%	75.0%	280-290	90.0%
1,1-diphenyl-butene-1	64.0%	79.0%	295-305	95.0%
1,1-diphenyl-2-methyl-propene-1	55.0%	74.0%	298-308	95.0%
1-phenyl-1-p-tolyl-propene-1	85.0%	90.5%	285-295	96.0%

Cyclic Hydrocarbons:

Cyclobutane	Condensation		Heat	
	0°	20°	Temp.	yield
1,1,3,3-tetraphenyl-2,4-dimethyl	40.0%	20.0%	280-290	8.0%
1,1,3,3-tetraphenyl-2,4-diethyl	32.0%	10.0%	295-305	3.0%
1,1,3,3-tetraphenyl-2,2,4,4-tetramethyl	42.0%	20.0%	298-308	4.0%
1,3-diphenyl-1,3-di-p-tolyl-2,4-dimethyl	13.0%	8.0%	285-295	2.0%

All unsaturated compounds soluble in ethyl and petrolium ether and cold methyl and ethyl alcohols.

All cyclobutane derivatives insoluble in cold ethyl and methyl alcohols, ethyl and petrolium ether, and are soluble in cold benzene giving a very faint violet fluorescence. Heat yield obtained by condition of distillation.

Physical Constants

Unsaturated Hydrocarbons:

Compound	M.P.	B.P.	D^{20}_{4}	N^{20}_{D}
1,1-diphenyl-propene-1	48.5-49°	280-281°	------	------
1,1-diphenyl-butene-1	-----	295-297°	1.0349	1.5794
1,1-diphenyl-2-methyl-propene-1	-----	298-299°	1.0288	1.5810
1-phenyl-1-p-tolyl-propene-1	-----	285-287°	1.0197	1.5890

The refractive index measured by the Abba Refractometer.

Cyclic Hydrocarbons:

Cyclobutane	M.P.	B.P.	From hot 95% ethyl alc.
1,1,3,3-tetraphenyl-2,4-dimethyl	104-105°	198-200°/2 mm	Small white rhombic
1,1,3,3-tetraphenyl-2,4-diethyl	175-175.5°	260-265°/62 mm	Small white needles
1,1,3,3-tetraphenyl-2,2,4,4-tetramethyl	201-201.5°	215-217°/3 mm	Small white plates
1,3-diphenyl-1,3-di-p-tolyl-2,4-dimethyl	203-204°	210-215°/2 mm	Small white needles

Distillation of cyclobutane derivatives at standard pressure was impossible because they were found to decompose.

Analysis and Molecular weights

Cyclobutanes

Analysis:

Cyclobutane	Sample gr.	CO_2 gr.	H_2O gr.	Hydrogen calc.	Hydrogen found	Carbon calc.	Carbon found
Tetraphenyl-di-methyl ($C_{30}H_{28}$)	.2164	.7357	.1408	7.20%	7.28%	92.80%	92.4%
Tetraphenyl-di-ethyl ($C_{32}H_{32}$)	.2049	.6911	.1406	7.75%	7.68%	92.25%	92.0%
Tetraphenyl-tetra-methyl ($C_{32}H_{32}$)	.2002	.6774	.1581	7.75%	7.72%	92.25%	92.3%
Diphenyl-di-p-tolyl-dimethyl ($C_{32}H_{32}$)	.2004	.6767	.1591	7.75%	7.77%	92.25%	92.1%

Carbon and hydrogen analysis made according to the method described by Fisher (55).

Molecular Weights:

Cyclobutane	Calculated	Observed 1	Observed 2
Tetraphenyl-dimethyl-	388.22	385.00	394.00
Tetraphenyl-diethyl-	416.26	400.00	414.00
Tetraphenyl-tetramethyl-	416.26	418.00	422.00
Diphenyl-di-p-tolyl-di-methyl-	416.26	424.00	419.00

Molecular weight determinations made by boiling point method described in Findlay (56).

-Summary-

An increase in temperature shows a marked increase in the formation of the unsaturated derivative in all cases.

The carbinol when subjected to the normal distillation temperature of its respective unsaturated derivative, underwent dehydration without the presence of aluminum chloride. The cyclobutane derivatives were formed as well as the unsaturated hydrocarbons.

In condensations, a decrease in temperature resulted in an increase in the formation of cyclic hydrocarbons. Increase in temperature with the presence of aluminum chloride favored the formation of tar.

The presence of branched chain alkyl group in the carbinol favored the formation of cyclic hydrocarbons on condensation, while the presence of methyl substituted aryl groups had the reverse effect.

Bromination of Unsaturated Hydrocarbons

Into a small R.B. flask 250 cc fitted with a mechanical stirrer and placed into an ice bath, were placed 5 gr. 1,1-diphenyl-propene-1 from a constant boiling fraction 280-280.5° in 20 cc of dry chloroform. To the above mixture was added a 1.3 cc quantity of bromine in 10 cc of chloroform. During the early part of the addition, complete decolorization was observed to take place. After allowing the mixture to stand for 12 hours, during which time HBr was given off in considerable quantities, the chloroform was evaporated off on a steam bath. The remainder, a dark brown liquid, was subjected to many fractionations and a month of cooling, and resolved into crystals of the bromo derivative.

Table of constants and analysis will be found on the next page.

Crystallization of these compounds is very difficult since they are found to decompose on standing in liquid form. Two of the derivatives are known to be solid, the diphenyl propene and the diphenylmethyl propene. It is predicted they all are solid though only the diphenyl propene derivative could be crystallized. Fractionation and seeding with the lower bromo homolog failed.

All bromo derivatives were prepared in a similar manner to the above, 1:1 molar proportions being used in all cases.

Constants and Analysis

Constants:

Compound	M.P.	B.P.	Description
2-bromo-1,1-diphenyl-propene-1	48-49°	171-172°/14 mm	White needles
2-bromo-1,1-diphenyl-butene-1	---	175-178°/2 mm	Yellow liquid
3-bromo-1,1-diphenyl-2-methyl-propene-1	---	183-185°/2 mm	Yellow liquid
2-bromo-1-phenyl-1-p-tolyl-propene-1	---	195-200°/11 mm	Yellow Liquid

Fractionation at standard pressure could not be carried out due to decomposition.

Analysis for bromine:

Compound	Formula	Calc.	found
2-bromo-1,1-diphenyl-propene-1	($C_{15}H_{13}Br$)	29.30%	29.16%
2-bromo-1,1-diphenyl-butene-1	($C_{16}H_{15}Br$)	27.80%	27.57%
3-bromo-1,1-diphenyl-2-methyl-propene-1	($C_{16}H_{15}Br$)	27.80%	27.42%
2-bromo-1-phenyl-1-p-tolyl-propene-1	($C_{16}H_{15}Br$)	27.80%	27.50%

Bromine analysis made by Parr bomb according to the procedure of Fisher (57).

Nitration of Cyclic Hydrocarbons

Nitrations were carried out according to the method of Gomberg (58 and 59) who states that all phenyl groups are nitrated in the para position.

1 gr. of hydrocarbon is treated with 15 gr. of fuming nitric acid (sp. gr. 1.58-1.6) at a temperature of 0°. The hydrocarbon is added to the nitric acid very slowly. After nitration is complete, (repeated nitrations may be required) the nitro derivative is removed from the acid by dilution with water at 0°, filtered, washed free of acid, and allowed to dry.

Gomberg designates that three nitrations be used, he does not state the concentration of the acid he used. These hydrocarbons were found to nitrate completely on one nitration. Several nitrations were used to make sure that complete nitration had taken place.

Cyclobutane	M.P.	Description
1,1,3,3-tetra-(p-nitro-phenyl)-2,4-dimethyl-	94-95°	Yellow powder
1,1,3,3-tetra-(p-nitro-phenyl)-2,4-diethyl-	135-36°	Dk yel powder
1,1,3,3-tetra-(p-nitro-phenyl)-2,2,4,4-tetramethyl-	265-67° D	Lt yel powder
1,3-di-(p-nitro-phenyl)-1,3-di-p-tolyl-2,4-dimethyl-	Dec. 240°	Lt yel powder

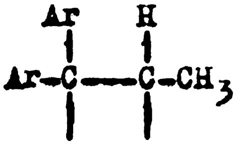
Distillation in vacuo resulted in decomposition.

-DISCUSSION-

As to an explaination, why these carbinols act the way they do as a result of the effects of aluminum chloride and heat, may be shown by several facts.

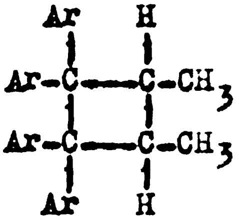
According to the literature, intramolecular dehydration of carbinols of this type have been known for some time. The fact that this dehydration will take place shows that there must be a distorted condition within the molecule. This distortion may be looked upon as, the hydrogen of the beta and the hydroxyl of the alpha carbon atoms being rendered highly mobile as a result of the influence of the two aryl substituents.

The cyclobutane formation, however, can not be conclusively explained from the standpoint of intramolecular dehydration. If such be the case, the only explaination possible would be the formation of a free radical with unsatified bonds on two adjacent carbon atoms:

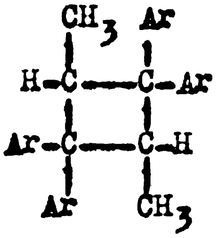


$\mathrm{Ar_2C{-}CH{-}CH_3}$

which, if possible, on combination of two such free radicals should give us two possible cyclobutanes:

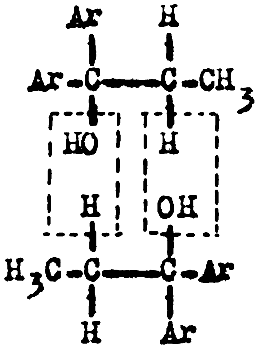


and



the possibility of the first case being very slight since there are too many like charged and bulky groups on one side of the molecule.

Another explaination of cyclobutane formation, one which seems very possible since the yields are quite low, would be:



an intermolecular dehydration as shown. The position of the aryl sustituents being favored by the fact that there is a repulsion of the like charged aryl groups and an attraction between positive hydrogen and negative hydroxyl.

-SUMMARY-

The aryl-alkyl carbinols are found not to react to conditions of intermolecular dehydration between carbinol and benzene.

These carbinols are found to dehydrate intramolecularly to form unsaturated diaryl hydrocarbons, and intermolecularly to form aryl-alkyl substituted cyclobutanes.

The effect of heat is the same as the effect of aluminum chloride but favors intramolecular dehydration. The formation of cyclobutane derivatives as a result of heat effect is very slight, though present.

Branched chain alkyl and methyl substituted aryl substituents in carbinols of this type as well as the diphenyl alkyl carbinols will not condense with benzene in the presence of aluminum chloride.

Considerable difficulty was encountered in the isolation of the compounds prepared. The fractions, though well defined, required twenty to thirty fractionations and repeated fractional crystallization before any state of purity could be attained.

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