

PRODUCTS AND RATES OF THE REACTION
OF SELECTED ARYL CHLOROFORMATES
WITH SILVER NITRATE

Thesis for the Degree of Ph. D.
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Matthew J. Zabik
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This is to certify that the

thesis entitled

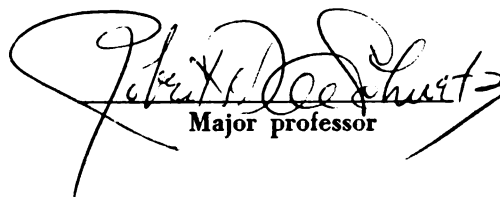
PRODUCTS AND RATES OF THE REACTION
OF SELECTED ARYL CHLOROFORMATES
WITH SILVER NITRATE

presented by

Matthew J. Zabik

has been accepted towards fulfillment
of the requirements for

— Ph. D. degree in Chemistry



Major professor

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ABSTRACT

PRODUCTS AND RATES OF THE REACTIONS OF SELECTED ARYL CHLOROFORMATES WITH SILVER NITRATE

by Matthew J. Zabik

The purpose of this investigation was to obtain information concerning the nature of the reactions of aryl chloroformates with silver salts including product analyses, reaction kinetics, and mechanistic studies. Thirteen aryl chloroformates were prepared by the reaction of phosgene with the appropriate phenol. The product studies and reaction kinetics of the reaction of the aryl chloroformates with silver nitrate were conducted in acetonitrile as a reaction medium. The reaction kinetics were determined for the 4-substituted phenyl chloroformates with equal molar concentrations of reactants and also in the presence of excess silver nitrate.

The products obtained in high yield from the reaction of the 4-substituted phenylchloroformates (4-methoxy, 4-methyl, 4-phenyl, 4-bromo, 4-chloro, 4-nitro) with silver nitrate were the 4-substituted-2-nitro phenols. From the interaction of 2,6-disubstituted phenylchloroformates (2,6-dimethyl, 2,6-diisopropyl) with silver nitrate, two products

were obtained; the expected 4-nitro-2,6-disubstituted phenols and biphenyl quinones. The 2,4,6-trisubstituted phenylchloroformate (2,4,6-trimethyl) on reaction with silver nitrate yielded substituted stilbenequinones as the major product. The α - and β -naphthylchloroformates on treatment with silver nitrate yielded 2-nitro-1-naphthol and 1-nitro-2-naphthol, respectively, as the major products.

At equal molar concentrations the initial rates of reaction of the 4-substituted phenylchloroformates with silver nitrate at 10, 21, and 31° were found to be second order. In the presence of a five-fold molar excess of silver nitrate, the initial rates at 21° were determined to be pseudo first order. This was accepted as good evidence that the rate determining step is the initial reaction of the 4-substituted phenylchloroformate with silver nitrate to form a nitro-carbamate.

The energy of activations determined in the rate controlling step of the reaction of the 4-substituted phenyl chloroformates with silver nitrate varied from 8.0 kcal/mole for the 4-nitro to 18.8 kcal/mole for the 4-methoxy substituent. The change in entropy, ΔS , for the same reactions were found to be negative and ranged from -40.7 for the 4-nitro to -5.1 for the 4-methoxy substituent. A plot of the Hammett equation, $\log \left(\frac{k}{k_H} \right)$ versus σ , for the reaction of the 4-substituted phenylchloroformates gave good straight line

plots with positive slopes, ρ , which had values of 1.5017 at 10°, 1.1482 at 21°, and 0.9211 at 31° for the reactions at equal molar concentrations of reactants and 0.9383 at 21° for the reaction in excess silver nitrate. This indicates a negative charge was developed in the transition state. The isokinetic temperature was determined to be 52° which is well above the highest reaction temperature used in the present investigation.

Several cursory investigations involving the reactions of 4-substituted phenylchloroformates with silver acetate and silver trifluoroacetate are also described.

PRODUCTS AND RATES OF THE REACTION OF SELECTED
ARYL CHLOROFORMATES WITH SILVER NITRATE

By
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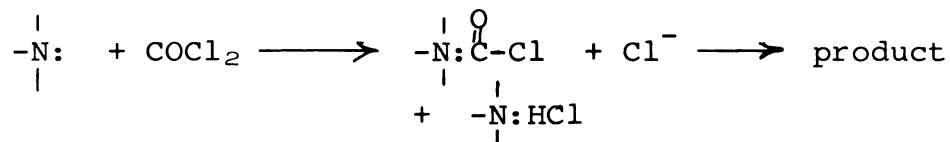
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INTRODUCTION

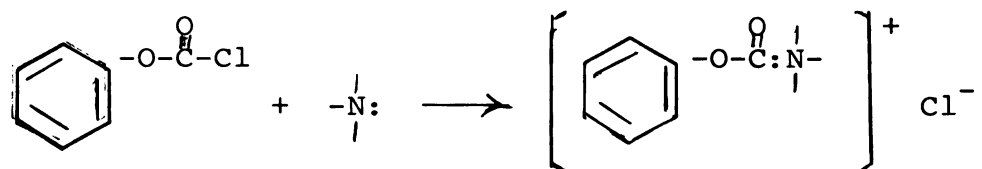
Although considerable research has been reported on aryl chloroformate, very little investigational work has been done with reactions of aryl chloroformates with inorganic salts. Wolfrom and Chaney (1) in 1960, reported on an attempt to prepare phenyl nitrate by the interaction of phenylchloroformate with silver nitrate. These investigators obtained o-nitrophenol in a 65% yield as a rearrangement product instead of the expected aryl nitrate. Since their initial article, no other reports concerned with this type of aromatic chloroformate rearrangement reaction have appeared in the literature. The purpose of the present investigation was to obtain information concerning the nature of the reactions of aryl chloroformates with silver salts including product analysis, reaction kinetics, and mechanistic studies.

The aryl chloroformates were conveniently prepared (2,3) by the addition of dimethylaniline to a stirred solution of phenol and liquid phosgene in benzene as a reaction media. The products are obtained pure by distillation or recrystallization. The tertiary amine is essential for the reaction to occur at a reasonable rate. Mechanistically it has been postulated (4) that the amine initially forms a complex with phosgene in addition to binding with the

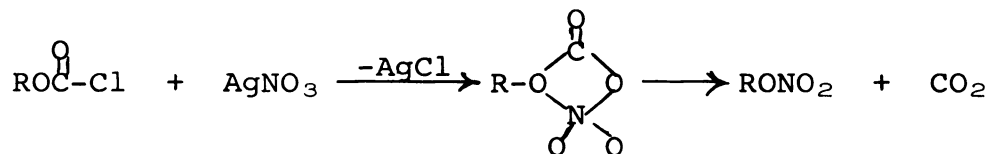
hydrogen chloride



reaction product. It has also been found that aryl chloroformates react with tertiary amines to yield a complex.



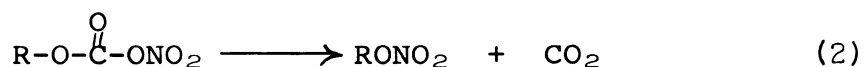
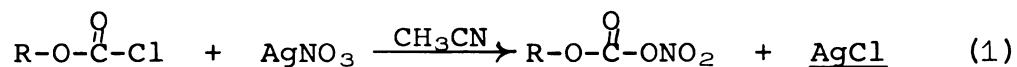
In contrast to the lack of information on the aryl chloroformates, considerable research has been reported on the reactions of aliphatic chloroformates. Some of this work has a direct bearing on the reactions of aryl chloroformates with silver salts. In 1959 Boschan (5) reported the preparation of aliphatic nitrate esters in high yields by the reaction of silver nitrate with aliphatic chloroformates. He determined that 75% of the R-O bond in the chloroformate remained intact by O^{18} labeling experiments and that the reaction proceeded mainly with retention of configuration (70% retention, 30% inversion) in the R group.



Hence, it was postulated that an $\text{S}_{\text{N}}\text{i}$ -type of decomposition of the intermediate was operative. Some reaction was thought to occur by an ionic mechanism as shown in the following equation.

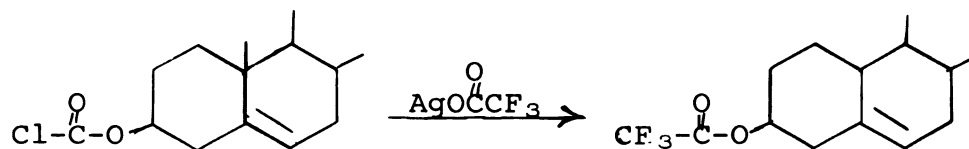


Mortimer (6) found in a study of alkyl nitratocarbonates that reaction 2 roughly paralleled reaction 1 at moderate

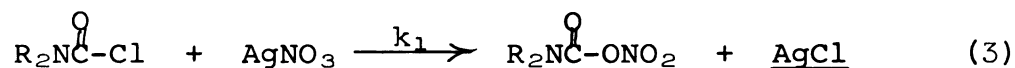


temperatures (40°), but was considerably slower than reaction 1 at temperatures below 0°. However, reaction 1 was too slow at temperatures below 0° to be of practical value. He further reported that pyridine was an excellent catalyst for the metathesis in step 1 of the overall reaction. In a reaction conducted at -17° and examined by vapor phase chromatography it was shown that only 40% of the chloroformate had reacted after two hours and that no carbon dioxide evolution had been initiated. This indicated that reaction 1 was taking place but not reaction 2. When the reaction temperature was allowed to reach room temperature, he found only nitrate product (100%) and thus reaction 2 must have occurred at the higher temperature.

Boschan (5) further reported that cholesteryl chloroformate reacts with silver trifluoroacetate to yield cholesteryl trifluoroacetate (77%). This is another example of a chloroformate reacting with silver salt to yield a rearranged product.



An additional example of a similar type of a rearrangement reaction is that reported by Norris (7) in which dialkylcarbamyyl chlorides react with silver nitrate to give dialkylnitramines (14-48%) as the main product. He further determined the rate determining step to be



represented by equation (3) with a value of 1.5×10^{-2} l/mole sec at 38.90° , for the rate constant k_1 .

In all the aliphatic chloroformate rearrangement reactions reported, it was postulated that the reaction proceeded in two steps; reaction of the nitrate ion with the chloroformate to yield a nitratocarbamate and silver chloride followed by rearrangement of the nitratocarbamate to yield the nitrate ester and carbon dioxide.

RESULTS AND DISCUSSION

I. Preparation of Aryl Chloroformates

The aryl chloroformates were conveniently prepared, in half molar quantities, by the addition of N,N-dimethylaniline to a stirred solution of the phenol and phosgene in benzene as a reaction media. The benzene layer obtained on addition of cold water to the reaction mixture was washed with dilute hydrochloric acid, dilute sodium hydroxide, water, and then dried over anhydrous magnesium sulfate. Distillation of the aryl chloroformates with the exception of p-nitrophenylchloroformate gave yields of pure products in the range 85.4-98.8%. The lower yields were obtained with the more hindered phenylchloroformates. Attempts to distill p-nitrophenylchloroformate were unsuccessful even though the literature (8) reports a boiling point for this material. On two successive attempts to distill this compound at high vacuum (0.1 mm) the product decomposed violently. However the material was readily recrystallized from petroleum ether (70.2%). The use of the tertiary amine as a catalyst in the reaction is necessary to have any reasonable reaction rate since in its absence the starting phenol is quantitatively recovered. Table (I) summarizes the physical properties

Table I. Physical Data for the Aryl Chloroformates

Chloroformate	B.p., °C/mm Hg	M.p., °C	n_D^{20}	$\bar{\nu}_{C=O}$ cm ⁻¹	Yield %	Reference
p-Methoxyphenyl	49/0.27	--	1.5110	1778	96.3	--
p-Methylphenyl	109/30.0	--	1.5110	1780	98.1	9
p-Phenylphenyl	120/4	39-40	--	1780	91.8	10
Phenyl	83/12	--	1.5007	1780	96.7	11
p-Bromophenyl	80/2.0	--	1.5583	1780	91.8	--
p-Chlorophenyl	108/19.0	--	1.5401	1769+1788	95.1	12
p-Nitrophenyl	159-162 ^a /19.0	81-81.5 ^b	--	1765	70.2	8
2,4,6-Trimethyl- phenyl	46/3	--	1.5114	1777	95.5	--
2,6-Dimethylphenyl	71-72/5.5-6.0	--	1.4993	1777	85.4	13
2,6-Diisopropylphenyl	89/2.8	--	1.5001	1781	98.8	--
α -Naphthyl	130-2/5.0	--	--	1778	82.8	12
β -Naphthyl	158/9.7	65-65.5	--	1777	92.0	14

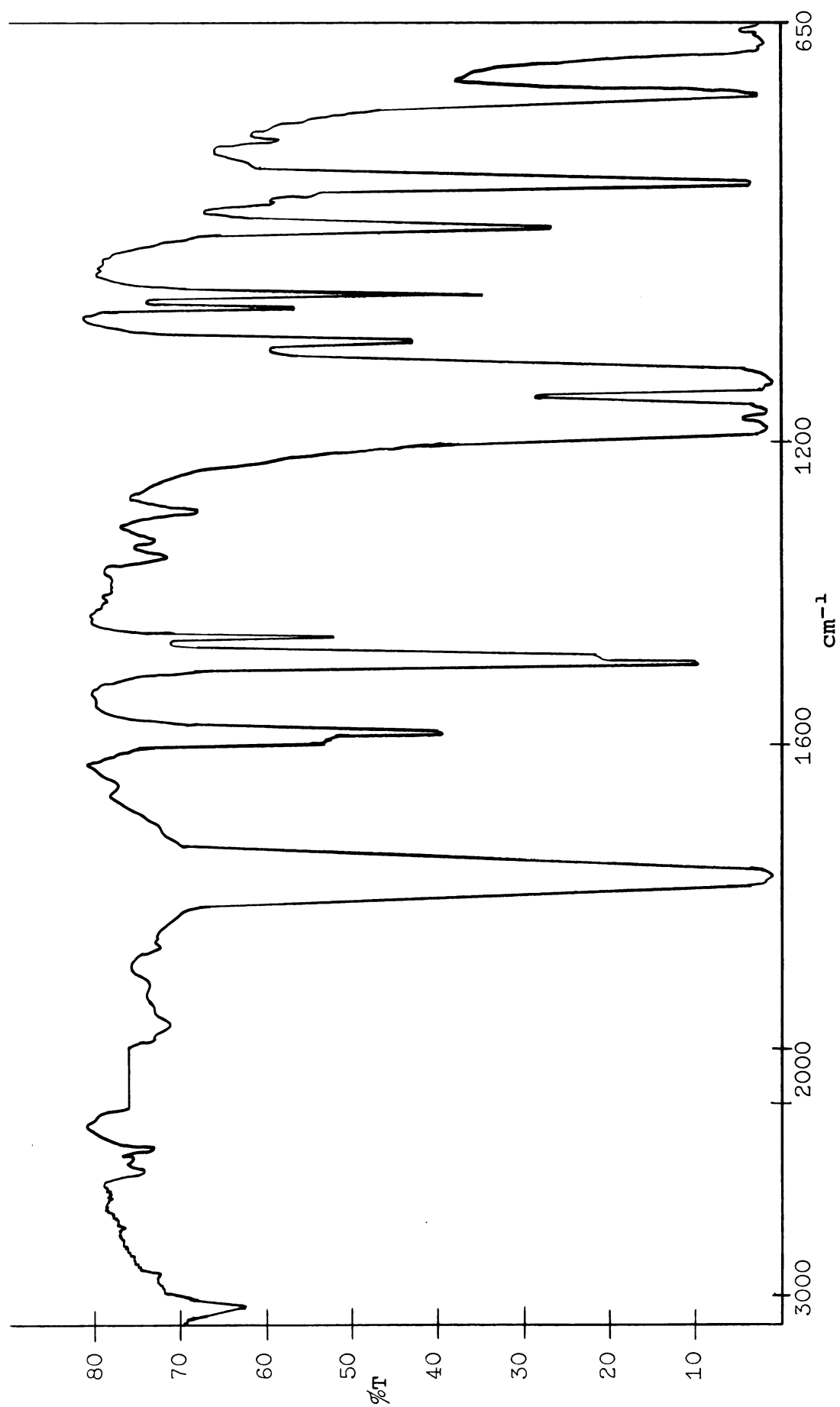
^aUnderwent violent decomposition in an attempt at distilling.^bRecrystallized from petroleum ether.

and the spectra 1-13 give the infrared spectra for the aryl chloroformates prepared in the course of this investigation.

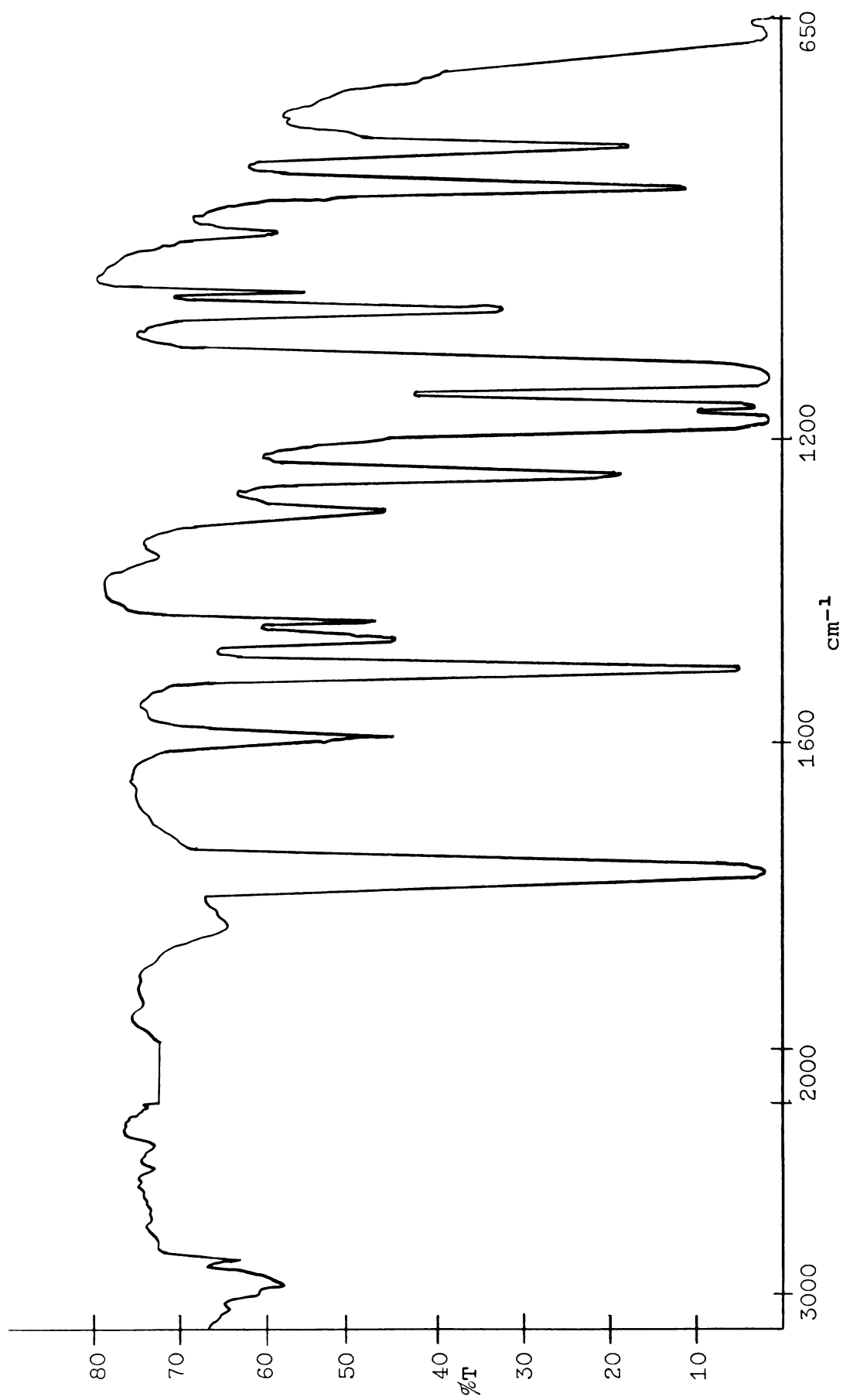
II. Product Analyses

A. Products from the Reaction of Phenylchloroformates with Silver Nitrate

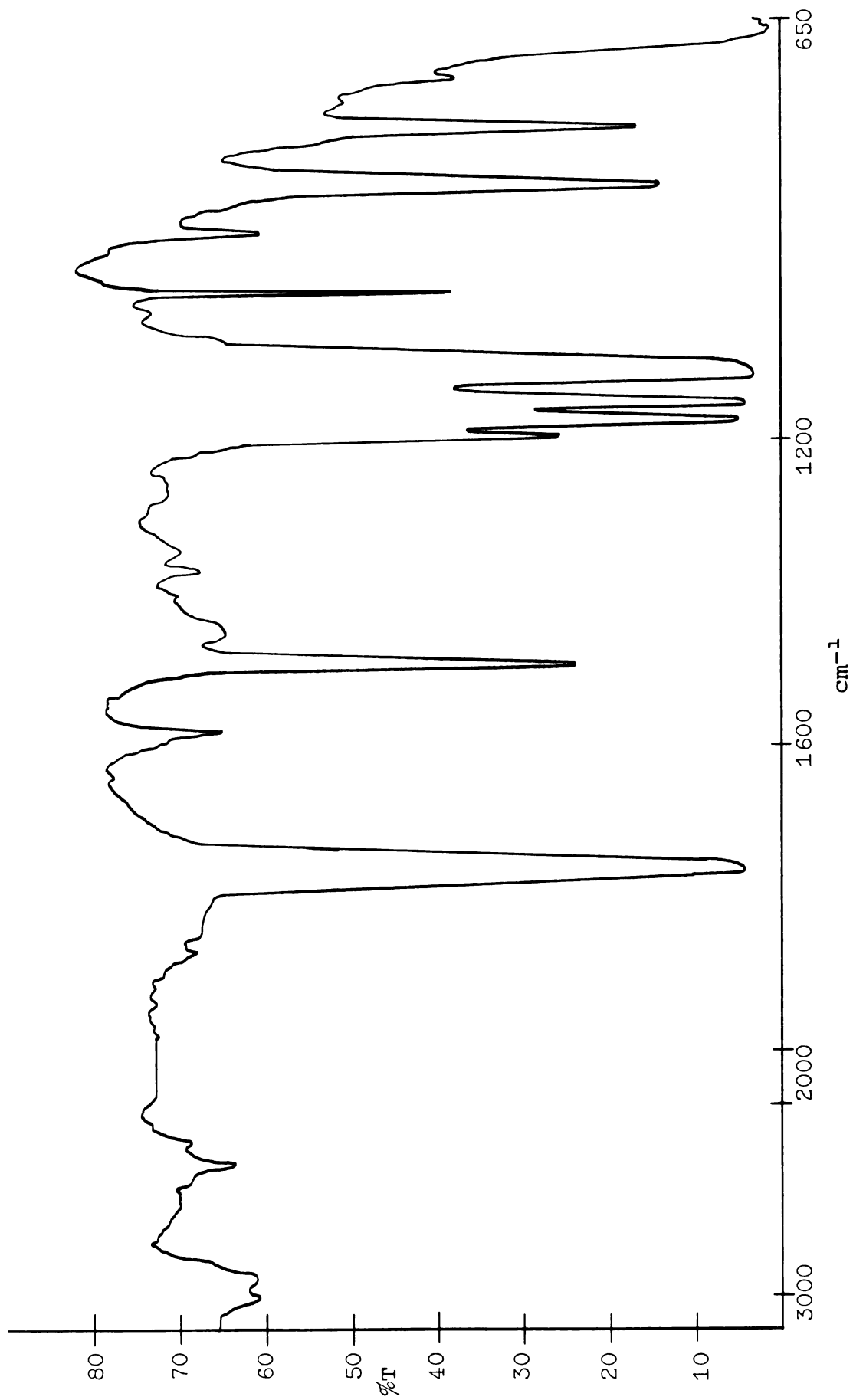
The reaction of phenylchloroformate with silver nitrate was reinvestigated to determine whether o-nitrophenol was the only product obtained as reported by Wolfrom and Chaney (1). The reaction was conducted on a 0.1 mole scale, at 20°, using acetonitrile as the reaction solvent. In subsequent reactions, acetonitrile was the choice of reaction solvents since it dissolves both the chloroformate and the silver nitrate resulting in a homogeneous reaction solution. The reaction can be run in a heterogeneous (ether) manner but the results are not as reproducible. The acetonitrile solution of the products obtained from the reaction was diluted to a specific volume and a 10 ml. aliquot was chromatographed on an alumina column using anhydrous ethyl ether as the elutant. The initial band from the column was light yellow and was established as o-nitro phenol. On further elution a second yellow band was obtained which was identified as p-nitro phenol. The percent of each isomer present varied from 65-70% and 15-20% of o- and p-nitro phenol, respectively. The yields of carbon dioxide and silver chloride obtained were 95.2% and 98.6%, respectively. No meta nitro phenol



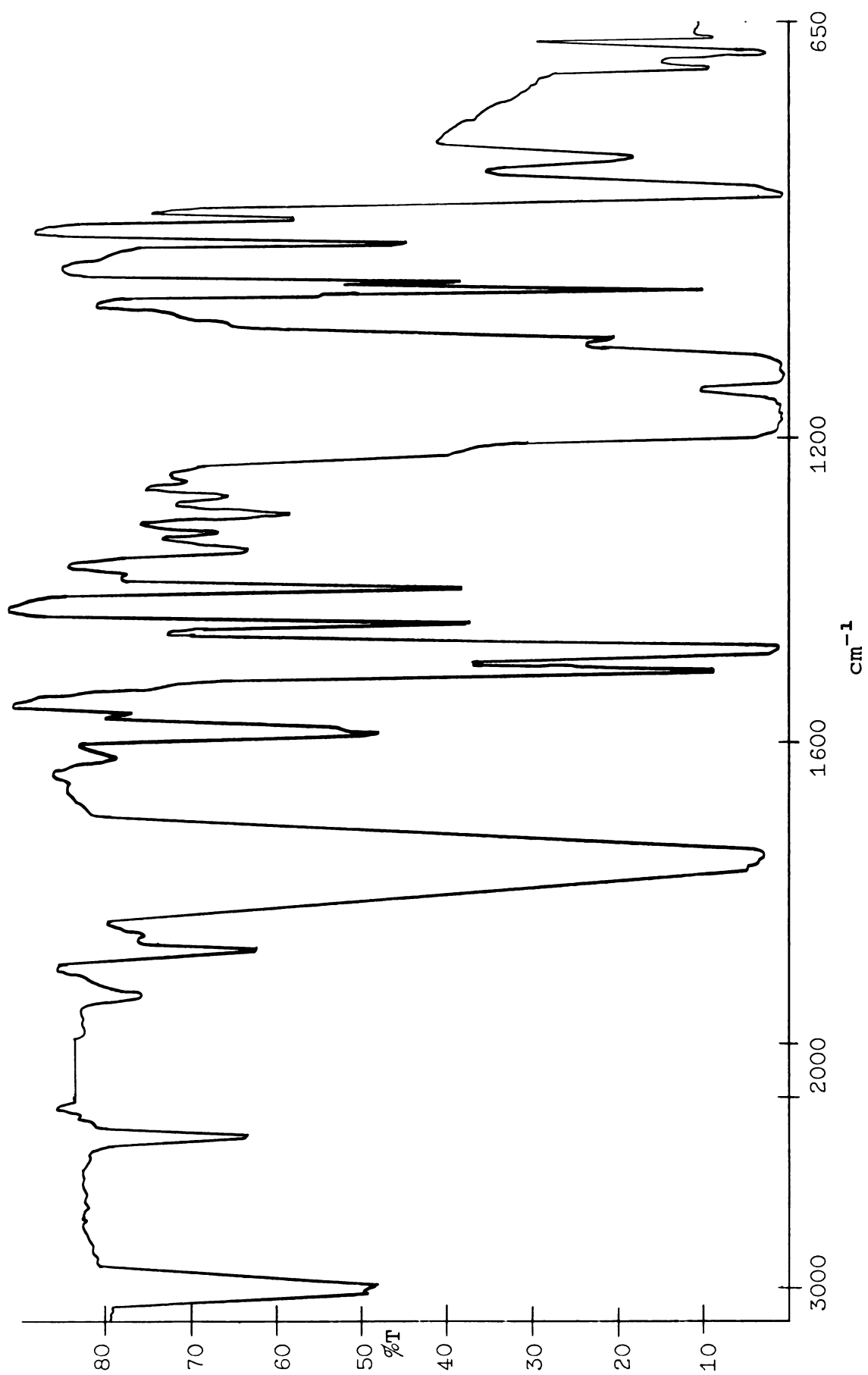
Infrared Spectrum 1. Phenylchloroformate



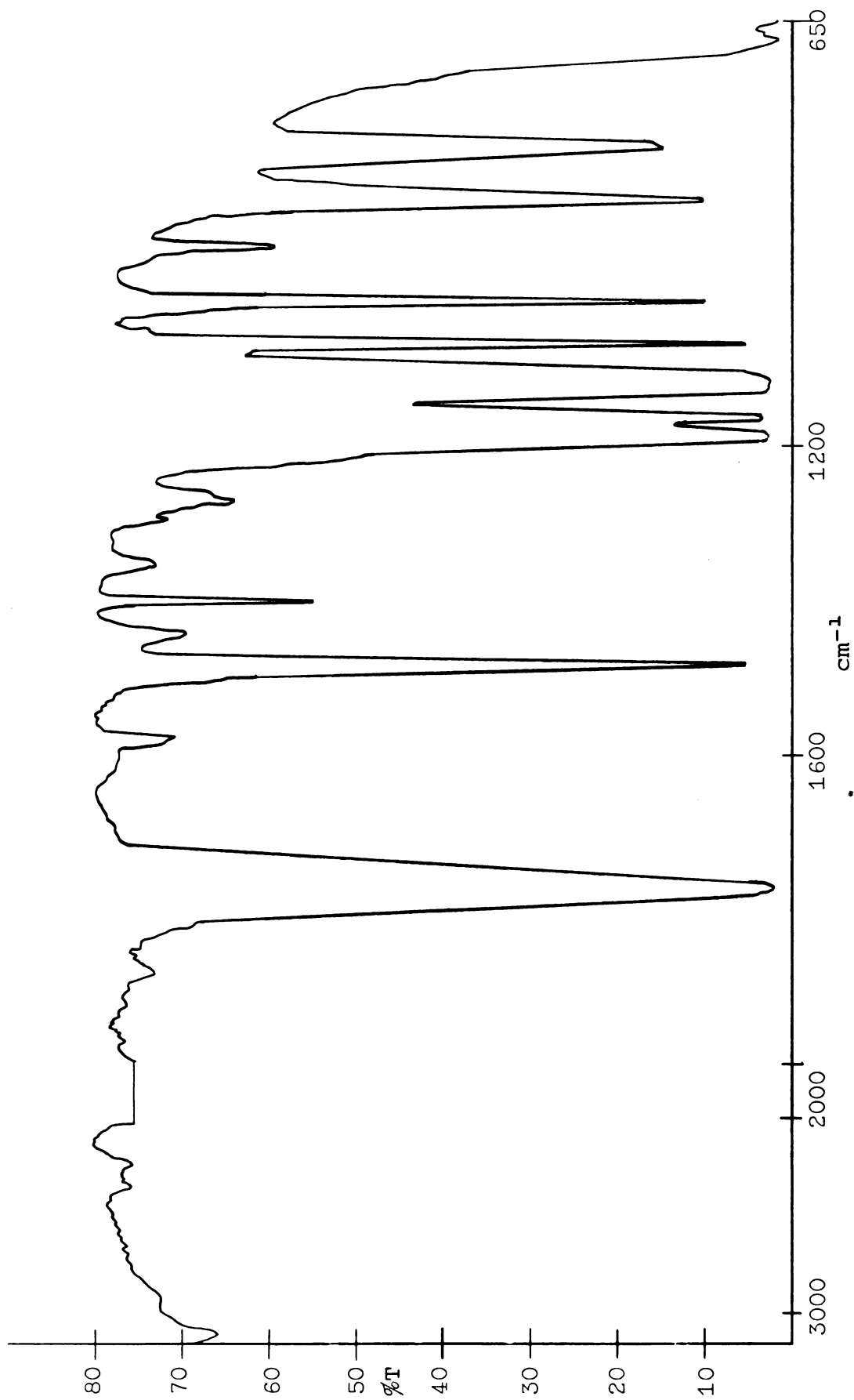
Infrared Spectrum 2. p-Methoxyphenylchloroformate



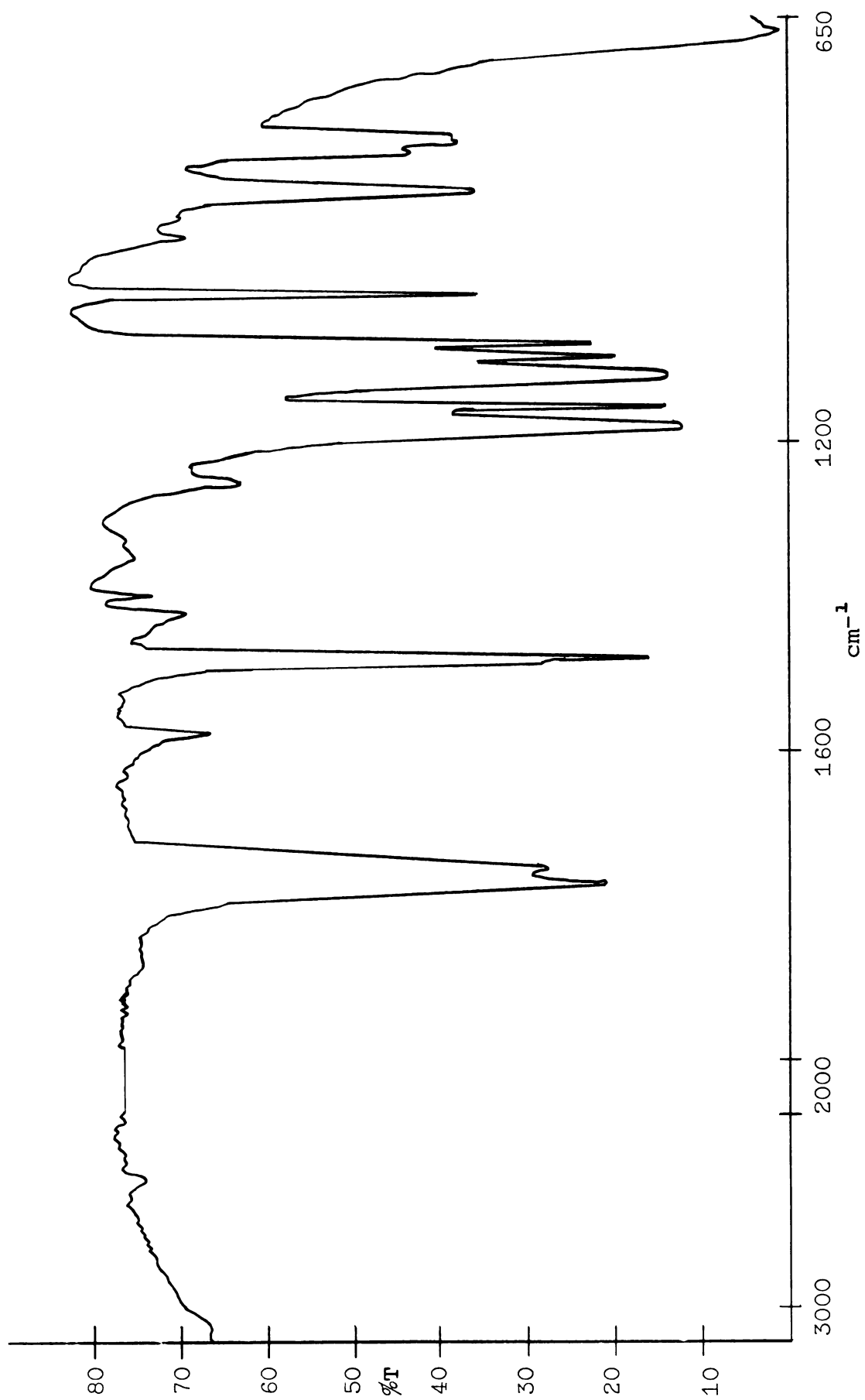
Infrared Spectrum 3. p-Methylphenylchloroformate



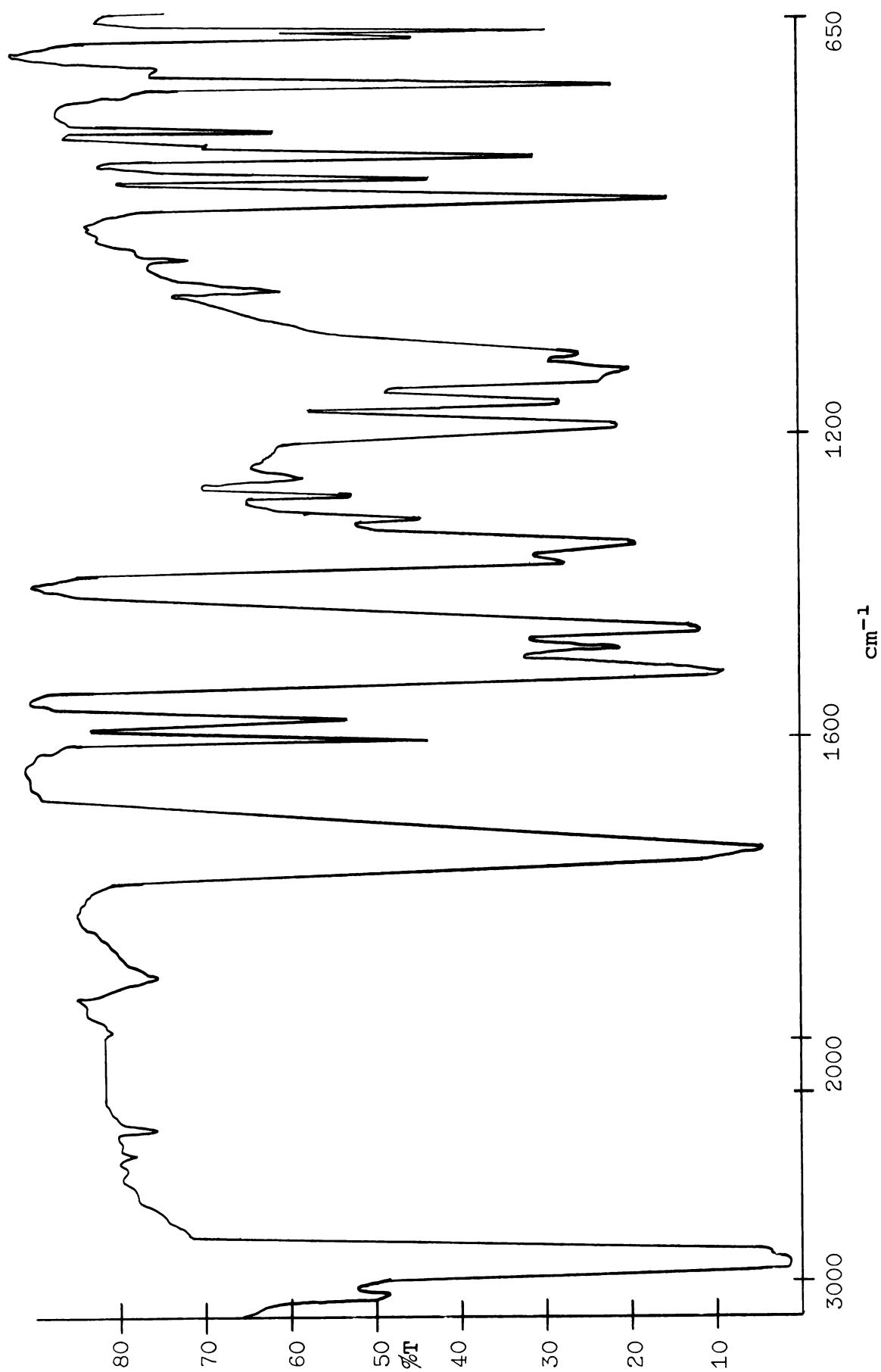
Infrared Spectrum 4. p-Phenylphenylchloroformate



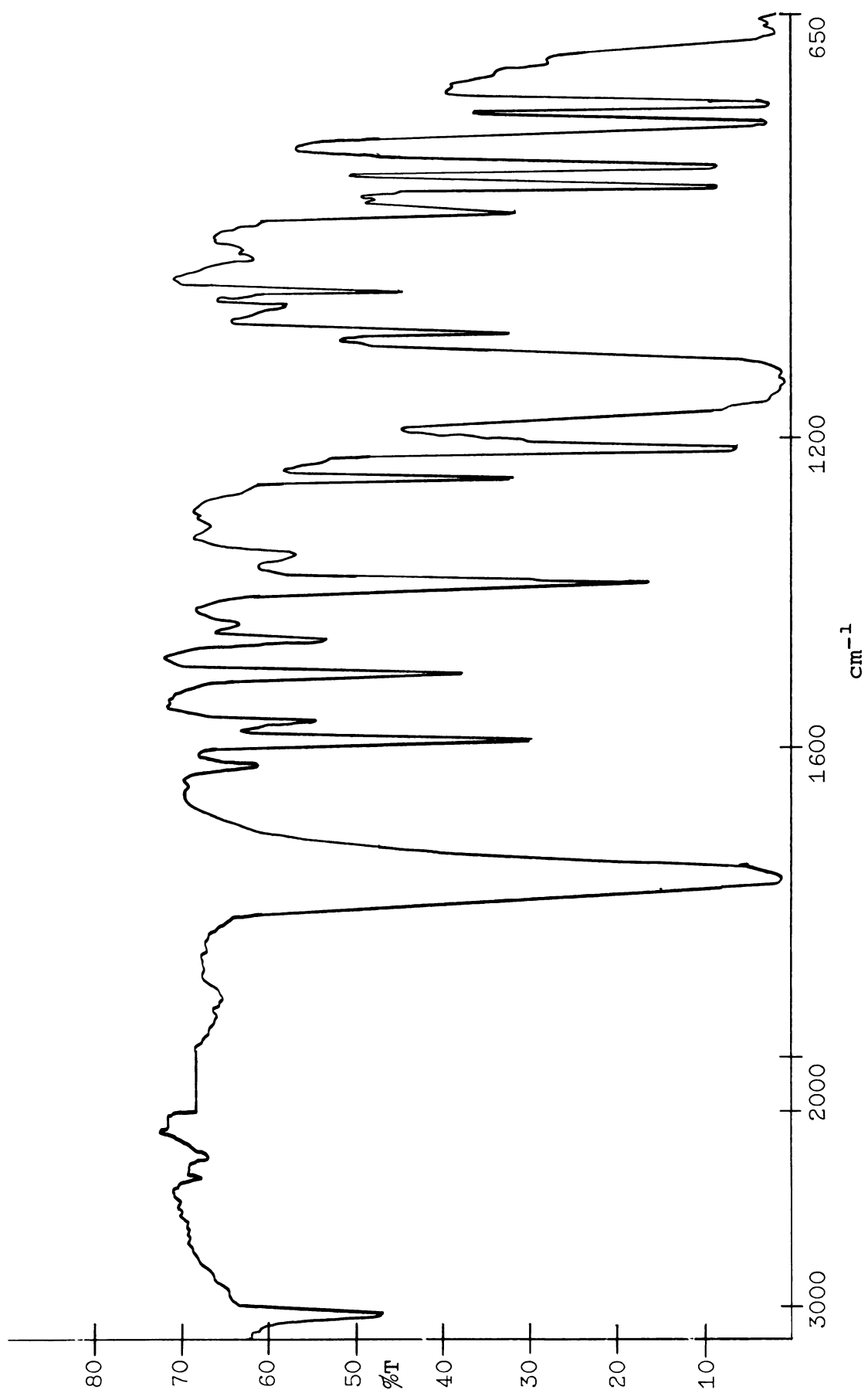
Infrared Spectrum 5. p-Bromophenylchloroformate



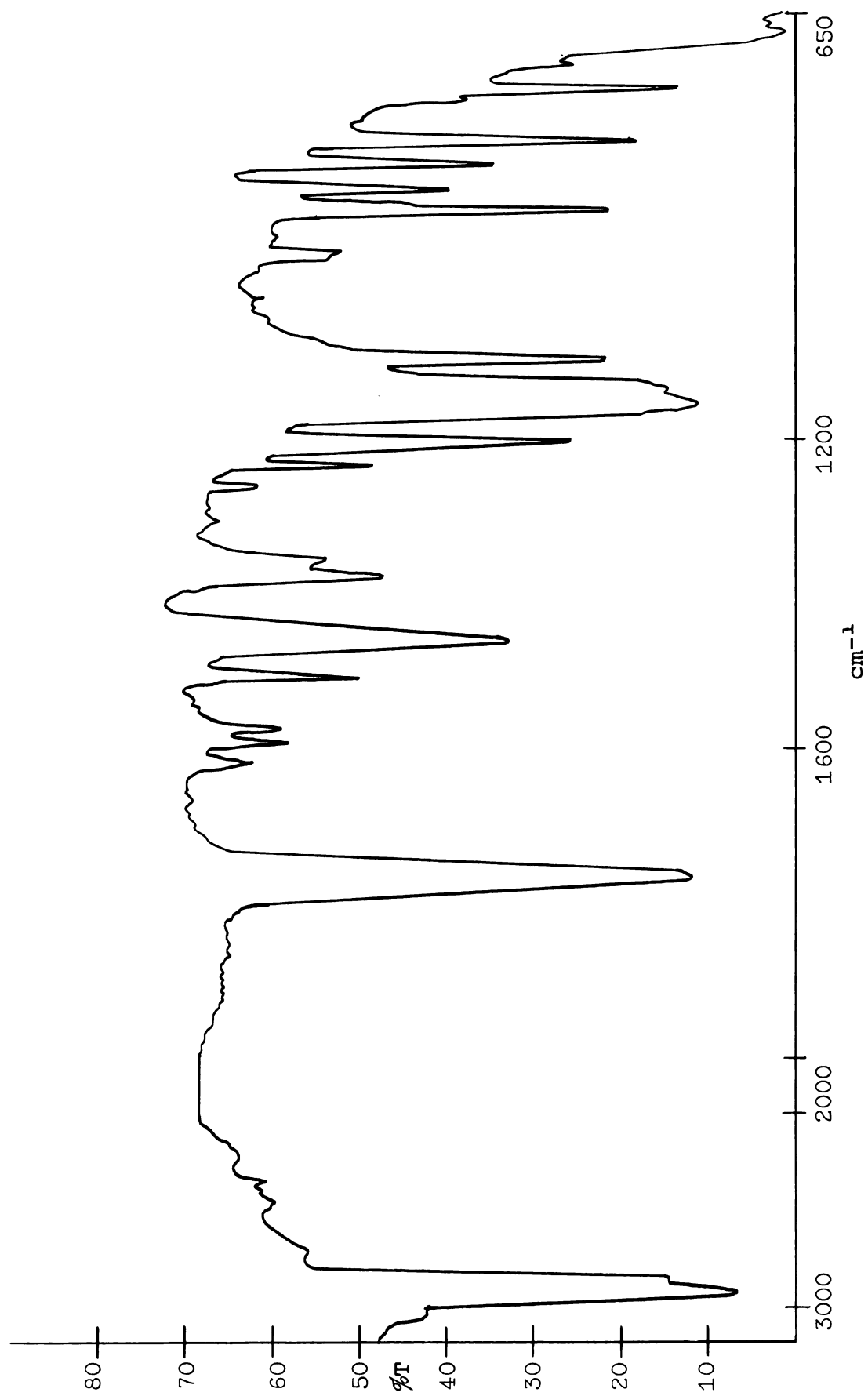
Infrared Spectrum 6. p-Chlorophenylchloroformate



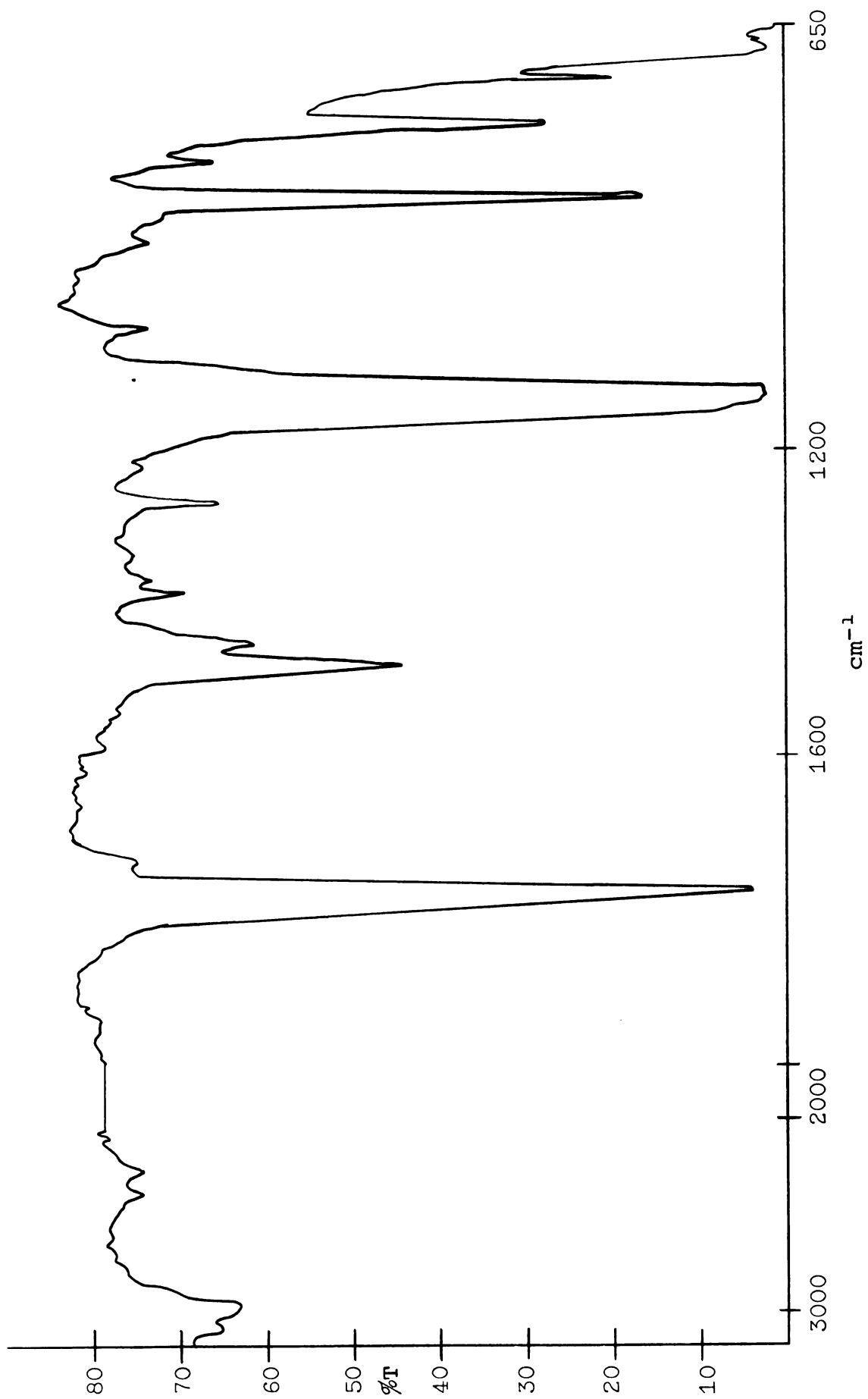
Infrared Spectrum 7. p-Nitrophenylchloroformate (Mull)



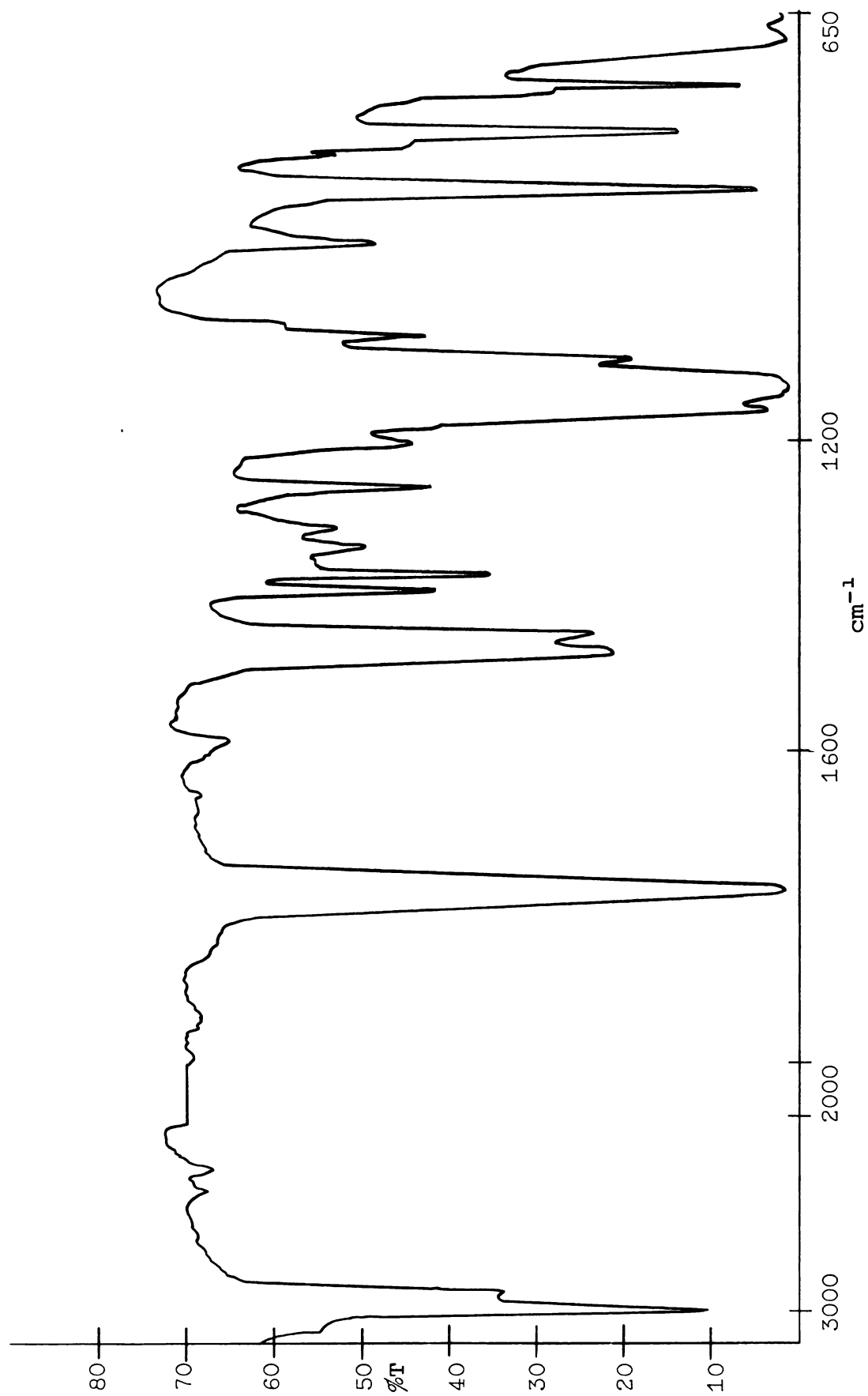
Infrared Spectrum 8. α -Naphthylchloroformate



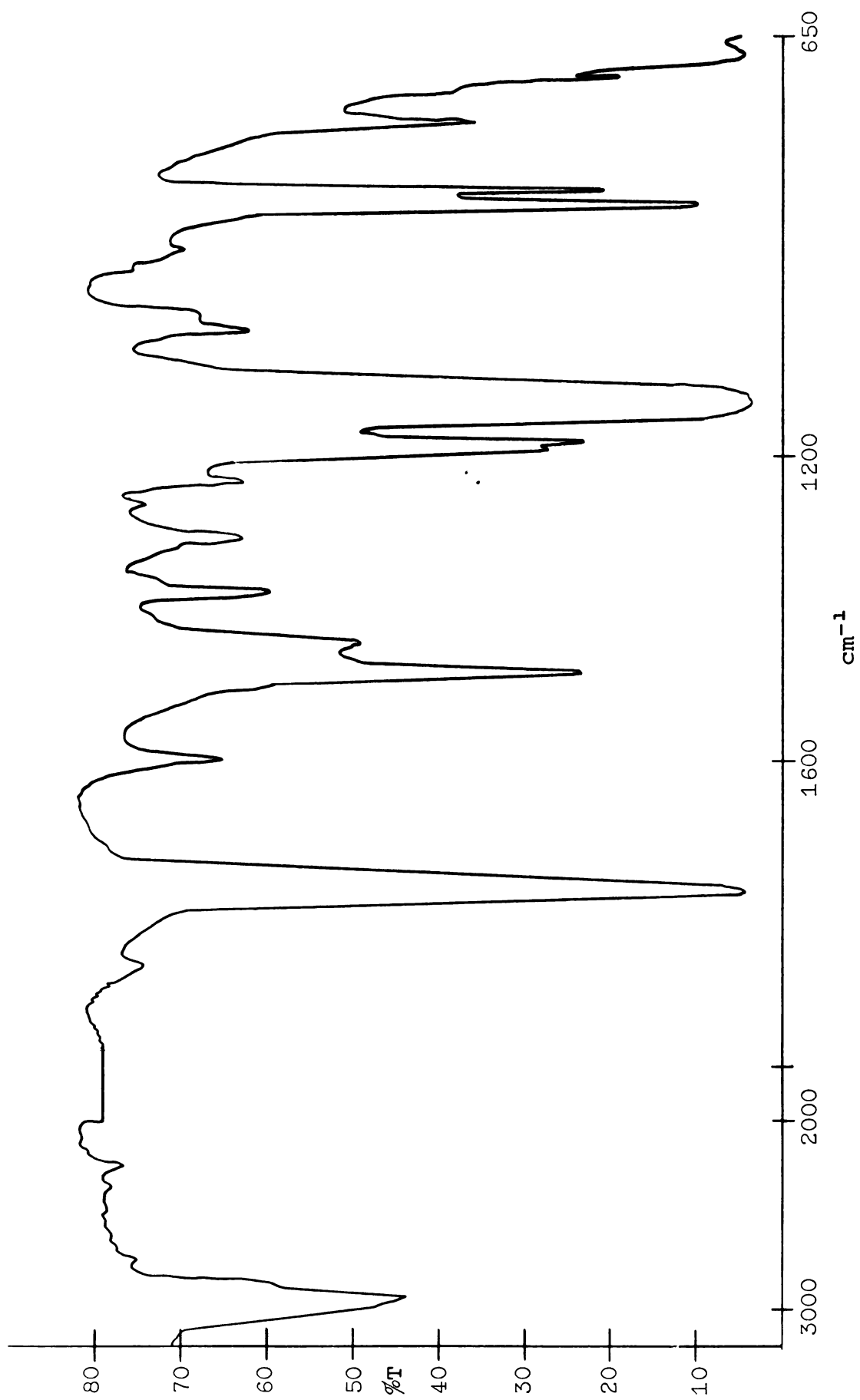
Infrared Spectrum 9. β -Naphthylchloroformate (Mull)



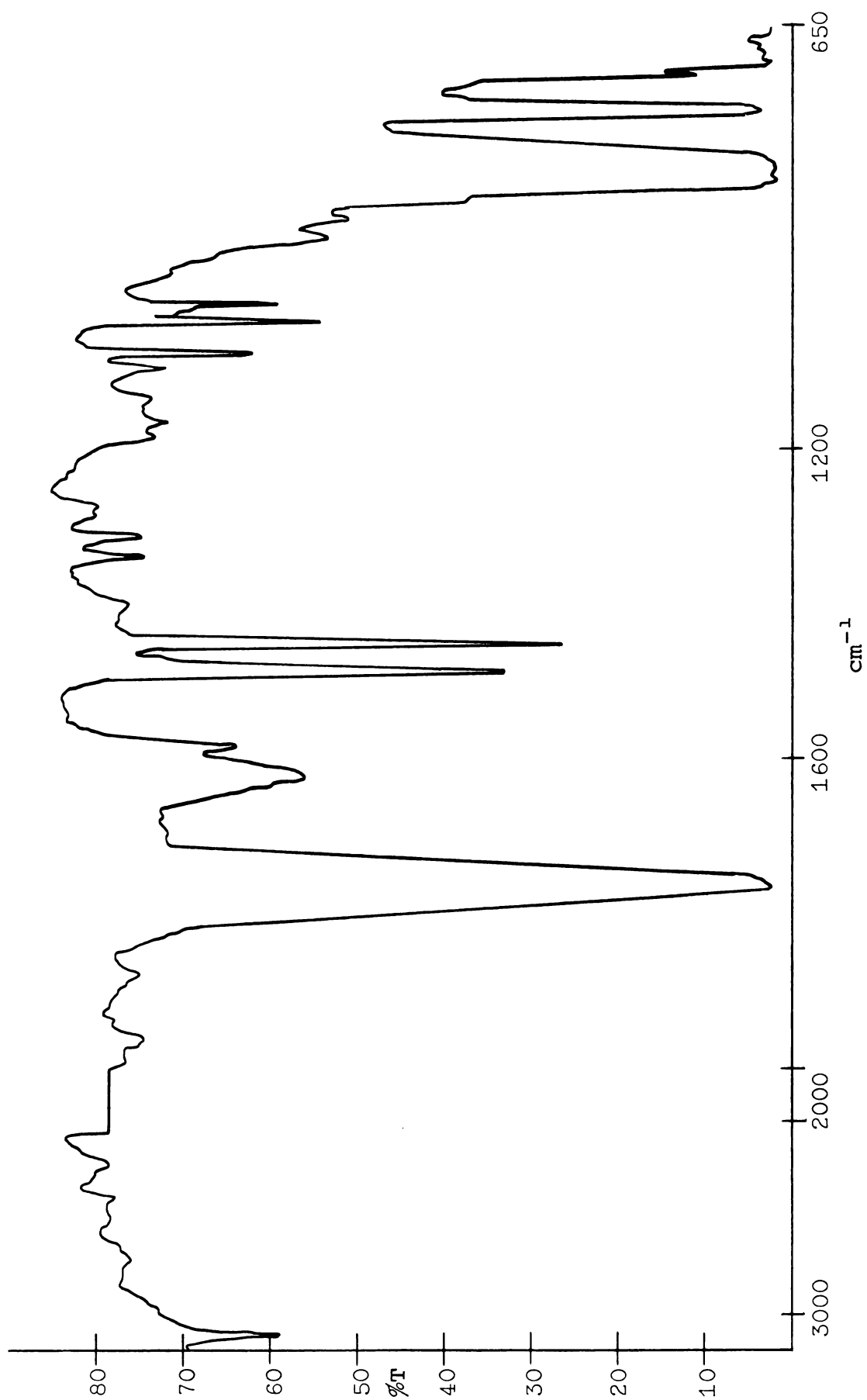
Infrared Spectrum 10. 2,6-Dimethylphenylchloroformate



Infrared Spectrum 11. 2,6-Diisopropylphenylchloroformate

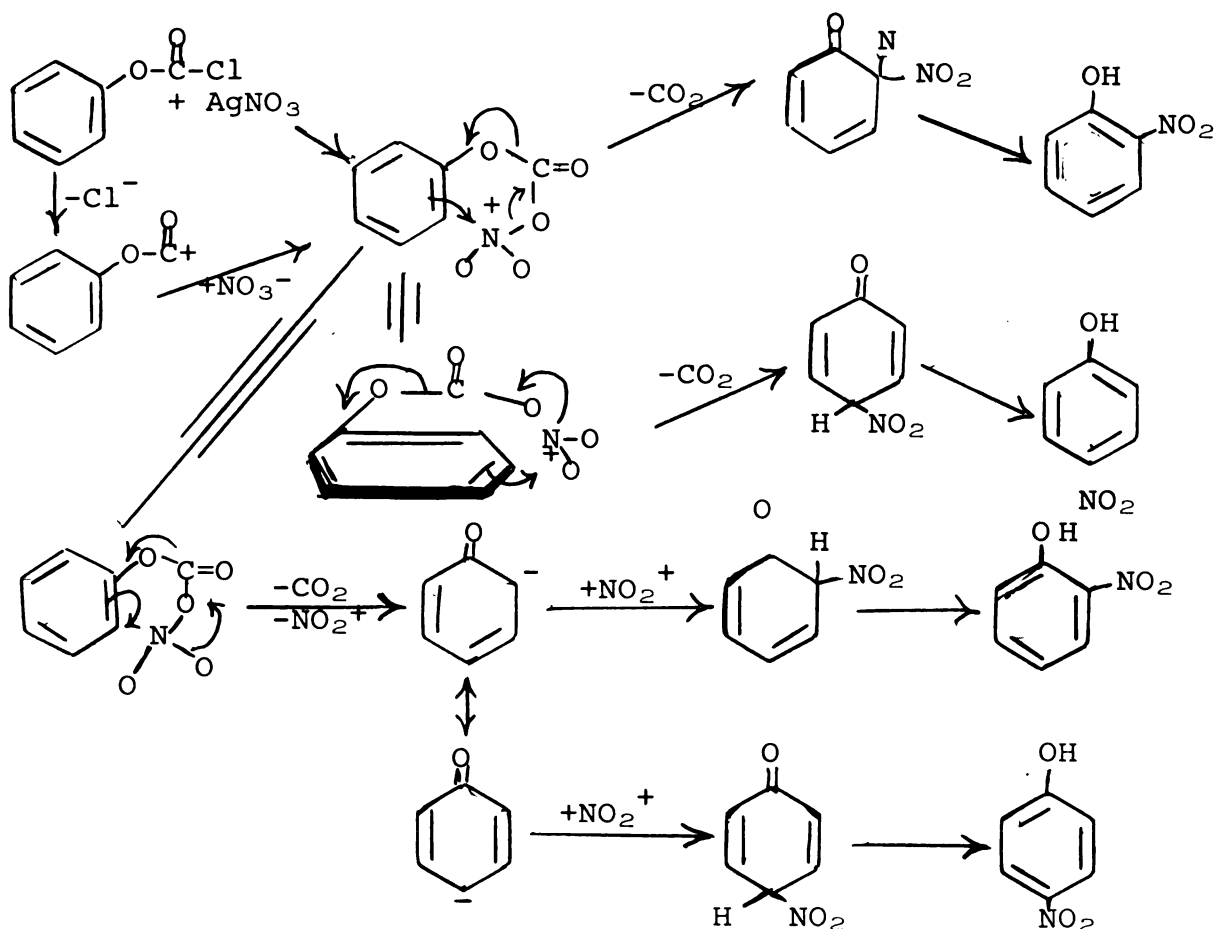


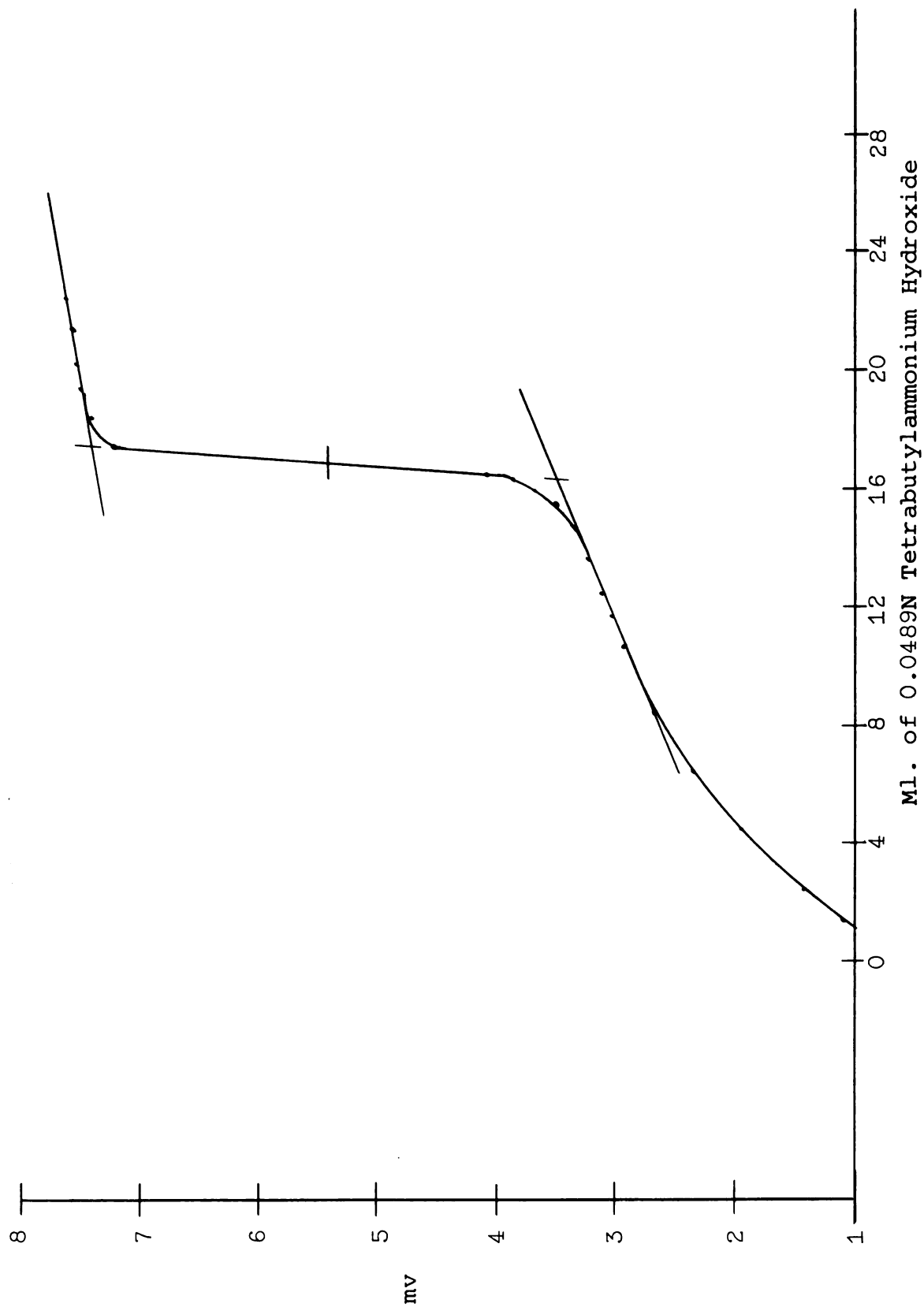
Infrared Spectrum 12. 2,4,6-Trimethylphenylchloroformate



Infrared Spectrum 13. Phenylchloroethiolformate

was detected in the reaction products. The total nitro phenolic content of the reaction mixture was determined by titration with standard methanolic tetrabutylammonium hydroxide (29,30). This procedure is incapable of distinguishing between the o and p-nitro phenols [See Graph (1)]. The total per cent yield (84%) calculated from this titration corresponds very closely to the total yield obtained from the column chromatography (84.7%). It was not surprising that a para nitrated phenol was obtained since numerous ortho rearrangement reactions reported in the literature also give the corresponding para products. There are several possible mechanisms by which this rearrangement reaction could proceed.





Graph 1. Titration curve for a mixture of o and p-nitrophenol with tetrabutylammonium hydroxide (glass versus calomel electrodes).

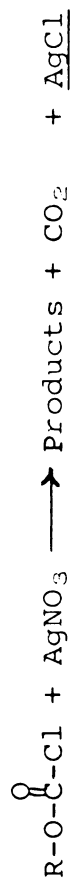
In an effort to determine which mechanism is operative and the scope of the reaction, a product, kinetic, and mechanistic investigation was undertaken of the reaction of various aryl chloroformates with silver nitrate.

B. Products from the Reaction of p-Substituted Phenylchloroformates with Silver Nitrate

The reaction of p-substituted phenylchloroformates was carried out at 20° on a 0.05 mole basis using acetonitrile as the reaction media. The p-substituents included methyl, methoxy, phenyl, bromo, chloro, and nitro. In all cases the products obtained were 4-substituted-2-nitrophenols, produced in excellent yields (72.8% to 99.1%). The products were obtained by the evaporation of the acetonitrile followed by recrystallized of the crude product from an appropriate solvent. Table (II), summarizes the pertinent data for these reactions. In all reactions a small quantity of tarry material was formed from which no identifiable compounds could be isolated.

The same reactions were rerun using a five-fold excess of silver nitrate. The reactions proceeded considerably faster than when equal molar-quantities of reactants were used as evidenced by the visual observation of the rate of precipitation of silver chloride. This increase in the concentration of silver nitrate and enhanced rate of reaction had no major effect on the yields of the 4-substituted-2-nitrophenols as indicated in Table (II).

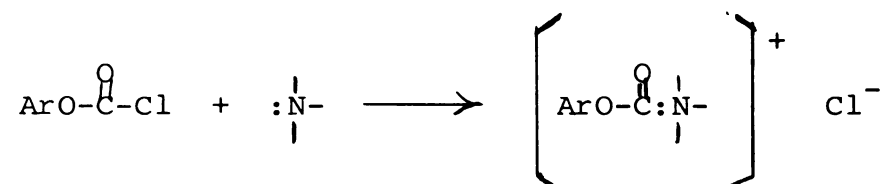
Table II. Product data from the Reaction of p-Substituted Phenyl and Naphthyl Chloroformates with Silver Nitrate



R	Product	Recrystallization Solvent	M.p. °C	Reaction Number	Percent Yield		Reference
					Product	AgCl CO ₂	
p-Methoxyphenyl	2-Nitro-4-methoxyphenol	90 to 120° Ligroin	79	1. ^a	72.8	98.8	88.3
			to	2. ^b	83.4	98.9	87.3
			80	3. ^c	80.9	97.6	88.2
p-Methylphenyl	2-Nitro-4-methylphenol	Amyl alcohol	31	1.	89.0	98.9	93.2
			to	2.	94.4	97.7	90.1
			32	3.	90.1	99.3	92.7
p-Phenylphenyl	2-Nitro-4-phenylphenol	Ethyl ether	65	1.	99.1	99.8	97.2
			to	2.	98.6	98.8	92.3
			66	3.	95.3	96.8	98.1
Phenyl	2-Nitrophenol and 4-Nitrophenol	Ethyl ether	44.5	1.	67.3-o	98.6	95.2
			to -o	.	18.9-p		
			45.0	2.	69.3-o	99.3	96.5
p-Bromophenyl	2-Nitro-4-bromophenol	Ethyl ether	113.5	3.	22.4-p		
			to -p		69.1-o	97.3	97.3
			114.0		18.3-p		
p-Chlorophenyl	2-Nitro-4-chlorophenol	Ethyl ether	88	1.	97.7	99.0	98.5
			to	2.	98.0	99.1	98.4
			89	3.	95.3	95.2	97.3
p-Nitrophenyl	2-4-Dinitrophenol	Ethyl ether	86.5	1.	87.2	97.7	90.3
			to	2.	92.6	98.1	91.5
			87.0	3.	92.2	96.3	95.5
α-Naphthyl	2-Nitro-1-naphthol	Ethyl alcohol	110.3	1.	93.5	95.3	94.1
			to	2.	95.1	98.4	95.1
			112.7	3.	93.9	96.7	94.0
β-Naphthyl	1-Nitro-2-naphthol	Water	128.0	1.	66.6	97.5	73.2
			to				
			103 to 104	1.	38.6	91.9	83.2

^aReactions number 1 have equal concentrations of reactants.
^bReactions number 2 have equal concentrations of reactants plus 0.01 ml of pyridine.
^cReactions number 3 have a five-fold excess of silver nitrate.

The p-substituted phenylchloroformate reactions were also conducted in the presence of pyridine. Here again the reaction is considerably accelerated. In one run, started at an initial temperature of 20° and an equal molar amount of pyridine, the reaction commenced to boil after 30 seconds of reaction and was essentially complete in two minutes. This reaction time compares to 3 or 4 hours for a reaction run in the absence of pyridine. It is well-known (4) that tertiary amines form complexes with aryl



chloroformates and this suggests the possibility that the rate determining step in the rearrangement of aryl chloroformates with silver nitrate is the initial attack by the nitrate ion on the chloroformate. The presence of pyridine helps break the C-Cl bond and thus enhances the reaction rate. It was determined that only a trace (0.001 ml) of pyridine is required for this large rate enhancement, suggesting that the pyridine is regenerated and is reused by successive chloroformate molecules.

The fact that the yields in these rearrangement reactions were quite high indicates that the reaction is a good preparative procedure to obtain o-nitro phenols. The two step process of preparing the chloroformate and its

subsequent rearrangement with silver nitrate gives overall yields of 70-80% of mononitrated phenol. Besides the mildness of the reaction conditions, this procedure is superior to the classical nitration procedures employing mixtures of nitric and sulfuric acids where not only mono nitration but also large amounts of dinitrated products are obtained.

C. Products from the Reaction of α and β Naphthylchloroformates with Silver Nitrate

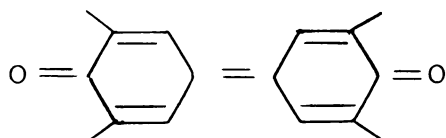
The reactions of the naphthylchloroformates were run at 20° on a 0.05 mole scale in acetonitrile as a reaction solvent. Following completion of the reaction the acetonitrile was removed on a rotary evaporator and water was added to the black oily reaction mixture. The aqueous suspension on steam distillation yielded 38.6% of 1-nitro-2-naphthol and 66.6% of 2-nitro-1-naphthol from β and α naphthylchloroformates, respectively. In each case some black tarry material remained after steam distillation. This was chromatogrammed on an alumina column using ether as the eluent, and in each case yielded numerous bands which could not be identified.

D. Products from the Reaction of 2,6-Disubstituted Phenylchloroformates with Silver Nitrate

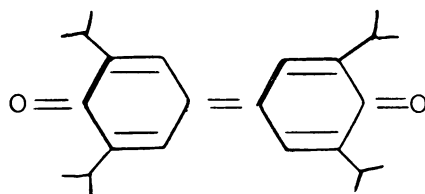
Reactions of aryl chloroformates with substituents blocking the ortho positions were conducted to determine if

only the para product resulted if a reaction occurred. Compounds used in this work included the 2,6-dimethyl and 2,6-diisopropyl phenylchloroformates. The highly hindered and ortho blocked 2,6-di-t-butylphenylchloroformate, an obvious choice for this type of study, could not be prepared, very probably due to steric hindrance. These reactions were run at 20° on a 0.05 mole scale.

On reaction with silver nitrate the 2,6-dimethylphenylchloroformate yielded a redish acetonitrile solution of the products. This solution on being chromatographed yielded 62.6% of 4-nitro-2,6-dimethyl phenol (p-rearrangement, m.p. 172-3°) and 0.78 g of a dark red compound which decomposed at 224°. The latter material was identified as 3,5,3',5'-tetramethyldiphenquinone-(4,4'), a quinone dimer (24).



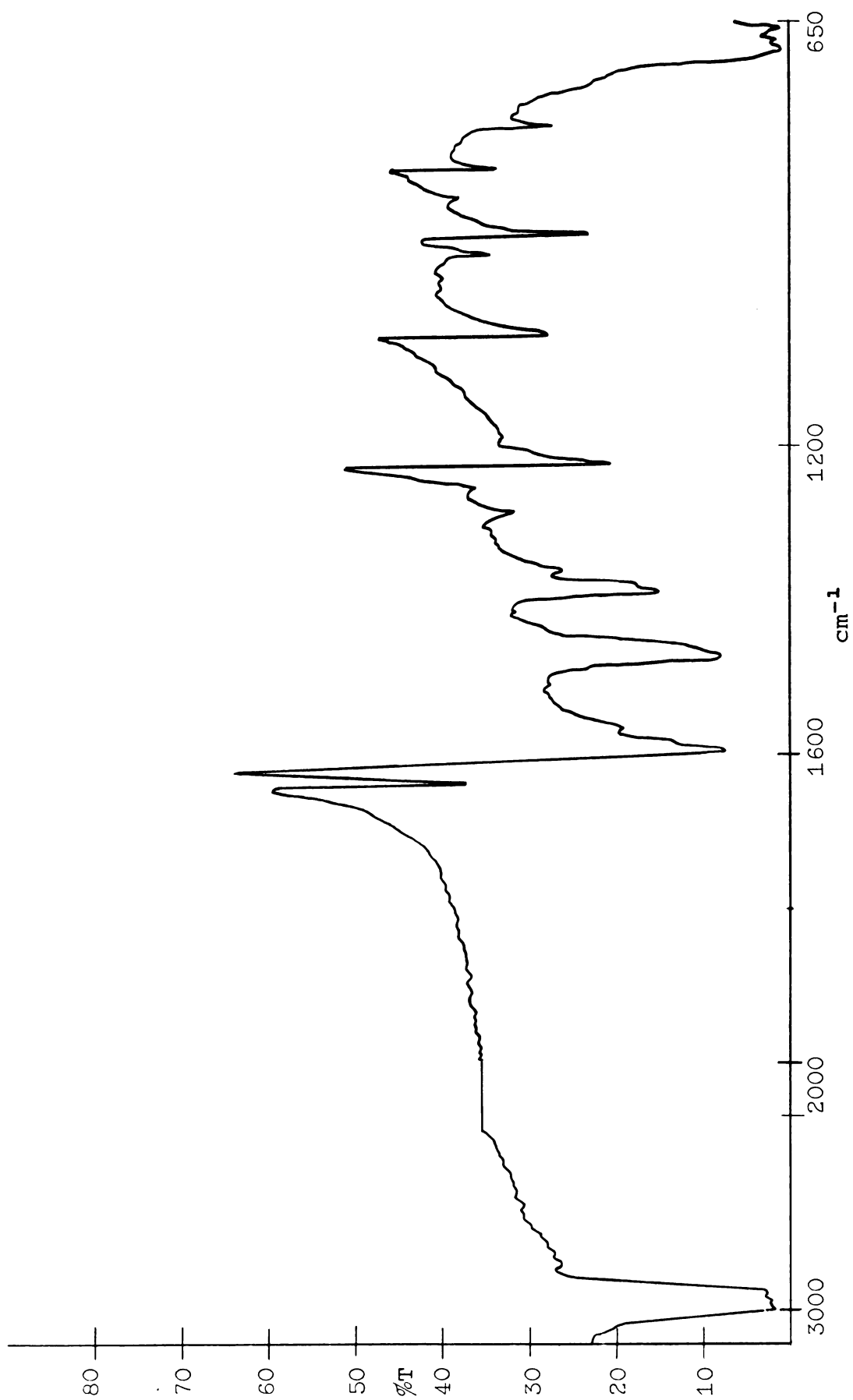
The 2,6-diisopropylphenylchloroformate, under the same reaction conditions and product isolation as described for the 2,6-dimethyl compound, yielded 4-nitro-2,6-diisopropyl phenol (73%) and again a small amount of a dark red colored compound identified as 3,5,3',5'-tetraisopropyldiphenquinone-(4,4') (24) which melted at 214°.



The fact that the p-nitro compound is the major product indicates that the p-rearrangement is not hindered to any great extent by blocking the ortho positions. The similarity in yields between the diisopropyl and dimethyl compounds further indicates that there is no significant effect on the p-rearrangement due to the size of groups in the ortho position.

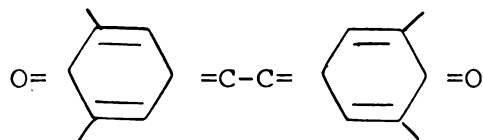
E. Products from the Reaction of 2,4,6-Trimethyl-phenylchloroformates with Silver Nitrate

The reaction of 2,4,6-trimethylphenylchloroformate with silver nitrate was run to determine whether the nitro group could be forced to enter the meta position. The same experimental procedure was used as already described for the other hindered phenylchloroformate reactions investigated. As the reaction proceeded in this case, dark red crystals separated from solution along with the precipitation of the silver chloride. On completion of the reaction the red crystals and silver chloride were collected by filtration. Some of the red crystals were picked out of the product mixture by hand and used in an attempt to determine a solvent from which they could be recrystallized. These were insoluble in all available solvents and the silver chloride had to be dissolved away from them with ammonium hydroxide. The crystals melted (decomposed) at 245° and had the infrared spectrum shown in spectrum (14).



Infrared Spectrum 14. 3,5,3',5',-Tetramethylstilbenequinone-(4,4') (Mull)

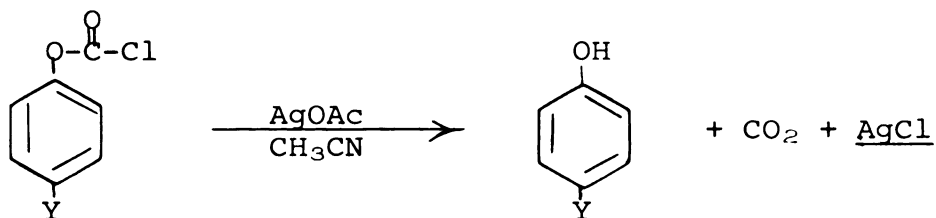
The red crystalline compound was identified as 3,5,3',5'-tetramethylstilbenequinone (4,4').



F. Products from the Reaction of p-Substituted Phenylchloroformates with Silver Acetate or Silver Trifluoroacetate

Reactions of aryl chloroformates with the silver salts of acetic and trifluoroacetic acid were conducted in the same experimental manner as with silver nitrate, to determine whether the acetyl or trifluoroacetyl groups would enter the aromatic nucleus similarly to the nitro group.

In the case of silver acetate the only organic phenolic products obtained are the nonacylated phenols (90% yields).

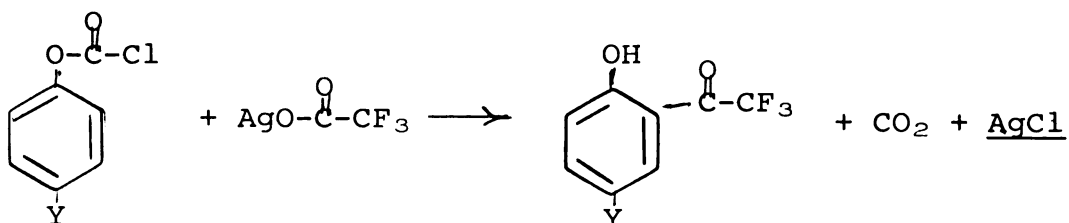


The silver chloride was obtained in practically quantitative yields.

Table III. Products Obtained From the Reaction of
p-Substituted Phenylchloroformates with
Silver Acetate

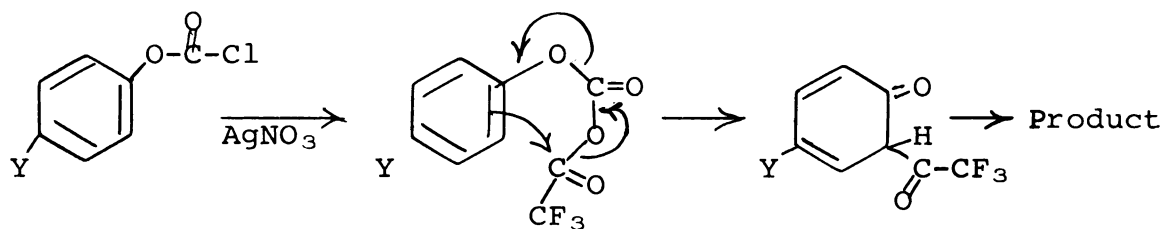
p-Substituted Phenylchloroformate	Phenol Obtained	Percent Yield	Percent Yield of AgCl
p-Phenyl	p-Phenyl	97.3	99.8
p-Chloro	p-Chloro	95.2	98.3
p-Methoxy	p-Methoxy	96.3	98.5
p-Nitro	p-Nitro	94.2	98.9

When silver trifluoroacetate was used, substituted phenyl trifluoromethyl ketones were obtained in greater than 95% yields. Conceivably this reaction could proceed



Y = phenyl and bromo

through the same type of postulated mechanism for the silver nitrate.

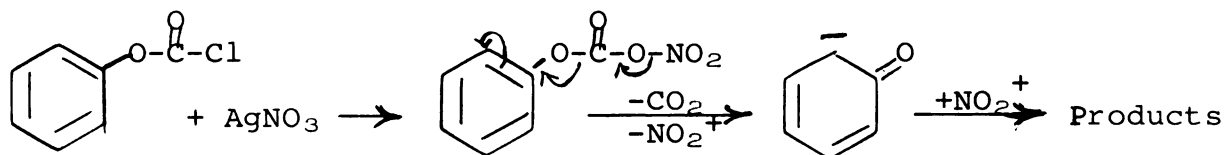


The carbonyl carbon of the trifluoromethyl acetate is more positive, due to the electron withdrawing effect (-I) of the three fluorine atoms, than the acetate carbonyl and

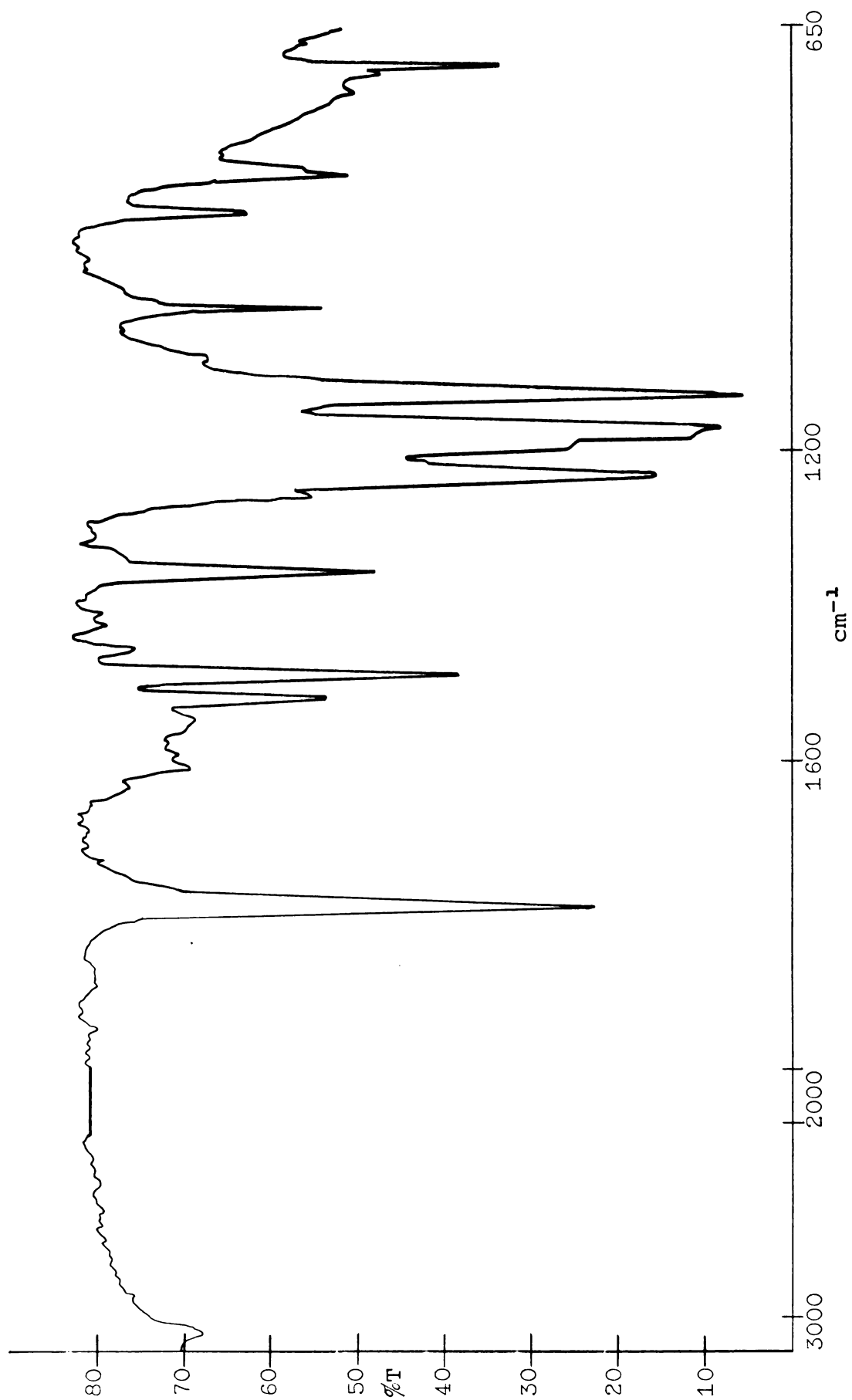
therefore would be expected to participate more readily in the cyclic rearrangement reactions postulated above. This could account for the observation that silver acetate failed to yield rearranged products in the reactions studied. There is similarity between the nitro group and the trifluoromethyl in that both have positive charges on the atom involved in the migration (nitrogen atom and carbonyl carbon atom, respectively). Thus, it appears that this is a prerequisite for this type of a rearrangement to occur.

G. Products Obtained from the Reaction of p-Phenyl-phenylchloroformate with Silver Nitrate in the Presence of Various Trapping Agents

Experiments were run in which p-methoxyphenol or p-methoxyphenoxide were added to the reaction medium in an effort to determine whether a nitronium ion (NO_2^+) was formed in the reaction sequence which in turn reacted with the aryl ring in an intermolecular process.



Para methoxy phenol was added to the reaction 10 minutes after it was initiated, and at the conclusion of the reaction product isolation was conducted in the usual manner. The sole product isolated in these experiments was



Infrared Spectrum 15. 2-Hydroxy-5-phenylphenyltrifluoromethyl Ketone

2-nitro-4-phenylphenol in 93.1% yield. These results showed that no intermolecular reaction had occurred. However, this left unanswered the possibility that perhaps a phenol group could not successfully compete with the intermediate methoxide ion which is normally formed during any reaction sequence that could produce the NO_2^+ ion. Therefore, sodium p-methoxyphenoxide was prepared and added to the reaction medium containing p-phenylphenylchloroformate and silver nitrate at the initiation of the reaction; then, 10 minutes after the initiation of the reaction; and finally 60 minutes after initiation of the reaction in an attempt to trap any NO_2^+ ion that might be formed. An immediate problem, encountered with the use of sodium p-methoxyphenoxide, was that it reacts instantly with the silver nitrate to yield a black precipitate. The latter slowly (12 hrs.) changes in color to a light cream-colored material. Thus, the overall mechanism for the reaction between phenylphenylchloroformate and silver nitrate may be changed and the results of this trapping experiment must be taken with some reservation. In all three cases examined the sole organic product isolated in high yields (97-99%) was 4-phenyl-2-nitrophenol, again indicating that no intermolecular reaction had occurred. These results, however, do not rule out the possibility of a closely bound ion pair where the NO_2^+ if formed was not able to participate in an intermolecular reaction mechanism.

These reactions were also conducted in the presence of α -methylstyrene and galvinoxyl to determine if the reaction proceeded by a free radical process. In separate experiments the galvinoxyl or α -methylstyrene were added at the initiation of the reaction between p-phenylphenylchloroformate and silver nitrate. In both cases, the yield of 4-phenyl-2-nitrophenol ranged between 94-98%. These results were again very close to the yield obtained without the addition of either trapping agent. This observation then rules out the possibility of a free radical mechanism being operative in the rearrangement reaction under the experimental conditions studied in the present investigation.

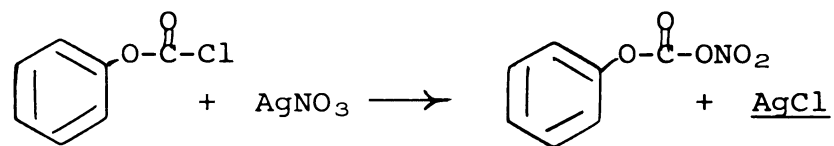
H. Carbon Dioxide Analysis

The quantitative determination of the carbon dioxide liberated during the rearrangement reaction of the various arylchloroformates studied was carried out on the reactions conducted at 20° in acetonitrile as a reaction media. The carbon dioxide evolved was absorbed on Ascarite and weighed directly. The results are summarized in Table II.

These data indicate that the amount of carbon dioxide evolved essentially follows the per cent yield of the various nitrated phenol products formed in the rearrangement. Where the yields of carbon dioxide are low as in the case of the hindered phenols, the yield of nitrated phenol was also low.

I. Silver Chloride Analysis

A semi-quantitative determination of the silver chloride was made by recovering the silver chloride formed by filtration, washing it with acetonitrile and anhydrous ether, drying in an oven at 105° for 1 1/2 to 2 hours and then weighing it directly. This procedure was of sufficient accuracy for the purpose of this investigation. In all cases the silver chloride was obtained in high yield indicating that all the chlorine from the chloroformates is lost as the chloride ion and forms silver chloride. From the mechanisms postulated the first step in the rearrangement is always the loss of the chloride ion followed by either rearrangement or decomposition occurring after this step.

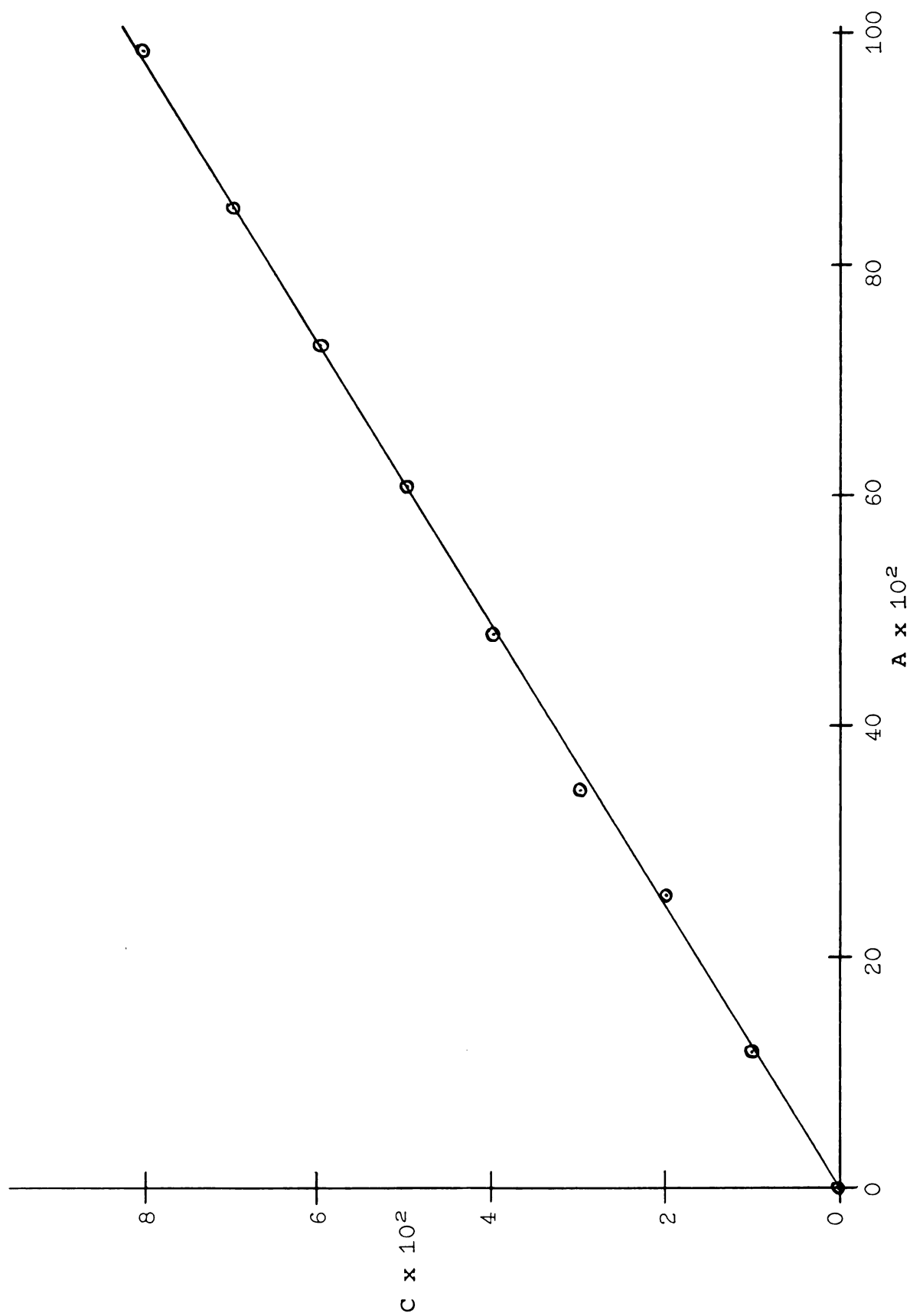


The above results would indicate that the first step is very probably quantitative but that subsequent steps (elimination of carbon dioxide) may or may not be depending on the particular chloroformate involved in the rearrangement. The yield of carbon dioxide, lost in a subsequent step of the reaction, follows the yield of product more closely and therefore is probably involved in the final step of the rearrangement.

III. Rates of the Reactions of the p-Substituted Phenylchloroformates with Silver Nitrate

The reaction rates of the various p-substituted phenylchloroformates were followed by determining the rate of disappearance of the 1777 cm^{-1} chloroformate carbonyl peak in the infrared spectra. All the p-substituted phenylchloroformates examined in this study were checked and found to follow Beer's Law in the concentrations used in this investigation. Initially, the experimental analyses procedures were attempted by conductimetric, amperometric, and carbon dioxide evolution methods. However, these procedures proved to be unreliable and not reproducible. The conductimetric and amperometric analyses probably failed due to the use of acetonitrile as the solvent for the reaction since both of these procedures are very satisfactory when used in aqueous solutions.

A Unicam S. P. 200 recording spectrophotometer was employed for the infrared measurements. The infrared cell used was a Research and Industrial Instruments Company variable temperature cell equipped with silver chloride windows and modified to permit a sample to be injected or withdrawn without disassembling the cell. Silver chloride windows had to be employed since silver nitrate, one of the reactants, would react with the normal cell windows of sodium chloride or potassium bromide. Further, the silver chloride window had an advantage in that the reaction does



Graph 2. Typical Beer's Law Plot (1778 cm^{-2} p-methoxyphenylchloroformate absorption)

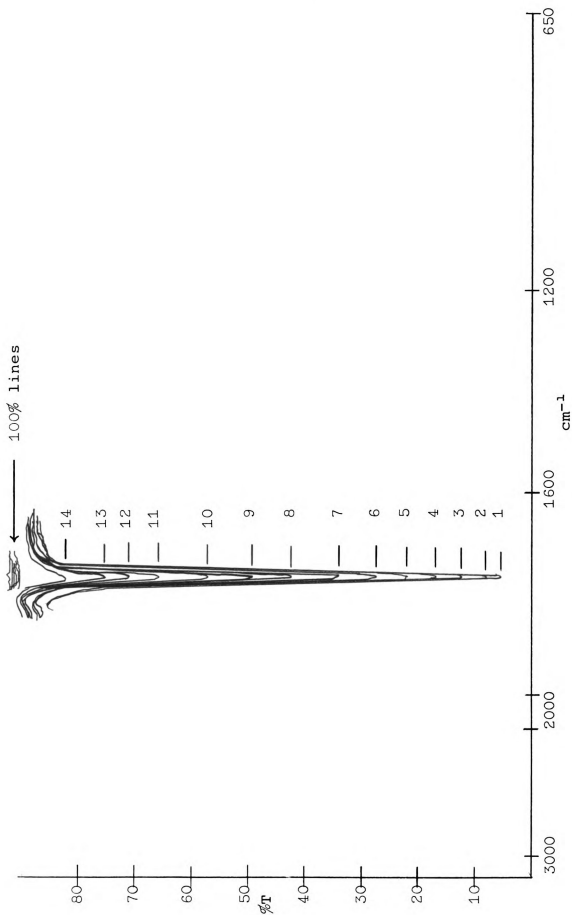
not come in contact with a salt different from that which the reaction mixture already contained. Thus, the cell material could not affect the rate of the reaction in any way. A variable temperature cell had to be utilized in this study since the kinetics were determined at three different temperatures, 10, 21, and 31°. The cell temperature was controlled to $\pm 0.3^\circ$. Temperature in the constant temperature water bath was controlled by a Thyatron electronic relay to $\pm 0.01^\circ\text{C}$ and was equipped with a stirrer. The reaction flask contained a carbon dioxide outlet; a liquid withdrawal tube (fitted with a fine sintered glass filter on the end immersed in the reaction solution and a standard taper female syringe joint at the outlet); a magnetic stirrer bar whose rotational velocity was controlled by a magnet fitted to an electric motor (glass enclosed) and immersed in the constant temperature bath.

The kinetic determinations were conducted by placing 50 ml. of a p-substituted phenylchloroformate solution in a reaction vessel supported in the constant temperature water bath. The solution was allowed to reach the bath temperature. A sample of this solution was injected into the variable temperature infrared cell to obtain the transmittance of the initial concentration. The cell was then washed with acetonitrile and air-dried in preparation for the next determination. To the solution in the bath was injected 4 ml. of standard silver nitrate solution. Samples were then withdrawn

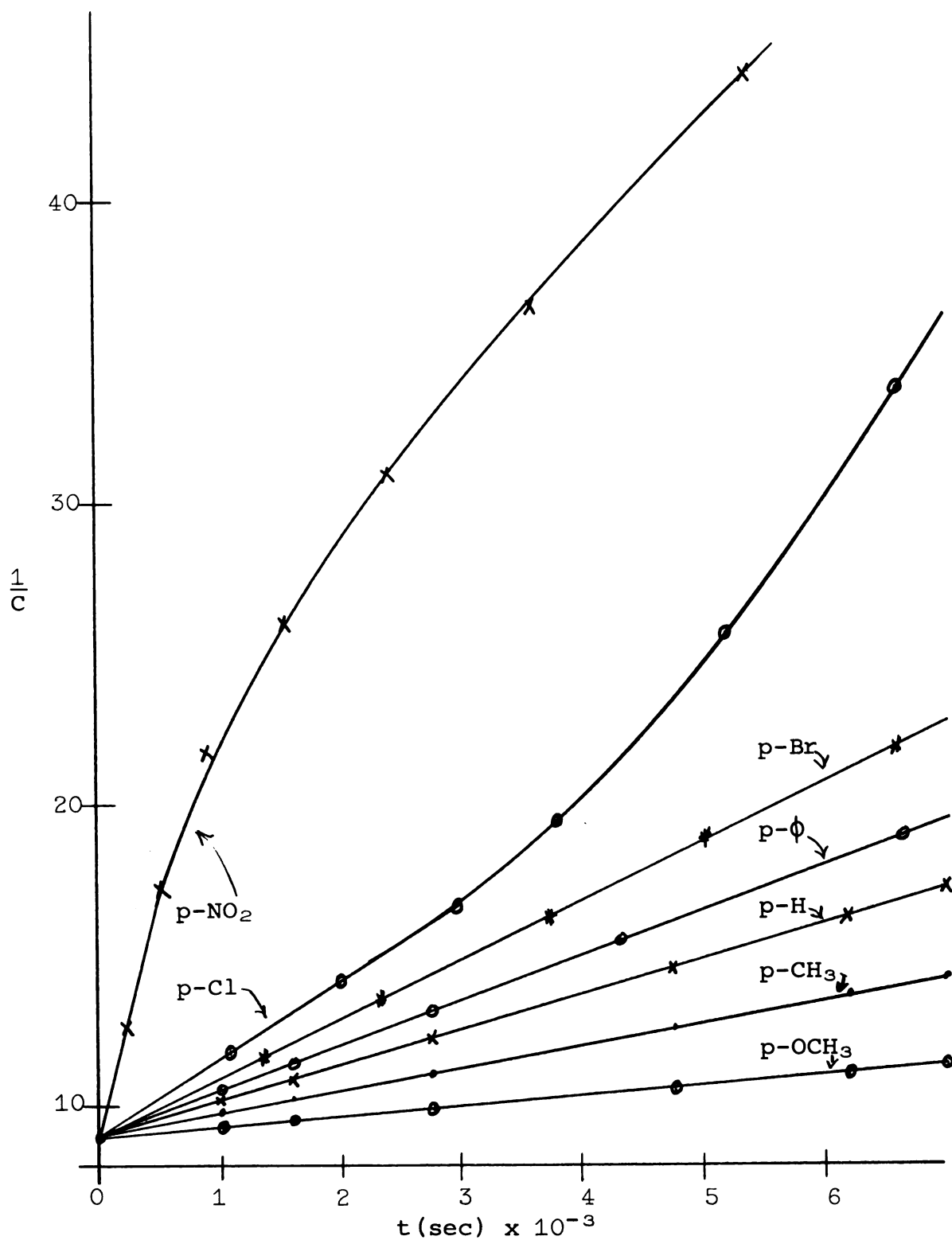
at predetermined times and injected into the cell to determine the transmittance of the reaction mixture. The time at which the minimum transmittance was reached was recorded. Following each concentration time determination, the cell was rinsed with acetonitrile and a acetonitrile versus acetonitrile (100% line) was determined. This procedure was necessary since silver chloride precipitates from the reaction solution in the cell and as a result would change the 100% transmittance line. The cell was then dried with air in preparation for the next determination. At the end of the kinetic run the transmittance for the initial concentration was corrected for dilution due to the addition of the four ml of silver nitrate solution.

The per cent transmittance was determined by measuring the distance between the 0% base line and the 100% line (determined for each time-concentration determination) and dividing this value by the distance between the 0% base line and the tip of the transmittance peak and then multiplying by 100.

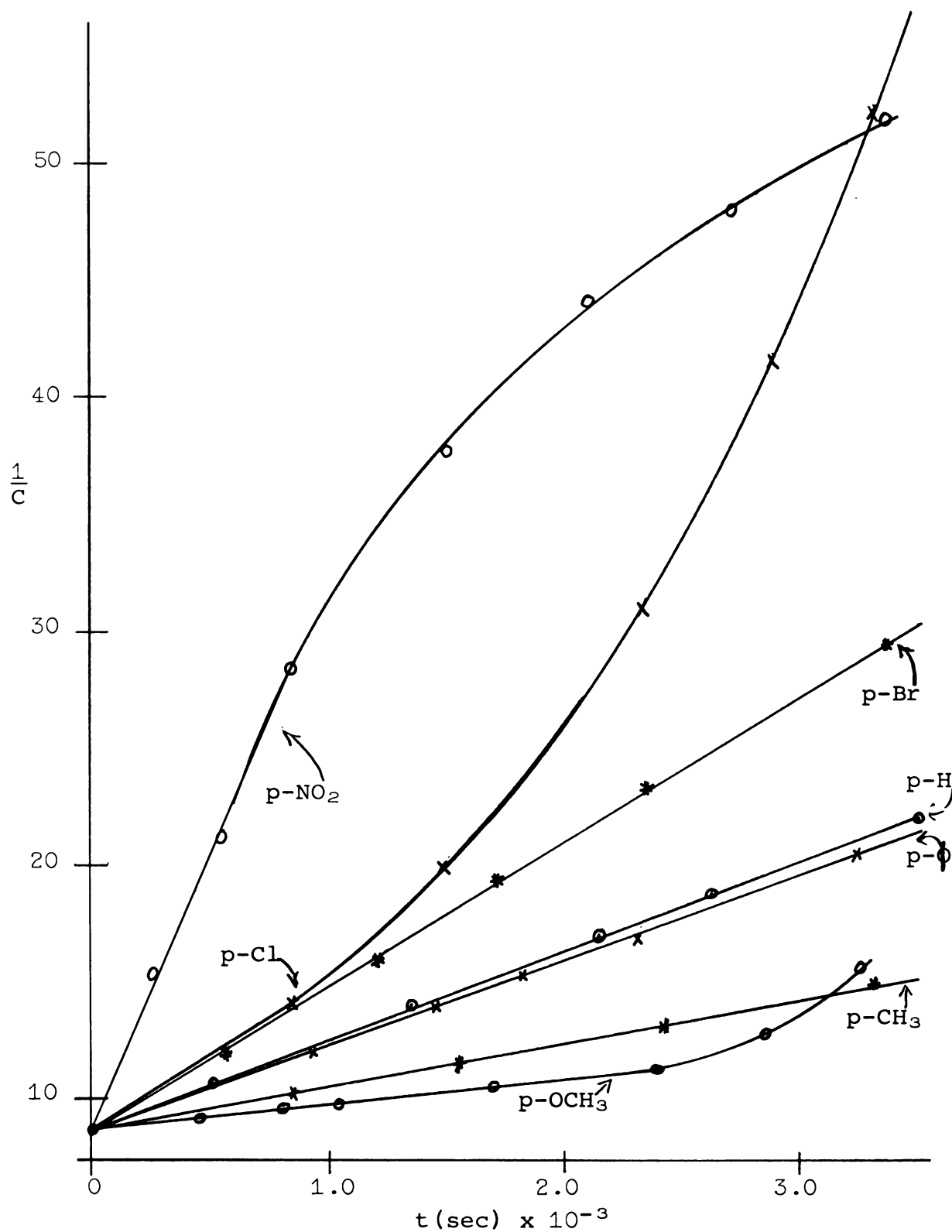
The results of the kinetic determinations at equal molar concentrations of the reactants on a second order plot are shown in Graphs 3, 4, and 5 for determination at 10, 21, and 31°, respectively. There are a number of conclusions that can be drawn from these plots. First, that as the reaction temperature was increased, the results became more erratic, especially at 31°. Second, the plots for the determinations at 10 and 21° are very comparable.



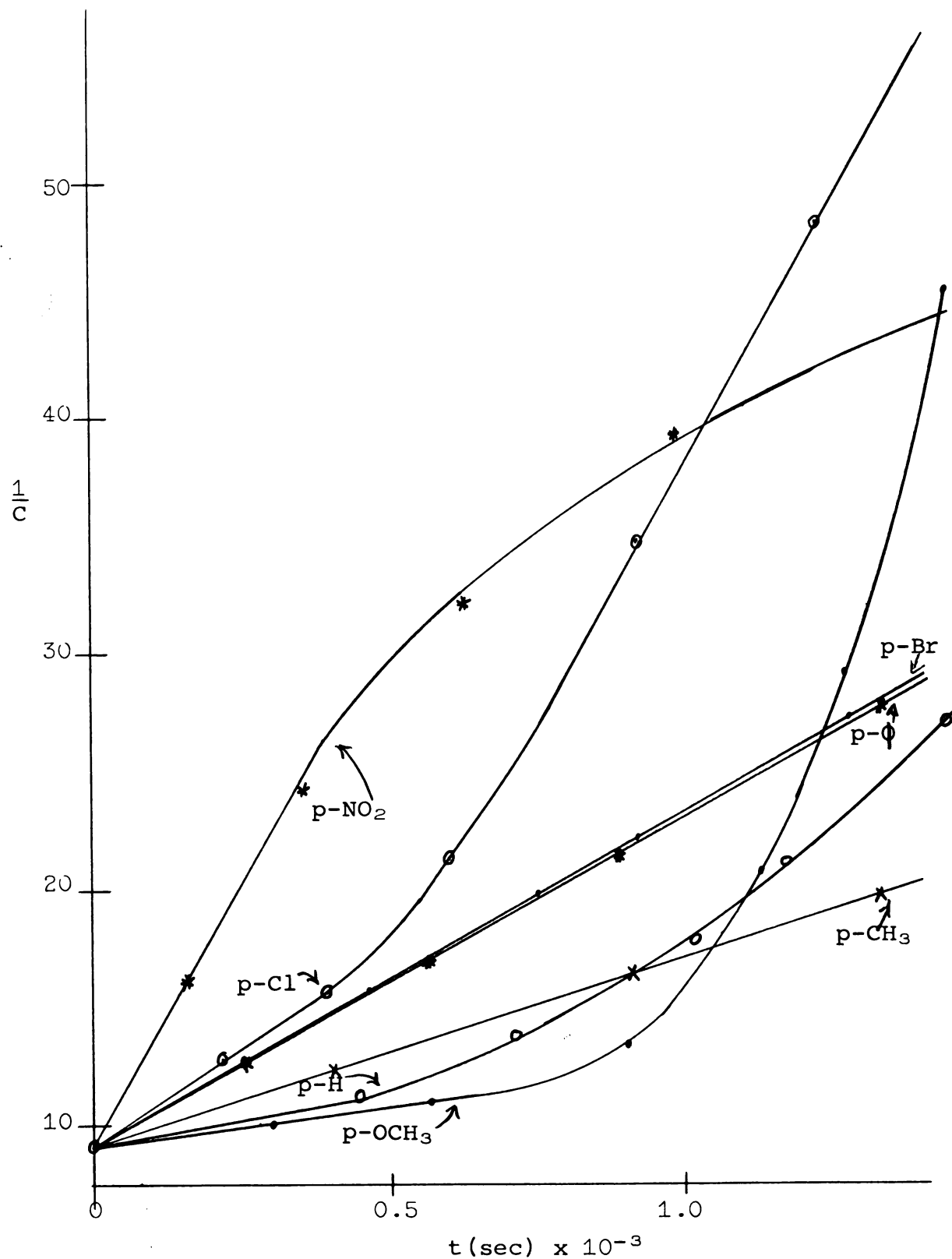
Infrared Spectrum 16. Typical Kinetic Run: Reaction of p-Methoxyphenylchloroformate with Silver Nitrate (Equal Molar Concentrations) at 21°.



Graph 3. Second Order Kinetic Plots for the Reactions of p-Substituted Phenylchloroformate with Silver Nitrate (Equal Molar Concentrations) at 10°.



Graph 4. Second Order Kinetic Plot for the Reaction of p-Substituted Phenylchloroformates with Silver Nitrate (Equal Molar Concentration) at 21°.



Graph 5. Second Order Kinetic Plots for the Reactions of p-Substituted Phenylchloroformates with Silver Nitrate (Equal Molar Concentrations) at 31°.

The most important conclusion to be drawn is that there is no simple overall reaction order. However, if only the first 20% of each of the kinetic determinations is examined it is noted that these portions of the plots are straight lines and follow a second order rate law. Additionally, it is observed that in the initial 20% of the reaction there is a definite increase in the reaction rate in going from p-methoxy (+I) to p-nitro (-I) phenylchloroformate. Thus, it is emphasized that all of the following data were determined from the initial 20% of the kinetic determinations and that all subsequent discussion deals with the initial rates (20% completion) and are not related to overall rates of reaction. This is followed even in the cases of p-methyl and p-phenylphenylchloroformate reactions, both of which followed a second order plot to 90% completion at 10 and 21^o.

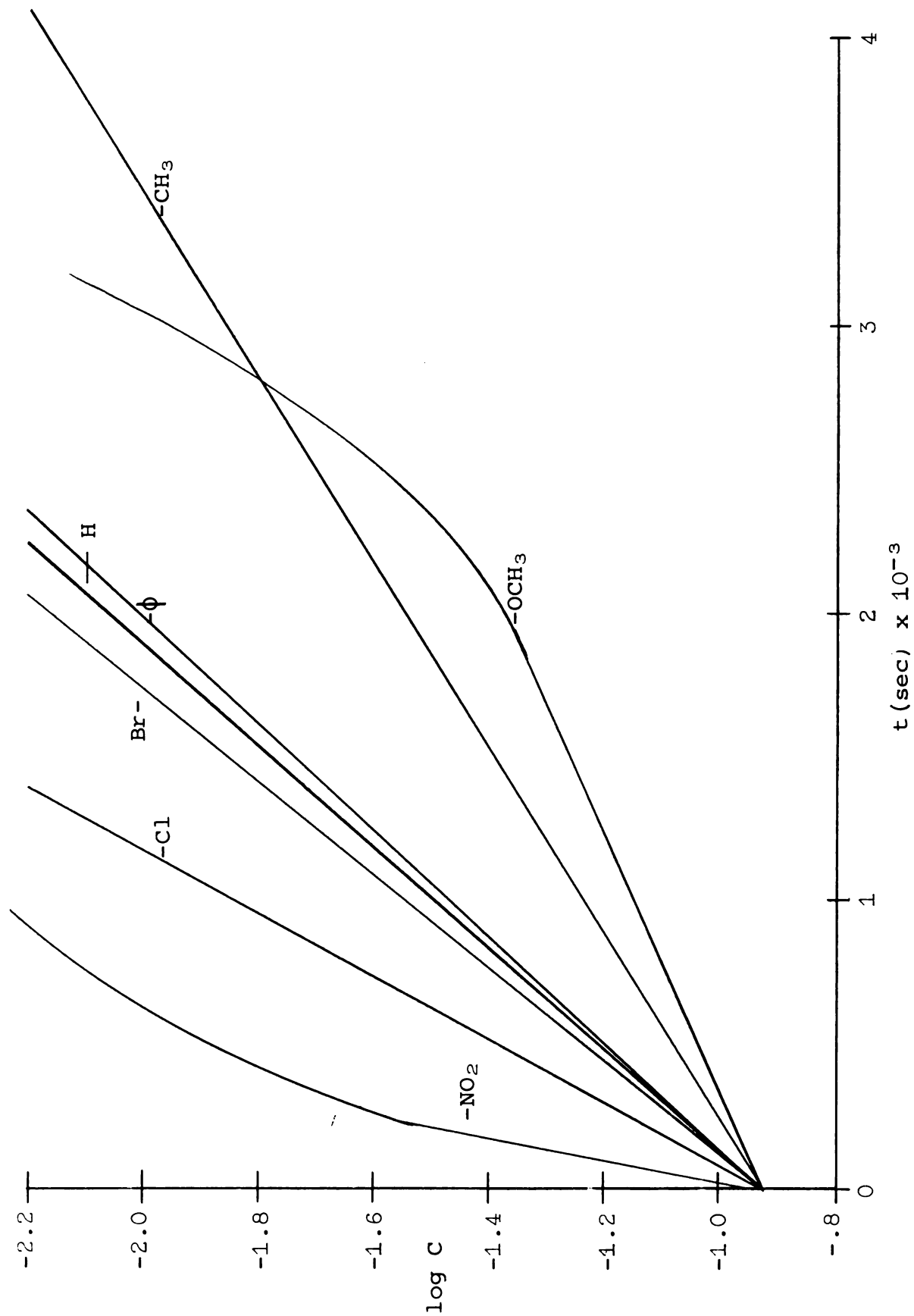
Possibly the abnormalities were due to the autocatalytic effects of one of the products formed during the reaction or to a surface area effect. To examine these possibilities experimentally kinetic determinations were conducted with; product added at the initiation of the reaction, freshly precipitated silver chloride added at the initiation of the reaction, and finally glass wool added to the reaction flask. All three variables were determined to have no effect on the rate of the reaction. However, these observations do not rule out any effect which an unstable

intermediate could have on the reaction rate. The effect of water in the reaction was also studied experimentally. Water effectively decreased the rate of the reaction probably due to the formation of a heterogeneous mixture (the chloroformate separates from the reaction solution on the addition of water) (Graph 7).

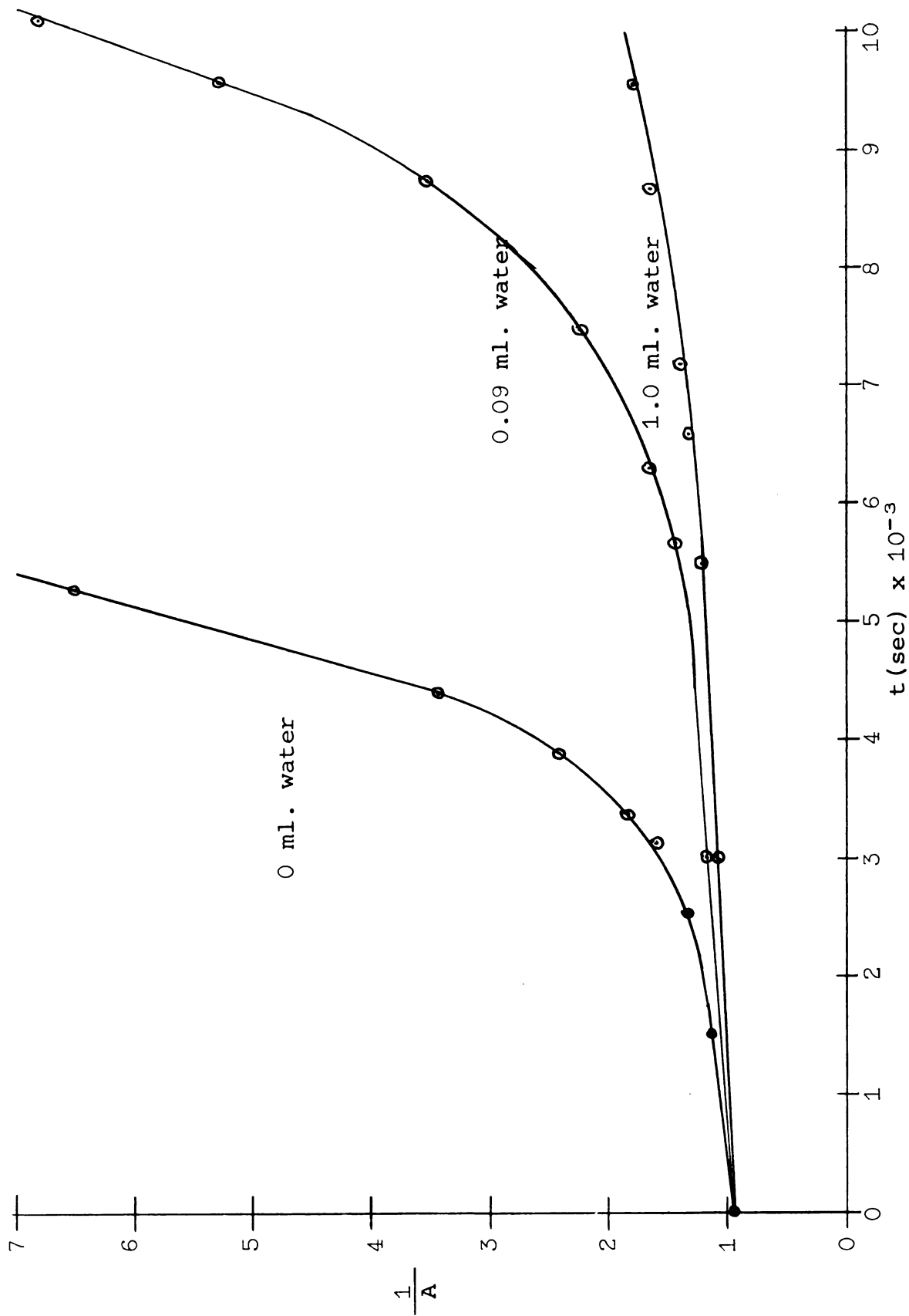
Pseudo first order reaction rates for the p-substituted phenylchloroformates with silver nitrate were determined by flooding the reaction with a five-fold excess of silver nitrate at 21°. In this case first order plots gave good straight lines for 80% of the reaction and then started to drop off. As in the previous cases the rate constant and subsequent data were determined for the initial rates only. The fact that pseudo first order kinetics were obtained under these reaction conditions indicates that the silver nitrate must take part in the rate determining step, of these rearrangement reactions.

Collective examination of the second order and pseudo first order kinetic data indicates that the first step in the reaction sequence is rate determining.

The activation parameters indicate that the substituent on the benzene ring has a large effect on the overall rate of the reaction. The energy of activation varies from 8.0 for p-nitro to 18.8 kcal/mole for p-methoxy phenylchloroformate.



Graph 6. Pseudo 1st Order Kinetic Plot at 21°C for the Reaction of p-Substituted Phenylchloroformate with a Five-fold Excess of Silver Nitrate.



Graph 7. Effect of Water on the Rate of the Reaction of p-Methoxyphenylchloroformate with Silver Nitrate.

Table IV. Initial Rate Constants and Activation Parameters for the Reaction of p-Substituted Phenylchloroformates with Silver Nitrate

p-Substituent	Temp °C	$k_1 \times 10^3$ l./mole sec	E_a kcal/mole	ΔS^* e.u.
Hydrogen	10	1.12	18.8	-6.7
	21	3.79		
	31	5.01		
Methoxy	10	0.34	20.1	-5.1
	21	1.27		
	31	3.95		
Methyl	10	0.72	19.6	-6.1
	21	2.16		
	31	8.24		
Phenyl	10	1.40	19.0	-6.6
	21	3.62		
	31	14.82		
Bromo	10	1.85	16.8	-13.7
	21	5.81		
	31	14.74		
Chloro	10	2.68	14.6	-20.9
	21	6.62		
	31	16.34		
Nitro	10	16.41	8.0	-40.7
	21	23.52		
	31	44.41		

The negative entropy (ΔS^*) values indicate that there is a decrease in the freedom of the reactants with a very large ΔS^* difference between the p-methoxy ($\Delta S^* = -5.1$) and p-nitro ($\Delta S^* = -40.7$) phenylchloroformate.

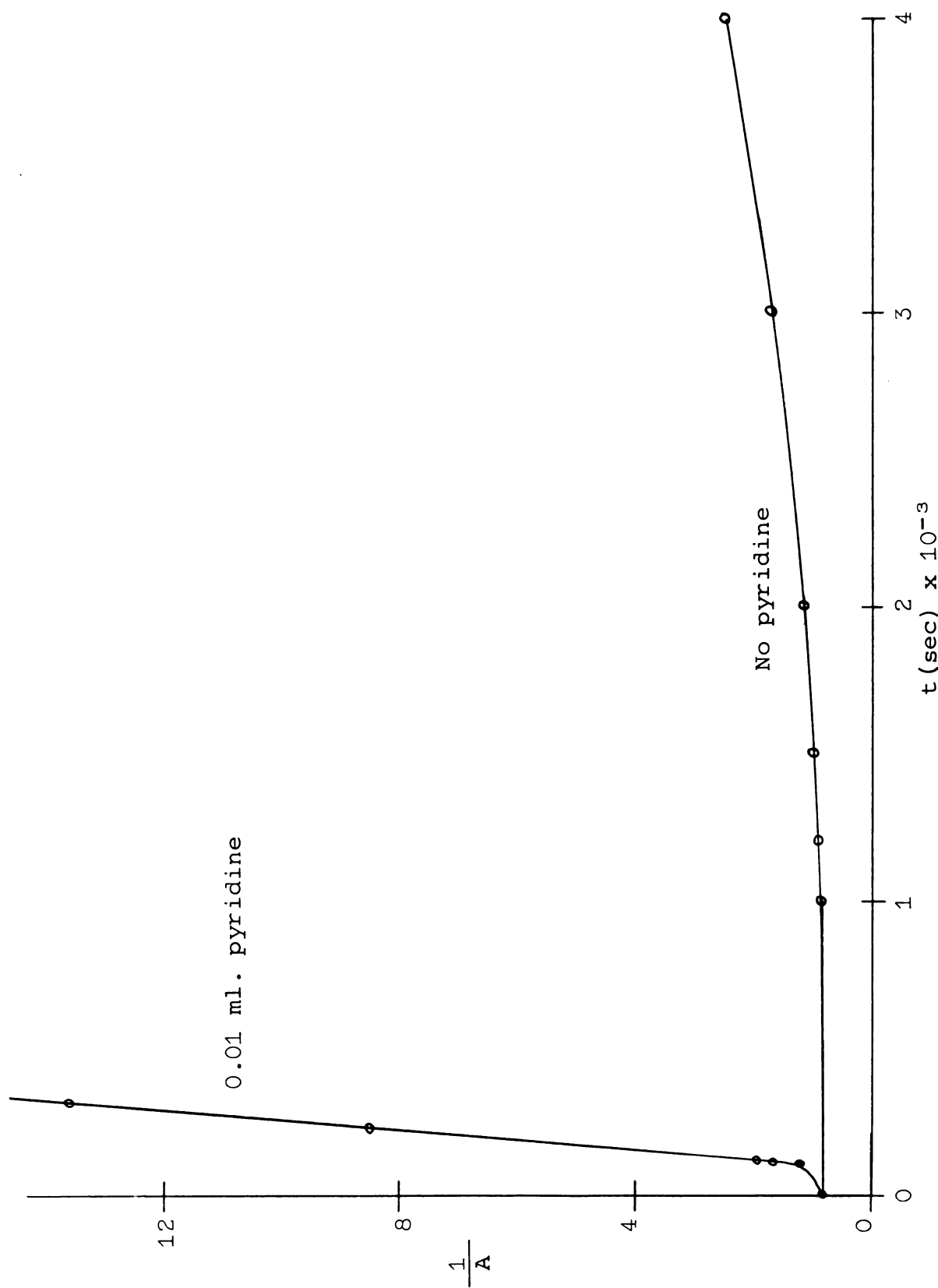
Table V. Initial Pseudo First Order Rate Constants for the Reaction of p-Substituted Phenylchloroformates with a Five-fold Excess of Silver Nitrate at 21°

Compound	$k_1 \times 10^4/\text{sec}$
p-Methoxyphenylchloroformate	6.37
p-Methylphenylchloroformate	7.34
p-Phenylphenylchloroformate	12.48
Phenylchloroformate	13.01
p-Bromophenylchloroformate	14.17
p-Chlorophenylchloroformate	21.28
p-Nitrophenylchloroformate	63.66

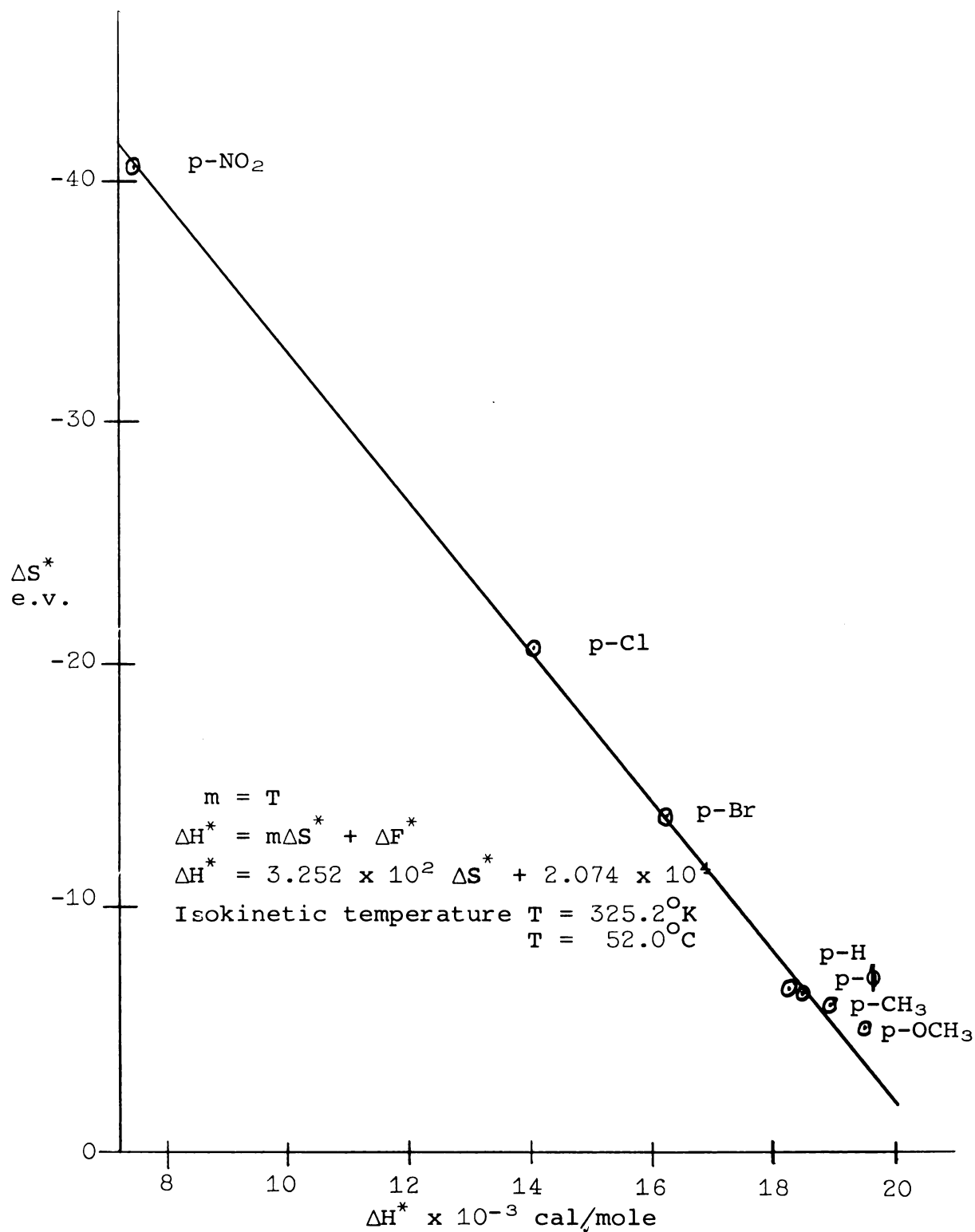
The rate of the reaction in the presence of pyridine was also examined. As shown in Graph 8, the rate is indeed enhanced but the overall shape of the curve is not changed indicating that whatever causes the abnormalities of the second order plot is not affected by the presence of pyridine in the reaction medium.

From the physical data an isokinetic temperature for the reaction was determined by plotting ΔS^* versus ΔH^* , see Graph 9. The isokinetic temperature determined was 52.0° which is 21° above the highest temperature used in the kinetic determinations. Thus, subsequent data for the Hammett relationship should be valid.

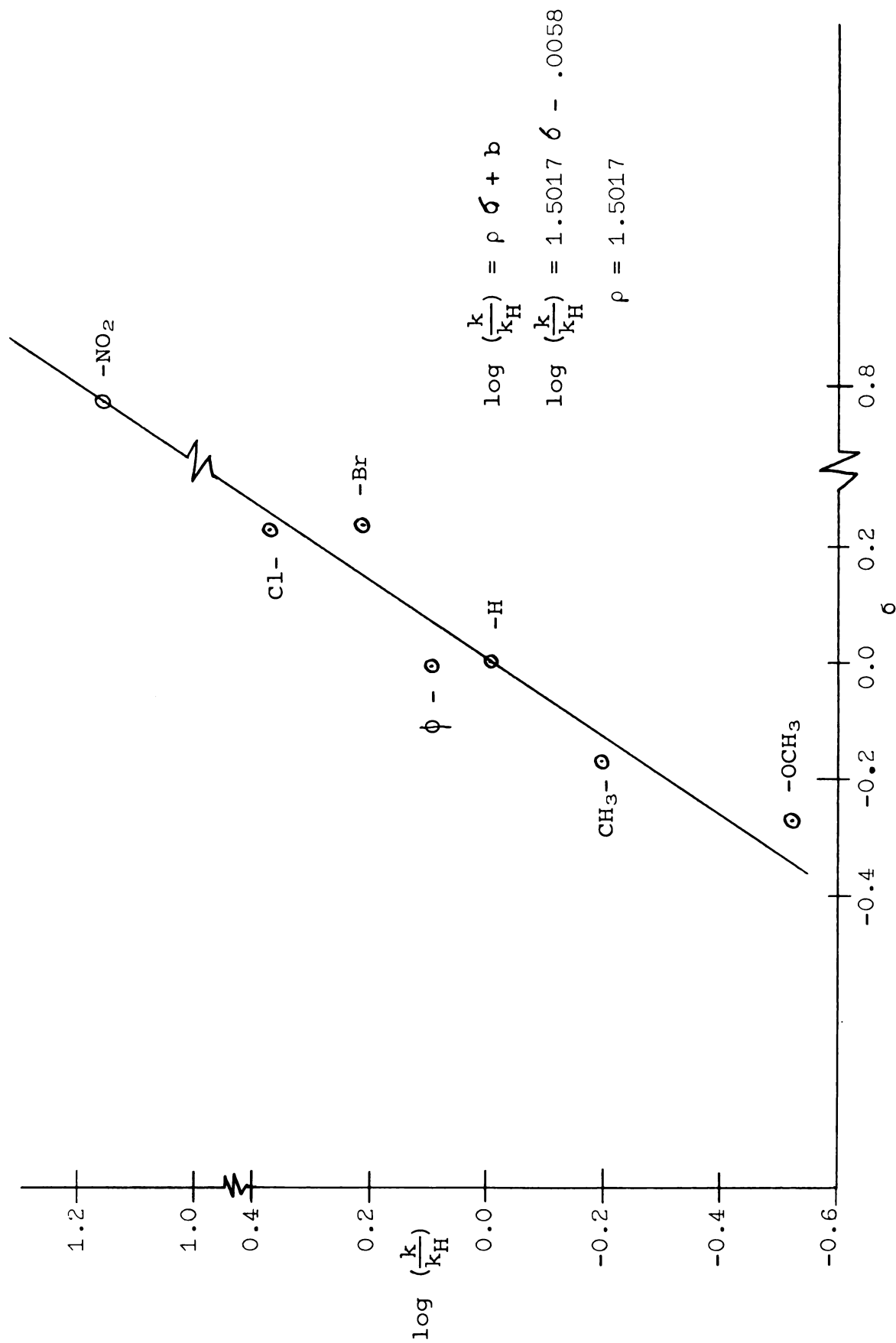
A Hammett plot of the reaction rates at 10, 21, and 31° (equal molar concentration) give a reasonably straight line when the p- σ substituent values are plotted versus $\log (\frac{k}{k_H})$. The values for ρ obtained were positive (10°, 1.5017; 21°, 1.1482; 31°, 0.9211) (see Graphs 10, 11, 12).



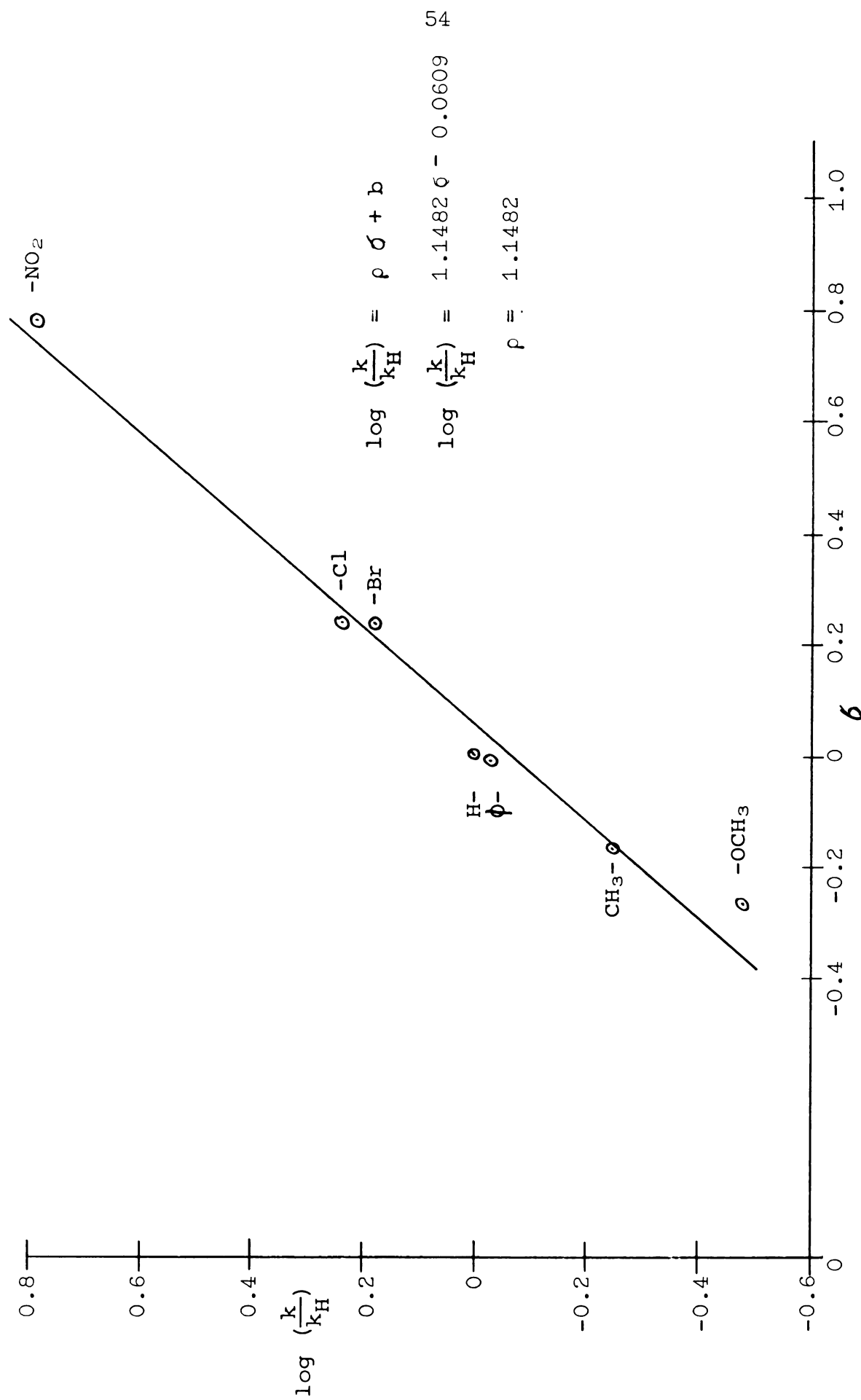
Graph 8. Effect of Pyridine on the Rate of Reaction of p-Methoxyphenylchloroformate (0.10 mole) with Silver Nitrate (0.10 mole).



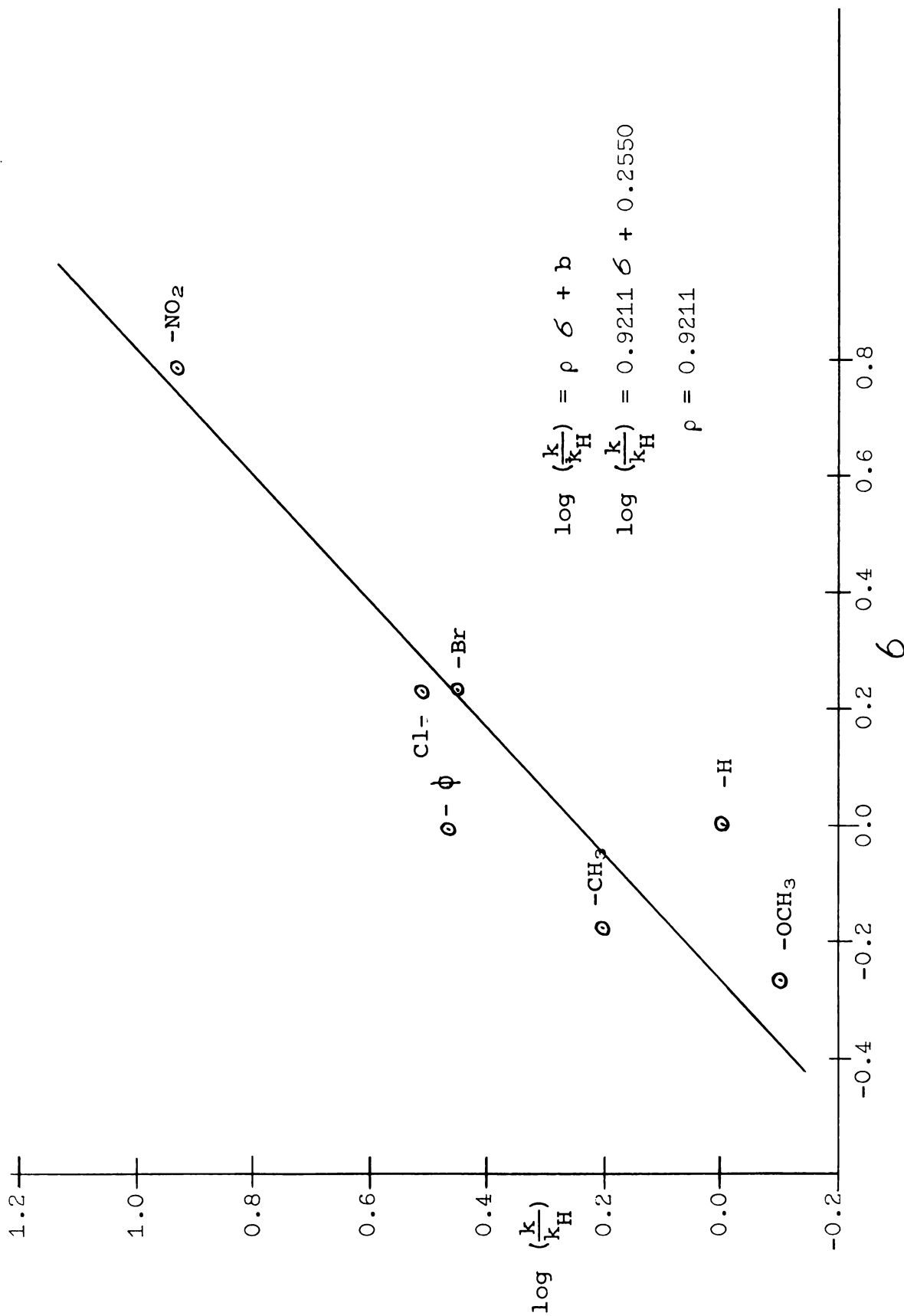
Graph 9. Graph of ΔS^* versus ΔH^* for the determination of the Isokinetic Temperature for the Reaction of p-Substituted Phenylchloroformates with Silver Nitrate (Equal Molar Concentrations).



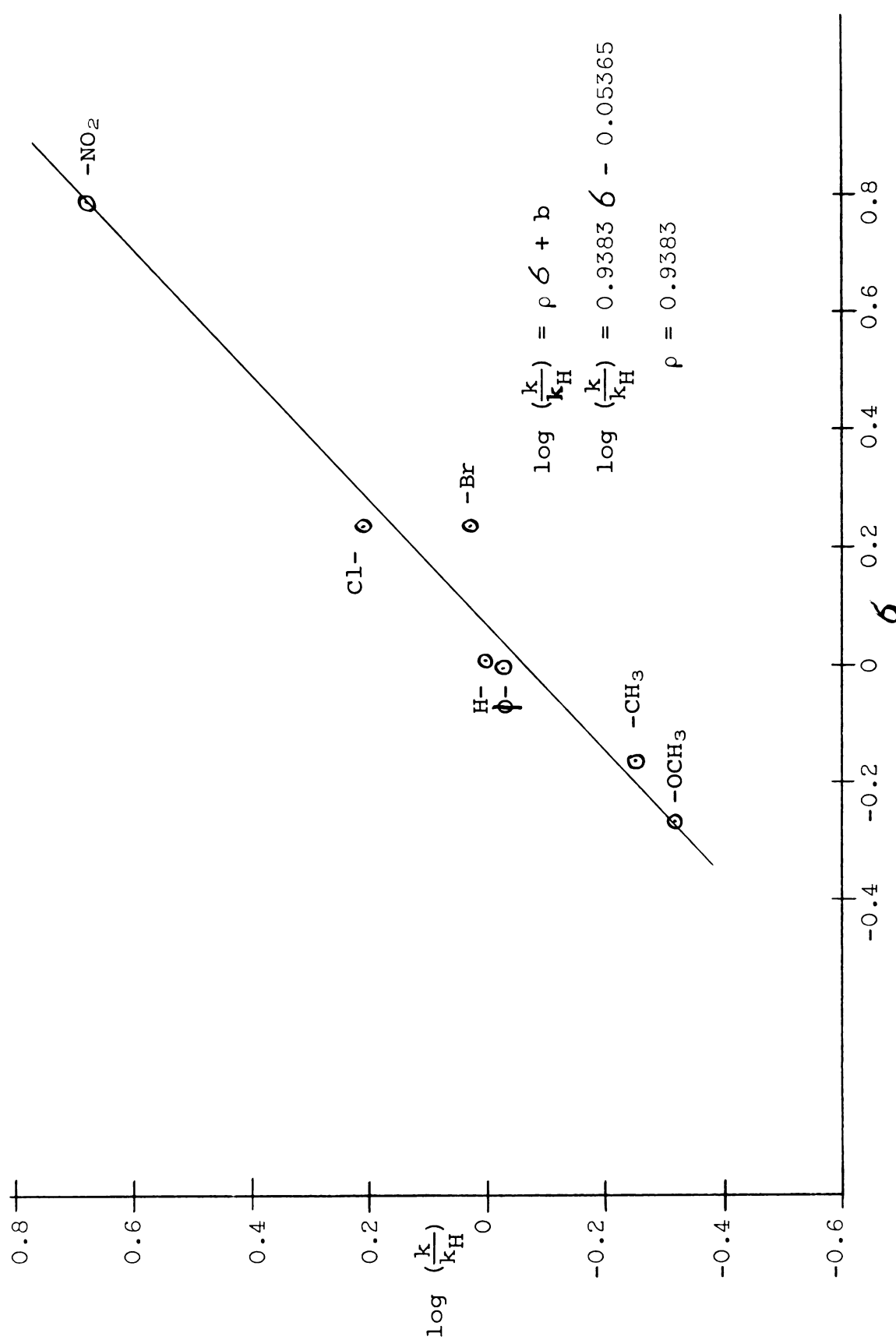
Graph 10. Plot of the Hammett Equation for the Reaction of p-Substituted Phenyl-chloroformates with Silver Nitrate (Equal Molar Concentrations) at 10° .



Graph 11. Plot of the Hammett equation for the Reaction of p-Substituted Phenylchloroformates with Silver Nitrate (Equal Molar Concentrations) at 21°.



Graph 12. Plot of the Hammett Equation for the Reaction of p-Substituted Phenylchloroformates with Silver Nitrate (Equal Molar Concentrations) at 31°.



Graph 13. Plot of the Hammett Equation for the Reaction of p-Substituted Phenyl-chloroformates with a Five-fold Excess of Silver Nitrate at 21°.

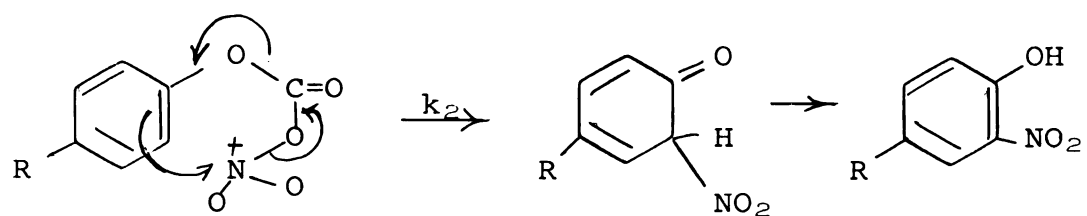
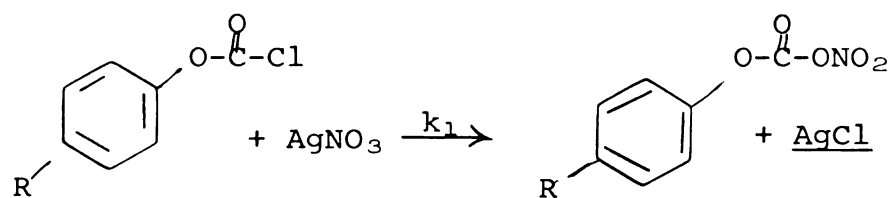
These values indicate that a negative charge is being developed in the transition state and since the ρ 's are relatively large a negative charge of some magnitude is being developed. In reaction with a five-fold excess of silver nitrate, a ρ value of 0.9383 was obtained, again indicating a negative charge was formed in the transition state.

Conclusions based on the experimental evidence determined in an investigation of the rearrangements of arylchloroformates in reaction with silver nitrate in acetonitrile as a reaction media are:

- a) the major products are 2-nitro-4-substituted phenols;
- b) a free radical mechanism is not operative;
- c) an intermolecular mechanism is not operative;
- d) the reaction rate is enhanced by the addition of pyridine to the reaction media;
- e) the initial reaction rate is second order for equal molar concentrations of silver nitrate and aryl chloroformate;
- f) the initial rate is pseudo first order in the presence of excess silver nitrate;
- g) the entropy change, ΔS , is negative, and
- h) the value of ρ in the Hammett relationship is positive.

These observations suggest the mechanism for the rearrangement reaction of p-substituted phenylchloroformate with

silver nitrate in acetonitrile is a two step sequence,



with step one as being rate determining,

EXPERIMENTAL

I. Reagents

A. Acetonitrile

Acetonitrile was distilled from calcium hydride through a two-foot column packed with fine glass helices. The fraction boiling in the range 81.1-81.5 was collected and stored over calcium hydride until use.

B. α -Methylstyrene

Eastman's Reagent Grade α -methylstyrene was fractionated through a glass helic-packed column and the material boiling in the range from 164.5-165.5 was used in the present investigation.

C. Galvinoxyl

Obtained from Sheldon Lande, and used as received.

D. Phenylchlorothiolformate

This compound was obtained from the Aldrich Chemical Company and was used as obtained.

E. Standard Silver Nitrate

Standard silver nitrate was prepared by weighing the required quantity of salt directly (Baker Certified Reagent) and dissolving it to volume in Acetonitrile.

F. Standard Tetrabutylammonium Hydroxide

Standard tetrabutylammonium hydroxide (0.0489N) was obtained from Professor K. G. Stone, of this department.

G. Silver Acetate

This material was obtained from the K & K Laboratories and was used as obtained.

H. Silver Trifluoroacetate

This compound was obtained from the K & K Laboratories and used as received.

II. Preparation of Aryl Chloroformates

A. Typical Preparation

In a typical preparation of an aryl chloroformate a liter three-necked flask fitted with a dropping funnel, dry ice-acetone reflux condenser (methanolic potassium hydroxide and water traps connected to the outlet), liquid addition tube, magnetic stirrer, and immersed in a dry ice-acetone cooling bath, was charged with 325 ml. of benzene and 62.07 g. (0.50 mole) of p-methoxyphenol. Through the addition tube, 67.8 ml. of liquid phosgene was cautiously added to the benzene solution of the phenol. The addition tube was then replaced with a glass stopper. To the vigorously stirred reaction mixture 66.92 ml. (0.05 mole) of N,N-dimethylaniline was added from the dropping funnel

while maintaining the reaction temperature between 0 and 5°. During the addition of each drop of N,N-dimethylaniline, the reaction solution underwent a color change from light blue to light green. On the addition of the final milliliter of the amine the reaction solution changed to a yellow colored slush. The reaction mixture was set aside for 10 minutes and 50 ml. of water was cautiously added, since a violent reaction took place if the water was added too rapidly. The benzene layer was separated; washed with dilute hydrochloric acid, dilute sodium hydroxide, and finally with water after which it was dried over anhydrous magnesium sulfate. The benzene was removed in a rotary evaporator and the crude product was distilled in vacuo to obtain 89.9 g. (96.3%) of clear colorless p-methoxyphenylchloroformate boiling at 49°/0.27 mm. and having a refractive index of n_D^{19} 1.5237. (See Table VI for the other arylchloroformates prepared in the course of this investigation.)

B. Attempted Preparation of 2,6-Di-t-Butylphenylchloroformate

An attempt to prepare 2,6-di-t-butylphenylchloroformate by the procedure described was unsuccessful. The starting phenol was recovered in 99%.

A variety of reaction conditions were employed unsuccessfully. These included higher concentration of phosgene or amine, no solvent, higher reaction temperature (15-20°), and various combinations of these. Aqueous sodium

Table VI. Elemental Analyses of the Aryl Chloroformates

Chloroformate	Elemental Analyses					
	Carbon		Hydrogen		Halogen	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
p-Methoxyphenyl	51.50	51.80	3.78	3.45	19.00	18.81
p-Methylphenyl	56.33	57.05	4.14	4.38	20.78	20.37
p-Phenylphenyl	67.11	67.00	3.90	3.67	15.24	15.24
p-Bromophenyl	35.71	36.05	1.71	1.74	48.99	49.17
p-Chlorophenyl	44.02	46.79	2.11	2.49	37.12	34.78
p-Nitrophenyl	41.71	42.45	2.00	2.19	17.59	16.68
Phenyl	53.70	53.71	3.22	3.23	22.64	22.43
2,6-Dimethylphenyl	58.55	58.64	4.91	4.97	19.20	19.41
2,6-Diisopropylphenyl	64.86	64.13	7.12	7.58	14.73	13.97
2,4,6-Trimethylphenyl	60.46	63.12	5.58	6.02	17.85	15.78
α -Naphthyl	63.94	64.00	3.41	3.51	17.16	16.86
β -Naphthyl	63.94	63.72	3.41	3.40	17.16	16.88

hydroxide was tried in place of the N,N-dimethylaniline as a base but to no avail. The steric hinderance of the two t-butyl groups ortho to the hydroxyl group evidently is great enough to prevent reaction with phosgene.

III. Product Analyses

A. Reaction of Naphthyl and p-Substituted Phenyl-chloroformates with Silver Nitrate

Using the apparatus illustrated in Diagram 1, a solution (precooled to 0°) containing 11.77 g. (0.05 mole) of p-bromophenylchloroformate in 150 ml. of acetonitrile was added to a solution (precooled to 0°) containing 8.50 g. (0.05 mole) of silver nitrate in 150 ml. of acetonitrile. The temperature of the solution was maintained at 0° while a continuous stream of nitrogen was passed through the apparatus throughout the entire reaction period. A half-hour after initiation of the reaction a considerable quantity of silver chloride had precipitated and the reaction solution had turned a light yellow in color. After four hours of reaction the solution had turned a dark orange in color and after twenty hours the reaction was complete as evidenced by the absence of a precipitate when chloride ion was added to an aliquot of the clear reaction solution. The silver chloride was removed by filtration, washed with two 20 ml. portions of cold acetonitrile and then with two 10 ml. portions of cold anhydrous ether, dried at 105° for

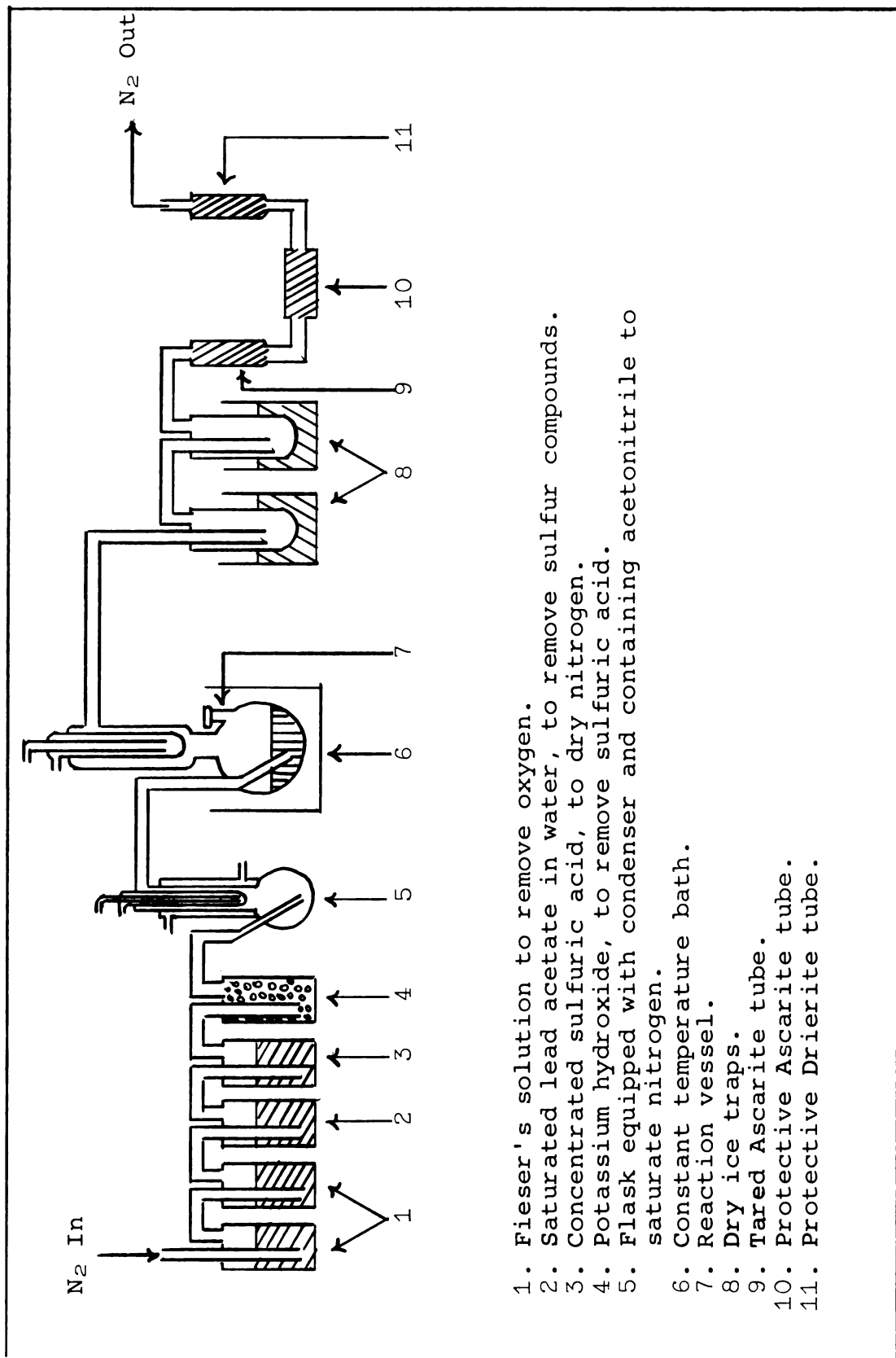


Diagram 1. Carbon Dioxide Absorption Train.

two hours and weighed (7.10 g. 99.0%). The combined acetonitrile washings were added to the original filtrate and the acetonitrile was removed in a rotary evaporator. The residue was dissolved in approximately 150 ml. of anhydrous ethyl ether, decolorized with Norite A, and the volume of the ether solution was concentrated to 50 ml. Cooling the concentrated solution in an ice bath yielded 7.8 g. of yellow colored crystals; reduction of the mother liquor to 15 ml. and cooling yielded a second quantity of the crystalline solid (2.8 g.). The total yield of 2-nitro-4-bromophenol obtained was 10.60 g. (97.7%) melting at 88-89°. Literature value (19): melting point 89°.

After setting the dry ice traps aside at room temperature for one hour the tared carbon dioxide absorption tube, packed with a 2:1 mixture of ascarite and anhydrous magnesium perchlorate, was reweighed and the gain in weight (2.2 g., 98.5%) of the tube was taken as equivalent to the weight of the carbon dioxide evolved during the reaction.

The results for all of the naphthyl and p-substituted phenylchloroformates reaction with silver nitrate are tabulated in Table II.

B. Reaction of the Hindered Phenylchloroformates with Silver Nitrate

1. Reaction of 2,6-dimethylphenylchloroformate with silver nitrate

Using the apparatus illustrated in Diagram 1, 9.23 g. (0.05 mole) of 2,6-dimethylphenylchloroformate dissolved

in 25 ml. of acetonitrile was added to a solution containing 8.50 g. (0.05 mole) of silver nitrate in 50 ml. of acetonitrile. Five minutes after initiation of the reaction the solution had become dark yellow in color, silver chloride had started to precipitate and the reaction mixture had to be cooled by immersion in an ice bath to maintain the reaction temperature below 30° . After 14 hours of reaction the silver chloride was removed by filtration, washed with two 20 ml. portions of acetonitrile and then two 10 ml. portions of anhydrous ether, dried at 105° for 90 minutes and weighed (7.12 g., 99.2%). The combined acetonitrile washings were added to the filtrate and it was decolorized. On cooling it yielded yellow colored crystals of product which on recrystallization from methylene bromide gave 5.23 g. (62.6%) of light yellow colored 4-nitro-2,6-dimethylphenol melting at $167.5-168.3^{\circ}$. A mixed melting point with an authentic sample of 4-nitro-2,6-dimethylphenol gave a melting point of $167-168^{\circ}$. Literature value (25): melting point $169-170^{\circ}$.

Concentration of the mother liquor yielded 0.78 g. of dark red colored crystals which decomposed at 224° . This material was identified as 3,5,3',5'-tetramethyldiphenequinone-(4,4') (24).

The carbon dioxide evolved during the reaction was determined as described for the p-substituted chloroformates. The yield was 83%.

2. Reaction of 2,6-diisopropylphenylchloroformate with silver nitrate

Using the experimental procedure described for the 2,6-dimethylphenylchloroformate 8.9 g. (0.05 mole) of 2,6-diisopropylphenylchloroformate was allowed to interact with 8.50 g. (0.05 mole) of silver nitrate. Following the product isolation previously described a dark reddish-yellow colored solution was obtained. This was diluted to 125 ml. in a volumetric flask with acetonitrile, and a 10 ml. aliquot was chromatographed on an acid-washed alumina column using acetonitrile as the elutant. The initial band which came off the column was dark yellow in color and on evaporation of the solvent yielded 8.2 g., equivalent to a 73% yield of 4-nitro-2,6-diisopropylphenol which melted at 112° . Literature value (28): melting point 112° . A second band was obtained which yielded a dark red compound (1.2 g.) This material decomposed at 245° , and was identified as 3,5,3',5'-tetra~~is~~propyldiphen~~o~~quinone-(4,4'). The yield of silver chloride and carbon dioxide in this reaction were 96.0% and 74.1%, respectively.

3. Reaction of 2,4,6-trimethylphenylchloroformate with silver nitrate

Using the procedure already described 20.00 g. (0.10 mole) of 2,4,6-trimethylphenylchloroformate was allowed to interact with 17.12 g. (0.10 mole) of silver nitrate in 300 ml. of acetonitrile as a reaction media.

After the reaction mixture had been set aside for 24 hours at room temperature, it was heated to 30° and held at this temperature, for an additional 24 hours resulting in the formation of a dark red solution containing silver chloride and a red crystalline product. Filtration of the solution gave a mixture of silver chloride and red crystals plus a dark red filtrate. The red crystals were insoluble in the common organic solvents, and the silver chloride was separated from the red crystals with ammonium hydroxide. The red crystalline solid was then washed with water and acetone yielding 4.73 g. of material which decomposed at $224-230^{\circ}$. It was identified as 3,5,3',5'-tetramethylstilbenequinone-(4,4'). Literature value (26): melting point $224-226^{\circ}$.

Calc'd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81.

Found: C, 81.16; H, 6.66

The red filtrate was subjected to column chromatographic analysis on an acid-washed alumina column. Forty distinct bands appeared on the column. None of these bands were identified.

C. Reaction of Phenylchlorothiolformate with Silver Nitrate

The apparatus illustrated in Diagram 1, and the experimental procedure as described for the p-substituted phenylchloroformates were used in this reaction. The sole "product" obtained was a black untracable amorphous solid

that failed to react with acetic anhydride indicating the absence of any phenolic monomer. In subsequent reaction of phenylchlorothioformate with silver nitrate, acetic anhydride was added after the reaction had proceeded for 30 minutes and 60 minutes. However, in each case only a black tarry material was formed from which no acetylated phenol could be obtained. In all cases the silver chloride and carbon dioxide was isolated in yields between 95-98% and 70-85%, respectively.

D. Trapping Experiments

1. Reaction of p-phenylphenylchloroformate with silver nitrate in the presence of sodium p-methoxyphenoxide

To 4.5 g. (0.025 mole) of silver nitrate in 150 ml. of acetonitrile, precooled to 0°, in a 250 ml. flask fitted with a reflux condenser, drying tube, cooling bath, and magnetic stirrer were added a solution containing 5.82 g. (0.025 mole) of p-phenylphenylchloroformate in 50 ml. of acetonitrile and a second solution containing 3.65 g. (0.025 mole) of sodium p-methoxyphenoxide in 25 ml. of acetonitrile. A black precipitate formed immediately in the reaction mixture; simultaneously the reaction solution underwent a color change from light green to yellow. The mixture was allowed to warm to room temperature. On being set aside for 12 hours, with stirring, the black precipitate turned

to a light yellow colored precipitate. Product isolation from the reaction mixture was then conducted in the same manner as for the reactions of other p-substituted phenylchloroformates. The yield of 4-phenyl-2-nitrophenol obtained was 5.23 g. (97.3%) melting at 65.5-66°. Literature value (17): melting point 66°. For the investigation, additional rearrangement reactions with the organic base as a catalyst, the same experimental procedure was used as described except that the sodium p-methoxyphenoxide was added 10 minutes and 60 minutes after initiation of the reaction with yields of 98.3% and 97.9%, respectively, being obtained of the expected product.

2. Reaction of p-phenylphenylchloroformate with silver nitrate in the presence of p-methoxyphenol

The experimental procedure described above was used for this trapping experiment. To 11.63 g. (0.05 mole) of p-phenylphenylchloroformate in 100 ml. of acetonitrile was added a solution containing 8.50 g. (0.05 mole) of silver nitrate in 200 ml. of acetonitrile. After the reaction had proceeded for 10 minutes, a solution containing 12.4 g. (0.10 mole) of p-methoxyphenol in 50 ml. of acetonitrile was added to the reaction mixture. Following the usual product isolation procedure 10.01 g. (93.1%) of 2-nitro-4-phenylphenol melting at 65-66° was obtained. Literature value (17): melting point 66°.

3. Reaction of p-phenylphenylchloroformate with silver nitrate in the presence of α -methylstyrene and galvinoxyl

The same procedures, compound and molar ratios of reactant as described above for the reaction in the presence of p-methoxyphenol were employed in this study of a possible free radical mechanism being operative in these rearrangements. The yield of 2-nitro-4-phenylphenol in the presence of α -methylstyrene and galvinoxyl was 95.1% and 96.3%, respectively.

E. Reaction of p-Substituted Phenylchloroformates with Silver Salts Other than Silver Nitrate

1. Reaction of p-substituted phenylchloroformates with silver acetate

To 0.25 mole of p-substituted phenylchloroformate in 25 ml. of acetonitrile was added 0.25 mole of silver acetate in 25 ml. of acetonitrile. A precipitate was immediately formed. The reaction mixture was set aside for 24 hours with constant stirring and product isolation was then carried out in the same manner as for reactions with silver nitrate and the arylchloroformates. In all cases only non-nitrated phenol was obtained (see Table III).

2. Reaction of p-phenylphenylchloroformate with silver trifluoroacetate

To 1.36 g. (0.0058 mole) of phenylphenylchloroformate in 25 ml. of acetonitrile was added 1.28 g. (0.0058 mole) of silver trifluoroacetate in 25 ml. of acetonitrile

whereupon an immediate precipitation of silver chloride occurred. After the reaction had been set aside for 24 hours, the silver chloride was removed by filtration, washed with acetonitrile and ether, dried at 106° for 2 hours and weighed (0.75 g., 94%). The acetonitrile washings were added to the filtrate, and the acetonitrile solvent was evaporated in a rotary evaporator leaving a white solid melting at $95-105^{\circ}$. On recrystallization from a 2:1 ether-pentane mixture 1.51 g. (98%) of white crystals melting at 98 to 103° was obtained. The compound was identified as 2-hydroxy-5-phenyl-trifluoromethyl ketone. This compound decomposes on standing.

Calc'd for $C_{14}H_9F_3O_2$: C, 63.16; H, 3.14; F, 21.41.

Found: C, 63.46; H, 3.15; F, 22.01.

F. Reaction of p-Methoxyphenylchloroformate with Silver Nitrate in the Presence of Pyridine

To a solution containing 0.1085 mole of p-methoxyphenylchloroformate in 50 ml. of acetonitrile was added 0.1085 mole of silver nitrate and 0.01 ml. of pyridine. A rapid evolution of carbon dioxide occurred after approximately 50 seconds. The reaction was set aside for 2 hours and then product isolation in the usual manner. The yields of silver chloride and 2-nitro-4-methoxyphenol was 98.9% and 83.4%, respectively.

IV. Kinetics of the Reactions of p-Substituted Phenylchloroformates with Silver Nitrate

The rates of the reaction were determined by measuring the rate of disappearance of the chloroformate absorption band at approximately 1777 cm^{-1} employing a Unicam S. P. 200 recording infrared spectrophotometer in conjunction with a variable temperature I. R. cell, equipped with silver chloride windows, and apparatus as illustrated in Diagram 2. This method was chosen after initial attempts to use conductometric, amperometric, and carbon dioxide evolution methods proved unfeasible in their attempted application to this system.

The following experimental procedure was used in a typical kinetic determination. A 50 ml. aliquot of a standard p-substituted phenylchloroformate was added to the reaction flask and magnetically stirred. The solution was then allowed to reach bath temperature which was controlled to $\pm 0.01^{\circ}$ with a thyratron electronic relay. The solution was then injected with a 4 ml. aliquot of a standardized silver nitrate solution. At predetermined time intervals, samples were filtered, withdrawn from the reaction and injected into the sample cell. The carbonyl absorption of the chloroformate was scanned and the time noted at which the minimum transmittance occurred. The sample was withdrawn from the cell with a hypodermic syringe and the cell was washed with acetonitrile. Acetonitrile was injected into the cell and

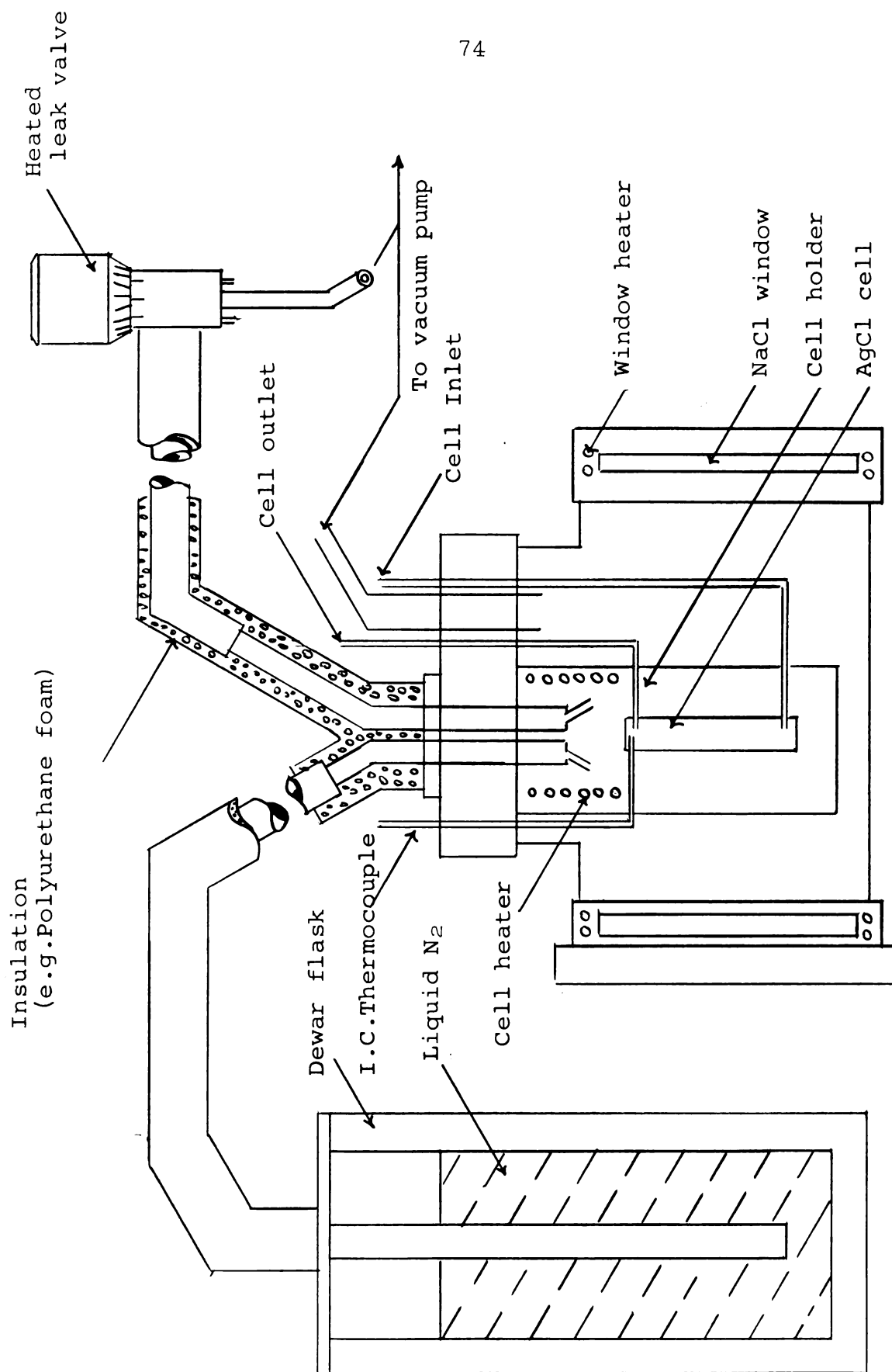


Diagram 2. Side View Variable Temperature I. R. Cell

the 100% point determined; the 100% transmittance point had to be determined after each sample was examined since silver chloride precipitated onto the cell windows during the measurements and thus affected the 100% point. In preparation for the determination of the next point, the cell was dried by forcing dry air through it. In this manner the rate of the disappearance of the chloroformate peak was followed. See Table I, page 6, for the absorption of the carbonyl band of the aryl chloroformates.

The second order rate constants were calculated from equation (1)

$$\frac{1}{C} = k_2 t + \frac{1}{C_0} \quad (1)$$

(where k is the second order rate constant, C is the concentration in liters/mole, and t is the time in sec.) by plotting the reciprocal of the concentration versus time and using the least squares method to determine the slope (k_2) and intercept (C_0). The first order constants were determined from equation (2) by plotting the logarithm

$$\ln C = -k_1 t + \ln C_0 \quad (2)$$

of the concentration versus time and using the method of least squares to determine the slope ($\frac{-k_1}{2.303}$) and the intercept ($\log C_0$). It was previously established that the absorbance of the various aryl chloroformates varies linearly

with concentration throughout the concentration range employed in this investigation.

The energy of activation, E_a , was calculated using equation (3)

$$k = s e^{-E_a/RT} \quad (3)$$

where k is the rate constant, E_a is the experimental activation energy in calories, R is the gas constant per mole (1.987 calories/ $^{\circ}$ K), and s is the frequency factor (pre-exponential factor). Taking the logarithm of both sides (4)

$$\log k = \log s + \frac{-E_a}{2.303RT} \quad (4)$$

and plotting $\log k$ versus $1/T$, the energy of activation was obtained by multiplying the slope of the line, which was determined by the method of least squares, by $-2.303R$. The least squares method also gave the value for the logarithm of the frequency factor, s , which is the intercept for equation (4).

The entropy of activation, ΔS^* , was calculated from the Eyring Equation (5)

$$k = \frac{ek'T}{h} e^{\Delta S^*/R} e^{E_a/RT} \quad (5)$$

where k is the rate constant, k' is Boltzmann's constant, T is the absolute temperature, h is Planck's constant, ΔS^* is the entropy difference between the initial and activated

states in entropy units, E_a is the experimental activation energy in calories, R is the gas constant in calories/ $^{\circ}\text{K}$, and e is the base of the natural logarithm system.

Combining equations (1) and (5) results in equation (6)

$$s = \frac{ek'T}{h} e^{\Delta S^*/R} \quad (6)$$

Taking the logarithms of both sides and rearranging gives

$$\Delta S^* = R \ln S - R \ln (ek'T/h) \quad (7)$$

therefore at $T = 21^{\circ}$ $\Delta S^* = 4.5765 (\log s - 13.2218) \quad (8)$

The entropy of activation was obtained by solving equation (8) by substituting the values of $\log s$ that had been previously determined (see the calculations for E_a).

The enthalpy, ΔH^* , was calculated from equation (9)

$$\Delta H^* = E_a - RT \quad (9)$$

by substituting the appropriate values for E_a , R , and T .

The isokinetic temperature was determined from equation (10)

$$\Delta H^* = T\Delta S^* + \Delta F^* \quad (10)$$

by a plot of ΔH^* versus ΔS^* using the least squares method to determine the slope which is the isokinetic temperature.

Rho (ρ) of the Hammett relation was determined from equation (11) by plotting the $\log (\frac{k}{k_h})$ versus σ again using

$$\log \left(\frac{k}{k_h} \right) = \sigma \rho \quad (11)$$

the least squares method to determine the slope.

V. Miscellaneous Preparations

A. Preparation of Sodium p-Methoxyphenoxide

To a solution containing 6.45 g. (0.16 mole) of sodium hydroxide in 100 ml. of water was added 20 g. (0.16 mole) of p-methoxyphenol. The resulting solution was evaporated to dryness under high vacuum to obtain 21.9 g. (0.15 mole) of light brown colored product.

B. Preparation of p-Methylphenylcarbamate

An excess of anhydrous ammonia gas was passed into a solution 1.00 g. (0.0059 mole) of p-methylphenylchloroformate in 50 ml. of anhydrous ethyl ether until precipitation ceased. The reaction mixture was washed twice with water; the ether layer was separated, dried over anhydrous sodium sulfate and the ether distilled under vacuum leaving a fluffy white residue. This, on recrystallizing from petroleum ether, yielded 0.80 g. (90.4%) of a white product melting at 155-156^o. Literature value (27): melting point 154^o.

SUMMARY

1. Four previously undescribed aryl chloroformates, p-bromophenyl, p-methoxyphenyl, 2,6-diisopropylphenyl, and 2,4,6-trimethylphenyl, were prepared and characterized.

2. The rates and products of the reactions of seven p-substituted phenylchloroformates with silver nitrate were studied. The products found were 2-nitro-4-substituted phenols. The initial rates of the reactions were found to be second order at equal molar concentrations of reactants and first order in the presence of excess silver nitrate. The Hammett equation was found to be applicable to these reactions with a positive rho (ρ) value. This suggests that the rate determining step is the first step; that is, the initial reaction of the chloroformate with silver nitrate to form a nitratocarbamate.

3. A product study was conducted on the reaction of silver nitrate with phenylchloroformates substituted in both ortho positions and both ortho positions plus the para position. The major product obtained when the ortho positions were blocked was p-nitro compound. When all three positions (ortho and para) were blocked, a dimer quinoid product was obtained.

4. The major products from the reaction of α - and β -naphthylchloroformates with silver nitrate were found to be 2-nitro-1-naphthol and 1-nitro-2-naphthol, respectively.

5. The reactions of some p-substituted phenylchloroformates with silver acetate and silver trifluoroacetate were also examined. With silver trifluoroacetate the products were substituted phenyl trifluoromethyl ketones.

6. In addition the reaction of phenylchlorothiolfomate with silver nitrate was investigated.

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