

[CONTRIBUTION FROM AVERY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

The Synthesis of Certain Organophosphorus Compounds Containing the Trichloromethyl Group

BY KENNETH C. KENNARD¹ AND CLIFF S. HAMILTON

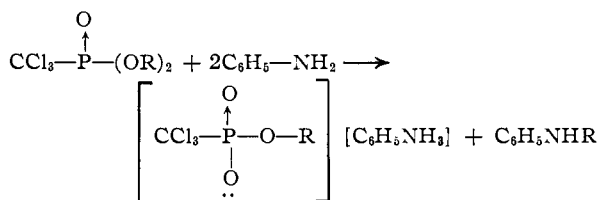
RECEIVED AUGUST 31, 1954

Trichloromethylphosphonic dichloride was treated with various amines and the resulting amides were isolated and characterized. The difference in the extent of reaction of these amines was studied and certain conclusions were reached. Hydrolysis of the red compound, produced by the reaction of *N*-methylaniline, trichloromethylphosphonic dichloride and pyridine, resulted in a derivative of glutaconic dialdehyde, showing that the pyridine ring had opened in the course of the initial reaction. Trichloromethylphosphonamidic chloride possessed acidic properties which were studied. This compound was also reacted with hydrazine, sodium alkoxides, cyclohexylamine and diazomethane.

This problem was undertaken to investigate the synthesis and reactions of organophosphorus compounds containing the trichloromethyl group.

Trichloromethylphosphonic dichloride (I),^{2,3} prepared by the aluminum chloride method⁴ from carbon tetrachloride and phosphorus trichloride was esterified with ethanol, in the presence of a tertiary base, to yield diethyl trichloromethylphosphonate. The physical constants of the ester, thus prepared, coincided with the physical constants of the same ester prepared by means of a Michaelis-Arbusov reaction from triethylphosphite and carbon tetrachloride.⁵

When diethyl trichloromethylphosphonate was heated with aniline in a hydrocarbon solvent, one of the ethyl groups was removed, forming anilinium *O*-ethyl-*P*-trichloromethylphosphonate (II). Russian workers³ later reported this reaction for both the methyl and ethyl esters.

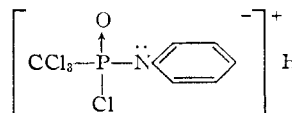


The melting point of II as prepared in this Laboratory was 196–198° dec. while the Russians reported a melting point of 176°. Both analysis and infrared spectra studies confirmed the structure of the compound prepared here.

Trichloromethylphosphonic dichloride (I) reacted with aniline to give trichloromethylphosphonamidic chloride (VIII), but did not react further with aniline, to yield the dianilide. The monoanilide (VIII) was shown to be acidic by its ready solubility in a cold, basic solution. The surprising stability of the acid chloride function was shown by the fact that acidification of the basic solution of VIII caused VIII to be returned unchanged.

The presence of the trichloromethyl group, which is strongly electron withdrawing,⁶ together with the influence of the chlorine atom apparently

causes a low electron density on the phosphorus atom and thence on the nitrogen atom. The evident result is an ionizable hydrogen.



The importance of the chlorine atom in aiding this effect is illustrated by the fact that when it is replaced by an amide or ester group, the effect vanishes and the compound is no longer base soluble.

Further evidence of this mobile hydrogen was afforded by the reaction of diazomethane with VIII. The product was a monomethylated derivative whose infrared absorption spectra showed no *N*-H peak. The melting point of this compound, *N*-methyl-*N*-phenyltrichloromethylphosphonamidic chloride was about 55° lower than the melting point of the starting material, VIII. The effect of destroying the hydrogen bonding possibilities was also shown by the cyclohexylamides. *N*-Cyclohexyltrichloromethylphosphonamidic chloride (VII) was a solid while *N*-cyclohexyl-*N*-methyltrichloromethylphosphonamidic chloride (VI) was a viscous oil at room temperature. Compound VI was prepared by the reaction of I with *N*-methylcyclohexylamine.

Trichloromethylphosphonamidic chloride (cpd. VIII) also reacted readily with a water-aniline mixture, sodium alkoxides, cyclohexylamine and hydrazine to give compounds IV, IX, X, XII, and XIV, respectively, which appear in Table II.

The acid chloride I did not undergo the anticipated facile reactions with all amines. The following table summarizes the behavior of this acid chloride with the various amines employed.

TABLE I

Amines	Moles of amine which reacted with one mole of I	
	Mild conditions ^a	Forcing conditions
<i>p</i> -Nitroaniline	0	0
<i>p</i> -Anisidine	1	0
Aniline	1	0
<i>N</i> -Methylaniline	0	0
Cyclohexylamine	1	1
<i>N</i> -Methylcyclohexylamine	1	0
Piperidine	2	...

^a Mild conditions are defined as 15 to 30 minutes of heating in benzene and forcing conditions are defined as 4 to 9 hours of heating in solvents which boil at 80° or above (benzene, dioxane, toluene, xylene).

(1) Parke, Davis and Co. Fellow 1952–1954, Research Laboratories, Eastman Kodak Co., Rochester, N. Y.

(2) All organophosphorus compounds discussed herein are named according to the nomenclature rules set up by the American Chemical Society, *Chem. Eng. News*, **30**, 4515 (1952).

(3) A. Ya. Yakubovich and V. A. Ginsbury, *Doklady Akad. Nauk S.S.S.R.*, **82**, 273 (1952); *C. A.*, **47**, 2685 (1953).

(4) A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952).

(5) G. M. Kosolapoff, *This Journal*, **69**, 1002 (1947).

(6) G. M. Kosolapoff, *ibid.*, **75**, 5738 (1953).

TABLE II

Letters A and B refer to the structure $\text{CCl}_3-\overset{\text{O}}{\underset{\text{B}}{\text{P}}}-\text{A}$. The Roman numerals correspond to the numbers in the Experimental Part where the compounds are named.

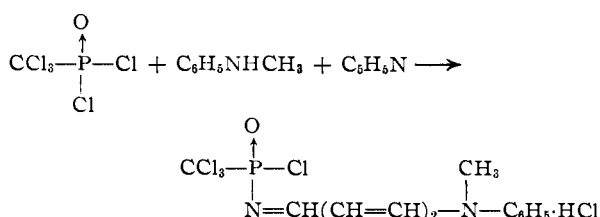
	A	B	Yield, %	M.p., °C.	Carbon Calcd.	Carbon Found	Chlorine Calcd.	Chlorine Found	Nitrogen Calcd.	Nitrogen Found
I	Cl	Cl	81-84	155-156
II	OC_2H_5	OH^a	71	196-198 ^b	33.72	33.41	33.18	32.98	4.37	4.57
III	$\text{NHC}_6\text{H}_4\text{OCH}_3$	OH^b	76	169-170 ^b	42.12	41.93	24.87	24.72	7.24	7.20 ^c
IV	NHC_6H_5	OH^a	84	190-191 ^b	42.52	42.50	28.97	28.87	7.63	7.80 ^d
V	NC_6H_{10}	NC_6H_{10}	84	238-240	39.59	39.98	31.88	32.06	8.39	8.56
VI	$\text{N}(\text{CH}_3)_2\text{C}_6\text{H}_{11}$	Cl	100	B.p. 144-145 ^e at 0.5 mm.	30.70	30.48	4.48	4.48
VII	$\text{NHC}_6\text{H}_{11}$	Cl	100	118-119	28.02	28.14	4.69	4.92
VIII	NHC_6H_5	Cl	100	112-113	28.70	28.84	4.78	4.80
IX	NHC_6H_5	OCH_3	60	146-147	33.30	33.25	36.87	36.79	4.86	5.05
X	NHC_6H_5	OC_2H_5	45	135.5-136.5	35.73	35.83
XI	$\text{N}(\text{CH}_3)_2\text{C}_6\text{H}_5$	Cl	70	57-58	31.30	31.54	46.20	46.41	4.56	4.46
XII	NHC_6H_5	$\text{NHC}_6\text{H}_{11}$	34	198-199	29.91	30.11	7.88	8.01
XIII	$\text{NHC}_6\text{H}_{11}$	$\text{NHC}_6\text{H}_{11}$	23	191-192	43.17	42.90	7.75	7.97
XIV	NHC_6H_5	$\text{NH}-\text{NH}_2$	82	191-193 ^b	14.56	14.62
XV	NHC_6H_5	$\text{NH}-\text{N}=\text{C}(\text{CH}_3)_2$	100	147-148	36.55	36.28	12.79	13.06
XVI	NHC_6H_5	$\text{NH}-\text{N}=\text{CHC}_6\text{H}_5$	90	195.5-197	44.65	44.22	11.16	11.27
XVII	Cl	$\text{N}=\text{CH}-(\text{CH}=\text{CH})_2^f$	76	155.5-157 ^a	36.95	36.72	41.95	42.11	6.62	6.41
XVIII	Cl	$\text{N}=\text{CH}-(\text{CH}=\text{CH})_2^f$ $\text{C}_6\text{H}_5-\text{N}-\text{CH}_3$	85	184-185 ^b	34.17	34.47	46.55	46.65	6.13	5.88
XIX	OH	$\text{NH}-\text{P}(\text{O})(\text{OH})\text{CCl}_3^g$ $\text{Cl}-\text{C}_6\text{H}_4-\text{N}-\text{CH}_3$	45	286-288 ^b	29.71	29.46	37.59	36.60	7.42	7.32
XX	$\text{C}_6\text{H}_5\text{N}-(\text{CH}=\text{CH})_2-\text{CHO}$ CH_3		100	81-82	7.48	7.59
XXI	$\text{ClC}_6\text{H}_4-\text{N}-(\text{CH}=\text{CH})_2-\text{CHO}$ CH_3		100	115-116	16.00	15.79	6.32	6.38

^a Aniline salt. ^b *p*-Anisidine salt. ^c Per cent. phosphorus. ^d Phosphorus calcd. 8.44, found 8.66%. ^e B.p. 164° at 1.5 mm. ^f Hydrogen chloride salt. ^g Dianiline salt. ^h Melted with decomposition.

The basicity of the amines plainly exerted influence on these reactions. However, if the basicity had been the only factor involved then *N*-methylaniline should have reacted at least once and *N*-methylcyclohexylamine should have reacted twice under forcing conditions.

The electronic environment of the phosphorus atom in the acid chloride (three electron withdrawing groups) and the reaction medium used (hydrocarbon solvents) appear favorable for an $\text{S}_{\text{N}}2$ reaction. In view of the irregular behavior of the *N*-alkylamines, the presence of a steric factor is a possibility. Coulombic repulsion between the electro-negative groups in the acid chloride and the amino nitrogen is a possible factor also.

During the attempts to treat *N*-methylaniline with I, pyridine was employed as the solvent on one occasion. Treatment of the reaction mixture with cold, dilute hydrochloric acid produced a dark red



solid which proved to be a derivative of glutamic dialdehyde.

This compound, *N*-[5-(methylphenylamino)-2,4-pentadienyldene] *P*-trichloromethylphosphonamidic chloride hydrochloride produced 5-(methylphenylamino)-2,4-pentadienal^{7,8} when hydrolyzed. *p*-Chloro-*N*-methylaniline reacted similarly to give *N*-[5-(*p*)-chlorophenylmethylamino]-2,4-pentadienyldene] *p*-trichloromethylphosphonamidic chloride hydrochloride. Hydrolysis of this compound afforded 5-(*p*-chlorophenylmethylamino)-2,4-pentadienal in high yield.

Amines which reacted with I under the conditions given in Table I gave only the substituted amides, and not the unsaturated, straight chain products, when pyridine was used as the solvent.

Experimental⁹

1. Trichloromethylphosphonic Dichloride (I).—In equip-

(7) T. Zincke, *Ann.*, **338**, 107 (1905).

(8) R. C. Elderfield, "Heterocyclic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 425-433.

(9) Melting and boiling points are uncorrected. Nitrogen analyses were made by the method of Dumas. Carbon analyses were run by the method of D. D. Van Slyke and J. Folch (*J. Biol. Chem.*, **136**, 509 (1940)) using the procedure for macroanalysis. Chlorine analyses were run gravimetrically using a Parr bomb for combustion of the sample. The infrared spectra were determined on a Perkin-Elmer machine, Model 21, by Mr. Rook and Dr. Robison of the University of Nebraska Instrumentation Laboratory.

ment protected from moisture, were placed 1 mole of anhydrous, powdered aluminum chloride, 1 mole of phosphorus trichloride and 1.2 moles of carbon tetrachloride. The reactants were stirred slowly until they were thoroughly mixed and then heat was applied carefully until the exothermic reaction began. When the mixture became solid it was allowed to cool for 30 minutes. The solid was then suspended in 1 l. of methylene chloride (redistilled over aluminum chloride) by vigorous stirring and the suspension was cooled in a Dry Ice-acetone bath to -10 to -20° . Distilled water (10 moles) was added dropwise over a period of 25 minutes with vigorous stirring followed by 15 minutes of stirring without the cooling bath.

The solid aluminum chloride hydrate was filtered and the filter cake was washed with three 50-ml. portions of methylene chloride. The filtrate was concentrated by distillation to about 250 ml. and the hot concentrate was poured into a 500-ml. round-bottomed flask. The remaining solvent was removed under reduced pressure.

2. Diethyl Trichloromethylphosphonate.—A solution of 200 ml. of absolute ethanol and 45 g. of triethylamine was heated to boiling and 47.3 g. of trichloromethylphosphonic dichloride was added in portions so as to maintain gentle boiling. After the addition was complete the reaction mixture was heated for 2 hours. Then about 125 ml. of ethanol was distilled and the remaining solution was poured into 300 ml. of dry ether. The triethylamine hydrochloride was filtered and the ether was distilled. The residue was distilled under reduced pressure to give 72.2 g. (53%) of colorless oil. This oil was twice distilled through an 8-inch Vigreux column; b.p. 130 – 131° at 14 mm., n_D^{25} 1.4580 (reported b.p. 135 – 37° at 16 mm., n_D^{25} 1.4582).⁵

3. Anilinium O-Ethyl-P-trichloromethylphosphonate (II).—A solution of 12.8 g. of diethyl trichloromethylphosphonate, 10.2 g. of aniline and 100 ml. of dry benzene was heated at reflux temperature for 15 hours. Then 50 ml. of solvent was removed by distillation and the remaining reaction mixture was cooled in an ice-bath. White crystals of product precipitated. An analytical sample was prepared by recrystallization from ethanol. This compound became gray during lengthy exposure to light or when dried at a temperature greater than 70° .

4. *p*-Anisidinium N-(*p*-Methoxyphenyl)-P-trichloromethylphosphonamide.—The reaction mixture of 23.7 g. of I, 54.3 g. of *p*-anisidine and 300 ml. of benzene was shaken until the initial reaction was complete and then was heated at reflux temperature for 30 minutes. The *p*-anisidinium chloride was filtered from the cooled solution and the filter cake was washed with two 20-ml. portions of benzene. The filtrate was evaporated on a steam-bath in the presence of 200 ml. of water. When the benzene was entirely evaporated the solid was well broken up in the warm water and was then filtered. One recrystallization from water gave a light gray solid. An analytical sample was prepared from ethanol. This compound was also sensitive to light and decomposed if dried above 40° .

5. Anilinium Trichloromethylphosphonilidate (IV).—This compound was synthesized, using aniline, by the same procedure as described in 4. The analytical sample was prepared by recrystallization from ethanol.

An alternative preparation consisted of heating 1 mole of VIII with 2 moles of aniline and an excess of water. In this case the yield was 95%.

6. Alkyl Substituted Amides of Trichloromethylphosphonic Acid.—The general method is described here. Specific details or departures from the general method are reported under the heading of the individual amide.

In a round-bottomed flask fitted with a reflux condenser were placed I, benzene (100 ml. for every one-tenth mole of amine) and the amine (2.1 moles for every mole of I). The reaction mixture was heated at reflux temperature for 15 to 30 minutes after the initial exothermic reaction was complete. The cooled mixture was then filtered and dry hydrogen chloride was bubbled into the filtrate. The amine hydrochloride was again filtered and the filtrate was evaporated under reduced pressure.

A. Trichloromethylphosphonic Dipiperidide (V).—In this case 4.1 moles of piperidine was used for every mole of I. The product was a white, granular, water soluble solid. The analytical sample was prepared by recrystallization from methanol-ether mixtures.

B. N-Cyclohexyl-N-methyl-P-trichloromethylphosphonamidic Chloride (VI).—This compound was a viscous oil

which was distilled twice through an 8-cm. Vigreux column under reduced pressure.

C. N-Cyclohexyl Trichloromethylphosphonamidic Chloride (VII).—Recrystallization from ethanol produced white platelets.

D. Trichloromethylphosphonilidic Chloride (VIII).—Dry ether was used instead of benzene. Evaporation of the ether to about one-fifth of the starting volume produced a first crop of crystals which melted at 109 – 110° and was adequate for use in further reactions. The analytical sample was recrystallized from ether.

7. Methyl Trichloromethylphosphonilidate (IX).—The mixture of 4.4 g. of VIII, 100 ml. of dry benzene and 1.0 g. of sodium methylate was heated at reflux temperature for 3 hours. It was then cooled and extracted with water. The benzene was evaporated under reduced pressure to give the product which was recrystallized from methanol.

Alternative preparations included treatment of IV with diazomethane in ether solution and treatment of IV with methyl sulfate in alkaline solution. The products obtained from all three preparative methods melted and mixed melted at 146 – 147° .

8. Ethyl Trichloromethylphosphonilidate (X).—A solution of 14.6 g. of VIII in 50 ml. of ethanol was added through the condenser to a solution of sodium (2.3 g.) in 100 ml. of absolute ethanol. The reaction was heated at reflux temperature for three hours. The reaction mixture was concentrated to about 75 ml. by evaporation under reduced pressure and was then poured into water. The soft product which precipitated was filtered and recrystallized from ethanol.

9. N-Methyl-N-phenyl-trichloromethylphosphonamidic Chloride (XI).—A solution of 14.6 g. of VIII and 100 ml. of ether was cooled to 5° and 3.4 g. of diazomethane¹⁰ in ether, also at 5° , was added in portions with swirling of the reaction flask in an ice-bath. The reaction solution was kept at 5° for 1 hour and then was allowed to stand at room temperature overnight. The ether was evaporated in the strong draft of the hood and the residue, a yellow oil, was distilled. The compound boiled at 152° at 0.5 mm. and crystallized in the receiver. Recrystallization from ethanol afforded an analytical sample.

10. N-Cyclohexyl-N-phenyl-P-trichloromethylphosphonic Diamide (XII).—The reaction solution of 14.6 g. of VIII, 11.9 g. of cyclohexylamine and 200 ml. of benzene was heated at reflux temperature for 7.25 hours after which it was cooled and the solid was filtered. The excess amine was removed by treatment of the filtrate with dry hydrogen chloride followed by filtration. The benzene was removed under reduced pressure giving an oily solid. Numerous recrystallizations from ethanol produced a white compound of constant melting point. Less than about eight recrystallizations gave a lower melting compound which analyzed high for nitrogen.

11. N,N'-Dicyclohexyltrichloromethylphosphonic Diamide (XIII).—Compound I (12 g.) was added to 200 ml. of toluene and 22 g. of cyclohexylamine. Cyclohexylamine hydrochloride was removed periodically to avoid bumping and to follow the course of the reaction. In all, the reaction was heated at reflux temperature for 4.0 hours. Excess amine was removed by treatment of the toluene solution with hydrogen chloride. The toluene was evaporated under reduced pressure to produce a soft, yellow solid. Numerous recrystallizations from ethanol afforded a white solid of constant melting point.

12. Trichloromethylphosphonilidic Hydrazide (XIV).—Anhydrous hydrazine¹¹ (3.2 g.) was placed in a flask with 100 ml. of C.P. dioxane. The flask was shaken in an ice-bath and 14.6 g. of VIII in 50 ml. of dioxane was added through the condenser. Shaking was continued until the initial reaction was complete and the mixture was allowed to stand overnight. The precipitate of hydrazine hydrochloride and product were filtered, dried on the filter paper and ground under water in a mortar. The water-insoluble solid was filtered, dried and the analytical sample was prepared by recrystallization from ethanol.

13. 2-Propanal Trichloromethylphosphonilidic Hydrazide (XV).—A solution of 2.0 g. of XIV and 100 ml. of acetone was heated at reflux temperature for 12 hours. The acetone was evaporated and the residue was recrystallized from ethanol to yield a white, crystalline solid.

(10) *Org. Syntheses*, **15**, 3 (1935).

(11) *ibid.*, **24**, 53 (1944).

14. **Benzal Trichloromethylphosphonanilidic Hydrazone (XVI).**—The reaction solution of 2 g. of XIV, 100 ml. of ethanol and 22.2 g. of freshly distilled benzaldehyde was heated at reflux temperature for 3.5 hours. The reaction mixture was poured into 200 ml. of dilute sodium bisulfite solution and the insoluble product was filtered and warmed to 60° in 100 ml. of dilute sodium bisulfite solution. The insoluble product was again filtered and recrystallized from ethanol to afford a white fiber-like compound.

15. **N-[5-(Methylphenylamino)-2,4-pentadienylidene] P-Trichloromethylphosphonamidic Chloride Hydrochloride (XVII).**—In a 500-ml. erlenmeyer flask were placed 23.7 g. of I, 150 ml. of pyridine and 42.8 g. of redistilled N-methyl-aniline. The reaction was allowed to stand for four days, after which the contents of the flask were poured into cold dilute hydrochloric acid (100 ml. of concd. acid and 300 ml. of distilled water) with good stirring. The stirring was continued for 15 minutes and the solid was then filtered, washed with water and pressed down well on the filter paper. Since the compound was unstable to prolonged heating, it was dried in a vacuum desiccator for 24 hours. A pure sample was best prepared by one recrystallization each from chloroform, acetone and ethanol. The product was a dark red colored compound which formed glistening needles from ethanol.

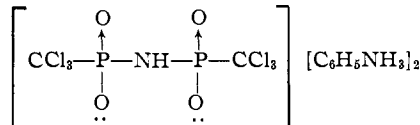
16. **N-[5-(*p*-Chlorophenylmethylamino)-2,4-pentadienylidene] P-Trichloromethylphosphonamidic Chloride Hydrochloride (XVIII).**—The *p*-chloro-N-methylaniline used in this reaction was prepared by the reduction¹³ of *p*-chloroformanilide¹² with lithium aluminum hydride according to the directions for similar compounds.

The preparation of this red compound was carried out in the same manner as described in 15. The reaction time in this case was 3.0 days.

(13) V. M. Micovic and M. Lj. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

(12) *Org. Synthesis*, **20**, 66 (1940).

17. **Imido Bis-(anilinium trichloromethylphosphonate).**—After filtration of XX in part 18, the filtrate was treated with charcoal and filtered until the solution was colorless. It was then acidified and evaporated under reduced pressure to about 75 ml. Aniline (3 g.) was added to the cooled solution and a gray solid precipitated. This was recrystallized from water to give a white compound. Apparently the phosphorus-containing half of the molecule coupled during the hydrolysis to form this compound.



18. **5-(Methylphenylamino)-2,4-pentadienal (XX).**—In a 250-ml. erlenmeyer flask were placed 3 g. of XVII and 40 ml. of ethanol. Potassium hydroxide (1.2 g.) in 30 ml. of ethanol and 10 ml. of water was added slowly while swirling the reaction flask in an ice-bath. The color changed from red to yellow and became cloudy when 100 ml. of water was added. The flask was placed in the refrigerator for 2 hours. The yellow solid was filtered and recrystallized from ethanol.

19. **5-(*p*-Chlorophenylmethylamino)-2,4-pentadienal (XXI).**—This compound was prepared from XVIII in exactly the same way that XX was prepared from XVII. The compound was a yellow to orange colored solid when recrystallized from ethanol.

Acknowledgment.—The authors wish to thank Dr. H. Armin Pagel for his continued interest and aid in the problems of analysis. The authors also wish to express their appreciation to Parke, Davis and Company for financial aid.

LINCOLN 8, NEBRASKA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

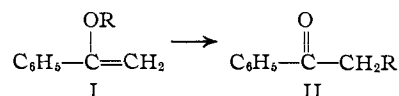
1,3-Shifts. II. The Stereochemistry of the Rearrangement of α -Alkoxystyrenes¹

BY KENNETH B. WIBERG AND BERTRAM I. ROWLAND

RECEIVED AUGUST 16, 1954

The thermal rearrangement of optically active α -2-butoxystyrene to β -methylvalerophenone was found to give over 95% racemization. The α -2-butoxystyrene and the product ketone were found to be configurationally stable under the conditions of the rearrangement. α -Neopentoxystyrene was found to rearrange to γ,γ -dimethylvalerophenone without rearrangement in the migrating group, indicating that a carbonium ion intermediate was unlikely. The reaction could be initiated by *t*-butyl peroxide, but the usual type of inhibition of a free radical chain reaction could not be realized. The kinetics of the rearrangement of α -2-butoxystyrene was found not to follow any simple rate law.

The rearrangement of α -alkoxy-styrenes (I) to the corresponding substituted acetophenone (II) was first reported by Claisen² in 1896. Subsequently, the rearrangement of α -methoxystyrene (III) re-



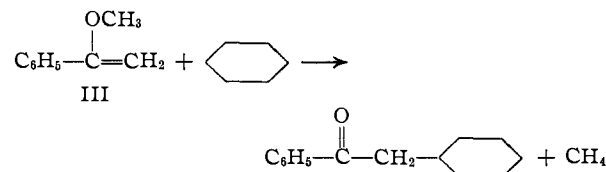
ceived considerable study by Lauer, Spielman and Mortenson.³ They found that the reaction was kinetically of the second order, and that the by-products, 1,2-dibenzoylpropane and methane, also were formed by a second-order process. Their data

(1) Abstracted from part of a thesis submitted by Bertram I. Rowland to the University of Washington in partial fulfillment of the requirement for the degree of Doctor of Philosophy, 1954.

(2) L. Claisen, *Ber.*, **29**, 2931 (1896).

(3) E. H. MacDougall, W. M. Lauer and M. A. Spielman, *THIS JOURNAL*, **55**, 4089 (1933); W. M. Lauer and M. A. Spielman, *ibid.*, **55**, 4923 (1933); M. A. Spielman and C. W. Mortenson, *ibid.*, **61**, 606 (1939); **62**, 1609 (1940).

were however not very precise, and the kinetic order is still not certain. They observed that III would react with a hydrocarbon solvent to give methane and a substituted acetophenone having the substituent derived from the solvent as, for example, in the case of cyclohexane. It was noted also that III reacted with alkyl halides in a similar man-



ner giving methyl halide and the substituted acetophenone.

They suggested that the reaction involved a cyclic eight-membered transition state, in which the driving force was a "heteroenoid" system. This would explain the intermolecular nature of the re-