

stirring for about 15 min., the olefin mixture was added in one portion. The solution remained blue after the addition of the olefin mixture and the undissolved lithium eventually caked into a silvery ball, from which blue streamers emerged as it was agitated around the flask. After 2 hr. the reaction mixture was poured slowly into ice-water and the resulting top layer was separated. The hydrocarbon layer was washed once with ice-water and dried over potassium carbonate. This sample was used for the vapor phase chromatographic analysis. The following analysis was obtained using a UCon polar column.

Cyclopentene reduction		Cyclohexene reduction	
Cyclopentene	55.0%	Cyclohexene	87.2%
Cyclopentane	45.0%	Cyclohexane	12.8%

Other Pairs of Olefins.—Using the experimental procedure described above, the observations summarized in Table V were made.

Several competitive and individual reduction experiments were performed in ethylamine which yielded isomeric olefinic products along with the expected reduction products. The effect

TABLE VI

Olefin or olefin pair ^a	Reduction, %	Isomer and % isomerization
Norbornene	42.2	
1-Hexene (TCP)	11.9	<i>cis</i> - and <i>trans</i> -2-hexene 33.8
Cyclohexene	None	...
1-Hexene (TCP or U)	39.0	<i>cis</i> - and <i>trans</i> -2-hexene 36.0
1-Hexene (TCP or U)	35.0	<i>cis</i> - and <i>trans</i> -2-hexene 20.0
1-Hexene ^b	31.0	None detected
2-Methyl-1-pentene	36.7	2-Methyl-2-pentene 16.7
Cyclohexene (TCP)	2.4	...
1-Hexene (U)	42.6	<i>cis</i> - and <i>trans</i> -2-hexene 11.9
3,3-Dimethyl-1-butene (S)	13	...
Cyclopentene ^c	6.0	...
Cyclohexene	5.8	...

^a All runs were performed with ethylamine as the solvent and the proton source, except where noted. Lithium was used to effect about 50% reduction in the competition experiment, and the stoichiometric amount of metal was utilized in the noncompetition runs. ^b The olefin was added with an equimolar amount of *t*-butyl alcohol. ^c The olefins were added with an equimolar amount of *t*-butyl alcohol to the lithium in ethylamine.

of adding alcohol to the system was also studied. The experiments were all performed according to the previous typical procedure and the results of these experiments are presented in Table VI.

Typical Reduction Procedure in Liquid Ammonia (1-Hexene Reduction).—In a 500-ml., three-necked flask equipped with an ammonia inlet, a Dry Ice condenser, and a dropping funnel were placed 250 ml. of liquid ammonia, and 1-hexene (15 g., 0.18 mole) was added. To this solution was added a portion of the lithium (2.5 g., 0.36 mole), upon which a blue color immediately developed. A portion of methanol (total added, 23 g., 0.72 mole) was added dropwise until the blue coloration was discharged. This process was repeated until all the lithium and the methanol was added. The ammonia was allowed to evaporate partially and the residual ammonia was decomposed by the addition of ice. The top layer was separated and dried over potassium carbonate; weight 5.7 g. (41%). This was analyzed by vapor phase chromatography. The following analysis was obtained using a tricesyl phosphate column: *n*-hexane, 17.0%; 1-hexene, 83.0%.

The results of other experiments performed in the ammonia medium are recorded in Table VII. No isomeric products were detected in any of the runs performed in this medium.

TABLE VII

Olefin or olefin pair	Reduction, %
1-Hexene (TCP)	17.0
Methylenecyclohexene ^a (U)	80.0
Norbornene ^b (TCP)	5
1-Hexene ^c (U)	49.0
3,3-Dimethyl-1-butene (S)	13.1
1-Hexene ^d	22.0
Norbornene (TCP)	2

^a Treated successively with two stoichiometric amounts of lithium followed by ethanol addition after each portion to discharge the color. ^b Following the typical procedure for 1-hexene except that 3 equivalents of metal were utilized with methanol as the proton source. ^c Using equimolar quantities of olefins and lithium and ethanol as the proton source. ^d Equimolar amounts of olefins and lithium utilized, with methanol as the proton source.

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The Reaction of Triphenylphosphine Oxide with Alkylolithium and Grignard Reagents¹

BY DIETMAR SEYFERTH,^{2a} DEAN E. WELCH,^{2b} AND JAMES K. HEEREN^{2c}

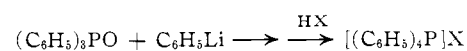
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The reaction of RCH_2Li in ether or of RCH_2MgBr in refluxing tetrahydrofuran with triphenylphosphine oxide results in formation of benzene and $(C_6H_5)_2P(O)CH(R)M$ ($M = Li$ and $MgBr$, respectively). Some characteristic reactions of such diphenylphosphinylalkyl organometallic reagents are described. The mechanism of formation of these reagents from triphenylphosphine oxide is shown to involve a very rapid exchange step, $(C_6H_5)_3PO + RCH_2M \rightarrow (C_6H_5)_2P(O)CH_2R + C_6H_5M$, followed by a slower (but still rapid) metalation reaction, $(C_6H_5)_2P(O)CH_2R + C_6H_5M \rightarrow C_6H_6 + (C_6H_5)_2P(O)CH(R)M$, when M is lithium. Both exchange and metalation steps are slower when M is $MgBr$.

Our recent work³ on the mechanism of the reaction of organolithium reagents with phosphonium salts, in which phosphorus bears a full positive charge, prompted further investigations of the action of organolithium reagents on tertiary phosphine oxides, in which phosphorus bears a partial positive charge. Of particular interest to us were those reactions which conceivably might proceed *via* transient pentasubstituted phosphorus intermediates. We report here

on the reaction of alkylolithium and Grignard reagents with triphenylphosphine oxide (TPPO).

A clue that these particular reactions might be of interest was provided by a synthesis used by Wittig and Rieber⁴ for tetraphenylphosphonium iodide



It seemed possible that here a P(V) intermediate, $(C_6H_5)_4PO^- Li^+$, might be involved. In order to obtain further information concerning this reaction, we treated TPPO with alkylolithium reagents.

Addition of 1 molar equivalent of methylolithium to a slurry of TPPO in diethyl ether at room temperature resulted in formation of a reddish brown, homoge-

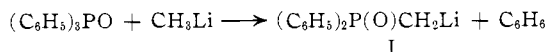
(1) (a) Presented in part at the Symposium, "Current Trends in Organometallic Chemistry," Cincinnati, Ohio, June 12–15, 1963; (b) preliminary communication; D. Seyferth, D. E. Welch, and J. K. Heeren, *J. Am. Chem. Soc.*, **85**, 642 (1963).

(2) (a) Alfred P. Sloan Research Fellow; (b) National Institutes of Health Predoctoral Fellow, 1962–1963; (c) Fellow of the M.I.T. School for Advanced Study, 1961–1962.

(3) D. Seyferth, J. K. Heeren, and W. B. Hughes, *J. Am. Chem. Soc.*, **84**, 1764 (1962).

(4) G. Wittig and R. Rieber, *Ann.*, **562**, 187 (1949)

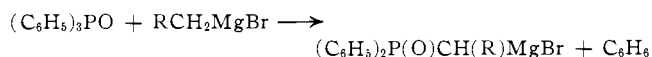
neous solution containing a new organolithium reagent, diphenylphosphinylmethyl lithium (I), and benzene.



A Gilman Color Test I⁵ on the solution was positive. The yield of benzene always was nearly quantitative. Quenching the reaction mixture with aqueous HBr gave methyl diphenylphosphine oxide in 84% yield, carbonation resulted in $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{COOH}$ (47%), and addition of triphenyltin chloride to the reagent solution gave $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{Sn}(\text{C}_6\text{H}_5)_3$ (76%).

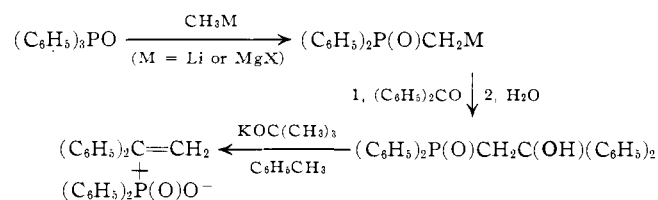
The reaction of ethyllithium and of *n*-butyllithium with TPPO produced $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CHLiCH}_3$ and $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CHLiC}_3\text{H}_7$, respectively. Reactions of these reagents as well as other reactions of I itself are described in the Experimental section. Such α -lithioalkyldiphenylphosphine oxides were not new, having been prepared previously by Horner, *et al.*,⁶ by metalating certain alkyldiphenylphosphine oxides. After a preliminary communication^{1b} describing the initial results of the present study had been submitted for publication, a much more extensive report appeared concerning the preparation of such reagents by the treatment of tertiary phosphine oxides containing at least one primary alkyl group with organolithium reagents.⁷ These studies demonstrated that such reagents undergo reactions typical for organolithium compounds.

A similar reaction was found to occur between aliphatic Grignard reagents and TPPO, provided it was carried out in refluxing tetrahydrofuran (THF) solution.



With methyl-, ethyl-, and *n*-propylmagnesium bromides the diphenylphosphinylalkyl Grignard reagent and benzene yields were *ca.* 80%. However, the action of benzylmagnesium chloride and isopropylmagnesium bromide on TPPO gave only low benzene yields. The diphenylphosphinylalkyl Grignard reagents derived from methyl-, ethyl-, and *n*-propylmagnesium bromide were characterized by reaction with triphenyltin chloride to form $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}(\text{R})\text{Sn}(\text{C}_6\text{H}_5)_3$ derivatives.

These reactions of aliphatic organolithium and Grignard reagents with TPPO represent a very convenient route to organofunctional phosphine oxides. Such a synthesis based on TPPO is more economical and practical than that based on alkyldiphenylphosphine oxides,^{6,7} since TPPO is a product of the Wittig reaction which usually is discarded when the Wittig reaction is performed on a laboratory scale. It may be mentioned that most of this work was carried out using TPPO recovered from Wittig reaction residues. It is interesting to note that this recovered TPPO, *via* the reactions reported here, can serve again in the synthesis of olefins, for instance, of 1,1-diphenylethylene



This reaction sequence is based on the use of α -meta-

(5) H. Gilman and P. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

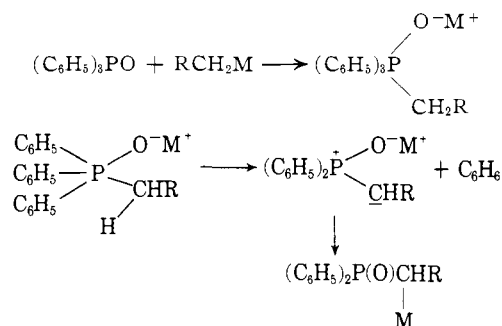
(6) L. Horner, H. Hoffmann, H. G. Wippl, and G. Klahre, *Chem. Ber.*, **92**, 2499 (1959).

(7) J. J. Richard and C. V. Banks, *J. Org. Chem.*, **28**, 123 (1963).

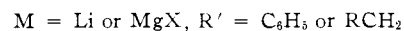
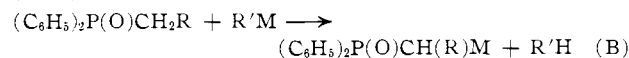
lated alkylphosphine oxides in olefin synthesis as reported by Horner and co-workers.⁶

Of primary interest to us in this study was the mechanism of the alkylmetallic-TPPO reactions. Two possibilities were considered:

(1) Intramolecular loss of benzene from a P(V) intermediate



(2) An exchange-metalation sequence



Mechanism 2 involves phenyllithium or phenylmagnesium bromide as an intermediate; mechanism 1 does not. Therefore experiments were performed to inquire into the question of the intermediacy of phenylmetallics in these reactions.

The clearer picture was obtained in a study of the methylmagnesium bromide-TPPO reaction. The observed results are in agreement with the exchange-metalation mechanism. They demonstrate that at room temperature in THF methylmagnesium bromide and TPPO react slowly to give a solution containing methyl diphenylphosphine oxide and phenylmagnesium bromide. Table I illustrates this. Thus after 8 hr. the benzene produced in 79% yield after treatment of the reaction mixture with D₂O contained 88% monodeuteriobenzene, *i.e.*, 88% of the benzene obtained was derived from the reaction of $\text{C}_6\text{H}_5\text{MgBr}$ with D₂O. At room temperature the metalation reaction B is extremely slow: only 12% of the benzene obtained had been produced in the metalation step. However, the results were quite different when this reaction was carried out in refluxing THF (Table I).

TABLE I

Temp., °C.	Time, hr.	A STUDY OF THE REACTION $(\text{C}_6\text{H}_5)_3\text{PO} + \text{CH}_3\text{MgBr} \xrightarrow{\text{THF}} \xrightarrow{\text{D}_2\text{O}}$	
		Benzene ^a yield, %	$\text{C}_6\text{H}_5\text{D}$ in benzene, %
25	0.5	14	Not detd.
25	1	24	Not detd.
25	3	56	96
25	5	65	Not detd.
25	8	79	88
Reflux	2	87	53
Reflux	6	86	0.0
Reflux	22	85	Not detd.

^a C_6H_6 from metalation reaction B + $\text{C}_6\text{H}_5\text{D}$ from hydrolysis of $\text{C}_6\text{H}_5\text{MgBr}$ formed in exchange reaction A.

The benzene yield after treatment of the reaction mixture with D₂O was nearly 90% after only 2 hr., and the deuteriobenzene content of the benzene dropped to zero within 6 hr., *i.e.*, the benzene produced in the 6-hr. reaction period resulted from the metalation reaction B which had consumed all of the $\text{C}_6\text{H}_5\text{MgBr}$ formed in reaction A.

Confirmation of these results was obtained by studying the metalation of methyldiphenylphosphine oxide by phenylmagnesium bromide separately. One equivalent of phenylmagnesium bromide was added to a solution of 1 equivalent of methyldiphenylphosphine oxide in THF. Samples were removed at successive time intervals and quenched in D₂O. Analysis of the benzene showed that after 8 hr. at room temperature the benzene contained 90% monodeuteriobenzene (10% metalation), and after 4 hr. at reflux the benzene contained no monodeuteriobenzene (100% metalation). The intermediacy of phenylmagnesium bromide in the RMgBr-TPPO reaction also was proved by a positive Gilman Color Test III⁸ and carbonation to give benzoic acid. Separate experiments demonstrated that (C₆H₅)₂P(O)CH₂MgBr did not give a positive Gilman Color Test III.

The results obtained in a study of the methyl lithium-TPPO and ethyllithium-TPPO reactions were not as clear-cut, since the exchange reaction A and the metalation reaction B could not be separated. However, the evidence compels one to the conclusion that mechanism 2 is operative in these reactions as well.

Experiments in which TPPO was allowed to react with ethereal methyl lithium and the resulting mixture was quenched after *ca.* 1 min. with D₂O showed that phenyllithium was indeed present in solution. When the ratio of CH₃Li to TPPO was 1:1, the benzene formed (97%) in the reaction (C₆H₆ from reaction B + monodeuteriobenzene from the reaction of unconsumed phenyllithium present with D₂O) contained 2% monodeuteriobenzene. When the CH₃Li/TPPO ratio was increased to 2 and 3, respectively, the monodeuteriobenzene content of the benzene formed (*ca.* 90-95%) rose to 9 and 13%, respectively. Similar results were obtained in a study of the ethyllithium-TPPO reaction. When these reagents were used in 1:1 molar ratio, quenching of the reaction mixture with D₂O gave benzene in 97% yield, which contained 14% deuteriobenzene. The same experiment with the C₂H₅Li/TPPO ratio increased to 2 and 3 gave benzene in *ca.* 98% yield, which now contained 25 and 50% monodeuteriobenzene, respectively. In a similar 3:1 experiment the phenyllithium remaining in solution owing to unsuccessful competition with ethyllithium in reaction B was characterized by its reaction with trimethylchlorosilane to give trimethylphenylsilane in 47% yield.

The possibility of the metalation reaction B was verified experimentally before the paper by Richard and Banks⁷ appeared. However, generation of α -lithioalkyldiphenylphosphine oxide reagents from alkyl-diphenylphosphine oxide and alkyl- or aryllithium reagents gave yellow to reddish yellow solutions. In contrast, the TPPO-RLi reaction mixtures always gave light-to-deep red solutions. This puzzling color phenomenon is not understood, but possibly could be due to a minor side reaction in the latter system.

The high yields of the (C₆H₅)₂P(O)CH(R)Li reagents obtained in those reactions in which RCH₂Li/TPPO = 1 suggested that here one was dealing with a very rapid exchange step followed by a slower (but still rapid) metalation step. Support for this idea was obtained in the following manner. If this were true, *i.e.*, if the original lithium reagent is completely consumed before the extent of metalation of the alkyl-diphenylphosphine oxide formed in reaction A is significant, then, for example, the reaction of 2 molar equivalents of methyl lithium with 1 equivalent of TPPO should lead very rapidly to a solution containing 1 molar equivalent each of CH₃Li, C₆H₅Li, and (C-

H₅)₂P(O)CH₃. Subsequent to this the two lithium reagents present should compete in the metalation of methyldiphenylphosphine oxide. Thus the final reaction mixture, in terms of unconsumed CH₃Li and C₆H₅Li due to this competition, should be the same as that obtained in a separate experiment involving the addition of 1 molar equivalent each of methyl lithium and phenyllithium to 1 molar equivalent of methyldiphenylphosphine oxide. These reactions were carried out, and in each case the reaction mixture was quenched with D₂O after 1 min. The benzene formed in nearly quantitative yield contained 9% deuteriobenzene in the former case, 10% deuteriobenzene in the latter reaction. The results of similar experiments with methyl- and ethyllithium are listed in Table II. All support the idea presented above.

TABLE II
D₂O QUENCHING EXPERIMENTS

System	% benzene	% C ₆ H ₆ D in benzene
(C ₆ H ₅) ₃ PO + 2CH ₃ Li	90	9
(C ₆ H ₅) ₂ P(O)CH ₃ + CH ₃ Li + C ₆ H ₅ Li	92	10
	90	10
(C ₆ H ₅) ₃ PO + 3CH ₃ Li	95	12
	97	13
(C ₆ H ₅) ₂ P(O)CH ₃ + 2CH ₃ Li + C ₆ H ₅ Li	92	11.4
(C ₆ H ₅) ₃ PO + 2C ₂ H ₅ Li	100	25
(C ₆ H ₅) ₂ P(O)C ₂ H ₅ + C ₂ H ₅ Li + C ₆ H ₅ Li ^a	95	25
(C ₆ H ₅) ₃ PO + 3C ₂ H ₅ Li	98	51
	91	45
	99	50
(C ₆ H ₅) ₂ P(O)C ₂ H ₅ + 2C ₂ H ₅ Li + C ₆ H ₅ Li ^a	91	46

^a In a separate experiment it was found that the action of ethyllithium alone on ethyldiphenylphosphine oxide gave a low (7%) yield of benzene presumably through attack of ethyllithium on phosphorus. In order to assess the seriousness of such a side reaction leading to benzene in the competition experiments mentioned above, a solution containing 1 molar equivalent each of ethyllithium and *p*-tolyllithium was allowed to react with 1 equivalent of ethyldiphenylphosphine oxide. No benzene was formed. Thus the benzene-producing side reaction is not important in the competition experiments.

In order for an interpretation of the D₂O quenching experiments described above to be meaningful, it was necessary to demonstrate that the metalation reaction B was essentially complete under the conditions of the quenching experiments. This was found to be the case. Thus, treatment of (C₆H₅)₂P(O)CH₃ separately with either methyl- or phenyllithium using the same reaction conditions and reaction times used in the D₂O experiments, followed by quenching with a triphenyltin chloride solution, gave (C₆H₅)₂P(O)CH₂Sn(C₆H₅)₃ in *ca.* 80% yield. Using an equimolar mixture of methyl- and phenyllithium, a similar yield (86%) of this tin derivative was obtained, along with methyl-triphenyltin (86%), benzene (88%), and a small amount of tetraphenyltin. Similar results were obtained in the experiments with ethyllithium.

The question as to whether the exchange reactions occurring between TPPO and RCH₂MgBr and RCH₂Li proceed *via* a P(V) intermediate or by direct S_N2 displacement at phosphorus remains unanswered at the present time. The TPPO-C₆H₅Li reaction cited earlier, which leads to a product in which all three phenyl groups of TPPO as well as the phenyl group derived from the lithium reagent are present, suggests that the former alternative is possible in the systems studied by us.

It is suggested by the experiments described in Table II that phenyllithium metalates ethyldiphenylphosphine oxide at a faster rate than does ethyllithium,

(8) H. Gilman and H. L. Yablunsky, *J. Am. Chem. Soc.*, **63**, 839 (1941).

a surprising result in view of previous reports⁹ that the reactivity of organolithium reagents in metalation reactions decreases in the order $C_2H_5Li > C_6H_5Li > CH_3Li$. It may be that in the case of rapid metalations, as in the present experiments, factors other than the basicity of "monomeric" RLi species (dissociated or undissociated) are important. Since the accepted order of reactivity of organolithium reagents was established using relatively unreactive substrates requiring half-life reaction times of several hours, perhaps in rapid metalations in ether the degree of association of the metalating agent¹⁰ as well as the reactivity of the substrate become important. Preliminary experiments in these laboratories support this.

Experimental

General.—All benzene yields were calculated using quantitative gas chromatography with toluene as an internal standard. The columns used were Dow Corning 710 silicone fluid or General Electric SE-30 silicone grease on Chromosorb W, with helium as the carrier gas. Normal operating conditions were: 80–100° jacket temperature, 10 p.s.i. He, 70° preheater temperature. Diethyl ether and tetrahydrofuran were purified by distillation from lithium aluminum hydride and stored over sodium wire. All experiments involving organolithium or Grignard reagents were carried out in an atmosphere of prepurified nitrogen. Melting points are uncorrected. Analyses were performed by Dr. S. M. Nagy, M.I.T. Microchemical Laboratory, and by the Schwarzkopf Microanalytical Laboratory.

Preparation of Starting Materials.—Methyl- and ethyllithium were prepared from the corresponding bromide and lithium wire in diethyl ether. *n*-Butyllithium was prepared from *n*-butyl chloride. Ethyl- and *n*-butyllithium were prepared at ca. 0° and used immediately thereafter. All solutions were standardized by the double titration method of Gilman¹¹ using 1,2-dibromoethane in place of benzyl chloride.

Triphenylphosphine oxide was obtained from Wittig reaction residues or was prepared by the method of Michaelis and Gleichmann.¹² Before use, TPPO (m.p. 155–157°) was dried over P_2O_5 at 110° (0.5 mm.).

The Reaction of TPPO with Alkyl Lithium Reagents.—The preparation of $(C_6H_5)_2P(O)CH_2Sn(C_6H_5)_3$ is given as an example of the general procedure used.

Treatment of a suspension of 13.9 g. (50 mmoles) of TPPO in 100 ml. of ether with 50 mmoles of methyllithium, followed by stirring for 2 hr., gave a deep red homogeneous solution.¹³ This mixture then was treated with 19.25 g. (50 mmoles) of triphenyltin chloride in 50 ml. of ether and 25 ml. of THF. A precipitate started to form rapidly after ca. 10 min. and stirring was continued for 3 hr. The mixture was filtered and ammonia was bubbled through the filtrate for 3 hr. (to remove unreacted triphenyltin chloride). Another filtration and removal of solvents from the filtrate under vacuum gave an oil which could be crystallized from benzene–heptane to give a white solid; 20.5 g. (76%), m.p. 135–141°. Two additional recrystallizations from benzene–heptane gave 17.0 g. (60%) of white solid, m.p. 141–142°, whose infrared spectrum (KBr pellet) showed principal absorption bands at 3020, 1485, 1440, 1430, 1173, 1120, 1075, 1025, 1000, 780, 763, 725, and 700 cm^{-1} ; n.m.r.¹⁴: doublet (2H, $J = 11.0$ c.p.s., $P-CH_2-$) centered at 2.38 p.p.m., flanked by two satellite doublets due to splitting by the tin nucleus (Sn^{117} and Sn^{119}) with $J = 58$ c.p.s.; complex phenyl absorption at 7.55 p.p.m. (10H, C_6H_5-P); complex phenyl absorption at 7.15 p.p.m. (15H, C_6H_5-Sn).

Anal. Calcd. for $C_{31}H_{27}POSn$: C, 65.87; H, 4.82; P, 5.48. Found: C, 65.52; H, 4.68; P, 5.68.

The following other preparative scale reactions were carried out to give the products described below.

(1) *Via TPPO + CH_3Li : $(C_6H_5)_2P(O)CH_2Si(C_6H_5)_3$.*—The reagent solution (10 mmoles in 33 ml. of ether) was treated with 10 mmoles of triphenylchlorosilane (Dow Corning Corp.) in 25 ml. of THF. The color of the reaction mixture faded rapidly to a pale yellow and stirring was continued for 2 days. The solvent was removed under vacuum to give a yellow, oily residue. Three

(9) H. Gilman, F. W. Moore, and O. Baine, *J. Am. Chem. Soc.* **63**, 2479 (1941).

(10) G. E. Coates, "Organometallic Compounds," 2nd Ed., Methuen & Co., Ltd., London, 1960, p. 20.

(11) R. G. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 339–366.

(12) A. Michaelis and L. Gleichmann, *Ber.*, **15**, 801 (1882).

(13) In a separate experiment this deep red solution was found to contain 96.5% of the theoretical benzene yield.

(14) Chemical shifts are downfield from tetramethylsilane, determined at 60 Mc. with a Varian Model A-60 n.m.r. spectrophotometer.

treatments in chloroform with Norit removed most of the color. The filtered solution was treated with 30 ml. of heptane and heated to boiling. When the mixture became cloudy it was left to stand for 2 days. A white solid precipitated. Three recrystallizations from benzene–heptane and chloroform–heptane gave 3.0 g. (65%) of white powdery solid, m.p. 149–152°. Its infrared spectrum (KBr pellet) showed major absorption at 3050, 1420, 1120, 1100, 1030, 1000, 850, 740, and 700 cm^{-1} .

Anal. Calcd. for $C_{31}H_{27}SiPO$: C, 78.45; H, 5.74; Si, 5.93. Found: C, 78.34; H, 5.61; Si, 6.03.

$(C_6H_5)_2P(O)CH_2COOH$.—The reagent solution (50 mmoles) was poured quickly into excess Dry Ice. After the mixture had warmed to room temperature, 100 ml. of water was added, and the aqueous layer was acidified with concentrated hydrochloric acid. The organic layer was found to contain 42.8 mmoles (85.5%) of benzene. The aqueous phase was extracted with chloroform, and the chloroform extracts were dried over anhydrous magnesium sulfate. The chloroform solution was concentrated to ca. 25 ml. under vacuum. Addition of cyclohexane precipitated a yellow solid, 6.7 g. (51.5%), m.p. 136–143°. Recrystallization from chloroform gave 6.05 g. (46.5%), m.p. 142–143°, reported¹⁵ m.p. 142–144° for carboxymethyldiphenylphosphine oxide. Its infrared spectrum (KBr pellet) showed major absorption at 1710, 1438, 1420, 1280, 1220, 1175, 1145, 1130, 1095, 1000, 905, 840, 815, 755, and 695 cm^{-1} .

Anal. Calcd. for $C_{14}H_{13}PO_3$: C, 64.61; H, 5.03; neut. equiv., 260.22. Found: C, 64.44; H, 4.97; neut. equiv., 260.60.

$(C_6H_5)_2P(O)CH_3$.—The reagent solution (50 mmoles) was quenched with 25 ml. of 48% aqueous HBr. The organic layer was found to contain 43.7 mmoles (87.5%) of benzene. The aqueous layer was saturated with potassium bromide and extracted with 100 ml. of chloroform. The chloroform extracts were dried over anhydrous magnesium sulfate and the chloroform removed under vacuum. The yellow, oily residue crystallized on standing. The solid was washed with warm cyclohexane and dried; 9.0 g. (83.5%), m.p. 104–111°. Recrystallization from benzene–heptane gave 8.2 g. (76%) of methyldiphenylphosphine oxide, m.p. 109–111°. A mixture melting point with authentic methyldiphenylphosphine oxide showed no depression.

$(C_6H_5)_2P(O)CH_2C(OH)(C_6H_5)_2$.—The reagent solution (50 mmoles) was treated dropwise over ca. 20 min. with 9.11 g. (50 mmoles) of benzophenone in 25 ml. of ether. The red color faded almost immediately and a heavy white solid precipitated. The mixture then was heated to reflux for 2 hr., cooled, and hydrolyzed with 3% HCl. The heavy, white precipitate was removed by filtration and dried over P_2O_5 to give 16.0 g. (81%) of white, crystalline solid, m.p. 184–186°. Two recrystallizations from benzene gave 14.7 g. (74%) of white crystals, m.p. 192–193°, lit.⁸ m.p. 192–193°, whose infrared spectrum (chloroform solution) showed principal absorption at 3325, 3020, 2995, 1490, 1445, 1430, 1160, 1118, 980, and 690 cm^{-1} .

$(C_6H_5)_2P(O)CH_2P(S)(C_6H_5)_2$.¹⁶—The reagent solution (40 mmoles) was treated with 40 mmoles of $(C_6H_5)_2PCl$ (Victor Chemical Works) in 25 ml. of ether. The mixture was heated to reflux for 12 hr., then was evaporated at reduced pressure. The residue was treated with 0.045 g.-atom of sulfur in hot benzene. Evaporation of the benzene left a yellow oil, which was dissolved in chloroform. The chloroform solution was extracted with water, dried, and evaporated. A pale yellow oil (8.28 g.) remained, which began to crystallize in long needles. The oil and the needles were crystallized from isopropyl alcohol to give 5.31 g. (25%) of product, m.p. 213–214° (lit.¹⁷ m.p. 209°). The infrared spectrum ($CHCl_3$) exhibited maxima at 3055, 2990, 1590, 1480, 1440, 1360, 1310, 1195, 1155, 1125, 1110, 1000, and 690 cm^{-1} .

Anal. Calcd. for $C_{23}H_{22}OSP_2$: C, 69.44; H, 5.13. Found: C, 69.09; H, 5.33.

(2) *Via TPPO + C_2H_5Li : $(C_6H_5)_2P(O)CH(CH_3)Sn(C_6H_5)_3$.* by reaction with triphenyltin chloride, in 81% crude yield, m.p. 170–175°, pure m.p. 176–177° (from benzene–heptane). The infrared spectrum (KBr pellet) showed major absorption at 3040, 1485, 1430, 1190, 1120, 1075, 735, and 700 cm^{-1} .

Anal. Calcd. for $C_{32}H_{29}POSn$: C, 66.35; H, 5.05; P, 5.34; Sn, 20.60. Found: C, 66.20; H, 4.89; P, 5.27; Sn, 20.88.

$(C_6H_5)_2P(O)CH(CH_3)COOH$: by reaction with Dry Ice, in 49.5% crude yield, m.p. 135–139°, m.p. 138–140° (from chloroform–hexane). The infrared spectrum (KBr pellet) showed principal absorption at 1745, 1440, 1295, 1230, 1160, 1117, 845, 720, and 695 cm^{-1} ; n.m.r.: quartet [3H, $J = 17$ c.p.s. ($P-C-CH_3$), $J = 8$ c.p.s. ($CH-CH_3$), at 1.34 p.p.m.]; quartet with some further splitting (1H, $J = 8$ c.p.s., centered at 3.63 p.p.m.); com-

(15) K. Issleib and G. Thomas, *Chem. Ber.*, **94**, 2244 (1961). Prepared by HCl

$[(C_6H_5)_2P(CH_2CO_2C_2H_5)_2]Br + NaOH \rightarrow$

(16) Experiment by Miss Patricia Selby, B.S. Thesis, M.I.T., June, 1963.

(17) K. Issleib and L. Baldauf, *Pharm. Zentralhalle*, **99**, 329 (1960).

plex phenyl absorption at 7.30–7.90 p.p.m. (10H, C₆H₅-P); singlet [1H at 11.12 p.p.m. (-COOH)].

Anal. Calcd. for C₁₅H₁₅PO₃: C, 65.69; H, 5.51; neut. equiv., 274.3. Found: C, 65.61; H, 5.66; neut. equiv., 273.6.

(C₆H₅)₂P(O)C₂H₅: by reaction with 48% hydrobromic acid, in 77.5% crude yield, m.p. 117–122°, m.p. 121–122° from benzene-heptane. A mixture melting point with authentic material was not depressed.

(C₆H₅)₂P(O)CH(CH₃)(OH)(C₆H₅)₂: by reaction with benzophenone, in 84% yield, m.p. 260–262° (from benzene). The infrared spectrum (CHCl₃) showed principal absorption at 3300, 3005, 2990, 1480, 1440, 1430, 1160, 1110, 1020, and 680 cm.⁻¹.

Anal. Calcd. for C₂₇H₂₅O₂: C, 78.62; H, 6.11; P, 7.51. Found: C, 78.85; H, 6.06; P, 7.48.

(3) *Via TPPO + n-C₄H₉Li*: (C₆H₅)₂P(O)CH[Sn(C₆H₅)₃]CH₂-CH₂CH₃: by reaction with triphenyltin chloride, m.p. 148–151° (from ether), in 69% yield. The infrared spectrum (CHCl₃) showed principal absorption at 3020, 2950, 1480, 1430, 1420, 1175, 1118, 1100, 1078, 1000, and 690 cm.⁻¹.

Anal. Calcd. for C₃₄H₃₃POSn: C, 67.24; H, 5.48; P, 5.10. Found: C, 66.91; H, 5.50; P, 4.96.

D₂O Quenching Experiments.—The experiments listed in Tables III and IV were carried out by rapidly (over *ca.* 15 sec.) adding the lithium reagent (or mixture of lithium reagents) to a suspension of the phosphine oxide in ether. The reaction mixture immediately became homogeneous and turned reddish brown. The mixture then was stirred vigorously for the designated time, cooled quickly, and the resulting reddish brown homogeneous solution was quenched with fresh D₂O. The benzene produced in these reactions was collected by preparative scale gas chromatography and analyzed by mass spectrometry, using a CEC, Model 21-130, mass spectrometer. Typical operating conditions were 20 μ and voltage setting = 250.

TABLE III

D₂O QUENCHING EXPERIMENTS, TRIPHENYLPHOSPHINE OXIDE

Phosphine oxide (mmoles)	RLi (mmoles)	Et ₂ O, ml.	T, °C.	Time (min.)	be-fore quench	Ben-zene, %	C ₆ H ₆ D in benzene	%		
(C ₆ H ₅) ₃ PO (25)	CH ₃ - (25)	50	25	1	97	2	97	13		
									97	13
(C ₆ H ₅) ₃ PO (10)	CH ₃ - (20)	25	25	1	90	9	91	13		
									91	13
(C ₆ H ₅) ₃ PO (25)	C ₂ H ₅ - (25)	50	25	1	97	14	91	13		
									91	13
(C ₆ H ₅) ₃ PO (10)	C ₂ H ₅ - (20)	25	25	1	100	25	91	45		
									91	45
(C ₆ H ₅) ₃ PO (25)	C ₂ H ₅ - (75)	50	25	5	98 ^a	51	91	45		
									91	45

^a The reaction mixture was concentrated to an aqueous slurry under vacuum and extracted with chloroform. Ethyldiphenylphosphine oxide (76%), m.p. 120–122°, was recovered from the chloroform extracts.

TABLE IV

D₂O QUENCHING EXPERIMENTS, ALKYL-DIPHENYLPHOSPHINE OXIDES

Phosphine oxide (mmoles)	RLi (mmoles)	Et ₂ O, ml.	T, °C.	Time (min.)	be-fore quench	Ben-zene, %	C ₆ H ₆ D in benzene	%
(C ₆ H ₅) ₂ P(O)CH ₃ (10)	CH ₃ - + C ₆ H ₅ - (10)	25	25	1	90	10	92	10
(C ₆ H ₅) ₂ P(O)CH ₃ (10)	CH ₃ - + C ₆ H ₅ - (20)	25	25	1	92	11.4	95	25
(C ₆ H ₅) ₂ P(O)C ₂ H ₅ (10)	C ₂ H ₅ - + C ₆ H ₅ - (10)	25	25	1	91	46	91	46
(C ₆ H ₅) ₂ P(O)C ₂ H ₅ (10)	C ₂ H ₅ - + C ₆ H ₅ - (20)	25	25	1	91	46	91	46

TPPO + 3C₂H₅Li. Trimethylchlorosilane Quench.—A suspension of 6.95 g. (25 mmoles) of triphenylphosphine oxide in 50 ml. of ether was treated rapidly (over *ca.* 0.5 min.) with 75 mmoles of ethyllithium. The mixture refluxed briefly during the addition and very rapidly became homogeneous and turned reddish brown.

The mixture was stirred rapidly for 5 min. and then quickly quenched with 8.15 g. (75 mmoles) of freshly distilled trimethylchlorosilane (Dow Corning Corp.) in 20 ml. of ether. The color of the reaction mixture faded rapidly to a pale yellow, and a white solid separated. Analysis of the reaction mixture by gas chromatography showed that it contained 15.3 mmoles (61%) of benzene and 8.70 mmoles (35%)¹⁸ of trimethylphenylsilane (collected by preparative scale gas chromatography), *n*_D²⁰ 1.4878, reported¹⁹ *n*_D²⁰ 1.4883 for trimethylphenylsilane. The infrared spectrum was identical with that of an authentic sample of trimethylphenylsilane.²⁰ The yield of (CH₃)₃SiC₆H₅ was measured by injecting a 50-ml. sample on a v.p.c. column (30% Dow Corning 710 silicone fluid on Chromosorb W, jacket at 190°, 10 p.s.i. helium pressure, preheater at 240°), measuring the area of the (CH₃)₃SiC₆H₅ peak, adding a known amount of authentic (CH₃)₃SiC₆H₅ to the mixture, and then measuring the increase in the area of the (CH₃)₃SiC₆H₅ peak using a 50-μl. sample.

Determination of Conversions for D₂O Quenching Experiments.—These experiments were performed in order to determine whether the reaction time and conditions used in the D₂O quenching experiments were sufficient to allow the metalation reaction B to go essentially to completion. This was found to be the case in all room temperature experiments. One example is described.

A suspension of 2.78 g. (10 mmoles) of TPPO in 35 ml. of ether was treated very rapidly with 13.08 ml. of 1.53 *N* (20 mmoles) methylolithium in ether. The resulting red solution was stirred for 1 min. and quenched with 7.72 g. (20 mmoles) of triphenyltin chloride in 20 ml. of THF. The color of the reaction mixture faded rapidly and stirring was continued for 6 hr. Then the mixture was treated with 10 ml. of KF solution. The organic phase was found to contain 9.1 mmoles (91%) of benzene. The mixture was filtered. Drying the residue gave 0.4 g. (0.93 mmole) of white solid, m.p. 223–227°. A mixture melting point with authentic tetraphenyltin was not depressed. The filtrate was saturated with KBr and the organic phase decanted. The residue was extracted with chloroform and the extracts were combined and dried over magnesium sulfate. The solvent was removed under vacuum to give a yellow, oily residue. Extraction of the oil with pentane and concentration of the pentane gave an oily residue which crystallized from cold ether; 3.04 g. (8.35 mmoles), m.p. 57–59°. A mixture melting point with authentic methyltriphenyltin²² was not depressed and their infrared spectra were identical. The portion of the oil which was not soluble in pentane was treated with ether. On standing, crystals formed; 4.5 g. (80%), m.p. 138–141°. A mixture melting point with authentic (C₆H₅)₂P(O)CH₂Sn(C₆H₅)₃ showed no depression.

A similar experiment, substituting ethyllithium for methylolithium, gave: benzene (71%); ethyltriphenyltin²³ (2.6 g., 6.87 mmoles, m.p. 53–55°; a mixture melting point with authentic C₂H₅Sn(C₆H₅)₃¹⁷ was not depressed and their infrared spectra were superimposable); tetraphenyltin (1.92 mmoles, m.p. 222–226°, identified by mixture melting point with authentic (C₆H₅)₄-Sn); and (C₆H₅)₂P(O)CH(CH₃)(C₆H₅)₂ (4.5 g., 77%, m.p. 166–171°).

Preparation of (C₆H₅)₂P(O)CH(R)Sn(C₆H₅)₃ Compounds by the Grignard Route.—A solution of *n*-propylmagnesium bromide [prepared from 1.46 g. (0.06 g.-atom) of magnesium turnings and 6.8 g. (55 mmoles) of *n*-propyl bromide in 90 ml. of THF] was added to a solution of 13.9 g. (50 mmoles) of TPPO in 40 ml. of THF. The mixture was then heated at reflux for 6 hr., during which time the color of the reaction mixture changed from dark green to deep red. The mixture was cooled, treated with 23.2 g. (60 mmoles) of triphenyltin chloride in 60 ml. of THF, and refluxing was continued for 20 hr. The resulting light brown solution was cooled and hydrolyzed with 20 ml. of saturated aqueous ammonium chloride solution. The mixture contained 38 mmoles (76%) of benzene. The organic phase was decanted and the residue was washed with 150 ml. of THF. The organic layers were combined and dried over magnesium sulfate. The mixture was filtered and ammonia was bubbled through the filtrate for 4 hr. The solution was then filtered and the filtrate was concentrated under vacuum to a colorless, opaque oil which crystallized on standing in ether; 17.9 g. (60%), m.p. 221–223°. Two recrystallizations from chloroform–heptane gave 16.5 g. (56%) of

(18) Separate experiments gave 13.8 mmoles (55%) and 11.8 mmoles (47%) of benzene; 10.4 mmoles (42%) and 11.7 mmoles (47%) of trimethylphenylsilane.

(19) A. Bygdén, *Z. physik. Chem.*, **90**, 243 (1915).

(20) Prepared by M. A. Weiner, Ph.D. Thesis, M.I.T., Dec., 1960.

(21) *Anal.* Calcd. for C₁₅H₁₅Sn: C, 62.51; H, 4.97. Found: C, 62.27; H, 5.17.

(22) Prepared by the reaction (C₆H₅)₃SnCl + RMgBr in THF. (C₆H₅)₃SnCH₃, m.p. 60–61° (from ether at -10°); R. H. Bullard and W. R. Robinson, *J. Am. Chem. Soc.*, **49**, 1368 (1927), report m.p. 61°. (C₆H₅)₃SnC₂H₅, m.p. 54–56°; M. Lesbre, R. Buisson, J. G. A. Luijten, and G. J. M. van der Kerk, *Rec. trav. chim.*, **74**, 1036 (1955), report m.p. 55–56°.

(23) *Anal.* Calcd. for C₂₀H₁₅Sn: C, 63.36; H, 5.32. Found: C, 63.64; H, 5.35.

white, crystalline solid, $(C_6H_5)_2P(O)CH(C_2H_5)Sn(C_6H_5)_3$, m.p. 225–227°, whose infrared spectrum (KBr pellet) showed principal absorption at 3000, 1478, 1418, 1075, 1020, 995, 725, and 690 cm^{-1} .

Anal. Calcd. for $C_{33}H_{51}PO_2Sn$: C, 66.80; H, 5.27, P, 5.22. Found: C, 66.49; H, 5.02; P, 5.03.

Similar experiments with benzylmagnesium chloride, methylmagnesium bromide, isopropylmagnesium bromide, and ethylmagnesium bromide gave benzene yields of 12, 84, 14, and 81%, respectively. The intermediates from the methyl and ethyl Grignard reagent reactions were converted to $(C_6H_5)_2P(O)CH_2-Sn(C_6H_5)_3$ (60%) and $(C_6H_5)_2P(O)CH(CH_3)Sn(C_6H_5)_3$ (9%), whose structures were confirmed by melting point and mixture melting point and by comparison of their infrared spectra with authentic samples prepared by the organolithium route.

D_2O Quenching Experiments. Grignard Procedure.—A solution of 6.95 g. (25 mmoles) of TPPO in 40 ml. of THF was treated with 23.2 ml. of 1.08 *N* (25 mmoles) methylmagnesium bromide in THF. Samples (2 ml.) were removed at successive time intervals and quenched in D_2O (1 ml.). The results are summarized in Table I.

Carbonylation of the TPPO- CH_3MgBr Reaction Mixture.—A solution of 13.9 g. (50 mmoles) of TPPO in 75 ml. of THF was treated with 46.3 ml. of 1.08 *N* (50 mmoles) methylmagnesium bromide in THF. The mixture then was stirred for 7 hr. at room temperature²⁴ and poured onto a slurry of Dry Ice in THF. The resulting suspension was left to stand for 15 hr. and then acidified with 1 *N* HCl. The entire mixture was then concentrated on a rotary evaporator to an aqueous slurry. The residue was extracted with three 100-ml. portions of ether. The ether solutions were combined, washed with 20 ml. of water, and dried over magnesium sulfate. The mixture was filtered and the ether was removed on a rotary evaporator. Sublimation of the residue at 60–80° (0.3 mm.) gave 2.22 g. (37%) of white, crystalline solid, m.p. 121–122°. A mixture melting point with authentic benzoic acid showed no depression. The anilide was prepared and recrystallized from ethanol; m.p. 158–160°. A mixture melting point with the anilide prepared from authentic benzoic acid was not depressed.

(24) A Gilman Color Test III was positive (deep purple).

Synthesis of Diphenylethylene.—An ethereal solution of $(C_6H_5)_2P(O)CH_2Li$ [generated from 13.9 g. (50 mmoles) of TPPO and 50 mmoles of methyl lithium in ether] was treated with 9.11 g. (50 mmoles) of benzophenone in ether. The resulting suspension was heated to reflux for 3 hr., cooled, and hydrolyzed with 3% HCl. The reaction mixture was filtered and the residue dissolved in 200 ml. of benzene. The benzene solution was dried over magnesium sulfate, filtered, and the filtrate concentrated under vacuum. The crude, white crystalline residue was dried under vacuum over P_2O_5 , suspended in 150 ml. of reagent toluene, and heated to reflux for 3 hr. with 5.73 g. (51 mmoles) of potassium *t*-butoxide (MSA Research Corp.). Analysis of the reaction mixture by gas chromatography at 200° with Dow Corning 710 silicone fluid on firebrick showed that it contained 36.4 mmoles (73%) of 1,1-diphenylethylene. A sample was collected which gave m.p. 6° and n_D^{25} 1.6065 (*Anal.* Calcd. for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.29; H, 6.83) and whose infrared spectrum and retention time were identical with that of authentic material. A sample of authentic 1,1-diphenylethylene gave m.p. 6° and n_D^{25} 1.6056. The yield of olefin was measured by the increase in peak area, using the same injection volume, after adding a known amount of diphenylethylene to the reaction mixture. The solid remaining in the reaction mixture was removed by filtration and dissolved in 25 ml. of 0.1 *N* NaOH. Careful acidification gave diphenylphosphonic acid in 86% yield, m.p. 188–190°, as a white precipitate. The reported melting point for $(C_6H_5)_2P(O)OH$ is 190–192°.²⁵

The same procedure using $(C_6H_5)_2P(O)CH_2MgBr$ in THF resulted in formation of 1,1-diphenylethylene in 71% yield.

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(25) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **64**, 2982 (1942).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY, DURHAM, N. C.]

Isolation of Intermediate Alkali Salt in *ortho*-Substitution Rearrangement of Benzyltrimethylammonium Ion as Benzophenone Adduct¹

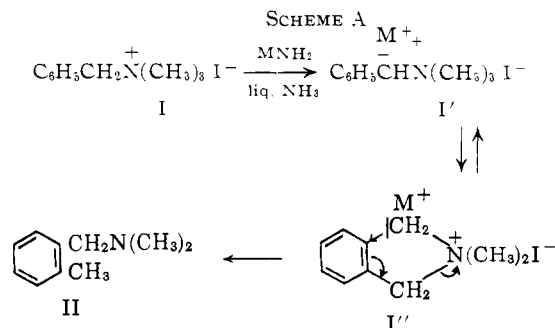
BY WALTER H. PUTERBAUGH² AND CHARLES R. HAUSER

RECEIVED SEPTEMBER 9, 1963

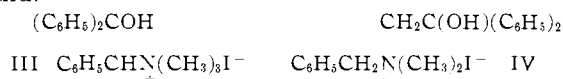
Although the *o*-substitution rearrangement of the benzyltrimethylammonium ion (I) by potassium amide or sodium amide in liquid ammonia occurs very rapidly at –33°, the initially formed benzyl carbanion (I') was isolated at –80° as its benzophenone adduct III. That the benzyl carbanion I' was an intermediate in the rearrangement was shown by its conversion at –33° to rearranged amine II in 87% yield within 3 min. Ionization of the benzylic hydrogen and also the *o*-rearrangement occurred more slowly with lithium amide than with potassium amide or sodium amide. Adduct III underwent thermal conversion to benzylidene phenyl ketone, and the *o*-substitution rearrangement with excess potassium amide in liquid ammonia to give carbinolamine V.

The *o*-substitution rearrangement of benzyltrimethylammonium iodide (I) by alkali amides in liquid ammonia to form amine II has been assumed³ to involve the initial formation of the benzyl carbanion I'; this carbanion would be in equilibrium with the methyl carbanion I'' which rapidly undergoes the rearrangement (Scheme A).⁴

In agreement with this theory, intermediate alkali salt I' has now been isolated as its benzophenone adduct III in yields of 71–73, 70, and 19% when M was potassium, sodium, and lithium, respectively. None of the isomeric adduct IV, which might have arisen



through condensation of salt I'' with the ketone, was found.



Isolation of III was accomplished by addition of

(1) Supported in part by Army Research Office (Durham).

(2) National Science Foundation Science Faculty Fellow, on leave from Thiel College.

(3) See S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951); F. N. Jones and C. R. Hauser, *J. Org. Chem.*, **26**, 2979 (1961).

(4) It has not been determined whether the conversion of I' to I'' occurs intramolecularly or intermolecularly. A possible mechanism might involve a six-membered ephemeral ring with a molecule of ammonia.