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 $C_{33}H_{31}POSn$: 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 $(C_6H_5)_2P(O)CH_2Sn(C_6H_5)_3$ (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.

Carbonation 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 temperature[24] 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.

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 methyllithium 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 $n^{25}D$ 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 $n^{25}D$ 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.

Acknowledgments.—The authors are grateful to the U. S. Army Research Office (Durham) (Grant DA-ARO (D)-31-124-G207) and to the United States Air Force (Contract AF 33(657)-8532, monitored by Materials Central, Aeronautical Systems Division, Wright Patterson AF Base, Ohio) for generous support of this work and to M and T Chemicals, Inc., for gifts of chemicals.

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

[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 Adduct[1]

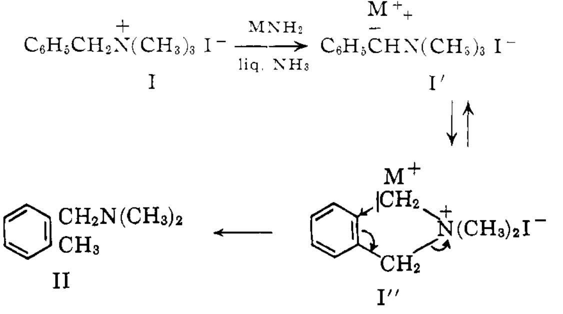
BY WALTER H. PUTERBAUGH[2] AND CHARLES R. HAUSER

RECEIVED SEPTEMBER 9, 1963

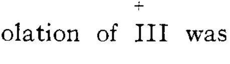
Although the *o*-substitution rearrangement of the benzyltrimethylammonium ion (I) by potassium amide or sodium amide in liquid ammonia occurs very rapidly at −33°, the initially formed benzyl carbanion (I′) was isolated at −80° as its benzophenone adduct III. That the benzyl carbanion I′ was an intermediate 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 benzhydryl 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 assumed[3] 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]

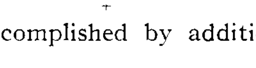
SCHEME A



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.

III 

$$\overset{(C_6H_5)_2COH}{C_6H_5CH\underset{+}{N}(CH_3)_3I^-}$$

 IV

$$\overset{CH_2C(OH)(C_6H_5)_2}{C_6H_5CH_2\underset{+}{N}(CH_3)_2I^-}$$

Isolation of III was accomplished by addition of

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[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.

quaternary salt I to a molecular equivalent of the alkali amide in liquid ammonia at −80°, followed by a molecular equivalent of benzophenone in ether. Besides III, some rearranged amine II and recovered ketone were obtained (Table I).

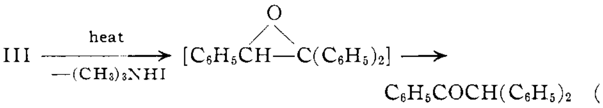
TABLE I

CONVERSION OF I TO I′ BY ALKALI AMIDES AT −80° CONDENSATION WITH BENZOPHENONE TO FORM III

Alkali amide	Color of salt I′	Adduct III yield, %[a]	Amine II yield, %	Recovd. ketone, %
KNH_2	Yellow-green	71 (73)[b]	2 (3)[b]	24 (26)[b]
$NaNH_2$	Orange-brown	70	8	27
$LiNH_2$	Gray	19	2	79

[a] Obtained on adding the benzophenone after 30 min. [b] Obtained on adding the benzophenone after 10 min.

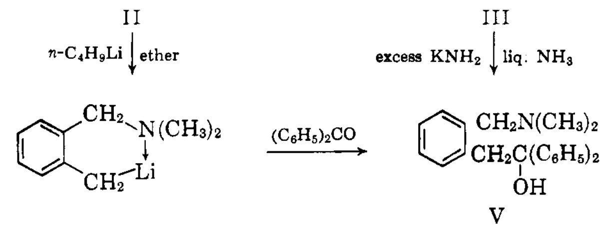
That the adduct was III, not IV, was supported by thermal conversion to benzhydryl phenyl ketone in 70% yield. This reaction presumably involved the intermediate formation of an epoxide, which underwent rearrangement (eq. 1).



(1)

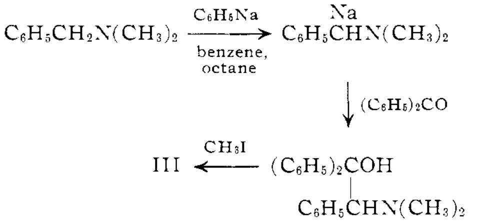
Structure III was further supported by its *o*-substitution rearrangement to form carbinolamine V (88%), which was independently synthesized through metalation of amine II (Scheme B).[5] The rearrangement of III presumably involved the intermediate formation of the alkali salt of an alkoxide-type ion.[6] Also, quaternary iodide I was converted to V without isolation of intermediate III (see Experimental).

SCHEME B



Structure III was confirmed by independent synthesis from benzyldimethylamine, benzophenone, and methyl iodide (Scheme C).[7]

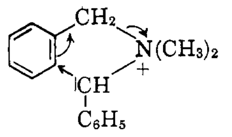
SCHEME C



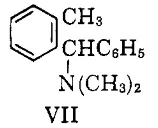
$$\begin{tikzcd} C_6H_5CH_2N(CH_3)_2 \arrow[r, "C_6H_5Na", "\text{benzene, octane}"'] & C_6H_5\overset{Na}{C}HN(CH_3)_2 \arrow[d, "(C_6H_5)_2CO"] \\ III & (C_6H_5)_2\underset{C_6H_5CHN(CH_3)_2}{COH} \arrow[l, "CH_3I"'] \end{tikzcd}$$

The success of the isolation of the alkali salts I′ as benzophenone adduct III appeared to be dependent not only on retarding their rate of rearrangement by lowering the temperature to −80°, but also on their precipitation. Interestingly, these salts I′ were stable under these conditions for at least 30 min. (see Table I), whereas at −33° the sodium and potassium salts rearrange rapidly. That the yellow-green potassium salt I′ from which adduct III was obtained at −80° is an intermediate in the *o*-substitution rearrangement was established by allowing the reaction mixture (without addition of benzophenone) to warm to −33°, at which temperature rearranged amine II was obtained in 87% yield after only 3 min.

The relatively low yield (19%) of adduct III obtained when quaternary salt I was treated with lithium amide (see Table I) indicates a relatively slow rate of ionization of the benzylic hydrogen of I by this base, compared to sodium amide and potassium amide. This slow ionization of I by lithium amide furnishes a partial explanation of the earlier observation that the rearrangement of I occurs much more slowly with this base than with potassium amide or sodium amide.[8] However, this relatively slow rate of rearrangement by lithium amide is evidently also due to a relatively slow conversion of lithium salt I′ to I″ (see Scheme A), since the rate of ionization of I to I′ with lithium amide (19% after 30 min. at −80°) is faster than the rate of *o*-rearrangement (8% after 1 hr. at −33°) with this base. Moreover, the dibenzyldimethylammonium ion, in which the initial benzylic carbanion VI is the carbanion that undergoes rearrangement, affords rearranged amine VII in 70% yield with lithium amide as well as with sodium amide after 1 hr. in liquid ammonia at −33°.[9]

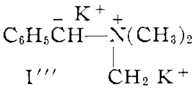


VI



VII

It seemed possible that benzylic carbanion I′ might undergo secondary ionization with excess amide ion to form dicarbanion I‴, which might rearrange even at −80°. However, when quaternary salt I was added to 2 molecular equivalents of potassium amide in liquid ammonia at −80° and the reaction mixture neutralized after 30 min., rearranged amine II was obtained in only 1% yield. Furthermore, when compound I was added to 2 equivalents of potassium amide at −80° followed by 1 equivalent of benzophenone, none of adduct IV, which would be expected from I‴, was evidently formed. Thus none of the rearrangement product of IV was isolated on warming the reaction mixture to −33° for 3 hr. Instead, rearranged amines II and V were obtained in yields of 72 and 12%, respectively, and 81% of the ketone was recovered. Apparently, the benzophenone was largely tied up as its potassium amide adduct, leaving most of the monopotassium salt I′ to undergo the rearrangement.



$$\underset{I'''}{}\quad C_6H_5\overset{-\ K^+}{C}H-\overset{+}{N}(CH_3)_2\underset{\underset{-}{CH_2}\,K^+}{|}$$

Experimental[10]

Conversion of I to I′ by Alkali Amides at −80°. Condensation with Benzophenone to Form III (Table I). (A) With Potassium Amide.—A stirred solution of 0.105 mole of potassium amide in 400 ml. of liquid ammonia[11] was cooled to −80° in a Dry Ice–

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(5) The details of this method will be published soon. For deuteration at the 2-methyl position of II through metalation, see F. N. Jones, M. F. Zinn, and C. R. Hauser, *J. Org. Chem.*, **28**, 663 (1963).

(6) The *o*-substitution rearrangement of certain other quaternary ammonium ion-alcohols through the alkali salt of alkoxide-type ions have recently been effected: G. C. Jones and C. R. Hauser, *ibid.*, **27**, 806 (1962).

(7) For the details of this method, see W. H. Puterbaugh and C. R. Hauser, *ibid.*, **28**, 3465 (1963).

(8) Whereas potassium amide and sodium amide have afforded II in 90% yield within a few minutes,[3] lithium amide has produced II in only 8% yield after 1 hr. and in 50% yield after 8 hr.: unpublished results of G. C. Jones, P. L. Bayless, and C. R. Hauser.

(9) P. L. Bayless and C. R. Hauser, unpublished results.

(10) Melting points were taken on a Fisher-Johns melting point stage which had been calibrated with standard samples. Analyses by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were taken on a Perkin-Elmer Model 237 Infracord using potassium bromide pellets.

acetone bath while a rapid stream of dry nitrogen was passed over the reaction mixture. The mixture was stirred for 15 min. at this temperature, and 27.7 g. (0.10 mole) of benzyltrimethylammonium iodide (I) was added during 2 min. The resultant yellow-green suspension containing potassium salt I′ was stirred for 10 min. and a solution of 18.2 g. (0.10 mole) of benzophenone in 150 ml. of dry ether was added. After stirring for 10 min., the cooling bath was removed. The gray mixture was stirred for 20 min. and then neutralized by pouring it into a solution of 17.4 g. (0.12 mole) of ammonium iodide in 150 ml. of liquid ammonia. The liquid ammonia was evaporated on the steam bath as 150 ml. of ether was added. The resulting ethereal suspension was stirred with 150 ml. of water. The precipitate that remained was removed by filtration and washed with water and ether. Recrystallization from methanol afforded 33.5 g. (73%) of 2-hydroxy-1,2,2-triphenylethyltrimethylammonium iodide (III), m.p. 181–182°, and at 182–183° after a second recrystallization from methanol.

The layers of the aqueous ethereal filtrate, obtained on filtering III (see above), were separated. The organic layer was combined with an ether extract of the aqueous layer after the latter had been made strongly basic with sodium hydroxide. The ethereal solution was extracted with 2 *M* hydrochloric acid, then washed with saturated sodium chloride solution, and dried over sodium sulfate. The solvent was removed to leave 4.8 g. (26%) of benzophenone, m.p. 45–48°, undepressed on admixture with an authentic sample.

The acidic extract (see above) was made basic with sodium hydroxide solution and the resulting mixture extracted with ether. The ether extract was dried and the solvent removed to leave 0.5 g. (3%) of amine, presumably II.

When the above reaction was effected similarly, except that the reaction mixture containing potassium salt I′ was stirred for 30 min. at −80° before adding the benzophenone, there was obtained 32.4 g. (71%) of III, m.p. 181–182.5°, along with 4.3 g. (24%) of benzophenone and 0.24 g. (2%) of II.

(B) **With Sodium Amide.**—This reaction was effected essentially as described above under (A) employing 0.105 mole of sodium amide.[12] The reaction mixture containing an orange-brown suspension of sodium salt I′ was stirred 30 min. at −80° before adding the benzophenone. There was obtained 32.3 g. (70%) of adduct III, m.p. and mixture m.p. with III from (A) above, 182–184°, along with 4.9 g. (27%) of recovered benzophenone and 1.2 g. (8%) of II.

(C) **With Lithium Amide.**—This reaction was similarly effected employing 0.105 mole of lithium amide[13] to give a gray suspension containing lithium salt I′ which was stirred for 30 min. before adding the benzophenone. There was obtained 8.7 g. (19%) of III, m.p. 177–180°, mixture m.p. with III from (A) above, 180–183°; together with 14.3 g. (79%) of benzophenone and 0.3 g. (2%) of II.

Proof of Structure of III. (A) Thermal Rearrangement to Benzhydryl Phenyl Ketone.—In a test tube flushed with dry nitrogen was placed 4.6 g. (0.01 mole) of III. After heating to 200–210° in an oil bath for 15 min., the mixture was cooled and triturated with water. The precipitate was filtered and recrystallized from 95% ethanol to yield 1.9 g. (70%) of benzhydryl phenyl ketone, m.p. 135–136°, reported[14] m.p. 136°. The melting point was not depressed on admixture with an authentic sample.[15]

(B) ***o*-Rearrangement of III to Form V with Excess Potassium Amide.**—To a solution of 0.15 mole of potassium amide in 600 ml. of ammonia was added 23.0 g. (0.05 mole) of III. The mixture, containing a blue-gray solution above a white precipitate, was stirred for 6.5 hr. and then poured into a solution of 21.8 g. (0.15 mole) of ammonium iodide in 200 ml. of liquid ammonia. The ammonia was replaced by 300 ml. of ether and 150 ml. of water was added. Since no precipitate formed (indicating the absence of unreacted III), the layers were separated. The organic layer was combined with an ether extract of the aqueous layer (previously made alkaline) and extracted with hydrochloric acid. The acidic extract was made basic and the liberated amine taken up in ether. The solvent was removed from the dried ether solution of the basic fraction to leave 14.7 g. (88%) of 2-(dimethylaminomethyl)-benzyldiphenylcarbinol (V), m.p. 122.5–125°. The analytical sample melted at 126–127° after two recrystallizations from hexane–benzene.

Anal. Calcd. for $C_{23}H_{25}NO$: C, 83.34; H, 7.60; N, 4.23. Found: C, 83.44; H, 7.58; N, 4.33.

The melting point was not depressed on admixture with a sample of V independently synthesized through metalation of 2-methylbenzyldimethylamine with *n*-butyllithium and condensation with benzophenone.[5] The infrared spectra of the two samples were identical.

The picrate melted at 185.5–186.5° after recrystallization from 95% ethanol.

Anal. Calcd. for $C_{29}H_{28}N_4O_8$: C, 62.13; H, 5.03; N, 10.00. Found: C, 61.96; H, 4.84; N, 10.21.

Removal of solvent from the dried ether solution of the neutra fraction left 1.1 g. (12%) of yellow partial solid, presumably benzophenone.

(C) **Independent Synthesis of Adduct III.**—This compound was independently synthesized through metalation of benzyldimethylamine with phenylsodium, condensation with benzophenone, and methylation essentially as described previously[7] (see Scheme C). This product melted at 181.5–183°, undepressed on admixture with a sample of III obtained from condensation of alkali salt I′ with benzophenone as described above.

Conversion of I to V without Isolation of III.—A suspension of potassium salt I′ prepared from 0.105 mole of potassium amide and 0.10 mole of I was stirred for 10 min. at −80°, and a solution of 18.2 g. (0.10 mole) of benzophenone in 150 ml. of ether was added. After stirring for 10 min. at −80° and for 20 min. with the cooling bath removed, a solution of 0.20 mole of potassium amide in 300 ml. of liquid ammonia was added from an inverse addition flask. The resultant mixture was stirred for 3 hr. and then poured into a solution of 16.6 g. (0.31 mole) of ammonium chloride in 150 ml. of liquid ammonia. From the basic fraction there was obtained 21.9 g. of partial solid, which was refluxed with 35 ml. of hexane, cooled, and filtered to give 13.5 g. (41%) of V, m.p. 124.5–126°, undepressed on mixture m.p. with independently synthesized V. The filtrate was distilled to give 5.8 g. (39%) of II, b.p. 79–80°. Recrystallization of the residue from the distillation afforded another 0.8 g. (2%) of V. From the neutral fraction there was obtained 10.0 g. (55%) of benzophenone, m.p. 44–47°.

Rearrangement of Potassium Salt I′ to II by Warming to −33°.—The yellow-green suspension of potassium salt I′ prepared as described above from 0.105 mole of potassium amide and 0.10 mole of I was stirred 10 min. at −80°. On removing the cooling bath, the yellow-green precipitate persisted until the temperature reached −33°, at which point it rapidly disappeared to leave a brown mixture. After 3 min., 16.0 g. (0.11 mole) of ammonium iodide was added rapidly, and the ammonia replaced by 200 ml. of ether. The resulting ethereal suspension was shaken with 50 ml. of 2 *M* sodium hydroxide and the mixture was worked up in the usual manner. Removal of solvent from the dried basic fraction left 14.0 g. of oil, which on distillation gave 13.0 g. (87%) of 2-methylbenzyldimethylamine (II), b.p. 82–83° at 15 mm., reported[3] b.p. 80–80.2° at 14 mm. The picrate melted at 112–113°, reported[3] m.p. 112.5–113°. The melting point was not depressed on admixture with an authentic sample.

Treatment of I with 2 Equivalents of Potassium Amide at −80°. (A) Without Benzophenone.—A solution of 0.21 mole of potassium amide in 450 ml. of liquid ammonia was cooled to −80° for 15 min. and 27.7 g. (0.10 mole) of I was added. The yellow-green suspension was stirred for 30 min. and then neutralized by adding 11.8 g. (0.22 mole) of ammonium chloride. From the basic fraction there was obtained only 0.2 g. (1%) of II. No material was found in the neutral fraction.

(B) **With Benzophenone.**—A solution of 0.21 mole of potassium amide in 450 ml. of liquid ammonia was cooled to −80° for 15 min. and 27.7 g. (0.10 mole) of I was added. After stirring for 10 min., a solution of 18.2 g. (0.10 mole) of benzophenone in 150 ml. of ether was added. The mixture was stirred for 10 min. at −80° and then for 3.5 hr. with the cooling bath removed. The mixture was neutralized by pouring it into a solution of 32 g. (0.22 mole) of ammonium iodide in 150 ml. of liquid ammonia. From the basic fraction there was obtained 16.2 g. of residue, which on distillation afforded 10.7 g. (72%) of II, b.p. 79–81° at 13 mm. The residue from the distillation was recrystallized from hexane to give 3.9 g. (12%) of V, m.p. 126–127.5°, undepressed on admixture with independently synthesized V. From the neutral fraction there was obtained 14.8 g. (81%) of recovered benzophenone, m.p. 44–47°.

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[11] See C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

[12] See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **8**, 122 (1954).

[13] See C. R. Hauser and W. H. Puterbaugh, *J. Am. Chem. Soc.*, **75**, 1068 (1953).

[14] H. Biltz, *Ber.*, **26**, 1957 (1893).

[15] R. S. Yost and C. R. Hauser, *J. Am. Chem. Soc.*, **69**, 2325 (1947).