This product is oxidatively unstable, losing about 6% of its reducing capacity in one day in spite of special precautions to keep it away from air. When treated with oxygen, this ditin is converted quantitatively to IV.

CONCLUSION

All the data available on the products of the dibutyltin dichloride reaction are given in Table II. On the basis of these results it is concluded that the products of Johnson and co-workers are actually bis(dialkyl-halotin) oxides (IV), rather than ditin compounds as claimed. Furthermore, these oxides are very stable compounds, readily formed by partial hydrolysis of the disubstituted tin dichlorides. That this stability is representative of the class of compounds will be shown in further papers.

EXPERIMENTAL[9]

Dibutylchlorotin hydroxide (III). Dibutyltin dichloride (150 g.) was dissolved in 300 ml. of methyl alcohol and treated with a large volume of water. A white solid formed and was filtered, powdered with a mortar and pestle, and reslurried with more water. The solid was again filtered and dried under reduced pressure, yielding 132 g. (93%) of a white solid, m.p. 105–107°. The infrared spectrum showed a small band at 3509 cm.$^{-1}$

Anal. Calcd. for $C_8H_{19}ClOSn$: Sn, 41.75; Cl, 12.47. Found: Sn, 40.71; Cl, 12.39.

The molecular weight was determined in chloroform by the isopiestic method of Barger[10] except that the solutions were measured gravimetrically rather than volumetrically.

Anal. Calcd: 285.4; Found: 250. Attempts to recrystallize led to dehydration and yielded only compound IV.

Bis-(dibutylchlorotin) oxide (IV). (a) Using the procedure of Johnson, Fritz, *et al.*[3,4] 0.025 mole of dibutyltin dichloride in 50 ml. anhydrous ether reacted with 0.025 mole of triethylamine and 20 ml. of absolute ethanol. After removal of the amine hydrochloride, 5.27 g. of a white solid, m.p. 111–113°, was obtained. Recrystallization from acetone yielded 3.37 g., m.p. 112–114°.

Anal. Calcd. for $C_{16}H_{36}Cl_2OSn$: Sn, 42.95; Cl, 12.80. Found: Sn, 42.6, 43.11; Cl, 13.06, 12.85.

(b) When Compound III was recrystallized from acetone, a white solid resulted, m.p. 112–113°, which gave no depression in a mixed melting point determination with the product from (a).

(c) Dibutyltin dichloride 9 g. (0.03 mole) and 7.5 g. (0.03 mole) of dibutyltin oxide were melted to a clear solution and allowed to cool. The solid, when recrystallized from acetone, melted 112–114°.

(d) In the course of another investigation, dibutyltin dihydride and dibutyltin dichloride were mixed in equimolar quantities and oxygen bubbled into the mixture. A solid product was obtained which was shown by melting point and mixture melting point to be identical with the product obtained by the procedure of Johnson and Fritz.[4,5] Recrystallization from petroleum ether (b.p. 40–60°) gave a solid m.p. 112–114°.

Anal. Calcd. for $C_{16}H_{36}Cl_2OSn_2$: Sn, 42.95; Found Sn, 42.51, 42.44.

RAHWAY, N. J.
DURHAM, N. H.

---

(9) Melting (or decomposition) points are uncorrected. Tin analyses were done in duplicate by the method of Farnsworth and Pekola. This method has been extremely reliable for many hundreds of analyses (M. Farnsworth and J. Pekola, *Anal. Chem.*, **31**, 410–414 (1959).

(10) A. Steyermark, *Quantitative Organic Microanalysis*, Blakiston Co., Philadelphia, p. 292 *ff.* (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Influence of the Metallic Cation of Certain Organometallic Compounds on the Courses of Some Organic Reactions[1,2]

WILLIAM IVO O'SULLIVAN,[3] FREDERIC W. SWAMER, WILBERT J. HUMPHLETT
AND CHARLES R. HAUSER

Received August 22, 1960

The ratios of ionization of the α-hydrogen *versus* addition to the carbonyl group of acetophenone by phenylpotassium phenylsodium, and phenyllithium were approximately 10:1, 1.5–2:1 and 1:23, respectively. Similar results were obtained in certain related reactions. They are interpreted on the basis of the influence of the metallic cation. The 1,2- *versus* 1,4-addition of the reagents to benzalacetophenone was studied.

The courses of certain organic reactions with strongly basic or nucleophilic anions are known to be influenced considerably by the metallic cation associated with the anion. Two examples are the substitution *versus* elimination reactions of alkyl halides with alkali diethylamides or phenylalkalies[4] and the condensation of alkali esters with the carbonyl group of ketones *versus* the ionization of their α-hydrogen.[5] In both examples the lithium reagent favors the nucleophilic reaction at the carbon, and the sodium reagent the basic attack at the hydrogen.

---

(1) Supported by the Office of Ordnance Research, U. S. Army, and by the Office of Naval Research.

(2) A portion of this work was reported at the Philadelphia meeting of the American Chemical Society, April 1950.

(3) On leave from the University College, Dublin, Ireland.

(4) W. H. Puterbaugh and C. R. Hauser, *J. Org. Chem.*, **24**, 416 (1959).

(5) C. R. Hauser and W. H. Puterbaugh, *J. Am. Chem. Soc.*, **75**, 4756 (1953); C. R. Hauser and W. R. Dunnavant, *J. Org. Chem.*, **25**, 1296 (1960).

TABLE I

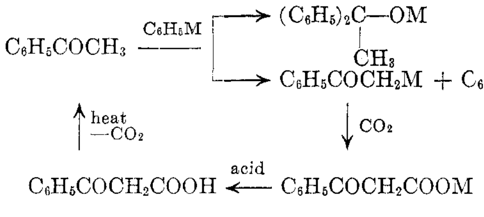
REACTIONS OF α-HYDROGEN COMPOUNDS WITH ORGANOMETALLIC REAGENTS FOLLOWED BY CARBONATION

Exp. No.	α-Hydrogen Compound	Organo-metallic Reagent	Solvent	Temp.	Time, Hr.	Regenerated α-H Compd. Yield, %[a]	Addition Product, Yield, %	Ratio of Ioniz. of α-H to Addition
1	Acetophenone	C_6H_5K	Isooctane	50	3	54	5	11:1
2	Acetophenone	$C_6H_5K^b$	Hexane-octane	50	3	60	6	10:1
3	Acetophenone	$C_6H_5Na^c$	Heptane	50	3	48	34	1.4:1
4	Acetophenone	$C_6H_5Na^d$	Hexane-octane	50	3	36	24	1.5:1
5	Acetophenone	$C_6H_5Na^{d,e}$	Hexane-octane	50	3	43	24	1.8:1
6	Acetophenone	C_6H_5Li	Ether	35	0.75	4	91	1:23
7	Acetophenone	C_6H_5MgBr	Ether	35	0.75	—[f]	90	Low
8	Acetophenone	$C_5H_{11}K$	Hexane-isooctane	50	3	48	—	High
9	Acetophenone	$C_5H_{11}Na$	Hexane-octane	50	3	38	12	3.2:1
10	Ethyl phenylacetate	$C_6H_5Na^c$	Heptane	25–30	3	65	4	16:1
11	Ethyl phenylacetate	C_6H_5Li	Ether	25–35	3	6	70	1:12
12	Phenylacetonitrile	$C_6H_5Na^c$	Benzene	40	1.5	90	5	18:1
13	Phenylacetonitrile	C_6H_5Li	Ether	35	8	45	9	5:1
14	Phenylacetonitrile	C_6H_5MgBr	Ether	35	5	15	33	1:2
15	Acetomesitylene	$C_6H_5Na^c$	Heptane	50	3	80	—	High
16	Acetomesitylene	C_6H_5Li	Ether	35	2	all	—	High
17	Mesitylacetonitrile	$C_6H_5Na^c$	Benzene	40	1.5	71	5	14:1
18	Mesitylacetonitrile	C_6H_5Li	Ether	35	4	—[g]	80	Low
19	Mesitylacetonitrile	C_6H_5MgBr	Ether	35	6	—	78	Low
20	Phenylacetonitrile	C_4H_9Li	Ether	35	2	28	—	High
21	Phenylacetonitrile	C_4H_9Li	Benzene	40	3	13	49	1:3.8
22	Mesitylacetonitrile	C_4H_9Li	Ether	35	6	35	21	1.7:1
23	Mesitylacetonitrile	C_4H_9Li	Benzene	40	4	14	51	1:3.6

[a] The regenerated α-hydrogen compounds generally boiled within a range of 2–5°. [b] The phenylpotassium–potassium methoxide reagent also contained a molecular equivalent of potassium chloride. [c] Reagent prepared by the earlier procedure. [d] Reagent prepared by newer procedure. [e] The phenylsodium–sodium chloride reagent also contained sodium methoxide. [f] No regenerated acetophenone was isolated but some of the magnesium bromide enolate of the ketone might have been formed and then condensed with unchanged ketone to give the aldol product. [g] The reaction product was not carbonated and thus regenerated mesitylacetonitrile was not expected.

We have found that, whereas phenyllithium and phenylmagnesium bromide add to the carbonyl group of acetophenone, phenylsodium, and especially phenylpotassium, react mainly with the α-hydrogen of this ketone effecting its ionization to form the alkali enolate. These two possible courses of reaction are shown in Scheme A, in which M represents potassium, sodium, lithium, or magnesium bromide.

Scheme A



As indicated in Scheme A, the relative extents of the two courses of reaction were determined by carbonation to convert the alkali enolate to the β-keto acid salt, which was separated from the carbinol. The free β-keto acid was liberated from the salt and decarboxylated to regenerate acetophenone, the yield of which represented the extent of ionization of the α-hydrogen. This yield as well as that of the carbinol from the addition reaction is given in Table I along with those from related reactions. Since 10–15% of the acetophenone was generally recovered in the reactions with the potassium and sodium reagents, the conversion yields would be correspondingly greater. The extent of the α-hydrogen reaction may be slightly higher than that indicated since the method did not take into account the possible aldol condensation.

Since phenylpotassium was obtained from anisole and phenylsodium from chlorobenzene, their preparations produced as by-products potassium methoxide and sodium chloride, respectively. Attempts to prepare the former reagent from chlorobenzene and the latter reagent from anisole[6] under similar conditions were unsatisfactory. In experiments 2 and 5 of Table I, the phenylpotassium–potassium methoxide reagent contained an equivalent of potassium chloride, and the phenylsodium–sodium chloride reagent an equivalent of sodium methoxide (see Experimental). The pressence of the potassium chloride in the former reagent had no appreciable effect on the two courses of reaction (compare Exps. 1 and 2) but that of the sodium methoxide favored slightly the α-hydrogen reaction (compare Exps. 3, 4, and 5).

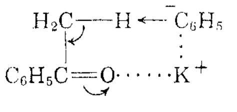
The last column of Table I shows that the ratio of ionization of the α-hydrogen of acetophenone to reaction at the carbonyl group was approximately 10:1 with phenylpotassium, 1.5–2:1 with phenyl-

---

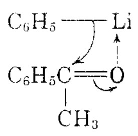
[6] See A. A. Morton and A. E. Brachman, *J. Am. Chem. Soc.*, **76**, 2975 (1954).

sodium and 1:23 with phenyllithium. Since the reactions with the potassium and sodium reagents were carried out under essentially the same conditions (Exps. 2 and 5), the considerable difference in the ratio of the two courses of reaction may be ascribed to the influence of the metallic cation. The great difference in the ratio of the two courses of reaction with the sodium and lithium reagents may be due not only to the influence of the metallic cation but also to the difference in solvents, which were an alkane and ether, respectively. An indication that the metallic cation is the more important factor is the observation that, in the related reactions of phenyl- and mesitylacetonitriles with butyllithium, the ratio of ionization of the α-hydrogen to addition was greater in ether than in benzene (Exps. 20–23). Consequently an even lower ratio in the two courses of reaction of acetophenone with phenyllithium might be expected if the solvent were a hydrocarbon instead of ether.

These results may be rationalized on the basis of the degree of ionization of the phenylalkalies, which should decrease as the metallic cation is varied in the order: K > Na > Li. Thus, phenylpotassium is effectively the strongest base attacking mainly the α-hydrogen, and phenyllithium the strongest nucleophilic reagent attacking largely the carbonyl carbon(indicated in I and II, respectively).

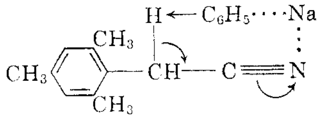


I

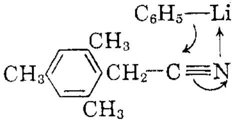


II

Similar results were obtained in several related reactions (see Table I). Interestingly, phenyllithium effected mainly ionization of the α-hydrogen of phenylacetonitrile but the addition reaction with mesitylacetonitrile lead to the formation of the corresponding ketone (Exps. 13 and 18). Phenylsodium, however, effected largely ionization of the α-hydrogen of both of these nitriles (Exps. 12 and 17). The predominant course of reaction of mesitylacetonitrile with the sodium and lithium reagents is indicated in III and IV, respectively.



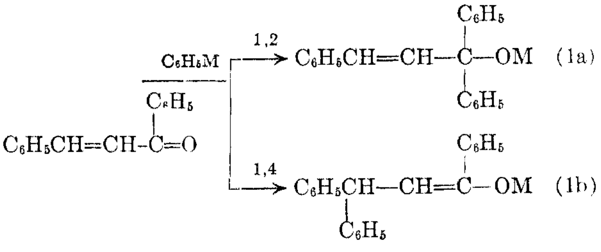
III



IV

As might be expected phenylsodium underwent the addition reaction with benzaldehyde to form benzhydrol. This reagent has previously been shown to add to benzophenone to give triphenylcarbinol.[7]

1,2-Versus 1,4-addition. Earlier workers have shown that benzalacetophenone undergoes mainly 1,2-addition with phenylpotassium, phenylsodium[8] and phenyllithium[8,9] in ether but largely 1,4-addition with phenylmagnesium bromide.[10] These two courses of reaction may be represented by equation 1a and 1b, respectively.



We have confirmed the predominant 1,2-addition with the three former reagents. Whereas the previous reaction with phenylpotassium and phenylsodium were carried out in ether,[8] we have employed appropriate hydrocarbon solvents. The reaction mixtures were carbonated to convert the metal enolate of the 1,4-addition product to the salt of the carboxylic acid which was separated from the carbinol. The results, including the earlier ones, are summarized in Table II.

TABLE II

1,2- Versus 1,4-Addition of Benzalacetophenone with Phenylalkalies and Phenylmagnesium Bromide

Metallic Cation	1,2-Addition Yield, %	1,4-Addition Yield, %
K	67 (52)[a]	—
Na	60 (39)[a]	14 (3.5)[a]
Li	75 (69)[a]	14 (13)[a]
MgBr	—	94[b]

[a] Ref. (8). [b] Ref. (10).

EXPERIMENTAL[11]

Potassium and sodium reagents. Phenylpotassium was prepared from potassium and anisole[12] in an appropriate alkane employing a creased flask and high speed stirrer. Carbonation of the suspension gave benzoic acid in 55–60% yield.

Phenylsodium was prepared in an alkane or in benzene from chlorobenzene and commercially dispersed sodium[13] (earlier procedure) or dispersed sodium prepared in this laboratory with a high speed stirrer (newer procedure.)[14]

---

(7) S. F. Acree, *Am. Chem. J.*, **29**, 588 (1903).

(8) H. Gilman and R. H. Kirby, *J. Am. Chem. Soc.*, **63**, 2046 (1941).

(9) A. Luttringhaus, Jr., *Ber.*, **67**, 1602 (1934).

(10) E. P. Kohler, *Am. Chem. J.*, **38**, 511 (1907).

(11) Boiling points and melting points are uncorrected.

(12) A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **23**, 1638 (1958).

(13) We are indebted to Dr. V. L. Hansley of Electrochemical Dept., E. I. du Pont de Nemours and Co., Niagara Falls, N. Y., and later of U. S. Industrial Chemical Co., Division of National Distillers, Cincinnati 37, Ohio, for generous samples.

(14) See U. S. Industrial Chemical Co., Division of National Distillers Production Corp., New York, N. Y., *Sodium Dispersions*, 1957, p. 36.

Carbonation of the suspension gave practically quantitative yields of benzoic acid.

n-Amylpotassium and *n*-amylsodium were prepared from *n*-amyl chloride and the alkali metal in an alkane.[15] An 80% yield of the reagent was assumed.[15]

Lithium and Grignard reagents. These reagents were prepared in ether in the usual mnner and transferred to the reaction flask under nitrogen pressure. Butyllithium was also prepared in benzene.[16]

Reactions of α-hydrogen compounds with reagents. (Table I.) (A) *With phenylpotassium.* In Exp. 1 of Table I, the phenylpotassium–potassium methoxide reagent prepared as described above was treated directly with acetophenone but, in Exp. 2, dry potassium chloride (11.17 g., 0.15 mole) was added with stirring to a 0.15 mole preparation of the reagent before adding 0.15 mole of the ketone. Experiment 1 is described below.

To the stirred reagent (0.2 mole preparation) was added a solution of 24.03 g. (0.2 mole) of acetophenone in 50 ml. of iso-octane during 20 min., maintaining the temperature at about 50°. After stirring for 3 hr. at this temperature, the reaction mixture was cooled and poured onto excess Dry Ice. When the excess Dry Ice had evaporated some isobutyl alcohol was added (to destroy potassium) followed by 200 ml. of water. After shaking, the two layers were separated. The aqueous layer was extracted three times with ether and the extracts were added to the organic layer. The two solutions were worked up as described below.

The aqueous solution was acidified and heated on the steam bath for 1 hr., cooled, and extracted three times with ether. The combined ether extracts were washed with a saturated solution of sodium bicarbonate, then with water, dried over anhydrous magnesium sulfate, and the solvent removed. The residual oil was distilled to give 13.0 g. (54%) of acetophenone, b.p. 90–92° at 19 mm.; 2,4-dinitrophenylhydrazone m.p. 248–249°.

The organic solution was washed with water, dried over anhydrous magnesium sulfate, and the solvent removed. The residual oil was distilled to give 3.05 g. (13%) of acetophenone, b.p. 91–94° at 19 mm. The residue was cooled and shaken with *n*-hexane. The mixture was filtered. The solid (0.85 g., 2.2%) was crude diphenylmethylcarbinol, m.p. 75–77° after recrystallization from benzene. It did not depress melting point of an authentic sample of the carbinol. The *n*-hexane filtrate was evaporated, and the residual oil was distilled to give 1.0 g. (2.8%) of 1,1-diphenylethylene, b.p. 142–147° at 19 mm., lit.[17] b.p. 147° at 16 mm. This olefin, which resulted from dehydration of the carbinol, readily decolorized bromine in carbon tetrachloride; total yield of carbinol is estimated to be 5%. A sample of the olefin, prepared by dehydration of the carbinol with concentrated sulfuric acid, boiled at 155–158° at 25 mm., lit.[18] b.p. 156° at 25 mm.

(B) *With phenylsodium.* In Exps. 3 and 4 of Table I, the phenylsodium–sodium chloride reagent prepared as described above was treated directly with acetophenone. In Exp. 5, methanol (6.4 g., 0.2 mole) was slowly added with cooling to a 0.4 mole preparation of phenylsodium to give 0.2 mole each of phenylsodium and sodium methoxide. Acetophenone (0.2 mole) in 50 ml. of *n*-hexane was then added. After stirring at about 50° for 3 hr., the reaction mixture was worked up as described for phenylpotassium.

The aqueous solution was acidified and heated on the steam bath to give 10.2 g. (43%) of acetophenone, b.p. 93° at 21 mm.; 2.4-dinitrophenylhydrazone, m.p. 249–250°.

The organic solution yielded 5.15 g. of diphenylmethylcarbinol, m.p. 78–81° (no depression on admixture with authentic sample), 1.6 g. of less pure carbinol, m.p. 66–73°, and 0.75 g. of 1,1-diphenylethylene, b.p. 115–120° at 11 mm., n_D^{26} 1.600, lit.[17] n_D^{14} 1.610. The total yield of carbinol is estimated to be 24%. Acetophenone (9%) was obtained as a forerun.

The reactions of other α-hydrogen compounds with phenylsodium (Exps. 10, 12, 15, and 17, Table I) were carried out similarly. The product obtained from the organic solution in Exp. 10 was distilled to give 1.2 g. of recovered ethyl phenylacetate and 6.1 g. of higher boiling material which, after a week in the refrigerator, deposited 1.7 g. of phenyl benzyl ketone, m.p. 56–60° after recrystallization from ligroin (b.p. 90–120°), lit.[19] m.p. 60°, oxime m.p. 97–98°, lit.[19] m.p. 98°.

The product obtained from the organic solution in Exp. 12 was added to dilute hydrochloric acid and heated on a steam bath for 1–2 hr. (to hydrolyze the ketimine hydrochloride). There was obtained phenyl benzyl ketone m.p. 55°[19]; semicarbazone (recrystallized from methanol), m.p. 146–147°, lit.[19] m.p. 148°.

The product obtained from the organic solution in Experiment 17 yielded 2,4,6-trimethylbenzyl phenyl ketone (5%), m.p. 162° (see below).

(C) *With amylpotassium and amylsodium.* The reaction of these reagents with acetophenone (Exps. 8 and 9) was carried out as described for phenylpotassium.

The product obtained from the organic layer in Experiment 9 was distilled to give recovered acetophenone (14%). b.p. 92–95° at 20 mm. (2,4-dinitrophenylhydrazone m.p. 251–253°) and 2-phenylheptane-2-ol (12%), b.p. 81–82° at 0.4 mm., $n_D^{25.5}$ 1.5065, lit.[20] b.p. 169° at 50 mm. and 108° at 0.6 mm., n_D^{25} 1.5028. The infrared spectrum of this product was identical with that of the carbinol (b.p. 80° at 0.3 mm., n_D^{24} 1.5042) prepared from *n*-amylmagnesium bromide and acetophenone in ether.

(D) *With phenyllithium and phenylmagnesium bromide.* Experiment 11 is described below. To a stirred solution of approximately 0.4 mole of phenyllithium in 500 ml. of ether was added 35.8 g. (0.2 mole) of ethyl phenylacetate in 100 ml. of ether. The mixture was refluxed 2 hr., cooled, and poured onto excess Dry Ice. There was obtained 2.15 g. (6%) of regenerated ethyl phenylacetate, b.p. 178–190° at 20 mm. (identified by infrared spectrum), and 36.8 g. (70%) of 1,1,2-triphenylethanol, m.p. 81–88° and at 87–88° after recrystallization from *n*-hexane. A mixed melting point with an authentic sample showed no depression. Also 9.2 g. of residual gum was obtained.

Experiments 6, 7, 13, 14, 16, 18, and 19 were carried out similarly. In Exps. 6, 7, and 16, slightly more than a 1:1 mole ratio of reagent to active hydrogen compounds was used. In Exps. 13, 14, and 18, a 10–50% excess of the reagent was employed. The products from Exps. 6, 7, and 16 were worked up as described in Exp. 1, and those from Exps. 13, 14, 18, and 19 as described in Exp. 12. In exps. 18 and 19, there was obtained 2,4,6-trimethylbenzylphenyl ketone, m.p. 162°.

Anal. Calcd. for $C_{17}H_{18}O$:C, 85.67; H, 7.61. Found: C, 86.06; H, 7.90.

(E) *With n-butyllithium.* These reactions (Exps. 20–23) were carried out essentially as described for Exp. 11, and the products were worked up as described for Exp. 12. In Exp. 20, no ketone was isolated under the conditions used and a considerable amount of the starting nitrile was recovered. In Exp. 21, *n*-butyl benzyl ketone (49%) was obtained, b.p.

---

(15) A. A. Morton, F. D. Marsh, R. D. Coomles, A. L. Jones, S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little, and R. L. Letsinger, *J. Am. Chem. Soc.*, 72, 3785 (1950).

(16) H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Am. Chem. Soc.*,**54**, 1957 (1932).

(17) I. Heilbron, *Dictionary of Organic Compounds*, **Vol. II**, Oxford University Press, New York, 1953, p. 415.

(18) A. Klages, *Ber.*, **35**, 2647 (1902).

(19) See Ref. 17, p. 12.

(20) W. C. Davies, R. S. Dixon, and W. J. Jones, *J. Chem. Soc.*, 471 (1930); M. Protiva, O. Exner, M. Borovick, and J. Pliml, *Chem. Listy*, **46**, 37 (1952).

128–138° at 13 mm., lit.[21] 130–131° at 12 mm. This experiment was repeated at room temperature for 118 hr. to give 17% of *n*-butyl benzylketone, 5% of regenerated nitrile, and some high boiling residue. In Exp. 23, 2,4,6-trimethylbenzyl *n*-butyl ketone was obtained, b.p. 142–147° at 7 mm.; 2,4-dinitrophenylhydrazone (yellow needles), m.p. 99° (recrystallized from ethanol).

Anal. Calcd. for $C_{12}H_{26}O_4N_4.C_2H_5OH$: N, 14.17. Found: N, 14.03.

Addition of reagents to benzalacetophenone. (Table II). These reactions were carried out as described in Exp. 1 by addition of benzalacetophenone in an appropriate solvent to the stirred reagent; the reaction mixtures were carbonated and worked up essentially as described for the α-hydrogen compounds.

In the experiment with phenylpotassium, no 1,4-addition product was isolated. A 67% yield of crude diphenylstyryl carbinol was obtained. After recrystallization from ligroin, the product melted at 109–111° (lit.[9] m.p. 108–111°). Some unidentified residue was obtained.

In the experiment with phenylsodium, β,β-diphenylpropiophenone, m.p. 94–95° (lit.[10] m.p. 96°) was obtained on acidifying the aqueous solution and decarboxylating the product. Diphenylstyrylcarbinol was isolated from the organic solution.

Reaction of phenylsodium with benzaldehyde. This reaction was carried out with 0.3 mole of phenylsodium and 0.21 mole of benzaldehyde in heptane (2 hr. at room temperature, 1 hr. at 50°). There was obtained 28 g. (72%) of benzhydrol, b.p. 175–180° at 17 mm. The product solidified; after recrystallization from ligroin (b.p. 90–120°), it melted at 66–67°. A mixed melting point with an authentic sample showed no depression.

DURHAM, N. C.

---

(21) D. Ivanov, *Bull. Soc. Chem.*, [5], **4**, 682 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

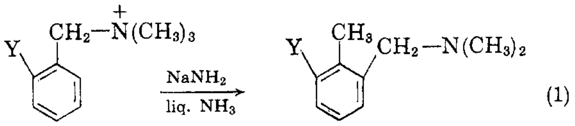
Ortho Substitution Rearrangement of Certain 3-Substituted and 3,5-Disubstituted Benzyltrimethylammonium Ions by Sodium Amide[1]

WILLIAM Q. BEARD, JR., DONALD N. VAN EENAM, AND CHARLES R. HAUSER

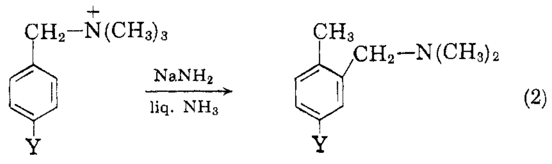
Received August 5, 1960

The 3-methoxy-, 3-methyl-, and 3-chloro-benzyltrimethylammonium ions underwent the ortho substitution rearrangement with sodium amide in liquid ammonia to form mixtures of the two possible types of isomeric amines in yields of 92, 90, and 16%, respectively. With the first two quaternary ions, rearrangement into the *ortho* position versus the *para* position occurred in the ratio of 2:1 and 1.2:1, respectively. The 3-bromo and 3-trifluoromethyl quaternary ions failed to yield isolable amounts of rearrangement products. The 3,5-dimethoxy- and 3,5-dimethyl-benzyltrimethylammonium ions underwent the rearrangement in 93% yield.

Previous papers[2-4] have described the *ortho* substitution rearrangements of several 2- and 4-substituted benzyltrimethylammonium ions (Equations 1 and 2, respectively) in which the substituents Y were such groups as alkyl, methoxy and chlorine.

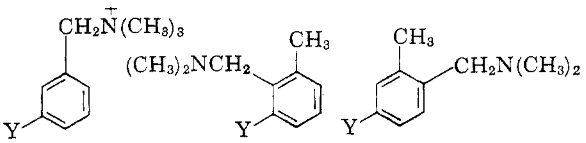


(1)



(2)

The present paper describes a similar study of certain 3-substituted and 3,5-disubstituted benzyltrimethylammonium ions with sodium amide in liquid ammonia. Whereas the rearrangement of a 2- or a 4- substituted benzyltrimethylammonium ion can form but a single amine (Equation 1 or 2), that of a 3-substituted quaternary ion of Type I (such as Ia) may afford a mixture of isomeric rearranged amines of Types II and III (such as IIa and IIIa). These isomers would arise through rearrangements into the *ortho*- and *para*- positions, respectively, relative to the 3-substituent.



Ia. Y = OCH_3
Ib. Y = CH_3
Ic. Y = Cl
Id. Y = Br
Ie. Y = CF_3

IIa. Y = OCH_3
IIb. Y = CH_3
IIc. Y = Cl

IIIa. Y = OCH_3
IIIb. Y = CH_3
IIIc. Y = Cl

Actually each of the three quaternary ions Ia–c produced a mixture of the possible isomeric amines of Types II and III. In Table I are summarized the yields of the amine mixtures and the relative proportions of the two isomers.

---

(1) Supported by the National Science Foundation.

(2) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951).

(3) C. R. Hauser and A. J. Weinheimer, *J. Am. Chem. Soc.*, **76**, 1264 (1954).

(4) W. Q. Beard, Jr., and C. R. Hauser, *J. Org. Chem.*, **25**, 334 (1960).