[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE COLLEGE AND SOUTHWESTERN COLLEGE]

Benzylalkali Compounds[1]

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Benzylsodium was found to be the most effective organometallic compound of a series examined in the metalation of furan.[2] In extension of interconversion reactions of organometallic compounds, we have examined procedures which might make the highly effective benzylalkali compounds more accessible.

Rearrangement of Sodium in *p*-Tolylsodium.—Bachmann and Clarke[3] isolated benzoic acid (34%), *p*-toluic acid (30%) and phenylacetic acid (0.36%) after carbonation of a reaction mixture of di-*p*-tolylmercury, sodium and benzene which had been allowed to stand for one month. The formation of phenylacetic acid establishes a migration of sodium to benzylsodium, and is an interesting variation of the lateral metalation of toluene by ethylsodium which was first examined by Schorigin.[4] However, it is uncertain in the Bachmann–Clarke experiment whether migration took place directly or involved first the metalation of benzene, used as a medium, inasmuch as phenylsodium must have formed because of the high yield of benzoic acid. We have carried out the same reaction using as a medium petroleum ether, which is not metalated by organosodium compounds, and find that phenylsodium is no necessary intermediate, benzylsodium being formed in quite satisfactory yields.

Ziegler[5] prepared *p*-tolylsodium from *p*-chlorotoluene and found that by omitting strong heating a migration of the metal from the nucleus to the side-chain did not occur. This result is also consistent with the long time, room temperature experiment of Bachmann and Clarke. Apparently the migration of sodium is not only independent of the intermediate formation of phenylsodium, but also takes place very slowly at room temperature. Actually, as we have shown, the reaction can be carried out for a short time and without refluxing to give exclusively *p*-tolylsodium; and, with refluxing, to give exclusively benzylsodium. This is also strikingly illustrated with the reaction of *m*-chlorotoluene and sodium.[6]

Benzylpotassium.—The existence of benzylpotassium has been postulated reasonably in some reactions, but the compound has not hitherto been accessible. Marcus,[7] in some studies with Schlenk, mentioned that 1,1,1,2-tetraphenylethane was cleaved by potassium to triphenylmethylpotassium and benzylpotassium.

$$(C_6H_5)_3CCH_2C_6H_5 + 2K \longrightarrow (C_6H_5)_3CK + C_6H_5CH_2K$$

Subsequently, Ziegler and Thielmann,[8] in an orienting experiment, carried out a similar reaction with sodium–potassium alloy and isolated, subsequent to carbonation, triphenylacetic acid but no phenylacetic acid. Wooster and Mitchell[9] added one equivalent of benzyl bromide to two equivalents of potassium in liquid ammonia. A deep red color developed, and this faded gradually until the solution was colorless. They concluded that the red color was due to benzylpotassium.

We now find that it is possible to prepare benzylpotassium in workable quantities by two different procedures. First, di-*p*-tolylmercury and potassium are heated in petroleum ether.

$$(p\text{-}CH_3C_6H_4)_2Hg \xrightarrow{[K]} p\text{-}CH_3C_6H_4K \longrightarrow C_6H_5CH_2K \qquad [I]$$

Second, toluene is metalated laterally in essential accordance with Schorigin's procedure in which ethylsodium was used. In one of these syntheses phenylpotassium (prepared from benzene and *n*-butylpotassium) was used as the metalating agent.

$$C_6H_5CH_3 + C_6H_5K \longrightarrow C_6H_5CH_2K + C_6H_6 \qquad [II]$$

In the other synthesis, the transitorily formed phenylpotassium was used as the metalating agent.

$$\begin{aligned} C_6H_5Cl + 2K &\longrightarrow [C_6H_5K] \\ [C_6H_5K] + C_6H_5CH_3 &\longrightarrow C_6H_5CH_2K \qquad [III] \end{aligned}$$

Phenylpotassium is most probably formed as an intermediate in reaction [III], although we have not as yet succeeded in interrupting the reaction to capture the phenylpotassium by carbonating to benzoic acid. Our present interpretation is that phenylpotassium is formed from chloro-

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(1) This is paper XXXI in the series entitled: "Relative reactivities of organometallic compounds," and an account of the studies was presented at the Eighth National Organic Symposium, St. Louis, Dec. 30, 1939. The preceding paper is in THIS JOURNAL, **62**, 1243 (1940).

(2) Gilman and Breuer, *ibid.*, **56**, 1123 (1934).

(3) Bachmann and Clarke, *ibid.*, **49**, 2096 (1927).

(4) Schorigin, *Ber.*, **41**, 2723 (1908); **43**, 1931, 1938 (1910).

(5) Ziegler, *Angew. Chem.*, **49**, 455 (1936).

(6) Gilman and Pacevitz, THIS JOURNAL, **62**, 673 (1940).

(7) Marcus, Dissertation on "Triarylmethyls," Jena, 1914.

(8) Ziegler and Thielmann, *Ber.*, **56**, 1740, 2453 (1923).

(9) Wooster and Mitchell, THIS JOURNAL, **52**, 688 (1930).

benzene and potassium in toluene, and then rapidly metalates the toluene to give benzylpotassium. This reaction, by the way, is one of choice for the preparation of benzylpotassium inasmuch as the 82–84% yield of pure phenylacetic acid indicates an even higher yield of benzylpotassium.

In sharp contrast with the reaction of chlorobenzene and potassium is the related reaction with sodium. Bockmühl and Ehrhart[10] were probably the first to prepare phenylsodium (in 70–80% yields) from chlorobenzene and sodium. We have found that it is possible to prepare phenylsodium in at least an 87% yield, and in a few hours, by appropriately cooling a mixture of chlorobenzene and sodium in toluene. If, however, the mixture is refluxed then the phenylsodium metalates the toluene to give benzylsodium in an 80% yield. Morton and co-workers[11] have prepared benzylsodium by metalation of toluene with amylsodium directly, or with phenylsodium prepared by metalation of benzene by amylsodium.

An examination of the reaction of *p*-chlorotoluene with sodium in some solvents has shown that *p*-tolylsodium can be prepared in 80% yield in toluene. When the reaction mixture is refluxed, a migration of the sodium takes place and benzylsodium is formed in a 79% yield. This migration is not peculiar to *p*-tolylsodium, for we have observed that benzylsodium is also formed from *o*-tolylsodium (prepared from di-*o*-tolylmercury and sodium), and from *m*-tolylsodium (prepared from *m*-chlorotoluene and sodium,[6] as well as from di-*m*-tolylmercury and sodium). As illustrated in reaction [I], *p*-tolylpotassium also undergoes a thermal rearrangement to give benzylpotassium.

Benzyllithium.—Although benzylsodium and benzylpotassium can now be obtained very conveniently and in highly satisfactory yields, benzyllithium is relatively inaccessible. Hein and coworkers[12] have prepared benzyllithium from dibenzylmercury and ethyllithium.

$$(C_6H_5CH_2)_2Hg + 2C_2H_5Li \longrightarrow 2C_6H_5CH_2Li + (C_2H_5)_2Hg \qquad [IV]$$

Ziegler and Dersch[13] have used two different reactions for the synthesis of benzyllithium. One of these is the interaction of benzylmagnesium chloride in ether with metallic lithium.

$$C_6H_5CH_2MgCl + Li \longrightarrow C_6H_5CH_2Li + Mg + LiCl \qquad [V]$$

The other is probably a two-stage reaction between benzylmagnesium chloride and phenyllithium.

$$C_6H_5CH_2MgCl + C_6H_5Li \longrightarrow C_6H_5CH_2MgC_6H_5 + LiCl$$
$$C_6H_5CH_2MgC_6H_5 + C_6H_5Li \longrightarrow C_6H_5CH_2Li + (C_6H_5)_2Mg \qquad [VI]$$

No one of these procedures is quite satisfactory. Reaction [IV] involves the relatively inaccessible dibenzylmercury, and may be incomplete; reaction [V] is quite slow and, if conditions are not followed rigorously, may be erratic; and reaction [VI] produces a mixture of two different but relatively reactive organometallic compounds.

Unfortunately, we have not succeeded as yet in effecting a rearrangement of *p*-tolyllithium to benzyllithium under conditions where *p*-tolylsodium and *p*-tolylpotassium (reaction [I]) rearrange to benzylsodium and benzylpotassium, respectively. It is possible to prepare benzyllithium by metalating toluene laterally with *n*-butyllithium. However, the yield is not much greater than that required to establish definitely that benzyllithium is formed. Interestingly enough, Mr. F. W. Moore has shown that benzene can be metalated by *n*-butyllithium under corresponding conditions to give a 15% yield of phenyllithium. In general, our experience is that alkylsodium and alkylpotassium compounds are distinctly more effective for lateral metalations than are alkyllithium compounds.

Lateral Metalations.—We have extended lateral metalations by organosodium and organopotassium compounds to mesitylene and to β-methylnaphthalene. In the absence of functional groups that would undergo secondary transformations, it is probable that lateral metalation will prove serviceable in effecting indirectly such reactions as oxidation. For example, there is no known procedure for oxidizing a methylcarbazole to a corresponding carbazolecarboxylic acid.[14] Lateral metalation followed by oxidation or carbonation would undoubtedly facilitate conversion of a methyl group to a carboxyl group. Occasional cases of oxidation-resistant methyl groups are

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(10) Bockmühl and Ehrhart, French Patent 736,428 [*Chem. Zentr.*, **104**, II, 2193 (1933)]; see, also, Ziegler, ref. 5.

(11) (a) Morton and Hechenbleikner, THIS JOURNAL, **58**, 2599 (1936). (b) Morton and Fallwell, Jr., *ibid.*, **60**, 1429 (1938). (c) Morton, Fallwell, Jr., and Palmer, *ibid.*, **60**, 1426 (1938). It is interesting to note that Morton, LeFevre and Hechenbleikner, *ibid.*, **58**, 754 (1936), obtained a 95% yield of *p*-toluic acid from *p*-chlorotoluene, sodium and carbon dioxide at 50° and under 500 pounds pressure. See, also, Morton and Massengale, *ibid.*, **62**, 120 (1940).

(12) Hein, Petzchner, Wagler and Segitz, *Z. anorg. allgem. Chem.*, **141**, 204 (1924).

(13) Ziegler and Dersch, *Ber.*, **64**, 448 (1931).

(14) Dunlop and Tucker, *J. Chem. Soc.*, 1945 (1939).

found in other types, for example, dibenzofuran.[15]

Rates of Carbonation.—It has long been known that the kind and ratio of products obtained by carbonation of organometallic compounds are influenced markedly by the rate and temperature of carbonation,[16a] particularly with organolithium compounds.[16b] Low temperature together with a large excess of carbon dioxide, conditions realized by pouring RM compounds on crushed solid carbon dioxide, give predominantly the acid and little of the ketone or tertiary alcohol. Furthermore, carbonation by solid carbon dioxide depresses markedly the formation of malonic acids from benzylmetallic types.[16c] For example, benzylpotassium under such conditions gives an 82% yield of phenylacetic acid and no significant quantity of phenylmalonic acid. However, slow carbonation with gaseous carbon dioxide gives 55% of phenylacetic acid and 23% of phenylmalonic acid. Related observations were made in the carbonation of 3,5-dimethylbenzylpotassium. What probably happens predominantly in such cases is the metalation of the active methylene group formed after the initial carbonation. The following reactions were investigated in some detail by Ivanoff and Spassoff[17] with benzylmagnesium chloride.

$$C_6H_5CH_2MgCl + CO_2 \longrightarrow C_6H_5CH_2COOMgCl \quad [VII]$$

$$C_6H_5CH_2COOMgCl + C_6H_5CH_2MgCl \longrightarrow [C_6H_5CHCOOMgCl][MgCl] + C_6H_5CH_3 \quad [VIII]$$

$$[C_6H_5CHCOOMgCl][MgCl] + CO_2 \xrightarrow{[H_2O]} C_6H_5CH(COOH)_2 \quad [IX]$$

Slow carbonation undoubtedly would facilitate metalation of the methylene group by the RM compound in essential accordance with reaction [VIII]. This mechanism for the carbonation of benzylsodium has been established by Morton and co-workers.[11c]

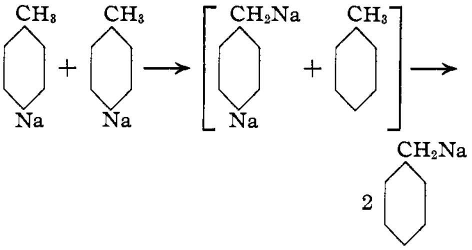
Reaction Mechanisms.—It is quite clear that there are at least two stages in the formation of benzylsodium from toluene, chlorobenzene and sodium.

$$C_6H_5Cl + 2Na \longrightarrow C_6H_5Na + NaCl \quad [X]$$

$$C_6H_5Na + C_6H_5CH_3 \longrightarrow C_6H_5CH_2Na + C_6H_6 \quad [XI]$$

The same reactions are probably the predominant ones when potassium is used in place of sodium, even though no direct evidence has been obtained as yet for the precursory formation of phenylpotassium. Reaction [XI] is apparently irreversible, for no benzoic acid has been isolated after carbonation of a reaction mixture of benzylsodium (free of toluene) and benzene which was stirred for fourteen hours at room temperature.

The migration of sodium in the transformation of *o*- and *p*-tolylsodiums to benzylsodium may be due to an allylic rearrangement of the type frequently observed with organometallic compounds. It is, however, difficult to account on such a basis for the conversion of *m*-tolylsodium to benzylsodium. Another possible mechanism that may involve all three isomeric tolylsodiums is the following



[XII]

That is, one molecule of *p*-tolylsodium may first metalate another molecule, and the resulting *p*-sodiobenzylsodium may then metalate the toluene formed in the first metalation to give benzylsodium. The apparent absence of any homoterephthalic acid, *p*-$HO_2CC_6H_4CH_2CO_2H$, suggests that reaction [XII] is either invalid or that *p*-sodiobenzylsodium metalates toluene with great ease.

It has been suggested that the difficulties of applying an allylic rearrangement for the tolylsodiums can be avoided by assuming the presence of traces of toluene, possibly formed by hydrolysis. This toluene would be metalated by the tolylsodium to give benzylsodium and toluene. Since the toluene is regenerated during the reaction, a small quantity would be adequate as a sort of catalyst. This sequence of reactions must be rapid because of the observed fairly prompt conversion of tolylsodium to benzylsodium.

Thermal Stabilities.—It has long been known that methylsodium, ethylsodium and methylpotassium are thermally labile, and that some decomposition occurs at room temperature,[18] particularly at initial stages.[19] Also, it appears that phenylalkali compounds are less thermally stable

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(15) Gilman, Van Ess and Hayes, This Journal, **61**, 643 (1939).

(16) (a) Some general references together with experimental work are given in the paper by Gilman and Parker, *ibid.*, **46**, 2816 (1924); (b) Gilman and Van Ess, *ibid.*, **55**, 1258 (1933); (c) Gilman and Pauvitz, *ibid.*, **62**, 1301 (1940).

(17) Ivanoff and Spassoff, *Bull. soc. chim.*, **49**, 19 (1931).

(18) Carothers and Coffman, This Journal, **51**, 588 (1929); **52**, 1254 (1930).

(19) Gilman and Young, *J. Org. Chem.*, **1**, 315 (1936).

than benzylalkali types. In our lateral metalations by phenylsodium no benzoic acid was isolated. This is strikingly illustrated in the metalation of β-methylnaphthalene which gave an almost analytically pure β-naphthylacetic acid. The non-isolation of benzoic acid may not have been due to thermolysis of small amounts of phenylsodium, but rather to a rapid, irreversible metalation. However, the action of heat on *m*-tolylsodium in petroleum ether illustrates a marked difference in thermal stabilities of *m*-tolylsodium and benzylsodium. When *m*-tolylsodium is prepared from *m*-chlorotoluene and sodium in petroleum ether, and with no refluxing, there results an 85% yield of *m*-toluic acid unaccompanied by any phenylacetic acid. But with only a ten-minute period of refluxing, phenylacetic acid (6.4% yield) but no *m*-toluic acid was formed. The benzylsodium formed intermediately in such reactions is relatively little affected by prolonged refluxing. The products of thermolysis other than benzylsodium have not as yet been examined.

Organolithium compounds differ markedly from other organoalkali compounds in thermal stabilities. For example, *p*-tolyllithium was found neither to decompose nor to rearrange after relatively long periods of refluxing in petroleum ether.

Experimental Part

Reaction of Sodium with Di-*p*-tolylmercury.—In a three-necked flask provided with stirrer, condenser and nitrogen inlet, was placed a mixture of 10 g. (0.43 g. atom) of sodium, 7.7 g. (0.02 mole) of di-*p*-tolylmercury, and 160 cc. of petroleum ether (b. p. 85–115°). The di-*p*-tolylmercury is not totally soluble in the solvent, but apparently reacted completely inasmuch as none was recovered at the end of the reaction. A reaction set in after the mixture was refluxed for ten minutes. The yellow-brown reaction mixture, after nineteen hours of refluxing, was cooled, carbonated by solid carbon dioxide, and then hydrolyzed. The yield of phenylacetic acid (mixed melting point) was 3.1 g. or 57%. In addition, the mother liquor yielded 0.13 g. of an oily solid which appears to be mainly phenylacetic acid.

When toluene was substituted for the petroleum ether, the yield of phenylacetic acid was 3.6 g. or 66%.

A sealed tube experiment now in progress indicates that di-*p*-tolylmercury and sodium in petroleum ether react very slowly at room temperature if there be no shaking or stirring.

Reaction of Sodium with Di-*o*-tolylmercury and Di-*m*-tolylmercury.—The di-*o*-tolylmercury and di-*m*-tolylmercury were prepared by conventional procedures using the Grignard reagents. Parallel experiments were made with each isomer, using three-necked flasks, 7.7 g. (0.02 mole) of mercurial, 10 g. (0.43 g. atom) of sodium wire and 160 cc. dry, unsaturate-free petroleum ether (b. p. 85–100°). Each mixture was stirred and refluxed for eighteen hours; and before carbonation with solid carbon dioxide, the red color characteristic of benzylsodium was evident.

The yield of phenylacetic acid from the di-*o*-tolylmercury experiment was 0.95 g. or 17.5%; and the yield from the di-*m*-tolylmercury experiment was 2.02 g. or 37.2%. No phenylmalonic acid was isolated from either carbonation product. Also, no toluic acid (*o*- or *m*-) was isolated from either reaction mixture, although the slightly lower melting point of the phenylacetic acid from the di-*o*-tolylmercury experiment may indicate the possible presence of traces of *o*-toluic acid.

The approximate times noted for inception of reaction between the mercurials and sodium were: di-*o*-tolylmercury, twenty minutes; di-*m*-tolylmercury, fifteen minutes; and di-*p*-tolylmercury, ten minutes.

Preparation of Phenylsodium in Toluene.—In a 500 cc. three-necked flask, equipped with a nitrogen inlet, condenser, mercury-sealed stirrer and thermometer, was placed a mixture of 150 cc. of toluene, 11.5 g. (0.5 g. atom) of sodium sand, and 22.5 g. (0.2 mole) of chlorobenzene. After stirring at room temperature for about forty-five minutes, the temperature started to rise. By appropriate cooling, the temperature was not allowed to exceed 40° during the entire reaction period, which was about two hours. When the temperature started to fall, the mixture was immediately poured jet-wise upon crushed solid carbon dioxide. The yield of benzoic acid (mixed melting point) was 21.2 g. or 87%.

Apropos the thermal stability of phenylsodium, two parallel preparations were made in a customary manner from 5 g. (0.014 mole) of diphenylmercury, 2 g. of sodium wire and 100 cc. of benzene. One of these was refluxed for twenty-four hours and after carbonation yielded 2.13 g. (62%) of benzoic acid. The other, stirred at room temperature for twenty-four hours, yielded 2.96 g. (86%) of benzoic acid.

Attempt to Prepare Phenylpotassium in Toluene.—To a mixture of 7.4 g. (0.19 g. atom) of potassium sand in 100 cc. of toluene, cooled to 0°, was added 11.2 g. (0.1 mole) of chlorobenzene in 45 cc. of toluene at such a rate that the temperature at no time rose above 0°. The time required for the addition in this orienting experiment was four and one-half hours. Carbonation, at the end of this time, gave 7.3 g. or a 60% yield of phenylacetic acid. On concentration of the mother liquors from the crystallization of an aliquot of the total acidic material, no benzoic acid was isolated.

Preparation of *p*-Tolylsodium.—In each of the experiments, the results of which are given in Table I, 12.7 g. (0.1 mole) of *p*-chlorotoluene, 5.5 g. (0.23 g. atom) of sodium sand and 75 cc. of solvent were used. The sodium sand should be as fine as possible, inasmuch as the reaction starts more promptly and runs a smoother course when the sand is very fine. It is also recommended that the fine sodium be freshly prepared. The conventional procedure of heating sodium in xylene was used for the preparation of the fine sodium. Reaction sets in almost immediately when the *p*-chlorotoluene is added to the sodium in the organic medium, and is accompanied by a temperature rise and the formation of black specks on the sodium. The mixture is stirred rapidly, and the temperature is held between 35–40°. After about one and one-half hours the temperature shows no further tendency to rise. Then the cooling-bath is removed, and stirring is continued until room temperature is reached. In carbonating by solid carbon dioxide it is desirable to add 100–200 cc. of dry ether when benzene is used as the medium, in order to reduce freezing of the benzene. The excess sodium is destroyed by the cautious dropwise addition of ethanol and water.

Table I

Preparation of *p*-Tolylsodium in Some Solvents
[0.1 Mole of *p*-Chlorotoluene]

Solvent	Yield of *p*-toluic acid G.	%
Benzene	8.9	65.5
Benzene	9.5	70.0
Cyclohexane	7.8	57.3
Cyclohexane	7.6	56.0
Pet. ether (70–80°)	10.1	74.3
Pet. ether (70–80°)	9.7	71.3
Toluene	10.9	80.1
Toluene	10.8	80.0

Preparation of Benzylsodium

A. From Chlorobenzene, Sodium and Toluene.—The preliminary operations in the following experiment were those described in the preparation of phenylsodium in toluene. After the formation of phenylsodium the suspension was refluxed for three hours. As soon as refluxing started, the black suspension assumed a brick-red color, and at the end of three hours the color was typical of benzylsodium. Carbonation, in the usual manner by solid carbon dioxide, gave 20.9 g. or a 77% yield of phenylacetic acid (mixed melting point). Carbonation after refluxing for six hours gave an 80% yield of phenylacetic acid. There was no perceptible formation of phenylmalonic acid under either of these sets of experimental conditions.

B. From *p*-Tolylsodium by Heating.—In each of the experiments, the results of which are given in Table II, the *p*-tolylsodium was prepared in accordance with directions given earlier from 0.1 mole of *p*-chlorotoluene, 0.23 g. atom of sodium sand, and 75 cc. of the solvent designated. The yields of phenylacetic acid are based on the initial 0.1 mole of *p*-chlorotoluene, and not on the % of *p*-tolylsodium obtained from the *p*-chlorotoluene.

Table II

Preparation of Benzylsodium by Heating *p*-Tolylsodium in Some Solvents

Solvent	Reflux period, hours	Yield of phenylacetic acid G.	%
Benzene	24	7.1	52.2
Benzene	16	6.8	50.0
Benzene	12	6.6	48.5
Toluene	4	8.5	62.0
Toluene	14	10.75	79.0
Toluene	14	10.7	79.0
Cyclohexane	18	7.3	53.7
Cyclohexane	14	7.9	58.1
Pet. ether (70–80°)	18	8.5	62.5

Rapid and Slow Carbonation of Benzylsodium.—The general conclusions drawn from the results reported recently[16c] on the rapid and slow carbonation of amylsodium were substantiated with benzylsodium. Two parallel preparations of benzylsodium were made from 11.2 g. (0.1 mole) of chlorobenzene, 5.75 g. (0.25 g. atom) of sodium sand, and 75 cc. of toluene. One of these was carbonated by pouring on solid carbon dioxide (time, five seconds); yield of phenylacetic acid 9.9 g. (72.9%); and no phenylmalonic acid isolated. The other was carbonated by gaseous carbon dioxide (time, four to five hours); yield of phenylacetic acid, 2.4 g. (17.6%); and yield of phenylmalonic acid, 3.8 g. (42.2%).

The mode of formation of benzylsodium is without essential effect, for benzylsodium from dibenzylmercury, sodium wire and toluene gave on rapid carbonation (five seconds) 3.3 g. (61%) of phenylacetic acid, and 0.03 g. or less than 1% of phenylmalonic acid; on slow carbonation (five hours, gaseous carbon dioxide), 0.46 g. (8.5%) of phenylacetic acid and 0.81 g. (22.8%) of phenylmalonic acid.

Preparation of Benzylpotassium

A. From Chlorobenzene, Potassium and Toluene.—In a 500-cc. round-bottomed flask, provided with the customary appurtenances mentioned previously, was placed a mixture of 8.5 g. (0.22 g. atom) of potassium sand and 100 cc. of toluene. A solution of 11.2 g. (0.1 mole) of chlorobenzene in 50 cc. of toluene was added very slowly, the temperature being kept between 30–35°. Since there is no induction period, the temperature starts rising with the addition of the first few drops of chlorobenzene. Occasional cooling with an ice-bath is necessary. The average time necessary for the addition of the chlorobenzene is one and one-half hours. At the conclusion of this preliminary operation, the reaction mixture was refluxed for one hour, during which time the color changed from black to a brilliant brick-red. On completion of the refluxing, the mixture was cooled and poured jet-wise upon solid carbon dioxide. The yield of pure phenylacetic acid was 11.2 g. or 82%.

B. From Phenylpotassium and Toluene.—A mixture of 5 g. (0.016 mole) of di-*n*-butylmercury, 3 g. (0.077 g. atom) of potassium and 50 cc. of benzene was stirred for sixty hours at room temperature. At the end of this time an aliquot, which was removed and carbonated and then hydrolyzed and acidified, gave no odor of valeric acid, thereby establishing the absence of *n*-butylpotassium. Subsequent to the addition of 50 cc. of toluene to the main reaction mixture, refluxing was carried out for six hours. The mixture was then cooled, and carbonated by pouring on solid carbon dioxide. Large pieces of potassium were removed by filtration, and then the carbonation mixture was hydrolyzed carefully and in sequence with butanol, ethanol and water. The yield of phenylacetic acid was 1.9 g. or 44%.

C. From Di-*p*-tolylmercury and Potassium.—A mixture of 7.7 g. (0.02 mole) of di-*p*-tolylmercury, 7.8 g. (0.2 g. atom) of potassium and 160 cc. of petroleum ether (b. p., 85–115°) was refluxed for 18.5 hours. Subsequent to cooling and carbonation, hydrolysis was effected by ethanol and then by water. The yield of phenylacetic acid was 0.9 g. or 16.5%. In addition, there was obtained 0.17 g. of a water-insoluble acid which charred at about 300°.

Reaction of Benzylpotassium with Gaseous Carbon Dioxide.—A suspension of benzylpotassium was prepared in accordance with the directions given in the preparation from potassium, chlorobenzene and toluene. At the end of the refluxing period, the mixture was cooled and then carbonated by passing carbon dioxide over the surface of the well-stirred suspension. The temperature was kept between 35–40°, and a negative color test[20] was obtained in fifteen minutes. The weight of the total acids was 10.1 g., and this mixture was separated, on the basis of solubility differences in chloroform, to give 2.1 g. or a 23% yield of phenylmalonic acid and 7.5 g. or a 55% yield of phenylacetic acid.

Reaction of Benzylpotassium with Benzophenone.—To benzylpotassium prepared from potassium (0.1 g. atom), chlorobenzene and toluene, was added 18.2 g. (0.1 mole) of benzophenone in 50 cc. of toluene over a one and one-half hour period. The brick-red color slowly disappeared and the solution assumed a deep emerald-green color, possibly due (in part) to the formation of the potassium ketyl of benzophenone. The temperature was not allowed to exceed 40°, and the mixture was stirred for one hour after the temperature ceased rising. Subsequent to hydrolysis, there was isolated 22 g. or a 59% yield of diphenylbenzylcarbinol melting at 87–88°.

Preparation of 3,5-Dimethylbenzylpotassium.—To a mixture of 8.5 g. (0.22 g. atom) of potassium sand and 100 cc. of dry mesitylene, was added slowly a solution of 11.2 g. (0.1 mole) of chlorobenzene and 39 cc. of mesitylene. The time of addition was one and one-half hours, and the temperature was kept between 30–35°. The black suspension changed slowly to the characteristic brick-red color upon refluxing for one hour. After carbonation by solid carbon dioxide and hydrolysis, there was isolated 13 g. or a 79% yield of 3,5-dimethylphenylacetic acid melting at 99.5–101°.

Under corresponding conditions, when sodium sand was used in place of the potassium sand, 3.3 g. or a 20% yield of 3,5-dimethylphenylacetic acid was obtained, in addition to some as yet unidentified tarry oil.

Slow Carbonation of 3,5-Dimethylbenzylpotassium.—In an orienting experiment, 3,5-dimethylbenzylpotassium was carbonated by the slow addition of gaseous carbon dioxide. The yield of 3,5-dimethylphenylacetic acid was 30%. In addition, there was obtained a 15% yield of 3,5-dimethylphenylmalonic acid, which softened at 149–150° and melted with decomposition at 154–155°.

Anal. Calcd. for $C_{11}H_{12}O_4$: neut. equiv., 104; C, 63.46; H, 5.77. Found: neut. equiv., 106, 107; C, 63.55, 63.57; H, 5.85, 5.81.

β-Naphthylmethylsodium.—Phenylsodium was prepared from 5.7 g. (0.25 g. atom) of sodium sand and 11.2 g. (0.1 mole) of chlorobenzene in 100 cc. of benzene. To the phenylsodium was added 28.4 g. (0.2 mole) of β-methylnaphthalene. No reaction was evident after stirring at room temperature for one hour. The mixture was refluxed for twenty-one hours, carbonated by solid carbon dioxide and then worked up in a customary manner to yield 0.8 g. or 4.3% of β-naphthylacetic acid melting at 137–139°. The yield of acid was 31% when metalation was effected by *n*-butylsodium (from di-*n*-butylmercury) in petroleum ether (b. p. 85–100°) at room temperature for twenty-six hours.

Phenylisopropylsodium (By Richard V. Young).—A mixture of 2.6 g. (0.01 mole) of diethylmercury, 0.035 g. atom of sodium and 25 cc. of cumene was stirred for twelve hours. In the course of the reaction a red precipitate formed, and this gave a positive color test. Carbonation of the reaction mixture by solid carbon dioxide gave a 41% yield of phenyldimethylacetic acid (mixed melting point). This preparation was carried out some time ago, and in view of the other results reported at this time it is quite possible that the widely used phenylisopropylpotassium might be prepared readily by metalation of cumene by benzylpotassium.

Benzyllithium from Toluene and *n*-Butyllithium.—To a filtered ether solution of *n*-butyllithium, prepared from 27.4 g. (0.2 mole) of *n*-butyl bromide,[21] was added 180 cc. of toluene. Within five minutes of the application of heat, a heavy white precipitate (probably lithium bromide) formed. After refluxing for nineteen hours, carbonation was effected by solid carbon dioxide, and the yield of phenylacetic acid was 0.06 g. or 0.22%.

Experiment on Thermal Stability

Dangers in Handling Organopotassium Compounds and Potassium.—In our experiments, we have generally used the conventional three-necked flasks provided with a mercury-sealed stirrer, condenser, and inlet tube for dry nitrogen. Inasmuch as dry organopotassium compounds, like benzylpotassium, are spontaneously inflammable on atmospheric exposure, there are occasional fire risks when the apparatus is disconnected. At times some of the benzylpotassium splashes up into parts of the apparatus attached to the flask, and is dried there by the stream of nitrogen. This risk can be decreased by stirring the solution vigorously at the end of the reaction so that some of the solvent wets any benzylpotassium and thereby prevents premature ignition.

Potassium residues should not be allowed to accumulate, and should not be added to sodium residues. There are two cases, in different laboratories, where sodium residues under kerosene have ignited and exploded. The causes of these accidents are not known, but it is possible that potassium residues in the sodium residues may be responsible. Potassium peroxide appears to form readily, and in contact with fresh potassium surfaces may give rise to violent explosions. If this is one of several possible explanations, then shaking a container of potassium residues may increase the hazard by exposing fresh surfaces.

Acknowledgment.—The authors are grateful to F. W. Moore for assistance.

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[20] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

[21] Gilman, Zoellner and Selby, *ibid.*, **54**, 1957 (1932).

Summary

The pronounced effectiveness of benzylalkali compounds in some interconversion reactions of organometallic compounds made desirable improved and convenient directions for the preparation of benzyl types. Benzylpotassium, now available for the first time in workable quantities, is readily prepared in 82% yield from toluene, chlorobenzene and potassium. Benzylsodium can be obtained in 80% yield by heating *p*-tolylsodium (from *p*-chlorotoluene and sodium in 80% yield) in petroleum ether; and in 80% yield by heating phenylsodium (from chlorobenzene and sodium in 87% yield) with toluene.

There is a lateral migration of sodium to give benzylsodium when *o*-, *m*-, or *p*-tolylsodium is heated. *p*-Tolyllithium is stable under these conditions. However, *n*-butyllithium metalates toluene laterally to give benzyllithium (0.2% yield).

In addition to other lateral metalations, an account is given of rates of carbonation, thermal stabilities, reaction mechanisms and some hazards in manipulating organopotassium compounds and potassium.

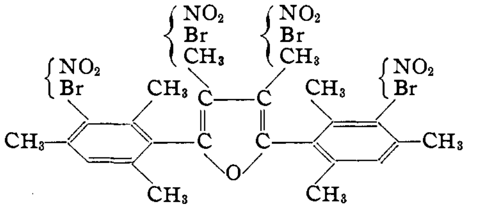
AMES, IOWA RECEIVED FEBRUARY 26, 1940

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Some Substituted 2,5-Dimesitylfurans

BY ROBERT E. LUTZ AND CHARLES J. KIBLER

This investigation has been made in order to study the effect of substitution of mesityl groups on the reactions of the furan nucleus, and also to test the possibility of stereoisomerism involving restricted rotation on the inter-nuclear bonds.

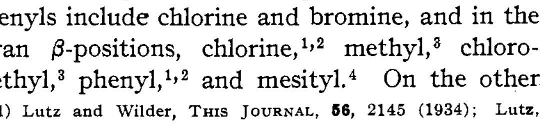


I

Five 2,5-dimesitylfurans of the type I have been prepared by methods in which the final step has completed the introduction of groups requisite for diastereoisomerism due to restricted rotation. In no case was there found any evidence of the existence of isomers. It would appear, therefore, that under the somewhat drastic preparative conditions involved in all but one case, stereoisomers are not stable enough for independent existence, as would be expected since interference effects in this type of compound should be small. It is, of course, possible that labile isomers, once formed, might be stable enough to exist under ordinary conditions; and further investigation should be made, including an attempt to resolve a suitable derivative which presumably would have the more stable *trans-dl* configuration.

In the preparation and study of the compounds mentioned above, it was found that the mesityl groups offer very little hindrance to nitration and bromination at the furan β-positions and that these β-positions are generally more reactive than the unsubstituted positions in the mesityl nuclei. The results parallel those obtained in the halogenation of 2,5-diphenylfuran.[1]

The most striking generalization arising from this investigation concerns oxidative ring fission, which is a reaction characteristic of 2,5-diarylfurans with no ortho substituents in the aryl nuclei. The *cis* unsaturated 1,4-diketone is produced whenever this stereoisomer is stable under the reaction conditions,[2] as is illustrated in the case of the oxidation of diphenyldimethylfuran (II) to the new *cis* unsaturated diketone, III. There are



II III

over 25 examples of this reaction among the 2,5-diaryl types alone, and there is now no authentic failure of the reaction when tried. Substituents in these compounds in the para position of the phenyls include chlorine and bromine, and in the furan β-positions, chlorine,[1,2] methyl,[3] chloromethyl,[3] phenyl,[1,2] and mesityl.[4] On the other

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(1) Lutz and Wilder, THIS JOURNAL, **56**, 2145 (1934); Lutz, Tyson, Sanders and Fink, *ibid.*, **56**, 2679 (1934).

(2) Lutz and Wilder, *ibid.*, **56**, 978 (1934), and references cited; *cf.* also examples cited by Gilman and Wright, *Chem. Rev.*, **11**, 523 (1932).

(3) Lutz and McGinn, results to be published shortly.

(4) Lutz and Kibler, THIS JOURNAL, **61**, 3007 (1939).