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Condensations by Sodium. XIX. Reactions of Compounds with Dichloro Ethers and Mercuric Chloride[1]

BY AVERY A. MORTON, JOHN T. MASSENGALE AND THOMAS R. P. GIBB, JR.

This paper records results from a study of (a) the reactions of three typical organosodium compounds, *viz.*, benzyl-, amyl- and phenylsodium on bis-(β-chloroethyl) ether and bis-(chloromethyl) ether and (b) the reaction of amylsodium with mercuric chloride. Replacement of both chlorine atoms in these dichlorides by organic radicals was expected.

Benzylsodium was the only reagent which reacted with bis-(β-chloroethyl) ether in the abovementioned manner (see equation 1)

$$2C_6H_5CH_2Na + (ClCH_2CH_2)_2O \longrightarrow (C_6H_5CH_2CH_2CH_2)_2O + 2NaCl \quad (1)$$

giving bis-(γ-phenylpropyl) ether in fair yield. This result is typical of the generally good behavior of this reagent in Wurtz[1a] syntheses.

All three organosodium reagents reacted with bis-(chloromethyl) ether forming the expected bis-(β-phenylethyl), hexyl, and benzyl ethers (equation 2) from which the corresponding alco-

$$2RNa + (ClCH_2)_2O \longrightarrow (RCH_2)_2O + 2NaCl \quad (2)$$

hols, phenylethyl, hexyl, and benzyl, respectively, were subsequently derived. A small quantity of each alcohol was also produced simultaneously with formation of the ether presumably because of the well-known breaking of the ether linkage by organometallic reagents. In view of the ease with which dichloromethyl ether is obtained and the readiness with which the ethereal product is hydrolyzed, this type of synthesis may be of some interest for preparation of alcohols where use of formaldehyde often proves unsatisfactory.

In contrast to the above reactions, neither phenyl- nor amylsodium gave an isolable quantity of the expected product from bis-(β-chloroethyl) ether. Carbonation of the mixture after each reaction led frequently to the finding of small quantities of succinic acid. Consumption of the dichloro ether by phenylsodium was determined by (a) observing cessation of the marked heat evolution when the dichloride was being added and (b) performing a series of experiments in which the quantity of dichloro ether was gradually increased until the products from carbonation showed that phenylsodium had disappeared. In this manner one molecule of the ether was found to be adequate for five molecules of phenylsodium. This quantity is enough to remove all of the halogen atoms, break the ether linkage in the known[2] manner, and add sodium atoms to the ethylene residue. Carbonation of such a product would account for the succinic acid formed. It was not possible, however, to obtain this acid consistently and there appeared to be other volatile acids present in the mixture which suggested instability of any supposed disodium product.

A general over-all equation which expresses some of the behavior is given below.

$$5C_6H_5Na + (ClCH_2CH_2)_2O \longrightarrow NaCH_2CH_2Na + NaOCH_2CH_2C_6H_5 + 2NaCl + 4C_6H_5^- \quad (3)$$

The equation demands the presence of phenylethyl alcohol and products from the phenyl radical. The former was indeed obtained. Disposition of the four phenyl radicals is not certain. No diphenyl was found. Insignificant amounts of phenylated polymers or tarry materials were present. No chlorobenzene nor products of the action of chlorobenzene with sodium or phenylsodium could be located. Phenyl might well have acquired a hydrogen atom from the solvent or some other by-product. Wieland[3] has noted such an effect in the decomposition of phenylazotriphenylmethane in petroleum ether. Because of the presence of solvent benzene in the reaction mixture, evidence for a similar disposition of phenyl radicals in our reactions was not sought.

It had been supposed that mercuric chloride would form diamylmercury from reaction with amylsodium. No trace of this compound could be obtained. The sole organic product was amylmercuric chloride. Some reduction to mercurous chloride and metallic mercury simultaneously occurred. The former can be accounted for by the reaction of excess sodium on mercuric chloride.

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(1) Original manuscript received March 27, 1940.

(1a) Morton and Fallwell, Jr., THIS JOURNAL, **60**, 1429 (1938).

(2) Schorigin, *Ber.*, **41**, 2717 (1908).

(3) Wieland, Popper and Seefried, *Ber.*, **55**, 1816 (1922); Wieland, *Rec. trav. chim.*, **41**, 276 (1922).

Experiments

General Directions for Reactions with Ethers. (By J. T. M.).—The experimental method was in general the same as used in previous work[4] with the exception that a deeply creased flask[5] was employed. The sodium sand (2.7 atoms per mole of chloride) was always activated just before use with 5 ml. of *n*-amyl alcohol per 37 g. of sodium. Addition rate was 0.6 mole of chloride per two and a half hours. Addition temperature was 20–25° for amyl chloride and 30–35° for chlorobenzene. Stirring time after addition was one hour at room temperature. The mixture was usually carbonated after a Wurtz reaction was completed, particularly if color remained. For decomposition water was added directly to the flask in an atmosphere of carbon dioxide. The first 15 or 20 ml. of water must be added very carefully over a half hour time because the action is at times sluggish and the operator may be deceived into believing that water can be added rapidly.

Reaction of Benzylsodium with bis-(β-Chloroethyl) Ether.—Three experiments were made in each of which 300 ml. of toluene was added to phenylsodium in petroleum ether prepared from 68 g. (0.6 mole) of chlorobenzene. Exchange was carried out by stirring at 83° for two hours. The temperature was then lowered and 60 g. (0.42 mole) of the ether added at 32–35° over a one hour period. Evolution of heat was very vigorous but ceased after about 50 ml. of reagent had been added. After decomposition the hydrocarbon layers were combined, the low boiling solvent removed, and the residue fractionated carefully in a packed column of fifteen theoretical plates. The only definite products isolated were: unreacted dichloroethyl ether (25 g.) boiling from 53 to 68° at 10 mm., diphenyl (34.5 g. or 15%) boiling from 100 to 110° at 10 mm., and bis-(γ-phenylpropyl) ether (141 g. or 37%) from 186 to 187° at 6 mm. A 10-g. sample of the last named material was refluxed for two hours with 40 ml. of 58% hydrobromic acid and partially converted to γ-phenylpropyl bromide, b. p. 108–110° (12 mm.). This material in turn gave benzoic acid only on oxidation with permanganate.

Reaction of Amylsodium with Bis-(β-chloroethyl) Ether.—Amylsodium was prepared from 106.5 g. (1 mole) of amyl chloride in 400 ml. of petroleum ether. The dichloroethyl ether, 30 g. (0.23 mole) was added over a period of two hours. Evolution of heat was vigorous during addition of the first 26 g. of this reagent. Since the reaction mixture still had a blue color it was carbonated. From the aqueous layer 0.05 formal equivalents (5.9 g.) of acid was extracted with ether. The material was recrystallized from alcohol solution by diluting with petroleum ether, giving a small amount of material, m. p. 181–181.5°. Recorded[6] for succinic acid 182°. Neutralization equivalent: 59.4; calculated value, 59.0. At least three experiments were made and in each case the hydrocarbon layer was fractionated in order to locate other products. Apart from the usual decane and excess dichloroethyl ether, no fraction was obtained which would give an identifiable derivative after treating with hydrobromic acid, although at 104° (7 mm.) a small amount of material boiling near the supposed diheptyl ether was collected.

Reaction of Phenylsodium with Bis-(β-chloroethyl) Ether.—Phenylsodium was prepared from 64 g. (0.6 mole) of amyl chloride in 600 ml. of benzene. β,β'-Dichloroethyl ether, 20 g. (0.15 mole) was added at 30–35°. Little heat was given off after 15 g. of the reagent had been added, but the color changed from green to blue. Stirring was continued for an hour and the mixture then carbonated. Succinic acid was isolated as in the reaction with amylsodium and identified by comparison with the previous sample. In order to discover the quantity of phenylsodium which reacted as well as to find out more about the other products of the reaction, four experiments were made in which 7.2 g. (0.05 mole or 0.1 chlorine equivalent) of the dichloroethyl ether was added over a period of forty-five minutes to varying quantities of phenylsodium. The mixture was stirred for two hours and then carbonated. After decomposition and acidification, the mixture was extracted with benzene to remove benzoic acid, then saturated with salt and extracted with ether to recover the mixture of acids from which succinic acid could sometimes be isolated. Quantities of reagents and yields are given in Table I. Percentage yields are calculated on the amount of amyl chloride used in preparing phenylsodium. The acid content was estimated by titration. Quantities are expressed in equivalents for convenience in calculation; percentages are determined on the basis of one carboxyl group for one amyl chloride without regard to any equation expressing the derivation. It is apparent that on the average ten molecules of phenylsodium are required for one equivalent of acid or five molecules for every dicarboxylic acid as in equation (3).

TABLE I

Amyl chloride G.	Amyl chloride Mole	Benzene, ml.	Benzoic acid Equiv.	Benzoic acid %	Other acids, equiv.	Ratio of phenylsodium to acid[a]
21.2	0.2	200	0.0	0	0.014	11
32	.3	350	0	0	.023	10
42.6	.4	400	0	0	.039	8
63.9	.6	600	0.1	17	.033	11[b]

[a] The usual quantity of phenylsodium is 78% of the amyl chloride used. [b] Value corrected for the unconsumed phenylsodium determined from the benzoic acid obtained.

The hydrocarbon layers were combined, the solvent removed and the residue fractionated through a packed column of fifteen theoretical plates. Amyl alcohol, 11 ml., and decane, 16 ml., were recovered at 130–142° and 62–73° (27 mm.), respectively. A negative Beilstein test indicated absence of chlorobenzene. At 73–91, 91–98, 98–102, 102–108°, all at 27 mm., there was collected 5, 4, 3 and 6 g., respectively. Hydrogen was evolved when sodium was added to the last three fractions, suggesting presence of phenylethyl alcohol. The portion boiling from 108–112° (27 mm.), amounting to 8.3 g. (about one-fourth of the amount predicted by equation 3), contained phenylethyl alcohol. Its presence was proven by the phenyl urethan derivative, 77–78° (recorded[7] value 79°)

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(4) Morton and Massengale, THIS JOURNAL, **62**, 120 (1940).

(5) Morton, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 170 (1939).

(6) Phelps and Hubbard, *Z. anorg. allgem. Chem.*, **53**, 361 (1907).

(7) Bickel and French, THIS JOURNAL, **48**, 747 (1926).

and by the α-naphthylurethane derivative, m. p. 116–117° (recorded value 119°). Dichromate oxidation of the alcohol produced benzoic acid only.

Reaction of Organosodium Compounds with Bis-(chloromethyl) Ether.—The *sym*-dichloromethyl ether was prepared[8] from formalin solution and hydrochloric acid, dried with concentrated sulfuric acid, and used without further purification. In each instance, 31 g. of this ether was added to the organosodium compound. Alcohols as well as ethers were always found among the reaction products, possibly because the ethereal products may be sensitive to organosodium reagents and possibly because of some paraformaldehyde in the reagent. Identification of the ether was made by hydrolysis to the corresponding alcohol.

Benzylsodium, from 64 g. of amyl chloride in benzene solution followed by heating for three hours at 75° with 150 ml. of toluene, was treated dropwise with dichloromethyl ether at 35° for one and one-half hours. Upon decomposing and fractionating, β-phenylethyl alcohol, 11 g. (15%), was obtained at 102–107° (14 mm.) and bis-(β-phenylethyl) ether, 13 g. (19%), at 161–164° (6 mm.). The alcohol was identified by the α-naphthyl isocyanate derivative, m. p. 114–116°, and by comparison with the product from phenylsodium and β,β′-dichloroethyl ether. The ether was hydrolyzed with 58% hydrobromic acid, and the bromide dried over calcium chloride and distilled under vacuum. The derived phenylethylmercuric bromide melted at 167–167.5°; recorded[9] value 169°.

Phenylsodium from 64 g. of amyl chloride in 600 ml. of benzene was treated with 30 g. of the ether. Upon fractionation of the product 9.7 g. of benzyl alcohol was recovered at 85–89° (16 mm.) and 4.8 g. (8.1%) of benzyl ether at 125–129° (3 mm.). Identification of the alcohol was made by means of the α-naphthyl carbamate derivative melting at 133°; recorded value[7] 134.5°. The ether after refluxing with 58% hydrobromic acid and then with aqueous alkali was treated with 3-nitrophthalic anhydride in order to obtain the half ester melting at 174–175°; recorded[10] value 176°.

Amylsodium from 64 g. of amyl chloride in petroleum ether reacted with 30 g. of the ether to give 14.3 g. (23%) of hexyl alcohol boiling at 106–109° (155 mm.) and 7 g. (13%) of hexyl ether at 153° (79 mm.). The α-naphthyl carbamate of the alcohol melted at 158°; recorded value 58°. The ether was converted to the bromide, as before, from which the hexylmercuric bromide was prepared; m. p. 118°; recorded[11] value 118.5°.

Attempted Reaction of Bis-(β-chloroethyl) Ether with Sodium.—Eight grams (0.6 mole) of the ether was added to 6 g. (0.3 atom) of sodium sand, previously activated by amyl alcohol, in 100 ml. of petroleum ether at 35° during thirty minutes. The surface of the sodium became red but no reaction appeared to occur. After refluxing for three hours the mixture was carbonated but no absorption of carbon dioxide took place nor could any acid be isolated. Neither was any evidence of reaction noted in 150 ml. of benzene after heating for one and one-half hours at 70°.

Reaction with Mercuric Chloride. (By T. R. P. G.).—The reagents for preparing amylsodium were 75 ml. (0.4 mole) of amyl chloride in an equal volume of petroleum ether, 35 g. (1.5 atoms) of sodium sand which had been activated by 5 ml. of *n*-amyl alcohol while suspended in 575 ml. of petroleum ether. The reaction was carried out in a 1-liter flask with vertical indentations. Addition of chloride was completed in about three hours at 16–18°. The mixture was stirred for one and one-quarter hours longer, after which 125 g. (0.46 mole) of powdered and dried mercuric chloride suspended in 300 ml. of petroleum ether was added. Owing to the difficulty of adding a suspension from the dropping funnel commonly used in these experiments, a large ordinary funnel connected to the reaction flask by a piece of rubber tubing closed with a pinchcock to regulate the addition of the salt was employed. Considerable heat was evolved during this thirty-five minute period but the temperature was kept at 25–35°. The reaction mixture changed from the dark blue color of the amylsodium stage to a dark gray with white striations. Stirring was continued for forty-five minutes at 33° after addition of mercuric chloride was completed. The mixture was cooled in an atmosphere of carbon dioxide, and the clear liquid decanted. The residue was extracted with three 300 ml. portions of petroleum ether, after which a final treatment with water and petroleum ether was made. Although no evidence of unreacted sodium was noted, the mixture was allowed to stand overnight to ensure complete decomposition. The petroleum ether layer was then added to the previous extracts, making a total of 900 ml. from which 4.1 g. of faintly yellow crystals melting at 115° was obtained after evaporation. On recrystallization from ethyl ether and acetone, waxy white crystals melting at 121° were secured.

After removing the water layer the gray-white residue was washed several times with water until freed from alkali and then dried in a vacuum desiccator. This material, amounting to 98 g., was extracted in a Soxhlet apparatus with petroleum ether yielding 57.8 g. of the waxy-white crystals which melted at 121°. The residue, 40 g., in the thimble consisted of semi-colloidal and larger globules of mercury, a white amorphous powder, and traces of sodium chloride. It gave a marked black coloration when dusted on a filter paper moistened with ammonia, showing the presence of mercurous salt. A neutralized nitric acid solution gave a strong test for mercuric and chloride ions. No organic material could be found.

The waxy-white crystals were shown to be amylmercuric chloride by mixed melting point with a sample prepared from diamylmercury and excess mercuric chloride, in acetone. The crystals could be purified by crystallization from a mixture of ethyl ether and petroleum ether. The melting point of the purest sample was 121–122° and the yield 46% based on the mercuric chloride added. *Anal.* Cl, 11.55. Calcd.: 11.56. Mol. wt.: 293, determined by the elevation of the boiling point of methanol. Calcd. 316.

Summary

The reaction of a benzyl-, aryl and alkylsodium compound with dichloro ethers has been investigated.

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(8) Stephen, Short and Gladding, *J. Chem. Soc.*, **117**, 510 (1920).

(9) Hill, THIS JOURNAL, **50**, 167 (1928).

(10) Monier, Ph.D. Thesis, M. I. T., 1932.

(11) Marvel, Gauerke and Hill, THIS JOURNAL, **47**, 3009 (1925).

Benzylsodium reacted smoothly with bis-(β-chloroethyl) and bis-(chloromethyl) ethers to give the corresponding bis-(γ-phenylpropyl) and bis-(β-phenylethyl) ethers, respectively.

Phenyl- and amylsodium reacted with the dichloromethyl ether to give the corresponding benzyl and heptyl ethers, respectively. Both reagents reacted vigorously with the dichloro ethyl ether, forming, however, products of a more extensive action on the ether molecule. Succinic acid was isolated from the carbonation products.

No reaction occurred between the dichloro ethyl ether and sodium metal.

Amylsodium reacted with mercuric chloride to form amylmercuric chloride.

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Condensations by Sodium. XX. Preparation and Properties of Organosodium Compounds Derived from Butyl and Propyl Chlorides[1]

BY AVERY A. MORTON, GRAHAM M. RICHARDSON AND A. THOMAS HALLOWELL

When *n*-butyl and *n*-propyl are used instead of *n*-amyl chloride in preparation of organosodium compounds, the change to alkyl radicals of lower molecular weight is progressively accompanied by (1) more difficulty in effecting reaction between alkyl chloride and sodium metal, (2) poorer yields, (3) greater tendency toward disproportionation as judged by the proportion of malonic acid formed when the organosodium compounds are carbonated under comparable conditions (0.35 to 0.8 to 1.3 for amyl, butyl and propyl, respectively), and (4) greater stability of the alkylsodium toward benzene and toluene. So much does the reactivity with these hydrocarbons decrease that they can be used to advantage as solvents for the reaction. In a mixture of benzene and petroleum ether, for example, the yield of organosodium reagent from butyl chloride was nearly as high as any from amyl chloride and the best conditions for propylsodium were in fact realized in toluene as a solvent.

By raising the temperature of toluene to 72° the propylsodium first formed in the reaction exchanges with the toluene rapidly enough to be effective for preparation of butylbenzene in 42% yield according to the sequence of changes previously discovered[1a] for syntheses of *n*-alkylbenzenes.

$$\mathrm{RX} \xrightarrow[\text{Toluene}]{\text{Na in}} \mathrm{RNa} \xrightarrow{\text{Toluene}} \mathrm{C_6H_5CH_2Na} \xrightarrow{\mathrm{RX}} \mathrm{C_2H_5CH_2R}$$

Accompanying this product was a high boiling fraction which appeared to be chiefly *m*-butylpropylbenzene together with some of the *p*-isomer. Metalation of butylbenzene therefore occurs in the nucleus rather than in the side chain with meta orientation predominating.

Other by-products from the reaction at 72° were unsaturated hydrocarbons boiling in the hexene and nonene range. Ozonolysis of one fraction showed that 3-methylpentene-2 was one component. Its presence might be explained by breaking of a carbon–carbon linkage during polymerization of an active propylene fragment. A somewhat similar break during dehydration and subsequent polymerization of methylisopropylcarbinol under influence of sulfuric acid has been noted already by Drake, Kline and Rose.[2]

Experiments

Butyl Chloride and Sodium. (By G. M. R.).—The apparatus was an ordinary three-necked flask with triple addition tube, stirrer, etc., as described in earlier[3] work. Conditions and results in a number of experiments are given in Table I.

Special attention is called to (a) the proportion of di- to mono- acid which is much higher than observed[3] with the products from reaction between amyl chloride and sodium, (b) the gradual loss in experiments 1, 2, and 3 of butylsodium (valeric acid) with no proportionate gain in propylmalonic acid when the mixture was heated at 42°, (c) the peculiar increase in yields of octane without parallel decrease in yields of valeric acid when the mixture was heated at 42° and (d) the relatively low yields of acids as compared with those from amyl chloride since an experiment[3] exactly comparable to the fourth using amyl chloride instead of butyl chloride gave 68% of mono- and 21% of dicarboxylic acids or a total of 89%.

Efforts to increase the yield by use of fine carborundum as an abrasive on the theory that a coating on the sodium surface inhibited the reaction improved the result by a few per cent. only.

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[1] Original manuscript received March 27, 1940.

[1a] Morton and Fallwell, Jr., THIS JOURNAL, **60**, 1429 (1938).

[2] Drake, Kline and Rose, THIS JOURNAL, **56**, 2076 (1934).

[3] Morton and Richardson, *ibid.*, **62**, 123 (1940).