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Condensations by Sodium. X. Some Side Reactions Occurring in Wurtz Syntheses and a Novel Formation of Iodobenzene

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Our method[1] for interrupting the Wurtz synthesis at the mono- and disodium intermediate stages affords opportunity to observe the different ways in which these reagents can react. The normal reaction of amylsodium with an alkyl halide yielding an amylalkyl can of course be predicted. We shall in this paper report our observations (1) that the amyl radical (or ion)[2] in amylsodium can be caused to dimerize to decane when the organometallic compound is treated with methyl iodide, (2) that phenylsodium treated with iodine can form iodobenzene; (3) that amylidenedisodium does not give branched chain compounds when treated with alkyl halides nor does amylsodium combine in the expected manner with methylene or ethylene dichloride, and (4) that high boiling materials, undoubtedly polymers, are present among the products of the reaction of these organosodium reagents with alkyl halides.

Accompanying the preparation of amylsodium is a certain amount, usually 14–16%, of decane probably resulting in large part from consecutive reactions of the organometallic compound with amyl chloride. If methyl iodide is added to amylsodium thus prepared the expected hexane is not obtained but additional decane is formed in yields totaling 50%. Such a large quantity of decane and the total absence of hexane leaves no doubt but that one of the reactions between these reagents can be expressed properly by the uncompleted equation

$$2C_5H_{11}Na + 2CH_3I \longrightarrow C_{10}H_{22} + 2NaI +$$

Methane, predominantly, and ethane as other products in the reaction were shown by analysis of evolved gases. No unsaturated hydrocarbon gases were found.

We also examined the reactions at room temperature between amylsodium and ethyl bromide, *n*-butyl chloride, *t*-butyl bromide, and benzyl chloride. Here the quantity of decane was in most cases a little higher (see Table I) than that found in the carbonation experiments, the normal products, *i. e.*, heptane, nonane, dimethylheptane, and hexylbenzene, were found in amounts less than the quantity of amylsodium (judged from the yields of caproic acid) present, both results being in agreement with those expected if a small amount of dimerization of amyl to decane as well as some disproportionation had occurred. Additional decane was formed too when ethyl bromide was added to the organometallic compound at −72°. The decane content rose to 28.4%, which is well above the 19.4% average for the other yields with ethyl bromide. In this instance the quantity of heptane was the same as when addition was carried out at room temperature, but was still below the value equivalent to the caproic acid obtained on carbonation. Such a decane increase may be due to an effect of temperature in shifting the ratio of coupling to disproportionation. Suggestive as these differences are, the example with methyl iodide provides indisputable evidence of the tendency toward dimerization of the amyl radical or ion attached to sodium.

When methyl iodide was added to phenylsodium or benzylsodium, both prepared by exchange reactions between amylsodium and the corresponding hydrocarbon, no diphenyl or dibenzyl but the normally expected product, toluene or ethylbenzene, was found. Stimulated by a desire to see whether union of two phenyl radicals or ions could be induced to occur, we next tried the addition of iodine to the organometallic compound. Upon a somewhat rapid addition of iodine in benzene to phenylsodium a yield of 6.3% of biphenyl was indeed obtained, but along with this product was 15% of iodobenzene, calculated on the basis of the amyl chloride used. Presence of this compound suggested that it was an intermediate in the formation of biphenyl and confirmation of this view was reached by adding the iodine solution gradually with some warming of the mixture. The yield of biphenyl rose to 12.5% while that of iodobenzene fell to 1.6%. Formation of bi-

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[1] Morton and Hechenbleikner, THIS JOURNAL, **58**, 1967 (1936).

[2] The term ion might be used to refer to the amyl radical in combination with sodium as amylsodium. The salt-like nature of organosodium compounds has already been mentioned by a number of investigators. The behavior of this ion is not necessarily that of a free radical.

TABLE I

REACTIONS OF AMYLSODIUM WITH ORGANO HALIDES

Constant factors: solvent, petroleum ether, P, or ligroin, L. Sodium sand, 35 g., in 100 ml. of solvent. Amyl chloride 66 g. in 75 ml. of solvent. 300–500 ml. more solvent added during the reaction to ensure rapid stirring. Temperature of addition of amyl chloride to sodium 18°. Time for addition two and one-half hours. Time for stirring after addition one hour. Time for addition of organic halide eighty minutes unless otherwise noted. Quantity of compound added was theoretically sufficient to combine with all of the organosodium compounds formed and the excess sodium present.

Expt.	Compound added	Solvent	Expected product	Yield		Yield of decane	
				G.	%	G.	%
1	Carbon dioxide	P	Caproic acid	21.9	30.4	7.0	16
				21.3	29.6	6.1	14
2	Methyl iodide	P	Hexane	0	0	22	50
3	Ethyl bromide	P	Heptane	14.2	22.8	8.6	19.4
4	Ethyl bromide	P	Heptane	14.0	22.6	12.5	28.4
5	*n*-Butyl chloride	P	Nonane	15.2	19.2	6.8	15.5
6	*t*-Butyl bromide	P	2,2-Dimethylheptane	4.0	5.5	5.0	11.4
7	Benzyl chloride	P	Hexylbenzene	8.1	8.1		..
8	Amyl chloride	P	Decane	28.0	36.0		..
9	Methylene chloride	L	Undecane		0	9.4	21.3
10	Methylene chloride	P	Undecane		0	8.5	19.4
11	Ethylene chloride	L	Dodecane		0	7.8	17.7

phenyl in an iodo-coupling reaction is therefore largely a matter of the novel formation of iodobenzene as an intermediate and its subsequent reaction with unchanged phenylsodium.

An unexpected angle in this study was furnished by the failure to find branched chain hydrocarbons from the action of alkyl halides on amylidenedisodium, though subsequent carbonation proved that this reagent had been consumed. Even cooling to dry ice temperatures during addition of ethyl bromide failed to produce the expected compound, 3-ethylheptane. Upon reflection, however, this behavior is not so surprising for Schlenk and Bergmann[3] have already recorded the failure of another disodium compound, tetraphenylethanedisodium, to combine in the expected manner with bromobenzene. Neither did Scott, Walker, and Hansley[4] find that dibenzyldihydronaphthalene was formed when dihydronaphthalenedisodium reacted with benzyl chloride. Our results, therefore, are in agreement with those of these other investigators.

Neither did amylsodium form any so-called normal product with methylene or ethylene dichloride. This complete failure of all disubstituted compounds tested, together with the failure to obtain 100% yield in the reactions between monosodium and monohalogen compounds, provokes the question as to the conditions which cause part of the radicals to unite and part to disproportionate when under the influence of such a powerful coupling agent. We have shown in the case of ethyl bromide that low temperature did not alter the ratio of coupling (heptane formation) to disproportionation. Reflection on the effect of nearness of radicals to each other at the moment of their liberation from the metal and halogen atoms leads us to suspect that spacing is of considerable importance, although no positive conclusion can be drawn from our experiments to date.

Comment should also be made on the presence of high boiling products invariably formed in all of these reactions. The quantity present in the experiments with ethyl bromide amounted to 9 or 11% calculated on the basis of the amyl chloride used in preparing the sodium compounds. The boiling range of this material is well above that which would result from any of the so-called normal reactions of the organosodium compounds with ethyl bromide. From the lack of a constant boiling point and the obvious high molecular weight, we judge these substances to be polymers formed from some of the unsaturated compounds. This deduction is supported by the absence of pentene in amount predicted from the quantity of pentane formed in the reactions where benzene was used as a solvent. More information relating to the process of polymerization in these reactions is being sought and will be published at a later date.

Experiments

The customary method of preparing the intermediate reagent, *viz.*, by addition of amyl chloride to excess sodium sand in a three-necked flask under an atmosphere of nitrogen as described in a previous paper, was followed. After suitable time was allowed for completion of this reaction, the alkyl chloride was added. Quantities and other condi-

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[3] Schlenk and Bergmann, *Ann.*, **463**, 15 (1928).

[4] Scott, Walker and Hansley, THIS JOURNAL, **58**, 2442 (1936).

TABLE II

REACTIONS IN BENZENE AS A SOLVENT

Constant factors: sodium sand, 35 g., in 100 ml. of benzene, 75 ml. of amyl chloride in 75 ml. of benzene, 300–400 additional benzene added in 100-ml. amounts during addition of amyl chloride whenever the mixture became too thick for easy stirring. Time of addition two and one-half hours, time of stirring after addition one and one-half hour. Temperature of addition of amyl chloride 18°.

			Yield		Decane	
Expt.	Compound added	Product	G.	%	G.	%
12	Methyl iodide	Toluene	20.5	39.2	4	9.1
13	Toluene followed by methyl iodide	Ethylbenzene	14.8	24.5	4.1	9.3
14	Iodine added rapidly	Iodobenzene	18.8	15.0	6.9	15.6
		Biphenyl	3.0	6.3		
15	Iodine added slowly	Iodobenzene	2.0	1.6	8.5	19.3
		Biphenyl	6	12.5		

tions are given in the tables. Analyses of the hydrocarbons obtained were made by fractionation through a column of 17 theoretical plates as determined by carbon tetrachloride–benzene mixture. The heptane range was 97 to 99°, the decane range 168 to 175°, that of other compounds was a proportionate amount. Care was always taken to fractionate the solvent employed in the reaction so that its boiling point did not interfere with the analysis of any so-called normal product. Pentane and pentene, the only other compounds obtained from amylsodium were indistinguishable from the solvent. Unless otherwise noted the yields are calculated on the amount of amyl chloride added. The reaction mixture was frequently carbonated to ensure that all of the reagent had been consumed by the alkyl chloride. Any details pertinent to the reactions are given in the numbered sections referring to the experiments.

Notes on Experiments

(1) In addition to the caproic acid, 8.7 and 7.8 g. (17.6 and 15.8%) of butylmalonic acid was obtained in these two runs.

(2) As many as six runs were made using methyl iodide without finding a trace of hexane. The run given is typical of all of the results. Gas uncondensed by a carbon dioxide snow trap was evolved when the reaction mixture was warmed slightly an hour after addition of methyl iodide had been completed. No unsaturated hydrocarbons were present in the gas. Combustions made in a slow combustion pipet showed that it consisted of 79% methane and 21% ethane. Some of this mixture could have been formed by reaction between methyl iodide and the excess sodium present. Material, 5.2 g., boiling above the decane range was found among the products.

(3) The average yield for three runs is recorded. Results for heptane were 23.4, 24.5, and 20.5%; those for decane were 19.5, 21.1, and 17.5%. Approximately 5 g. of material boiling above 180° was obtained in each of these reactions.

(4) Reaction mixture cooled in a dry-ice bath before ethyl bromide was added. Four grams of material boiling above the decane fraction was obtained.

(5) Fractionation showed that 2.3 ml. of octane was present among the products. Four grams of high boiling material, 180–209°, was also collected. Above 209° the amount of hydrocarbon was 4.6 g.

(6) No octane fraction was observed in this experiment. The quantity of material above the decane fraction was 7.6 g.

(7) Other products were not examined in this reaction.

(8) Amyl chloride was used as the reactant in this experiment in hope of obtaining as high an amount as possible of pentadecane from amylidenedisodium and amyl chloride. None could be found. The yield is calculated on the actual amount of amyl chloride used since a considerable excess had been added.

(9) This run is typical of three runs in none of which was any undecane found.

(10) Methylene chloride was added at dry ice temperature in the hope that undecane would be formed or that the quantity of decane would be increased. An attempt was made to collect gas from this reaction but so little was evolved that a satisfactory analysis was impossible.

(11) The recorded value is the average of three runs yielding 20.5, 16.6, and 16% decane.

(12) Pentane, 27 g., pentene, 5.2 g. (calculated from the dibromide), and residue, 4.5 g., boiling above the decane fraction were also recovered.

(13) Pentane, 25 g., pentene 3 g., and a liquid, 3.5 g., boiling from 180 to 250° were also found.

(14) Very little heat was evolved on addition of iodine to phenylsodium. It probably could be added in a very rapid stream with even better yields of iodobenzene than here obtained. The iodine was added until the solution changed color. The separation of iodobenzene from decane in the fractionating column was not perfect. Much decomposition product remained in the flask. Calculated on the amount of iodine used, 54 g., the yields were 39% iodobenzene and 9.2% biphenyl. Pentane, 21.4 g., and pentene, 3 g., were also recovered. The residue was black and tarry.

(15) Less iodine was needed to change the color of the solution than in the previous experiment. From 37.5 g. of iodine the calculated yields were 6.7% of iodobenzene and 28% of diphenyl. Pentane, 21.5 g., and pentene, 4 g., were also obtained.

Summary

Methyl iodide added to amylsodium causes the amyl radical to dimerize to decane rather than combine to form hexane.

Iodine added rapidly to a solution of phenylsodium forms chiefly iodobenzene; added slowly it forms biphenyl.

Amylidene disodium does not react with alkyl halides to form branched chain compounds nor

does methylene or ethylene dichloride react with amylsodium in the manner expected.

The result of nearness of groups to each other upon the nature of the products is discussed.

High boiling products are formed during reaction of these organosodium compounds with alkyl halides.

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

The Solubility Curves of the Systems Carbon Tetrachloride–*n*-Alkyl Acids–Water at 25°

BY HILTON A. SMITH AND M. BERMAN

In connection with studies of certain ternary alloys, Wright[1] investigated the system chloroform–acetic acid–water, giving his results in weight per cent. on a triangular coördinate system. Subsequently considerable data have been reported giving distribution coefficients of various organic acids between numerous organic solvents and water, but little work has been done in connection with locating the solubility curves of such three phase systems.

The present paper gives the results of investigations into the composition of homogeneous phases having the maximum possible concentration of carbon tetrachloride in water containing varying amounts of straight chain acids. The solubility curves are given in mole per cent. instead of weight per cent. in order to show the effect of the length of the carbon chain of the acids on the size and shape of the areas of mutual solubility.

Experimental

Materials.—Pure formic acid was prepared from the analytical reagent (89%) acid by distillation in a fractionating column, following the method of Ewins.[2] The pure acid froze at 8.3°. C. P. glacial acetic acid and C. P. carbon tetrachloride were used without further purification. The best grades of Eastman chemicals were used in the case of propionic and higher acids.

Methods.—The limits of mutual solubility of the three components were determined by titration of mixtures of two of the components with the third until two phases merged into a single phase or, when the two starting components were miscible, until a second phase separated. Calibrated burets were used, and all experiments were carried out at 25°. In the case of acids which were only partially miscible with one of the other components, the mutual solubility of each in the other was also determined by allowing the two to remain in contact with each other in a 25° thermostat for forty-eight hours after having first been shaken vigorously. Samples of each layer were then withdrawn and analyzed using standard potassium hydroxide solution.

Results and Discussion

The results of the determinations are given in Table I. The figures represent the maximum mole per cent. of carbon tetrachloride which may be dissolved in the indicated mixtures of acid and water. The solubility of water in carbon tetrachloride and that of carbon tetrachloride in water have been determined accurately by Clifford,[3] by Rosenbaum and Walton,[4] and by Gross and Saylor.[5] These values were not redetermined, but the figures given in the table were calculated from those given in the literature.

TABLE I

Mole % CCl_4	Mole % Acid	Mole % H_2O
Formic Acid		
0.01	0	99.99
.15	40	60
.30	49	51
.40	55	44
.60	63	36
.90	74	24
2.2	94	3.9
2.7	97.3	0
91.2	8.8	0
99.9	0	0.1
Acetic Acid		
0.01	0	99.99
.3	5.2	94.5
.3	9.5	90
.4	14.4	85
.4	20	79
.5	28	72
2.4	46	52
5.2	54	41
9.2	58	33
11.4	58	31
15	58	27
23	57	20
27	55	18
32	53	15
48	44	8.0
55	39	6.2
61	34	4.4
69	29	1.9
99.9	0	0.1
Propionic Acid		
0.01	0	99.99
.2	5.7	94
.5	19	80
1.5	26	72
5.0	33	62
13	40	47
17	44	39
31	47	22
42	46	12
49	43	8.3
55	40	5.5
63	35	2.4
75	25	0.1
99.9	0	0.1

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(1) Wright, *Proc. Roy. Soc.* (London), **49**, 174 (1891); **50**, 375 (1892).

(2) Ewins, *J. Chem. Soc.*, **105**, 350 (1914).

(3) Clifford, *Ind. Eng. Chem.*, **13**, 631 (1921).

(4) Rosenbaum and Walton, THIS JOURNAL, **52**, 3568 (1930).

(5) Gross and Saylor, *ibid.*, **53**, 1744 (1931).