The product of addition of toluene to phenylsodium at room temperature will yield ethylbenzene with methyl iodide but benzoic acid with carbon dioxide. Higher temperatures are needed to fix the sodium to the tolyl radical.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 171]

Condensations by Sodium. XIII. The Wurtz–Fittig Synthesis of Amylbenzene and Some Reactions of Benzylsodium

BY AVERY A. MORTON AND FRANKLIN FALLWELL, JR.

Previous work[1] has demonstrated that an important and possibly a sole cause of the Wurtz synthesis, namely, that phase involving the reaction between an organosodium compound and an alkyl halide, is by no means quantitative with respect to coupling. With a view of sifting the intermediates involved in a typical Wurtz–Fittig synthesis we have conducted an experimental inquiry into formation of amylbenzene. Amylsodium and chlorobenzene form chiefly a polymer and the phenylsodium and chlorobenzene pair react incompletely. Simultaneous addition of chlorobenzene and amyl chloride to metallic sodium, a circumstance which might favor combinations as free radicals, did not alter the above findings. Evidently the reactions involved in this particular Wurtz–Fittig synthesis may proceed through intermediate organosodium stages, yet give poor yields and a diversity of products.

As a means of arriving at a satisfactory preparation we have utilized a by-pass from phenyl- to benzylsodium and thence with butyl chloride to amylbenzene according to the sequence

$$C_5H_{11}Cl \xrightarrow[C_6H_6]{\text{Na in}} C_6H_5Na \xrightarrow{C_7H_8}$$

$$C_6H_5CH_2Na \xrightarrow{C_4H_9Cl} C_5H_{11}C_6H_5$$

Yields of 56% calculated on the amyl chloride used testify to the the success of this round-about procedure. Substitution of toluene for benzene in the first step of the above chain is impractical as a means of stopping the reaction at the benzylsodium stage (10% yield) but serves admirably for synthesizing hexylbenzene (61%), particularly if the reaction is carried out at 75°. Similar application to the amylbenzene synthesis using butyl chloride gave a 70% yield. Where the alkyl chloride is expensive it is preferable to prepare benzylsodium first via the amyl chloride–benzene–toluene route and then decolorize with the desired alkyl halide so that its conversion is practically quantitative. Incidentally, benzylsodium, in contrast to amyl- and phenylsodium, is the only one of those so far studied at length in this series which has consistently given the expected products with methyl iodide, ethyl bromide, amyl chloride, or methylene dichloride. In general its use is recommended for a Wurtz–Fittig reaction wherever the nature of the product permits.

Examination of the polymer from amylsodium and chlorobenzene showed that it consisted of one amyl and three phenyl residues. Possibility of its source from any secondary reaction involving amylbenzene was eliminated by an independent experiment (No. 7). Absence of free benzene suggested that the amyl and phenyl radicals had disproportionated giving pentane and phenylene, the doubly unsaturated radical then becoming the chief agent in polymerization.

The lack of complete reactivity exhibited by phenylsodium to amyl chloride is not a general behavior of this organometallic compound toward all substances for its reactions with toluene, iodine, and carbon dioxide have led to entire consumption of the reagent. Even chlorobenzene appears to react more readily with phenylsodium than does amyl chloride. Neither is benzylsodium outstandingly reactive toward all substances, for in an additional comparison with another reagent, namely, trioxymethylene, the three organometallic reagents in question yielded hexyl alcohol, benzyl alcohol and phenylethyl alcohol in 28, 19 and 17% yields, respectively.

Experiments

The general method of carrying out these reactions was the same as that previously described. Specific details are included in the tables or in the accounts of separate experiments. In all experiments a carbonation was performed as the last step in order to determine the amount of unconsumed reagent.

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(1) Morton and Fallwell, THIS JOURNAL, 59, 2387 (1937).

TABLE I

REACTION OF AMYL- OR PHENYLSODIUM

Constant factors: sodium sand, 35 g.; amyl chloride, 75 ml. or chlorobenzene, 100 ml., or an equivalent amount of the mixture of these two added to sodium during two hours. Solvent, petroleum ether, P, or benzene, B. Percentage yields are calculated either on the amount of amyl chloride (% a) or of chlorobenzene (% c) added.

No.	Major reaction	Solvent	Yields of acids Benzoic		Yields of acids Caproic		Amylbenzene		Diphenyl		Decane		Polymer	
			G.	% c	G.	% a	G.	% a	G.	% c	G.	% a	G.	% a
1	$C_5H_{11}Na + C_6H_5Cl$	P	5	10	..	..	5	5	4	13	9	20	18	30
2	$C_5H_{11}Na + C_6H_5Cl$	P	4	7	..	..	5	5	5	15	9	20	20	33
3	$C_6H_5Na + C_5H_{11}Cl$	P	16	21[a]	..	..	8	9	0	0	15	23	4	7
4	$C_6H_5Na + C_5H_{11}Cl$	B	16	21	..	..	9	10	0	0	7	10	4	7
5	$C_5H_{11}Cl + C_6H_5Cl + Na$	P	20	50	9	22	6	11	3	10	3	14	6	18
6	$C_5H_{11}Cl + C_6H_5Cl + Na$	B	18	42	..	..	4	5	3	10	4	17	9	27
7	$C_5H_{11}Cl + Na + C_6H_5C_5H_{11}$	P	..	..	21	29					8	18	..	..

[a] Yield calculated on amyl chloride basis.

SPECIAL COMMENTS

(1) Chlorobenzene, 100 ml., was added during twenty-five minutes to the amylsodium. After one and one-half hours at 40° the mixture was carbonated. The unused chlorobenzene recovered by distillation amounted to 56 ml. The yield is calculated on the remaining 44 ml. In addition to the products listed in the table, 2 g. of an amorphous powder was obtained. No benzene was observed among the products.

(2) The reaction was the same as No. 1 except that the addition of chlorobenzene consumed eighty minutes. Unused chlorobenzene amounted to 54 ml. The quantity of amorphous powder was 2 g.

(3) Phenylsodium was prepared by the reaction of amyl chloride with sodium in petroleum ether followed by stirring with 150 ml. of benzene for two hours at 40°. The additional amyl chloride added was 60 ml. of which 8 ml. was recovered after one hour of stirring at 40°. The yield is calculated on the amyl chloride originally used in preparation of phenylsodium. Less than 0.1 g. of triphenylcarbinol was also found among the products.

(4) Conditions for preparing phenylsodium were the same as in No. 3 except that benzene was used as the solvent. Amyl chloride, 75 ml., was added to ensure the presence of a great excess of the halide. The mixture was stirred for three hours at 25°. All but 30 ml. was recovered by distillation of the products. Triphenylcarbinol, 0.5 g.

(5) A mixture of amyl chloride, 42 ml., and chlorobenzene, 34 ml., was added to sodium sand in hope that the simultaneous presence of both halides and radicals would have a favorable influence on formation of amylbenzene. All of the amyl chloride and chlorobenzene was consumed in the reaction.

(6) Reaction was the same as No. 5 except that benzene instead of petroleum ether was used as the solvent in order to simplify analysis of the products.

(7) Amylbenzene, 35 ml., added to the petroleum ether used as a solvent during addition of amyl chloride to sodium. The yields of caproic acid and butylmalonic (8 g. 17%) were substantially the same as found in reactions using petroleum ether alone as a solvent.

TABLE II

REACTIONS WITH BENZYLSODIUM

Constant factor: Na, 35 g., used in all experiments. Amyl chloride, 75 ml., or the equivalent amount of butyl chloride.

No.	Source of benzylsodium Solvent[a]	Source of benzylsodium Alkyl-chloride	Temp., °C.	Reagent added to C_7H_8Na	Wurtz–Fittig product	Yield G.	Yield %
7	T	Amyl	22	None	Hexylbenzene	23	54
8	T	Amyl	75	None	Hexylbenzene	31	61
9	B, T[b]	Amyl	75	C_4H_9Cl	Amylbenzene	52	56
10	T	Butyl	18	None	Amylbenzene	0	0
11	T	Butyl	70	None	Amylbenzene	32	70

[a] T = toluene, B = benzene. [b] Benzene followed by toluene.

SPECIAL COMMENTS

(7) This experiment was carried out in the manner usually employed for interrupting the Wurtz reaction but carbonation yielded only 12 g. (14%) of phenylacetic and 4 g. (7%) of phenylmalonic acid. Decane, 3 g. (7%) was also found.

(8) The temperature was higher than in No. 7 in order to facilitate the reaction between benzylsodium and amyl chloride.

Carbonation at the end of the operation yielded 8 g. (10%) and 3 g. (5%) of phenylacetic and phenylmalonic acids, respectively. The decane content was 4 g. (8%).

(9) Toluene, 75 ml., followed by 60 ml. of butyl chloride, was added to the phenylsodium. Decane, 5 g. (10%), but no octane was found.

(10) Addition of butyl chloride was made at 18–20° after which the mixture was heated slowly to 80° and stirred for three hours. No colorimetric evidence of an exchange was seen until the temperature reached 50° at which point the mixture turned from blue to yellow. Phenylacetic acid, 1 g. (2%), phenylmalonic acid, 4 g., (7%), and octane, 6 g. (17%) were also obtained.

(11) This experiment was a repetition of No. 10 except that addition of butyl chloride was carried out at 70° in hope that the exchange would be favored. No octane was found and only a trace of phenylacetic acid could be isolated.

Examination of the Polymer.—Fractionation of the mixture obtained in experiment 34 gave 5 ml. boiling at 128–143° (4 mm.), 3 ml. boiling at 144–154° (4 mm.) and 3 ml. from 155–165° (4 mm.). Combustion of the last 3 ml. from 155–165° (4 mm.). Combustion of the last fraction showed C, 91.31%; H, 8.73%. The ratio of carbon to hydrogen is 10.46. Within the experimental error this figure is correct for one amyl and three phenyl residues. Molecular weight in camphor 294; calcd. for

$(C_6H_5)_3C_5H_{11}$, 302. The polymer was not oxidized by twenty hours of boiling with neutral permanganate solution, conditions which were effective in converting hexylbenzene to benzoic acid in six hours. No immediate decoloration with bromine occurred.

Diphenylpropane.—To benzylsodium, prepared as in experiment 9, was added gradually 30 ml. of methylene dichloride. The mixture was stirred for one-half hour after addition and then carbonated to ensure complete reaction of the organosodium compound. After the usual decomposition no acids could be found. Crude diphenylpropane (270–285°) 11 g. (18%), decane 5 g. (12%), and liquid boiling from 175–270°, 7 g. were obtained.

Hexyl-, Benzyl-, and Phenylethyl Alcohols.—Amylsodium, phenylsodium, and benzylsodium were prepared in the customary manner used in the reactions described in Tables I and II. Trioxymethylene, 30 g., suspended in the appropriate hydrocarbon solvent was added and the mixture stirred until the color of the organosodium compound was discharged, after which the mixture was heated to ensure completion of the reaction. The mixture was then carbonated and decomposed with ice. No acids were obtained. Upon fractionation of the hydrocarbon layer obtained in each experiment there was isolated 16 g. (28%), 11 g. (17%), and 13 g. (17%) of *n*-hexyl, benzyl, and phenylethyl alcohols, respectively. The corresponding decane and high boiling contents were 18, 20, and 14 g. The 3-nitrophthalic acid monoester derivative of this hexyl alcohol (boiling 149–152°) melted without further purification at 119–121° (pure 121°); that of the 190–200° boiling benzyl alcohol at 167–174° and when recrystallized at 172–176° (pure 176°). The phenylethyl alcohol which boiled at 205–212° was shown to be free from *o*-methylbenzyl alcohol by the absence of phthalic acid and the presence of benzoic acid after oxidation with neutral permanganate solution.

Summary

Possible combinations of organosodium compounds and organic chlorides in the Wurtz–Fittig synthesis of amylbenzene have been studied. The reaction is capable of giving high yields of products other than the expected coupling.

Benzylsodium reacts more smoothly and gives far better yields with alkyl halides than does amyl- or phenylsodium. In general its use is preferred where the nature of the product permits.

Diphenylpropane can be prepared by reaction of benzyl sodium with methylene dichloride.

Trioxymethylene reacts with amyl-, phenyl-, or benzylsodium yielding hexyl, benzyl, and phenylethyl alcohols, respectively.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Photolysis of Gaseous Hydrogen Sulfide

BY GEORGE S. FORBES, JAMES E. CLINE AND BENJAMIN C. BRADSHAW

Warburg and Rump,[1] in 1929, photolyzed hydrogen sulfide in hexane and in water. In hexane the quantum yield ϕ (molecules of hydrogen produced per light quantum absorbed by hydrogen sulfide) was close to unity, but in water it ranged from 0.2 to 0.3. The lower value in water they attributed to hydration of the photolyte. This conclusion appeared at first to be supported by differences in the absorption curves of hydrogen sulfide in the two solvents, respectively, but Arends and Ley,[2] using a more refined procedure, found the two curves to be identical.

Goodeve and Stein,[3] in 1931, investigated the absorption spectra of hydrogen sulfide, selenide and telluride, and concluded that the energy at the threshold of the optical dissociation, of hydrogen sulfide at least, indicated the reaction $H_2S + h\nu \longrightarrow H_2 + S\ (^1D)$.

Herzberg[4] dissented, pointing out that both hydrogen atoms should not be split off in a single act, since they are not bound together in the original molecule. Furthermore, the analogous dissociation $H_2O + h\nu \longrightarrow H_2 + O\ (^1D)$ requires 163.3 kcal., in contrast with the observed dissociation threshold at 153 kcal. Herzberg preferred to write $H_2S + h\nu \longrightarrow H + HS$ followed by $H + H_2S = H_2 + HS$, and by $HS + HS \longrightarrow H_2S + S$ to explain the formation of sulfur.

Stein,[5] in 1933, photolyzed gaseous hydrogen sulfide in approximately monochromatic light, $\lambda = 205$ mμ, and measured with a Pirani gage the very small quantity of hydrogen produced. When P_{H_2S} lay between 75 and 250 mm., ϕ was close to 2 but rose to 3.5 for a pressure of 1350 mm. These high values Stein attributed to short chains initiated by excited sulfur atoms or molecules, a hypothesis not entirely satisfactory.

In 1934, a preliminary series of quantitative photolyses in light of λ 208 mμ was undertaken (B. C. B.) using carefully purified gas. To spread

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(1) Warburg and Rump, *Z. Physik*, **58**, 291 (1929).

(2) Arends and Ley, *Z. physik. Chem.*, **15B**, 311 (1932).

(3) Goodeve and Stein, *Trans. Faraday Soc.*, **27**, 393 (1931).

(4) Herzberg, *ibid.*, **27**, 402 (1931).

(5) Stein, *ibid.*, **29**, 583 (1933).