7. **5-Chloro-1,4-dimethyl-2-thiolbenzene.**—The starting material was 2-amino-1,4-dimethylbenzene. All attempts to sulfonate this material were unsatisfactory. The amine was acylated with acetic anhydride and sulfonated according to the directions of Junghahn.[2] The acetyl group was removed by refluxing for three hours with concentrated hydrochloric acid. The reactions from this stage on were identical with those in the previous cases. The chlorosulfonyl chloride melted at 49–49.5°; the sulfonamide at 189–190°. It was possible to recrystallize the product from benzene if the solution was placed in a desiccator filled with paraffin shavings; the melting point was 92.5°.

Anal. Calcd. for C_8H_9ClS: S, 18.57. Found: S, 18.67.

8. **Disulfide of 5-Chloro-1,4-dimethyl-2-thiolbenzene.**—The product was recrystallized from a chloroform–alcohol mixture (1:2) and melted at 103°.

Anal. Calcd. for $C_{16}H_{16}Cl_2S_2$: C, 55.95; H, 4.69. Found: C, 56.15; H, 4.68.

9. **2-Chloro-1-thiolnaphthalene.**—The starting material was 2-amino-1-naphthalene sulfonic acid. The final product recrystallized from alcohol melted at 66.5°.

Anal. Calcd. for $C_{10}H_7SCl$: S, 16.47. Found: S, 16.58.

10. **Disulfide of 2-Chloro-1-thiolnaphthalene.**—After several recrystallizations from a chloroform–alcohol mixture (1:2) the product melted at 134°.

Anal. Calcd. for $C_{20}H_{12}Cl_2S_2$: C, 62.01; H, 3.12. Found: C, 62.08; H, 3.12.

11. **4-Chloro-1-thiolnaphthalene.**—The starting material was 1-naphthylamine-4-sulfonic acid. The product was purified by dissolving it in dilute alkali, clarifying the solution with kieselguhr, and precipitating it with dilute hydrochloric acid, melting point 51°.

12. **The Disulfide of 4-Chloro-1-thiolnaphthalene.**—Very easily formed; recrystallized from alcohol, it melted at 124–125°.

Anal. Calcd. for $C_{20}H_{12}Cl_2S_2$: C, 62.01; H, 3.12. Found: C, 62.00; H, 3.17.

Summary

Several new halogenated thiophenols and naphthols were prepared which are interesting because of a possible therapeutic application.

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[2] Junghahn, *Ber.*, **33**, 1364 (1900).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Reduction of Phenylated Olefins with Alkali Metals in Liquid Ammonia Solution

BY CHARLES BUSHNELL WOOSTER AND JOHN F. RYAN[1]

The present investigation was undertaken to obtain further information regarding the nature of the reactions which may occur between alkali metals and phenylated olefins in liquid ammonia at its boiling point. The compounds studied were styrene, stilbene, unsymmetrical diphenylethylene, triphenylethylene, tetraphenylethylene, 1,1-diphenylpropylene, 1,1,3,3-tetraphenylpropylene and tetraphenylallene; the general results may be summarized briefly as follows.

In no case did the alkali metal attack the phenyl groups, but it was found possible, under suitable conditions, to saturate the double bonds in the side chains of every hydrocarbon and to obtain the corresponding phenylated paraffins after decomposition of the intermediate organo-alkali compounds with ammonium chloride. In some cases the double bonds were partially or completely saturated with hydrogen before the addition of ammonium chloride due to ammonolysis of the intermediate organo-alkali compounds.

$$RNa + NH_3 = RH + NaNH_2$$

The occurrence and extent of the ammonolysis may in general be predicted on the basis of the benzohydryl rule;[2] that is, the alkali metal atoms were replaced with hydrogen except when they were present in the grouping $(C_6H_5)_2C(M)$—(M = alkali metal), as may be seen by inspection of Table I giving the reaction products obtained with *excess* sodium.

TABLE I

THE ACTION OF SODIUM ON PHENYLATED OLEFINS IN LIQUID AMMONIA

No.	Olefin	Products
I	$C_6H_5CH{=}CH_2$	$C_6H_5C_2H_5$ and styrene polymers
II	$C_6H_5CH{=}CHC_6H_5$	$C_6H_5CH_2CH_2C_6H_5$
III	$(C_6H_5)_2C{=}CH_2$	$(C_6H_5)_2CNaCH_3$ and $(C_6H_5)_2CNaCH_2CH_2CNa(C_6H_5)_2$
IV	$(C_6H_5)_2C{=}CHC_6H_5$	$(C_6H_5)_2CNaCH_2C_6H_5$
V	$(C_6H_5)_2C{=}C(C_6H_5)_2$	$(C_6H_5)_2CNaCNa(C_6H_5)_2$ and $(C_6H_5)_2CHNa$ or $(C_6H_5)_2CNa_2$?
VI	$(C_6H_5)_2C{=}CHCH_3$	$(C_6H_5)_2CNaCH_2CH_3$
VII	$(C_6H_5)_2C{=}CHCH(C_6H_5)_2$	$(C_6H_5)_2CNaCH_2CH(C_6H_5)_2$
VIII	$(C_6H_5)_2C{=}C{=}C(C_6H_5)_2$	$(C_6H_5)_2CNaCH_2CNa(C_6H_5)_2$

The alkali metals also reacted with some of the phenylated olefins in other ways, including

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[2] (a) Wooster and Mitchell, THIS JOURNAL, **52**, 688 (1930); (b) Wooster and Ryan, *ibid.*, **54**, 2419 (1932).

polymerization (I), dimerization (III), cleavage (V) and addition to but one of the two double bonds in tetraphenylallene.

The stable organo-alkali compounds were all red. They reacted with oxygen and with certain RX reagents: ethyl bromide, dimethyl sulfate and benzyl chloride. Oxygen and some of the RX reagents regenerated the double bond in organo-alkali compounds in which two alkali metal atoms were attached to adjacent carbon atoms. The RX reagents replaced alkali metal atoms in the other types of organo-alkali compounds with organic radicals or with *hydrogen.* Reactions of the latter type were probably due to the tendency of alkyl halides and sulfates to ammonolyze with formation of alkyl ammonium salts which behave as acids in the liquid ammonia system. The occurrence of hydrogen substitution was influenced both by the nature of the organo-alkali compound and of the RX reagents; it could often be avoided by using benzyl chloride in place of ethyl bromide or methyl sulfate. Thus $(C_6H_5)_2CNaCH_3$ and $(C_6H_5)_2CNaC_2H_5$ yielded $(C_6H_5)_2CHCH_3$ and $(C_6H_5)_2CHC_2H_5$, respectively, with either methyl sulfate or ethyl bromide, but formed $(C_6H_5)_2C(CH_2C_6H_5)CH_3$ and $(C_6H_5)_2C(CH_2C_6H_5)C_2H_5$ with benzyl chloride. On the other hand, $(C_6H_5)_2CNaCH_2C_6H_5$ formed hydrocarbons of the type $(C_6H_5)_2CRCH_2C_6H_5$ with all three reagents.

Experimental Part

The apparatus employed in the investigations which required the quantitative determination of reactant alkali metal and of gaseous products has been described previously.[3] Purely qualitative reactions were carried out in a three-necked flask of appropriate size, equipped with a dropping funnel and mechanical stirrer.

I. Styrene

Quantitative investigations of the reaction of this compound with sodium were carried out in two ways. In one experiment 3.08 g. (2.7 equivalents) of sodium was added to a solution of 5.18 g. of styrene in ammonia. At no time was the red color, indicative of an organo-alkali compound, apparent. Titration of the excess sodium with ammonium chloride evolved 750 cc. of hydrogen, at N. T. P. This volume of hydrogen corresponds to 1.54 g. of sodium, indicating that only 1.54 g. or 1.34 equivalents of sodium had reacted with each mole of styrene. In a second experiment 4.052 g. of styrene was added to a solution of 2.116 g. (2.36 equivalents) of sodium in ammonia. Treatment with ammonium chloride in this case yielded 426 cc. of hydrogen. This corresponds to 0.875 g. of sodium, indicating that 1.241 g. of sodium, or 1.38 equivalents, had reacted with the styrene.

This deviation from the expected ratio of two atoms of alkali metal for each molecule of hydrocarbon is explained by the rapid polymerization of the hydrocarbon in a solution of the alkali metals in ammonia. In each of the above experiments approximately half of the product consisted of ethylbenzene (b. p. 136°, n^{20}_{D} 1.4950). The rest of the product boiled gradually up to 200° at 13 mm. pressure, leaving a small glassy residue.

Polymerization of styrene under the influence of sodium in ethereal solution has also been reported by Schlenk and Thal.[4]

II. Stilbene

When sodium or potassium was added slowly to stilbene in ammonia, the blue color of the alkali metal solution was changed rapidly to a reddish brown, suggesting the formation of a colored addition product. The reddish color, however, rapidly faded until the solution became colorless, and the only organic product isolated after evaporation of the ammonia and steam distillation of the residue was dibenzyl. It is probable that in the reduction of stilbene by alkali metals, the first step is always formation of an addition product, $C_6H_5CHM\text{–}CHMC_6H_5$. At −78° this organo-alkali compound is apparently stable for some time,[5] and at the temperature of boiling ammonia it is stable long enough for its color to be apparent, but at room temperature it is ammonolyzed immediately.[6]

III. 1,1-Diphenylethylene

When a solution of 10 g. of the diphenylethylene in 2 volumes of dry ether was slowly added to a solution of about four times the theoretical amount of sodium in ammonia, the red color of an organo-alkali compound developed rapidly. Hydrolysis of this product with ammonium chloride yielded about 9 g. of a colorless oil boiling at 153° under 13 mm. Its boiling point and method of preparation together with its index of refraction (n^{20}_{D} 1.5756) indicate that it is 1,1-diphenylethane (n^{20}_{D} 1.5761). About one gram of 1,1,4,4-tetraphenylbutane (m. p. and mixed m. p. 120–121°) was also obtained. Treatment of the red organo-alkali compound with benzyl chloride yielded 1,2,2-triphenylpropane. Similar reactions using dimethyl sulfate and ethyl bromide did not lead to alkylation but to mixtures of 1,1-diphenylethane (about 60–70%) and 1,1,4,4-tetraphenylbutane (about 20–30%), showing that substitution of the alkali metal by hydrogen had occurred.

Ziegler[7] reported that when a solution of 2.3 g. of diphenylethylene in ether was added slowly to a solution of excess sodium in liquid ammonia, the sole product of hydrolysis was diphenylethane, but we have found that the use of larger quantities (8-10 g.) permits the isolation of 1,1,4,4-tetraphenylbutane to the extent of 10 to 30% of the reaction product.

IV. Triphenylethylene

Triphenylethylene adds two atoms of sodium, the addition product is semi-ammonolyzed and reacts normally

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(3) Wooster, THIS JOURNAL, **51**, 1856 (1929).

(4) Schlenk and Thal, *Ber.*, **47**, 473 (1914).

(5) Schlubach, *Ber.*, **48**, 13 (1913).

(6) Lebeau and Picon, *Compt. rend.*, **159**, 70 (1913).

(7) Ziegler and Colonius, *Ann.*, **473**, 35 (1929).

with ammonium chloride, ethyl bromide and benzyl chloride.[2b]

When the product obtained by treating 3.3 g. of triphenylethylene with potassium was decomposed with methyl sulfate, about 3 g. of 1,2,2-triphenylpropane, $(C_6H_5)_2C(CH_3)CH_2C_6H_5$, was obtained, identical with the product of the action of benzyl chloride on diphenylethylsodium (see Section III). It is evident that 1-sodium-1,1,2-triphenylethane, $(C_6H_5)_2CNaCH_2C_6H_5$, is much more easily alkylated than 1-sodium-1,1-diphenylethane, $(C_6H_5)_2CNaCH_3$.

V. Tetraphenylethylene

The disodium compound of tetraphenylethylene is stable in ammonia, and may be prepared by treating the olefin with two equivalents of sodium in this solvent. Its reactions in ammonia are similar to those observed in ether.[8] Its behavior when treated with RX reagents offers a sharp contrast to the behavior of most organo-alkali compounds, since alkylations do not occur. The general reaction leads to regeneration of the double bond, thus tetraphenylethylene resulted from the action of dry air, methyl sulfate and benzyl chloride. However, in one experiment in which an excess of sodium had been used, the action of ethyl bromide on the organo-alkali compound yielded two distinct products, tetraphenylethane, m. p. 211°, and a liquid boiling at 147–148° under 10 mm., the physical properties of which (n^{17}_D 1.5744; mol. wt., cryoscopic in cyclohexane, 193) compared closely with those of 1,1-diphenylpropane (b. p. 150–151° under 17 mm.; n^{17}_D 1.5744; mol. wt., 196). The formation of the latter product indicates cleavage of disodium tetraphenylethane by excess sodium, followed by reaction with ethyl bromide and ammonolysis. The occurrence of such cleavage was demonstrated by the following experiment.

Tetraphenylethylene (1 g.) was treated in liquid ammonia solution with 0.4420 g. of sodium (6.38 equivalents). The solution became deep red, then purple. At the end of twenty minutes the color was discharged with ammonium chloride. The volume of hydrogen evolved, 92 cc. at N. T. P., corresponds to 0.1889 g. of sodium indicating that 0.2531 g., or 3.65 equivalents of the metal, had reacted with each mole of tetraphenylethylene.

Distillation of the product of this reaction yielded about 0.2 g. of tetraphenylethane, and 0.6 g. of an oil boiling at 132° under 17 mm. (n_D at 28.4°, 1.5708) which was evidently diphenylmethane (b. p. 134° under 21 mm.; n_D at 28.4°, 1.5709).

VI. 1,1-Diphenylpropylene-(1)

Diphenylpropylene reacts readily with the alkali metals in ammonia, the primary addition product being semi-ammonolyzed. The stable product yields 1,1-diphenylpropane and 1,2,2-triphenylbutane with ammonium chloride and benzyl chloride, respectively.[2b]

In two experiments 5 g. of the diphenylpropylene, dissolved in ether, were added to a solution of 3.6 g. (6 equivalents) of sodium in liquid ammonia and the resulting organo-alkali compound was decomposed with methyl sulfate and ethyl bromide, respectively. In both cases about 4.4 g. of an oil was obtained, boiling at 152–153° under 20 mm. The physical constants of this substance (m. p. −6.2°; n^{17}_D 1.5640; mol. wt., cryoscopic in cyclohexane, 191) indicated that it was 1,1-diphenylpropane (b. p. 153–154° under 20 mm.; m. p. −6°; n^{14}_D 1.5657; mol. wt., 196), and the identification was confirmed by mixed melting point.

VII. 1,1,3,3-Tetraphenylpropylene

In ammonia solution, tetraphenylpropylene reacted with two atoms of alkali metal, yielded tetraphenylpropane after hydrolysis of the organo-alkali product with ammonium chloride. Treatment of the stable red addition product with methyl sulfate, ethyl bromide, and benzyl chloride led to the formation of derivatives melting at 118, 128 and 122–123°, respectively. The first two hydrocarbons have been identified as 1,1,3,3-tetraphenylbutane and 1,1,3,3-tetraphenylpentane by comparison with samples independently synthesized as follows.

1,1,3,3-Tetraphenylbutane resulted from the reduction of 1,1,3,3-tetraphenylbutene-(1) with sodium and alcohol. The butene was obtained in two ways, from tetraphenylallyl ethyl ether by the method of Schlenk and Bergmann[9] and from dypnone according to the procedure of Schoepfle and Ryan.[10]

1,1,3,3-Tetraphenylpentane was prepared in a similar manner. Cleavage of tetraphenylallyl ethyl ether followed by treatment with ethyl iodide gave a sticky oil which could not easily be crystallized, but direct reduction of this oil with sodium and alcohol yielded a hydrocarbon of melting point 128°, identical with that obtained from the treatment of potassium tetraphenylpropane with ethyl bromide.

The benzyl derivative by analogy is probably 1,1,3,3,4-pentaphenylbutane but its structure has not been established by independent synthesis.

VIII. Tetraphenylallene

Tetraphenylallene reacts readily with sodium in ammonia to form a deep red organo-alkali compound. In one experiment 1.3275 g. of tetraphenylallene in ammonia was treated with 0.6213 g. of sodium (7.00 equivalents). The addition of ammonium chloride after two hours of stirring evolved 140 cc. of hydrogen at N. T. P. Since this volume of hydrogen corresponds to 0.287 g. of sodium, it was evident that 0.334 g., or 3.76 equivalents of the metal, had reacted with each mole of tetraphenylallene. A second, similar, experiment indicated the reaction of 4.3 equivalents of sodium per mole of tetraphenylallene. In both cases the product isolated after evaporation of the ammonia was 1,1,3,3-tetraphenylpropane, in rather pure form (m. p. 135°) and in practically quantitative yield.

Attempts to prepare derivatives of the sodium compound by the use of alkyl halides were unsatisfactory, the reaction in every case leading to the formation of viscous uncrystallizable oils, but the following evidence indicates that two atoms of sodium are ammonolyzed and two remain in the organo-alkali compound.

A special reaction tube was so constructed that it could be removed from the system and weighed. Ammonia was condensed on a sample of tetraphenylallene, and a weighed amount of sodium added. After completion of the

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(8) *Cf.* Wooster, *Chem. Rev.*, **11**, 1–91 (1932).

(9) Schlenk and Bergmann, *Ann.*, **463**, 226 (1928).

(10) Schoepfle and Ryan, THIS JOURNAL, **54**, 3687 (1932).

reaction as usual, the ammonia was evaporated and the reaction tube evacuated at room temperature. Evacuation and weighing were repeated to constant weight. In two experiments using 0.3802 and 0.4024 g. of tetraphenylallene and 0.1430 and 0.1076 g. of sodium the increases in weight observed were 0.0366 and 0.0369. These values correspond to the ammonolysis of 1.95 and 1.86 atomic equivalents of sodium, respectively.

This evidence does not show whether the sodium atoms occupy the 1,2 or 1,3 positions, but the latter possibility is favored by the fact that oxidation of the organo-alkali compound did not result in the formation of tetraphenylpropylene. Accordingly, the more probable formula has been indicated in Table I.

When potassium was employed in place of sodium, the reactions were apparently similar, but in this case it was possible to obtain crystalline methyl, ethyl and benzyl derivatives. The principal products of the action of methyl sulfate, ethyl bromide and benzyl chloride were mono-substitution products of the type $(C_6H_5)_2CRCH_2$-$CH(C_6H_5)_2$ ($R = CH_3$, C_2H_5 or $CH_2C_6H_5$), which were identical with the corresponding derivatives obtained from tetraphenylpropylene (see Section VII). These may have resulted from a mono-potassium compound $(C_6H_5)_2CK$-$CH_2CH(C_6H_5)_2$, or a dipotassium compound, since the RX reagents are capable of replacing alkali metals with hydrogen upon occasion. In this connection it is significant that in every instance a second product was obtained in much smaller quantities. These were suspected to be disubstitution products but unfortunately several attempts to establish their constitution by independent syntheses were unsuccessful.

When 3.00 g. of tetraphenylallene was treated with just 0.406 g. (2 equivalents) of sodium, and the product hydrolyzed with water, the result was pure tetraphenylpropylene. suggesting that the addition of alkali metal to tetraphenylallene occurs in stages, one bond being saturated before the second bond is attacked.

Schlenk and Bergmann[9] obtained only a disodium compound of tetraphenylallene after three days of shaking in ether.

Summary

1. The action of liquid ammonia solutions of the alkali metals on styrene, stilbene, *unsym*-diphenylethylene, triphenylethylene, tetraphenylethylene, 1,1-diphenylpropylene, 1,1,3,3-tetraphenylpropylene and tetraphenylallene has been investigated.

2. In no case did the alkali metal attack the phenyl groups, but it was found possible to saturate the double bonds in the side chain of every hydrocarbon and to obtain the corresponding phenylated paraffins after decomposition of the intermediate organo-alkali compounds with ammonium chloride.

3. In accordance with the benzohydryl rule some of the intermediate organo-alkali compounds were partly or completely ammonolyzed.

4. The stable organo-alkali compounds reacted with oxygen and certain RX reagents: ethyl bromide, methyl sulfate and benzyl chloride. Oxygen and some of the RX reagents regenerated the double bond in organo-alkali compounds in which two alkali metal atoms were attached to adjacent carbon atoms. The RX reagents replaced alkali metal atoms in the other types of organo-alkali compounds with organic radicals or with *hydrogen*.

5. The alkali metals also reacted with some of the phenylated olefins in other ways, including polymerization, dimerization, cleavage and addition to but one of the unsaturated bonds in tetraphenylallene.

6. The reactions observed in liquid ammonia are seldom identical with those which take place in indifferent solvents, the two chief differences being a tendency toward more extensive reaction with the concentrated solutions of the alkali metals obtainable in ammonia and the occurrence of reactions involving the solvent.

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