### **REACTIONS OF NON-ACTIVATED ARYL HALIDES** WITH NUCLEOPHILIC AGENTS INDUCED BY ALKALI AMIDES IN LIQUID AMMONIA\*

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Abstract-It has been shown that the reactions of nucleophiles with non-activated aryl halides, discovered by Bergstrom to be induced by alkali amides in liquid ammonia, proceed by way of a benzyne-type intermediate. The ease with which a given nucleophile can compete with amide ion does not appear to be a simple function of either its basic strength or nucleophilic character as measured in other reactions. Thus, the anions of a number of weak acids line up qualitatively in competitive power as follows: fluorenyl anion  $\sim$  anilide > thiophenolate  $\sim$  triphenylmethide > acetophenone enolate anion  $\sim$  phenylacetylide > phenolate > pyrrolate > alkoxides, iodide or cyanide. The results indicate benzyne to be a highly unstable entity.

IN 1936 Bergstrom and co-workers<sup>1,2</sup> reported that chlorobenzene, bromobenzene and iodobenzene react with sodium or potassium amide in liquid ammonia solution at  $-33^{\circ}$  to give approximately 50 per cent of aniline, along with smaller amounts of diphenylamine, triphenylamine and p-aminobiphenyl. They also observed that potassium anilide and potassium diphenylamide under the same conditions failed to react with chlorobenzene and bromobenzene, unless potassium amide was added. Potassium diphenylmethide and potassium triphenylmethide reacted very slowly with chlorobenzene in liquid ammonia solution at  $-33^{\circ}$ ; however, slow addition of potassium amide caused a marked increase in the reaction rate. The products were triphenylmethane and tetraphenylmethane, respectively. Potassium diphenylmethide was found to catalyze the reaction of potassium diphenylamide with chlorobenzene, possibly owing to the formation of amide ion through the following equilibrium:

$$(C_6H_5)_2CHK + NH_3 \rightleftharpoons (C_6H_5)_2CH_2 + KNH_2$$

Since potassium diphenylmethide  $(pK_a = 34)^3$  is a weaker base than potassium amide  $(pK_8 = 36)^3$ , the equilibrium would be expected to lie far on the left.

Bergstrom and co-workers<sup>4,5,6</sup> have reported that quinaldine, lepidine,  $\alpha$ -picoline, o-tolunitrile, acetonitrile and fluorene can be phenylated with chlorobenzene and bromobenzene in the presence of potassium amide in liquid ammonia as follows:

$$\mathrm{RCH}_{3} \xrightarrow[C_{6}\mathrm{H}_{5}\mathrm{X}]{} \mathrm{RCH}_{2}(C_{6}\mathrm{H}_{5}) + \mathrm{RCH}(C_{6}\mathrm{H}_{5})_{2} + \mathrm{RC}(C_{6}\mathrm{H}_{5})_{3}$$

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- <sup>6</sup> R. A. Seibert and F. W. Bergstrom, J. Org. Chem. 10, 544 (1945).
   <sup>6</sup> P. W. Bergstrom and R. Agostinho, J. Amer. Chem. Soc. 67, 2152 (1945).
   <sup>6</sup> P. H. Dirstine and F. W. Bergstrom, J. Org. Chem. 11, 55 (1946).

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 <sup>1</sup> F. S. Bergstrom, R. E. Wright, C. Chandler and W. Gilkey, J. Org. Chem. 1, 170 (1936).
 <sup>3</sup> R. E. Wright and F. W. Bergstrom, J. Org. Chem. 1, 179 (1936).
 <sup>3</sup> J. B. Conant and G. W. Wheland, J. Amer. Chem. Soc. 54, 1212 (1932).



Recently Leake and Levine<sup>7</sup> have shown that ketones can be similarly phenylated in liquid ammonia with the aid of potassium amide.

In all the above-mentioned reactions, aniline, diphenylamine and triphenylamine are formed as side-products. The formation of the various products can be easily rationalized on the assumption that the metallic amides dehydrohalogenate the aryl halide molecules with the formation of benzyne (I), which is then attacked by the various nucleophilic agents present in competition with amide ions. The purpose of this research was to establish whether the elimination-addition mechanism is involved



and, if so, to determine whether nucleophilicity or base strength determines the ease of attack of a given species on the benzyne intermediate.

In determining whether the reaction between aryl halides with nucleophilic agents with potassium amide in liquid ammonia proceeds through a benzyne intermediate, advantage was taken of the fact that substitutions by the elimination-addition mechanism invariably lead to rearrangement with tolyl halides or with isotopically labeled phenyl halides. The reaction between potassium triphenylmethide and chlorobenzene[1-<sup>14</sup>C] was first considered, since, if a way could be found to degrade the resulting isotopically labeled tetraphenylmethane to triphenylacetic acid, it would be possible to determine whether the reaction proceeded with rearrangement or by direct substitution. However, no successful degradation scheme was found for conversion of tetraphenylmethane to triphenylacetic acid.

The reaction between sodium phenylacetylide and aryl halides was investigated next. Diphenylacetylene was obtained in 26 per cent yield from the reaction of sodium phenylacetylide with bromobenzene. When *p*-bromotoluene was substituted for bromobenzene, the reaction product contained, besides small amounts of 3- and 4-methyldiphenylacetylenes, large amounts of diaryl- and triaryl-amines. Attempts to determine the ratio of the two acetylenes by oxidative degradation to a mixture of benzoic and toluic acids did not lead to satisfactory results, for it was found that the oxidation did not proceed quantitatively. Finally the phenyltolylacetylenes were separated from the other products by elution with hexane through an alumina column and analyzed by means of infrared spectroscopy. The reaction between sodium

<sup>7</sup> W. Leake and R. Levine, Chem. & Ind. (Rev.) 37, 1160 (1955).

phenylacetylide and o-bromotoluene was investigated in a similar way. In both cases, the reaction appeared to proceed through a benzyne intermediate, the isomer ratios of the phenyltolylacetylenes agreeing rather closely with the isomer ratios obtained in the amination of the corresponding halotoluenes.\*8 The results are summarized in Table 1.

In order to see whether nucleophilicity or base strength determines the ease of attack of an anion on benzyne, bromobenzene was treated with a variety of nucleophilic agents in the presence of potassium amide in liquid ammonia. The conditions and yields are summarized in Table 2. For the various nucleophiles, the relative yields of substitution products are considered to provide a rough measure of the competitive powers of the nucleophiles relative to amide ion. The complexity of the reactions makes more accurate measurements of competition factors difficult. The

$CH_3$ $X + Y^{\Theta} \xrightarrow{K N H_2} CH_3$ $Y$					
Isomer	x	Y <sup>o</sup>	Ortho (per cent)	Meta (per cent)	Para (per cent)
p	Br	C₅H₅C≡C <sup>⊙</sup>	0	57	43
0	Br	$NH_2^{\odot}$ $C_6H_6C \equiv C^{\odot}$	0 49	62 51	48 ; 0
	Br	NH₂ <sup>⊙</sup> *	48.5	51.5	0

TABLE 1. ORIENTATION IN THE REACTION OF HALOTOLUENES WITH PHENYLACETYLIDE AND AMIDE IONS

\* Data from Roberts et al.8

data of Table 2 clearly prove that, on the whole, benzyne shows a considerable lack of selectivity in its addition reactions. This is consonant with a high degree of exothermicity<sup>9</sup> in such additions, as would be expected from the substantial angle strain of (I).

It is evident from the data of Table 2 that the base strength is not the sole determining factor in the attack of a nucleophilic species on benzyne, for triphenylmethane, aniline, fluorene, acetophenone and thiophenol, whose  $pK_a$  values range from 33 to 8.4, give rather comparable yields of products. Similarly, it is not possible directly to correlate nucleophilicity with ease of attack on benzyne, for while nucleophilicity decreases in the following order:<sup>10</sup>  $C_6H_5S^- > I^- > CN^- > (CH_3)_3CO^- > C_6H_5O^-$ , the ease of attack on benzyne appears to decrease in the following order:  $C_6H_5S^- > C_6H_5O^- > I^-, CN^-, (CH_3)_3CO^-.$ 

The nucleophilic order mentioned above for various anions was determined with

<sup>\*</sup> Further indication that rather different nucleophiles may attack benzyne-type intermediates to give similar product ratios is provided by the results of Huisgen et al. [cf. Angew. Chem. 69, 389 (1957)], on the reactions which proceed by an elimination-addition mechanism of 1-halonaphthalenes with organolithium compounds and the lithium salts of secondary amines. In each case 1- and 2-substituted naphthalenes were formed in approximately equal ratios, despite the marked differences in the character of the addends.

<sup>&</sup>lt;sup>8</sup> J. D. Roberts, C. W. Vaughan, L. A. Carlsmith and D. A. Semenow, J. Amer. Chem. Soc. 78, 611 (1956). <sup>9</sup> G. S. Hammond, J. Amer. Chem. Soc. 77, 334 (1955).
 <sup>10</sup> A. Streitwieser, Jr., Chem. Rev. 56, 571 (1956).

aliphatic halides as substrates, and, since the transition state for attack of an anion on benzyne is almost certainly different in nature from the transition state in  $S_N^2$  reactions, it is perhaps not surprising that the order of reactivity is different. An additional complication is possibly provided by the differences in solvent used in the benzyne-type reactions and those employed in determining the nucleophilicities toward alkyl halides.

Of very considerable significance is the fact that amide ions and alkoxide ions appear to be much less effective competitors relative to the rather less powerfully basic, but unsaturated, phenolate, pyrrolate and thiophenolate ions than might reasonably be expected. Amide and alkoxide ions are relatively small anions with

TABLE 2. REACTION OF STRONG BASES AND NUCLEOPHILIC AGENTS WITH BROMOBENZENE

$C_6H_bBF + R^\circ  C_6H_bR + BF^\circ$ $NH_3$					
R—H	р <i>К</i> в	Reaction time (hr)	Mole ratio RH/C₀H₅Br	Yield (per cent)	
Ammonia*	36		0.7–1.5	56	
Triphenylmethane	33	4-25	0.33	39	
Aniline†	27		! _ !	57	
Fluorene	25	5.0	0.5	58‡	
Phenylacetylene	21	0.75	4.0	26	
Acetophenone§	19		· ·	28	
tertButyl alcohol	18	0.75	2.0	0	
Pyrrole	16.5	3.0	1.6	~1	
Phenol	10.0	2.5	1.0	~4	
Thiophenol	8-4	3.5	1.0	42	
Hydrogen cyanide	9.1	4.0	1.8	0	
Hydrogen iodide	<0	8.0	6.2	0	

$$C_{6}H_{8}Br + R^{\ominus} \xrightarrow{NH_{2}^{\ominus}} C_{6}H_{8}R + Br^{\ominus}$$

\* Data from Bergstrom et al.<sup>1</sup>

<sup>†</sup> Data from Wright and Bergstrom.<sup>2</sup>

<sup>±</sup> Combined yield of 9-phenyl- and 9,9-diphenylfluorene.

§ Data from Leake and Levine.7

concentrated charges presumably rather tightly solvated by ammonia molecules. The unsaturated anionic nucleophiles may be more reactive toward benzyne, because their relatively dispersed charges are more loosely solvated by ammonia molecules at the reactive site, thus reducing the degree of steric hindrance to attack on benzyne. In order that a factor of this sort dominant over the effects usually important in nucleophilic substitution, it is necessary that activation energies for addition to benzyne be small.<sup>9</sup>

#### EXPERIMENTAL

General procedure for reactions of nucleophilic agents with aromatic halides in the presence of alkali amides in liquid ammonia

The apparatus used for the reaction of various nucleophilic agents with aromatic halides in the presence of alkali amides in liquid ammonia was similar to that used by Schlatter<sup>11</sup> for the preparation of *cyclopropyl* cyanide. A 11. three-necked

<sup>11</sup> M. J. Schlatter, J. Amer. Chem. Soc. 63, 1733 (1941).

flask was fitted with a ball-and-socket sealed mechanical stirrer, a condenser containing solid carbon dioxide, and a tube extending to the bottom of the flask. A second 2 l. three-necked flask was fitted with a ball-and-socket sealed mechanical stirrer, a short inlet tube and a condenser containing solid carbon dioxide connected to a drying tower. The condenser attached to the 1 l. flask was connected by means of rubber tubing to a T-tube, through which flowed a very gentle stream of dry nitrogen.

After the apparatus had been thoroughly dried by flashing with a Bunsen burner and flushing with dry nitrogen, the two condensers were filled with acetonesolid carbon dioxide mixture, and the required amounts of liquid ammonia were condensed in the two flasks. Traces of water in the liquid ammonia were removed by adding small amounts of sodium or potassium metal until the blue color in the solution persisted for at least 1 min. Sodium or potassium amide was prepared in both flasks through the reaction of the required amounts of alkali metals with liquid ammonia in the presence of a small amount of anhydrous ferric chloride. The appropriate active hydrogen compound was added to the 21. flask and 15-30 min were allowed for the establishment of the following equilibrium, which in most cases was far to the right:

### $RH + MNH_2 \rightleftharpoons RM + NH_3$

The aryl halide was then added to the 2 l. flask and the tubes attached to the two flasks were connected by means of rubber tubing. The alkali amide solution (or slurry, in the case of sodium amide) was forced slowly in small amounts from the 1 l. flask into the 2 l. flask by momentarily closing the outlet tube of the nitrogen stream. In a few cases, a Fisher Electric Hosecock, operated by a solenoid timer, was advantageously employed. After all the amide had been added, the reaction mixture was set aside for various periods of time, and then the unreacted bases were decomposed by careful addition of an excess of ammonium chloride or water. The reaction flask was opened to the atmosphere and the liquid ammonia was allowed to evaporate overnight. The residue was mixed with an organic solvent and water, and the products were isolated as described below.

#### Tetraphenylmethane

Potassium amide (0.46 mole) in 500 ml of liquid ammonia was added during 41 hr to a solution of potassium triphenylmethide (0.10 mole) and bromobenzene (0.30 mole) in 500 ml of liquid ammonia. The reaction mixture was set aside for 30 min, then an excess of ammonium chloride was added and the solvent was allowed to evaporate. The solid residue was taken up in hot benzene and water. The organic layer was washed several times with dilute mineral acid and water and then filtered. The solvent was evaporated; the residue was washed several times with small amounts of ether and recrystallized from benzene. The yield of tetraphenylmethane, m.p.  $282.5-283.5^\circ$ , was 10.0 g (31 per cent).

### Diphenylacetylene

Sodium amide (0.62 mole) in 500 ml of liquid ammonia was added during 45 min to a solution of sodium phenylacetylide (0.93 mole) and bromobenzene (0.62 mole) in 500 ml of liquid ammonia. The reaction mixture was set aside for 30 min, an excess of ammonium chloride was added and the solvent was allowed to evaporate. The residue was dissolved in ether and water; the organic layer was washed several times with dilute hydrochloric acid and water. The ether was evaporated, and the unreacted phenylacetylene and bromobenzene were removed by distillation under reduced pressure.

The residue was dissolved in low-boiling light petroleum (boiling range  $30-60^{\circ}$ ); a small amount of an insoluble blue material was removed by filtration, and the solution was passed through a column packed with 250 g of acid-washed alumina which had been activated by being heated for 30 min to a dull red color in a nitrogen atmosphere. Diphenylacetylene (11.0 g, 26 per cent), m.p.  $51-60^{\circ}$ , was obtained by evaporation of the eluate. The product was identified by comparison of its infrared and ultraviolet spectra with those of an authentic sample.

Attempts to prepare anisylphenylacetylenes and trifluoromethyldiphenylacetylenes through the reactions of *o*-bromoanisole and *o*-chlorotrifluoromethylbenzene led only to undistillable tarry materials.

# Reaction of p-bromotoluene with sodium phenylacetylide in the presence of potassium amide in liquid ammonia

Potassium amide (0.38 mole) in 300 ml of liquid ammonia was slowly added during  $1\frac{1}{2}$  hr to 1 l. of liquid ammonia containing 0.72 mole of sodium phenylacetylide and 0.26 mole of distilled *p*-bromotoluene. After all the potassium amide had been added, the mixture was set aside for 30 min and then treated with an excess of ammonium chloride, and the solvent was allowed to evaporate overnight. The solid residue was dissolved in dilute hydrochloric acid and pentane. The organic layer was washed several times with dilute hydrochloric acid and water, then it was dried over anhydrous magnesium sulfate and the solvent was evaporated on a steam bath. The residue was distilled through a semimicro column<sup>12</sup> to 40° (2 mm) to remove phenylacetylene and *p*-bromotoluene.

Since preliminary experiments had shown that the diarylamines present in the product could not be removed either by distillation through a 100 cm spinning-band column or by extraction with concentrated mineral acid, the residue after the distillation was eluted with hexane through a  $3.4 \times 30$  cm column packed with acid-washed alumina that had been activated by being heated at 125° for 12 hr in vacuo. 3-Methyland 4-methyl-diphenylacetylene were eluted completely with 31. of solvent. A succeeding 1 l. fraction contained no high-boiling residue. The solvent was evaporated; an infrared spectrum of the residue showed the presence of only 3- and 4-methyldiphenylacetylene contaminated with a small amount of p-bromotoluene. The product was again eluted with 1 l. of carbon tetrachloride through a  $2 \times 20$  cm column packed with alumina that had been activated by the above-mentioned method to remove some silicon grease that contaminated the product. After the carbon tetrachloride had been removed by evaporation, 7.8 g (16 per cent) of a mixture of 3- and 4-methyldiphenylacetylenes containing some p-bromotoluene was obtained. This mixture was analyzed by using a Perkin-Elmer (Model 21) Infrared Spectrophotometer at 12.28, 12.48 and 12.85  $\mu$  with the aid of calibration graphs constructed from the absorptions of the pure constituents at each wavelength. Cells 0.1 mm thick were used and the solvent was carbon disulfide. Known mixtures were found to be analyzable to  $\pm 2$  per cent and showed no change in composition when passed through an alumina column in hexane solution. The reaction mixture was found to

<sup>18</sup> C. W. Gould, Jr., G. Holzmann and C. Niemann, Analyt. Chem. 20, 361 (1948).

contain 3- and 4-methyldiphenylacetylenes in the ratio of 57 to 43 and 15 per cent of p-bromotoluene.

Preparation of authentic samples of 3- and 4-methyldiphenylacetylenes will be described below.

## Reaction of o-bromotoluene with sodium phenylacetylide in the presence of potassium amide in liquid ammonia

The reaction of o-bromotoluene with sodium phenylacetylide in the presence of potassium amide in liquid ammonia was carried out as with the p-isomer.

The crude product, after the starting materials had been removed by distillation, was eluted with hexane through a column containing 300 g of activated alumina. Both 2- and 3-methyldiphenylacetylene were completely eluted with 21. of solvent. An infrared analysis showed that small amounts of o-bromotoluene and aliphatic hydrocarbons (probably from impurities in the hexane) were present along with the two acetylenes.

An elemental analysis showed that the bromine content of the mixture was 1.65 per cent, which corresponds to 3.5 per cent of *o*-bromotoluene.

A carbon disulfide solution of the mixture, containing 42.9 mg of the mixture per g of solution, was analyzed by infrared spectroscopic procedures with the aid of a calibration curve for 3-methyldiphenylacetylene at  $12.85 \mu$  and found to contain 19.8 mg of 3-methyldiphenylacetylene (46 per cent of the mixture). Since none of the other components absorbed in the region of the spectrum used to determine the concentration of this compound, the error in the analysis was probably no more than 2 per cent. No direct determination of 2-methyldiphenylacetylene could be made, since no suitable peak was found in the infrared spectrum.

The infrared absorption of the three methyldiphenylacetylenes are practically identical in the  $3\cdot0-3\cdot7\mu$  region of the infrared spectrum. The amount of aliphatic hydrocarbons present in the mixture was estimated roughly by spectroscopic analysis of solutions of 3-methyldiphenylacetylene and hexane in carbon disulfide in different proportions and at different concentrations. When the 3-methyldiphenylacetylene to hexane ratio was 95 to 5, the spectra of the above mixture and the mixture obtained from the reaction of *o*-bromotoluene and phenylacetylene matched very closely. The amount of 2-methyldiphenylacetylene present in the mixture was then obtained by difference. The composition (by weight) was estimated to be: 46 per cent of 3-methyldiphenylacetylene, 45 per cent of 2-methyldiphenylacetylene, 4 per cent of *o*-bromotoluene and 5 per cent of aliphatic hydrocarbons. The ratio of 3- to 2-methyldiphenylacetylene was 51 to 49.

#### 2-Methyl-, 3-methyl- and 4-methylstilbenes

4-Methylstilbene was prepared by the method of Meerwein *et al.*<sup>13</sup> From 70 g (0.65 mole) of *p*-toluidine and 90 g (0.61 mole) of cinnamic acid there was obtained, after one recrystallization from ethanol, 33.0 g (24 per cent) of 4-methylstilbene; m.p.  $118-120.5^{\circ}$  (m.p.  $119.5^{\circ 14}$ ).

3-Methylstilbene was prepared by the same method in 17 per cent yield; after two recrystallizations from methanol, the m.p. was  $40-45^{\circ}$  (m.p.  $48^{\circ 14}$ ).

<sup>&</sup>lt;sup>18</sup> H. Meerwein, E. Büchner and J. van Emster, J. Prakt. Chem. 152, 237 (1939).

<sup>&</sup>lt;sup>14</sup> F. Bergman and D. Shapiro, J. Org. Chem. 12, 57 (1949).

2-Methylstilbene was prepared by the same method in 5 per cent yield; b.p. 125-140° (1 mm) [b.p. 125° (0.15 mm <sup>14</sup>)].

#### 2-Methyl-, 3-methyl- and 4-methyldibromostilbenes

4-Methyldibromostilbene was prepared by the method described in Organic Syntheses.<sup>15</sup> From 33 g (0.17 mole) of 4-methylstilbene was obtained 35 g of crude product, m.p. 184–187°. Upon evaporation of the mother liquors, 1.0 g of additional product, m.p. 194–196.5°, was obtained. The yield of pure 4-methyldibromostilbene was 31.0 g (51.5 per cent); m.p. 199–200° (m.p. 188°<sup>14</sup>). Since the m.p. of the product was appreciably different from the one reported in the literature, the product was submitted for elemental analysis. Anal. Calcd. for C<sub>15</sub>H<sub>14</sub>Br<sub>2</sub>: C, 50.88; H, 3.98; Br, 45.14. Found: C, 50.78; H, 4.05; Br, 45.16.

3-Methyldibromostilbene was prepared by the same method in 70 per cent yield; m.p. 182-183°. Anal. Calcd. for  $C_{15}H_{14}Br_2$ : C, 50.88; H, 3.98; Br, 45.14. Found: C, 51.00; H, 4.04; Br, 45.12.

2-Methyldibromostilbene was prepared by the same method in 55 per cent yield; m.p.  $159-161^{\circ}$  (m.p.  $159^{\circ 14}$ ).

#### 2-Methyl-, 3-methyl- and 4-methyldiphenylacetylene

4-Methyldiphenylacetylene was prepared by the general method described in Organic Syntheses.<sup>15</sup> From 31 g (0.0865 mole) of 4-methyldibromostilbene was obtained 16 g (96 per cent) of 4-methyldiphenylacetylene, m.p.  $71.5-72.5^{\circ}$ . After one sublimation *in vacuo*, the m.p. of the product was raised to  $72.5-73.5^{\circ}$ . Anal. Calcd. for C<sub>15</sub>H<sub>14</sub>: C, 93.71; H, 6.29. Found: C, 93.74; H, 6.23.

3-Methyldiphenylacetylene was prepared by the same method in 76.5 per cent yield from 3-methyldibromostilbene; b.p. 126–128° (2 mm), m.p. 30–31°. Anal. Calcd. for  $C_{15}H_{12}$ : C, 93.71; H, 6.29. Found: C, 93.78; H, 6.25.

2-Methyldiphenylacetylene was prepared by the same method in 92 per cent yield from 2-methyldibromostilbene; b.p. 120–122° (2 mm). The product was further purified by elution with hexane through a column packed with acid-washed alumina and very slow distillation at 70° in a short-path distillation apparatus. Anal. Calcd. for  $C_{15}H_{12}$ : C, 93.71; H, 6.29. Found: C, 93.58; H, 6.43.

### Reaction of potassium pyrrolate with bromobenzene in the presence of potassium amide in liquid ammonia

Potassium amide (0.45 mole) in 500 ml of liquid ammonia was added during 3 hr to a solution containing 0.5 mole of potassium pyrrolate and 0.311 mole of bromobenzene in 600 ml of liquid ammonia. The solvent was allowed to evaporate slowly, so that the total volume of solution was kept approximately constant.

The reaction mixture, after all the potassium amide had been added, was set aside for 45 min, and then an excess of ammonium chloride was added, followed by 500 ml of ether. After the solvents had evaporated, the residue was dissolved in ether and water; the organic layer was washed five times with dilute hydrochloric acid and twice with distilled water. The ether was evaporated and the residue distilled through a semimicro column.<sup>12</sup> One gram of distillate, b.p. 64–70° (1 mm), was collected. This material solidified upon standing; m.p. 53–58°. After a sublimation

<sup>&</sup>lt;sup>6</sup> Organic Syntheses Coll. Vol. III, p. 350. John Wiley, New York (1955).

and three recrystallizations from 70 per cent ethanol, the m.p. was raised to  $59-60^{\circ}$ . The infrared and ultraviolet spectra were identical with those of N-phenylpyrrole; and the m.p. of the product showed no depression when mixed with an authentic sample of N-phenylpyrrole.<sup>16</sup> The yield of crude N-phenylpyrrole was 1.0 g (1.4 per cent).

# Reaction of 9-fluorenylpotassium with bromobenzene in the presence of potassium amide in liquid ammonia

Potassium amide (0.53 mole) in liquid ammonia was added during 5 hr to a solution of 9-fluorenylpotassium (0.229 mole) and bromobenzene (0.45 mole) in 200 ml of ether and 500 ml of liquid ammonia. The reaction mixture was set aside for 15 min, an excess of ammonium chloride was added, and the solvents were allowed to evaporate. The residue was dissolved in benzene and water; the organic layer was washed several times with dilute hydrochloric acid and water, and then the solvent was evaporated.

9-Phenylfluorene is soluble in 95 per cent ethanol to the extent of less than 50 mg/ 100 ml, while 9,9-diphenylfluorene is practically insoluble in the same solvent, so the crude reaction product was digested with 100 ml of 95 per cent ethanol, cooled and washed with 100 ml of 95 per cent ethanol to separate diphenylamine and triphenylamine as well as much of the excess of fluorene. The treatment was then repeated with two 500 ml portions of 95 per cent ethanol. The residual alcohol-

Compound	Concentration (mg/l.)	Absorption (optical-density units)			Amount present in
		301∙5 mµ	305∙0 mµ	310-0 mµ	ture (mg/l.)
Fluorene	231	1.35	0.45	0.03	30
9-Phenylfluorene	378	0.62	1.37	0.14	218
9,9-Diphenylfluorene	464	0.53	0.45	1.13	127
Reaction mixture	375	0.68	0.97	0.40	
		I			

TABLE 3. ANALYSIS OF A MIXTURE OF FLUORENE, 9-PHENYLFLUORENE AND 9,9-DIPHENYLFLUORENE

insoluble product weighed 39.3 g. The strong band at 2.95  $\mu$  of diphenylamine was absent from the infrared spectrum of the product and there was an absorption minimum at 297 m $\mu$  in the ultraviolet spectrum where triphenylamine shows strong absorption.

The mixture was analyzed with the aid of its ultraviolet spectrum in benzene solution by using 1.00 mm cells in a Cary Recording Spectrophotometer (Model 11 M). The results of this analysis are summarized in Table 3. The yield of 9-phenylfluorene was  $22.3 \pm 1.5$  g (40 per cent) and the yield of 9,9-diphenylfluorene was  $13.8 \pm 0.8$  g (18 per cent).

A sample weighing 2.9 g was fractionally sublimed *in vacuo*. A fraction of 1.40 g, which sublimed at a bath temperature of  $80-130^\circ$ , was recrystallized twice from ethanol; its m.p. was  $148.5-149.0^\circ$ . The ultraviolet spectrum of this compound was identical with that of 9-phenylfluorene. The m.p. showed no depression when

mixed with an authentic sample<sup>17</sup> of the above compound. A final fraction of 0.95 g, which sublimed at  $135-170^{\circ}$ , showed m.p. of  $222-224^{\circ}$ , after two recrystallizations from benzene. The m.p. was not depressed when the substance was mixed with an authentic sample of 9,9-diphenylfluorene.<sup>18</sup> The ultraviolet spectrum was identical with that of 9,9-diphenylfluorene.

### Reaction of potassium thiophenolate with bromobenzene in the presence of potassium amide in liquid ammonia

Potassium amide (0.44 mole) in 250 ml of liquid ammonia was added during 3.5 hr to a solution of potassium thiophenolate (0.34 mole) and bromobenzene (0.346 mole) in 700 ml of liquid ammonia. An excess of ammonium chloride was then added and the solvent was allowed to evaporate. The residue was dissolved in water and ether; the organic layer was washed first with dilute hydrochloric acid, then with sodium hydroxide solution and finally with water. It was dried over anhydrous magnesium sulfate; the ether was evaporated and the residue was distilled from a distilling flask. The results of this distillation at a pressure of 3 mm were as follows:

Fraction	1	2	3	4
Temperature (°C)	120-128	128–136	136–144	144–164
Weight (g)	7·9	10-4	11.5	11.6

The ultraviolet spectra of the first three fractions showed them to consist mostly of diphenyl sulfide; the infrared spectra showed the presence of diphenylamine. The infrared and ultraviolet spectra of fraction 4 were similar to the corresponding spectra of pure diphenyl disulfide.

The first three fractions were combined and found by combustion analysis to contain 16.79% sulfur and 0.55% nitrogen. From these data, the combined first three fractions were calculated to consist of 89% diphenyl sulfide, 5% diphenyl disulfide and 6% diphenylamine. The total amount of diphenyl sulfide present was 26 g (0.14 mole, 41 per cent).

A small amount of the combined first three fractions was oxidized at room temperature with 30% hydrogen peroxide in acetic acid. The resulting product melted at 125°, and showed no m.p. depression when mixed with an authentic sample of diphenyl sulfone. Its infrared and ultraviolet spectra were also identical with those of diphenyl sulfone.

Fraction 4 was found to contain  $21 \cdot 1\%$  sulfur as compared to  $29 \cdot 4\%$  calculated for pure diphenyl disulfide, and may have contained some diphenyl sulfide. This fraction solidified partially after a few days in a refrigerator. The supernatant liquid was removed by filtration; 8 g of a slightly yellow solid, m.p.  $50-56^\circ$ , was obtained. After two recrystallizations from ethanol, the m.p. of the solid was raised to  $60^\circ$ ; no m.p. depression was observed when the solid was mixed with an authentic sample of diphenyl disulfide. Its infrared and ultraviolet spectra were identical with those of diphenyl disulfide. Presumably, the disulfide arises from oxidation of excess of thiophenolate in the isolation procedures.

F. Ullmann and R. von Wusteinberger, Ber. Dtsch. Chem. Ges. 37, 73 (1904).
 W. E. Bachmann, J. Amer. Chem. Soc. 55, 2135 (1933).

## Reaction of potassium phenolate with bromobenzene in the presence of potassium amide in liquid ammonia

Potassium amide (0.64 mole) in 500 ml of liquid ammonia was added to a mixture of 0.5 mole of potassium phenolate and 0.51 mole of bromobenzene in 500 ml of liquid ammonia during 2.5 hr. The solution was set aside for 1 hr, and then the unreacted amides were carefully hydrolyzed with 20 ml of water. Water (750 ml) was added, and the mixture was extracted with two 300 ml portions of benzene. The combined extracts were washed successively with 500 ml of 2% sodium hydroxide, two 500 ml portions of 2% hydrochloric acid and water. The organic layer was dried over anhydrous magnesium sulfate and distilled through a semimicro column.<sup>12</sup> The amount of bromobenzene recovered was 15 g (0.095 mole).

The fraction (3.8 g) of b.p. 76–108° (2 mm) was shown to contain diphenylamine and diphenyl ether by its ultraviolet and infrared spectra. A ferric chloride test was positive, indicating the presence of some phenol. The mixture was analyzed by means of its ultraviolet spectrum in 95% ethanol and shown to contain about 78% diphenyl ether, 14% diphenylamine and 7% phenol (by difference). The yield of diphenyl ether was 3.0 g (3.5 per cent or 4.2 per cent based on unrecovered bromobenzene).

Part of the product (1.2 g) was dissolved in anhydrous ether and treated with anhydrous hydrogen chloride. Diphenylamine hydrochloride was removed by filtration; the filtrate was washed with a dilute sodium hydroxide solution to remove the phenol present and dried over anhydrous magnesium sulfate. The solvent was removed and the residue was nitrated by the method of Matsumara.<sup>19</sup> The resulting 4-nitro-diphenyl ether, after four recrystallizations from acetic acid, showed m.p. 194–196°, 195–197°<sup>19</sup>.

## Attempted reaction of potassium tert.-butoxide with bromobenzene in the presence of potassium amide in liquid ammonia

A suspension of sodium amide (0.6 mole) in 250 ml of liquid ammonia was added during 45 min to a solution of potassium *tert*.-butoxide (1.2 mole) and bromobenzene (0.6 mole) in 750 ml of liquid ammonia. The solution was set aside for 1 hr, the unreacted bases were decomposed by dropwise addition of water and the solvent was allowed to evaporate. The residue was dissolved in ice-cold water and ether; the organic layer was washed three times with an ice-cold solution of 0.5% hydrochloric acid and then with a solution of potassium carbonate. The basic water extract was treated with bromine water, but no precipitate formed.

The ether layer was washed with cold water, dried over anhydrous magnesium sulfate and distilled. Seventeen grams of bromobenzene was recovered. The product that distilled next was diphenylamine. No *tert*.-butyl phenyl ether was detected.

### Attempted reaction of sodium cyanide with bromobenzene in the presence of sodium amide in liquid ammonia

Anhydrous sodium cyanide (0.81 mole) and 0.45 mole of bromobenzene were added to 700 ml of liquid ammonia. A suspension of 0.652 mole of sodium amide in liquid ammonia was added in small portions during 4 hr. The unreacted sodium amide was neutralized with an excess of ammonium chloride. The solvent was evaporated with a stream of nitrogen and the residue was extracted with ether and water.

<sup>19</sup> K. Matsumara, J. Amer. Chem. Soc. 52, 3199 (1932).

The organic layer was dried over anhydrous magnesium sulfate, the solvent was evaporated and the residue was distilled through a semimicro column.<sup>12</sup> Bromobenzene, aniline, diphenylamine and triphenylamine were collected. The distillation was interrupted because the distillate solidified in the condenser. The residue (7.0 g) was heated under reflux with 100 ml of ethanol containing 10.0 g of potassium hydroxide for 60 hr. The solution was evaporated to dryness under reduced pressure. The residue was dissolved in water, extracted with ether, acidified and again extracted with ether. Evaporation of the ethereal solution gave less than 10 mg of a yellow oil.

## Attempted reaction of potassium iodide with bromobenzene in the presence of potassium amide in liquid ammonia

A solution of 0.436 moles of potassium amide in 500 ml of liquid ammonia was added during 8 hr to a solution of 450 g (2.71 mole) of anhydrous potassium iodide and 79 g (0.5 mole) of bromobenzene. The total volume of solution in the reaction flask was maintained constant by allowing the solvent to evaporate slowly. The unreacted base was neutralized with an excess of ammonium chloride, the solvent was evaporated and the residue was extracted with water and ether. The organic layer was washed several times with dilute mineral acid and water, dried over anhydrous magnesium sulfate and distilled through a semimicro column.<sup>12</sup> Bromobenzene (33.5 g), b.p. 51° (18–19 mm),  $n_D^{20} = 1.5592$ , was collected. An infrared spectrum of this fraction showed the total absence of all the bands characteristic of iodobenzene. The next appreciable fraction was diphenylamine.