

3.02 g (48.0%) of 1,2,4-tribromobenzene, mp 44–44.5° (sample E). Both products were then recrystallized from 95% ethanol.

**Degradation of Sample E.** The methods used were as for degradation of sample A. From 1.0 g of sample E, 0.57 g (76%) of *p*-dibromobenzene, mp 86–87° after two recrystallizations, was obtained. This is sample F. From 1.0 g of sample E, 0.74 g (83%) of 3,4-dibromobenzoic acid, mp 233–234.5°, twice recrystallized from aqueous ethanol, was obtained; this is sample G.

**Isomerization of 1a in the Presence of 2b.** By the procedure described above, a solution of potassium anilide in ammonia (450 ml) was prepared from 0.391 g of potassium metal and 1.86 g of aniline, a solution of 3.15 g of inactive 1a and 1.05 g of sample D in 50 ml of ether was added to it, reaction was allowed to occur for 15 min, and the two tribromobenzenes were separated by chromatography on alumina. Obtained were 0.88 g of 1,3,5-tribromobenzene, mp 119.5–120° (sample H), and 2.68 g of 1,2,4-tribromobenzene, mp 43–43.5° (sample I). Both were recrystallized from 95% ethanol.

**Counting Procedures.** A liquid Geiger-Muller tube (20th Century Electronics, Type M6H) was used. Flatness of the Geiger plateau between applied voltages of 410 and 500 V was established using a <sup>32</sup>P sample. Also, the counter was shown to respond

linearly to the amount of <sup>32</sup>P in the sensitive counter volume (about 8 ml). For <sup>82</sup>Br counting, weighed samples were dissolved in an 80% absolute ethanol–20% acetone solvent, which was then washed into the counter. The solution was made up to 8 ml, to a mark on the counter. For counting the dibromobenzoic acid samples, absolute ethanol was used as solvent. At least 20,000 counts were recorded for each sample. All samples were recrystallized to constant specific activity. Counting rates were referred back to an arbitrary zero time, the time of counting sample A. Other count rates were corrected to zero time<sup>9</sup> by means of the first-order decay formula with attention to the 35.3-hr half-life of <sup>82</sup>Br. Background counts were about 60–100 cpm, and appropriate corrections were made.

**Acknowledgment.** We thank Professor A. L. Odell of the University of Auckland for making the facilities of the Urey Radiochemical Laboratory available to us, and for his valuable advice.

(9) G. Friedlander, J. W. Kennedy, and J. M. Miller, "Nuclear and Radiochemistry," 2nd ed, Wiley, New York, N. Y., 1964, p 541.

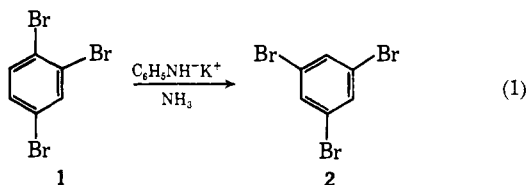
## Factors Limiting the Extent of Isomerization of 1,2,4-Tribromobenzene in the Potassium Anilide–Ammonia System<sup>1</sup>

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**Abstract:** Rates of both the potassium anilide catalyzed isomerization of 1,2,4- to 1,3,5-tribromobenzene and of bromide ion forming side reactions are strongly depressed by aniline. This is attributed in part to repression of aryl anion formation in acid–base equilibria, and in part to complexing with anilide ions to form bianilide ions of reduced activity. 1,3,5-Tribromobenzene is much less soluble than its 1,2,4 isomer in liquid ammonia, and isomer proportions at equilibrium may be predominantly determined by solubilities. However, both isomers are quite soluble in 50% ammonia–50% diethyl ether.

Under the influence of potassium anilide in liquid ammonia or 50% ammonia–50% diethyl ether, 1,2,4-tribromobenzene (**1**) isomerizes to its 1,3,5 isomer **2**.<sup>2–4</sup> The latter isomer does not revert to the former under the same conditions, but reversion does occur, at



least in 50% ammonia–50% ether, if a small amount of 1,2,3,5-tetrabromobenzene is added as a cocatalyst.<sup>4</sup> These reactions find interpretation in the seven-halogen version of the positive halogen transfer mechanism, as sketched in Scheme II of an accompanying paper.<sup>4</sup>

Except for the original report of Wotiz and Huba,<sup>5</sup> isomerization of **1** to **2** had never been observed to go to

completion. Some **1** always remained unconverted. *A priori*, completion of isomerization might be limited either by kinetic factors (such as the consumption of catalyst in side reactions) or by the attainment of a state of equilibrium. Evidence that the transformation of **1** to **2** is reversible providing that 1,2,3,5-tetrabromobenzene or similar substance is supplied as a cocatalyst has been presented,<sup>4</sup> and it is known that disproportionation of **1** to di- and tetrabromobenzenes occurs on exposure to potassium anilide.<sup>3,4</sup> It is therefore plausible that equilibrium between **1** and **2** may be attained with cocatalysis by internally generated tetrabromobenzene.

Nevertheless puzzling was the great variability in the extent of isomerization of **1** to **2** observed in ammonia or ammonia–ether systems. Thus, in experiments of Moyer,<sup>3,6</sup> all seemingly conducive to isomerization, the final ratio of **2**:**1** varied from as low as 0.39 to as high as 9.4. An occasional low conversion (or even complete failure of rearrangement) might be ascribed to the accidental admission of water or CO<sub>2</sub> to the system, but the persistence of variable results despite care to exclude contaminants made that an unlikely cause for the fluctuations observed.

(6) C. E. Moyer, Jr., Ph.D. Dissertation, Brown University, 1964; *Diss. Abstr.*, 25, 4412 (1965).

(1) Support by the National Science Foundation is gratefully acknowledged.

(2) C. E. Moyer, Jr., and J. F. Bunnett, *J. Amer. Chem. Soc.*, 85, 1891 (1963).

(3) J. F. Bunnett and C. E. Moyer, Jr., *ibid.*, 93, 1183 (1971).

(4) J. F. Bunnett and G. Scorrano, *ibid.*, 93, 1190 (1971).

(5) J. H. Wotiz and F. Huba, *J. Org. Chem.*, 24, 595 (1959).

**Table I.** Reactions of Tribromobenzenes with Potassium Anilide in Refluxing Ammonia or Ammonia-Ether Mixtures

Run no.	$C_6H_3Br_3$		Ether in solvent, % (v/v)	$[C_6H_5NHK]$ , $[C_6H_5NH_2]^a$		$[C_6H_2Br_4]^b$	Reaction time, hr	1,3,5/1,2,4 isomer ratio	$C_6H_3Br_3$ recovered, %	$Br^-$ , % <sup>c</sup>
	Initial configuration	Concn, M		M	M					
1a	1,2,4	0.019	0	0.022	0.016		0.5	7.2	76	31
1b	1,2,4	0.019	0	0.020	0.018		2.0	7.2	66	39
2a	1,2,4	0.095	0 <sup>d</sup>	0.100	0.092		2.0	500	73	27
2b	1,2,4	0.095	0 <sup>d</sup>	0.102	0.090		4.0	500	74	23
3a	1,2,4	0.019	50	0.056	0.048		0.5	1.19	94	14
3b	1,2,4	0.019	50	0.055	0.049		2.0	1.25	67	33
4a	1,3,5	0.019	0	0.061	0.069	0.0006	1.0	∞	98	15
4b	1,3,5	0.019	0	0.063	0.067	0.0006	2.0	∞	87	19
5a	1,3,5	0.019	50	0.022	0.016	0.0005	1.0	1.85	75	24
5b	1,3,5	0.019	50	0.023	0.015	0.0005	2.0	1.85	71	27
6a	1,2,4	0.019	50	0.024	0.014	0.0005	1.5	1.52	70	33
6b	1,3,5	0.019	50	0.020	0.018	0.0005	1.5	1.72	84	23
7a	1,2,4	0.019	0	0.042	0	0.0005	1.0	4.2	29	86
7b	1,2,4	0.019	0	0.040	0.134	0.0005	1.0	2.3	91	23
8a	1,3,5	0.019	0	0.056	0.004		2.0	∞	67	44
8b	1,3,5	0.019	0	0.061	0.059		2.0	∞	88	19
9a	1,3,5	0.019	50	0.025	0.013	0.0006	1.5	1.79	60	34
9b	1,3,5	0.019	50	0.020	0.018	0.0006 <sup>e</sup>	1.5	1.72	69	36

<sup>a</sup>  $C_6H_5NH_2$  remaining after formation of  $C_6H_5NHK$ . <sup>b</sup> 1,2,3,5-Tetrabromobenzene unless otherwise specified. <sup>c</sup> Based on one  $Br^-$  per  $C_6H_3Br_3$  as 100%. <sup>d</sup> 100 ml of solvent used instead of the usual 500 ml. <sup>e</sup> 1,2,4,5-Tetrabromobenzene.

The present experiments were addressed to gaining an understanding of the factors governing the extent of isomerization.

## Results

**Retardation by Aniline.** Earlier experiments<sup>3,6</sup> had indicated that the extent of isomerization of **1** to **2** and the recovery of tribromobenzenes were substantially as great after, say, 0.5-hr reaction as after 8 hr. In giving further attention to this phenomenon we set up experiments in pairs, two runs being performed side by side with care to maintain all factors the same in both flasks except the one variable under study. Several pairs of experiments are summarized in Table I. Runs 1a and 1b comprise a pair, etc.

The data in Table I show that the side reactions releasing bromide ion tend to proceed to a certain point and then stop. According to the balanced equation (eq 2),<sup>7</sup> reaction of potassium anilide with a tribromo-

$$C_6H_3Br_3 + 2C_6H_5NHK \longrightarrow C_6H_3Br_3NH-K^+ + KBr + C_6H_5NH_2 \quad (2)$$

benzene should form half as much bromide ion as potassium anilide supplied as long as the supply of aryl bromide is sufficient. However, the observed yields are much less than the expectation. For example, one would anticipate the yields of bromide ion (on the basis of one  $Br^-$  per  $C_6H_3Br_3$  molecule) to be 53% for runs 2a-2b whereas 27 and 23% were observed, and one would expect 100%  $Br^-$  for runs 3a-3b whereas only 14 and 33% were produced. Moreover, with one possible exception, yields of  $Br^-$  among the first five pairs of runs are scarcely greater when the reaction time is doubled. The possible exception concerns pair 3a-3b, for which the base is in excess, solubility is very favorable, and the reaction time for 2b is four times that for 2a.

Runs 6a-6b involve 1,2,4- and 1,3,5-tribromobenzenes reacting under identical conditions, including co-

(7) Unpublished experiments (of I. N. Feit) show that the chief nitrogenous products are dibromoanilines, which are stronger Brønsted acids than aniline.

catalysis by 1,2,3,5-tetrabromobenzene. The ratios of 1,3,5 to 1,2,4 isomer attained were 1.52 starting from the 1,2,4 and 1.72 starting from the 1,3,5 isomer. This substantiates a previous estimate<sup>4</sup> that the 1,3,5/1,2,4 ratio at equilibrium in 50% ammonia-50% ether is about 1.6. In cases where equilibrium was not attained (pairs 3a-3b and 5a-5b), doubling or quadrupling the reaction time caused little further progress to equilibrium. Thus isomerization, as well as bromide release, tends to stop even though base remains in the system.

The possibility that a side reaction (e.g., oxidation) destroys the base is excluded by the fact that a solution of potassium anilide in ammonia that had been allowed to stand at reflux for 2 hr gave the same bromide ion yield from **2** as when a freshly prepared solution was used. Also, it was found possible to recover 99% of the aniline introduced into a typical reaction.

A possible clue was the previously noted indication that aniline retards the reaction.<sup>4</sup> The effect of aniline concentration was therefore investigated, in runs 7a-7b and 8a-8b. In both pairs of runs, bromide ion release was sharply decreased by having aniline present in high concentration. Also, in 7a-7b, the extent of isomerization was considerably less when excess aniline was present.

Runs 9a-9b show that 1,2,4,5-tetrabromobenzene is about as effective as its 1,2,3,5 isomer as a cocatalyst for isomerization of **2**.

**Solubility Effects.** In the exploratory investigation of Moyer,<sup>2,3,6</sup> the solvent was liquid ammonia except for small but unmeasured amounts of diethyl ether usually used to wash trihalobenzene reactants into the reaction flask. Precipitates were often present in reaction mixtures,<sup>3,6</sup> but time did not permit investigation of the kinetic or thermodynamic consequences they might have. Clearly, the equilibrium ratio of two isomers would be affected by solubility factors if one isomer were soluble and the other insoluble in the reaction medium.

The solubilities of **1** and **2** in refluxing liquid ammonia and certain ammonia-ether mixtures have now been determined. Results are set forth in Table II.

**Table II.** Solubilities of Tribromobenzenes in Refluxing Ammonia and Ammonia-Ether Mixtures

Diethyl ether, % (v/v)	Stirring time, hr	Concn in solution, g/l. <sup>a</sup>	
		1,2,4	1,3,5
0	1.0	3.0 ± 0.6	0.38 ± 0.08
	3.5	3.6 <sup>b</sup>	0.38 ± 0.23
25	2.5	14.1 ± 0.1	1.85 ± 0.17
50	1.5	29.4 ± 0.6	6.0 ± 0.4
	3.5	29.0 ± 0.2	7.0 ± 0.2

<sup>a</sup> Except as noted, each determination was performed in triplicate.

<sup>b</sup> Single determination.

The results show that **1** is more soluble than **2** and that both compounds are more soluble in solvents with greater proportions of ether. Under conditions normally used in this and in previous studies,<sup>2, 3, 6</sup> **1** is largely soluble and **2** largely insoluble in liquid ammonia. However, unless the concentration of **2** at equilibrium exceeds 0.022 *M*, both isomers are completely soluble in 50% ammonia-50% ether. Therefore under most conditions the equilibrium proportions of **1** and **2** for reactions run in ammonia should be strongly shifted toward **2** by the low solubility of the 1,3,5 isomer, but the equilibrium proportions in 50% ammonia-50% ether should be unaffected by solubility factors. It is also conceivable that small but variable amounts of ether in ammonia media might appreciably affect the isomer proportions at equilibrium.

The actual effect of solubility on the isomer ratio was observed in two ways. First, the effect of added ether in the solvent was studied systematically by running reactions side by side as described previously. Some results are given in Table III.

**Table III.** Effect of Diethyl Ether on the Rearrangement of 1,2,4-Tribromobenzene with Potassium Anilide in Refluxing Ammonia<sup>a</sup>

Run no.	Diethyl ether, % (v/v)	1,3,5:1,2,4 isomer ratio	C <sub>6</sub> H <sub>3</sub> Br <sub>3</sub> recovd, %
10a	0	1.21	79
10b	10	4.2	84
11a	10	3.2	72
11b	20	2.2	80
12a	20	2.9	82
12b	30	1.43	78
13a	10	2.6	84
13b	50	1.12	83

<sup>a</sup> Conditions: total solvent volume, 500 ml; 1.9-2.4 × 10<sup>-2</sup> *M* potassium anilide; 1.4-1.9 × 10<sup>-2</sup> *M* aniline; 1.9 × 10<sup>-2</sup> *M* (3 g) tribromobenzene); 0.5-hr reflux.

The added ether had the expected effect of decreasing the ratio of 1,3,5 to 1,2,4 isomer as long as at least 10% ether was present. The low 1,3,5:1,2,4 ratio observed in neat ammonia (run 10a) undoubtedly represents incomplete equilibration owing to kinetic limitations. It should be noted that in other experiments (runs 1a-1b and 2a-2b, Table I) extensive isomerization of **1** occurred in neat ammonia.<sup>8</sup>

(8) In other, unreported reactions in neat ammonia, in the present study as well as in Moyer's work,<sup>6</sup> the isomer ratio varied considerably. It is conceivable that another factor, perhaps differences in stirring rate or in temperature, affected the concentration of **1** in solution in the early minutes of reaction, and thereby the outcome of competition between reactions of differing kinetic order.

The effect of the solubility difference was verified in another way. It was observed that when **1** was treated with potassium anilide in refluxing ammonia, a thick precipitate appeared within a few minutes. This precipitate was expected to be the insoluble 1,3,5 isomer **2**.

This was shown to be the case by filtering the reaction mixture under the normal reaction conditions. This experiment was done twice, with free aniline present one time and absent the other. Without free aniline, bromide ion release was extensive (86%) and recovered tribromobenzenes totaled only 29%, of which 19% was in the precipitate and 10% in the filtrate. The precipitate was almost entirely (>94%) **2**, and the 1,3,5:1,2,4 isomer ratio in the filtrate was 0.8.

In the experiment with free aniline present, only 23% bromide ion was released, and recovered tribromobenzenes totaled 91%, being 61% in the precipitate and 30% in the filtrate. Again the precipitate was mainly (95%) **2**; the 1,3,5:1,2,4 isomer ratio in the filtrate was 0.18.

In both experiments the concentration of **2** in solution (0.26 g/l.) was in substantial agreement with the solubility determinations of Table II. In both, the isomer ratio in the filtrate was considerably less than at equilibrium in 50% ammonia-50% ether, suggesting that in neither case was equilibrium established in the solution phase.

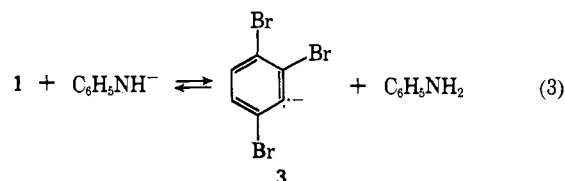
## Discussion

This research has served to identify two factors which limit the extent of isomerization of **1** to **2**.

**Solubility Effects.** Our solubility determinations (Table II) show that **1** is much more soluble than **2** in liquid ammonia. Therefore, except at very low tribromobenzene concentrations, the precipitation of **2** as formed by isomerization of **1** in neat ammonia shifts the product isomer ratio strongly toward **2**. We have verified that the precipitate which forms as isomerization proceeds is mainly **2**.

The solubility factor should be most pronounced, affording a very high 1,3,5:1,2,4 tribromobenzene isomer ratio, at rather high tribromobenzene concentrations, and indeed the anticipated effect appears in runs 2a-2b, Table I. Presumably the initial concentration of **1** was also quite high in the experiment of Wotiz and Huba;<sup>9</sup> in these terms one can reconcile their report of complete isomerization of **1** to **2** with subsequent observations<sup>3, 4</sup> of incomplete isomerization.

**Retardation by Aniline.** Aniline may inhibit the isomerization reaction and the release of bromide ion by repressing the acid-base reactions in which aryl anions are formed, such as that represented in eq 3.



The key roles that aryl anion intermediates play in the isomerization and disproportionation reactions have

(9) Wotiz and Huba<sup>9</sup> stated that 0.3 mol of **1** and 0.6 mol of NaNH<sub>2</sub> were allowed to react in an unspecified volume of ammonia for 18 hr, and that 0.1 mol of **2** was formed.

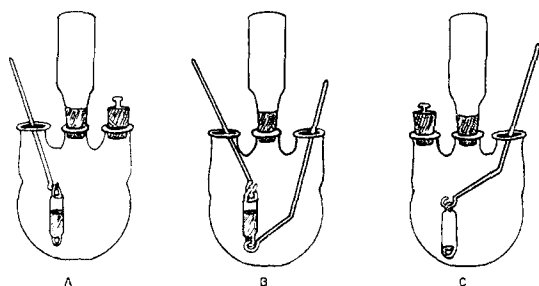
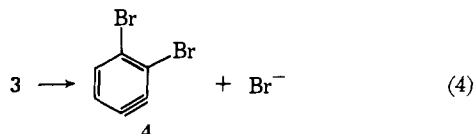


Figure 1. Addition of substrate, catalyst, and internal standard to reaction flask.

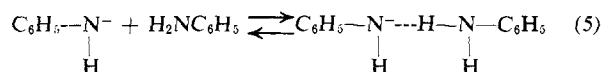
been discussed in previous papers.<sup>3,4,10</sup> *o*-Bromoaryl anions, such as **3**, may also expel bromide ion so as to form arynes, as in eq 4. The observation of complete



hydrogen isotope exchange on treatment of perdeuterated **1** with potassium anilide in ammonia<sup>3</sup> requires bromide ion expulsion to be the rate-limiting step in aryne formation.

Both isomerization and bromide ion release are thus kinetically dependent on the concentrations of aryl anions (**3** and isomers thereof). The inhibition by aniline owing to repression of equilibria such as that of eq 3 resembles the inhibitory effect of piperidine on the lithium piperidide induced dehydrofluorination of fluorobenzene in ether.<sup>11</sup>

A second inhibitory effect is proposed to be reversible complexing, through hydrogen bonding, of aniline molecules with anilide ions to form bianilide ions (eq 5).



Analogies for this exist in the formation of bifluoride ion from fluoride ion and HF, and in the formation of biphenoxide ion which has been proposed to explain the deactivation of phenoxide ion by phenol.<sup>12</sup>

To the extent that equilibrium 5 lies on the side of bianilide ion, and if this complex is itself ineffective as either acid or base, the formation of bianilide ion will decrease the concentrations of both anilide ions and aniline, and thus will diminish both the numerator and denominator of the equilibrium constant expression for reaction 3. The relative effect, however, will be greater in respect to the species (anilide ion or aniline) present in lesser amount. If bianilide ion is a tight complex and if aniline is in excess, this becomes a powerful factor to retard the rate of any reaction proceeding *via* aryl anion intermediates.

The release of one bromide ion in a side reaction involves the consumption of *two* anilide ions and the generation of one aniline molecule (eq 2). Therefore aniline inhibition becomes rapidly more pronounced as the bromide ion forming side reactions occur, first by altering the (magnified) significance of the species in excess (eq 5), and then by affecting equilibrium 3.

Irrespective of whether this interpretation is correct in all details, the phenomenon of aniline inhibition is a fortunate one in regard to the isomerization and disproportionation reactions. Isomerization is often sufficiently fast for equilibrium between the tribromobenzene isomers to be established before consumption of anilide ion and formation of aniline have reduced the rate to a negligible level. Then, as side reactions forming bromide ion occur, they "shut themselves off." In these terms one can understand why potassium anilide is so much more satisfactory than potassium amide as an isomerization catalyst.

## Experimental Section

Infrared spectra were taken on a Perkin-Elmer Model 337 grating spectrophotometer. Nuclear magnetic resonance spectra were taken on a Varian A56/60A spectrometer in  $\text{CCl}_4$  solution using tetramethylsilane as internal standard. Mass spectra were taken on a Hitachi Perkin-Elmer RMU-6E mass spectrometer.

**Materials.** **1,2,4-** and **1,3,5-tribromobenzene** were obtained commercially (Aldrich). The 1,2,4 isomer was used as received, mp 42–43° (lit.<sup>13</sup> mp 44°). The 1,3,5 isomer was purified by recrystallization from *tert*-butyl alcohol or passage through a column of acidic alumina, mp 119–121° (lit.<sup>5</sup> mp 121–122°). **1,2,3,5-Tetrabromobenzene** was prepared by treating 1,3,5-tribromoaniline<sup>14</sup> (35 g, 0.11 mol) with sodium nitrite (15.2 g, 0.22 mol) in 600 ml of glacial acetic acid and 200 ml of concentrated HBr at 65° according to Flürscheim and Simon.<sup>15</sup> The 15–20% of the product that was **2**, determined by nmr and glpc analysis, was removed by sublimation at 70° (0.2 mm) for 4 hr. Recrystallization from ethanol–ether gave 18.5 g (43% yield) of product, mp 97–98.5 (lit.<sup>16</sup> mp 98°).

**Reactions of Tribromobenzenes with Potassium Anilide.** When a particular reaction variable was being studied, two reactions were run side by side. Care was taken to ensure that all other reaction variables were held constant.

**General Reaction Procedure.** Two three-necked round-bottomed flasks were each fitted with a nitrogen inlet tube and a Dry Ice condenser to which was attached a potassium carbonate drying tube. A slow stream of nitrogen was dried by passage through a drying tube filled with Molecular Sieve (type 4A) and swept through the reaction flasks while they were flame dried. After the apparatus cooled to room temperature, the nitrogen inlet tubes were replaced with ammonia inlet tubes, and the reaction flasks were placed in Dry Ice–isopropyl alcohol slurries. Diethyl ether, freshly distilled from lithium aluminum hydride, was added to the reaction flasks in the experiments utilizing ammonia–ether solutions as solvent. Ammonia was then distilled through a potassium carbonate–potassium hydroxide drying tube into the reaction flasks until the solvent was of the desired volume.

A piece of potassium was scraped clean, washed with *tert*-butyl alcohol, and washed again with toluene. The ammonia or ammonia–ether solution was dried by adding small slivers of the clean potassium until the blue color persisted for at least 15 min. The desired weight of potassium was then added to the dried solvents along with a trace of ferric nitrate to catalyze the reaction of the ammonia and the potassium. The disappearance of the blue color indicated the complete reaction of the potassium. Pure, dry aniline was then added to convert the potassium amide to ammonia and potassium anilide.

When no ether was to be used in the solvent, special precautions were taken to get all of the tribromobenzene into contact with the ammonia solution. This was necessitated by the tendency of the tribromobenzene to cluster as fine, long needles on the walls of the reaction flask and to adhere to any funnel. A carrier tube was therefore fashioned from a glass tube sealed at one end with glass handles placed at both ends. This tube, containing the desired quantities of substrate, internal standard, and in some cases, catalyst, was introduced into the reaction flask by means of a glass hook (Figure 1A). A second glass hook, placed in the reaction flask through another neck, grabbed the lower handle (Figure 1B).

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Removal of the hook from the upper handle led to the inversion of the tube (Figure 1C). The inverted tube was then rinsed with solvent until transfer of its contents was complete. Finally, the inverted tube was removed from the flask through the neck. This procedure eliminated the necessity of rinsing the walls of the flask with ether, as had been done previously.<sup>3,6</sup>

When ether-ammonia solutions were used as solvent, a more convenient procedure was to add the substrate, internal standard, and catalyst dissolved in a small amount of ether.

An uncoated magnet was then placed in the flask and the reaction mixture was stirred rapidly. At the end of the desired time period, the reaction was quenched by the addition of excess ammonium nitrate. The ammonia was allowed to evaporate, and the residue was taken up in a mixture of 50 ml of ether and 50 ml of water. (If 50 ml of ether remained after the ammonia evaporated, no more ether was added.)

The ether-water mixture was then separated, and the water solution was washed with ether (two 10-ml portions). The combined ether extracts were washed with water (two 10-ml portions), and then with 10-ml portions of 6 *M* HCl until there was no further reaction evident on mixing. Usually, two or three washings were sufficient. The combined water layers were analyzed for bromide ion by potentiometric titration with silver nitrate and the combined ether layers were analyzed by glpc.

**Glpc Analysis.** The ether extracts were analyzed on an Aerograph A-90P3 gas chromatograph using a 4 ft × 0.25 in. column of 10% SE54 on Chromosorb P operated at 160° with a helium flow rate of 75 cc/min. The order of elution (with retention times relative to air in parentheses) was dibromobenzene (3 min), biphenyl (7 min), **2** (9 min), and **1** (11 min). Identity of the peaks was made by comparison of retention times with those of authentic compounds as well as by co-injection. No correction for the molar response of the instrument to biphenyl (internal standard) relative to tribromobenzene was needed; the molar response ratio was found to be unity.

**Solubility Determinations.** Saturated solutions were prepared by stirring actively, for an extended period of time, an excess of solid **1** or **2** with the solvent under study, allowing the undissolved solid to settle to the bottom of the unstirred mixture, removing an aliquot of the clear solution by means of a calibrated pipet jacketed at -78°,<sup>17</sup> evaporating the solvent from the aliquot, and weighing the residue. Results are set forth in Table III. It is significant that determinations made after different stirring times gave substantially the same results; this gives assurance that the determinations represent equilibrium solubilities rather than rates of solution.

**Analysis of Soluble and Insoluble Fractions from Isomerization of **1** to **2** in Ammonia.** Isomerization reactions were carried out in the usual way, except that the reaction mixture (in ammonia at -33°) was filtered and the filtrate and precipitate were separately analyzed. Filtration was accomplished by inserting a gas dispersion tube with fritted glass tip into the reaction mixture and applying pressure to the flask so as to force the liquid phase out through the filter, retaining the precipitate in the flask. Immediately following filtration, NH<sub>4</sub>NO<sub>3</sub> was added to the filtrate to quench any potassium anilide remaining.

This experiment was done twice, with 3.00 g (0.0095 mol) of **1** and 0.02 mol of potassium anilide in 500 ml of ammonia being used each time. In the experiment without free aniline, filtration was performed after 1.0 hr. The precipitate (0.58 g) contained >94% **2** and <6% **1**; evaporation of the filtrate afforded 0.30 g of tribromobenzenes, shown by glpc to comprise 0.17 g of **1** and 0.13 g of **2**; also, 86% bromide ion was formed. In the other experiment, aniline (0.067 mol) was present, and the reaction time was 1.0 hr. The precipitate (1.83 g) comprised 0.10 g of **1** and 1.73 g of **2**. The filtrate contained 0.89 g of tribromobenzenes, being 0.74 g of **1** and 0.13 g of **2**; 23% of bromide ion was formed.

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(17) Designed by G. Scorrano.