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SOLVOLYSIS OF HYDRAZOBENZENE IN METHYL IODIDE

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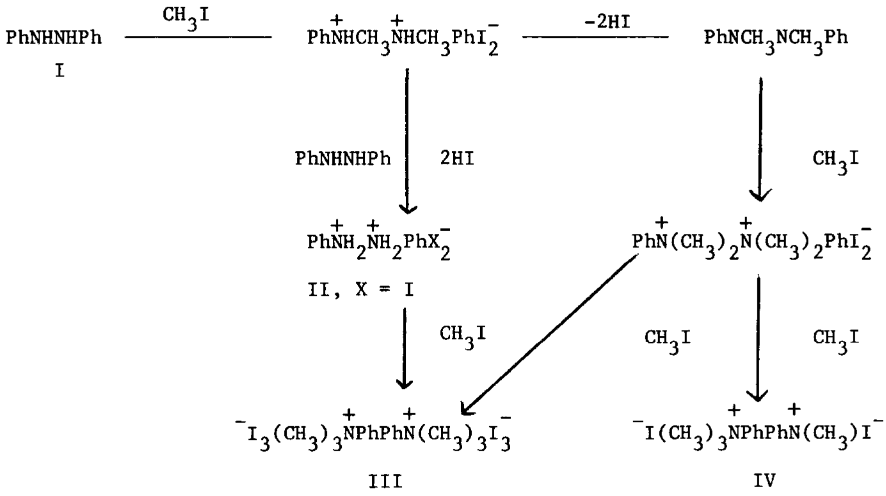
During our studies of solid state reactions[1,2] we investigated the reaction of crystalline hydrazobenzene (I) with HCl gas in hopes of isolating $Ph\overset{+}{N}H_2\overset{+}{N}H_2PhX_2^-$ (II, X = Cl). However, the major product was benzidine dihydrochloride as shown by comparison of its NMR spectrum to an authentic sample. These results are consistent with the studies of Carlin, Nelb and Odioso who also found that the benzidine rearrangement occurred upon reacting solid hydrazobenzene with HCl gas.[3]

In contrast, Pongratz and co-workers reported that hydrazobenzene reacted with methyl iodide and methyl bromide to yield the second conjugate acid of hydrazobenzene $Ph\overset{+}{N}H_2\overset{+}{N}H_2PhX_2^-$ (II (X = I, Br)).[4,6] They suggested the following mechanism:



Since neither $Ph\overset{+}{N}H_2\overset{+}{N}H_2PhX_2^-$ nor $Ph\overset{+}{N}H_2NHPhX^-$ has ever been isolated during studies of the benzidine rearrangement[3,7-11] and since even in the absence of solvent in a crystalline matrix no II (X = Cl) could be isolated, the solvolysis of hydrazobenzene in methyl iodide, where II was reportedly isolated, was reinvestigated. In addition, N-methylhydrazobenzene and N,N-dimethylhydrazobenzene were prepared[12] and their solvolysis in methyl iodide was studied.

We have found that the solid obtained by the Pongratz group in this solvolysis reaction was aniline hydroiodide instead of hydrazobenzene dihydroiodide as reported. Also trimethylphenylammonium triiodide ($Ph\overset{+}{N}(CH_3)_3I_3^-$) and trimethylphenylammonium iodide ($Ph\overset{+}{N}(CH_3)_3I^-$) have been isolated instead of tetramethylbenzidine diiodomethylate tetraiodide (III) and tetramethylbenzidine diiodomethylate (IV).

A solution of 1 g hydrazobenzene in 10 ml methyl iodide was allowed to react without agitation and the precipitated solid was collected. This solid was a mixture containing $Ph\overset{+}{N}H_3\overset{-}{I}$, $Ph\overset{+}{N}(CH_3)_3I^-$, and $Ph\overset{+}{N}(CH_3)_3\overset{-}{I_3}$. The filtrate after removal of methyl iodide contained PhN = NPh, $PhNHNCH_3Ph$, $PhNCH_3NCH_3Ph$, $Ph\overset{+}{N}(CH_3)_3\overset{-}{I_3}$, $Ph\overset{+}{N}(CH_3)_2H\overset{-}{I}$, and $Ph\overset{+}{N}CH_3H_2\overset{-}{I}$. Table I shows the yields of these products under various conditions.

Table I

Reaction of Hydrazobenzene (1 g) with Methyl Iodide (10 ml)

Reaction conditions and reaction time	Yield % of Products Formed[a,b] $Ph\overset{+}{N}H_3I$	$Ph\overset{+}{N}(CH_3)_3\overset{-}{I}$	$Ph\overset{+}{N}(CH_3)_3\overset{-}{I_3}$	PhN=NPh	$PhNHNCH_3Ph$	PhNHNHPh
air, dark, 25°, for 3 days	43	11	trace	28	9	8
air, light, 25°, for 3 days	44	14	trace	25	7	10
N_2, dark, 25°, for 3 days	43	14	1	27	7	8
N_2, dark, 25°, for 10 days	41	27	7	15	7	3
air, dark, reflux for 3 days	49	18	13	20	-	-
air, dark, 0° for 21 days	38	11	trace	32	7	12

[a] In addition to these products shown, a trace of $Ph\overset{+}{N}H(CH_3)_2\overset{-}{I}$, $Ph\overset{+}{N}H_2CH_3\overset{-}{I}$, $PhNCH_3NCH_3Ph$ have also been found in these reactions.

[b] The yields of these products were calculated as follows: The NMR spectrum of the precipitated solid in D_2O showed the proton ratio of aromatic and methyl group which was used to calculate the ratio of $Ph\overset{+}{N}H_3\overset{-}{I}$ and $Ph\overset{+}{N}(CH_3)_3\overset{-}{I}$, and the yield was calculated using the total weight of the precipitates. The NMR spectrum of the orange solid in $CDCl_3$ showed the different chemical shifts of aromatic protons of PhN=NPh and PhNHNHPh, and methyl group proton of $PhNHNCH_3Ph$ and $PhNCH_3NCH_3Ph$ which were confirmed by the mixture of authentic samples and were used to calculate their ratio and yield %.

These products were identified as follows: After 3 days the reaction was stopped (otherwise as indicated in Table I). The precipitated solid was then removed by filtration and washed with anhydrous ether. The solid was reacted with ammonia gas in an attempt to reisolate hydrazobenzene (I) which would be produced if II were present. However, we obtained a gummy material which upon extraction with $CDCl_3$ gave an NMR spectrum identical with that of aniline.

If the solid was recrystallized from methanol, the first crystals obtained were $Ph\overset{+}{N}(CH_3)_3I^-$ based on comparison of NMR and IR spectra to that of an authentic sample and elemental analysis (calcd. for $C_9H_{14}NI$: C, 41.06; H, 5.32, N, 5.32, I, 48.29. Found C, 41.31; H, 5.46; N, 5.58; I, 48.00). After removal of these crystals a third batch of crystals was obtained and identified as $Ph\overset{+}{N}H_3I^-$ by comparison of NMR and IR spectra to that of an authentic sample and by elemental analysis (calcd. for C_6H_8NI: C, 32.6; H, 3.62; N, 6.34; I, 57.46. Found: C, 32.69; H, 3.63; N, 6.13; I, 57.70).

The methyl iodide was then evaporated from the filtrate. The solid was extracted with ether and the residue was recrystallized from methanol to yield $Ph\overset{+}{N}(CH_3)_3I_3^-$ which was identified by comparison of its NMR and IR spectra with that of an authentic sample and by elemental analysis (calcd. for $C_9H_{14}NI_3$: C, 20.89; H, 2.71; N, 2.71; I, 73.68. Found: C, 21.12; H, 2.85; N, 2.59; I, 73.40).

The ether extract was evaporated to dryness to give an orange solid which was recrystallized from methanol and was identified as azobenzene by comparing its spectra with the NMR and IR spectra of an authentic sample.

Under similar conditions, N-N-dimethylhydrazobenzene was reacted with methyl iodide; after 4 days N,N-dimethylhydrazobenzene was recovered almost completely unreacted; in a week we obtained a small amount of solid containing $Ph\overset{+}{N}(CH_3)_3I^-$ and $Ph\overset{+}{N}(CH_3)_3I_3^-$. The reaction of N-methylhydrazobenzene with methyl iodide in 3 days gave $Ph\overset{+}{N}H_3I^-$ (9%), $Ph\overset{+}{N}CH_3H_2I^-$ (3%), $Ph\overset{+}{N}(CH_3)_2HI^-$ (7%), $Ph\overset{+}{N}(CH_3)_3I^-$ (23%), $Ph\overset{+}{N}(CH_3)_3I_3^-$ (8%), $PhNHNCH_3Ph$ (42%), $PhNCH_3NCH_3Ph$ (8%).

In contrast, reactions of hydrazobenzene in air in the solvents methanol, ethanol, chloroform, carbon tetrachloride always gave azobenzene as the only product and no reaction occurred in a nitrogen atmosphere.

In methyl iodide the reaction of hydrazobenzene was obviously more complicated. It was insensitive to light or air, and even in the presence of nitrogen we still obtained a large amount of azobenzene and other products, as shown in Table I.

It is interesting to compare the products of the methyl iodide reactions with those obtained in the photobenzidine and benzidine rearrangement of N,N'-dimethylhydrazobenzenes. The photobenzidine rearrangement of N-methylhydrazobenzenes and 1,4-diaryl-1,4-dimethyl-1,2-tetrazines produced N-methylanilines in yields ranging from a trace to 36% and semidines in yields ranging from 6 to 65%.[13-15] These reactions have been shown to involve aniline radicals. Reaction of N,N'-dimethylhydrazobenzenes in acetonitrile in the presence of acid produced a high yield (>70%) of N-methylanilines.[16] This reaction was explained by formation of a semidine which then acted as an oxidizing agent for the reductive clevage of N,N'-dimethylhydrazobenzene.

Although efforts were made to elucidate the mechanism of this reaction, at the present time it remains uncertain.

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References:

1. S.R. Byrn, J. Pharm. Sci., 65, 1 (1976).
2. S.R. Byrn and C.T. Lin, J. Amer. Chem. Soc., 97, 4004 (1976).
3. R.B. Carlin, R.G. Nelb and R.C. Odioso, J. Amer. Chem. Soc., 73, 1002 (1951).
4. A. Pongratz and K. Scholtis, Ber., 75, 138 (1942).
5. A. Pongratz, S. Bohmert-Süb and K. Scholtis, Ber., 77, 651 (1944).
6. A. Pongratz and H. Wustner, Ber., 73, 423 (1940).
7. G.S. Hammond and H.J. Shine, J. Amer. Chem. Soc., 72, 220 (1950).
8. L. Croce and J.D. Gettler, J. Amer. Chem. Soc., 75, 874 (1953).
9. M.D. Cohen, and G.S. Hammond, J. Amer. Chem. Soc., 75, 880 (1953).
10. G.S. Hammond and W. Grudemeier, J. Amer. Chem. Soc., 77, 2444 (1955).
11. C.A. Bunton and R.J. Rubin, J. Amer. Chem., Soc., 98, 4236 (1976).
12. G. Wittig, Angew. Chem., 53, 244 (1940).
13. H.J. Shine and J.D. Cheng, J. Org. Chem., 36, 2787 (1971).
14. J.D. Cheng and H.J. Shine, J. Org. Chem., 39, 336 (1974).
15. V.J. Hull and H.J. Shine, J. Amer. Chem. Soc., 95, 8102 (1973).
16. J.D. Cheng and H.J. Shine, J. Org. Chem., 40, 703 (1974).