Photobenzidine Rearrangements. II. Rearrangements of *N,N'*-Dimethylhydrazo Aromatics[1,2]

HENRY J. SHINE* AND JIIN D. CHENG[3]

Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

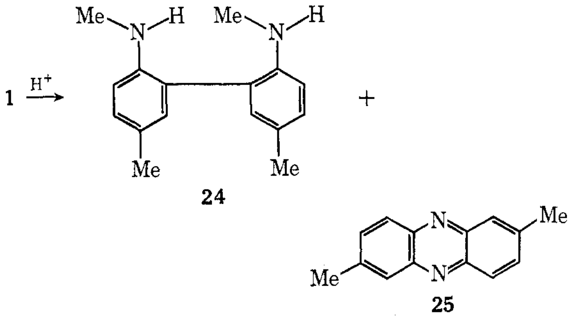
Received February 9, 1971

N,N'-Dimethyl-*p*-hydrazotoluene (**1**), *N,N'*-dimethyl-*p*-hydrazoanisole (**2**), and *N,N'*-dimethyl-*p*-hydrazobiphenyl (**3**) rearranged to the corresponding *o*-semidines (compounds **5**, **12**, and **23**) when irradiated in cyclohexane solution. Rearrangement of **1** was relatively slow but clean. That is, after 10 hr 19% of **1** had rearranged, while 74% was recovered. In contrast, after 3 hr 65% of **2** had rearranged, 11% had undergone scission to *N*-methylanisidine, and 17% was recovered. After 17 hr of irradiation of **3**, 34% was recovered, 24% had rearranged, and 35% had undergone scission to *N*-methyl-4-aminobiphenyl. Some 4-aminobiphenyl was also formed. Irradiation of *N,N'*-dimethylhydrazomesitylene (**4**) caused scission to *N*-methylmesidine and some demethylation–scission to mesidine. The photochemical rearrangements of *N,N'*-dimethylhydrazobenzenes are the first photobenzidine rearrangements known to occur in more than trace amounts. Acid-catalyzed rearrangement of **1** gave the *o*-benzidine type product **24** and 2,7-dimethylphenazine (**25**) in 9 and 5% yields, respectively. Three other unidentified compounds were also obtained. Acid-catalyzed rearrangement of **2** gave 46% of the *o*-semidine (**12**) and 42% of *N*-methylanisidine. Mechanistic details of the photorearrangement have not been explored, but it is evident that the rearrangement pathways are different from those of the well-known acid-catalyzed rearrangements.

Although acid-catalyzed and thermally induced benzidine rearrangements are well known,[4] almost nothing about photochemical rearrangements has appeared in the literature. Hashimoto and coworkers[5] have reported the chromatographic detection of *o*- and *p*-semidine in 0.25% yields from the irradiation of hydrazobenzene. As far as we know, no other example of rearrangement of simple hydrazo aromatics has been reported. This is not surprising, since it is now known that hydrazobenzenes, which do not have substituents on the hydrazo-group nitrogen atoms, undergo dehydrogenation and, in small part, N,N bond scission when irradiated.[6,7] The dehydrogenation reaction is almost quantitative at 290 nm (whereas some scission to anilines occurs at 250 nm) and involves the solvent, since the use of *N,N'*-dideuteriohydrazobenzene in cyclohexane gave large amounts of HD.[7] Hydrogen-atom formation from singlet hydrazobenzene followed by disproportionation of hydrazyl radicals has been proposed by Shizuka[6] to explain the behavior of hydrazobenzene. In contrast with the behavior of simple hydrazobenzenes, we have found that *N,N'*-dimethylhydrazobenzenes undergo rearrangement. The case of *N,N'*-dimethylhydrazobenzene was reported briefly recently.[2] We have been exploring the scope of the rearrangement of *N,N'*-dimethylhydrazobenzenes and now report on four of them.

N,N'-Dimethyl-*p*-hydrazotoluene (**1**), *N,N'*-dimethyl-*p*-hydrazoanisole (**2**), and *N,N'*-dimethyl-*p*-hydrazobiphenyl (**3**) rearrange to the *o*-semidine (eq 1 in Table I). Authentic *o*-semidines **5** and **12** were synthesized, but synthesis of authentic **23** was not attempted.

Another product of rearrangement, the *o*-benzidine type, is possible in principle. This was not formed. The *o*-benzidine type product was obtained from acid-catalyzed rearrangement of *N,N'*-dimethylhydrazobenzene,[8] and in the present work from acid-catalyzed rearrangement of **1** (eq 2). Not only was the *o*-benzidine (**24**) obtained but also 2,7-dimethylphenazine (**25**). Evidently, the photobenzidine rearrangement does not follow the same pathway(s) as the acid-catalyzed rearrangement. We do not know at this stage if the rearrangement is intramolecular (in analogy with acid-catalyzed rearrangement). Irradiation of **1**, **2**, and **3** also gave some of the scission product, the *N*-methylarylamine. Thus, it is probable that *N*-methylarylamino radicals are formed as precursors to the scission products, but whether or not these radicals are also involved in forming rearrangement products has not been explored yet.



(2)

Compound **4**, of course, cannot rearrange, and it is not surprising that its major photochemical pathway is to give the scission product, *N*-methylmesidine.

All reports, with one exception,[5] on the photochemistry of ordinary hydrazobenzenes show that these compounds do not rearrange, but, instead, undergo dehydrogenation and, to a small extent, scission at the N,N bond.[6,7,9] The easy loss of hydrogen atom from an excited hydrazobenzene molecule[6] is contrasted with rearrangement when both of the N,N' hydrogen atoms are replaced with methyl groups. Azobenzenes are not formed. The formation of demethylated anilines (*e.g.*, mesidine) in the present work may be attributable to the photochemical demethylation of the first-formed *N*-methylanilines.[10]

---

[1] Supported by Grant No. D-028 from the Robert A. Welch Foundation.

[2] Part I: J. F. Sullivan, K. Hailey, and H. J. Shine, *Tetrahedron Lett.*, 2007 (1970).

[3] Predoctoral Fellow.

[4] H. J. Shine, "Aromatic Rearrangements," Elsevier, Amsterdam, 1967, pp 126–179.

[5] S. Hashimoto, J. Sunamoto, and S. Nishitani, *Bull. Chem. Soc. Jap.*, **41**, 623 (1968).

[6] H. Shizuka, H. Kayoiji, and T. Morita, *Mol. Photochem.*, **2**, 165 (1970).

[7] Unpublished work by C. M. Baldwin and J. H. Harris in these laboratories.

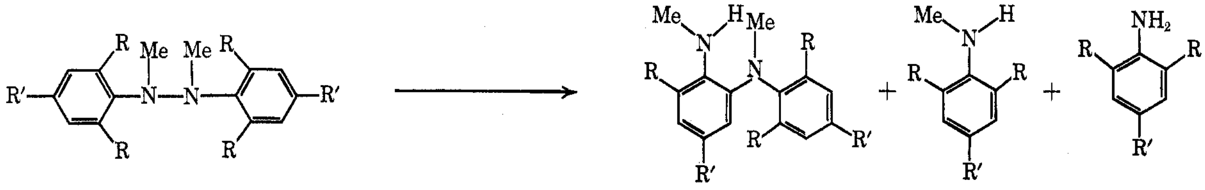
[8] W. N. White and E. E. Moore, *J. Amer. Chem. Soc.*, **90**, 526 (1968).

[9] P. F. Holt and B. P. Hughes, *J. Chem. Soc.*, 1666 (1953).

[10] Y. Ogata and K. Takagi, *J. Org. Chem.*, **35**, 1642 (1970).

TABLE I

PRODUCTS[a] OF IRRADIATION OF *N,N'*-DIMETHYLHYDRAZO AROMATICS



(1)

Compd	R	R'	Time, hr	Compd	%	%	%
1	H	Me	10	**5**	19	+	−
2	H	OMe	3	**12**	65	11	−
3	H	C_6H_5	17	**23**	24	35	+
4	Me	Me	7			36	30

[a] Some of the hydrazo compound was recovered: **1**, 74%; **2**, 17%; **3**, 34%.

Experimental Section

Irradiation Equipment.—Irradiations were carried out with a Rayonet reactor, "Merry-Go-Round," Model Type RS, and a Bausch and Lomb monochromator, Model 33-86-07.

***N,N'*-Dimethyl-*p*-hydrazotoluene** (**1**) was prepared by methylating *p*-hydrazotoluene with butyllithium and methyl iodide[11] in 43% yield, mp 65–66° (ethanol).

Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.96; H, 8.39; N, 11.65. Found: C, 80.17; H, 8.34; N, 11.53.

***N,N'*-Dimethyl-*p*-hydrazoanisole** (**2**).—Because *p*-hydrazoanisole was so sensitive to air oxidation and acid-catalyzed rearrangement, **2** was prepared by methylating *p*-azoanisole with sodium and methyl iodide in tetrahydrofuran (THF)[12] in 42% yield, mp 105–106° (cyclohexane–dioxane).

Anal. Cacld for $C_{16}H_{20}N_2O_2$: C, 70.60; H, 7.35; N, 10.29. Found: C, 70.45; H, 7.34; N, 10.40.

***N,N'*-Dimethyl-*p*-hydrazobiphenyl** (**3**) was prepared from hydrazobiphenyl in 99% yield, mp 173–174° (THF–methanol).

Anal. Calcd for $C_{26}H_{24}N_2$: C, 85.68; H, 6.64; N, 7.69. Found: C, 85.69; H, 6.52; N, 7.75.

***N,N'*-Dimethylhydrazomesitylene** (**4**).—Because hydrazomesitylene is so sensitive to air oxidation,[13] **4** was prepared from azomesitylene[14] directly. The crude product was chromatographed on alumina to give a red oil which when triturated with ethanol gave **4**, mp 117–120°. Crystallization from benzene–ethanol gave a 49% yield, mp 118–119°.

Anal. Calcd for $C_{20}H_{28}N_2$: C, 81.03; H, 9.52; N, 9.45. Found: C, 81.07; H, 9.63; N, 9.50.

N,N'*,3,4'-Tetramethyl-6-aminodiphenylamine** (N,N'*,3,4'-tetramethyl-*o*-semidine**) (**5**).—This compound was prepared in six steps (Scheme I) beginning with 3,4-dinitrotoluene.

3-Amino-4-nitrotoluene (**6**) was prepared from 3,4-dinitrotoluene by the method of Boyer.[15]

3,4'-Dimethyl-6-nitrodiphenylamine (**7**).—A mixture of 5.1 g of **6**, 3 g of anhydrous potassium carbonate, 1 g of cuprous iodide, and 40 ml of *p*-bromotoluene was boiled for 12 hr.[16] Excess *p*-bromotoluene was removed under vacuum. The remaining red oil was triturated with carbon tetrachloride to leave 0.25 g of unused **6**. Evaporation of the solution gave an oil which with ether–ethanol gave 5 g (62%) of **7**, mp 97–97.5° (ethanol).

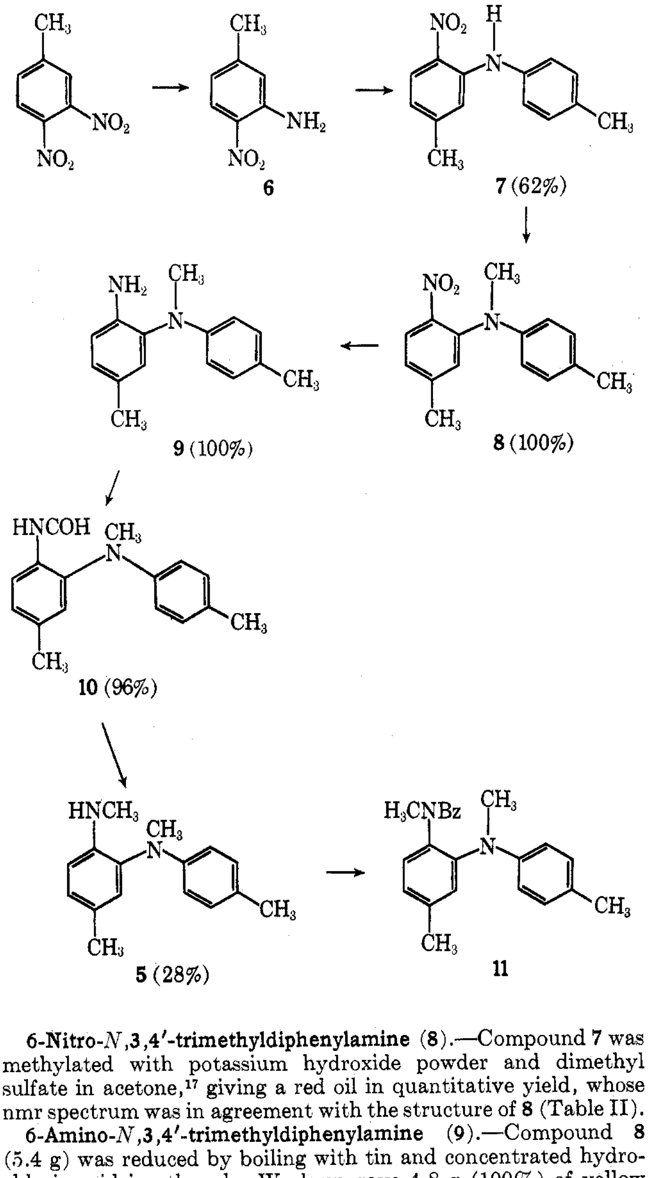
Compound **7** was also prepared by heating a mixture of 9.5 g of 3-bromo-4-nitrotoluene, 6.7 g of *N*-acetyltoluidine, 0.2 g of copper powder, 6.1 g of potassium carbonate, and 1 g of potassium iodide in 40 ml of nitrobenzene for 21 hr at 160°, according to the procedure of Goldberg.[16] The product, *N*-acetyl-3,4'-dimethyl-6-nitrodiphenylamine (29%), had mp 157–157.5° (ether).

Anal. Calcd for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.88. Found: C, 67.53; H, 5.73; N, 9.58.

This product was hydrolyzed with methanolic sodium hydroxide to give **7**, mp 96–97° (ethanol), in quantitative yield.

Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.82; N, 11.57. Found: C, 69.11; H, 5.88; N, 11.72.

SCHEME I



6-Nitro-*N*,3,4'-trimethyldiphenylamine (**8**).—Compound **7** was methylated with potassium hydroxide powder and dimethyl sulfate in acetone,[17] giving a red oil in quantitative yield, whose nmr spectrum was in agreement with the structure of **8** (Table II).

6-Amino-*N*,3,4'-trimethyldiphenylamine (**9**).—Compound **8** (5.4 g) was reduced by boiling with tin and concentrated hydrochloric acid in ethanol. Work-up gave 4.8 g (100%) of yellow oil, whose nmr spectrum was in agreement with the structure of **9** (Table II).

6-Formamido-*N*,3,4'-trimethyldiphenylamine (**10**).—Formylation of compound **9** was carried out by boiling a toluene solution of 4.8 g of **9** with 27 ml of 88% formic acid and removing water as it was formed. The formamide **10** (5.2 g, 96%) was obtained as a brown oil.

---

[11] G. Wittig, *Angew. Chem.*, **52**, 241 (1940).

[12] J. W. Reesor and G. F. Wright, *J. Org. Chem.*, **22**, 375 (1957).

[13] Unpublished work in this laboratory.

[14] L. Hanner and W. Kirmse, *Justus Liebigs Ann. Chem.*, **597**, 48 (1955).

[15] J. H. Boyer, R. F. Reinisch, M. J. Danzis, G. A. Stoner, and F. Sahhar, *J. Amer. Chem. Soc.*, **77**, 5688 (1955).

[16] I. Goldberg, *Ber.*, **40**, 4541 (1907).

[17] I. J. Pachter and M. C. Kloetzel, *J. Amer. Chem. Soc.*, **74**, 1321 (1952).

TABLE II

NMR DATA FOR NEW COMPOUNDS

Compd	Spectrum pattern[a]
1[b]	2.33 (s, 6), 3.02 (s, 6), 7.05 (d, 4), 7.40 (d, 4)
2[b]	2.85 (s, 6), 3.73 (s, 6), 6.75 (s, 8)
3[c]	3.07 (s, 6), 6.95 (d, 4), 7.50 (m, 14)
4[b]	2.17, 2.25 (2 s, 18), 2.80 (s, 6), 6.69 (s, 4)
5[b]	2.17, 2.19 (2 s, 6), 2.70 (s, 3), 3.05 (s, 3), 3.94 (s, 1), 6.44, 6.48 (2 d, 3), 6.75 (s, 1), 6.88 (d, 3)
7[b]	2.25 (s, 3), 2.42 (s, 3), 6.48 (d, 1), 6.89 (s, 1), 7.15 (s, 4), 8.02 (d, 1), 9.44 (s, 1)
8[b]	2.21 (s, 3), 2.43 (s, 3), 3.2 (s, 3), 6.57 (d, 2), 6.93 (d, 3), 7.04 (s, 1), 7.67 (d, 1)
9[b]	2.05, 2.20 (2 s, 6), 3.06 (s, 3), 3.48 (s, 2), 6.47 (d, 3), 6.73 (s, 1), 6.90 (d, 3)
12[b]	2.70 (s, 3), 3.03 (s, 3), 3.58, 3.60 (2 s, 6), 3.90 (s, 1), 6.60 (m, 7)
17[c]	3.70 (s, 3), 3.82 (s, 3), 6.29 (m, 2), 6.93 (d, 2), 7.22 (d, 2), 8.10 (d, 1), 9.65 (s, 1)
19[b]	3.19 (s, 3), 3.65, 3.73 (2 s, 6), 6.56 (m, 6), 7.77 (d, 1)
20[b]	3.05 (s, 3), 3.38 (s, 2), 3.58, 3.63 (2 s, 6), 6.60 (m, 7)
23[c]	2.87 (s, 3), 3.2 (s, 3), 3.75 (s, 1), 6.67, 6.72 (2 d, 3), 7.32 (m, 14)
24[c]	2.29 (s, 6), 2.78 (s, 6), 3.58 (s, 2), 6.70 (d, 2), 6.98 (s, 2), 7.18 (d, 2)

[a] In δ units. [b] Solvent CCl_4. [c] Solvent $CDCl_3$.

***N,N'*3,4'-Tetramethyl-*o*-semidine (5).**—The formamide **10**, 5.2 g, was reduced by boiling with lithium aluminum hydride in ether. Work-up gave 4.4 g of an oil which was fractionally distilled twice to give 1.37 g (28%) of **5**, bp 118–143° (1 mm). The nmr spectrum was in agreement with the structure of **5** (Table II). The tetramethyl-*o*-semidine was characterized as the benzamide **11**, using Schotten–Bauman conditions, mp 107–108.5° (ethanol).

Anal. Calcd for $C_{23}H_{24}N_2O$: C, 80.21; H, 7.02; N, 8.12. Found: C, 80.37; H, 7.09; N, 8.21.

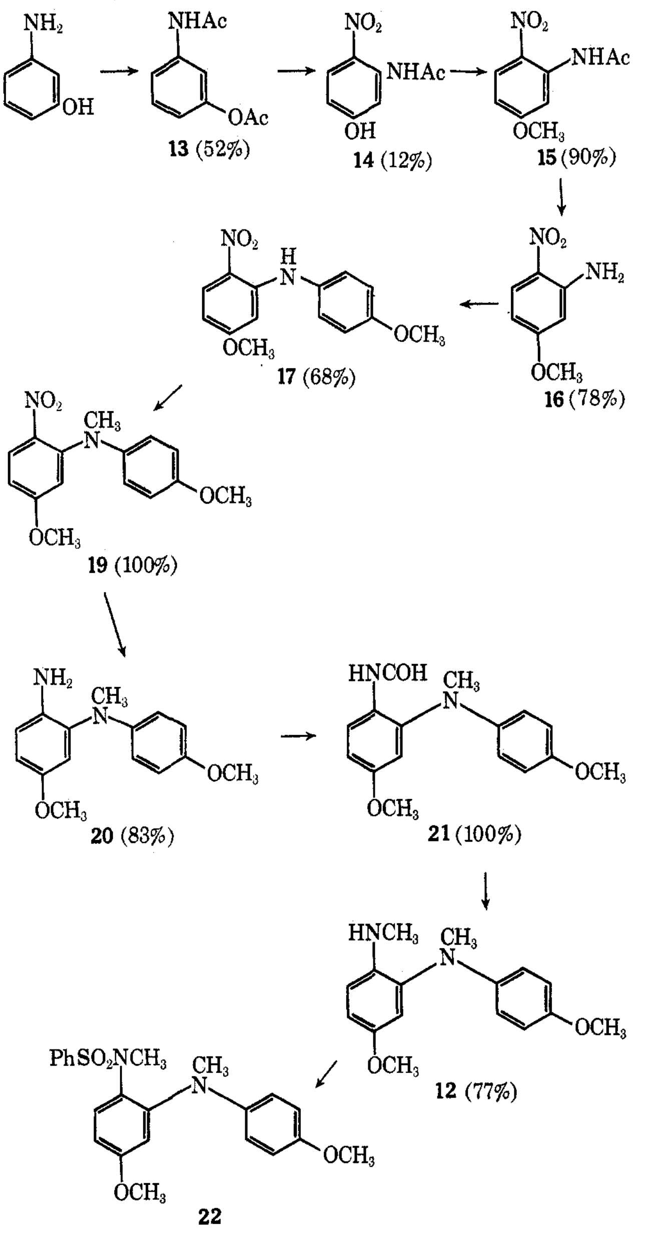
3,4'-Dimethoxy-*N,N'*-dimethyl-6-aminodiphenylamine (3,4'-Dimethoxy-*N,N'*-dimethyl-*o*-semidine) (12).—This compound was prepared in nine steps (Scheme II) beginning with *m*-aminophenol.

***N,O*-Diacetyl-*m*-aminophenol (13)** was prepared in 52% yield by boiling *m*-aminophenol in acetic anhydride.[18] Compound **13** was nitrated in poor yield by modifying Meldola's procedure.[19] **13** (40 g) was added in portions to 80 ml of ice-cold nitric acid (sp gr 1.4) in 5 min. To this was added dropwise 40 ml of fuming nitric acid in 10 min, and the solution was stirred at 19–22° for 3 hr, after which it was poured into 500 ml of ice water. The precipitate was crystallized from ethanol to give 5.7 g (12%) of 3-acetomido-4-nitrophenol (**14**), mp 262–263° (lit.[19] mp 266°). These conditions for nitration were chosen after several other attempts to follow Meldola's recipe gave even poorer results. The nitro compound **14** was methylated by treating 4 g with 4 g of dry potassium carbonate and 6 ml of methyl iodide in 60 ml of dimethylformamide for 90 min at room temperature. Pouring the mixture into 200 ml of water gave 3.9 g (90%) of 3-acetamido-4-nitroanisole (**15**), mp 126–127° (lit.[19] mp 124°). Compound **15** (4 g) was hydrolyzed with 3 g of sodium hydroxide in 70 ml of methanol at room temperature for 45 min, giving 2.5 g (78%) of 3-amino-4-nitroanisole (**16**), mp 129–130° (lit.[19] mp 131°).

3,4'-Dimethoxy-6-nitrodiphenylamine (17).—A mixture of 2.5 g of compound **16**, 2.5 g of dry potassium carbonate, 0.6 g of cuprous iodide, and 20 ml of *p*-bromoanisole was boiled at 217° for 7 hr. The mixture was filtered through a bed of Celite filter aid, and the excess of *p*-bromoanisole was steam distilled. The residue was stirred with portions of ether. Evaporation of the ether gave a solid which was dissolved in carbon tetrachloride and chromatographed on a silica gel column, by elution with carbon tetrachloride containing a small amount of ether (98:2). A total of 2.78 g (68%) of 3,4'-dimethoxy-6-nitrodiphenylamine (**17**), mp 104–105° (ether), was obtained.

Anal. Calcd for $C_{14}H_{14}N_2O_4$: C, 61.31; H, 5.15; N, 10.21. Found: C, 61.28; H, 5.17; N, 10.27.

SCHEME II



On some occasions compounds **14–16** were used in sequence in crude condition, in which case trituration of the *p*-bromoanisole condensation product with carbon tetrachloride left behind small amounts of a compound believed, on the basis of nmr and elemental analysis, to be 3-amino-6-nitroanisole (**18**), mp 157.5–158° (methanol) (lit.[20] mp 169°). Evidently, nitration of **13** gives at least two isomers (the 4- and 6-nitro derivatives), both of which are carried through the methylation and hydrolysis stages, too. Apparently condensation with *p*-bromoanisole is more facile with 3-amino-4-nitroanisole (**16**) than with 3-amino-6-nitroanisole (**18**). When these facts were recognized, however, preparation of **17** was carried out only with the reliably recrystallized isomer **16**.

3,4'-Dimethoxy-*N*-methyl-6-nitrodiphenylamine (19) was prepared from compound **17** with powdered potassium hydroxide and dimethyl sulfate in acetone.[17] The product was a red oil, obtained in quantitative yield, whose nmr spectrum agreed with the structure of **19** (Table II).

6-Amino-3,4'-dimethoxy-*N*-methyldiphenylamine (20) was obtained in 83% yield by reducing compound **19** with tin and hydrochloric acid in ethanol. The product was an oil whose nmr spectrum agreed with structure **20** (Table II). Formylation of compound **20** gave the formamide **21** also as an oil, in quantitative yield. This was reduced with lithium aluminum hydride in tetrahydrofuran, giving 3,4'-dimethoxy-*N,N'*-dimethyl-6-

---

[18] M. Ikuta, *Amer. Chem. J.*, **15**, 41 (1893).

[19] R. Meldola and F. G. C. Stephens, *J. Chem. Soc.*, **89**, 923 (1906).

[20] F. Reverdin and K. Widmer, *Ber.*, **46**, 4072 (1913).

aminodiphenylamine (**12**), bp 168–169° (1 mm), in 77% yield. The nmr spectrum agreed with structure **12**. The benzenesulfonyl derivative **22** had mp 94–95° (ether).

Anal. Calcd for $C_{22}H_{24}N_2O_4S$: C, 64.06; H, 5.87; N, 6.79; S, 7.77. Found: C, 64.05; H, 5.97; N, 7.06; S, 7.96.

Photochemical Rearrangement of *N*,*N*′-Dimethyl-*p*-hydrazotoluene (1).—A solution of 1 g of **1** in 200 ml of spectrograde cyclohexane (Eastman) was degassed by the freeze–thaw technique and irradiated in the Rayonet reactor with 300-nm lamps for 10 hr. During this time, the reactor was flushed continuously with refrigerated air and the temperature ranged between 15–29°. Evaporation of the cyclohexane gave 1.1 g of solid. Chromatography on a column of alumina gave 0.74 g of recovered **1** (elution with petroleum ether). Continued elution with 95: 5 petroleum ether–ether gave 0.19 g (19%) of rearrangement product **5** as an oil. The nmr spectrum agreed well with that of authentic **5**, the benzamide **11** had mp 106.5–107.5 (ether–petroleum ether), and the mixture melting point with authentic **11** was not depressed.

Similar, additional experiments showed that *N*-methyl-*p*-toluidine was also formed, but the amounts were not determined.

Photochemical Rearrangement of *N*,*N*′-Dimethyl-*p*-hydrazoanisole (2).—The procedure was the same as with compound **1**, except that 0.68 g of **2** in 190 ml of cyclohexane was irradiated for only 3 hr. Successive elutions with 98:2 petroleum ether–ether from an alumina column gave 0.117 g of **2** (17.2% recovery), 0.450 g (65.1%) of rearrangement product **12**, and 0.074 g (10.7%) of *N*-methylanisidine. Product **12** was characterized as the benzenesulfonyl derivative **22**, mp 94–95°, mixture melting point with authentic **22**, 95–95.5°.

Photochemical Rearrangement of *N*,*N*′-Dimethyl-*p*-hydrazobiphenyl (3).—A solution of 0.50 g of **3** in 450 ml of cyclohexane was irradiated for 17 hr at 25°. Evaporation of the solvent gave a brown oil which was chromatographed on a silica gel column. Elution with 1 l. of petroleum ether–ether (99:1) gave 0.17 g (34%) of **3**, mp 173.5–174.5°. Elution with 750 ml of petroleum ether–ether (98:2) gave 0.12 g (24%) of a compound, mp 171–171.5° (ethanol-benzene), mixture melting point with **3** 147–164°, which is believed to be the *o*-semidine (*N*,*N*′-dimethyl-6-amino-3,4′-diphenyl diphenylamine) (**23**). The nmr spectrum is listed in Table II.

Anal. Calcd for $C_{26}H_{24}N_2$: C, 85.68; H, 6.64; N, 7.69. Found: C, 85.41; H, 6.42; N, 7.84.

Continued elution of the column with 500 ml of petroleum ether–ether (95:5) gave 0.174 g (35%)) of *N*-methyl-4-aminobiphenyl, identified through its benzenesulfonyl derivative, mp and mmp 152–153°. Elution with 750 ml of petroleum ether–ether (85:15) gave 0.10 g of a tacky solid, which was not identified but whose nmr spectrum suggested the presence of a cyclohexyl group. Stripping the column with ether gave 0.06 g of brown oil whose nmr spectrum indicated the presence of 4-aminobiphenyl, confirmed by preparation of the benzamide, mp 233–234° (lit.[21] mp 230°). The melting point was not depressed by mixture with an authentic sample.

Photolysis of *N*,*N*′-Dimethylhydrazomesitylene (4).—A solution of 0.5 g of **4** in 400 ml of cyclohexane was degassed, sealed, and irradiated with 300-nm lamps for 7 hr at 24–29°. Removal of solvent left 0.69 g of orange oil which was chromatographed on alumina. Elution with petroleum ether gave 0.18 g (36%) of *N*-methylmesidine, identified by nmr and its benzenesulfonyl derivative, mp 116–117° (ether). Elution with 90:10 petroleum ether–ether gave 0.14 g (30%) of mesidine, identified by nmr and its dibenzenesulfonyl derivative, mp 176.5–177° (ether).

Anal. Calcd for $C_{21}H_{21}NS_2O_4$: C, 60.70; H, 5.09; N, 3.37; S, 15.43. Found: C, 60.96; H, 5.15; N, 3.65; S, 15.62.

Stripping of the column with methanol gave 0.11 g of an unidentified oil.

Acid-Catalyzed Rearrangement of *N*,*N*′-Dimethyl-*p*-hydrazotoluene (1).—To a solution of 4.8 g of **1** in 500 ml of methanol at 0° was added 100 ml of a cold, 0.18 *N* solution of methanolic hydrogen chloride. The solution was stirred for 75 min and neutralized with 30 ml of 2.5 *N* aqueous sodium hydroxide. Solvent was removed at room temperature on a rotary evaporator, and the residue was dissolved in ether which was then washed and dried over magnesium sulfate. Column chromatography on alumina gave five compounds, as follows. Elution with petroleum ether gave 0.42 g (8.8%) of 5,5′-dimethyl-2,2′-bis(methylamino)biphenyl (*N*,*N*′,5,5′-tetramethyl-*o*-benzidine) (**24**), mp 124–125° (ethanol). Identification was made by nmr spectroscopy and by elemental analysis.

Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.96; H, 8.39; N, 11.65. Found: C, 80.20; H, 8.56; N, 11.67.

Elution with 60:40 petroleum ether–benzene gave 0.21 g (5%) of 2,7-dimethylphenazine (**25**), mp 161–162.5° (ether–petroleum ether) (lit.[22] mp 162.5–163°). Identification was made by nmr spectroscopy and elemental analysis. Elution with 50:50 petroleum ether–ether gave 0.22 g of an unidentified brown oil, while elution with methanol gave 0.70 g of an unidentified red solid.

Acid-Catalyzed Rearrangement of *N*,*N*′-Dimethylhydrazoanisole (2).—To an ice-cold solution of 0.5 g of **2** in a nitrogen-flushed mixture of 20 ml of dioxane and 80 ml of methanol was added a cold solution of 0.2 ml of 12 *N* hydrochloric acid in 20 ml of methanol. The solution was stirred at 0° for 30 min, and 0.4 g of potassium hydroxide in 10 ml of methanol was added. Evaporation of the solution under reduced pressure and extraction with ether gave an oil which was chromatographed to give 0.23 g (46%) of *o*-semidine (**12**), benzenesulfonyl derivative, mp 95–95.5° (ether), and 0.21 g (42%) of *N*-methylanisidine benzenesulfonyl derivative, mp 75.5–76° (ethanol), mmp 76–76.5°.

Registry No.—**1**, 30724-66-4; **2**, 30724-67-5; **3**, 30788-03-5; **4**, 30788-04-6; **5**, 30724-68-6; **7**, 30788-05-7; **8**, 30788-06-8; **9**, 30788-07-9; **11**, 30788-08-0; **12**, 30745-00-7; **17**, 4793-90-2; **19**, 30788-09-1; **20**, 30788-10-4; **22**, 30788-11-5; **23**, 30724-70-0; **24**, 30788-12-6; mesidine dibenzenesulfonyl derivative, 30724-71-1; *N*-acetyl-3,4′-dimethyl-6-nitrodiphenylamine, 30724-72-2.

---

[21] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1967, p 328.

[22] G. A. Swan and D. G. I. Felton, "The Chemistry of Heterocyclic Compounds—Phenazine," Interscience, New York, N. Y., 1957, p 24.