Photochemistry of Dimethylamine in Hydrocarbon Solvents. Striking Differences between Solution- and Gas-Phase Photochemical Reactivity

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Generation of dimethylamino radicals both thermally and photochemically from a variety of chemical precursors has produced discordant results.[1-4] However, one widely accepted generalization has been that dimerization to tetramethylhydrazine is a prominent reaction of dimethylamino radicals;[1b,3,4h] indeed, the reaction has even been touted as a practicable synthetic route to the hydrazine.[3a,c] Complicating interpretation of dimethylamino radical reactivity have been numerous other reaction products, apparently varying with the precursor, medium, and method for generating the dimethylamino moiety.[2-4] Among these, *N,N,N′,N′*-tetramethylmethanediamine (1) has often been found,[2,3a,c,5] but never adequately explained.

We wish to report the results of our study of the solution-phase photochemistry of dimethylamine (2) in hydrocarbon solvents, which (a) contrast sharply with the gas-phase photochemistry of dimethylamine;[3,4] (b) indicate that dimerization of dimethylamino radicals may be almost totally suppressed under some reaction conditions; (c) offer an extremely clean, easy, and high-yield synthesis of the interesting[6] diamine 1; and (d) support for the first time a viable mechanism for the formation of 1 from dimethylamino radicals.

Hydrocarbon (most conveniently, *n*-nonane; cf. Experimental Section) solutions of 2 (*ca.* 1 *M*) were degassed and irradiated at 35° with a Vycor-filtered mercury arc; reaction was monitored by GLC (Carbowax 20M on firebrick). At about 70% conversion, 100 mmol of 2 gave (eq 1) 22

$$\underset{2}{\mathrm{Me_2NH}} \xrightarrow[\mathrm{C_9H_{20}}]{h\nu} \underset{1}{\mathrm{Me_2NCH_2NMe_2}} + \underset{3}{\mathrm{MeNH_2}} + \begin{matrix}\text{trace}\\ \text{products}\end{matrix} \qquad (1)$$

mmol of diamine 1, 7 mmol of methylamine (3), and traces (<2%) of two minor products (vide infra). Diamine 1 was isolated by spinning-band distillation (alternatively, preparative GLC) and identified by comparison with authentic material. It is noteworthy that, assuming the minimum 3:1 stoichiometry demanded for the 2 → 1 reaction, the observed yields of 1 are above 90% and thus synthetically quite attractive.[7] The two minor products were identified by GLC–MS techniques as *N,N,N′*-trimethylmethanediamine (4) and tetramethylhydrazine (5). No methane, solvent

$$\underset{4}{\mathrm{Me_2NCH_2NHMe}} \qquad \underset{5}{\mathrm{Me_2N{-}NMe_2}}$$

reaction products, or *N,N′*-dimethylethanediamine were observed within our detection limits (estimated at ca. 1%); no analysis for hydrogen was made. Monitoring the reaction with time by GLC and NMR showed only continued and proportional increases in the yields of the four volatile products (1, 3, 4, and 5) with increasing time of irradiation; no transient accumulation of 4, 5, or other species was detected. Oligomerization was minimal, judging from the relatively small nonvolatile photolysate residue.

Formation of 1 from 2 may thus be explained mechanistically (Scheme I) in terms of consecutive (i) photolytic scission of the N–H bond of 2 (eq 2), generating dimethylamino radicals 6;[3,4] (ii) oxidation of 6 to *N*-methylenemethylamine (7) via autodisproportionation (eq 3a), bimolecular disproportionation (eq 3b), and/or a hydrogen transfer sequence involving solvent (eq 3c);[9] (iii) addition of 2 to 7, giving 4 (eq 4); and (iv) transamination of 4 with 2 (eq 5) to give 1 and 3, the observed products.

Scheme I

$$\underset{2}{\mathrm{Me_2NH}} \xrightarrow{h\nu} \underset{6}{\mathrm{Me_2N\cdot}} + \mathrm{H\cdot} \qquad (2)$$

$$[\mathrm{Me_2N\cdot} + \mathrm{H\cdot}] \longrightarrow \mathrm{H_2} + \underset{7}{\mathrm{MeN{=}CH_2}} \qquad (3a)$$

and/or

$$\underset{6}{\mathrm{2Me_2N\cdot}} \longrightarrow \mathbf{2} + \underset{7}{\mathrm{MeN{=}CH_2}} \qquad (3b)$$

and/or

$$\mathrm{RH} \xrightarrow{\mathrm{Me_2N\cdot\ or\ H\cdot}} \mathrm{R\cdot} \xrightarrow{\mathrm{Me_2N\cdot}} \underset{7}{\mathrm{MeN{=}CH_2}} + \mathrm{RH} \qquad (3c)$$

$$\underset{2}{\mathrm{Me_2NH}} + \underset{7}{\mathrm{CH_2{=}NMe}} \longrightarrow \underset{4}{\mathrm{Me_2NCH_2NHMe}} \qquad (4)$$

$$\underset{4}{\mathrm{Me_2NCH_2NHMe}} + \underset{2}{\mathrm{Me_2NH}} \longrightarrow \underset{1}{\mathrm{Me_2NCH_2NMe_2}} + \underset{3}{\mathrm{MeNH_2}} \qquad (5)$$

An alternative a priori explanation would have the sequence of events as primary photochemical conversion of 2 to hydrazine 5, followed by secondary photolysis of 5 to the observed products. However, the failure to detect (GLC–NMR monitoring) short-term accumulation of 5 in the photochemical reaction of 2 suggests that hydrazine 5 is not involved as a cul-de-sac for dimethylamino radicals.

In the proposed mechanism the photochemical cleavage and disproportionation steps are well documented.[3,4] The subsequent addition and transamination steps follow not only from isolation of 4 from reaction mixtures after irradiation of 2, but also from the observed stoichiometry and general absence of other by-products. However, conversion of independently synthesized 4 to 1 under the conditions employed for photosynthesis of 1 from 2 needs to be demonstrated before the transamination step is unequivocally established. The smaller than theoretical yields of 3 may be attributed both to analytical limitations and to the known photolability of 3. Irradiation of 3 gives 7,[11] which would then give 4 and, ultimately, 1.

Resemblance of the photolytic conversion of 2 to 1 in nonane to the photochemical behavior of dimethylamine in chlorocarbons[2] is compatible with the intermediacy of 6 in both mechanisms. However, in nonane, photolysis of 2 gives 6 directly; in chlorocarbons, photodissociation of the charge-transfer complex of 2 gives the aminium cation radical (8), which then generates 6 in a hydrogen transfer reaction with 2 (eq 6). Thus, although diamine 1 and methylamine 3 are the major amine photoproducts from 2 in both nonane and carbon tetrachloride, involvement of the charge-transfer mechanism in the chlorocarbon solvent leads to formation of by-products (amine hydrochloride 9 and chloroform) which are absent when the photochemical reaction is carried out in a hydrocarbon solvent.

$$\mathrm{Me_2NH\cdot CCl_4} \xrightarrow[\mathrm{Pyrex}]{h\nu}$$

$$\mathrm{Cl_3C\cdot} + \underset{8}{[\mathrm{Me_2\overset{+\cdot}{N}H}]\mathrm{Cl^-}} \xrightarrow{\mathrm{Me_2NH}} \underset{9}{\mathrm{Me_2NH\cdot HCl}} + \underset{6}{\mathrm{Me_2N\cdot}} \qquad (6)$$

Results of our investigation contrast dramatically with earlier studies of the dimethylamino radical under gas-phase conditions,[3,4a,b,h] since we observed only minimal levels of radical recombination (to give hydrazine 5) and very little formation of higher molecular weight oligomers of imine **7** (e.g., 1,3,5-trimethylhexahydro-*s*-triazine, polymeric material). The smaller proportion of oligomers seems clearly due to efficient trapping of **7** in solution by excess dimethylamine. The minimum yields of hydrazines are of less certain origin, corresponding to an unusual situation in which a radical dimer product is formed in the gas phase, but not in solution. An explanation involving intermediacy of the isomeric C-centered radicals in solution rather than **6**, an a priori possibility in light of Allan and Swan's photochemical studies of diethylamine,[12] seems incompatible with the absence of *N,N'*-dimethylethanediamine here and the known proclivity of α-aminoalkyl radicals toward recombination rather than disproportionation.[1a,12] The most likely explanation would appear to be the source of the dimethylamino radical. When **6** is generated from **2** by photolysis in solution, oxidation to imine **7**, either via autodisproportionation within the solvent cage (eq 3a) or via the hydrogen transfer sequence with solvent as hydrogen carrier (eq 3c), should be optimized, conditions favoring subsequent formation of **1**. In contrast, when **6** is generated from tetramethyltetrazene or even from **2** in the gas phase, conditions for oxidation of **6** to **7** are no longer optimal; diffusion and recombination reactions of **6** become more important.

Our observations differ superficially from those of Niu and Stenberg,[10] who reported 90% yields of imines analogous to **7** (and no diamines analogous to **1**) resulting from photodehydrogenation of several secondary amines (e.g., **10**, eq 7). Although shorter periods of irradiation were employed in the **10** → **11** (eq 7) conversion (6 hr[10] vs. 96 hr for **2** → **1**), unreported sample size in the earlier study[10] makes direct, meaningful comparisons difficult. It is likely, however, that the failure to detect even transient buildup of **7** from **2** during the NMR–GLC monitoring of photolyses of **2** partly reflects the higher concentrations of amine ($\geq 1\ M$) used in our study than in Niu and Stenberg's work ($10^{-2}\ M^{10}$), since higher concentrations of amine would lead to more efficient bimolecular destruction of imine (Scheme I, eq 4). Similar concentration dependence of imine yields in secondary amine photolysis has been reported by Ratcliff and Kochi.[1a] Another important factor in accounting for the differing reactivities of **2** and amines such as **10** may be stereochemical. Relative to imine **7**, the imine **11** derived from **10** may be less reactive toward nucleophilic addition of amine (as in eq 4) because of the steric hindrance posed by bulky substituents in **10** and **11**.

$$\underset{\mathbf{10}}{(n\text{-}C_6H_{13})_2NH} \xrightarrow[\text{cyclohexane}]{h\nu,\ 6\ \text{hr}} \underset{\mathbf{11}}{n\text{-}C_6H_{13}N{=}CHC_5H_{11}} \qquad (7)$$

Finally, the origin of diamine **1**, which was once considered "obscure," [3a] and later considered to be the reaction of methyl radicals with trimethylamine,[3c] is, in all likelihood, neither. Unlike previous mechanisms offered for formation of **1**, the one outlined in Scheme I involves only species whose presence in photolysates is now well documented.

Experimental Section

Photolysis of Dimethylamine in Nonane. In a typical experiment, a 1.3 *M* solution of dimethylamine (3.77 g, 83.7 mmol) in 65 ml of *n*-nonane in a quartz tube was degassed by three freeze–pump–thaw cycles, then sealed, and irradiated at 35° with an adjacent Vycor-filtered mercury arc lamp (Hanovia medium-pressure 450-W). Progress of reactions was monitored by NMR and by GLC on a 5 ft × 0.25 in. column of 20% w/w alkali-treated Carbowax 20M on 60/80 firebrick at 65°. After 96 hr, NMR, mass spectral, and GLC analysis indicated 68% reaction, with 27 mmol of dimethylamine remaining, formation of 18 mmol (95% yield) of *N,N,N',N'*-tetramethylmethanediamine, 6 mmol of methylamine, and traces (<2% each) of tetramethylhydrazine and *N,N,N'*-trimethylmethanediamine (identified by tandem GC–MS). Prolonged irradiation was inefficient in raising the yield of *N,N,N',N'*-tetramethylmethanediamine because of secondary photochemical reactions. Similar procedures were followed for irradiating samples containing from 2 to 100 mmol of dimethylamine, with approximately proportional irradiation times and with identical results.

Nitrogen was bubbled through the photolysate to remove most of the methylamine and some of the dimethylamine. *N,N,N',N'*-tetramethylmethanediamine was isolated from the residue by spinning-band distillation, bp 82–84° (lit.[8] bp 82–84°), of larger samples or by preparative GLC of smaller ones in ca. 85% yields; it was identified by comparison of ir, NMR, and mass spectra to those of authentic material.[2,8]

Use of pentane or cyclohexane as solvent gave comparable results by GLC analysis; however, isolation by distillation was facilitated using the higher boiling *n*-nonane as solvent (and distillation chaser).

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Registry No.—**1**, 51-80-9; **2**, 124-40-3; nonane, 111-84-2.

References and Notes

(1) For brief discussions, see (a) M. A. Ratcliff, Jr., and J. K. Kochi, *J. Org. Chem.*, **37**, 3268 (1972); (b) J. R. Roberts and K. U. Ingold, *J. Am. Chem. Soc.*, **95**, 3228 (1973).

(2) (a) K. G. Hancock and D. A. Dickinson, *J. Chem. Soc., Chem. Commun.*, 783 (1973); (b) K. G. Hancock and D. A. Dickinson, *J. Org. Chem.*, **39**, 331 (1974).

(3) (a) J. S. Watson, *J. Chem. Soc.*, 3677 (1956); (b) F. O. Rice and C. J. Grelecki, *J. Am. Chem. Soc.*, **79**, 2679 (1957); (c) B. G. Gowenlock, and D. R. Snelling, *Adv. Chem.*, **36**, 150 (1962); (d) B. G. Gowenlock, P. P. Jones, and D. R. Snelling, *Can. J. Chem.*, **41**, 1911 (1963).

(4) (a) C. H. Bamford, *J. Chem. Soc.*, 17 (1939); (b) G. H. Booth and R. G. W. Norrish, ibid., 188 (1952); (c) B. R. Cowley and W. A. Waters, ibid., 1228 (1961); (d) D. Mackay and W. A. Waters, *J. Chem. Soc. C*, 813 (1966); (e) S. G. Hadley and D. H. Volman, *J. Am. Chem. Soc.*, **89**, 1053 (1967); (f) D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, **53**, 3932 (1970); (g) W. C. Danen and T. T. Kensler, *J. Am. Chem. Soc.*, **92**, 5235 (1970); (h) P. W. Jones and H. D. Gesser, *J. Chem. Soc., B*, 1873 (1971); (i) R. W. Dennis and B. P. Roberts, *J. Organomet. Chem.*, **43**, C2 (1972).

(5) (a) F. Klages, G. Nober, F. Kircher, and M. Bock, *Justus Liebigs Ann. Chem.*, **547**, 1 (1941); (b) G. Smith and G. A. Swan, *J. Chem. Soc.*, 886 (1962); (c) W. H. Urry and J. Sheeto, *Photochem. Photobiol.*, **4**, 1067 (1965).

(6) Among the interesting properties of diamine **1** may be mentioned its apparent tumor cytostatic effect; cf. H. Schönenberger and A. Adam, *Arzneim.-Forsch.*, **14**, 1168 (1964).

(7) Both yield and operational simplicity appear to distinguish this method from the alternatives.[2,8]

(8) J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, **22**, 355 (1957); L. Henry, *Bull. Cl. Sci., Acad. R. Belg.*, **26**, 203 (1893).

(9) Which pathway predominates depends on other reaction conditions,[1,3,4,10] and has not yet been determined under the conditions we employed for photochemical synthesis of **1**.

(10) C. H. Niu and V. I. Stenberg, *Chem. Commun.*, 1430 (1971).

(11) J. S. Watson and B. deB. Darwent, *J. Chem. Phys.*, **20**, 1041 (1952).

(12) L. T. Allan and F. A. Swan, *J. Chem. Soc.*, 4822 (1965).

3-Thiabicyclo[3.2.0]hepta-1,4-dienes. Synthesis of Tetraphenyl-2,5-dithiabisnorbiphenylene

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3-Thiabicyclo[3.2.0]hepta-1,4-dienes are members of a class of strained heterocyclic systems which have only recently been prepared.[1-4] Two of the reported synthetic routes[1,3] involve closure of the four-membered ring as the final synthetic step, one the formation of the thiophene ring[2] and in the other formation of both rings in one reac-