The Photochemical Reaction of Dimethylamine in Polychloromethanes. A Photochemical Synthesis of Bis(dimethylamino)methane

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Irradiation of *ca.* 1.0 *M* solutions of dimethylamine in carbon tetrachloride at 300 nm and 35° gave *N,N,N′,N′*-tetramethylmethanediamine (22 mol %), dimethylamine hydrochloride (32 mol %), and chloroform (25 mol %), plus lesser amounts of methylamine. Quantum yields at zero conversion were 4.7 mol einstein^{-1} for disappearance of dimethylamine, and 1.2, 1.1, and 1.2 for appearance of diamine, amine hydrochloride, and chloroform, respectively. Similar reactions of dimethylamine were observed in chloroform and α,α,α-trichlorotoluene, but with longer irradiation times. Diamine formed in irradiations of dimethylamine in deuteriochloroform showed no deuterium incorporation. A mechanism involving photodissociation of an amine–halocarbon charge-transfer complex, followed by disproportionation and/or combinations of dimethylamino radicals, and, finally, by aminal disproportionation is supported by control experiments, quantum yields, and the protochemistry of potential and actual intermediates. The 4:1 reaction stoichiometry of dimethylamine to diamine corresponds to *ca.* 88% of theoretical yield for production of diamine.

Despite the significance of amino radicals and cation radicals in organic and biological chemistry, the mechanisms of reactions involving these species have not been thoroughly elucidated. Unstudied key compounds and insufficient quantitative data have contributed to the complexity of the problem. In particular, the complicated reactions of amines with compounds of high electron affinity have generated sporadic investigations spanning 60 years.[1] During this time, however, some of the simplest amines have oddly escaped scrutiny.

It is now generally appreciated that halogenated solvents cannot be used unwarily for spectroscopic analysis of amines because of possible donor–acceptor complexation between the amine and halocarbon solvent. Such interactions may be reflected subtly by changes in molecular polarization and dipole moments or,[2] more directly, by appearance of a new band in the electronic absorption spectrum.[3-5] In numerous cases, the interaction is visibly manifested in direct reaction of an amine with the halocarbon solvent, leading to amine hydrochloride salts and a variety of other products.[5,6]

The complexes between amines and halocarbons have been shown to have a 1:1 stoichiometry by vapor-pressure measurements,[7] spectroscopic techniques,[2-5] and adduct isolation.[8] That the amine functions as electron donor and the halocarbon as acceptor has been supported by noting the parallel increases of complex strength and halocarbon electron affinity: $BrCCl_3 > CCl_4 > FCCl_3$[3] and $CCl_4 > CHCl_3 > CH_2Cl_2$.[4] The reactions of the charge-transfer complexes are general for primary, secondary, and tertiary amines,[6] but are extremely susceptible to variations in reactant structure and reaction conditions such as amine basicity;[2,9] steric hindrance;[2,9] uv-visible light;[3-5,10] presence of oxygen;[5,9,11,12] catalysis by metal salts, particularly copper;[5,6,11,13] concentration;[4,5] and the identity of the polyhalocarbon.[2-4,8] Both ionic[9,12,14] and homolytic mechanisms[3,5,6,11] have been suggested, with the most recent and extensive investigations[5,6] supporting existence of radical chain processes initiated *via* an amino radical cation. Depending upon reaction conditions, nitrogen-containing products have included amine hydrohalides, imines, nitriles, isocyanides, lower molecular weight amines, and ureas, generally as complicated mixtures.[5,6]

This report describes the photochemical reaction of dimethylamine in polychlorocarbons. Strangely, reactions of this simplest of secondary amines appear to have been passed over. In fact, the reaction of dimethylamine (1) in polychlorocarbons is unique, giving rise to only methylamine and one other volatile nitrogen-containing photoproduct of unusual structure, apparently *via* an equally unusual mechanism.

Results

Irradiations were carried out at 300 nm and 25–40° on *ca.* 1.0 *M* solutions of dimethylamine (1) in carbon tetrachloride which had been purged with argon. Irradiations were carried out on scales ranging from 2 to 200 mmol of **1**. In a typical microscale irradiation, *ca.* 50% of 3 mmol of **1** was consumed in 1 hr.[15] During irradiation, a white precipitate formed which was collected by filtration and analyzed by Volhard titration with silver nitrate[16] and nmr (in D_2O) as dimethylamine hydrochloride (2). In addition to solvent, the liquid phase contained chloroform, methylamine (3), and one other photoproduct, which was best isolated by preparative glpc (Carbowax 20M, alkali-treated, 20% on firebrick) at 100°. Based on ir, nmr (12 H singlet at δ 2.15, 2 H singlet at 2.60), and mass spectra (and glpc retention times) identical with those of authentic material, the photoproduct was identified as *N,N,N′,N′*-tetramethylmethanediamine (4) (eq 1).

$$\underset{\mathbf{1}}{Me_2NH} \xrightarrow[CCl_4]{h\nu} \underset{\mathbf{2}}{Me_2NH{\cdot}HCl} + \underset{\mathbf{3}}{MeNH_2} + \underset{\mathbf{4}}{Me_2NCH_2NMe_2} + CHCl_3 \quad (1)$$

At 50% conversions or less, the reaction was remarkably clean, with 100 mmol of **1** giving 32 mmol of hydrochloride **2**, *ca.* 7 mmol of methylamine **3**, 22 mmol of diamine **4**, and 25 mmol of chloroform. As both methylamine (3) and diamine **4** were also demonstrated to be somewhat photolabile, secondary reactions reduced the yields of both **3** and **4** at higher conversions.

As Table I indicates, products **2** and **4** were also observed, albeit in somewhat reduced yields and with longer irradiation times required, using either deuteriochloroform or α,α,α-trichlorotoluene as solvent. For purposes of comparison, irradiation times and product yields at 50% conversions of **1** are recorded, in consideration of the secondary reactions which complicate analysis beyond that point.

In light of known ground-state syntheses of $R_2N(CH_2)_nNR_2$ diamines from amines and dihalogenated hydrocarbons,[17] solvent was an *a priori* possibility for the source of the central carbon in the bis(dimethylamino)methane photoproduct **4**. In fact, in methylene chloride, rapid production of **4** by conventional ground-state amine alkylation occurs. However, the only products formed in the ground-state alkylation are the amine hydrochloride **2**

Table I
Formation of Bis(dimethylamino)methane and Dimethylamine Hydrochloride in Chlorocarbon Solvents

Solvent	Conditions	Conversion, %	Reaction time, hr	Yield of **4**, mol %	Yield of **2**, mol %
CCl_4	300 nm[a]	50	1	22	32
$PhCCl_3$	300 nm[a]	50	20	11	b
$CDCl_3$	300 nm[a]	50	40	17	b
CH_2Cl_2	45°, dark	90	16	25	b
CD_2Cl_2	45°, dark	94	21	22, d_2	46

[a] Duplicate dark controls at 45° indicated ≤3% thermal reaction. [b] Not analyzed at 50% conversion in these runs.

and diamine **4**, in the 2:1 ratio expected from stoichiometry. In dideuteriomethylene chloride the product is bis(dimethylamino)dideuteriomethane (**4**-d_2), confirming solvent incorporation during the amine-alkylation reaction. Parenthetically, the preparative value of this reaction for preparing **4**-d_2 should be noted.

$$\underset{\mathbf{1}}{4Me_2NH} + CH_2Cl_2 \xrightarrow{25°} \underset{\mathbf{2}}{2Me_2NH\cdot HCl} + \underset{\mathbf{4}}{Me_2NCH_2NMe_2}$$

Clearly, however, the photochemical reaction of **1** is drastically different. Rapid thermal reaction precluded photochemical reaction of dimethylamine in methylene chloride, but the isolation of diamine **4** rather than deuterated or phenylated **4** from irradiations in deuteriochloroform and benzotrichloride rules out solvent incorporation in the photochemical synthesis of **4**.

Mechanistic Probes. The solvent independence of the identity of diamine **4** as the dominant (other than hydrochloride salt) photoproduct established dimethylamine itself, *and not solvent, as the source of the central carbon in* **4**. The uniqueness of the photoproduct prompted attempts to at least partially unravel the reaction mechanism, which was obviously anomalous among amine–halocarbon interactions.

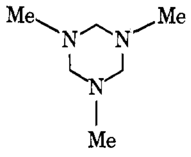
Quantum yields for the photochemical reaction of **1** in carbon tetrachloride were determined, employing the potassium ferrioxalate actinometer of Hatchard and Parker.[18] Measured quantum yields showed a dependence on both concentration and extent of conversion of amine **1**. However, at 1.1 *M* initial concentrations of dimethylamine (*cf.* Experimental Section), extrapolation from a series of determinations at differing photolysis times and conversions gave zero-conversion quantum yields of 4.70 mol einstein^{-1} for disappearance of **1** and 1.1, 1.2, and 1.2 for appearance of amine hydrochloride **2**, diamine **4**, and chloroform, respectively. Severe analytical difficulties prevented measurement of meaningful quantum yields for methylamine appearance.

The photochemical transformation of **1** to **4** could be mimicked using cuprous chloride as the initiator. Results in the copper-initiated and photochemical reactions were comparable. Solutions of dimethylamine in carbon tetrachloride also displayed the usual ability[6] to bleach the color caused by added galvinoxyl free radical when exposed to light.

The possible mechanistic involvement of *N*-chlorodimethylamine (**5**) was tested by photolysis of independently prepared **5**[19] in carbon tetrachloride. Irradiation of **5** at 300 nm caused rapid decomposition of chloramine **5** and precipitation of amine hydrochloride, but gave no solvent-soluble, volatile photoproducts detectable by glpc or nmr. Similar results were obtained in photolysis of **5** containing added cumene; no dicumyl, tetramethylhydrazine,[20] chloroform, or other glpc- or nmr-detectable photoproducts were formed. Control runs at 45° in the dark showed both chloramine **5** and mixtures of **5** and **1** to be thermally stable.

Similarly, irradiation of a carbon tetrachloride solution of 1,3,5-trimethylhexahydro-*s*-triazine (**6**, trimer of *N*-methylenemethylamine, **7**) caused precipitation of amine hydrochloride. Chloroform was the only solvent-soluble photoproduct noted by glpc and nmr. Triazine **6** was shown to be thermally stable at 45° in the dark.

Me_2NCl
5



6

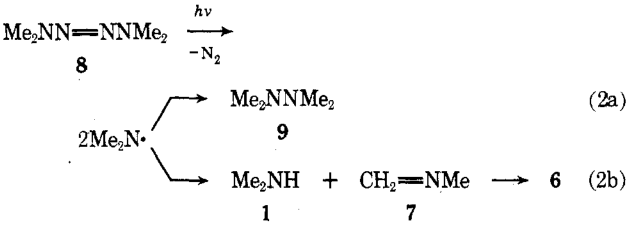
$CH_2{=}NCH_3$
7

Irradiation of tetramethyltetrazene (**8**) in carbon tetrachloride again gave chloroform as the only solvent-soluble photoproduct and a precipitate of amine hydrochloride. Reaction, however, was inefficient. Added cumene had no measurable effect. The absences of **4** and of tetramethylhydrazine[20] (**9**) were specifically noted.

Discussion

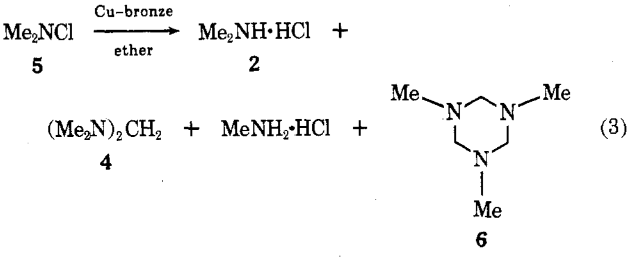
The plethora of nitrogen-containing products noted in earlier reports of amine–halocarbon reactions[5,6] (*vide supra*) did not include diamines. Formation of **4** from **1** is thus both anomalous in its deviation from the usual pattern of *amine–halocarbon interactions and* unique in the specificity with which the novel photoproduct is formed.

Only scant precedent for the **1** → **4** transformation can be found in the literature. Watson has reported that diamine **4** is a 1% by-product in photolysis of tetramethyltetrazene to tetramethylhydrazine (**9**) and triazine **6**.[21] In support of the proposed mechanism, which involved combination of and/or disproportionation of dimethylamino radicals (eq 2), allusion was made to an unpublished study of the mercury-sensitized decomposition of gaseous dimethylamine,[21] in which **4** had been observed as a minor product of "obscure origin." Diamine **4** has also been produced in 2–4% yields during the autoxidation of tetrakis(dimethylamino)ethylene (**10**);[22] as a minor product from γ irradiation of trimethylamine, the major products being **9** and *N,N,N',N'*-tetramethylethanediamine (**11**);[23] and as a major product from treatment of *N*-chlorodimethylamine (**5**) with copper-bronze in ether[24] (eq 3). Pyrolysis of **8** gives **4**, often as a major product, but re-



$$\underset{\mathbf{8}}{Me_2NN{=}NNMe_2} \xrightarrow[-N_2]{h\nu} 2Me_2N\cdot \longrightarrow \underset{\mathbf{9}}{Me_2NNMe_2} \quad (2a)$$

$$2Me_2N\cdot \longrightarrow \underset{\mathbf{1}}{Me_2NH} + \underset{\mathbf{7}}{CH_2{=}NMe} \longrightarrow \mathbf{6} \quad (2b)$$



Scheme I
Mechanism for the Photochemical Reaction of Dimethylamine in Carbon Tetrachloride

$$\underset{\mathbf{12}}{Me_2NH{\cdot}CCl_4} \xrightarrow{h\nu} \underset{\mathbf{13}}{\overset{+\bullet}{[Me_2NH]}Cl^-} + \underset{\mathbf{14}}{Cl_3C\cdot} \quad (4)$$

$$\underset{\mathbf{13}}{\overset{+\bullet}{[Me_2NH]}Cl^-} + \underset{\mathbf{1}}{Me_2NH} \longrightarrow \underset{\mathbf{2}}{Me_2NH{\cdot}HCl} + \underset{\mathbf{15}}{Me_2N\cdot} \quad (5)$$

$$\underset{\mathbf{14}}{Cl_3C\cdot} + \underset{\mathbf{1}}{Me_2NH} \longrightarrow HCCl_3 + \underset{\mathbf{15}}{Me_2N\cdot} \quad (6)$$

$$\underset{\mathbf{15}}{Me_2N\cdot} + CCl_4 \longrightarrow \underset{\mathbf{5}}{Me_2NCl} + \underset{\mathbf{14}}{Cl_3C\cdot} \quad (7)$$

$$\underset{\mathbf{15}}{2Me_2N\cdot} \longrightarrow \underset{\mathbf{7}}{MeN{=}CH_2} + \underset{\mathbf{1}}{Me_2NH} \quad (2b)$$

$$\underset{\mathbf{1}}{Me_2NH} + \underset{\mathbf{7}}{MeN{=}CH_2} \longrightarrow \underset{\mathbf{16}}{Me_2NCH_2NHMe} \quad (8)$$

$$\underset{\mathbf{16}}{Me_2NCH_2NHMe} + \underset{\mathbf{1}}{Me_2NH} \longrightarrow \underset{\mathbf{4}}{Me_2NCH_2NMe_2} + \underset{\mathbf{3}}{MeNH_2} \quad (9)$$

ported yields showed large temperature and surface effects.[25]

Despite the lack of a close precedent for the photochemical synthesis of **4** from **1** in polychloromethanes, there is considerable evidence to support a free-radical mechanism such as the one in Scheme I.

In this mechanism, initiation is envisioned as occurring through photodissociation of the carbon tetrachloride–dimethylamine charge-transfer complex (**12**) into the chloride salt of dimethylamine radical cation (**13**) and trichloromethyl radical (**14**) (eq 4). Photodissociation of amine–halocarbon charge-transfer complexes has been generally accepted[3-6] as satisfactorily accounting for the photolability of amine–halocarbon mixtures. The catalytic effect of cuprous chloride on the **1** → **4** transformation has ample parallel. In other amine–halocarbon reactions,[5,6,11] copper initiation has been considered to involve either a redox or ligand-transfer process.

Hydrogen transfer between radical cation **13** and excess dimethylamine (eq 5) produces the observed dimethylamine hydrochloride (**2**) and a dimethylamino radical **15**. Although, in principle, radical **15** could be N centered, C centered ($MeNHCH_2\cdot$), or even H bridged, the N-centered formalism seems most rational in view of Lindsay Smith and Malik's study of *tert*-butylamine,[6] and an earlier study of *N*-chlorobenzylamine by Heublein.[9] However, the precise structure of radical **15** is incidental to its place in this mechanism.[26]

Trichloromethyl radical (**14**) abstracts hydrogen from **1**, also giving a dimethylamino radical **15** and chloroform (eq 6). Involvement of free radicals such as **14** and **15** at some stage of the reaction was clearly indicated by the effect of galvinoxyl. Together, reactions 5 and 6 generate two dimethylamino radicals, and could constitute the beginning of a radical chain propagation sequence.

A disproportionation of two amino radicals **15** to dimethylamine (**1**) and *N*-methylenemethylamine (**7**) (eq 2b), followed by nucleophilic addition of **1** to **7** (eq 8), would give *N,N,N'*-trimethylmethanediamine (**16**). Trimethyldiamine **16** could equally well arise directly by radical combination of N-centered radical **15** with the C-centered $MeNHCH_2\cdot$ isomeric radical. Both sequences are plausible, and would constitute termination steps for radical chains. The disproportionation of dimethylamino radicals (eq 2b) has been well studied,[21,25,27,28] and addition of amine **1** to imine **7** parallels the conversion of RCH=NH imines by R'NH₂ to RCH=NR' imines in the photochemical reactions of other amine–halocarbon systems.[5,6] The alternative route of direct radical combination of **15** with the C-centered isomer would have precedent in Watson's explanation[26] for the gas-phase photoreactivity of methylamine (eq 10).

$$\underset{\mathbf{3}}{MeNH_2} \xrightarrow[Hg]{h\nu} Me\underset{\bullet}{\ddot{N}}H + \dot{C}H_2\ddot{N}H_2 \longrightarrow [MeNHCH_2NH_2] \longrightarrow NH_3 + \underset{\mathbf{7}}{MeN{=}CH_2} \quad (10)$$

N-Methylenemethylamine (**7**), formed as an intermediate in the disproportionation–addition route to trimethyldiamine **16** (eq 2b, 8), is known to trimerize to 1,3,5-trimethylhexahydro-*s*-triazine (**6**).[21] Failure to detect **6** in photolyses of **1**, however, cannot be construed as evidence against the occurrence of **7**, since independent photolysis of **6** showed it to be quite photolabile. Further, it is likely that the lifetime of **7** in solution in the presence of excess dimethylamine could be too short to allow much trimerization.

Finally, trimethyldiamine **16** would react rapidly with excess **1** to give diamine **4** and methylamine (**3**), the observed products (eq 9). The transamination parallels the imine exchange reaction observed in other amine–halocarbon systems[5,6] (*vide supra*). Although **16** was not detected in photolysates, a low steady-state concentration would be anticipated since dimethylamine is in excess during most of the photolysis. Additionally, **16** would probably be about as photolabile as the closely related diamine **4**; thus, any **16** not rapidly consumed in reaction with **1** could be photochemically destroyed. An alternate route from **16** to **4** would be photochemical dissociation of the N–H bond in **16**, followed by S_H2 displacement on **1**. No precedent exists for this possibility, however.

The preceding sequence (eq 4, 5, 6, 2b, 8, 9) constitutes a nonchain radical mechanism, and predicts a 4:1 stoichiometry for the **1** → **4** transformation (eq 11). The observed yields are in good agreement with these predictions, and the 22 mol % yield of diamine **4** would thus correspond to 88% of theoretical. That the yield of **4** is slightly low and that of amine hydrochloride **2** is somewhat high (32 mol %) relative to chloroform (25 mol %) is to be expected. Diamine **4**, once formed, can act as the base in eq 5, giving the hydrochloride salt of **4** and the dimethylamino radical **15**. However, the hydrochloride of diamine **4** is known to be unstable, decomposing to chlorotrimethylamine (**17**) and dimethylamine hydrochloride (**2**).[29] Photolability of diamine **4** was also demonstrated.

$$\underset{\mathbf{1}}{4Me_2NH} + CCl_4 \xrightarrow[CCl_4]{h\nu} \underset{\mathbf{2}}{Me_2NH{\cdot}HCl} + \underset{\mathbf{3}}{MeNH_2} + \underset{\mathbf{4}}{Me_2NCH_2NMe_2} + CHCl_3 \quad (11)$$

Another source of amine hydrochloride **2** at the expense of diamine **4** is the involvement of the *N*-chlorodimethylamine (**5**) in the mechanism. Involvement of **5** would presumably involve formation *via* chlorine abstraction from solvent by dimethylamino (**15**, eq 7) and disappearance *via* a secondary photochemical reaction, since control experiments indicated thermal stability and photochemical lability for **5** at 45°. Incorporation of eq 7 completes a radical chain propagation sequence within the mechanism.

The report of Klages, *et al.*[24] (eq 3), made the intermediacy of chloramine **5** a strong *a priori* possibility. The absence of triazine **6**, formed in Klages' experiments, would not be surprising in view of the photolability already discussed. However, the irradiations of **5**, with and without added cumene, clearly ruled out **5** as a photochemical precursor of diamine **4**. Chloramine **5** was also shown to be thermally stable in the dark, as were mixtures of **5** and amine **1**. Thus, chloramine **5** cannot be a direct precursor of the diamine **4**.

In other amine–halocarbon photoreactions, the intermediacy of *N*-chloramines has been implicated as an important step in the radical-chain propagation sequence.[5] High quantum yields characterize these reactions. In the case of dimethylamine, the observed quantum yields (*e.g.*, 4.7 for disappearance of **1**) are only *ca.* 20% in excess of those predicted for the stoichiometry summarized in eq 11 and the mechanism excluding participation of chloramine **5**, *i.e.*, a free-radical nonchain process. The slight deviations of actual yields and quantum yields from the idealized values for eq 11 suggest some participation of a short-chain process including involvement of chloramine (eq 7 and photochemical decompositions of **5**) in the overall mechanism. Both the quantum yields and the dark and photochemical reactions of **5** suggest that such participation is real, but minor.

Finally, the larger deviations from theoretical of the yields of methylamine (**3**) are attributed in part to analytical difficulties, but also to secondary reactions. Photochemical decomposition of methylamine to imine **7** (which would then give **4**) has been established.[27] It is also probable that a small amount of methylamine hydrochloride is formed, which would have gone undetected in the accuracy of the Volhard titration–nmr analysis.

In summary, the photochemical reaction of dimethylamine in carbon tetrachloride and other polychlorocarbons is indeed unusual. Not only is formation of a diamine unique; the mechanism of reaction is anomalous in both the apparent lack of significant involvement of a chain process and in the unusual aminal transamination which is suggested as the final step. The high yields of diamine suggest potential preparative value. Investigation of the implications of these findings to related systems is in progress.

Experimental Section

Materials. Spectrograde (Mallinckrodt) carbon tetrachloride, chloroform, and dichloromethane were passed through alumina and dried over Linde Type 3A Molecular Sieves. Deuteriochloroform, deuteriomethylene chloride, and α,α,α-trichlorotoluene (Matheson Coleman and Bell) were also dried over molecular sieves. *N,N,N′,N′*-Tetramethylmethanediamine (Eastman) and 1,3,5-trimethylhexahydro-*s*-triazine (Aldrich) were used as received after checking for purity by glpc. Dimethylamine (Eastman, anhydrous) was stored in the dark at 0° over molecular sieves. Tetramethyltetrazene was provided by Professor A. L. Balch and Mr. J. Boehm.

N-Chlorodimethylamine was synthesized by the method of Heasley, Kovacic, and Lange[19] in 60% yield from dimethylamine hydrochloride and sodium hypochlorite at 0°, nmr (CCl_4) resonance at δ 2.83.

Tetramethylhydrazine was synthesized by the method of Beltrami and Bissell[20] by successive methylation of *unsym-N,N*-dimethylhydrazine with methyl formate and isolated by preparative glpc on a 5 ft × 0.25 in. Carbowax 20M (alkali-treated, 20% on firebrick) column, nmr (CCl_4) resonance at δ 2.21.

Sample Handling and Analysis. Heeding warnings concerning catalysis by hidden traces of metals,[5] only glass and Teflon storage and transfer apparatus was employed. Dimethylamine samples were prepared in red, low actinic glassware in a darkened cold room at 0°. Solvents were flushed with argon and cooled to 0° before mixing. Initial concentrations were determined by glpc (corrected for detector response) and nmr analysis using undecane as internal standard.

Irradiations were carried out at 25–40° in a Rayonet reactor equipped with eight RUL-3000 Å lamps. Duplicate control runs for thermal reaction were carried out in the dark at 45°.

Following irradiations, samples were placed in a −23° slush in the dark. Immediate analysis of solvent-soluble products was done using both glpc (5 ft × 0.25 in. alkali-treated Carbowax 20M, 20% on firebrick, 100°) and nmr *vs.* the undecane standard. Hydrochloride salt analysis was then done by quenching the sample with 5 *M* nitric acid and determining chloride content by Volhard titration with silver nitrate.[16] In duplicate runs, the precipitated amine hydrochloride was collected by filtration, mp 164–167° (lit.[30] mp 170°), and then analyzed by nmr in D_2O. Analysis for methylamine was done by quantitative mass spectrometric measurements of volatile components removed on a high-vacuum system.

Photolysis in Carbon Tetrachloride. In a typical microscale experiment, 101.6 mg (2.254 mmol) of dimethylamine and 52.6 mg (0.336 mmol) of undecane were brought to 2.0-ml volume in a 5-mm Pyrex tube with argon-flushed carbon tetrachloride and then were sealed. After 60 min irradiation, analysis (*vide supra*) showed 45% conversion of dimethylamine; the photolysate contained 0.25 mmol (25 mol %) of chloroform, 0.23 mmol (22 mol%) of *N,N,N′,N′*-tetramethylmethanediamine, and 0.39 mmol (39 mol %) of dimethylamine hydrochloride. Hexachloroethane, 1,3,5-trimethylhexahydro-*s*-triazine, and tetramethylhydrazine were not detected by glpc. Analysis of parallel thermal controls run in the dark at 45° showed that less than 7 μmol of diamine had formed during handling and 60 min in the dark.

Photolyses in Deuteriochloroform, Chloroform, and α,α,α-Trichlorotoluene. In irradiations conducted similarly to parallel runs in carbon tetrachloride (*vide supra*), 128 mg (2.84 mmol) of dimethylamine in deuteriochloroform containing 122 mg (0.784 mmol) of undecane showed 50% reaction in 40 hr and 70% reaction in 50 hr. Diamine was formed without deuterium incorporation and in 17 mol % yield (0.32 mmol). Identical results were obtained in protiochloroform. Blank runs at 45° showed no dark reaction.

Dimethylamine (106 mg, 2.35 mmol) in benzotrichloride containing 124 mg (0.795 mmol) of undecane showed 50% conversion in 20 hr, with formation of 0.14 mmol (11 mol %) of bis(dimethylamino)methane as the principal photoproduct. No dark reaction was detected in control runs.

Reaction of Dimethylamine with Dichloromethane. Dimethylamine (220 mg, 4.88 mmol), with 142 mg (1.69 mmol) of cyclohexane as internal standard, in 0.5 ml (7.60 mmol) of dichloromethane was heated for 16 hr at 45° in the dark, giving 1.10 mmol (25 mol %, 100% of theoretical yield) of *N,N,N′,N′*-tetramethylmethanediamine at 90% conversion.

In 0.50 ml (7.60 mmol) of dideuteriodichloromethane, 352 mg (7.80 mmol) of dimethylamine, with 147 mg (0.939 mmol) of undecane internal standard, was heated for 5 hr in the dark at 45°, after which time nmr analysis indicated 70% reaction. After 21 hr at 45°, 94% conversion of dimethylamine had occurred, forming 1.60 mmol (22 mol %, 88% of theoretical) of *N,N,N′,N′*-tetramethyldideuteriomethanediamine and 3.38 mmol (46 mol %, 92% of theoretical) of dimethylamine hydrochloride.

Photochemical and Thermal Control Experiments. *N*-Chlorodimethylamine (0.368 mmol, measured *vs.* 0.432 mmol of cyclohexane internal standard) in 1.0 ml of carbon tetrachloride was irradiated for 75 min. Analysis of the photolysate indicated 67% consumption of the chloramine, but revealed no solvent-soluble photoproducts detectable by glpc or nmr. A parallel photolysis of 0.368 mmol of *N*-chlorodimethylamine in 1.0 ml of carbon tetrachloride containing 36.8 mg (0.306 mmol) of cumene and 49.2 mg (0.558 mmol) of dioxane as internal standard gave identical results. No dicumyl, chloroform, or other solvent-soluble photoproducts were detected. Precipitated amine hydrochloride was not quantitatively analyzed. Controls at 45° in the dark indicated no reaction of either *N*-chlorodimethylamine or mixtures of the chloramine and dimethylamine in comparable time periods.

A 1.0-ml carbon tetrachloride solution of 1,3,5-trimethylhexahydro-*s*-triazine (32.0 mg, 0.248 mmol) with 35.8 mg (0.229 mmol) of undecane internal standard was irradiated for 3 hr at 300 nm, showing 100% decomposition of starting material and formation of chloroform as the only detectable solvent-soluble photoproduct. Precipitated amine hydrochloride was not analyzed quantitatively. No thermal reaction occurred in the dark at 45°.

N,N,N′,N′-Tetramethylmethanediamine (33.2 mg, 0.325 mmol) in 1.0 ml of carbon tetrachloride with 34.7 mg (0.222 mmol) of undecane as internal standard was 85% consumed in 3 hr of irradiation, with formation of 0.172 mmol of chloroform as the only volatile solvent-soluble photoproduct. Precipitated amine hydrochloride was not quantitatively measured. On a qualitative scale, photochemical destruction of the diamine was thus *ca.* one fourth as efficient as formation of diamine from dimethylamine.

Tetramethyltetrazene (145 mg, 1.25 mmol) in 0.5 ml of carbon tetrachloride with 155 mg (1.84 mmol) of cyclohexane as internal standard irradiated for 1.5 hr at 300 nm analyzed for 25% reaction of tetrazene with chloroform as the lone detectable photoproduct. Continued photolysis with 69 mg (0.59 mmol) of added cumene caused 67% reaction in 30 hr, with no new solvent-soluble photoproducts (specifically excluding bicumyl) formed. Precipitation of amine hydrochloride was observed but not quantitatively measured.

Addition of cuprous chloride (50 mg, 0.51 mmol) to a 2.0-ml solution of dimethylamine (100 mg, 2.22 mmol) in carbon tetrachloride resulted in formation of bis(dimethylamino)methane, chloroform, and dimethylamine hydrochloride as in photochemically irradiated samples. Solutions of dimethylamine in carbon tetrachloride were also found to decolorize added galvinoxyl when exposed to light.

Quantum Yields. Quantum yields were determined in 2.0-ml 5-mm cylindrical Pyrex tubes surrounded by 15-mm cylindrical Pyrex filter vessels containing a solution of 1.0 M cobaltous sulfate and 1.0 M nickelous sulfate in 5% aqueous sulfuric acid. The filter assemblies containing the reaction vessels were mounted in a carousel inside a Rayonet chamber reactor of eight RUL-3000 Å lamps. In adaptation of the method of Hatchard and Parker,[18] 2.00-ml aliquots of 0.15 M potassium ferrioxalate solution were irradiated for 0.75 min, then withdrawn and assayed for ferrous content spectrophotometrically.

Using 1.1 M dimethylamine–carbon tetrachloride solutions, the samples and actinometer had comparable absorbances, and neither transmitted more than 0.1% of incident light. Following determination of light flux by irradiation of the actinometer, amine solutions were irradiated for varying periods, then analyzed as previously described for substrate disappearance and photoproduct appearance. Quantum yields from multiple runs were extrapolated to values at zero conversion. For a 1.08 M dimethylamine solution, quantum efficiencies were 4.70 mol einstein^{-1} for dimethylamine disappearance, and 1.23, 1.17, and 1.10 for appearance of chloroform, bis(dimethylamino)methane, and dimethylamine hydrochloride, respectively. Individual determinations were reproducible to within ±10%. Quantum yields were concentration dependent with higher values obtained at higher concentrations of dimethylamine.

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References and Notes

(1) W. M. Dehn and A. H. Dewey, *J. Amer. Chem. Soc.*, **33**, 1588 (1911).

(2) A. N. Sharpe and S. Walker, *J. Chem. Soc.*, 2794 (1961); 157 (1962).

(3) D. P. Stevenson and G. M. Coppinger, *J. Amer. Chem. Soc.*, **84**, 149 (1962).

(4) K. M. C. Davis and M. F. Farmer, *J. Chem. Soc. B*, 28 (1967).

(5) W. J. Lautenberger, E. N. Jones, and J. G. Miller, *J. Amer. Chem. Soc.*, **90**, 1110 (1968), and references cited therein.

(6) J. R. Lindsay Smith and Z. A. Malik, *J. Chem. Soc. B*, 617 (1970); 920 (1970), and references cited therein.

(7) H. Wolff and H. E. Hoeppel, *Ber. Bunsenges, Phys. Chem.*, **70**, 874 (1966); H. Wolff and R. Wuertz, *ibid.*, **72**, 101 (1968).

(8) B. J. Pullman and B. O. West, *J. Inorg. Nucl. Chem.*, **19**, 262 (1961).

(9) G. Drefahl and G. Heublein, *J. Prakt. Chem.*, **20**, 323 (1963); G. Heublein, *ibid.*, **31**, 76 (1966).

(10) R. F. Collins, *Chem. Ind. (London)*, 704 (1957); R. Foster, *ibid.*, 1354 (1960).

(11) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 2261 (1961); M. Asscher, *Chem. Ind. (London)*, 1430 (1965).

(12) M. Pesez and J. Bartos, *Bull. Soc. Chim. Fr.*, 1122 (1963).

(13) N. H. Cromwell, P. W. Foster, and M. M. Wheeler, *Chem. Ind. (London)*, 228 (1959); G. J. Beichl, J. E. Colwell, and J. G. Miller, *ibid.*, 203 (1960).

(14) T. G. Bonner and R. A. Hancock, *Chem. Ind. (London)*, 267 (1965).

(15) Owing to inefficient light capture in microscale runs, irradiation times are potentially misleading. On larger scales employing more efficient optics, 50% reaction could also be achieved in 1-hr irradiations.

(16) J. Volhard, *J. Prakt. Chem.*, **117**, 217 (1874); W. J. Blaedel and V. W. Meloche, "Elementary Quantitative Analysis," 2nd ed, Harper and Row, New York, N. Y., 1963, p 301.

(17) R. Damiens, *Ann. Chim. (Paris)*, **6**, 835 (1951), and references cited therein.

(18) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

(19) V. L. Heasley, P. Kovacic, and R. M. Lange, *J. Org. Chem.*, **31**, 3050 (1966).

(20) R. T. Beltrami and E. R. Bissell, *J. Amer. Chem. Soc.*, **78**, 2467 (1956).

(21) J. S. Watson, *J. Chem. Soc.*, 3677 (1956).

(22) W. H. Urry and J. Sheeto, *Photochem. Photobiol.*, **4**, 1067 (1965).

(23) G. Smith and G. A. Swan, *J. Chem. Soc.*, 886 (1962).

(24) F. Klages, G. Nober, F. Kircher, and M. Bock, *Justus Liebigs Ann. Chem.*, **547**, 1 (1941).

(25) (a) B. G. Gowenlock and D. R. Snelling, *Advan. Chem.*, **36**, 150 (1962); (b) B. G. Gowenlock, P. P. Jones, and D. R. Snelling, *Can. J. Chem.*, **41**, 1911 (1963). The differences in source, phase and solvent, temperature, and surface effects between the work of Gowenlock, *et al.*, and the present work probably vitiate application of the mechanisms postulated for thermal formation of **4** from **8** to the photochemical production of **4** from **1** in carbon tetrachloride.

(26) J. S. Watson and B. deB. Darwent, *J. Chem. Phys.*, **20**, 1041 (1952), suggested that the photochemistry of methylamine involved both C-centered and N-centered radicals.

(27) F. O. Rice and C. J. Grelecki, *J. Amer. Chem. Soc.*, **79**, 2679 (1957).

(28) J. R. Roberts and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 3228 (1973).

(29) H. Böhme, W. Lehners, and G. Keitzer, *Chem. Ber.*, **91**, 340 (1958).

(30) "Handbook of Chemistry and Physics," 48th ed, R. C. Weast and S. M. Selby, Ed., Chemical Rubber Co., Cleveland, Ohio, 1967.