methyl substituent (entries 13 and 14), since we have also found that a para methyl group is better than a para methoxy with respect to the identical problem (entries 4 and 5, and 10 and 12). This latter point appears indicative of the lack of, or at least greatly attenuated, specialized long-range stabilization by through-resonance interactions. Deviations of this type which are not normally expected from the simple through-resonance picture for +T substituents[12] have been previously reported.[11]

In conclusion, our studies indicate a definitive interplay of three neighboring-group effects (i.e., the 5,6 double bond of the substrate, the sulfur atom, and the ortho nitro group) in the additions of arenesulfenyl chlorides to bicyclo[2.2.1]hepta-2,5-diene, wherein the kinetically controlled product distributions reflect the effect of increasing electron demand in the product-determining transition state. Further studies are currently under way to determine if such interactions are of importance in the analogous rate-determining step.

Experimental Section

General Methods. All melting points were measured on a Fisher-Johns block and are uncorrected. ^{1}H NMR spectra were recorded on Varian Associates T-60 and HA-100 spectrometers. ^{13}C NMR spectra were recorded on a Varian FT80-16K spectrometer. Chloroform-*d* was used as an internal lock and reference. All spectral parameters are referenced to Me_4Si as an internal standard.

Bicyclo[2.2.1]hepta-2,5-diene was available commercially (Aldrich) and purified by distillation; bp 88–89 °C (758 mmHg).

2,4-Dinitrobenzenesulfenyl chloride was prepared by the method of Lawson and Kharasch from bis(2,4-dinitrophenyl) disulfide. The compound was recrystallized from CCl_4; mp 96–96.5 °C (lit.[7] mp 97–98 °C).

2-Nitro-4-chlorobenzenesulfenyl chloride was prepared by the method of Turner and Conner using 1,4-dichlorobenzene as starting material; mp 98 °C (lit.[8] mp 97.5–98 °C).

2-Nitrobenzenesulfenyl chloride was commerically available (Aldrich) and was recrystallized from CCl_4; mp 76 °C (lit.[10] mp 74.5–75 °C).

2-Nitro-4-methylbenzenesulfenyl chloride was prepared from the analogous aniline by the procedure of Zincke and Röse[9] and was recrystallized from CCl_4; mp 89–90 °C.

2-Nitro-4-methoxybenzenesulfenyl chloride was prepared from the analogous aniline as above and crystallized as brillant orange needles from CCl_4; mp 106–107 °C.

The remaining arenesulfenyl chlorides were prepared from the corresponding commercially available thiols or disulfides by chlorination with molecular chlorine in CCl_4 with cooling (0–4 °C). All physical data were as expected.[10]

General Reaction Procedure. Product studies were carried out as previously described.[5] In the cases of 4-substituted-2-nitrobenzenesulfenyl chlorides, ^{1}H NMR analysis was carried out during the course of the reactions and thereafter to ensure the establishment of kinetically controlled product distributions. Because of the essentially instantaneous nature of the reactions of arenesulfenyl chlorides which lack the ortho nitro substituent, only the slow isomerizations postaddition were observable by ^{1}H NMR. Samples of individual adducts were isolable via preparative TLC on silica gel with CH_2Cl_2 or 80:20 cyclohexane–ethyl acetate as elutant depending upon the substituents. ^{13}C NMR parameters for the various adducts are listed in Tables II–IV.

Acknowledgment. Continued financial support from the National Research Council of Canada is appreciated.

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[7] D. Lawson and N. Kharasch, *J. Org. Chem.*, **24**, 857 (1956).

[8] R. A. Turner and R. Conner, *J. Am. Chem. Soc.*, **69**, 1009 (1947).

[9] T. Zincke and H. Rose, *Justus Liebigs Ann. Chem.*, **406**, 103, 127 (1914).

[10] N. Kharasch, *Intra-Sci. Chem. Rep.*, 1 (1969).

[11] See for example L. P. Hammett in "Physical Organic Chemistry, Reaction Rates, Equilibria, and Mechanisms", 2nd ed., McGraw-Hill, New York, 1970, pp 357–69.

[12] +T is Ingold's symbol; Wheland's corresponding symbol is –R.

Photochemical Reactions of Isomeric *N*,*N*-Dimethyltoluidines in CCl_4, $CHCl_3$, and CH_2Cl_2

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Products of photochemical reactions of *N*,*N*-dimethyl-*p*-toluidine (DMpT), *N*,*N*-dimethyl-*m*-toluidine (DMmT), and *N*,*N*-dimethyl-*o*-toluidine (DMoT) in CCl_4, $CHCl_3$, and CH_2Cl_2 have been isolated and identified. Mechanisms of partial reactions have been advanced to account for similarities and differences of photochemical transformations in the given media. Particular attention has been paid to participation of the methyl group bound with the benzene ring in the reactions.

Electronic excitation of *N*,*N*-dimethylaniline (DMA) in bromobenzene,[1] tetrachloromethane,[2,3] trichloromethane,[4] and dichloromethane[5] has been found to initiate two simultaneous photochemical processes: cleavage of the *N*-methyl bond and irreversible electron transfer onto the solvent molecule. The former process does not have a decisive effect on further transformations of the amine in these media. The latter affords a radical cation of DMA as well as the radical R and the halogen ion X^-, which are formed by heterolytic dissociation of the C–X bond of an electron-acceptor molecule. The extent of further transformations is determined by a high lability of the DMA radical cation and by the chemical reactivity of the radical R. Secondary reactions occurring in the cage of the solvent afford still other active species involving either the α radical or the carbocation β (eq 1 and 2).

In CH_2Cl_2, $CHCl_3$, and CCl_4 the recombination of the DMA radical cation with the appropriate chloromethane

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[1] Grodowski, M.; Latowski, T. *Tetrahedron* **1974**, *30*, 767.

[2] Latowski, T.; Zelent, B. *Rocz. Chem.* **1974**, *48*, 831.

[3] Latowski, T.; Zelent, B. *Rocz. Chem.* **1977**, *51*, 1883.

[4] Latowski, T.; Zelent, B. *Rocz. Chem.* **1977**, *51*, 1709.

[5] Latowski, T.; Zelent, B. *Rocz. Chem.* **1977**, *51*, 1405.

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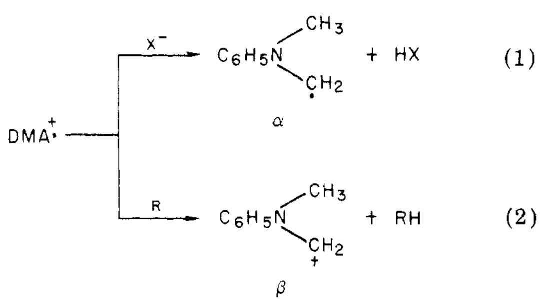
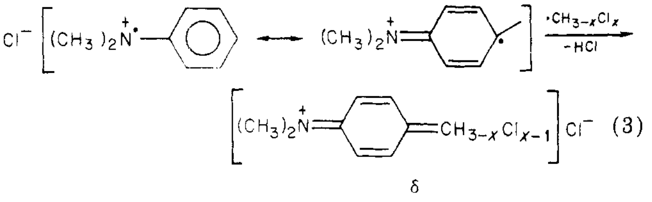


radical (·CH$_{3-x}$Cl$_x$, x = 1, 2, or 3) affords intermediates of the type δ (eq 3). In the presence of an excess of DMA, the α, β, and δ intermediates participate in further secondary reactions.

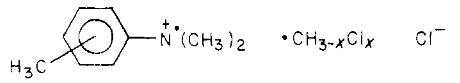


The observed diversity of photochemical transformations of DMA in the media is due to nitrogen-bound methyl groups on one hand and to the benzene ring on the other.[6] Consequently, a substitution in the ring should markedly differentiate photochemical activity of a tertiary aromatic amine.

In this article results have been presented of studies on photochemical reactions of three isomeric *N*,*N*-dimethyltoluidines in chlorinated methanes.

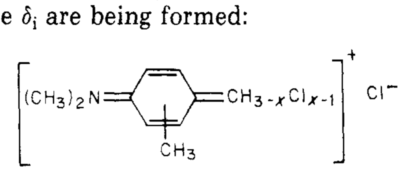
Results and Discussion

Products of photochemical transformations of isomeric *N*,*N*-dimethyltoluidines (DMT) in CCl$_4$, CHCl$_3$, and CH$_2$Cl$_2$ reveal, as in the case of DMA, two pathways of the primary photochemical process, namely, dissociation of the *N*-methyl bond and preionization of the amine. The pathway involving electron transfer is facilitated by electron-acceptor properties of the reaction medium[7] on one hand and by dissociative capture of an electron by a chloromethane molecule on the other. Products of these transformations in the cage of the solvent include the following species:



Secondary reactions in these systems are initiated by *N*-methyltoluidine radicals and by transformations in the solvent cage described by eq 1 and 2. They afford the α_i radical CH$_3$C$_6$H$_5$N(CH$_3$)ĊH$_2$ and the β_i carbocation CH$_3$C$_6$H$_5$N(CH$_3$)CH$_2^+$ (i denotes the para, meta or ortho isomer).

Products of photochemical transformations of DMmT and DMoT in CH$_2$Cl$_2$, as well as results of spectrophotometric measurements, indicate that colored transients of the type δ_i are being formed:



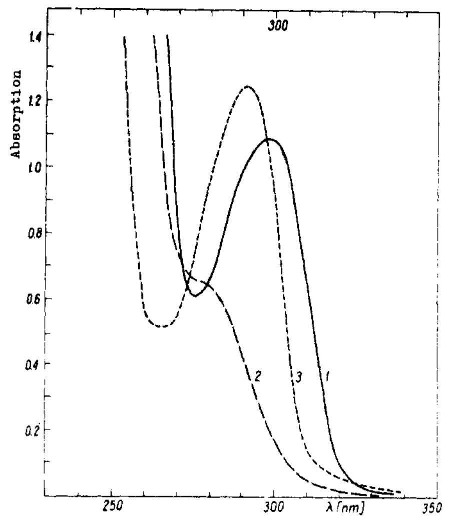


Figure 1. Absorption spectra of 5 × 10^{-4} M solutions of *N*,*N*-dimethylaniline (1), *N*,*N*-dimethyl-*o*-toluidine (2), and *N*-methyl-*o*-toluidine (3) in hexane (l = 1 cm).

The presence of *N*-methyltoluidine radicals in these systems is confirmed by the *N*-methyltoluidine isomers **9**, **17**, and **25** and by the hydrazine derivatives **3** and **12** found among the products (Table I).

As can be easily demonstrated by TLC chromatography, photolysis of the *N*-methyl bond of the DMT isomers in a medium saturated with ammonia affords almost equal quantities of the corresponding *N*-methyltoluidines in high yields. In an acid medium the quantities of the *N*-methyltoluidines are different. *N*-Methyl-*m*-toluidine is formed in small amounts, whereas the yields of *N*-methyl-*p*-toluidine and *N*-methyl-*o*-toluidine are high. These differences are probably due to an enhanced reactivity of DMT whose molecule has unoccupied ortho and para positions that are additionally activated by the methyl group, thus favoring participation of the benzene ring in further reactions. This observation has been confirmed by much higher quantum yields of HCl for DMmT than for DMpT and DMoT, particularly in the CCl$_4$ medium.

The photochemistry of DMoT deserves separate discussion. The photolysis of the *N*-methyl bond of this amine is facilitated by the steric effect of the ortho-standing methyl group.[8] A decrease in conjugation of the lone electron pair at the nitrogen atom with the π electrons of the benzene ring due to steric hindrance is particularly evident when absorption spectra of DMoT and DMA are compared (cf. Figure 1). Replacement of the methyl group at the nitrogen atom for a hydrogen atom facilitates a coplanar arrangement of the NHCH$_3$ and restores conjugation of the electron pair of nitrogen with the electronic sextet of the ring. The yield of *N*-methyl-*o*-toluidine is particularly high during irradiation of DMoT in CCl$_4$. Consequently, the solvent itself also affects the extent of demethylation. In the series of chloromethanes, CCl$_4$ is characterized by the highest value of electron affinity.[6] In CCl$_4$ the formation of electron donor–acceptor complexes with potential electron donors has been found to occur already in their ground electronic states.[9-12] Such an

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(6) Latowski, T.; Przytarska, M.; Zelent, B. *Rocz. Chem.* **1977**, *51*, 995.

(7) Dmitrievskii, O. D. *Opt. Spektrosk.* **1965**, *19*, 828. Bagdasar'yan, Kh. S.; Borovkova, V. A.; Pikel'ni, V. F. *Dokl. Akad. Nauk SSSR* **1971**, *200*, 1126. Saperstein, D.; Levin, E. *J. Chem. Phys.* **1975**, *62*, 3560.

(8) Uzan, R.; Dubois, J.-E. *Bull. Soc. Chim. Fr.* **1971**, 598. Klevens, H. B.; Platt, J. R. *J. Am. Chem. Soc.* **1949**, *71*, 1714. Grammaticakis, P. *Bull. Soc. Chim. Fr.* **1949**, 134. Remington, W. R. *J. Am. Chem. Soc.* **1945**, *67*, 1838. Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1957**, *76*, 357.

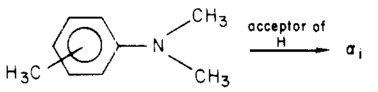
(9) Anderson, R.; Prausnitz, J. M. *J. Chem. Phys.* **1963**, *39*, 1225, Erratum **1964**, *40*, 3443. Hooper, H. O. *Ibid.* **1964**, *41*, 599. Weimer, R. F.; Prausnitz, J. M. *Ibid.* **1965**, *42*, 3643. Dörr, F.; Buttgereit, G. *Ber. Bunsenges. Phys. Chem.* **1963**, *67*, 867. Rosseinsky, D. R.; Kellawi, H. *J. Chem. Soc. A* **1969**, 1207. Hatano, M.; Ito, O. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 916.

interaction can also be expected between DMoT and CCl_4. The interaction between the amine and the solvent probably facilitates photolysis of the *N*-methyl bond.

Ammonia has been found to be an effective sweeper of radical cations of aromatic amines.[13] In our opinion, the interaction between the radical cation of the amine and ammonia can be accompanied by cleavage of the N–CH_3 bond. This assumption has been supported by high yields of the *N*-methyltoluidine radicals in solutions saturated with ammonia. A remarkable concentration of the radicals in the basic medium facilitates their recombination to appropriate hydrazine derivatives. This reaction was not observed in solutions of DMoT in CCl_4, $CHCl_3$, and CH_2Cl_2, probably owing to the steric effect.

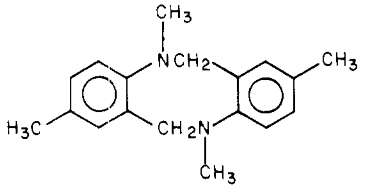
The formation of *N*-methyltoluidines gives rise to new radicals in the systems considered.

In most cases, especially in the CCl_4 medium, the amine acts as the hydrogen donor. The attack of radicals is mostly directed to nitrogen-bound methyl groups (eq 4).



(4)

The α_i radicals are produced mainly in reactions 1 and 4. The presence of α_i in the reaction medium is confirmed by such products as 1, 10, and 22 [$CH_3C_6H_5N(CH_3)CH_2CCl_3$] and 2, 11, and 23 [$CH_3C_6H_5N(CH_3)CH_2CHCl_2$]. In the CCl_4, $CHCl_3$, and CH_2Cl_2 solutions of DMpT other radical reactions also occur during irradiation. Reaction of the α_p radicals can explain the formation of 5.[14] Simple recombination of the α_p radical with the *N*-methyl-*p*-toluidine radical affords 6. Compound 5 is formed in acid medium, while the formation of 6 is promoted in a basic medium (Table I).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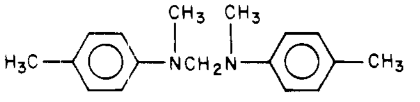
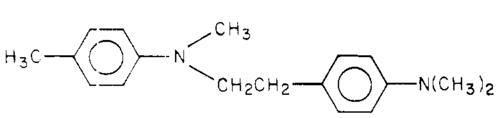
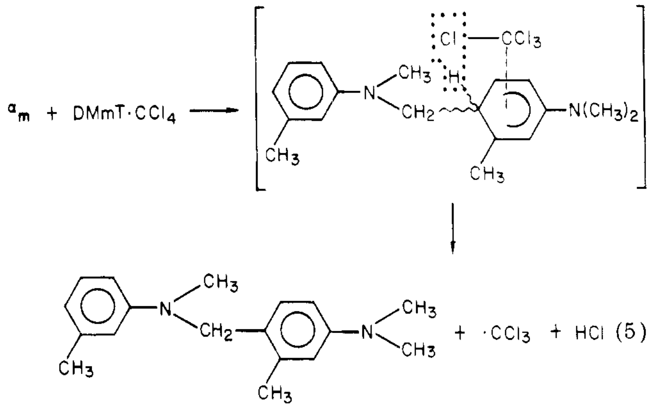

6

In the CCl_4 medium 7 is also formed in a low yield. This compound is indicative of a reaction occurring between the α_p radical and that of *p*-(*N,N*-dimethylamino)benzyl which can be produced from DMpT in the presence of a hydrogen acceptor. These reactions are characteristic for DMpT only. With DMmT and DMoT no counterparts of 5, 6, and 7 have been detected.


7

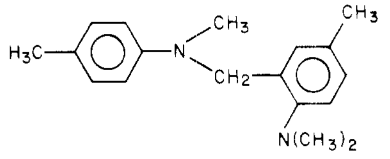
The α_i radicals can also exert an attack on the ring, as has been shown by detection of 4, 14, and 24, particularly in the CCl_4 and $CHCl_3$ media. A particularly high quantum yield of formation of HCl during irradiation of a DMmT solution in CCl_4 (Table II) suggests a chain mechanism of the reaction leading to 14. Similarly, as for DMA,[2] the reaction can be written as in eq 5 and 6.

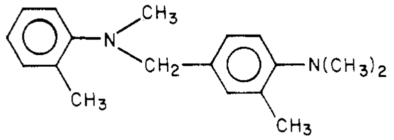


14

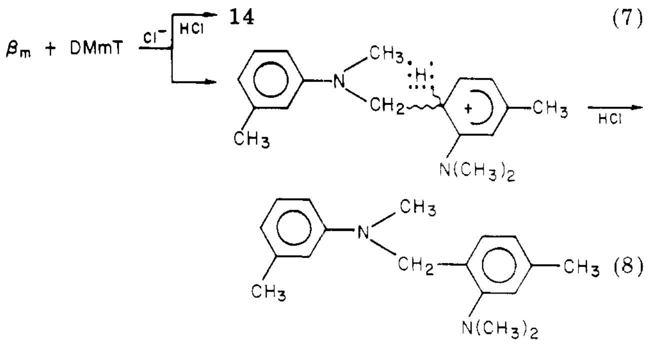
$$\mathrm{DMmT} + \cdot CCl_3 \longrightarrow a_m + CHCl_3 \qquad (6)$$
$$a_m + \mathrm{DMmT}\cdot CCl_4 \longrightarrow$$

In a similar way 4 and 24 are likely to be formed.


4


24

Compounds 4, 14, and 24 can also be formed in a reaction of carbocation β_i with the molecules of the amines in the presence of a proton acceptor. The reactions appear to be facilitated in a polar medium. In the CH_2Cl_2 medium, besides 14, 13 also is formed, thus suggesting the course of reaction shown in eq 7 and 8.



13

In a similar way as for *N*-(*p*-dimethylaminobenzyl)-*N*-methylaniline,[15] compounds 4, 13, 14, and 24 will undergo partial catalytic decomposition in acid medium to

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(10) Stevenson, D. P.; Coppinger, G. M. *J. Am. Chem. Soc.* **1962**, *84*, 149. Drefahl, G.; Heublein, G. *J. Prakt. Chem.* **1963**, *20*, 323. Heublein, G. *Z. Chem.* **1965**, *8*, 305. Heublein, G. *J. Prakt. Chem.* **1966**, *31*, 76. Lautenberger, W. J.; Jones, E. N.; Miller, J. G. *J. Am. Chem. Soc.* **1968**, *90*, 1110. Biaselle, C. J.; Miller, J. G. *Ibid.* **1974**, *96*, 3813.

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(14) Roy, R. B.; Swan, G. A. *Chem. Commun.* **1966**, 427. Swan, G. A. *Ibid.* **1966**, 1376. Swan, G. A. *J. Chem. Soc. C* **1971**, 2880.

(15) Fayadh, J. M.; Jessop, D. W.; Swan, G. A. *J. Chem. Soc. C* **1966**, 1605.

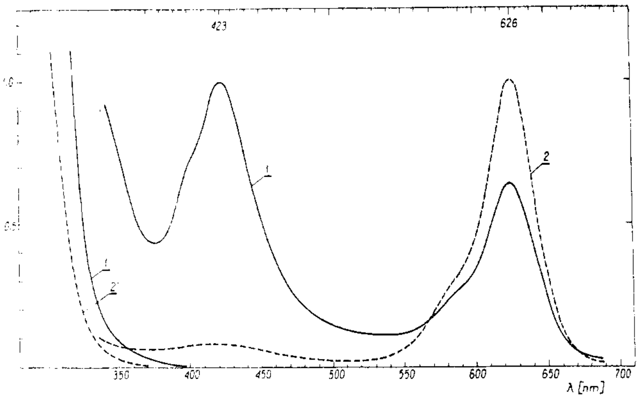
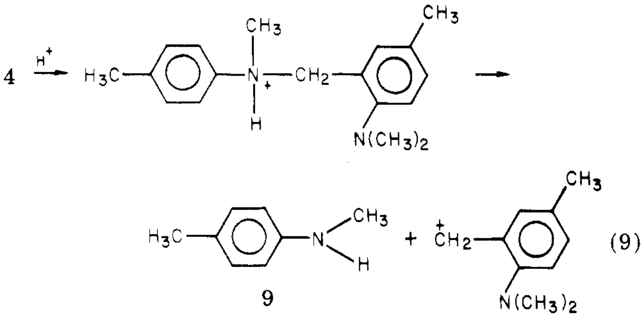


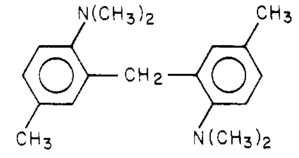
Figure 2. Absorption spectra of irradiated solutions of *N*,*N*-dimethyl-*m*-toluidine (5×10^{-3} M) in dichloromethane (1) and *N*,*N*,*N'*,*N'*-tetramethyl-4,4'-diamino-2,2'-dimethyldiphenylmethane ($\sim 1 \times 10^{-4}$ M) in dichloromethane (2). Curves 1' and 2' refer to solutions before irradiation.

afford the appropriate *N*-methyltoluidines (the second source of these compounds, the first being photolysis of the *N*-methyl bond) and carbocation γ_i (eq 9). In the presence of DMpT, carbocation γ_p can afford 8. Our observations show that 4 is unstable in CCl_4, while in $CHCl_3$ and in CH_2Cl_2 it presumably undergoes complete decomposition.



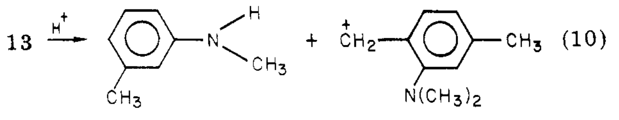
(9)

9 γ_p



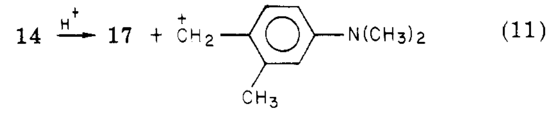
8

In the CCl_4, $CHCl_3$, and CH_2Cl_2 solutions of DMmT, reactions 10 and 11 are likely to occur. In the presence of DMmT, 14, and 17, carbocation γ_m participates in further transformations as shown in eq 12–16.



(10)

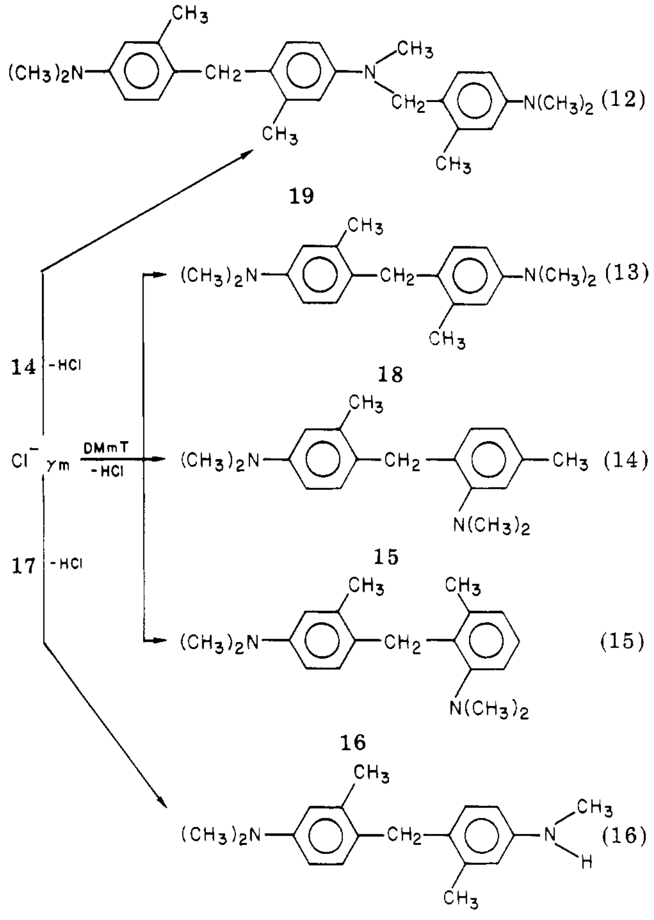
17 γ_m

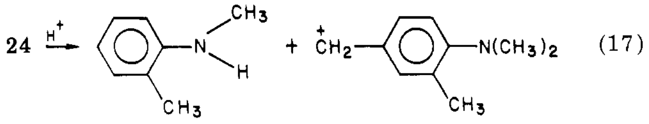


(11)

γ_m

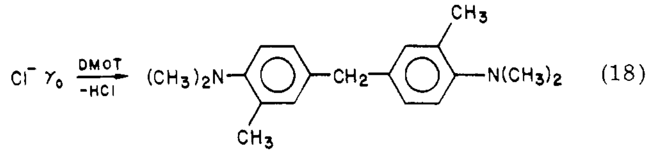
Compound 15 can also be formed in a reaction of γ_m' with DMmT. A similar explanation can be offered for the formation of certain products in DMoT solutions (eq 17 and 18).





(17)

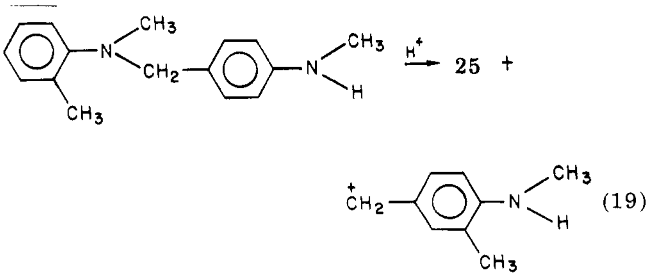
25 γ_o



(18)

26

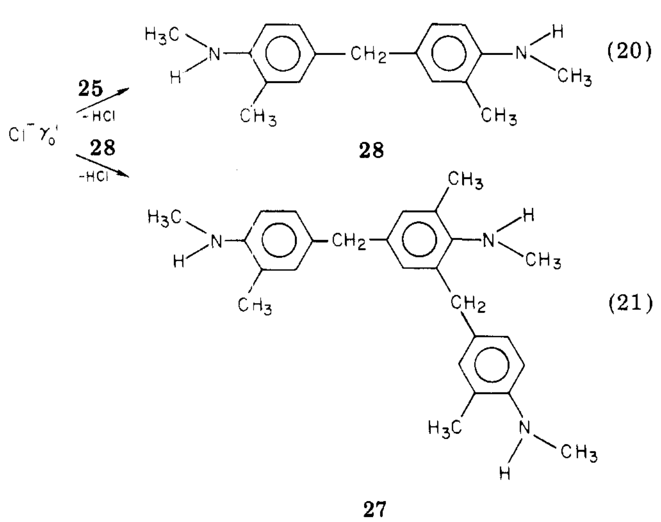
N-Methyl-*N*-(4-(*N*-methylamino)-3-methylbenzyl)-*o*-toluidine, providing the product of a reaction between α_o and *N*-methyl-*o*-toluidine, should also result in photochemical reactions of DMoT in the CCl_4, $CHCl_3$, and CH_2Cl_2 media. Decomposition of this compound (eq 19) and participation of carbocation γ_o' in further reactions would explain the appearance of 28 and 27 among the reaction products (eq 20 and 21).



(19)

γ_o'

Both the thermal (reactions 9–11, 17, and 19) and photochemical[4,5] decompositions of 4, 13, 14, and 24 are



promoted by increased polarity of the medium. Addition of acetonitrile to the $CHCl_3$ and CCl_4 solutions of DMmT results in a complete decomposition of the photochemically produced **14**, while **18** is formed in a high yield.

The mechanisms of photochemical reactions of DMT via radical cation → α_i radical or β_i carbocation → products bear many analogies with processes of chemical oxidation of DMA and its derivatives.[14-26]

On the basis of the foregoing evidence it is difficult to estimate the probability of the transformations of DMT occurring via the α_i radical or via the carbocation β_i. It seems that only in CCl_4 is $[\alpha_i] \gg [\beta_i]$, as has been revealed by a chainlike course of the reaction in this solvent. In the polar CH_2Cl_2 medium $[\alpha_i] \ll [\beta_i]$, as has been demonstrated by the absence of recombination products of α_i with $\cdot CH_2Cl$ and by finding **13** along with **14**. On the other hand, in the less polar $CHCl_3$ medium $[\alpha_i] \approx [\beta_i]$. The carbocation β_i is presumably formed only in the cage of the solvent, while the α_i radical can be formed both in the cage and outside it.

Saturation of solutions during irradiation with ammonia suppresses reactions 9, 10, 11, and 17. The formation of **15**, **16**, **18**, and **20** as well as of **26**, **27**, and **28** in ammoniacal solutions of CH_2Cl_2 shows that there are still other routes to the compounds in this solvent. In the CCl_4 and $CHCl_3$ media, the methylene group joining benzene rings in the molecules of **8**, **15**, **16**, **18**, **20**, **26**, **27**, and **28** is derived from the *N*-methyl group of the DMT molecule. In the CH_2Cl_2 medium the methylene group may be derived from the solvent. This suggestion was advanced during earlier studies of products of photochemical reactions of *N*,*N*-diethylaniline in CCl_4, $CHCl_3$, and CH_2Cl_2.[5] In the CH_2Cl_2 medium the aforementioned compounds can be formed by further reactions of the δ_i transient (eq 22–28, where R′ is CH_3 or H).

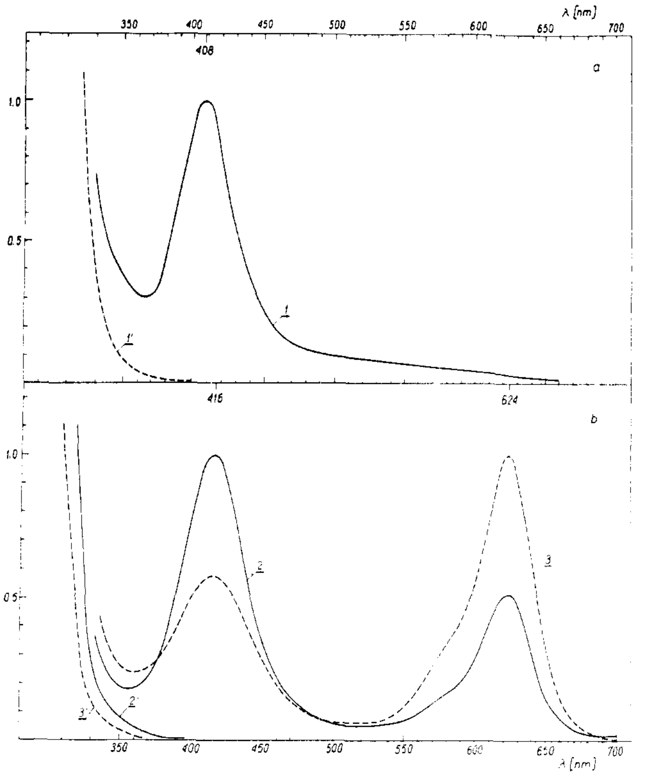
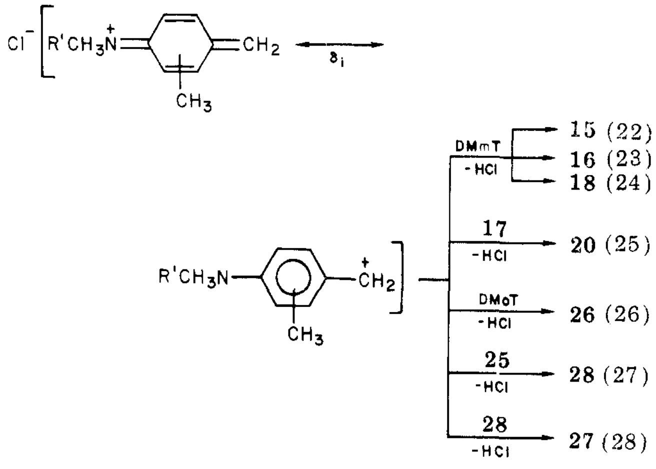


Figure 3. Absorption spectra of irradiated solutions of *N*,*N*-dimethyl-*m*-toluidine (5×10^{-3} M) in trichloromethane (1) and in a 1:2 (v/v) mixture of trichloromethane and acetonitrile (2), as well as of *N*,*N*,*N*′,*N*′-tetramethyl-4,4′-diamino-2,2′-dimethyldiphenylmethane ($\sim 1 \times 10^{-4}$ M) in the solvent mixture (3). Curves 1′, 2′, and 3′ refer to solutions before irradiation.



The UV radiation (λ 313 nm) absorbed by DMmT in CH_2Cl_2 produced two bands in the absorption spectrum, one at 423 nm and the other at 626 nm (cf. Figure 2).

Similarly, as in the case of DMA,[5] the first band can be assigned to the transient δ_m being formed in the reaction medium, while the second band is due to the dye **21**. Since **21** can be produced by photochemical oxidation of **18**, both the absorption spectrum and the identified products show that besides reactions of the type 3 and 24, another photochemical reaction occurs in CH_2Cl_2 (eq 29–31).

The absorption spectrum of an irradiated DMmT solution in $CHCl_3$ displays only one band at 408 nm (cf. Figure 3a). The band has been assigned to the δ_m' transient.

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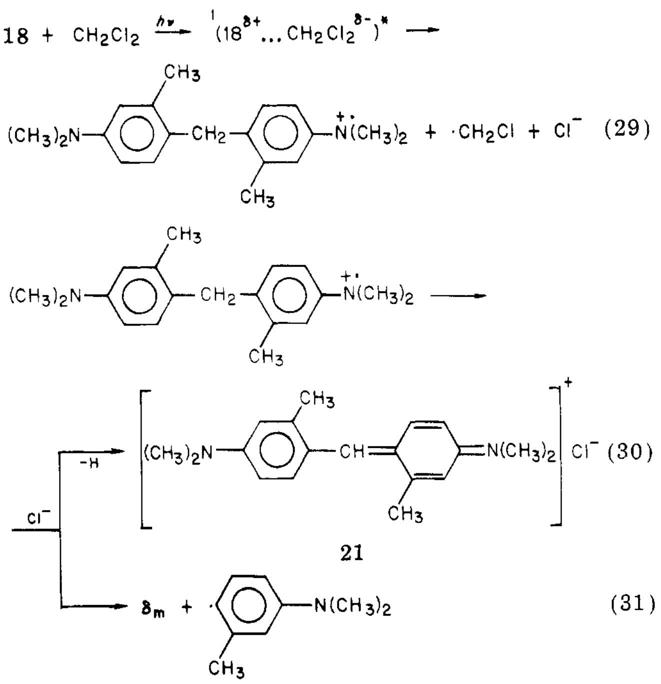

(29)

(30)

21

(31)

Upon irradiation of 18 in $CHCl_3$, no blue color characteristic for 21 has been observed, possibly due to a too low polarity of the medium, which is necessary for stabilization of an ionic form of the compound. For the same reason a band due to 21 is absent in the long-wavelength portion of a spectrum of an irradiated solution of DMmT in $CHCl_3$, although the compound should have been formed in a reaction of δ_m' with an excess of DMmT. There are variations in the absorption spectra with increasing polarity of the medium. In the $CHCl_3$–CH_3CN (1:2 v/v) system, photochemical degradation of 18 results in appearance of a long-wavelength absorption characteristic of 21. A band due to 21 (at 624 nm) also appears in a spectrum of irradiated DMmT solution in this solvent mixture, along with a bathochromically shifted band (416 nm) of the δ_m' transient (Figure 3b). These findings suggest that an increase in the polarity of the medium increases the probability of the photochemical reaction between DMmT and $CHCl_3$ via δ_m' to give 21.

A DMmT solution in CCl_4 behaves dissimilarly. Irradiation of the solution results in appearance of turbidity, whereas in the CCl_4–CH_3CN (1:4 v/v) system colored intermediates are formed. Notwithstanding that the probability of formation of the δ_m'' transient in this system appears to be high, further transformations of δ_m'' in the presence of DMmT fail to produce the expected violet crystal derivative. However, 18 and 21 are produced in high yields.

During irradiation of 0.01 M solutions of DMmT in CH_2Cl_2, $CHCl_3$, and CCl_4 under a layer of water, photochemically produced colored transients δ_m, δ_m', and δ_m'' pass from the organic layer to the aqueous one and undergo hydrolysis there. Variations in the time of the absorption spectra of aqueous solutions of these compounds are similar to those of forms of DMA.[3-5] The following hydrolysis products have been identified: 4-(*N*,*N*-dimethylamino)-2-methylbenzyl alcohol, 4-(*N*,*N*-dimethylamino)-2-methylbenzaldehyde and 4-(*N*,*N*-dimethylamino)-2-methylbenzoic acid.

Despite a close chemical similarity of DMmT and DMA, there are distinct differences in potential photochemical transformations of these amines. With DMmT in $CHCl_3$ and CCl_4, reactions of the δ_m' and δ_m'' transients fail to produce triphenylmethane derivatives. Our observations show that the δ_m transient is capable of reacting with one molecule of the amine only. Further reactions via the benzene ring of the amine are hampered by the steric effect of the methyl group.

The δ_o transients are also formed during irradiation of DMoT in the media studied. However, their behavior is unlike that observed for transients of DMmT and DMA. During irradiation of DMoT in CH_2Cl_2, the absorption spectrum of the solution shows that only one band appears at 418 nm. A similar spectrum is displayed by the DMoT solution in $CHCl_3$ (λ_{max} 404 nm). A solution of DMoT in CCl_4, like the DMmT and DMA solutions in this solvent, becomes turbid upon irradiation.

An increase in polarity of the medium caused by addition of acetonitrile does not lead to appearance of a new band in the long-wavelength portion of the spectrum. Instead, disappearance of bands due to δ_o species is observed. Among the transformation products of these species, only **26** appears in solution in slightly increased quantities. Apparently, the pattern of photochemical transformations of DMT is determined by photolysis of the *N*-methyl bond.

Quantum yields of formation of HCl (φ_{HCl}) measured during photochemical reactions of the DMT isomers in CCl_4, $CHCl_3$, and CH_2Cl_2 (Table II) seem to support the suggested mechanism of photochemical reactions.

The position of the methyl group in the benzene ring differentiates the mechanism of photochemical transformations, as is reflected, among other things, by the φ_{HCl} values. The differences in these values are especially large in CCl_4, and a high φ_{HCl} value for DMmT suggests that a chain reaction occurs in this system. Comparison of φ_{HCl} for DMA (12.70[12]) with those for DMpT (4.76) and for DMmT (17.36) calls attention to the reactivity of the para position. With DMpT, the para position does not participate in the reaction, whereas with DMmT it is additionally activated by the methyl group. The main link of the chain reaction of DMmT in CCl_4 is reaction 5. Accordingly, HCl is formed not only during dissociative capture of an electron by CCl_4 but also in reaction 5. The relatively low φ_{HCl} value for DMoT in CCl_4 (1.86) can be explained in terms of a faster photolysis rate of the *N*-methyl bond as compared to the rate of preionization.

Experimental Section

Reagents. *N*,*N*-Dimethyl-*p*-toluidine and *N*,*N*-dimethyl-*m*-toluidine (both from Fluka AG, Buchs SG, Switzerland) were purified in a manner similar to that of *N*,*N*-dimethylaniline.[2] *N*,*N*-Dimethyl-*o*-toluidine (Fluka AG, Buchs SG) was purified by column chromatography with silica gel and a petroleum ether–ethyl ether mixture. The purity of the amines was checked by TLC.

Analytical grade tetrachloromethane, trichloromethane, and dichloromethane (supplied by POCh, Gliwice, Poland) were purified as described elsewhere.[6,12]

N-Methyl-*o*-toluidine (ICN K and K Laboratories, Inc., Plainview, NY) was used as supplied.

N,*N*,*N*′,*N*′-Tetramethyl-4,4′-diamino-2,2′-dimethyldiphenylmethane was obtained by a sulfuric acid catalyzed condensation of *N*,*N*-dimethyl-*m*-toluidine with formaldehyde.[27] The crude product was repeatedly crystallized from ethanol to give white crystals, mp 82–83 °C.

Instrumentation. As a source of the UV–vis irradiation, a Hanau Q-400 analytical lamp with a mercury burner was employed. Solutions of the amines were irradiated in a Pyrex flask transmitting the wavelengths longer than 285 nm.

IR spectra were taken on a Perkin-Elmer Model 257 spectrophotometer.

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Table I. **Products of Photochemical Reactions of Isomeric *N*,*N*-Dimethyltoluidines in CCl_4, $CHCl_3$, and CH_2Cl_2 and Their R_f Values on Silica Gel**

		reaction medium			developing system[c]		
no.	compd	CCl_4	$CHCl_3$	CH_2Cl_2	5:1	15:1	100:1
DMpT	*N*,*N*-dimethyl-*p*-toluidine	*a*, *b*	*a*, *b*	*a*, *b*	0.70	0.45	0.18
1	*N*-methyl-*N*-(β-trichloroethyl)-*p*-toluidine	*a*, *b*			0.91	0.76	0.41
2	*N*-methyl-*N*-(β-dichloroethyl)-*p*-toluidine		*a*, *b*		0.87	0.72	0.39
3	*N*,*N*′-dimethyl-*N*,*N*′-bis(4-methylphenyl)hydrazine	*b*	*b*	*b*	0.85	0.71	0.38
4	*N*-methyl-*N*-[2-(*N*,*N*-dimethylamino)-5-methylbenzyl]-*p*-toluidine	*a*			0.82		
5	5,6,11,12-tetrahydro-2,5,8,11-tetramethylphenhomazine	*a*	*a*	*a*	0.78	0.52	0.24
6	*N*,*N*′-dimethyl-*N*,*N*′-bis(4-methylphenyl)diaminomethane	*b*	*b*	*b*	0.82		
7	*N*-methyl-*N*-[β-(4-(*N*,*N*-dimethylamino)-phenyl)ethyl]-*p*-toluidine	*a*			0.47	0.33	0.30
8	*N*,*N*,*N*′,*N*′-tetramethyl-2,2′-diamino-5,5′-dimethyldiphenylmethane		*a*	*a*	0.53	0.30	0.10
9	*N*-methyl-*p*-toluidine	*a*, *b*	*a*, *b*	*a*, *b*	0.43	0.26	0.05
DMmT	*N*,*N*-dimethyl-*m*-toluidine	*a*, *b*	*a*, *b*	*a*, *b*	0.81	0.53	0.25
10	*N*-methyl-*N*-(β-trichloroethyl)-*m*-toluidine	*a*, *b*			0.87	0.85	0.60
11	*N*-methyl-*N*-(β-dichloroethyl)-*m*-toluidine		*a*, *b*		0.86	0.82	0.57
12	*N*,*N*′-dimethyl-*N*,*N*′-bis(3-methylphenyl)hydrazine	*b*	*b*	*b*	0.85	0.80	0.47
13	*N*-methyl-*N*-[2-(*N*,*N*-dimethylamino)-4-methylbenzyl]-*m*-toluidine			*a*	0.81	0.72	0.35
14	*N*-methyl-*N*-[4-(*N*,*N*-dimethylamino)-2-methylbenzyl]-*m*-toluidine	*a*, *b*	*a*, *b*	*a*, *b*	0.63	0.40	
15	*N*,*N*,*N*′,*N*′-tetramethyl-4,2′-diamino-2,4′-dimethyldiphenylmethane	*a*	*a*	*a*, *b*	0.59	0.35	
16	*N*,*N*,*N*′,*N*′-tetramethyl-4,2′-diamino-2,6′-dimethyldiphenylmethane	*a*	*a*	*a*, *b*	0.59	0.35	
17	*N*-methyl-*m*-toluidine	*a*, *b*	*a*, *b*	*a*, *b*	0.47	0.28	0.16
18	*N*,*N*,*N*′,*N*′-tetramethyl-4,4′-diamino-2,2′-dimethyldiphenylmethane	*a*	*a*	*a*, *b*	0.44	0.20	
19	*N*-methyl-*N*-[4-(*N*,*N*-dimethylamino)-2-methylbenzyl]-*N*′,*N*′-dimethyl-4,4′-diamino-2,2′-dimethyldiphenylmethane	*a*			0.34	0.11	
20	*N*,*N*,*N*′-trimethyl-4,4′-diamino-2,2′-dimethyldiphenylmethane	*a*	*a*	*a*, *b*	0.26	0.09	
21	*N*,*N*,*N*′,*N*′-tetramethyl-4,4′-diamino-2,2′-dimethyldiphenylmethyl chloride			*a*			
DMoT	*N*,*N*-dimethyl-*o*-toluidine	*a*, *b*	*a*, *b*	*a*, *b*	0.81	0.50	0.33
22	*N*-methyl-*N*-(β-trichloroethyl)-*o*-toluidine	*a*, *b*			0.98	0.76	0.65
23	*N*-methyl-*N*-(β-dichloroethyl)-*o*-toluidine		*a*, *b*		0.93	0.69	0.50
24	*N*-methyl-*N*-[4-(*N*,*N*-dimethylamino)-3-methylbenzyl]-*o*-toluidine	*a*, *b*	*a*, *b*	*a*, *b*	0.70	0.40	
25	*N*-methyl-*o*-toluidine	*a*, *b*	*a*, *b*	*a*, *b*	0.60	0.34	0.20
26	*N*,*N*,*N*′,*N*′-tetramethyl-4,4′-diamino-3,3′-dimethyldiphenylmethane	*a*	*a*	*a*, *b*	0.48	0.19	
27	*N*-methyl-2,4-bis[4-(*N*-methylamino)-3-methylbenzyl]-6-methylaniline	*a*	*a*	*a*, *b*	0.35	0.09	
28	*N*,*N*′-dimethyl-4,4′-diamino-3,3′-dimethyldiphenylmethane	*a*	*a*	*a*, *b*	0.22	0.03	
29	trichloromethane	*a*, *b*					
30	hexachloroethane	*a*, *b*					
31	dichloromethane		*a*, *b*				

[a] Compound found in the deaerated solution. [b] Compound found in the ammonia-saturated solution. [c] Petroleum ether–ethyl ether (v/v).

^1H NMR spectra were recorded on an 80-MHz Tesla BS 487 C spectrometer.

Mass spectra were obtained on a Varian MAT-711 mass spectrometer.

The visible and UV spectra were recorded on a Perkin-Elmer Model 402 spectrophotometer.

Procedure. Preparative irradiations of both deaerated and ammonia-saturated ~0.4 M solutions of the DMT isomers in CCl_4, $CHCl_3$, and CH_2Cl_2 were accomplished as described earlier.[6] Mixtures of the photochemical reaction products were analyzed by TLC on glass plates (6 × 18 cm) covered with 1.6 g of silica gel. Spots were rendered visible with iodine vapor. Individual compounds were then isolated by column chromatography with silica gel (Merck) and a petroleum ether (boiling range 40–60 °C)–ethyl ether solvent system. Identified compounds have been listed in Table I.

Quantum yields of HCl were measured in 1×10^{-2} M solutions of the amines in CCl_4, $CHCl_3$, and CH_2Cl_2. Before irradiation, the solutions were deaerated with a stream of nitrogen. As a source of the 313-nm radiation, a HBO-200 (Osram) lamp with a combined Weller filter[28] was used. The radiation intensity was measured by means of a ferric oxalate actinometer.[29]

The concentration of HCl in solutions after irradiation was determined potentiometrically.

Quantum yields of HCl have been listed in Table II.

Spectral Characteristics of Photochemical Reaction Products of *N*,*N*-Dimethyltoluidine in CCl_4, $CHCl_3$, and CH_2Cl_2. A. Products of *N*,*N*-Dimethyl-*p*-toluidine. *N*-Methyl-*N*-(β-trichloroethyl)-*p*-toluidine (1): ^1H NMR (CCl_4) δ 2.14 (s, 3 H, $ArCH_3$), 3.13 (s, 3 H, NCH_3), 4.16 (s, 2 H, NCH_2), 6.52, 6.75 (2 d, $J = 9$ Hz, 4 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 2930 (s), 2860 (s), 1620 (s), 1515 (vs), 1345 (w), 805 (vs), ~800

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Table II. Quantum Yields of Formation of Hydrogen Chloride (φ_{HCl}) in Photochemical Reactions of Isomeric *N,N*-Dimethyltoluidines in CCl_4, $CHCl_3$, and CH_2Cl_2

isomer	solvent	φ_{HCl}	$\overline{\varphi}_{HCl}$
DMpT	CCl_4	4.84	4.76
		4.75	
		4.69	
	$CHCl_3$	3.07	3.02
		3.03	
		2.96	
	CH_2Cl_2	2.49	2.44
		2.46	
		2.37	
DMmT	CCl_4	17.08	17.36
		17.80	
		17.20	
	$CHCl_3$	3.37	3.28
		3.31	
		3.16	
	CH_2Cl_2	2.66	2.57
		2.45	
		2.60	
DMoT	CCl_4	2.13	1.86
		1.62	
		1.83	
	$CHCl_3$	2.87	2.81
		2.78	
		2.78	
	CH_2Cl_2	1.95	1.82
		1.82	
		1.69	

(s) cm^{-1}; mol wt of $C_{10}H_{12}NCl_3$, 252.57; mass spectrum (70 eV), *m/e* molecular ions 257, 255, 253, and 251, other ions 220, 218, 216, 134, 120, and 91.

***N*-Methyl-*N*-(β-dichloroethyl)-*p*-toluidine (2)**: ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 3 H, $ArCH_3$), 3.03 (s, 3 H, NCH_3), 3.86 (d, *J* = 6.5 Hz, 2 H, NCH_2), 5.78 (t, *J* = 6.5 Hz, 1 H, CH), 6.55, 7.01 (2 d, *J* = 9 Hz, 4 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 2950 (s), 2895 (s), 1620 (s), 1525 (vs), 1450 (m), 1345 (vs), 800 (vs), 755 (s) cm^{-1}; mol wt of $C_{10}H_{13}NCl_2$, 218.12; mass spectrum (70 eV), *m/e* molecular ions 221, 219, and 217, other ions 184, 182, 134, 119, and 91.

***N,N'*-Dimethyl-*N,N'*-bis(4-methylphenyl)hydrazine (3)**: ^{1}H NMR (CCl_4) δ 2.14 (s, 6 H, $ArCH_3$), 2.81 (s, 6 H, NCH_3), 6.65, 7.06 (2 d, *J* = 7 Hz, 4 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 2920 (s), 2860 (s), 1615 (s), 1515 (vs), 1450 (s), 1320 (s), 807 (vs) cm^{-1}. $C_{16}H_{20}N_2$ requires mol wt 240.35; mass spectrum (70 eV), *m/e* 240, 225, 120, 91.

***N*-Methyl-*N*-[2-(*N,N*-dimethylamino)-5-methylbenzyl]-*p*-toluidine (4)**: ^{1}H NMR (CCl_4) δ 2.10 (s, 6 H, $ArCH_3$), 2.55 (s, 6 H, NCH_3), 2.85 (s, 3 H, NCH_2Ar), 6.38–6.88 (m, 7 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 2990–2800 (s), 1625 (s), 1525 (vs), 1500 (s), 1450 (m), 1375 (m), 1345 (m), 1315 (m), 820 (s), 805 (s) cm^{-1}. $C_{18}H_{24}N_2$ requires mol wt 268.40; mass spectrum (70 eV), *m/e* 268, 148, 134, 120, 91.

5,6,11,12-Tetrahydro-2,5,8,11-tetramethylphenhomazine (5): white crystalline solid; ^{1}H NMR (CCl_4) δ 2.13 (s, 6 H, $ArCH_3$), 2.64 (s, 6 H, NCH_3), 4.07 (s, 4 H, $ArCH_2N$), 6.50–6.85 (m, 8 H, aromatic protons); IR (KBr) $\tilde{\nu}_{max}$ 3000–2800 (s), 1618 (s), 1515 (vs), 1385 (s), 1350 (s), 825 (s), 810 (s) cm^{-1}. $C_{18}H_{22}N_2$ requires mol wt 266.39; mass spectrum (70 eV), *m/e* 266, 251, 236, 222, 220, 146, 134, 132, 105, 91, 77.

***N,N'*-Dimethyl-*N,N'*-bis(4-methylphenyl)diaminomethane (6)**: ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 6 H, $ArCH_3$), 3.08 (s, 6 H, NCH_3), 3.88 (s, 2 H, CH_2), 7.16, 7.58 (2 d, *J* = 9 Hz, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 2940 (vs), 2860 (s), 1620 (s), 1520 (vs), 1350 (s), 805 (s) cm^{-1}; mol wt of $C_{17}H_{22}N_2$, 254.37; mass spectrum (70 eV), *m/e* 254, 239, 120, 91.

***N*-Methyl-*N*-[β-(4-(*N,N*-dimethylamino)phenyl)ethyl]-*p*-toluidine (7)**: ^{1}H NMR (CCl_4) δ 2.14 (s, 3 H, $ArCH_3$), 2.71 (s, 3 H, NCH_3), 2.78 (s, 6 H, NCH_3), 3.15–3.48 (m, 4 H, NCH_2CH_2Ar), 6.38–6.92 (4 d, 8 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 2940 (s), 2880 (s), 2840 (m), 1625 (s), 1530 (vs), 1360 (s), 800 (s) cm^{-1}; mol wt of $C_{18}H_{24}N_2$, 268.40; mass spectrum (70 eV), *m/e* 268, 253, 148, 134, 120, 119, 118, 91.

***N,N,N',N'*-Tetramethyl-2,2'-diamino-5,5'-dimethyldiphenylmethane (8)**: IR (film) $\tilde{\nu}_{max}$ 2980–2800 (s), 1625 (s), 1510 (vs), 1310 (m), 820 (s), 810 (m) cm^{-1}; mol wt of $C_{19}H_{26}N_2$ 282.43; mass spectrum (70 eV), *m/e* 282, 237, 222, 148, 134.

***N*-Methyl-*p*-toluidine (9)**: ^{1}H NMR (CCl_4) δ 2.10 (s, 3 H, $ArCH_3$), 2.62 (s, 3 H, NCH_3), 3.3 (s, 1 H, NH), 6.25, 6.76 (2 d, *J* = 9 Hz, 4 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 3420 (s), 3030 (m), 2990 (m), 2930 (s), 2880 (s), 2820 (m), 1622 (vs), 1525 (vs), 1450 (m), 1320 (s), 805 (vs) cm^{-1}; mol wt of $C_8H_{11}N$, 121.18; mass spectrum (70 eV), *m/e* 121, 120, 105, 91.

B. Products of *N,N*-Dimethyl-*m*-toluidine. *N*-Methyl-*N*-(β-trichloroethyl)-*m*-toluidine (10): ^{1}H NMR (CCl_4) δ 2.23 (s, 3 H, $ArCH_3$), 3.16 (s, 3 H, NCH_3), 4.2 (s, 2 H, NCH_2), 6.38–7.10 (m, 4 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 3050 (w), 2920 (m), 2810 (s), 2815 (w), 1610 (vs), 1590 (s), 1505 (vs), 1490 (m), 1450 (m), 1370 (s), 1350 (s), 1270 (s), 800 (vs), 770 (vs), 695 (s) cm^{-1}; mol wt of $C_{10}H_{12}NCl_3$, 252.57; mass spectrum (70 eV), *m/e* molecular ions 257, 255, 253, and 251, other ions 220, 218, 216, 134, 120, and 91.

***N*-Methyl-*N*-(β-dichloroethyl)-*m*-toluidine (11)**: ^{1}H NMR (CCl_4) δ 2.20 (s, 3 H, $ArCH_3$), 3.01 (s, 3 H, NCH_3), 3.86 (d, *J* = 6.5 Hz, 2 H, NCH_2), 3.78 (t, *J* = 6.5 Hz, 1 H, CH), 6.20–7.05 (m, 4 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 2930 (vs), 2860 (vs), 1610 (vs), 1590 (s), 1505 (vs), 1490 (m), 1450 (m), 1350 (s), 800 (vw), 770 (vs), 695 (m) cm^{-1}; mol wt of $C_{10}H_{13}NCl_2$, 218.12; mass spectrum (70 eV), *m/e* molecular ions 221, 219, and 217, other ions 184, 182, 134, 120, 119, 105, 91.

***N,N'*-Dimethyl-*N,N'*-bis(3-methylphenyl)hydrazine (12)**: ^{1}H NMR (CCl_4) δ 2.21 (s, 6 H, $ArCH_3$), 2.87 (s, 6 H, NCH_3), 6.46–7.15 (m, 8 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 3050 (m), 2930 (s), 2810 (w), 1610 (vs), 1590 (s), 1500 (vs), 1330 (m), 770 (s), 695 (s) cm^{-1}; mol wt of $C_{16}H_{20}N_2$, 240.35; mass spectrum (70 eV), *m/e* 240, 225, 120, 105, 91.

***N*-Methyl-*N*-[2-(*N,N*-dimethylamino)-4-methylbenzyl]-*m*-toluidine (13)**: ^{1}H NMR (CCl_4) δ 2.16, 2.21 (2 s, 6 H, $ArCH_3$), 2.50 (s, 3 H, NCH_3), 2.55 (s, 6 H, NCH_3), 4.38 (s, 2 H, NCH_2Ar), 6.28–7.04 (m, 7 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 3000–2790 (s), 1610 (vs), 1590 (vs), 1505 (vs), 1480 (vs), 1460 (vs), 1435 (m), 1355 (s), 1315 (m), 795 (s), 770 (s), 760 (s), 695 (s) cm^{-1}; mol wt of $C_{18}H_{24}N_2$, 268.40; mass spectrum (70 eV), *m/e* 268, 148, 134, 120, 105, 91.

***N*-Methyl-*N*-[4-(*N,N*-dimethylamino)-2-methylbenzyl]-*m*-toluidine (14)**: white crystalline solid; ^{1}H NMR (CCl_4) δ 2.18, 2.20 (2 s, 6 H, $ArCH_3$), 2.80 (s, 3 H, NCH_3), 2.82 (s, 6 H, NCH_3), 4.27 (s, 2 H, NCH_2), 6.32–7.10 (m, 7 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 3030 (w), 2920 (s), 2800 (m), 1615 (vs), 1605 (vs), 1510 (vs), 1500 (vs), 1445 (m), 1345 (vs), 800 (m), 776 (s), 690 (s) cm^{-1}; mol wt of $C_{18}H_{24}N_2$, 268.40; mass spectrum (70 eV), *m/e* 268, 148, 134, 120, 105, 91.

***N,N,N',N'*-Tetramethyl-4,2'-diamino-2,4'-dimethyldiphenylmethane (15)**: ^{1}H NMR (CCl_4) δ 1.97 (s, 3 H, $ArCH_3$), 2.17 (s, 3 H, $ArCH_3$), 2.55 (s, 6 H, $N'CH_3$), 2.76 (s, 6 H, NCH_3), 3.76 (s, 2 H, $ArCH_2Ar$), 6.20–7.00 (m, 6 H, aromatic protons).

***N,N,N',N'*-Tetramethyl-4,2'-diamino-2,6'-dimethyldiphenylmethane (16)**: ^{1}H NMR (CCl_4) δ 1.97 (s, 3 H, $ArCH_3$), 2.27 (s, 3 H, $ArCH_3$), 2.44 (s, 6 H, $N'CH_3$), 2.74 (s, 6 H, NCH_3), 3.87 (s, 2 H, $ArCH_2Ar$), 6.20–7.00 (m, 6 H, aromatic protons).

Compounds **15** and **16** could not be separated chromatographically. The ^{1}H NMR spectrum was taken for their mixture. As the compounds are formed in the mole ratio 2:1, appropriate δ values could be assigned to these compounds.

Also, the infrared spectrum and the mass spectrum were taken for the mixture of **15** and **16**: IR (film) $\tilde{\nu}_{max}$ 3000–2790 (s), 1620 (vs), 1515 (vs), 1480 (s), 1455 (s), 1355 (s), 1312 (m), 810 (m), 780 (m), 760 (w), 735 (w), 710 (vw), 695 (vw) cm^{-1}; mol wt of $C_{19}H_{26}N_2$, 282.43; mass spectrum (70 eV), *m/e* 282, 267, 148, 134.

***N*-Methyl-*m*-toluidine (17)**: ^{1}H NMR (CCl_4) δ 2.17 (s, 3 H, $ArCH_3$), 2.70 (s, 3 H, NCH_3), 3.34 (s, 1 H, NH), 6.20–7.06 (m, 4 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 3420 (vs), 3050 (s), 2990 (s), 2930 (vs), 2820 (s), 1615 (vs), 1600 (vs), 1520 (vs), 1500 (s), 1450 (m), 1335 (s), 775 (vs), 695 (vs) cm^{-1}; mol wt of $C_8H_{11}N$, 121.18; mass spectrum (70 eV), *m/e* 121, 120, 105, 91.

***N,N,N',N'*-Tetramethyl-4,4'-diamino-2,2'-dimethyldiphenylmethane (18)**: white crystalline solid. The compound was identified by comparison with an authentic sample (R_f and ^{1}H NMR and IR spectra).

_N_-Methyl-_N_-[4-(_N_,_N_-dimethylamino)-2-methylbenzyl]-_N'_,_N'_-dimethyl-4,4'-diamino-2,2'-dimethyldiphenylmethane (19): ^{1}H NMR (CCl_4) δ 2.11 (s, 6 H, $ArCH_3$), 2.17 (s, 3 H, $ArCH_3$), 2.74 (s, 3 H, NCH_3), 2.77, 2.79 (2 s, 12 H, NCH_3), 3.56 (s, 2 H, $ArCH_2Ar$), 4.17 (s, 2 H, NCH_2Ar), 6.10–6.90 (m, 9 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 3000–2800 (s), 1620 (vs), 1515 (vs), 1480 (m), 1450 (m), 1350 (s), 805 (s), 780 (w), 760 (w), 705 (vw), 695 (vw) cm^{-1}; mol wt of $C_{28}H_{37}N_3$, 415.62; mass spectrum (70 eV), *m/e* 415, 400, 354, 340, 281, 252, 148, 134.

_N_,_N_,_N'_-Trimethyl-4,4'-diamino-2,2'-dimethyldiphenylmethane (20): ^{1}H NMR (CCl_4) δ 2.05, 2.09 (2 s, 6 H, $ArCH_3$), 2.67 (s, 3 H, NCH_3), 2.75 (s, 6 H, NCH_3), 3.15 (s, 1 H, NH), 3.57 (s, 2 H, $ArCH_2Ar$), 6.05–6.65 (m, 6 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 3400 (s), 3000–2800 (vs), 1615 (vs), 1510 (vs), 1445 (s), 1348 (s), 1328 (s), 800 (s), 775 (m), 700 (w) cm^{-1}; mol wt of $C_{18}H_{24}N_2$, 268.39; mass spectrum (70 eV), *m/e* 268, 253, 148, 134, 133, 119, 118, 105, 104.

_N_,_N_,_N'_,_N'_-Tetramethyl-4,4'-diamino-2,2'-dimethyldiphenylmethyl Chloride (21). This compound was identified by comparison with an authentic sample (spectrum over the visible range). As the authentic sample, a dye obtained by photochemical oxidation of *N*,*N*,*N'*,*N'*-tetramethyl-4,4'-diamino-2,2'-dimethyldiphenylmethane in CH_2Cl_2 and in $CHCl_3$–acetonitrile and CCl_4–acetonitrile mixtures was used.

C. Products of _N_,_N_-dimethyl-_o_-toluidine. _N_-Methyl-_N_-(β-trichloroethyl)-_o_-toluidine (22): ^{1}H NMR (CCl_4) δ 2.32 (s, 3 H, $ArCH_3$), 2.96 (s, 3 H, NCH_3), 4.0 (s, 2 H, NCH_2), 6.95–7.30 (m, 4 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 2960 (s), 2940 (vs), 2860 (s), 1605 (w), 1495 (m), 1350 (m), 810 (m), 795 (s), 765 (s), 720 (s) cm^{-1}; mol wt of $C_{10}H_{12}NCl_3$, 252.57; mass spectrum (70 eV), *m/e* molecular ions 257, 255, 253, and 252, other ions 220, 218, 216, 134, 120, and 91.

_N_-Methyl-_N_-(β-dichloroethyl)-_o_-toluidine (23): ^{1}H NMR (CCl_4) δ 2.20 (s, 3 H, $ArCH_3$), 2.71 (s, 3 H, NCH_3), 3.49 (d, J = 6.5 Hz, 2 H, NCH_2), 5.44 (t, J = 6.5 Hz, 1 H, CH), 6.70–7.15 (m, 4 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 2990–2805 (s), 1605 (s), 1500 (vs), 1455 (s), 1425 (s), 1380 (w), 1350 (m), 800 (m), 790 (s), 775 (s), 730 (s) cm^{-1}; mol wt of $C_{10}H_{13}NCl_2$, 218.12; mass spectrum (70 eV), *m/e* molecular ions 221, 219, and 217, other ions 184, 182, 134, 120, 119, and 91.

_N_-Methyl-_N_-[4-(_N_,_N_-dimethylamino)-3-methylbenzyl]-_o_-toluidine (24): white crystalline solid; ^{1}H NMR (CCl_4) δ 2.20, 2.30 (2 s, 6 H, $ArCH_3$), 2.48 (s, 3 H, NCH_3), 2.58 (s, 6 H, NCH_3), 3.85 (s, 2 H, NCH_2), 6.84–7.18 (m, 7 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 3070 (w), 3030 (m), 2990–2800 (s), 1615 (w), 1605 (s), 1510 (vs), 1500 (vs), 1460 (s), 1445 (m), 1430 (w), 1380 (w), 1360 (s), 1315 (s), 765 (s), 730 (s) cm^{-1}; mol wt of $C_{18}H_{24}N_2$, 268.40; mass spectrum (70 eV), *m/e* 268, 148, 134, 132, 118, 105, 104, 91.

_N_-Methyl-_o_-toluidine (25). This compound was identified by comparison with an authentic sample (R_f and ^{1}H NMR and IR spectra).

_N_,_N_,_N'_,_N'_-Tetramethyl-4,4'-diamino-3,3'-dimethyldiphenylmethane (26): ^{1}H NMR (CCl_4) δ 2.10 (s, 6 H, $ArCH_3$), 2.76 (s, 12 H, NCH_3), 3.66 (s, 2 H, CH_2), 6.15–6.95 (m, 6 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 2980–2860 (s), 1615 (s), 1500 (s), 1470 (m), 1460 (m), 1380 (m), 1320 (vw), 775 (m), 760 (m), 730 (m) cm^{-1}; mol wt of $C_{19}H_{26}N_2$, 282.43; mass spectrum (70 eV), *m/e* 282, 267, 148, 134, 119.

_N_-Methyl-2,4-bis[4-(_N_-methylamino)-3-methylbenzyl]-6-methylaniline (27): ^{1}H NMR (CCl_4) δ 1.98 (s, 9 H, $ArCH_3$), 2.75 (s, 9 H, NCH_3), 3.80 (s, 3 H, NH), 4.19 (s, 4 H, CH_2), 6.25–7.15 (m, 8 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 3430 (s), 2980–2825 (s), 1625 (vs), 1525 (vs), 1475 (m), 1455 (s), 1375 (s), 1325 (s), 815 (s) cm^{-1}; mol wt of $C_{26}H_{33}N_3$, 387.57; mass spectrum (70 eV), *m/e* 387.

_N_,_N'_-Dimethyl-4,4'-diamino-3,3'-dimethyldiphenylmethane (28): white crystalline solid; ^{1}H NMR (CCl_4) δ 1.90 (s, 6 H, $ArCH_3$), 2.71 (s, 6 H, NCH_3), 3.10 (s, 2 H, NH), 3.60 (s, 2 H, CH_2), 6.22–6.90 (m, 6 H, aromatic protons); IR (film) $\tilde{\nu}_{max}$ 3440 (vs), 3075 (m), 3045 (m), 3005 (s), 2980 (s), 2910 (vs), 2815 (s), 1620 (vs), 1520 (vs), 1470 (s), 1450 (m), 1435 (m), 1415 (m), 1380 (m), 1335 (s), 1320 (s), 820 (s), 805 (s), 775 (w), 750 (m) cm^{-1}; mol wt of $C_{17}H_{22}N_2$, 254.38; mass spectrum (70 eV), *m/e* 254, 239, 224, 134, 120, 119, 105.

Trichloromethane (**29**), hexachloroethane (**30**) and dichloromethane (**31**) were identified as described previously.[2,6]

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Stereochemistry of Ene Reactions of Glyoxylate Esters

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The stereochemistry of the thermal and catalytic ene reactions of methyl glyoxylate is examined. With *cis*-2-butene at 200 °C, a 54% yield of a 7.4:1 mixture of endo–exo adducts is obtained. With cyclohexene and ferric chloride catalyst, a 4.4:1 mixture of endo–exo adducts is obtained. Trisubstituted alkenes give very little selectivity. The intramolecular ene reaction of prenyl glyoxylate proceeds at 90 °C, giving a 1:1 mixture of *cis*- and *trans*-3-isopropenyl-2-hydroxybutyrolactones.

The ene reaction, like the related Diels–Alder reaction, can proceed through an endo or exo transition state. Unlike the Diels–Alder reaction, very little is known about the stereochemistry of intermolecular ene reactions. β-Pinene has been investigated with a wide variety of enophiles,[1,2] and Gill has recently shown that Lewis acids can drastically influence the stereochemistry of the ene reaction of β-pinene with chloral.[2c] Ene reactions with 1,2-disubstituted or trisubstituted alkenes produce two adjacent chiral centers. If one diastereomer is highly

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