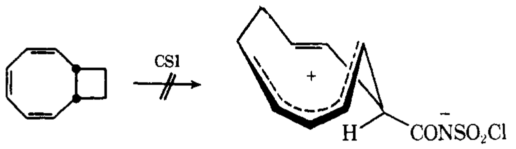
genesis is most satisfactorily rationalized in terms of the cis isomer of **15b**. The somewhat unique capability of **15b** to undergo detectable inversion of that methylene bridge which bears the $-CON^{-}SO_2Cl$ group would appear to be related to the enhanced ground-state strain of this ion which is engendered by the proximity of the methyl substituent.

The ring-methylated derivatives of **1** do behave as if the charge distribution in the intermediate zwitterions is that expected for **2b**; however, complicating factors (polymer formation) do exist. As a result, an accurate assessment of the extent of positive charge borne by C_6 and C_7 in the *trans*-1,3-bishomotropylium ions cannot be made at this time. The overriding energy factor is undoubtedly maximal charge localization on the longest linearly conjugated carbon segment; but "aromaticity," if inherent in such a structural type, necessitates the development of a certain amount of ring current. Further comments on this point are not warranted until additional studies, presently in progress, are completed. It is interesting that *cis*-bicyclo[6.2.0]-deca-2,4,6-triene (**17**) whose interaction with CSI might be expected to lead to pentadienyl cation **18** does not react with this electrophile (CH_2Cl_2, reflux 100 hr, 94.5% recovery). The failure of this cycloaddition may, however, be conformationally related.[2]



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Acknowledgment. We acknowledge with gratitude the financial support of the National Science Foundation and Eli Lilly and Company.

(9) Holder of a NATO Postdoctoral Fellowship (1970–1972) administered by the Science Research Council.

Leo A. Paquette,* Michael J. Broadhurst[9]
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received August 28, 1971

Photocyclization Mechanism of N-Substituted Diphenylamines

Sir:

The photocyclization of aromatic amines to carbazoles has been investigated by a number of authors.[1] In flash kinetic studies with *N*-methyldiphenylamine (A), Linschitz and Grellmann have found a transient with an absorption maximum at 610 nm.[2] They proposed that this 610 transient is the 11,12-dihydrocarbazole[3] which is formed *via* the amine triplet and which reacts further either to the carbazole or back to the amine (eq 1–6). This mechanism has been questioned

$$^3A^* \xrightarrow{k_1} 610 \tag{1}$$

$$^3A^* + M \xrightarrow{k_2} {}^1A + M \tag{2}$$

$$^3A^* + O_2 \xrightarrow{k_3} {}^1A + O_2 \tag{3}$$

$$610 \xrightarrow{k_4} \text{carbazole} + H_2 \tag{4}$$

$$610 + O_2 \xrightarrow{k_5} \text{carbazole} + H_2O_2 \tag{5}$$

$$610 \xrightarrow{k_6} {}^1A \tag{6}$$

recently.[5] We wish to present experimental results from flash photolytic studies which prove it to be correct. The apparatus used has been described elsewhere.[6]

In order to find out whether carbazole is indeed formed *via* 610 (step 4 or 5) we compared flash decay curves at 341 and 610 nm in degassed with those in aerated solutions.[7] At both wavelengths the amine does not absorb, at 341 nm both the carbazole and the transient absorb, and at 610 nm only the transient absorbs.

In the aerated solution the optical density at 341 nm changes irreversibly within the lifetime of the flash (Figure 1d). There are two explanations for this observation. (a) Carbazole is formed within the lifetime of the flash, *i.e.*, much faster than 610 decays. (b) The 610 decay and the carbazol growing in curves mutually compensate each other, because carbazole is formed *via* 610.

In a degassed solution, where there is practically no carbazole formation at room temperature ($k_4/k_6 \approx 10^{-2}$) the decay rate at 341 nm is exactly the same as at 610 nm (*cf.* Figure 1a and b). The ratio of the optical densities at zero time E_0^{610}/E_0^{341} (computed from the extrapolated curves in Figure 1, zero time being taken as the end of the flash excitation) has the same value in the aerated and in the degassed solution. Therefore the absorption in Figure 1d is, at zero time, entirely due to the 610 and, at infinite time, entirely due to carbazole absorption, which means explanation b is the correct one.

At low temperatures in degassed solutions, where (in contrast to room temperature) appreciable amounts of carbazole are formed ($k_4/k_6 \gg 1$), the transient absorptions at 341 and 610 nm show the same behavior as in the aerated solution, because the 610 transient is again the precursor of carbazole.

Steady state illumination experiments with propiophenone as sensitizer[8] already indicated that the formation of carbazole proceeds *via* the triplet state of the amine. In flash experiments at room temperature with a degassed solution containing 10^{-3} *M* *N*-methyldiphenylamine and 10^{-2} *M* propionphenone in methylcyclohexane, under conditions where only the propiophenone was excited, we could observe the 610 transient absorption. The direct formation (without sensitizer)

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(1) (a) C. A. Parker and N. J. Barnes, *Analyst (London)*, **82**, 606 (1957); (b) E. J. Bowen and J. H. D. Eland, *Proc. Chem. Soc.*, 202 (1963); (c) G. C. Terry, V. E. Uffindell, and F. W. Willets, *Nature (London)*, **223**, 1050 (1969).

(2) K. H. Grellmann, G. M. Sherman, and H. Linschitz, *J. Amer. Chem. Soc.*, **85**, 1881 (1963); H. Linschitz and K. H. Grellmann, *ibid.*, **86**, 303 (1964).

(3) In a pulse radiolytic study of triphenylamine,[4] Kemp, *et al.*, assigned the 610 transient erroneously to the amine triplet.

(4) T. I. Kemp, J. P. Robert, G. A. Salmon, and G. F. Thompson, *J. Phys. Chem.*, **71**, 3052 (1967); **72**, 1464 (1968).

(5) H. Shizuka, Y. Takayama, J. Tanaka, and T. Morita, *J. Amer. Chem. Soc.*, **92**, 7270 (1970); see also ref 1c.

(6) K. H. Grellmann, E. Heilbronner, P. Seiler, and A. Weller, *ibid.*, **90**, 4238 (1968).

(7) There is no wavelength detectable at which the photoproduct carbazole absorbs significantly stronger than the 610 transient. For this reason no "growing in curve" such as in Figure 2b can be observed.

(8) E. Tauer, M.S. Thesis, University Erlangen, Germany, 1966; see also ref 5.

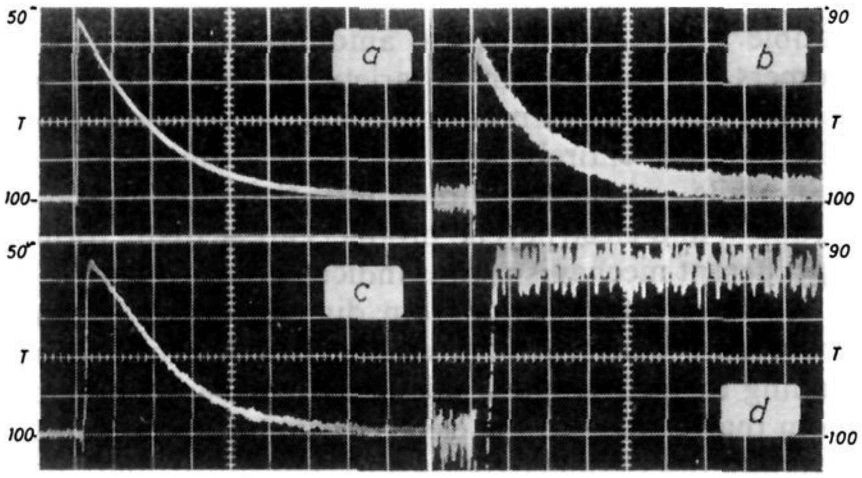

Figure 1. Oscilloscope traces at 610 (a and c) and 341 nm (b and d) after flashing a 2×10^{-4} *M* solution of *N*-methyldiphenylamine (A) in methylcyclohexane: a and b, degassed; c and d, aerated. Time scale: a and b, 20 msec/div; c and d, 0.2 msec/div. Vertical scale, per cent transmission (*T*). The flash intensity in c and d was twice as high as that in a and b.

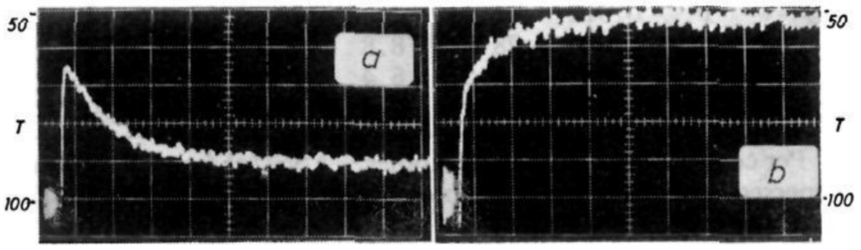

Figure 2. Oscilloscope traces at 520 (a) and 610 nm (b) after flashing a 2×10^{-4} *M* degassed solution of A in 3-methylpentane at −111°: time scale, 0.1 msec/div; vertical scale, per cent transmission (*T*)

of the 610 transient from the amine triplet state is measurable only at low temperatures. Between −100 and −160° the decay of the amine triplet is slow in comparison with the flash lifetime and we observed the triplet decay at 520 nm and at 610 nm the growing in of the 610 transient (Figure 2).

Both processes are first order and occur with the same rate, which clearly shows that the amine triplet is, at least in this temperature range, the precursor of 610. That this mechanism is also operative at room temperature can be shown as follows. The activation energy for the triplet decay is 5.5 kcal/mol in ethanol. The triplet lifetime at room temperature, $\tau_0 = 2 \times 10^{-8}$ sec, as obtained by extrapolation from the Arrhenius plot (Figure 3) agrees quite well with the value derived from the 610 quantum yields in flash experiments on degassed (ϕ_0^{610}) and aerated (ϕ^{610}) solutions using the Stern–Volmer equation, $\phi_0^{610}/\phi^{610} = 1 + k_3[O_2]\tau_0$, where (neglecting phosphorescence) $\tau_0 = 1/(k_1 + k_2[M])$. Since 610 decays by a first-order reaction both in the presence of oxygen ($\tau_{610} = 3 \times 10^{-4}$ sec) and in degassed solutions ($\tau_{610} = 3.5 \times 10^{-2}$ sec), the ratio of the 610 quantum yields is easily determined by extrapolating the decay curves back to zero time. In ethanol and methylcyclohexane $\phi_0^{610}/\phi^{610} = 2$; $k_3[O_2]$ is assumed to be 6×10^7 sec^{-1} (based on Ware's measurements[9]) so that $\tau_0 = 1.7 \times 10^{-8}$ sec. Tris-*p*-tolylamine has an absorption spectrum which makes this compound suitable for nitrogen-laser excitation at 337 nm.[10] The decay of the triplet state can therefore be measured directly at room temperature; we found $\tau_0 = 5 \times 10^{-8}$ sec. The agreement between the values of τ_0 determined from the laser experiment, from the extrapolated Arrhenius plot, and from the 610 quantum yield ratio ($\phi_0^{610}/\phi^{610} = 7$) is good (*cf.* Figure 3).

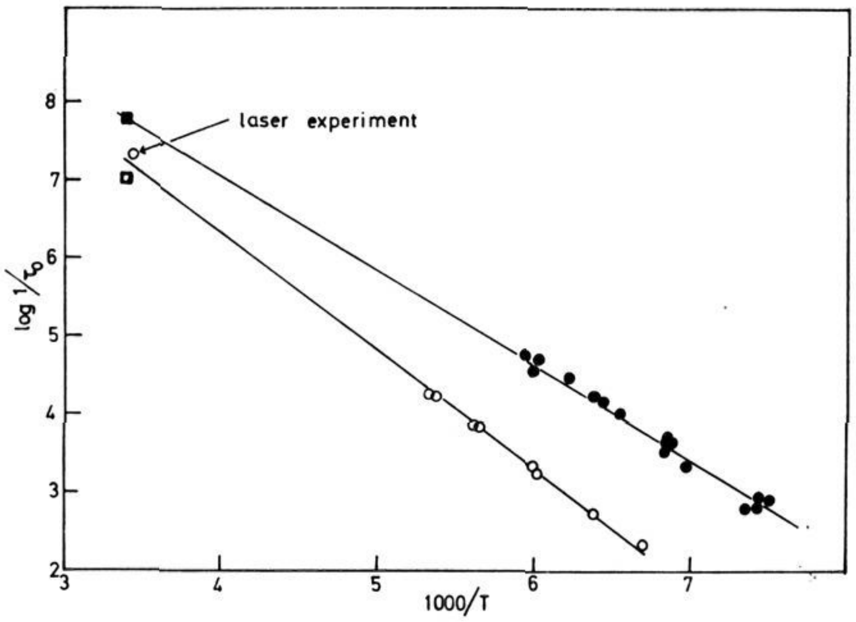

Figure 3. Arrhenius plot of the triplet decay of *N*-methyldiphenylamine (●) and tris-*p*-tolylamine (○). Points calculated from quenching experiments: ■; □.

The quantum yield for carbazole formation from A is, according to our measurements in aerated solutions, 0.42,[11] and therefore $\phi^{610} = k_1/(k_1 + k_2[M] + k_3 \cdot [O_2]) \geq 0.42$. Since $\phi_0^{610}/\phi^{610} = 2$, it follows that $\phi_0^{610} = k_1/(k_1 + k_2[M]) \geq 0.84$. These amazingly high yields imply that the chemical relaxation process 1 competes at room temperature very effectively with the normal triplet deactivation reactions (2 and 3). Process 1 is not suppressed in highly viscous media. Even solutions of A in polymethylmethacrylate matrices show the 610 absorption on flashing at room temperature. Presumably, $k_2[M] \ll k_1$, because in photochemically stable amines, such as tris-*p*-carbomethoxyphenylamine (I) or *N*-methylbis-*p*-carbomethoxyphenylamine, where there is no detectable 610 and carbazole formation, the triplet lifetime is 3 orders of magnitude longer and liquid solutions of I phosphoresce even at room temperature.[12]

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[9] W. Ware, *J. Phys. Chem.*, **66**, 455 (1962).

[10] The authors are indebted to Dr. H. Staerk of this institute who performed the experiment.

[11] The carbazole concentration was determined spectrophotometrically, using an extinction coefficient ϵ_{343} 5400 l./(mol cm). The value 3900 used by Tanaka, *et al.*,[5] is too low and consequently their quantum yield of 0.62 too high.

[12] K. H. Grellmann, *Ber. Bunsenges. Phys. Chem.*, **73**, 827 (1969).

[13] Part of Ph.D. Thesis, Göttingen, 1971.

E. W. Förster,[13] K. H. Grellmann*
Max-Planck-Institut für Biophysikalische Chemie
Abteilung Spektroskopie, 34 Göttingen, Germany

Received March 12, 1971

Competing Diradical and Electrocyclic Reactions. Difference in Activation Volumes

Sir:

Numerous examples are now known in which thermal reaction of a diene with a dienophile reagent produces mixtures of cyclohexenes and vinylcyclobutanes.[1] It is generally accepted that the cyclohexenes result from concerted, electrocyclic reaction allowed by orbital

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[1] (a) P. D. Bartlett, *Quart. Rev., Chem. Soc.*, **24**, 473 (1970); (b) C. A. Stewart, Jr., *J. Amer. Chem. Soc.*, **84**, 117 (1962); (c) J. C. Little, *ibid.*, **87**, 4020 (1965).