

and with carbon dioxide to give the acid II_d.³ The n.m.r. spectra of II_c and of the methyl ester of the acid II_e³ are again consistent with the proposed structures. It is interesting that in the latter case (II_e), the four protons on C-2 and C-3 are observed as a separate peak no longer lying under the *t*-butyl peak.

The formation of a carbanion at C-6 seems unprecedented, since there is no simple way to delocalize the negative charge. This property must be due to a change in hybridization resulting in increasing *s*-character for the C-6 H bond, brought about by the unusually small bond angles required in structure II_a. The correlation of acidity with *s*-character is well known,⁶ examples of such acidic protons being those on acetylenic carbons and the olefinic protons of cyclopropene.⁷ Since the carboxamide group is certainly converted into an anion in *n*-butyllithium solution and is therefore unlikely to aid in stabilization of the carbanion, and since the two-carbon bridge should not make a large difference in the C-C bond angles, the acidity of II_a would seem to be a property intrinsic in the bicyclo[1.1.0]butane portion of its skeleton. The validity of this conclusion is at present being investigated.

(6) A. D. Walsh, *Discussions Faraday Soc.*, **2**, 18 (1947).

(7) K. B. Wiberg, R. K. Barnes and J. Albin, *J. Am. Chem. Soc.*, **79**, 4994 (1957); G. L. Closs and L. E. Closs, *ibid.*, **85**, 99 (1963).

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Photo-Conversion of Diphenylamines to Carbazoles, and Accompanying Transient Species

Sir:

In the course of flash-excitation studies on *N*-substituted diphenylamines in solution, we have observed new transient species which are neither the triplet states nor the positive ions. The hypothesis that the transients are cyclized structures suggested that under oxidative conditions carbazoles should be formed, and this is indeed found to be the case. Our results are related to recent proposals of mechanisms and kinetic intermediates in analogous oxidative photocyclization reactions.^{1,2}

When triphenylamine is flashed³ in deoxygenated hexane, EPA or tetrahydrofuran solution, two main transients are observed, with absorption peaks at 530 $m\mu$ and 610 $m\mu$, respectively. At room temperature, the major product is the 610 $m\mu$ compound, but low temperature favors formation of the 530 $m\mu$ substance. In EPA solution, at -150° , phosphorescence, which decays at precisely the same rate as the 530 $m\mu$ absorption, is observed. This peak is therefore assigned to the lowest triplet state of triphenylamine.

The 610 $m\mu$ compound has a lifetime of 0.5 msec. at room temperature in hexane and a slightly longer lifetime in polar solvents. It undergoes strictly first-order decay to the ground state, with an activation energy of about 10 kcal./mole in the temperature range 25° to -70° . On flashing *N*-methyl-diphenylamine, two main transients are again formed, with absorption spectra similar to those obtained from triphenylamine. However, the lifetime of the 610 $m\mu$ transient of *N*-methyl-diphenylamine (16 msec. at room temperature,

(1) F. B. Mallory, J. T. Gordon and C. S. Wood, *J. Am. Chem. Soc.*, **85**, 828 (1963).

(2) W. M. Moore, D. D. Morgan and F. R. Stermitz, *ibid.*, **85**, 829 (1963).

(3) Discharge energies of about 100 w.-sec. were used, with flash durations of about 5 μ sec. Temperatures could be varied from 30° to -150° . The apparatus had the general configuration of that described earlier by H. Linschitz and K. Sarkanen, *ibid.*, **80**, 4826 (1958).

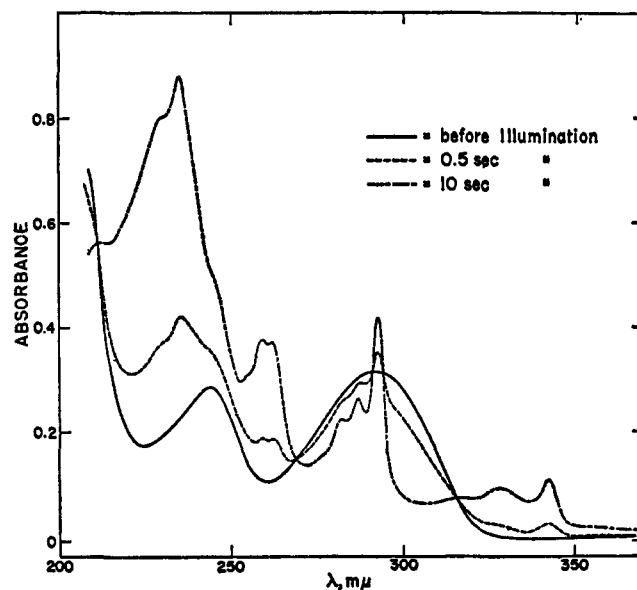
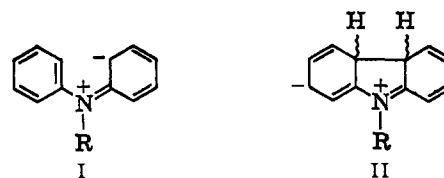


Fig. 1.—Photo-conversion of *N*-methyl-diphenylamine to *N*-methylcarbazole. Absorption spectrum of *N*-methyl-diphenylamine in aerated hexane: solid line, before illumination; dotted line, after half-second illumination; dashed-dotted line after 10-second illumination; concn. $2.6 \times 10^{-5} M$; sample in 1 cm. quartz cell, placed 5 cm. from Hanovia Type SH mercury lamp; room temperature.

in hexane) is much longer than that of the corresponding triphenylamine compound (0.5 msec.).

The positive ion of triphenylamine absorbs at 650 $m\mu$,⁴ with a spectrum easily distinguished from that of the 610 $m\mu$ product. Moreover, if the ion were formed by photo-ionization of the amine in fluid non-polar solvents, it would be expected to decay by extremely fast, second-order kinetics, with a low activation energy for recombination⁵ and with little lifetime dependence on *N*-methyl or *N*-phenyl substitution. Thus, the 610 $m\mu$ transient cannot be the positive ion. Two possibilities may be suggested for this transient, an excited ionic species I, stabilized by Franck-Condon effects, and the cyclized intermediate II.



Other resonance forms of I and II can evidently be written.

The assignment of structure II for the 610 $m\mu$ compound is supported by the high activation energy for decay and by the formation of carbazoles in high yield when the amines are illuminated in organic solvents, exposed to air. Figure 1 shows the changes in absorption spectrum of a hexane solution of *N*-methyl-diphenylamine, caused by brief illumination by a 150 w. mercury lamp. The final spectrum is identical with that of *N*-methylcarbazole and corresponds to about 70% conversion. In other experiments, *N*-methylcarbazole was isolated and identified by its m.p. (85.5 – 86.5°), mixture melting point (no depression) and infrared spectrum. The illumination of triphenylamine gave the ultraviolet spectrum of *N*-phenylcarbazole (about 65% yield) which was similarly isolated and further identified by its m.p. (88.5°), mixture melting point (no depression) and infrared spectrum. The photo-

(4) G. N. Lewis and D. Lipkin, *ibid.*, **64**, 2801 (1942).

(5) H. Linschitz and J. Eloranta, *Z. Elektrochem.*, **64**, 169 (1960).

conversion of triphenylamine is considerably slower than that of N-methyldiphenylamine consistent with the much shorter lifetime of the $610\text{ m}\mu$ intermediate of triphenylamine. Presumably, the rapid conversion of the intermediate to the ground state competes with its thermal oxidation to carbazole. Diphenylamine itself is also photo-converted to carbazole, but with considerable side reaction.

The formation of intermediate II in the course of the reaction may be understood as a consequence of charge migration from the nitrogen atom into the rings, in the excited state I, followed by bond formation by nucleophilic attack in the polar excited form, to yield II.

Further details of these and related experiments will be published shortly.

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RECEIVED APRIL 15, 1963

Measurement of an Amine Inversion Rate Using Nuclear Magnetic Resonance

Sir:

In spite of considerable interest in barriers to inversion of amines, it has thus far been possible to measure rates of inversion only for amines possessing NH bonds, where the observed large rates found using microwave spectroscopy have been attributed to tunneling,¹ or in

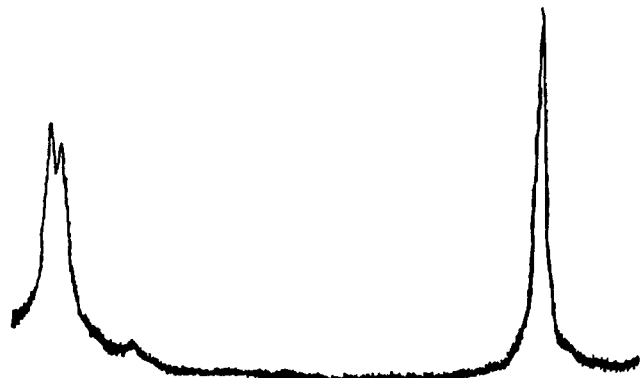


Fig. 1.—The CH_2 and CH_3 peaks in the n.m.r. spectrum of 0.35 M dibenzylmethyl ammonium chloride at pH 2.0.

ethyleneimines where it is suggested that the rates, observed using n.m.r. spectroscopy, are unusually slow due to steric restriction.^{2,3}

We wish to report a new method of employing n.m.r. spectroscopy to measure these rates, which is applicable over a wide range of values including the rates of typical tertiary amines.

When a benzyl group is bonded to an amine having two dissimilar groups attached as well, it is expected that the CH_2 hydrogens will experience different chemical shifts due to the asymmetric environment, which should be similar to that produced by an asymmetric carbon.^{4,5} Inversion of the amine then results in interchange of the chemical shifts. If this occurs rapidly enough, the expected AB quartet of the CH_2 will coalesce

to a singlet. Observation of this phenomenon with change of temperature would enable measurement of the rate, but only if the rate could be slowed to 50 sec.^{-1} or slower. This has thus far been impossible in the case of any amine tried at the lowest temperature attainable. Therefore, another method of reducing the rate was devised. Dibenzylmethylamine was dissolved in concentrated hydrochloric acid and the n.m.r. spectrum observed. In addition to splitting of the CH_2 and CH_3 peaks due to coupling with the NH, the CH_2 peak showed the effects of non-equivalence of the protons, since inversion cannot occur in the ammonium salt. It was found necessary to use low concentrations of the salt since the chemical shift between the CH_2 hydrogens was a function of the concentration and was a maximum at low concentration. Because of the high conductivity of these samples, it was found necessary to use the arrangement of pulse equipment suggested by Meiboom⁶ for eliminating noise produced by modulation of leakage. Decreasing the acid concentration resulted in coalescence of the methyl doublet because of NH exchange of the salt with free amine. The rate of this process was measured using the method of Meiboom.⁷ At 0.35 M salt concentration and 25° with 2 N HCl present, a pseudo first-order rate constant of 5 sec.^{-1} was found. Using a $\text{p}K_a$ of 7.5 ± 0.1 , which was obtained spectroscopically, a second-order rate constant for the proton transfer of $6 \pm 3 \times 10^8\text{ l./mole sec.}$ was obtained. On going to still weaker acid, the NH exchange becomes faster and the methyl peak becomes a singlet; however, the CH_2 hydrogens were found to be still not equivalent (Fig. 1). This demonstrates that the salt can lose its proton to give the amine and be re-protonated without inversion. On raising the pH to 2.5, the doublet was observed to coalesce. Since the inversion can occur only during the time spent as amine, and the rate of interconversion of amine and salt is rapid

$$k_{\text{interchange}} = k_{\text{inversion}} \cdot [\text{amine}]/([\text{salt}] + [\text{amine}])$$

The measured $\text{p}K_a$ permitted calculation of this fraction as a function of pH. The rate constant for interchange at pH 3.5 was found to be 21 sec.^{-1} using equations derived by Alexander⁸ to prepare a computer program which calculates line shape for the A-B system, including the effects of coupling between the protons, and natural line width. Taking account of the fraction of unprotonated amine, we obtained a rate constant for the inversion of $2 \pm 1 \times 10^6\text{ sec.}^{-1}$.

(6) S. Meiboom, personal communication.

(7) A. Lowenstein and S. Meiboom, *J. Chem. Phys.*, **27**, 1067 (1957).

(8) S. Alexander, *ibid.*, **37**, 966 (1962).

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RECEIVED MARCH 1, 1963

Diphenylquinocyclopropene

Sir:

Although the synthesis of the stable, basic diphenylcyclopropenone (I) in 1958¹ has been accompanied by preparation of several other cyclopropenium aromatic compounds,² attempts to isolate stable substances containing the methylenecyclopropene system (II) appear to have been unsuccessful.³ We wish to report the

(1) R. Breslow, R. Haynie and J. Mirra, *J. Am. Chem. Soc.*, **81**, 247 (1959); M. Volpin, Yu. Koreshev and D. Kursanov, *Izv. Akad. Nauk SSSR*, 560 (1959).

(2) R. Breslow, H. Höver and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962), and references cited therein; D. G. Farnum and M. Burr, *ibid.*, **82**, 2651 (1960).

(3) E.g., R. Breslow and M. Battiste, *ibid.*, **82**, 3626 (1960); H. Prinzbach and W. Rosswog, *Angew. Chem.*, **73**, 543 (1961).

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(2) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 5203 (1958).

(3) J. F. Kincaid and F. C. Henriques, Jr., *ibid.*, **62**, 1474 (1940).

(4) G. M. Whitesides, F. Kaplan, K. Nagarajan and J. D. Roberts, *Proc. Natl. Acad. Sci.*, **48**, 1112 (1962).

(5) H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2196 (1962).