conversion of triphenylamine is considerably slower than that of N-methyldiphenylamine consistent with the much shorter lifetime of the 610 mμ 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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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

(1) W. Gordy, W. V. Smith and R. F. Trambarillo, "Microwave Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1953.

(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).

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 Meiboom[6] 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 pK_a of 7.5 ± 0.1, which was obtained spectroscopically, a second-order rate constant for the proton transfer of 6 ± 3 × 10⁸ 1./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 reprotonated 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 pK_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 Alexander[8] to prepare a computer program which calulates 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 ± 1 × 10⁵ sec.$^{-1}$.

(6) S. Meiboom, personal communication.

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

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

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Diphenylquinocyclopropene

Sir:

Although the synthesis of the stable, basic diphenylcyclopropenone (I) in 1958[1] 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. Koreshkov 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).