

cyclo[2.2.1]hept-2-ene-*exo-cis*-5,6-dicarboxylic acid (3) by dissolving it in warm water (40–60°), and was used immediately for esr measurements. The oxygen-bridged olefinic acid anhydride was hydrogenated in acetone with 5% Pd/charcoal catalyst⁴² and then hydrolyzed into diacid 5 by dissolving it in hot water.

Bicyclo[2.2.1]hept-2-ene-*endo-cis*-5,6-dicarboxylic anhydride and its diacid, 4, were prepared according to the procedure of Fieser.⁴³ Bicyclo[2.2.1]heptane-*endo-cis*-5,6-dicarboxylic acid was prepared from the anhydride of 4 by hydrogenation with 5% Pd/charcoal catalyst in ethyl acetate followed by hydrolysis in boiling water.

The following reagents were obtained commercially from Nakarai Chemicals Ltd. and Wako Pure Chem. Ind. and used without further purification: 20% TiCl₃ aqueous solution, 30% H₂O₂ aqueous solution, hydroxylamine hydrochloride, 9% peroxyacetic acid in acetic acid, *tert*-butyl hydroperoxide, and thioglycolic acid.

(42) O. Diels and Olsen, *J. Prakt. Chem.*, **156**, 302 (1940).

(43) L. F. Fieser, "Organic Experiments," D. C. Heath, Boston, Mass., 1964, Chapter 15.

Generation of Radicals. For the generation and the esr measurement of the radicals, the Dixon-Norman⁴⁴ type rapid flow technique was used. Two aqueous solutions (A and B) flew into the mixing chamber and then into the sample cell in the esr cavity. The reagents and their concentrations in both solutions are summarized in Table II. When the solubility of the substrate was insufficient the solution was heated to increase the solubility.

Esr Measurement. The esr spectra were obtained with a JEOL 3BSX spectrometer with 100-kHz modulation. The flow system consists of a JEOL JES-SM-1 mixing chamber, a JES-LC-01 capillary-type aqueous sample cell. Hyperfine coupling constants and *g* factors were determined relative to the hfsc of ¹⁴N (13.07 G) and the *g* factor (2.00559) of potassium peroxyaminedisulfonate in aqueous solution filled in a capillary which was attached to the sample cell. The reported *g* factors were corrected to second order with respect to the hyperfine interactions.

(44) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963).

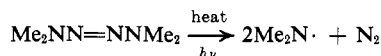
Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. X. Reactions of Some Alkylamino Radicals in Solution^{1,2}

J. R. Roberts³ and K. U. Ingold*

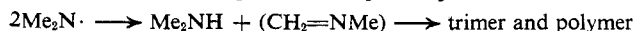
Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R9. Received September 29, 1972

Abstract: Dimethylamino, diethylamino, and diisopropylamino radicals have been generated in the cavity of an epr spectrometer by photolysis of the appropriate tetraalkyltetrazenes and by photolysis of di-*tert*-butyl peroxide in the presence of the dialkylaminodiethoxyphosphines. The second-order decay of dimethylamino and diethylamino occurs at the diffusion controlled limit, $(2 \pm 1) \times 10^9 M^{-1} \text{sec}^{-1}$. The decay of diisopropylamino is second order at temperatures below ambient ($k^2_{\text{epi}} \approx 1.0 \times 10^7 M^{-1} \text{sec}^{-1}$) and first order above. For radicals generated from the tetrazene, the first-order process is rather slow and represents thermal decomposition of an intermediate which is probably the *cis* tetrazene. For radicals generated from the phosphine the first-order process is quite rapid and probably corresponds to a true unimolecular reaction of diisopropylamino radicals, except when the solvent is a good hydrogen donor. 2,2,6,6-Tetramethylpiperidyl radicals were generated from the tetrazene. The decay is first order in hydrocarbon solvents. The variation in the rate constants for decay with hydrocarbon structure, the rate constants in perdeuterated solvents, and product studies show that this reaction is usually a hydrogen abstraction from the solvent. The tetramethylpiperidyl radical is more reactive in abstractions than are peroxy radicals. Tetramethylpiperidyl ($a_N = 14.66 \text{ G}$, $g = 2.0048$ in isopentane at 27°) reacts rapidly with oxygen and is converted to the corresponding nitroxide ($a_N = 15.3 \text{ G}$, $g = 2.0064$ at -100°). With ¹⁷O labeled oxygen this nitroxide has $a(^{17}\text{O}) = 19.35 \text{ G}$.

Studies of the chemistry of dialkylamino radicals in solution have generally been confined to the dimethylamino radical which has been generated by the thermolysis or photolysis of tetramethyl-2-tetrazene.



In the absence of any other reactant the principal products appear to arise from the combination and disproportionation of the dimethylamino radicals.^{4,5}



(1) Issued as N.R.C.C. No. 13197. Part IX: G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 2963 (1973).

(2) A preliminary account of this work has been published: J. R. Roberts and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 6686 (1971); **94**, 2159 (1972).

(3) N.R.C.C. Postdoctorate Fellow, 1970–1972.

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

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

Some hydrogen abstraction from the tetrazene, leading to induced decomposition, may also occur.^{4,6,7} Dimethylamino radicals appear to add to styrene⁸ and to α -methylstyrene^{9,10} but not to simple olefins^{7,9} or to aromatic systems.^{9,11,12} They abstract benzylic (and other activated) hydrogens "feebly" at elevated temperatures,^{7–9,12,13} and the relative reactivities of some substrates have been determined.^{7,13} However, they do not readily abstract benzylic hydrogens at room temperature which is a bit surprising since the

(6) W. C. Danen and T. T. Kensler *ibid.*, **92**, 5235 (1970).

(7) C. J. Michejda and W. P. Hoss, *ibid.*, **92**, 6298 (1970).

(8) B. L. Erusalimsky, B. A. Dolyoplosk, and A. P. Kavanenko, *Zh. Obshch. Khim.*, **27**, 267 (1957).

(9) B. R. Cowley and W. A. Waters, *J. Chem. Soc.*, 1228 (1961).

(10) See, however, R. S. Neale, N. L. Marcus, and R. G. Schepers, *J. Amer. Chem. Soc.*, **88**, 3051 (1966).

(11) R. E. Jacobson, K. M. Johnston, and G. H. Williams, *Chem. Ind. (London)*, 157 (1967).

(12) D. Mackay and W. A. Waters, *J. Chem. Soc. C*, 813 (1966).

(13) K. M. Johnston, G. H. Williams, and H. J. Williams, *J. Chem. Soc. B*, 1114 (1966).

N-H bond dissociation energy in dimethylamine has been estimated to be 95 kcal/mol.¹⁴ The abstraction of hydrogen from toluene should therefore be 10 kcal/mol exothermic and might be expected to be fairly rapid at ambient temperatures. The dimethylamino radical is also very unreactive toward cyclohexane.¹²

Work on other dialkylamino radicals¹⁵ in solution appears to be confined to a brief qualitative study of hydrogen abstraction by the piperidyl radical¹² and to epr spectroscopic investigations.^{2,6,16,17} Except for the preliminary account of this work² the absolute rate has not, so far as we are aware, been reported for any reaction involving any dialkylamino radical in solution. Even the question as to whether such radicals react with oxygen appears to be still in dispute.¹⁸⁻²¹

Danen and Kensler's⁶ exciting discovery that dialkylamino radicals can be observed by epr spectroscopy on photolyzing tetraalkyltetrazenes directly in the epr cavity prompted the present kinetic studies. Absolute rate constants have been measured for the bimolecular self-reactions of dimethylamino, diethylamino, and diisopropylamino radicals and for the reactions of 2,2,6,6-tetramethylpiperidyl with some hydrocarbons. The latter radical has been shown to react rapidly with oxygen to yield the nitroxide.

The dimethylamino, diethylamino, and diisopropylamino radicals have also been generated by photolysis in the epr cavity of di-*tert*-butyl peroxide containing the appropriate dialkylaminodiethoxyphosphine. This recently discovered reaction²² yields higher concentrations of dialkylamino radicals at lower temperatures than does tetrazene photolysis. Furthermore, the starting material is more easily prepared. Kinetic studies on diisopropylamino from this source have now shown that the previously reported² peculiarities in the decay of this radical above 25° are not due to the presence and thermal instability of the hydrazine. The unstable intermediate is probably the *cis* tetrazene.

Experimental Section

The general experimental procedure for kinetic studies of free radicals on our Varian E-3 epr spectrometer has been described previously.¹ The epr samples contained 5% or less tetrazene in order to reduce the importance of radical attack on the tetrazene.^{6,7} All samples were carefully degassed either by the freeze-thaw method after addition of the solvent or by distilling the solvent under vacuum directly into the epr tube. The solvents were the best grade available and were freed from any hydroperoxides by passage over alumina or by distillation from triphenylphosphine. Unless these precautions were observed, instead of the amino radicals the corresponding nitroxides would be formed by reaction

of the amino radicals with hydroperoxide,²³ with peroxy radicals²⁴ or, as is shown later, with oxygen. The problem of nitroxide formation was particularly acute with 2,2,6,6-tetramethylpiperidyl since the corresponding nitroxide is stable indefinitely at room temperature.

The nmr spectra were recorded on a Varian HA-100 spectrometer, and nmr data are quoted in ppm downfield from TMS, the relative intensities of the different peaks being given in brackets. Analysis by glpc was carried out on an F&M Model 1200 gas chromatograph using a 10-ft silicone rubber packed column.

Preparation of the Tetrazenes. Tetramethyltetrazene (bp 32° (15 Torr)),²⁵ tetraethyltetrazene (79° (12 Torr)),²⁶ and tetraisopropyltetrazene (50° (0.2 Torr))²⁶ were prepared *via* mercuric oxide oxidation of the corresponding 1,1-dialkylhydrazines.^{26,27} The nmr spectra of the tetrazenes were consistent with the literature.²⁸ The tetrazene of 2,2,6,6-tetramethylpiperidine was prepared in reasonable yield *via* nitrosation of the amine with sodium nitrite, reduction of the nitrosoamine to the hydrazine with LiAlH₄, and oxidation of the hydrazine with iodine as described below.

1-Nitroso-2,2,6,6-tetramethylpiperidine. A slurry of the hydrochloride was prepared by adding, dropwise, 25 g of 2,2,6,6-tetramethylpiperidine to 14 ml of cold, concentrated hydrochloric acid. After the slurry was heated to ≥85°, a solution containing 15 g of sodium nitrite in 20 ml of H₂O was added slowly. In order to keep the reaction mixture just acidic at all times, 2 *N* HCl was added when necessary. The solution was allowed to stir for several hours. An additional 6 g of sodium nitrite in 20 ml of H₂O was added slowly, and the solution was then allowed to stir for 10 hr at 95°. The reaction mixture was cooled, and extracted with ether, and the organic layer was dried over MgSO₄. By distillation, 12 g (40% yield, yellow liquid) of 1-nitroso-2,2,6,6-tetramethylpiperidine was collected from 97 to 98° (7-10 Torr) (lit.¹² bp 91-92° (12 Torr)).

1-Amino-2,2,6,6-tetramethylpiperidine. A slurry containing 5 g of LiAlH₄ in 75 ml of anhydrous ethyl ether and 75 ml of anhydrous *n*-butyl ether was prepared. A solution containing 11 g of 1-nitroso-2,2,6,6-tetramethylpiperidine in 25 ml of anhydrous ethyl ether was added slowly to the slurry. When no reaction occurred after 1 hr, the solvent was removed by distillation until the pot temperature reached 95°. A water cooled condenser was then attached and the refluxing was continued overnight. After destroying excess LiAlH₄ with a 50:50 mixture of methanol-ether, the slurry was poured into a separatory funnel containing ice and an excess of 10% sodium hydroxide. The aqueous layer was extracted with ether and the extract was dried over MgSO₄. By distillation, 4.4 g (44%) of 1-amino-2,2,6,6-tetramethylpiperidine was collected from 80 to 83° (20-21 Torr) (lit.¹² bp 80° (20 Torr)). The infrared spectrum contained a doublet at 3350 and 3220 cm⁻¹, which is consistent with the presence of the amino group (nmr 1.01 (6), 1.46 (3), 2.6 (1)).

1,1'-Azo-2,2,6,6-tetramethylpiperidine. A solution of 4.6 g of iodine in 120 ml of ethyl ether was added dropwise to an ice-cooled solution of 50 ml of ethyl ether containing 2.5 g of 1-amino-2,2,6,6-tetramethylpiperidine and 5.2 ml of diethylamine. The iodine solution was decolorized immediately with the concurrent formation of a fluffy white precipitate of diethylammonium iodide. The addition of the iodine solution was continued until the solution remained colored. The solution was filtered, washed with water, and dried over anhydrous calcium carbonate, and the solvent removed. Crystallization at -78° from pentane yielded 1 g of white crystalline material, mp 45-47°. This material could be further purified through sublimation to give samples free from any paramagnetic material: nmr (C₆D₁₂) 1.28 (2), 1.57 (1).

Anal. Calcd for C₁₈H₃₆N₄: C, 70.07; H, 11.76. Found: C, 70.22; H, 11.92.

Products of Tetrazene Photolysis. Tetraisopropyltetrazene. An unsuccessful attempt was made by nmr to detect the intermediate

(14) D. M. Golden, R. K. Solly, N. A. Gac, and S. W. Benson, *J. Amer. Chem. Soc.*, **94**, 363 (1972).

(15) A number of studies on NH₂, RNH, alkylarylamino, and diarylamino radicals have, however, been reported.

(16) (a) V. D. Sholle, E. G. Rozantsev, A. I. Prokof'ev, and S. P. Solodovnikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2628 (1967); (b) see also D. W. Pratt, J. J. Dillon, R. V. Lloyd, and D. E. Wood, *J. Phys. Chem.*, **75**, 3486 (1971).

(17) After submission of this paper it was reported [M. A. Ratcliffe, Jr., and J. K. Kochi, *J. Org. Chem.*, **37**, 3268, 3275 (1972)] that the bimolecular self-reaction of dibenzylamino radicals yields disproportionation products only, no dimerization occurring.

(18) G. G. Jayson, G. Scholes, and J. J. Weiss, *J. Chem. Soc.*, 2594 (1955).

(19) P. W. Jones and H. D. Gesser, *Chem. Ind. (London)*, 566 (1970).

(20) P. W. Jones and H. D. Gesser, *J. Chem. Soc. B*, 1873 (1971).

(21) M. Simic, P. Neta, and E. Hayon, *Int. J. Radiat. Phys. Chem.*, **3**, 309 (1971).

(22) R. W. Dennis and B. P. Roberts, *J. Organometal. Chem.*, **43**, C2 (1972).

(23) A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, p 113.

(24) See, e.g., O. L. Harle and J. R. Thomas, *J. Amer. Chem. Soc.*, **79**, 2973 (1957); J. R. Thomas, *ibid.*, **82**, 5955 (1960); J. C. Baird and J. R. Thomas, *J. Chem. Phys.*, **35**, 1507 (1961); K. Adamic, M. Dunn, and K. U. Ingold, *Can. J. Chem.*, **47**, 287 (1969); K. Adamic and K. U. Ingold, *ibid.*, **47**, 295 (1969).

(25) W. E. Bull, J. A. Seaton, and L. F. Audrieth, *J. Amer. Chem. Soc.*, **80**, 2516 (1958).

(26) D. M. Lemal, F. Menger, and E. Coats, *ibid.*, **86**, 2395 (1964).

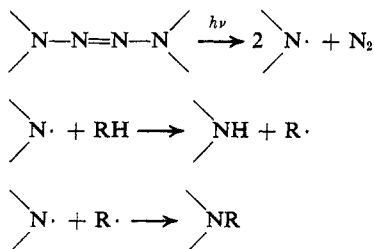
(27) H. Zimmer, L. F. Audrieth, M. Zimmer, and R. A. Rowe, *ibid.*, **77**, 790 (1955).

that the kinetic studies suggest is formed and is stable at low temperatures.

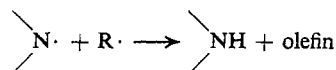
A degassed solution containing 0.14 g (5.8×10^{-4} mol) of the tetrazene in 1 ml of perdeuterio-*n*-heptane (containing <1% TMS) was photolyzed in a quartz tube in the epr cavity at -60° . The amino radical concentration was steady at $\sim 2 \times 10^{-6} M$ throughout the run. The nmr spectrum was recorded periodically, but the sample was kept below -40° at all times. The nmr peaks due to the tetrazene decreased and were supplanted by peaks due to diisopropylamine and the Schiff base, *N*-isopropylacetamine.^{28,29} After 2.3 hr the tetrazene had decreased 20% (as judged against the TMS internal standard). The decomposed tetrazene was apparently converted entirely to the amine and Schiff base (as estimated from the intensity of their nmr peaks and from the fact that no other peaks were present in the spectrum).³¹ Furthermore, the nmr spectrum obtained after warming the sample to 30° (and waiting till the epr signal due to diisopropylamino had completely decayed; see Results) was identical with that obtained cold. Since the amine and Schiff base peaks did not increase to any noticeable extent the yield of any unstable intermediate cannot have been greater than 2%. No intermediate could be detected by nmr when photolysis of this sample was continued at -60° through a Pyrex filter until a further 15% of the tetrazene had been decomposed.

1,1'-Azo-2,2,6,6-tetramethylpiperidine. A solution containing 0.0115 g of the tetrazene in 1.3 ml of tetramethylsilane was photolyzed for 5 hr through a Pyrex filter at room temperature. Nmr analysis indicated a 10% consumption of the tetrazene. The only major volatile product (glpc, mass spectrometer analysis) was tetramethylpiperidine.

A solution containing 0.0253 g of the tetrazene in 0.52 ml of *n*-octane was photolyzed for 10 hr in quartz at room temperature (almost complete tetrazene decomposition). The yield of tetramethylpiperidine was $60 \pm 5\%$ based on starting tetrazene. A 50% yield is expected on the basis of the reactions



The small excess of amine may be due to a cross-disproportionation reaction.



In analogous experiments in cyclopropane and in neopentane the yields of tetramethylpiperidine were ~ 2 and $\sim 5\%$, respectively, based on starting tetrazene. Some radical decay process other than hydrogen abstraction must occur in these solvents.

Dialkylaminodiethoxyphosphines. We are deeply indebted to Dr. B. P. Roberts for providing the three phosphines used in this work.

Results

Epr Spectra. Dimethylamino, diethylamino, and diisopropylamino radicals generated by photolysis of tetrazenes⁶ or by photolysis of di-*tert*-butyl peroxide in the presence of the dialkylaminodiethoxyphosphines²² gave epr spectra identical with those reported by Danen and Kensler.^{6,32}

(28) G. Slomp and J. G. Lindberg, *Anal. Chem.*, **39**, 60 (1967).

(29) Infrared analysis of a similar mixture photolyzed in perdeuterio-benzene at 5° showed a strong absorption at 1650 cm^{-1} due to the Schiff base.³⁰

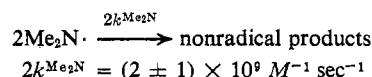
(30) C. Sandorfy in "The Chemistry of the Carbon-Nitrogen Double Bond," S. Patai, Ed., Interscience, New York, N. Y., 1970, p 37.

(31) In the gas phase at 150° dimethylamino radicals are reported to aut disproportionation to hydrogen and *N*-methylenemethylamine.²⁰ We see no evidence for such a reaction with any dialkylamino radicals in solution at lower temperatures (see also ref 17).

The epr spectrum of the 2,2,6,6-tetramethylpiperidyl radical consists of a triplet of multiplets. In isopentane at 27° the epr spectroscopic parameters are³³ $a_N = 14.66 \text{ G}$, $a_H = 0.82 \text{ G}$, $g = 2.0048$; and at -70° $a_N = 14.66$, $a_H = 0.63$, $g = 2.0048$. This radical is distinguishable from the corresponding nitroxide by its lower g value³⁴ and by its resolvable hydrogen couplings.^{16a,35} Under the best conditions, there are definitely 11 and probably at least 13 lines in each multiplet.³⁶ This splitting must arise principally from 12 equivalent protons in the four methyl groups. The spectrum was temperature dependent and the methyl splittings could not be resolved below -90° . However, the triplet that remains is split further on further cooling. In isopentane, at temperatures below -140° , a rather poorly resolved 9-line spectrum is obtained. The same spectrum is obtained by photolysis of the tetrazene at these temperatures or by its photolysis at -60° followed by cooling of the sample after cutting off the light. The spectrum is consistent with a triplet (1:1:1), $a_N = 14.6 \text{ G}$, of triplets (1:2:1), $a_H \approx 4.6 \text{ G}$ (2 H). Presumably, the radical is locked (on the epr time scale) into one conformation at these temperatures. The four methyl groups are therefore no longer equivalent (even if they are still rotating freely they will form axial and equatorial pairs). The two hydrogens responsible for the 4.6-G splittings are presumed to be in the 3 and 5 axial positions.

Kinetics of Amino Radical Decay. Dimethylamino.

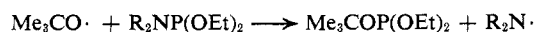
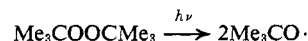
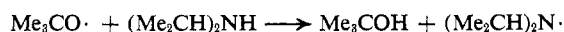
The spectra obtained with the tetrazene were too weak for kinetic studies. In isopentane at -80° the radicals from the phosphine decayed with "clean" second-order kinetics.



Under steady illumination the radical concentrations were proportional to the square root of the light intensity.

Diethylamino. In *n*-pentane at -90° decay was clean second order: $2k^{\text{Et}_2\text{N}} = (7 \pm 3) \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ for radicals from the tetrazene and $2k^{\text{Et}_2\text{N}} = (1.0 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ for radicals from the phosphine. The latter rate constant is probably the more accurate since a much higher concentration of diethylamino radicals was obtained from the phosphine than from the tetrazene. The "best" value for $2k^{\text{Et}_2\text{N}}$ is probably $(2 \pm 1) \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ in *n*-pentane at -90° . Under steady illumination the radical

(32) The diisopropylamino radical (but not the other two) could also be observed by thermolysis of the tetrazene at temperatures $\geq 150^\circ$, and by photolysis of di-*tert*-butyl peroxide in the presence of the amine.



(33) (a) Since this manuscript was submitted this radical has also been prepared by photolysis of the chloramine.^{33b} In benzene at room temperature, $a_N = 14.3$, $a_H = 0.78$, $g = 2.0041$. (b) T. Toda, E. Mori, H. Horuchi, and K. Murayama, *Bull. Chem. Soc. Jap.*, **45**, 1802 (1972). (c) For comparison, the splittings for the 2,2,6,6-tetramethylpiperid-4-on-1-yl radical in tetrahydrofuran at 20° are reported to be^{16a} $a_N = 15.5 \text{ G}$ and $a_H = 1.16 \text{ G}$.

(34) The g values of dialkyl^{16b} and diaryl²³ nitroxides are ~ 2.006 , while those of dialkyl- and diarylamino radicals are ~ 2.0045 .

(35) R. Briere, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 3273 (1965).

(36) Some uncertainty arises from splitting due to ^{13}C ; cf. ref 16a.

concentrations (tetrazene and phosphine) were proportional to the square root of the light intensity both at -90 and at -5° .

Diisopropylamino from the Tetrazene. At temperatures below -10° diisopropylamino radicals decay with "clean" second-order kinetics over a tenfold range in the initial radical concentration. Although decays were complete in about 0.1 sec, the buildup of the amino radical to its steady-state concentration required 30–50 sec of photolysis of a fresh sample of tetrazene but only ~ 0.1 sec for a sample that had been photolyzed already. However, if the tetrazene solution was allowed to warm to room temperature and was kept warm until the thermally produced diisopropylamino radicals had decayed (see below) a photolysis below -10° again required 30–50 sec for the steady-state concentration of radicals to be reached.

In *n*-pentane from -13 to -70° the radical concentration under steady illumination was proportional to $(h\nu)^{0.51 \pm 0.1}$. Over this temperature range the decay rate constant was

$$k_{\text{ep}}^2 = 2k^i\text{-Pr}_2\text{N} = (4.5 \pm 1.0) \times 10^6 M^{-1} \text{sec}^{-1}$$

and the activation energy for decay is 0 ± 1 kcal/mol.

This decay rate constant is consistent with the nmr measurements of the rate of loss of tetraisopropyltetrazene in the low temperature photolysis described in the Experimental Section (*viz.*, a 20% loss of a $5.8 \times 10^{-1} M$ solution in 2.3 hr). That is

$$2d[\text{tetrazene}]/dt = (2 \times 0.2 \times 0.58)/$$

$$(2.3 \times 3600) = 2.8 \times 10^{-6} M \text{sec}^{-1}$$

and this should be equal to the decay rate constant times the square of the amino radical concentration during the photolysis (*viz.*, $2 \times 10^{-6} M$), *i.e.*,

$$2k^i\text{-Pr}_2\text{N}[i\text{-Pr}_2\text{N}\cdot]^2 = 4.5 \times 10^6 \times (2 \times 10^{-6})^2 =$$

$$(2.3 \times 3600) = 1.8 \times 10^{-6} M \text{sec}^{-1}$$

The agreement between these two rates indicates that any route to the amine and Schiff base that does not involve *free* diisopropylamino radicals is only of minor importance.

If a sample of the tetrazene which has been photolyzed at temperatures below -10° is allowed to warm up after the *i*-Pr₂N \cdot radical has completely decayed, the signal due to this radical reappears at about -5° and increases as the temperature is raised further. In typical experiments a radical concentration of $\sim 5 \times 10^{-7} M$ is obtained at 10° and this does not decay appreciably in 20 min. In the range -5 to $+20^\circ$ the radical concentration can be increased and decreased reversibly by raising and lowering the temperature. In our initial report,² we suggested that in this temperature range the radical was in equilibrium with its dimer, tetraisopropylhydrazine. In the present paper it is shown that the species responsible for this behavior is an intermediate produced by photolysis of the tetrazene and that it does not arise from the diisopropylamino radicals. We suggest that this intermediate is the *cis* tetrazene³⁷ by analogy with azoalkanes,³⁸ in par-

ticular, azobisisobutane³⁹ and phenylazocumene.⁴⁰ The nmr experiments have shown that very little of this intermediate is formed (see the Experimental Section) which suggests that it is itself subject to photolysis. The slow buildup (in fresh tetrazene samples) but fast decay of diisopropylamino radicals implies that the intermediate is photolyzed to give these radicals. A low steady-state concentration of the intermediate is also indicated by the fact that the same radical concentration was produced at 20° on warming samples that had been photolyzed below -15° for 1 min or for 30 min.

Diisopropylamino radicals decay at a significant rate at 25° . At this and higher temperatures decay is first order, and in *n*-octane can be described by

$$k_{\text{ep}}^1 = 10^{14.4 \pm 1.2} e^{-(24000 \pm 2000 \text{ cal/mol})/RT} \text{sec}^{-1}$$

This expression was obeyed both by thermally and by photochemically produced radicals. In the latter case, an initial rapid decay was followed by the much slower first-order process. There is a distinct break in the decay curves at the point where the rate of *thermal* production of radicals from the intermediate equals their rate of decay. Despite the fact that decay is first order the amino radical concentration under steady illumination is approximately proportional to the square root of the light intensity (*e.g.*, $(h\nu)^{0.56 \pm 0.1}$ in *n*-octane at 70°).

The first-order-decay rate constants at 70° were independent of the tetrazene concentration (0.02–0.2 *M*), independent of the extent of photolysis of the tetrazene, and had the same value in cyclohexane as in perdeuteriocyclohexane (see Table I). However, k_{ep}^1

Table I. First-Order Decay of Diisopropylamino Radicals in Various Solvents

Solvent	$10^3 k_{\text{ep}}^1$, sec ⁻¹ at 70°	Log ($A^1_{\text{ep}}/$ sec ⁻¹)	E^1_{ep} , kcal/mol
Benzene	58 ± 6		
Toluene	41 ± 5	17 ± 3	27 ± 5
Cyclohexane	24 ± 3		
Cyclohexane- <i>d</i> ₁₂	24 ± 3		
<i>n</i> -Octane	17 ± 3	14.4 ± 1.2	24 ± 2
2,3-Dimethylbutanol	4 ± 0.4		
Di- <i>n</i> -butyl ether	2 ± 0.2		

does depend on the solvent. It is largest in benzene and toluene and smallest in 2,3-dimethylbutanol and *n*-butyl ether (see Table I). Photolysis of the tetrazene in methanol resulted in a very rapid evolution of nitrogen, possibly because of an induced decomposition of the tetrazene. The tetrazene reacted vigorously with glacial acetic acid, even in the absence of light. Carbon tetrachloride gave yellowish-green solutions upon adding the tetrazene and so kinetic studies were not undertaken. In tetrahydrofuran the radical concentration was too low for kinetic studies.

We have shown previously that first-order decay kinetics are consistent with radical destruction occurring *via* a bimolecular self-reaction if the radicals are

(37) Normal tetrazenes, like other azo compounds, are presumed to have *trans* configuration. Rather interestingly, a cyclic *cis* tetrazene has been found to be about as stable as the analogous acyclic *trans*-tetramethyl-2-tetrazene: S. F. Nelson and R. Fibiger, *J. Amer. Chem. Soc.*, **94**, 8497 (1972).

(38) I. I. Abram, G. S. Milne, B. S. Solomon, and C. Steel, *ibid.*, **91**, 1220 (1969).

(39) T. Mill and R. S. Stringham, *Tetrahedron Lett.*, 1853 (1969).

(40) N. A. Porter, L. J. Marnett, C. H. Lochmüller, G. L. Closs, and M. Shobataki, *J. Amer. Chem. Soc.*, **94**, 3664 (1972).

sured decay rate constants were $15 \times 10^6 M^{-1} \text{sec}^{-1}$ at -80° , $6 \times 10^6 M^{-1} \text{sec}^{-1}$ at -24° , $8 \times 10^6 M^{-1} \text{sec}^{-1}$ at 6° , and $20 \times 10^6 M^{-1} \text{sec}^{-1}$ at 33° . The "best" value for the bimolecular rate constant for decay of diisopropylamino radicals generated from the tetrazene and phosphine is $2k^{1-\text{Pr}_2\text{N}} = (1 \pm 0.5) \times 10^7 M^{-1} \text{sec}^{-1}$, in the temperature range -80 to 33° .

2,2,6,6-Tetramethylpiperidyl. In isopentane at 24° these radicals decay with clean first-order kinetics. The decay rate constant was independent of the tetrazene concentration (15-fold range), of the radical concentration (40-fold range), and of the extent of photolysis of the tetrazene. The radical concentration under steady illumination was proportional to the first power of the light intensity which indicates that the kinetics are not the result of a slow decay of an unstable intermediate. In isopentane this radical showed no sign of dimerizing even at temperatures as low as -120° .

The effect of solvents on the first-order rate constant indicates that in most solvents the decay is not a true unimolecular process, but instead is the result of hydrogen atom abstraction from the solvent. That is, k_{ep}^1 values increase as the hydrogens on the solvent become more labile (see Table II). Furthermore,

Table II. Decay of 2,2,6,6-Tetramethylpiperidyl in Various Solvents

Solvent (concn, M at 24°)	k_{ep}^1 , sec^{-1} (24°)	$10^2 k_{\text{abs}}^2$, $M^{-1} \text{sec}^{-1}$ (24°)	Log ($A^2_{\text{abs}}/M^{-1} \text{sec}^{-1}$)	E^2_{abs}
Toluene (9.4)	12.9	69	4	6 ± 2
Toluene- d_8 (9.4)	0.6	3.2	4	7 ± 2
Cyclohexane (9.2)	1.4	8.0	4	7 ± 2
Cyclohexane- d_8 (9.2)	0.09	0.48		
Hexamethyldisilane (5.0)	0.5	5.0		
Freon 113 (8.4)	0.6			
<i>n</i> -Heptane (6.9)	0.6	4.6	3	6 ± 2
<i>n</i> -Hexane (7.7)	0.5	3.3		
Isopentane (8.6)	0.25	1.5	4	8 ± 2
Tetramethylsilane (7.4)	0.2	1.4		
2,3-Dimethylbutane (7.7)	0.2	1.3	4	7 ± 2
Neopentane (8.1)	0.02			
Cyclopropane (17)	0.045			

there is a large deuterium isotope effect when cyclohexane is replaced by perdeuteriocyclohexane ($k_{\text{H}}/k_{\text{D}} = 16 \pm 3$ at 22° and 9 ± 2 at 90°) and when toluene is replaced by perdeuteriotoluene ($k_{\text{H}}/k_{\text{D}} = 24 \pm 3$ at -10° and 23 ± 3 at -25°). In addition, tetramethylpiperidine was a major product when the tetrazene was photolyzed in tetramethylsilane or *n*-octane (see Experimental Section). The bimolecular rate constants for hydrogen abstraction from the hydrocarbon solvents, k_{abs}^2 , which are listed in Table II were calculated from solvent concentrations and k_{ep}^1 values. It has been assumed in these calculations that each molecule of hydrocarbon traps two amino radicals.

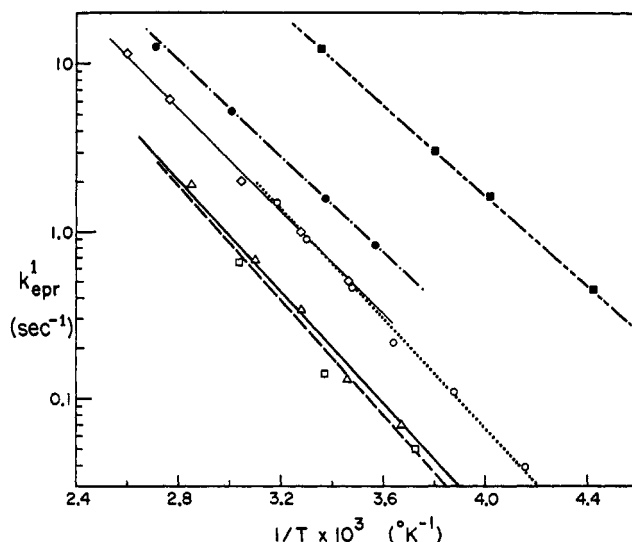
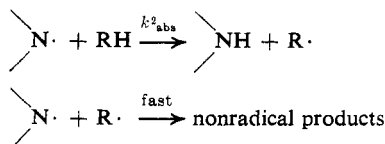


Figure 1. Hydrogen atom abstraction from hydrocarbon solvents by 2,2,6,6-tetramethylpiperidyl: (\square - - -) 2,3-dimethylbutane; (\triangle —) isopentane; (\diamond —) *n*-heptane; (\circ · · ·) perdeuteriotoluene; (\bullet —) cyclohexane; (\blacksquare - - -) toluene.

Arrhenius parameters for some of the abstractions are listed in Table II and the Arrhenius plots (for k_{ep}^1) are shown in Figure 1.

In cyclopropane and in neopentane very little tetramethylpiperidine was formed (see Experimental Section). In the former solvent decay may be due to an attack on the ring or perhaps to a true unimolecular decomposition of the radical. In neopentane it is likely that the principal mode of decay is a true unimolecular reaction. The nature of the decay process in Freon 113 ($\text{CF}_2\text{ClCFCl}_2$) is uncertain. Rates of decay in benzene were not reproducible.

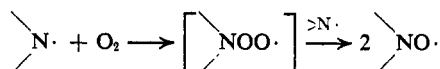
Reaction of 2,2,6,6-Tetramethylpiperidyl with Oxygen. The occurrence of a rapid direct reaction between tetramethylpiperidyl and oxygen was indicated by the immediate conversion of the amino radical to the corresponding nitroxide on venting a solution of the amino radical to the atmosphere at a temperature where the amino radical itself is virtually stable.⁵¹ That the new radical was indeed the nitroxide was shown as follows. A thoroughly degassed solution of the tetrazene in isopentane was photolyzed at -50° . The spectrum of the tetramethylpiperidyl radical was well resolved, and it was clear that the sample was completely free of nitroxide. The photolysis was stopped and the sample was rapidly cooled to -120° without any appreciable loss of the radical. At -120° tetramethylpiperidyl (which shows only three broad lines at this temperature) is remarkably stable, decaying less than 2% in 10 min. Oxygen enriched in ^{17}O ($\sim 47\%$) was then allowed to diffuse into the sample at ~ 50 Torr. The amino radical began to decay immediately and

(51) There is therefore no question of the amino radical abstracting hydrogen from the solvent and the resulting alkyl radical picking up the oxygen, with the nitroxide being formed by a peroxy radical-amino radical reaction. The reaction of this same amino radical with oxygen has also been reported in a paper that appeared after the present work was complete.^{33b} However, the radical was prepared by photolysis of the chloramine in oxygen saturated benzene and it is not unlikely that peroxy radicals were also produced via the highly reactive chlorine atom. A direct reaction between the amino radical and molecular oxygen was, therefore, not proved conclusively. Rather interestingly, 2,2,6,6-tetramethylpiperid-4-on-1-yl was reported to not react with oxygen.

three peaks centered at a lower field began to appear. After the piperidyl radical had decayed completely the sample was degassed. Splittings due to the ^{17}O could then be clearly observed. At -100° the following spectral data were obtained: $a_N = 15.35$ G, $a(^{17}\text{O}) = 19.35$ G, $g = 2.00636$. The a_N and g values are completely consistent with those found with an authentic sample of 2,2,6,6-tetramethylpiperidine nitroxide in isopentane at -100° . The ^{17}O splitting is smaller than the 19.71 G reported for ^{17}O labeled di-*sec*-butyl nitroxide in benzene.^{52,52a}

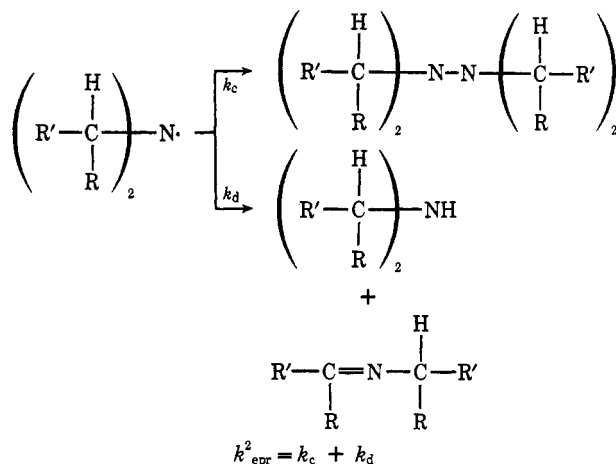
A solution of the tetrazene in air-saturated isopentane was photolyzed at room temperature to form $\sim 10^{-6}$ M nitroxide. The solution was then degassed and photolyzed at -60° to form about an equal quantity of the amino radical. The two radicals are both clearly visible. In the temperature range -75 to -100° the spectrum of both radicals changed only by an amount corresponding to the Boltzmann factor. This failure to observe any formation of an amino-nitroxide coupled product is disappointing, but may have been due to the rather low concentrations of the two radicals.

Attempts to measure the rate of the tetramethylpiperidyl-oxygen reaction were unsuccessful but indicated that it was extremely fast. The formation of nitroxide appears to be quantitative.



Discussion

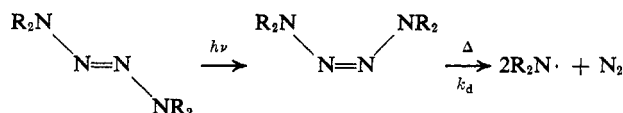
The second-order decays of dimethylamino, diethylamino, and diisopropylamino radicals at low temperatures indicate bimolecular self-reactions. Previous product studies on the self-reactions of dimethylamino^{4,5,44} and diethylamino⁴⁴ indicate that combination and disproportionation are of approximately equal importance.



Dimethylamino and diethylamino radicals react with one another at the diffusion controlled limit ($k_{\text{ep}}^2 = (2 \pm 1) \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$). Diisopropylamino radicals, which appear to disproportionate almost exclusively at low temperatures, react much

more slowly ($k_{\text{ep}}^2 = (1.0 \pm 0.5) \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$). Since this reaction has little or no activation energy the preexponential factor in the Arrhenius equation must be of comparable magnitude and the slowness of reaction is due to entropy rather than to enthalpy factors. That is, the duration of an average encounter between diisopropylamino radicals is not sufficient to ensure that a configuration which would permit reaction is achieved and so the radicals diffuse apart without reaction even though there is no real potential energy barrier to be surmounted. The same phenomenon has been observed with certain other sterically hindered radicals.⁵³

Diisopropylamino radicals generated by photolysis of the tetrazene decay with first-order kinetics at temperatures above 25° . For the reasons outlined in the Results section we suggest that this is due to the photolytic formation and thermal decomposition of the *cis* tetrazene.



The rate of the thermal decomposition to radicals is somewhat dependent upon the solvent (see Table I). In *n*-octane the activation energy is 24 kcal/mol.

Diisopropylamino radicals generated from the amino-diethoxyphosphine also decay with first-order kinetics at temperatures above ambient, but this decay is much faster than that of the radicals generated from the tetrazene. It is possible that this decay represents a true unimolecular reaction, either a β scission or an isomerization in which hydrogen is transferred from the α carbon to the nitrogen.⁴⁵

Tetramethylpiperidyl decays with first-order kinetics, abstracting hydrogen from most of the solvents in which it was studied. It is rather selective in hydrogen abstraction (see Table II). The relative reactivities per hydrogen at 24° are calculated to be

Primary aliphatic	≤ 0.0005
Secondary aliphatic	0.02 (paraffinic)
Secondary aliphatic	0.03 (cyclohexane)
Tertiary aliphatic	0.025
Primary benzylic	1

This reactivity pattern is unusual in that the secondary and tertiary aliphatic hydrogens are of comparable reactivity. This is probably due to the highly hindered nature of the attacking radical⁵⁴ and it is probably steric factors which cause cyclohexane to be, relatively, so reactive.

The selectivity of tetramethylpiperidyl is comparable to that found for bromine atoms and for peroxy radicals⁵⁵ even though the amino radical probably forms a much stronger bond to hydrogen than do these two species.⁵⁶

Previous studies on hydrogen abstraction by dialkylamino radicals appear to be confined to dimethylamino. They have indicated that this radical is only a feeble dehydrogenating agent and its low reactivity

(53) See, e.g., M. L. Morrell and G. Vincow, *J. Amer. Chem. Soc.*, **91**, 6389 (1969).

(54) See, e.g., N. C. Deno, R. Fishbein, and J. C. Wyckoff, *ibid.*, **93**, 2065 (1971).

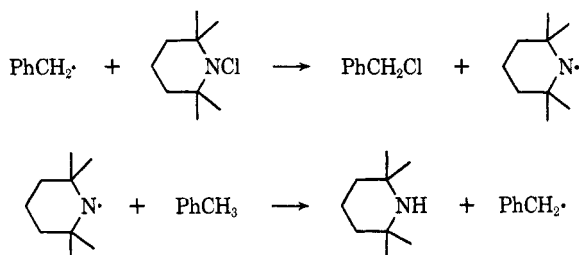
(55) K. U. Ingold in "Free Radicals," J. K. Kochi, Ed., Wiley, New York, N. Y., in press.

(56) $D[\text{R}_2\text{N}-\text{H}] = 95$ kcal/mol;¹⁴ $D[\text{ROO}-\text{H}] = 88-90$;⁵⁵ $D[\text{Br}-\text{H}] = 87$.⁵⁶

(52) J. C. Baird, *J. Chem. Phys.*, **37**, 1879 (1962).

(52a) NOTE ADDED IN PROOF. The $a(^{17}\text{O})$ values for 2,2,6,6-tetramethylpiperid-4-one-*N*-oxyl (^{17}O) have recently been measured in several solvents; H. Hayat and B. L. Silver, *J. Phys. Chem.*, **77**, 72 (1973).

has often been rationalized on the basis of an unrealistically low value for $D[\text{Me}_2\text{N}\cdot\text{H}]$. Tetramethylpiperidyl would, if anything, be expected to be less reactive in abstractions than dimethylamino. However, our results indicate that it is fairly active; in particular, it abstracts hydrogen from toluene at 24° ($k_{\text{abs}}^2 = 0.69 \text{ M}^{-1} \text{ sec}^{-1}$) considerably more easily than *tert*-butylperoxy ($k_{\text{abs}}^2 = 0.05 \text{ M}^{-1} \text{ sec}^{-1}$) or benzylperoxy ($k_{\text{abs}}^2 = 0.24 \text{ M}^{-1} \text{ sec}^{-1}$) at 30° .⁵⁷ It should be possible, therefore, to set up a chain reaction at ambient temperatures in which one step in the propagation involves abstraction of a benzylic hydrogen by a dialkylamino radical. The chain length could be quite long if the second propagation step was rapid and if the amino radical were tetramethylpiperidyl. A reaction that might fulfill these conditions is the chlorination of toluene using the chloramine in nonacidic media.



The deuterium isotope effects observed in the reaction of tetramethylpiperidyl with toluene and with cyclohexane are remarkably large for hydrogen abstractions.⁵⁸ Thus, the isotope effect for abstraction

(57) J. A. Howard, *Advan. Free-Radical Chem.*, **4**, 49 (1971).

(58) There will, of course, be some contribution from secondary isotope effects.

from toluene *vs.* perdeuteriotoluene by dimethylamino at 136° yields $k_{\text{H}}/k_{\text{D}} = 4.0$.⁷ Isotope effects are often enhanced in sterically hindered hydrogen transfers over the values found for their unhindered counterparts.^{59,60} This is normally attributed to tunneling⁵⁹⁻⁶¹ and to a more extensive loss of zero-point energy as the barrier becomes more symmetric.⁵⁹⁻⁶⁴ The rather low *A* factors found for hydrogen abstraction by tetramethylpiperidyl can also be ascribed to tunneling.⁶⁰⁻⁶² Low *A* factors are a common feature of hydrogen abstractions by sterically hindered radicals^{57,65} and by unhindered radicals from sterically hindered positions.⁵⁷

Tetramethylpiperidyl reacts rapidly and quantitatively with oxygen to yield the corresponding nitroxide. It must therefore be assumed that other dialkylamino radicals will react in a similar manner. Most workers^{18,21} seem agreed that this is the case. The occasional reports^{19,20} that dialkylamino radicals do not react with oxygen appear to be due to confusion of the amino radical with the nitroxide. The *N-tert*-butylanilino radical also reacts readily with oxygen⁶⁶ but product studies indicate that the *N*-phenyl-2-naphthylamino radical is relatively inert.⁶⁷

(59) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **40**, 1851 (1962).

(60) E. S. Lewis and L. H. Funderburk, *J. Amer. Chem. Soc.*, **89**, 2322 (1967).

(61) See E. F. Caldin, *Chem. Rev.*, **69**, 135 (1969).

(62) F. H. Westheimer, *ibid.*, **61**, 265 (1961).

(63) C. A. Bunton and V. J. Shiner, Jr., *J. Amer. Chem. Soc.*, **83**, 3214 (1961).

(64) W. A. Pryor and K. G. Kneipp, *ibid.*, **93**, 5584 (1971).

(65) E. T. Denisov, "Konstanti Skorosti Homolyticheskii Zhidko-fazni Reaktsii," Nauka, Moscow, 1971.

(66) S. F. Nelson, R. T. Landis, L. H. Kiehle, and T. H. Leung, *J. Amer. Chem. Soc.*, **94**, 1610 (1972).

(67) R. F. Bridger, *ibid.*, **94**, 3124 (1972).

Medium Effects on the Fluorine-19 Magnetic Resonance Spectra of Fluoropyridines

C. S. Giam* and J. L. Lyle

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77840. Received June 1, 1972

Abstract: The effects of some 30 different solvents on the ^{19}F nmr shifts of 2-, 3-, and 4-fluoropyridine have been studied. These solvent-induced chemical shifts could not be correlated with the widely used solvent function which contained the dielectric constant. Instead good correlations were obtained using Dimroth's *E_s* or Kosower's *Z* values. Explanations for these observations are discussed.

In the course of our study of relationships of substituent parameters—chemical shifts of substituted fluoropyridines,¹ we observed some unusual medium effects on the chemical shifts. In particular, unsatisfactory results were obtained in our plots of the fluorine chemical shifts with the function $(\epsilon - 1)/(\epsilon + 1)$ or the function $(\epsilon - 1)/(\epsilon + 0.789)$ where ϵ is the dielectric constant of the solvent. This frequently used function was proposed by Emsley and Phillips² from the Onsager

(1) C. S. Giam and J. L. Lyle, *J. Chem. Soc. B*, 1516 (1970).

(2) (a) J. W. Emsley and L. Phillips, *Mol. Phys.*, **11**, 437 (1966); (b) J. W. Emsley and L. Phillips, *Progr. Nucl. Magn. Resonance Spectrosc.*, **7**, 1 (1971); (c) W. T. Raynes and M. A. Raza, *Mol. Phys.*, **20**, 555 (1971).

model to explain solvent effects on the fluorine chemical shifts in aromatic compounds. This led us to look for an alternate parameter which would better explain and predict the effects of solvents on the fluorine chemical shifts of these compounds.

One such solvent parameter which we considered was Kosower's *Z* which is defined³ as the energy in kcal/mol of the first charge-transfer band of 1-ethyl-4-carboxymethylpyridinium iodide dissolved in the particular solvent. In general, proton chemical shifts have been found to give only *poor* correlations with *Z* values, pos-

(3) E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253 (1958).