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 catalyst[42] 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% $TiCl_3$ aqueous solution, 30% H_2O_2 aqueous solution, hydroxylamine hydrochloride, 9% peroxyacetic acid in acetic acid, *tert*-butyl hydroperoxide, and thioglycolic acid.

Generation of Radicals. For the generation and the esr measurement of the radicals, the Dixon–Norman[44] 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 ^{14}N (13.07 G) and the *g* factor (2.00559) of potassium peroxylaminedisulfonate 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.

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Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. X. Reactions of Some Alkylamino Radicals in Solution[1,2]

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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, $(2 \pm 1) \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$. The decay of diisopropylamino is second order at temperatures below ambient ($k^2_{\mathrm{epr}} \approx 1.0 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$) 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 G, g = 2.0048 in isopentane at 27°) reacts rapidly with oxygen and is converted to the corresponding nitroxide (a_N = 15.3 G, g = 2.0064 at −100°). With ^{17}O labeled oxygen this nitroxide has $a(^{17}O)$ = 19.35 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.

$$Me_2NN{=}NNMe_2 \xrightarrow[h\nu]{\text{heat}} 2Me_2N\cdot + N_2$$

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

$$2Me_2N\cdot \longrightarrow Me_2NNMe_2$$

$$2Me_2N\cdot \longrightarrow Me_2NH + (CH_2{=}NMe) \longrightarrow \text{trimer and polymer}$$

Some hydrogen abstraction from the tetrazene, leading to induced decomposition, may also occur.[4,6,7] Dimethylamino radicals appear to add to styrene[8] 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

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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 radicals[15] in solution appears to be confined to a brief qualitative study of hydrogen abstraction by the piperidyl radical[12] and to epr spectroscopic investigations.[2,6,16,17] Except for the preliminary account of this work[2] 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's[6] 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 reaction[22] 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 reported[2] 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 radicals[24] 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.[26] 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 $LiAlH_4$, 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 $\geq 85°$, a solution containing 15 g of sodium nitrite in 20 ml of H_2O was added slowly. In order to keep the reaction mixture just acidic at all times, 2 *N* HCl was added when necessary. The solituon was allowed to stir for several hours. An additional 6 g of sodium nitrite in 20 ml of H_2O 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 $MgSO_4$. 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 $LiAlH_4$ 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 $LiAlH_4$ 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 $MgSO_4$. 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 (C_6D_{12}) 1.28 (2), 1.57 (1).

Anal. Calcd for $C_{18}H_{36}N_4$: 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

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[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 $\dot{N}H_2$, R$\dot{N}$H, 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).

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[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).

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[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).

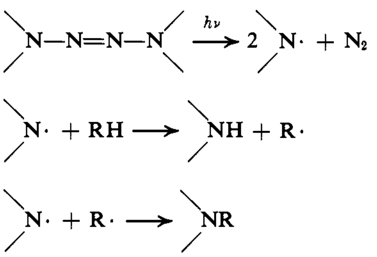
[27] H. Zimmer, L. F. Audrieth, M. Zimmer, and R. A. Rowe, *ibid.*, **77**, 790 (1955).

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 ~2 × 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 ± 5% based on starting tetrazene. A 50% yield is expected on the basis of the reactions

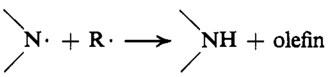


$$\mathrm{{>}N{-}N{=}N{-}N{<}} \xrightarrow{h\nu} 2\,\mathrm{{>}N\cdot} + \mathrm{N_2}$$

$$\mathrm{{>}N\cdot + RH \longrightarrow {>}NH + R\cdot}$$

$$\mathrm{{>}N\cdot + R\cdot \longrightarrow {>}NR}$$

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



$$\mathrm{{>}N\cdot + R\cdot \longrightarrow {>}NH + olefin}$$

In analogous experiments in cyclopropane and in neopentane the yields of tetramethylpiperidine were ~2 and ~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 tetrazenes[6] or by photolysis of di-*tert*-butyl peroxide in the presence of the dialkylaminodiethoxyphosphines[22] gave epr spectra identical with those reported by Danen and Kensler.[6,32]

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 are[33] a_N = 14.66 G, a_H = 0.82 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* value [34] 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 tempeatures 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 G, of triplets (1:2:1), $a_H \approx$ 4.6 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.

$$2\mathrm{Me_2N\cdot} \xrightarrow{2k^{\mathrm{Me_2N}}} \text{nonradical products}$$

$$2k^{\mathrm{Me_2N}} = (2 \pm 1) \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$$

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: $2k^{\mathrm{Et_2N}}$ = (7 ± 3) × 10^9 M^{-1} sec^{-1} for radicals from the tetrazene and $2k^{\mathrm{Et_2N}}$ = (1.0 ± 0.5) × 10^9 M^{-1} 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 $2k^{\mathrm{Et_2N}}$ is probably (2 ± 1) × 10^9 M^{-1} sec^{-1} in *n*-pentane at −90°. Under steady illumination the radical

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

[29] Infrared analysis of a similar mixture photolyzed in perdeuteriobenzene 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 autodisproportionate 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).

[32] The diisopropylamino radical (but not the other two) could also be observed by thermolysis of the tetrazene at temperatures ≥150°, and by photolysis of di-*tert*-butyl peroxide in the presence of the amine.

$$\mathrm{Me_3CO\cdot + (Me_2CH)_2NH \longrightarrow Me_3COH + (Me_2CH)_2N\cdot}$$

$$\mathrm{Me_3COOCMe_3 \xrightarrow{h\nu} 2Me_3CO\cdot}$$

$$\mathrm{Me_3CO\cdot + R_2NP(OEt)_2 \longrightarrow Me_3COP(OEt)_2 + R_2N\cdot}$$

[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 G and a_H = 1.16 G.

[34] The *g* values of dialkyl[16b] and diaryl[23] 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 beeh 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 $(h\nu)^{0.51\pm0.1}$. Over this temperature range the decay rate constant was

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

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 × 10^{-1} *M* solution in 2.3 hr). That is

$$2\text{d[tetrazene]}/\text{d}t = (2 \times 0.2 \times 0.58)/(2.3 \times 3600) = 2.8 \times 10^{-5}\ M\ \text{sec}^{-1}$$

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

$$2k^{i\text{-Pr}_2\text{N}}[i\text{-Pr}_2\text{N}\cdot]^2 = 4.5 \times 10^6 \times (2 \times 10^{-6})^2 = (2.3 \times 3600) = 1.8 \times 10^{-5}\ M\ \text{sec}^{-1}$$

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-Pr$_2$N· 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 ~5 × 10^{-7} *M* is obtained at 10° and this does not decay appreciably in 20 min. In the range −5 to +20° 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 tetrazene[37] by analogy with azoalkanes,[38] in particular, azobisisobutane[39] 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

$$k^1_{\text{epr}} = 10^{14.4\pm1.2}e^{-(24000\pm2000\ \text{cal/mol})/RT}\ \text{sec}^{-1}$$

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.*, $(h\nu)^{0.56\pm0.1}$ 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^1_{epr} 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.

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

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

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

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[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).

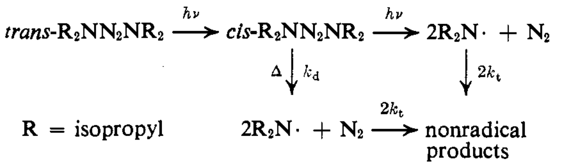
[38] I. I. Abram, G. S. Milne, B. S. Solomon, and C. Steel, *ibid.*, **91**, 1220 (1969).

[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).

present in equilibrium with their dimer.[2,41] Under such conditions the radical concentration serves merely to monitor the dimer concentration and hence to monitor decay of the dimer. A similar situation obtains for any other intermediate that decays slowly to yield radicals that disappear by fast bimolecular self-reactions. In particular, it applies to Scheme I.

Scheme I



$$\begin{tikzcd}
trans\text{-}R_2NN_2NR_2 \arrow[r, "h\nu"] & cis\text{-}R_2NN_2NR_2 \arrow[r, "h\nu"] \arrow[d, "\Delta"', "k_d"] & 2R_2N\cdot + N_2 \arrow[d, "2k_t"] \\
R = \text{isopropyl} & 2R_2N\cdot + N_2 \arrow[r, "2k_t"] & \text{nonradical products}
\end{tikzcd}$$

At temperatures below −10° where k_d is very small decay is fast and second order in $R_2N\cdot$ with $2k_t = 2k^{i\text{—}Pr_2N}$.

At temperatures above 25° where k_d is significant we have

$$-d[\text{cis}]/dt = k_d[\text{cis}]$$

and

$$d[R_2N\cdot]/dt = 2k_d[\text{cis}] - 2k_t[R_2N\cdot]^2$$

Provided $[R_2N\cdot] \ll [\text{cis}]$, then $d[R_2N\cdot]/dt \ll d[\text{cis}]/dt$ and hence

$$d[\text{cis}]/dt \approx -k_t[R_2N\cdot]^2 \qquad (1)$$

and

$$k_d[\text{cis}] \approx k_t[R_2N\cdot]^2 \qquad (2)$$

Differentiating eq 2 and combining with eq 1 yield

$$-d[R_2N\cdot]/dt = (k_d/2)[R_2N\cdot]$$

Radical decay is therefore first order and the measured rate constant $k^1{}_{epr} = k_d/2$.

At intermediate temperatures (−5 to 20°) $d[R_2N\cdot]/dt = 0$ within the time of the experiments and hence $2k_d[\text{cis}] = 2k_t[R_2N\cdot]^2$ which is the same expression as would be obtained if the amino radicals were in equilibrium with the intermediate. Since $2k_t$ is virtually independent of temperature the variation with temperature of the concentration of radicals produced thermally (after low temperature photolysis) yields the activation energy for decomposition of the intermediate, E_d. In isopentane E_d was found to be 25 ± 2 kcal/mol by this method, a value in excellent agreement with the 24 ± 2 found by decay measurements (in *n*-octane) at temperatures above 25°.

Diisopropylamino from Diisopropylaminodiethoxyphosphine. Decay of the amino radicals was rapid at all temperatures between −80 and 100°. The decays were complete in about 0.1 sec and, upon photolysis, the radicals reached a steady-state concentration in a similar time. No radicals could be generated thermally by warming samples to between 30 and 100° that had been photolyzed for short or long periods at temperatures below −20°. The intermediate that yields radicals thermally after photolysis of the tetrazene at low temperatures cannot, therefore, be derived from the amino radicals themselves. In particular, it cannot be the hydrazine.[42] The cis tetrazene would appear to be the most likely candidate.[38-40]

At temperatures above ∼110° the amino radicals are produced without photolysis as a result of the thermal decomposition of the peroxide. At temperatures of 70–110° the radical concentrations were proportional to the *first* power of the light intensity and the decays were first order. In neat peroxide the decay rate constants were independent of the phosphine concentration (over a range of ten). Virtually identical rate constants were also obtained with a solution containing 20% peroxide and 2% phosphine in benzene and with one of 20% phosphine in neat peroxide. However, the rate constants were slightly increased on changing the solvent from benzene, to perdeuteriotoluene, to toluene. The measured decay rate constants were: at 70°, 47 sec^{-1} in peroxide, 76 in C_6H_5-CD_3, and 120 in toluene; at 90°, 70 sec^{-1} in peroxide, *n*-octane[43] and benzene, and 160 in toluene; at 122°, 200 sec^{-1} in toluene. The fact that the rate constant was higher in toluene than in perdeuteriotoluene indicates that decay can involve hydrogen abstraction. However, the small magnitude of the isotope effect (*cf.* Table II, and a ratio k_H/k_D of 4.0 reported[7] for $Me_2N\cdot$ at 136°) and the small enhancement of the rate constant in toluene relative to peroxide and benzene suggest that hydrogen abstraction plays a relatively unimportant role in the decay process in solvents that do not contain fairly labile hydrogen atoms. This suggests that the first-order decay in peroxide and in benzene represents a true unimolecular reaction of the radical. Such a reaction might be either a *β* scission[44]

$$[(CH_3)_2CH]_2N\cdot \longrightarrow CH_3\cdot + (CH_3)_2CHN{=}CHCH_3$$

or an isomerization[45]

$$[(CH_3)_2CH]_2N\cdot \xrightarrow{\text{slow}} (CH_3)_2CHNH\dot{C}(CH_3)_2 \xrightarrow[{[(CH_3)_2CH]_2N\cdot}]{\text{fast}} (CH_3)_2CHNHC(CH_3)_2N[CH(CH_3)_2]_2$$

Below 70° a second-order decay process starts to come into play as judged by the dependence of the steady-state radical concentration on the light intensity. Second-order decay dominates the reaction completely at temperatures below ∼0°. In isopentane the mea-

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(41) More detailed kinetic treatments have also been given: S. A. Weiner and L. R. Mahoney, *J. Amer. Chem. Soc.*, **94**, 5029 (1972); J. L. Brokenshire, J. R. Roberts, and K. U. Ingold, *ibid.*, **94**, 7040 (1972).

(42) The possibility that the hydrazine is the intermediate but is destroyed by the phosphine was eliminated by mixing solutions of the tetrazene (∼5% in benzene) and of the peroxide–phosphine (20 and 2%, respectively, in benzene). Individually, these solutions gave about the same amino radical concentrations on photolysis at 24°. The diisopropylamino radicals produced by photolysis of this mixture at 40° behaved in exactly the same manner as those from tetrazene alone, *i.e.*, an initial rapid decay, followed by a very slow first-order process. Prolonged photolysis of the mixture gave new radicals.

(43) For comparison, radicals generated from the tetrazene decay with a rate constant of 1.0 sec^{-1} at this temperature in *n*-octane.

(44) B. G. Gowenlock and D. R. Snelling, *Advan. Chem. Ser.*, **No. 36**, 150 (1962).

(45) There is experimental evidence that 1,2-hydrogen shifts from the *α* carbon to the nitrogen can occur with suitably substituted alkylamino radicals[46-49] even though such isomerizations are normally considered to proceed only with difficulty when the two multivalent atoms involved are both from the first row of the periodic table.[50]

(46) G. V. Pukhal'skaya, A. G. Kotov, and S. Ya. Pshezhetskii, *Dokl. Akad. Nauk SSSR*, 171, 1380 (1966).

(47) N. H. Anderson and R. O. C. Norman, *J. Chem. Soc. B*, 933 (1971).

(48) P. Neta and R. W. Fessenden, *J. Phys. Chem.*, **75**, 738 (1971).

(49) P. Wardman and D. R. Smith, *Can. J. Chem.*, **49**, 1869, 1880 (1971).

(50) See, *e.g.*, P. S. Skell "Organic Reaction Mechanisms," *Chem. Soc., Spec. Publ.*, **No. 19**, 131 (1965); R. Kh. Freidlina, *Advan. Free-Radical Chem.*, **1**, 211 (1965); C. G. Pitt and M. S. Fowler, *J. Amer. Chem. Soc.*, **90**, 1928 (1968).

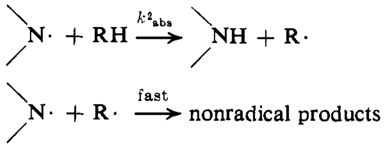
sured decay rate constants were 15 × 10^6 M^{-1} $\sec^{-1}$ at −80°, 6 × 10^6 M^{-1} $\sec^{-1}$ at −24°, 8 × 10^6 M^{-1} $\sec^{-1}$ at 6°, and 20 × 10^6 M^{-1} $\sec^{-1}$ at 33°. The "best" value for the bimolecular rate constant for decay of diisopropylamino radicals generated from the tetrazene and phosphine is $2k^{i\text{-}Pr_2N} = (1 \pm 0.5) \times 10^7$ M^{-1} $\sec^{-1}$, 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, $k^1{}_{epr}$ values increase as the hydrogens on the solvent become more labile (see Table II). Furthermore, there is a large deuterium isotope effect when cyclohexane is replaced by perdeuteriocyclohexane (k_H/k_D = 16 ± 3 at 22° and 9 ± 2 at 90°) and when toluene is replaced by perdeuteriotoluene (k_H/k_D = 24 ± 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, $k^2{}_{abs}$, which are listed in Table II were calculated from solvent concentrations and $k^1{}_{epr}$ values. It has been assumed in these calculations that each molecule of hydrocarbon traps two amino radicals.

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

Solvent (concn, M at 24°)	k'_{epr}, $\sec^{-1}$ (24°)	$10^2k^2{}_{abs}$ M^{-1} $\sec^{-1}$ (24°)	Log ($A^2{}_{abs}$/ M^{-1} $\sec^{-1}$)	$E^2{}_{abs}$
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			
n-Heptane (6.9)	0.6	4.6	3	6 ± 2
n-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			



$$\rangle N\cdot + RH \xrightarrow{k^2{}_{abs}} \rangle NH + R\cdot$$

$$\rangle N\cdot + R\cdot \xrightarrow{\text{fast}} \text{nonradical products}$$

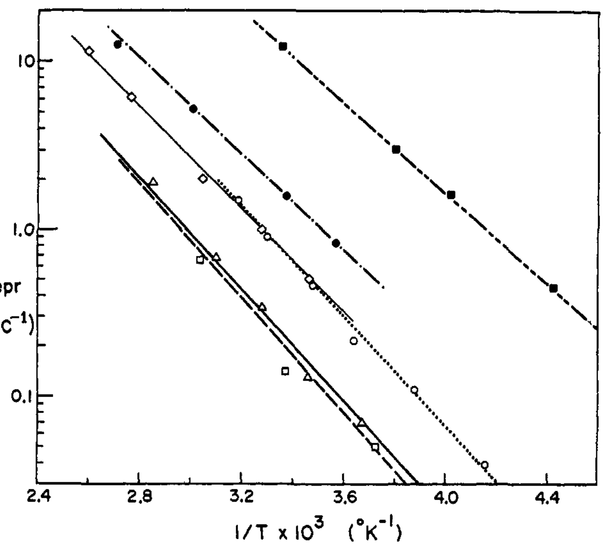


Figure 1. Hydrogen atom abstraction from hydrocarbon solvents by 2,2,6,6-tetramethylpiperidyl: (□ - - -) 2,3-dimethylbutane; (△ —), isopentane; (◇ —) n-heptane; (○ · · ·) perdeuteriotoluene; (—●—) cyclohexane; (■ — - -) toluene.

Arrhenius parameters for some of the abstractions are listed in Table II and the Arrhenius plots (for $k^1{}_{epr}$) 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 ($CF_2ClCFCl_2$) 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 (∼47%) was then allowed to diffuse into the sample at ∼50 Torr. The amino radical began to decay immediately and

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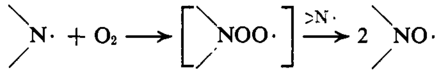
[51] There is therefore no question of the amino radical abstracting hydrogen from the solvent and the resulting alkyl radical picking up the oxygen, with the nitroxide being formed by a peroxy radical–amino radical reaction. The reaction of this same amino radical with oxygen has also been reported 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 obained: $a_N = 15.35$ G, $a(^{17}O) = 19.35$ 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]

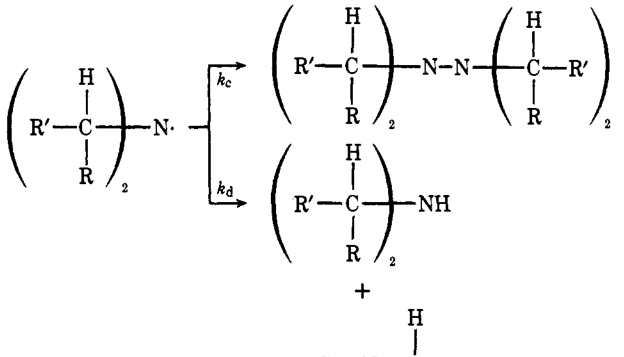
A solution of the tetrazene in air-saturated isopentane was photolyzed at room temperature to form $\sim 10^{-6}$ *M* nitroxide. The solution was then degassed and photolyzed at −60° to form about an equal quantity of the amino radical. The two radicals are both clearly visible. In the temperature range −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

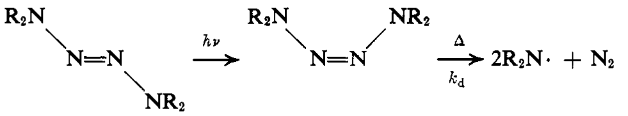
The second-order decays of dimethylamino, diethylamino, and diisopropylamino radicals at low temperatures indicate bimolecular self-reactions. Previous product studies on the self-reactions of dimethylamino[4,5,44] and diethylamino[44] indicate that combination and disproportionation are of approximately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



$$k^2_{\text{epr}} = k_c + k_d$$

Dimethylamino and diethylamino radicals react with one another at the diffusion controlled limit ($k^2_{\text{epr}} = (2 \pm 1) \times 10^9\ M^{-1}\ \text{sec}^{-1}$). Diisopropylamino radicals, which appear to disproportionate almost exclusively at low temperatures, react much more slowly ($k^2_{\text{epr}} = (1.0 \pm 0.5) \times 10^7\ M^{-1}\ \text{sec}^{-1}$). 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 aminodiethoxyphosphine 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 radical[54] 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 radicals[55] 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

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

(52a) NOTE ADDED IN PROOF. The $a(^{17}O)$ 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).

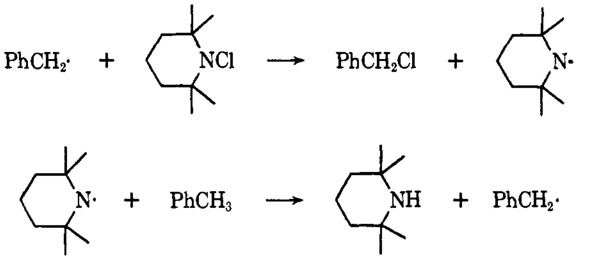
(53) See, *e.g.*, M. L. Morrell and G. Vincow, *J. Amer. Chem. Soc.*, 91, 6389 (1969).

(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) $D[R_2N–H] = 95$ kcal/mol;[14] $D[ROO–H] = 88–90$;[55] $D[Br–H] = 87$.[55]

has often been rationalized on the basis of an unrealistically low value for $D[\mathrm{Me_2N\text{-}H}]$. 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° ($k^2_{\mathrm{abs}} = 0.69\ M^{-1}\ \mathrm{sec}^{-1}$) considerably more easily than *tert*-butylperoxy ($k^2_{\mathrm{abs}} = 0.05\ M^{-1}\ \mathrm{sec}^{-1}$) or benzylperoxy ($k^2_{\mathrm{abs}} = 0.24\ M^{-1}\ \mathrm{sec}^{-1}$) 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 from toluene *vs.* perdeuteriotoluene by dimethylamino at 136° yields $k_{\mathrm{H}}/k_{\mathrm{D}} = 4.0$.[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 tunneling[59–61] 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 oxygen[66] but product studies indicate that the *N*-phenyl-2-naphthylamino radical is relatively inert.[67]

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

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

(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 Homolyticheski Zhidkofaeni 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

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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_{t} 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 Phillips[2] from the Onsager 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 defined[3] 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-

(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).

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