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Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XXI. Some Mono-, Di-, and Trialkylhydrazyls[1]

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Received October 29, 1974

Abstract: The kinetics, mechanism, and products of decay of some mono-, 1,2-di-, and trialkylhydrazyls have been examined. 1-Alkylhydrazyls decay with second-order kinetics at the diffusion-controlled limit. 1,2-Diisopropylhydrazyl undergoes a very rapid second-order decay, which is a β-disportionation to hydrazine and azo compound. According to their structure, trialkylhydrazyls may decay by a fast second-order β-disproportionation (alkyl-H → N) or by a slow β-scission (loss of alkyl and formation of an azo compound). These results, together with previously reported data on 2,2-dialkylhydrazyls,[14] are discussed in relation to the possibilities of isolating persistent alkyl hydrazyl radicals.

Interest in alkyl hydrazyls has grown dramatically in the 2 years since the uv[4] and EPR[5] spectra of the first of these radicals were reported. Attention has been focused primarily on the EPR spectra.[6-13] Apart from the usual qualitative statements about radical lifetimes, detailed kinetic and product studies have been confined to Nelsen and Landis' work on some bi- and multicyclic trialkylhydrazyls[6] and work from this laboratory on a series of 2,2-dialkylhydrazyls.[14] Further work on alkylhydrazyls is clearly justified when it is remembered that amongst arylhydrazyls is included diphenylpicrylhydrazyl (DPPH), one of the most persistent free radicals known.[15] In this paper, we report on the kinetics and products of the decay of some mono-, di-, and trialkylhydrazyls.

Experimental Section

Materials. Methyl hydrazine was obtained from Chemical Intermediates and Research Laboratories, Inc. Benzylhydrazine was prepared from benzyl chloride and hydrazine hydrate.[14] 1,2-Diisopropylhydrazine was obtained from Fluka, AG, and azotrifluoromethane from Merck Sharpe and Dohme, Ltd. *tert*-Butylhydrazine was prepared from chloramine and *tert*-butylamine.[16] Trialkylhydrazines were prepared by reduction of hydrazones with sodium cyanoborohydride.[17] The hydrazones were prepared by condensation of 1,1-dialkylhydrazine with a carbonyl compound. The following preparation of 1-isopropylamino-2,2,6,6-tetramethylpiperidine[18] is fairly typical of a slow and difficult reaction.

A mixture consisting of 2.5 g (0.016 mol) of $TMPNH_2$,[19] 0.9 g (0.016 mol) of acetone, and 0.07 g (0.0007 mol) of 2-hydroxypyridine (a catalyst) was refluxed 48 hr.[20] The reaction mixture was washed with water and ether, and the ether layer was dried and then distilled under vacuum. The hydrazone [$TMPN{=}C(CH_3)_2$] distilled at 85° (12 mm), yield 2.0 g. It was purified by preparative VPC. NMR spectrum in C_6D_6 (in ppm downfield from Me_4Si):[21] TMP, $(CH_3)_2$ 0.84 (s), $(CH_3)_2$ 1.30 (s), $(CH_2)_3$ 1.54 (m, broad), $=C(CH_3)_2$ 1.79 (d, J = 4 Hz). Anal. Calcd for $C_{12}H_{24}N_2$ (mol wt 196.34): C, 73.41; H, 12.32; N, 14.27. Found (mol wt (mass spectrometry) 196): C, 73.37; H, 12.30; N, 14.35.

To a stirred solution of 1.2 g (0.006 mol) of $TMPN{=}C(CH_3)_2$ in 25 ml of acetonitrile was added 0.2 g (0.003 mol) of $NaBH_3CN$ in 4 or 5 small portions over 30 min. After a further 45 min, ca. 1 ml of acetic acid was added slowly and the reaction mixture stirred for an additional 6 hr. Then 0.6 ml of concentrated HCl was added, the acetonitrile removed under vacuum, and the oily residue dissolved in 20 ml of H_2O, basified with KOH, saturated with NaCl, extracted with ether, and dried over $MgSO_4$. The ether was removed and the yellow oil distilled under high vacuum on a molecular still at room temperature (yield of $TMPNHCH(CH_3)_2$, 0.5 g). NMR spectrum in C_6D_6: TMP, $(CH_3)_4$ and $(CH_2)_3$ three broad peaks at 0.93, 1.14, and 1.43; $CH(CH_3)_2$ 1.01 (d, J = 6 Hz), $CH(CH_3)_2$ 3.14 (septet); NH 2.30 (broad). Anal. Calcd for $C_{12}H_{26}N_2$ (mol wt. 198.35): C, 72.66; H, 13.21; N, 14.12. Found

Table I. Percentage Yields of Products Formed by Oxidation of $TMPNHCH(CH_3)_2$ with Various Reagents

Oxidant	Temp, °C	Time, hr	A	B	C	TMPN=C(CH₃)₂
$[(CH_3)_3CON]_2$ [a]	50	48	45	38	8	9
$[(CH_3)_3CO]_2$	110	25	76	8	8	8
$[(CH_3)_3CO]_2$	140	2	79	6	6	9
$[(CH_3)_3CO]_2$ [b]	25	25	5	8	22	65
Ag_2O [a]	25	16	0	0	0	100
HgO [a]	25	16		No reaction		

[a] In benzene. [b] Photolysis.

(mol wt (mass spectrometry) 198): C, 72.58; H, 13.17; N, 14.22.

The NMR spectrum in C_6D_6 of some of the other hydrazines and of their dehydro derivatives (hydrazone or azo compound) are as follows. $[(CH_3)_2CHNH-]_2$: $(CH_3)_2$ 0.95 (d, J = 6 Hz); CH 2.73 (septet); NH 2.23 (broad). $[(CH_3)_2CHN=]_2$: $(CH_3)_2$ 1.14 (d, J = 6 Hz); CH 3.61 (septet). $TMPNHCH_3$: TMP $(CH_3)_4$ 1.02 (s); $(CH_2)_3$ 1.38 (s); CH_3NH 2.55 (s), NH 2.03 (broad). $TMPN=CH_2$: TMP $(CH_3)_4$ 1.14 (s); $(CH_2)_3$ 1.45 (s); CH_2 6.66 (d) and 6.90 (d, J = 14 Hz). $(CH_3)_2NNHCH(CH_3)_2$: $(CH_3)_2N$ 2.20 (s); $(CH_3)_2CH$ 0.99 (d, J = 6 Hz); $(CH_3)_2CH$ 2.83 (septet); NH not observed. $(CH_3)_2NN=C(CH_3)_2$: $(CH_3)_2N$ 2.38 (s); $(CH_3)_2C$ 1.69 (s).

Radical Production. The hydrazyl radicals were formed photolytically in the cavity of a Varian E-3 EPR spectrometer. All but one of the hydrazyls was generated by hydrogen abstraction from the parent hydrazine by *tert*-butoxy radicals.[10] Photolysis of $CF_3N=NCF_3$ in isopentane yielded the $C_2H_5(CH_3)_2C(CF_3)$-$NNCF_3$ radical.[10]

The EPR spectra of the hydrazyls have been reported previously.[9,10] Photolysis of $(CH_3)_3CNHNH_2$ in $(CH_3)_3COOC(CH_3)_3$ at room temperature immediately yields a strong signal due to the $(CH_3)_3\dot{C}$ radical (second-order lines are resolvable). The $(CH_3)_3\dot{C}$ radical is also formed when the photolysis is carried out in $(CD_3)_3COOC(CD_3)_3$, and it must therefore come from the hydrazine. After a few minutes of photolysis of either of these mixtures, a second spectrum builds up that certainly belongs to a hydrazyl (a^N = 9.45 and 12.8 G, a^H(1H) = 3.0 G, g = 2.0039). This spectrum is not completely inconsistent with that which might be expected from $(CH_3)_3CNNH_2$ provided splitting by one of the amino H's is less than the line width,[22] $\Delta H_{pp} \sim 1.1$ G. However, the fact that this hydrazyl signal does not reach a steady level until 5–8 min of continuous photolysis is very suspicious for a primary radical product and, on the basis of the nitrogen splittings, we therefore suggest[23] that this radical is $(CH_3)_3CNNHC(CH_3)_3$ produced as secondary product after a number of reactions, about which we prefer not to speculate.

The kinetic procedure used to follow radical decays has been described in previous papers in this series.[1,14,19]

Product Studies. Three trialkylhydrazines and one 1,2-dialkylhydrazine were allowed to react with ca. 50 mol % of thermally generated *tert*-butoxy radicals (from *tert*-butyl hyponitrite) in degassed C_6D_6 at 50° for 48 hr in the dark.[14] Since the decay kinetics of monoalkylhydrazyls could not be properly examined (see later), no product studies were undertaken on these radicals. The reactions were carried out in NMR tubes in the presence of a trace of Me_4Si. The hydrazine concentrations were ca. 0.4 M and the hyponitrite ca. 0.1 M. The NMR spectra were recorded immediately before and after the reaction. The NMR analysis of the products was confirmed, whenever possible, by VPC.

(i) $[(CH_3)_2CHNH-]_2$ gave only $[(CH_3)_2CHN=]_2$, and this was formed in an amount equal to the initial hyponitrite concentration. That is, 1 mol of azo compound was formed for every 2 mol of *tert*-butoxy (i.e., for every two hydrazyl radicals).

(ii) $TMPNHCH_3$ gave only $TMPN=CH_2$, 1 mol/2 mol of *tert*-butoxy.

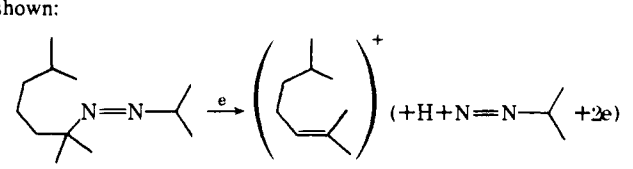
(iii) $(CH_3)_2NNHCH(CH_3)_2$ was, unfortunately, rather impure and, to judge from the NMR spectrum and VPC trace, gave a variety of different products, but none in overwhelming yield. After showing that $(CH_3)_2NN=C(CH_3)_2$ was not formed in significant amounts, this reaction was abandoned.

(iv) $TMPNHCH(CH_3)_2$ gave, after reaction, a complex NMR spectrum, in which $TMPN=C(CH_3)_2$ could be recognized in a yield of ca. 10% based on hydrazine consumed (which amounted to 1 mol/2 mol of *tert*-butoxy). Other tentatively identifiable product peaks in the NMR spectrum implied the presence of an $H_2C=C$ group (4.75, unresolved multiplet, $J \sim 2$ Hz) and two, or more, $(CH_3)_2CHN=N$ groups (3.66, 3.68, and perhaps 3.69, apparently overlapping septets with $J \approx 6$ Hz). The integrated intensities of these two groups indicated that the concentration of $H_2C=C$ was approximately half of that of all the $(CH_3)_2CHN=N$ groups together. VPC analysis on a 12-ft SE-30 column at 200° showed three unknown products, A, B, and C, with retention times of 8.4, 9.0, and 9.8 min, respectively, together with the hydrazone (13.3 min) and unreacted hydrazine (16.0 min). None of the unknown products was any of the following: $(CH_3)_2CH(CH_2)_3C(CH_3)=CH_2$ (3.2 min); $(CH_3)_2CH(CH_2)_2CH=C(CH_3)_2$ (3.5 min); TMPH (5.0 min); or $TMPN=CHCH_3$ (10.4 min).

Table II. ^1H and Decoupled ^{13}C NMR Spectra of A

^{13}C NMR		^1H NMR
	$(CH_3)_2$	0.85 (d, J = 6 Hz)
	CH	
	CH_2	Broad multiplet
	CH_2	Centered at 1.6
	CH_2	
69.4 (30.9)	$C(CH_3)_2$	1.18 (s)
	N	
	N	
68.5	CH	3.68 (septet)
21.3	$(CH_3)_2$	1.17 (d, J = 6 Hz)

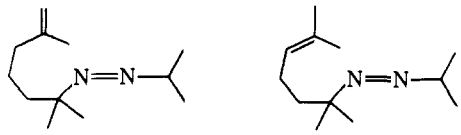
The percentage yields of A, B, C and hydrazone are given in Table I for the hyponitrite reaction and for oxidation under a variety of different conditions. The additional experiments were carried out in order to find conditions where the relative yield of one of the unknown products increased sufficiently to justify an attempt at separation by preparative VPC. Compound A was isolated as a yellowish oil by this technique, following reaction of 2.7 mmol of hydrazine with di-*tert*-butyl peroxide (2.7 mmol) at 140° for 7.5 hr (3 half-lives for the peroxide). It was not sufficiently pure (the major impurities being B and bleeding from the VPC column) for elemental anaysis. The ^1H and decoupled ^{13}C NMR spectra of A (in C_6D_6, chemical shifts in ppm downfield from Me_4Si) are consistent with those of the acyclic azo compound shown in Table II. The ^{13}C chemical shifts were assigned by comparison with azoisopropane (CH, 68.1; CH_3, 21.1) and 2,2'-azoisobutane (C, 66.5; CH_3, 27.6), taking into account possible β- and γ-substitution effects.[24] The other ^{13}C resonances were not assigned because of problems associated with the impurities present. The presence of an azo linkage is supported by the uv spectrum of A: λ_{max} 360 mμ (ϵ 14) in *n*-pentane. For comparison, azoisopropane has: λ_{max} 356 mμ (ϵ 14) in the same solvent. The ir spectrum of (neat) A [2900 (v broad), 1467 (s), 1458 (shoulder), 1379 (s), 1363 (s), 1309 (m), 1260 (w), 1171 (m), 1033 (w), and 804 (w) cm^{-1}] is also very similar to that of azoisopropane [2968 (s), 2927 (s), 2893 (s), 2864 (s), 1466 (s), 1458 (shoulder), 1378 (s), 1364 (s), 1310 (m), 1126 (s) cm^{-1}]. The mass spectrum of A did not show a parent peak. It has as its maximum m/e 126, corresponding presumably to the molecular ion $C_9H_{18}^+$ produced perhaps as shown:



A

The mass spectral cracking pattern of A is identical with that for $(CH_3)_2CH(CH_2)_2CH=C(CH_3)_2$. The mass spectra of B and C (combined VPC, mass spectrometer) both have maximum m/e 124. Combination of this fact with the observed yields of A, B, and

C and the relative intensities of the $H_2C{=}C$ and $(CH_3)_2CHN{=}N$ groups in the hyponitrite oxidation leads us to assign the following structures to B and C.



B C

This assignment receives some support from the relative VPC retention times of B and C and of $(CH_3)_2CH(CH_2)_3C(CH_3){=}CH_2$ and $(CH_3)_2CH(CH_2)_2CH{=}C(CH_3)_2$.

Results

Monoalkylhydrazyls. Methyl- and benzylhydrazine react with *tert*-butoxys to give $CH_3\dot{N}NH_2$ and $C_6H_5CH_2\dot{N}NH_2$, respectively.[9] The large number of lines in the EPR spectra of these radicals made the intensity of any individual line too low for kinetic study. However, the radical concentrations were proportional to the square root of the light intensity, which implies that they decay by radical-radical processes. From the radical concentrations under steady illumination and the known rate of *tert*-butoxy formation, the bimolecular rate constant for radical decay was estimated to be $(1.0 \pm 0.5) \times 10^9\ M^{-1}\ \text{sec}^{-1}$ at 25°; i.e., decay occurs at essentially the diffusion-controlled limit.

$$2CH_3\dot{N}NH_2 \longrightarrow \text{products}$$

The formation of the $(CH_3)_3\dot{C}$ radical when *tert*-butylhydrazine reacts with *tert*-butoxys, suggests that $(CH_3)_3CNH\dot{N}H$ rather than $(CH_3)_3C\dot{N}NH_2$ (which is the type of hydrazyl formed from less hindered monoalkyl hydrazines[9]) may be formed initially but is not detected either because it undergoes an unexpectedly rapid β-scission or because it is an unusually powerful hydrogen donor,[25] e.g.:

$$(CH_3)_3CNH\dot{N}H \longrightarrow (CH_3)_3\dot{C} + HN{=}NH$$

$$(CH_3)_3CNH\dot{N}H + (CH_3)_3COOC(CH_3)_3 \longrightarrow$$

$$[(CH_3)_3CN{=}NH + (CH_3)_3CO\cdot + (CH_3)_3COH] \longrightarrow$$

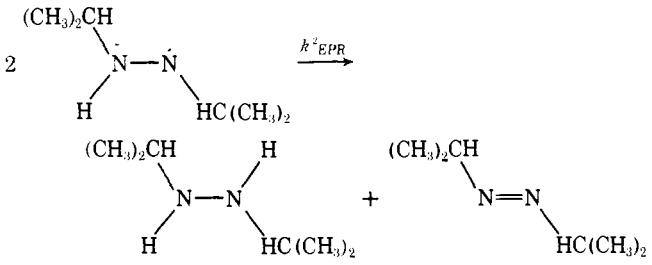
$$[CH_3)_3CN{=}\dot{N} + 2(CH_3)_3COH] \longrightarrow$$

$$(CH_3)_3C\cdot + N_2 + 2(CH_3)_3COH$$

1,2-Dialkylhydrazyl. At 20° and at concentrations in the range $1\text{-}20 \times 10^{-7}\ M$, 1,2-diisopropylhydrazyl decayed rapidly with "clean" second order kinetics:[26]

$$k^2_{EPR} = 9.8\,(\pm 1.3) \times 10^7 M^{-1}\,\text{sec}^{-1}$$

The formation of azoisopropane as the sole product upon oxidation of this hydrazine with *tert*-butoxys indicates that the overall reaction is a disproportionation involving the amino hydrogen.[27]



If this reaction is the process actually monitored by EPR, it has only a small deuterium kinetic isotope effect since decay of $(CH_3)_2CHND\dot{N}CH(CH_3)_2$ (from $[(CH_3)_2CHND]_2$ formed by D_2O addition to a solution of the hydrazine)[7,9,10,14] occurs at virtually the same rate, viz.:

$$(k^2_{EPR})_D = 9.5(\pm 1.3) \times 10^7\ M^{-1}\ \text{sec}^{-1}$$

While fast reactions rarely exhibit large deuterium isotope effects, it is quite possible that the reaction actually proceeds by a rate-controlling radical coupling to form a tetrazane. The observed products would then be formed by a subsequent slower 1,3-hydrogen transfer.

$$2(CH_3)_2CHNH\dot{N}CH(CH_3)_2 \xrightarrow{k^2_{EPR}}$$

$$[(CH_3)_2CHNHNCH(CH_3)_2]_2 \longrightarrow$$

$$(CH_3)_2CHNHNHCH(CH_3)_2 + (CH_3)_2CHN{=}NCH(CH_3)_2$$

This mechanism is analogous to that previously established for $(CH_3)_2N\dot{N}H$, $(CH_3CH_2)_2N\dot{N}H$, and $(C_6H_5CH_2)_2N\dot{N}H$ radicals.[14]

2,2-Dialkylhydrazyls. The decay kinetics and products have been described previously.[14]

Trialkylhydrazyls. (i) **TMP-1-aminomethyl** decayed with clean second-order kinetics. Within the limits of experimental accuracy, the rate constant was unaffected by temperature in the range −30 to 30° so the activation energy for decay is probably ≤2 kcal/mol.

$$k^2_{EPR} = 1.2(\pm 0.2) \times 10^7\ M^{-1}\ \text{sec}^{-1}$$

The formation of the hydrazone as the sole oxidation product implies that the observed reaction is a disproportionation involving alkyl hydrogen.

$$2\ TMP\dot{N}CH_3 \longrightarrow TMPNHCH_3 + TMPN{=}CH_2$$

(ii) 2,2-Dimethyl-1-isopropylhydrazyl was slightly longer lived. It decayed with second-order kinetics, and the rate constant was independent of the temperature from −30 to 30°.

$$k^2_{EPR} = 2.1(\pm 0.4) \times 10^6\ M^{-1}\ \text{sec}^{-1}$$

Since hydrazone was not formed, the expected disproportionation must be inhibited by steric factors. The most likely reaction would seem to be formation of a tetrazane that subsequently decays to yield a variety of products.

(iii) TMP-1-aminoisopropyl gave more problems than all the preceding hydrazyls. Brief irradiation of a fresh sample gave radicals that decayed rapidly (e.g., $\tau_{1/2} \ll 1$ sec at 25°, ~15 sec at −80°). On repeated irradiation, decay became slower and, at temperatures below −60°, the radical did not decay completely. This "residual" radical was destroyed on warming the sample to room temperature but, on reirradiation, radical decay remained "slow". Addition of the hydrazone $(TMPN{=}C(CH_3)_2)$ and of *tert*-butyl alcohol did not affect this pattern of behavior. Although it proved difficult to obtain reproducible results, it was easily established that all "slow" decays ($\tau_{1/2} \sim 1$ sec at 25°) followed *first*-order kinetics. Moderately reproducible decay data were obtained on a number of different samples provided they were first irradiated for a period of 30 sec to 2 min. In the temperature range 25 to −50°, the rate constant for decay could be represented by[26]

$$\log (k^1_{EPR}/\text{sec}^{-1}) = 6.7\,(\pm 1.2) - 9.2(\pm 1.7)/\theta$$

where $\theta = 2.3RT$ kcal/mol.

Under steady illumination, the radical concentration was very roughly proportional to the square root of the incident light intensity at all temperatures. This suggested that the hydrazyl radicals are destroyed by reaction with a second radical. The combination of first-order decay kinetics and radical concentrations proportional to (light intensity)$^{0.5}$ has been observed for quite a variety of sterically hindered radicals (e.g., phenoxys,[28,29] iminoxys,[30] aminos,[31] and 1,1-dialkylhydrazyls[14]). It has been shown to be due to the rapid and reversible formation of a dimer, with the equilibrium lying strongly in favor of the dimer under the conditions where the radical decay is followed.

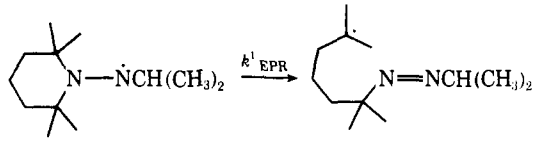
$$R\cdot + R\cdot \overset{\text{fast}}{\rightleftharpoons} R_2 \xrightarrow{\text{slow}} \text{products}$$

The measured decay rate corresponds to the slow, irreversible, decomposition of the dimer.

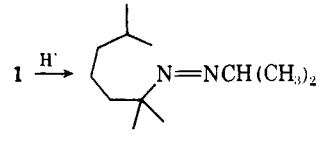
It has usually been possible to obtain independent evidence for the formation of the dimer by working at low temperatures. Provided radical decay becomes sufficiently slow, photolysis can be stopped and the radical concentration increased and decreased reversibly by raising and lowering the temperature. In the present case, this procedure yielded *no* evidence for a reversibly formed dimer. This prompted us to reexamine our use of the light intensity exponent to determine decay kinetics.

Suppose one generates a radical, R·, from RH with photochemically produced $(CH_3)_3CO\cdot$. If R· decays solely by a unimolecular process, then under steady-state conditions $[R\cdot]_{ss} \propto (h\nu)^{1.0}$. If this decay is slow, then R· is likely to compete with RH for the $(CH_3)_3CO\cdot$ radicals. Under limiting conditions where all R· are destroyed by *tert*-butoxys, $[R\cdot]_{ss}$ is independent of the light intensity.[32] These limiting conditions will apply at very high light intensities while, at very low intensities, all R· will decay by the unimolecular process. Therefore, $[R\cdot]_{ss}^{h\nu\to\infty} \propto (h\nu)^{0.0}$, and $[R\cdot]_{ss}^{h\nu\to 0} \propto (h\nu)^{1.0}$, so that over a considerable range of light intensities $[R\cdot]_{ss}$ will approximate to $(h\nu)^{0.5}$. This appears to be the situation with $TMPN\dot{C}H(CH_3)_2$. Close examination of the data reveals an increase in the exponent from ca. 0.4 at full intensity to ca. 0.7 at 2% of full intensity. We therefore believe that $TMPN\dot{C}H(CH_3)_2$ decays by a true unimolecular process when radical generation is stopped by cutting off the light. This suggestion is supported by the decay kinetics and by the products (see below). The irreproducible and rapid decay of this hydrazyl in the initial stages of a reaction we attribute to trace impurities that are efficient donors of hydrogen to the hydrazyl but are soon consumed.

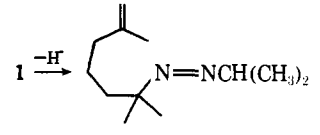
The identification of the saturated azo compounds (A) and the tentative identification of two unsaturated azo compounds (B and C) upon oxidation of $TMPNHCH(CH_3)_2$ suggest that the slow first-order decay is a unimolecular ring opening, β-scission.



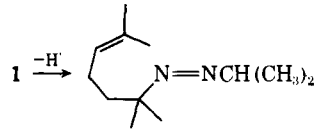
1



A



B



C

The activation energy measured for this reaction (9.2 kcal/mol) appears reasonable, but the preexponential factor ($10^{6.7}$ sec^{-1}) is much too low for a *simple* β-scission. However, since the alkyl radical center in **1** cannot diffuse away from the azo linkage, the ring opening may actually be reversible.[33] The small amount of hydrazone formed during *tert*-butoxy oxidation of this hydrazine may indicate that there is a small extent of hydrazyl disproportionation. Alternatively, it may represent a product formed by reaction of the hydrazyl with *tert*-butoxys.

The decay rates, kinetics, and general behavior of TMP-1-aminocyclohexyl were essentially identical with those of TMP-1-aminoisopropyl.

(iv) 1,2-Bis(trifluoromethyl)-2-*tert*-pentylhydrazyl is produced by photolysis of $CF_3N{=}NCF_3$ in isopentane.[10]

$$CF_3N{=}NCF_3 \xrightarrow{h\nu} 2\dot{C}F_3 + N_2$$

$$\dot{C}F_3 + RH \longrightarrow R\cdot + CF_3H$$

$$R\cdot + CF_3N{=}NCF_3 \longrightarrow CF_3(R)N\dot{N}CF_3$$

At ambient temperatures and at concentrations in the range $6\text{–}0.8 \times 10^{-6}$ M, this hydrazyl decays with clean second-order kinetics.[26]

$$k^2_{EPR} = 7.2(\pm 1.5) \times 10^4\ M^{-1}\ sec^{-1} \text{ at } 0°$$

The only conceivable product is the tetrazane. Moreover, the tetrazane must itself slowly decompose because, after the hydrazyl has decayed ($\tau_{1/2} \sim$ 1–3 sec at 0–25° and the usual concentrations), a second radical is produced slowly ($\tau_{1/2} \sim$ 60 sec for formation). This radical has been assigned the structure[10] $RCF_2(R)N\dot{N}CF_2R$. It is very much longer lived than the initial hydrazyl, perhaps because it is sterically more crowded around the reaction center. The following mechanism for the formation of the second radical has been suggested.[10]

$$2\ CF_3(R)N\dot{N}CF_3 \overset{k^2_{EPR}}{\rightleftharpoons} [CF_3(R)NNCF_3]_2$$

$$CF_3(R)N\dot{N}CF_3 + RH \xrightarrow{\text{slow}} (R\cdot + CF_3(R)NNHCF_3) \longrightarrow$$

$$(R\cdot + CF_3(R)NN{=}CF_2 + HF) \longrightarrow CF_3(R)N\dot{N}CF_2R \xrightarrow{\alpha\text{-}}$$

$$CF_3NN(R)CF_2R \xrightarrow{RH} \text{----} RCF_2\dot{N}N(R)CF_2R.$$

Discussion

Our work on alkyl hydrazyls[7,9,10,14] was begun with the hope that some of these radicals might have lifetimes sufficient for them to be isolated as pure materials (like DPPH). There seems little likelihood that this will be achieved with mono- or dialkylhydrazyls, but our results (and others) make trialkylhydrazyls look a bit more promising. Our results are summarized below.

(i) 1-Alkylhydrazyls [$R\dot{N}NH_2$ (e.g.,[9] $CH_3\dot{N}NH_2$)] decay by a diffusion-controlled bimolecular reaction. The reaction products have not been examined, but both combinations to (presumably unstable) tetrazanes and β-disproportionation seem likely to occur.

(ii) 2-Alkylhydrazyls (RNHṄH) have not been identified directly,[10] but we infer from the presence of the $(CH_3)_3\dot{C}$ radicals that we have produced $(CH_3)_3CNH\dot{N}H$ from its hydrazine. If this is correct,[34] at least one 2-alkylhydrazyl decays extremely rapidly.

(iii) 1,2-Dialkylhydrazyls (RṄNHR) are short lived (like 1,2-diarylhydrazyls)[27] because they undergo a facile β-disproportionation, amino-H → Ṅ; e.g., $(CH_3)_2CH\dot{N}NH\text{-}CH(CH_3)_2$.

$$2R\dot{N}NHR \longrightarrow RNHNHR + RN{=}NR$$

This reaction may involve the intermediate formation of a tetrazane.

(iv) 2,2-Dialkylhydrazyls ($R_2N\dot{N}H$) are relatively short lived even when the R groups are bulky because they can

undergo an α-disproportionation, amino-H $\rightarrow$ N.[14] The *N*-nitrene intermediate decays to hydrocarbon products and nitrogen,[14] e.g., TMPNH.

$$2R_2\dot{N}\dot{N}H \longrightarrow R_2NNH_2 + (R_2N{=}N) \longrightarrow R_2 + N_2$$

When the R groups are not bulky, decay involves a diffusion-controlled combination to yield a tetrazane, which then decays to yield the observed products, amine and nitrogen;[14] e.g., $(CH_3CH_2)_2N\dot{N}H$.

$$2R_2N\dot{N}H \longrightarrow (R_2NNH)_2 \longrightarrow 2R_2NH + N_2$$

(v) **Trialkylhydrazyls** having relatively small alkyl groups attached to the divalent nitrogen undergo rapid β-disproportionations, alkyl-H $\rightarrow$ N; e.g., $TMPN\dot{C}H_3$.

$$2R_2N\dot{N}CH_3 \longrightarrow R_2NNHCH_3 + R_2NN{=}CH_2$$

This process is strongly inhibited by steric protection of the radical center since it is unimportant with $TMPN\dot{C}H(CH_3)_2$. However, the latter radical decays, and presumably most other hindered trialkylhydrazyls can decay, by a unimolecular β-scission of a C-N bond.

$$R_2N\dot{N}R' \longrightarrow R\cdot + RN{=}NR'$$

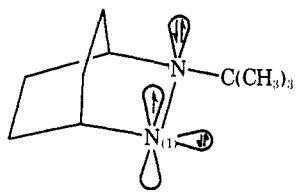
We would expect that a suitably substituted trialkylhydrazyl might decay by a unimolecular β-scission of a C-C bond.

$$R_2N\dot{N}CH_2R' \longrightarrow R_2NN{=}CH_2 + R'\cdot$$

While no example of this reaction has been observed, one can guess that it would be important with radicals such as $(CH_3)_2N\dot{N}CH_2CH_2C_6H_5$ or $TMPN\dot{C}H_2C(CH_3)_3$.

It is difficult to see how β-scission could be entirely prevented in trialkylhydrazyls in which rotation around the N-N bond is possible, but it should be minimized when all the radicals that could be eliminated are primary alkyls. This suggests that $(CH_3)_2N\dot{N}C(CH_3)_3$, $[(CH_3)_3CCH_2]_2N\dot{N}C(CH_3)_3$, and $(CH_2)_5N\dot{N}C(CH_3)_3$ might be fairly long lived, but so far we have not succeeded in preparing the appropriate hydrazines.

The Nelsen and Landis[6] approach to long-lived trialkylhydrazyls looks more promising than our own. Specifically, they have prepared a bicyclic hydrazyl (**2**) that contains



2

a *tert*-butyl group on $N_{(2)}$ but persists indefinitely in solution in the absence of air. The persistence of **2** is presumably related to (i) the (virtual)[35] impossibility of a β-disproportionation involving a bridgehead H $\rightarrow$ N (which would violate Bredt's rule) and (ii) to the (virtual) impossibility of a β-scission involving loss of the *tert*-butyl radical since the $N_{(1)}$ orbital, containing the unpaired electron, and the $N_{(2)}$-$C(CH_3)_3$ bond are almost orthogonal to one another.[25] Perhaps **2** or a radical related to it,[36] will indeed be isolated eventually.

The great persistence of $RCF_2(R)N\dot{N}CF_2R$ [R = $(CH_3)_2CC_2H_5$ or $(CH_3)_3C$][10] suggests that at least some partially (or fully) fluorinated trialkylhydrazyls may be isolable.

Acknowledgment. The authors are grateful to Dr. V. Malatesta for assistance in the synthesis of some of the trialkylhydrazines.

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