prepared by adding sodium acetate (1.50 g) to 1 M acetic acid (100 mL). The substrate (50 mg, 0.23 mmol) was then added followed by methanol (10 drops) to give a homogeneous mixture. After 3 h at room temperature, 15% sodium hydroxide (1 mL) was added followed by extraction with CH_2Cl_2 (2 × 3 mL) after which the extracts were dried and concentrated. The products were isolated as oils.

***trans*-1-Methyl-2-phenyl-4-(2-methylaminoethyl)pyrrolidine (8a):** bp 58–60 °C (0.005 mm) (bulb to bulb); NMR δ 7.2 (s, 5 H), 3.3 (d of d, 1 H), 3.1 (t, 1 H), 2.4 (s, 3 H), 2.2 (s, 3 H), 1.4–2.8 (m, 8 H), 1.1 (s, 1 H). Anal. Calcd for $C_{14}H_{22}N_2$: C, 77.01; H, 10.16; N, 12.83. Found: C, 77.12; H, 10.42; N, 12.80.

***cis*-1-Methyl-2-phenyl-4-(2-*N*-methylaminoethyl)pyrrolidine (8b):** bp 55 °C (0.005 mm) (bulb to bulb); NMR δ 7.1 (s, 5 H), 2.8–3.3 (m, 2 H), 2.4 (s, 3 H), 2.1 (s, 3 H), 1.2–2.8 (m, 9 H). Anal. Calcd for $C_{14}H_{22}N_2$: C, 77.01; H, 10.16; N, 12.83. Found: C, 76.88; H, 10.38; N, 12.87.

Registry No.—**2a,** 67505-92-4; **2b,** 67505-93-5; **2c,** 67505-94-6; **3a,** 67505-95-7; **3b,** 67505-96-8; **3c,** 67505-97-9; **4a,** 67505-98-0; **4b,** 67505-99-1; **4c,** 67506-00-7; **6b** isomer 1, 67506-01-8; **6b** isomer 2, 67506-02-9; **8a** (Ar = Ph), 67506-03-0; **8b** (Ar = Ph), 67506-04-1; 1-methyl-3-(2-chloro-1-hydroxy-1-phenylethyl)-2-pyrrolidone, 67506-05-2; *N*-methylpyrrolidone anion, 67506-06-3; *N*-methyl-2-pyrrolidone, 872-50-4; phenacyl chloride, 532-27-4; phenacyl bromide, 70-11-1; 1-methyl-3-carbethoxy-2-pyrrolidone, 30932-85-5; *p*-chlorophenacyl bromide, 536-38-9; *o*-methylphenacyl bromide, 51012-65-8; methylammonium acetate, 6998-30-7.

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2,2,6,6-Tetramethyl-4-oxo-1-(1,1-diphenylethoxy)piperidine: Synthesis and Thermal Stability[1]

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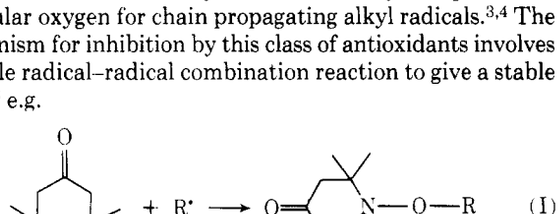
2,2,6,6-Tetramethyl-4-oxopiperidinyl-1-oxy reacts with the 1,1-diphenylethyl radical to give 2,2,6,6-tetramethyl-4-oxo-1-(1,1-diphenylethoxy)piperidine. In solution this ether appears to exist in equilibrium with the parent radicals with $\Delta H°_2 \sim -21.4$ kcal mol^{-1} and $\Delta S°_2 \sim -36$ cal deg^{-1} mol^{-1}. In degassed solution there is an irreversible first-order decay of this *O*-alkyl hydroxylamine to give 1,1-diphenylethylene and 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-one with $\log (k_3/s^{-1}) = 14.8 - 6425/T$. Decomposition is significantly faster when the solution contains dissolved oxygen because 1,1-diphenylethyl radicals are rapidly converted to 1,1-diphenylethylperoxy radicals and $\log (k_{-2}/s^{-1}) = 14.8 - 5354/T$. The strength of the O–C bond in 2,2,6,6-tetramethyl-4-oxo-1-(1,1-diphenylethoxy)piperidine must be ~21 kcal mol^{-1}. 2,2,6,6-Tetramethyl-4-oxo-1-cumyloxypiperidine can be prepared from 2,2,6,6-tetramethyl-4-oxopiperidinyl-1-oxy and cumyl radicals and it is significantly more stable in degassed and oxygen-containing solutions than the *O*-1,1-diphenylethyl analogue.

Introduction

Cyclic di-*tert*-alkylnitroxides such as 2,2,6,6-tetramethyl-4-oxopiperidinyl-1-oxy, TMPO·, are efficient inhibitors for autoxidation because they can successfully compete with molecular oxygen for chain propagating alkyl radicals.[3,4] The mechanism for inhibition by this class of antioxidants involves a simple radical–radical combination reaction to give a stable ether,[3] e.g.



(I)

The stability of these ethers is pertinent to the use of nitroxides as antioxidants[3,4] and as radical scavengers in the determination of rates of initiation for homolytic reactions.[5] In this context we have recently discovered that several of these ethers, e.g., 2,2,6,6-tetramethyl-4-oxo-1-(1,1-diphenylethoxy)piperidine, are thermally unstable. This discovery prompted us to embark on a kinetic and product study of the decomposition of this *O*-alkyl hydroxylamine and the closely related *O*-cumyl derivative and the results of this work are reported here.

Results and Discussion

During an attempt to measure the rate of production of 1,1-diphenylethyl from thermolysis of 2,2,3,3-tetraphenylbutane (3.3 mM) in oxygen-free *tert*-butylbenzene at 50 °C by monitoring the disappearance of 2,2,6,6-tetramethyl-4-oxopiperidinyl-1-oxy, TMPO· (initial concentration = 0.031 mM), we found (i) that the rate of nitroxide disappearance did not follow the expected zero-order kinetics, (ii) that the initial rate of nitroxide disappearance was about one-half the expected rate based on the known rate constant for decomposition of TPB[6] and the efficiency of radical production,[7] and (iii) that the nitroxide reached an apparent steady-state concentration of 0.002 mM (see Figure 1).

Now it is generally accepted that reactive alkyl radicals add rapidly to nitroxides to give *O*-alkyl hydroxylamines.[3,9–12] The reaction of 1,1-diphenylethyl with TMPO· would, therefore, be expected to give 2,2,6,6-tetramethyl-4-oxo-1-(1,1-diphenylethoxy)piperidine, $TMPOR_1$, and in the presence of excess TPB all the nitroxide should have been consumed.

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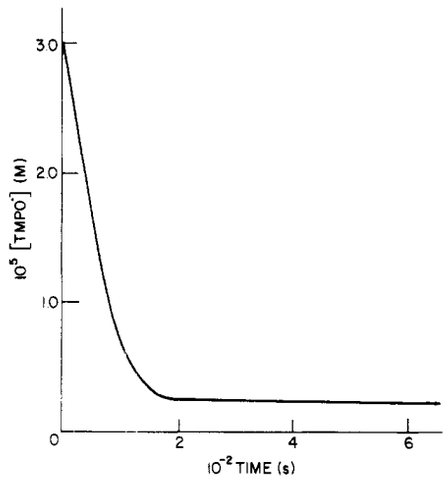
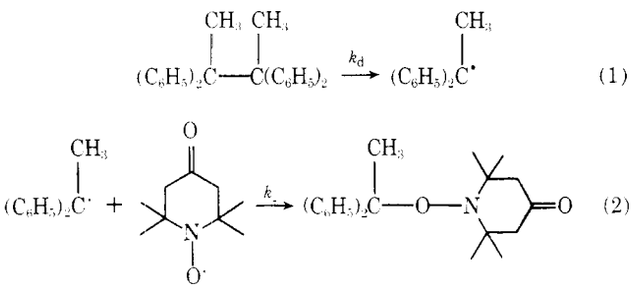
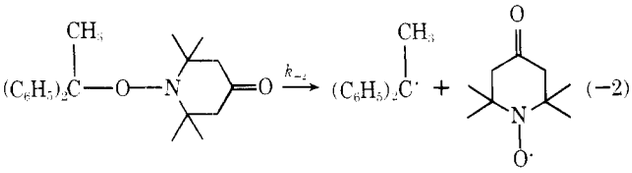


Figure 1. The concentration of TMPO· as a function of time in the presence of TPB (0.0033 M) in oxygen-free *tert*-butylbenzene at 50 °C.



We also discovered that the nitroxide concentration could be increased by raising the temperature and decreased by lowering the temperature with no apparent loss in nitroxide concentration, behavior that suggests that reaction 2 is reversible.[8]



Over a period of several hours the nitroxide concentration did not increase or decrease irreversibly and the radical concentrations given in Table I were measured. Above 100 °C increasing the temperature had no effect on [TMPO·] and if it was assumed that $[\text{TMPO}\cdot]_{max}$ was equal to the concentration of TMPOR_1, the equilibrium constants K_2, given in the last column of Table I, could be calculated from

$$K_2 = \frac{[\text{TMPOR}_1]}{[(C_6H_5)_2\dot{C}CH_3][\text{TMPO}\cdot]} = \frac{[\text{TMPOR}_1]}{[\text{TMPO}\cdot]^2}$$

A van't Hoff plot of ln K_2 against $1/T$ yielded thermodynamic parameters $\Delta H^\circ_2 = -21.4 \pm 1.5$ kcal mol^{-1} and $\Delta S^\circ_2 = -36 \pm 4$ cal deg^{-1} mol^{-1}.

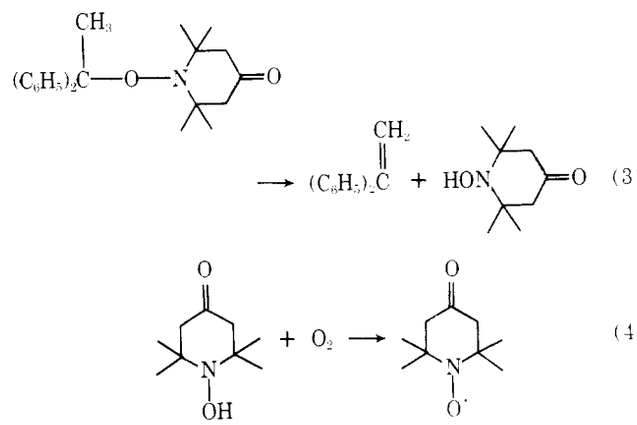
In aliphatic solvents, such as cyclohexane, the situation was somewhat different in that $-\text{d}[\text{TMPO}\cdot]/\text{d}t$ was independent of the radical concentration until about 90% of the radical had been consumed and was equal to twice the rate of decomposition of TPB. The rate then slowed down rapidly and stopped to leave a residual radical concentration equal to about 1% of the original concentration. This residual nitroxide concentration could be increased or decreased by raising or lowering the temperature between 100 and 20 °C.

An NMR study of the decomposition of TPB (0.053 M) in the presence of TMPO· (0.1 M) in $CDCl_3$ at 50 °C revealed

Table I. Steady-State Concentrations of 2,2,6,6-Tetramethyl-4-oxopiperidinyl-1-oxy in *tert*-Butylbenzene as a Function of Temperature after the Decomposition of Tetraphenylbutane (0.47 mM) in the Presence of TMPO· (0.031 mM) at 50 °C

temp, °C	10^6 [TMPO·], M	10^{-6} K_2, M^{-1}
38	0.81	8.2
60	1.5	2.4
80	3.4	0.47
70	2.4	0.94
90	4.4	0.28
60	1.7	1.87
50	1.0	5.4
38	0.74	9.86
90	4.26	0.30
100	5.0	0.22
112	5.4	
122	5.2	

that TPB disappeared exponentially with a first-order rate constant k_d equal, within experimental error, to the literature value,[6] and TMPOR_1 was formed initially at close to twice the rate of disappearance of TPB. The ether did, however, reach a maximum concentration of ca. 0.07 M while 1,1-diphenylethylene and 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-one, TMPOH, became major reaction products. On allowing air into the system the hydroxylamine was *slowly* oxidized to TMPO· ($\tau_{1/2} \sim 12$ h at 30 °C).



Decomposition of TMPOR_1. 2,2,6,6-Tetramethyl-4-oxo-1-(1,1-diphenylethoxy)piperidine was isolated and found to decompose in degassed $CDCl_3$ at 51.5 °C to give quantitative yields of 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-one and 1,1-diphenylethylene. There was no evidence for the formation of 1,1-diphenylethane. The kinetics of the decomposition at this temperature strictly obeyed the rate expressions

$$\frac{-\text{d}[\text{TMPOR}_1]}{\text{d}t} = \frac{\text{d}[\text{TMPOH}]}{\text{d}t} = \frac{\text{d}[(C_6H_5)_2C{=}CH_2]}{\text{d}t} = k_3[\text{TMPOR}_1]$$

with $k_3 = 1.1 \times 10^{-5}$ s^{-1}. Values of k_3 were obtained from 50 to 90 °C and an Arrhenius plot yielded the activation parameters $E_3 = 29.4 \pm 0.8$ kcal mol^{-1} and log $(A_3/\text{s}^{-1}) = 14.8 \pm 0.5$ (Table II). Decomposition in C_6D_6 appeared slightly slower with $k_3 = 5.6 \times 10^{-6}$ s^{-1} at 51.5 °C.

Decomposition of TMPOR_1 in the Presence of Oxygen. TMPOR_1 was very unstable in solvents containing dissolved oxygen and had a half-life of 43 s in oxygen-saturated chlorobenzene at 50 °C. A kinetic study of this oxidation revealed that the rate of oxygen absorption was proportional to the

Table II. Rate Constants for Thermal Decomposition of 2,2,6,6-Tetramethyl-4-oxo-1-(1,1-diphenylethoxy)-piperidine

solvent	temp, °C	$10^4 k_3/s^{-1}$
$CDCl_3$	51.5	0.11
	62.5	0.4
	74.2	1.9
	91.3	15
C_6D_6	51.5	0.056

concentration of $TMPOR_1$ to the first power and equal to the rate of formation of TMPO·, i.e.

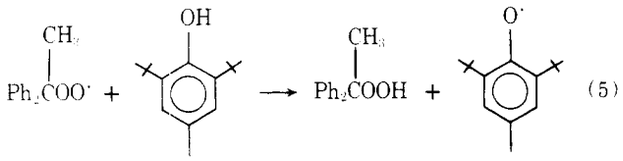
$$\frac{-d[O_2]}{dt} = \frac{d[TMPO\cdot]}{dt} = k_{-2}[TMPOR_1]$$

where k_{-2} is the first-order rate constant for decomposition of $TMPOR_1$. Values of k_{-2} were determined from 20 to 50 °C (Table III) and obey the Arrhenius equation

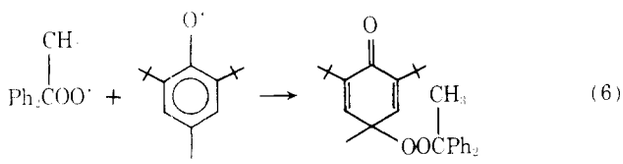
$$\log (k_{-2}/s^{-1}) = 14.8 \pm 0.6 - (5348 \pm 180)/T$$

Atmospheric oxidation gave almost quantitative yields of TMPO· along with somewhat lower yields of acetophenone, benzophenone, and 1,1-diphenylethanol (Table III). These ketones and alcohol suggest the intermediacy of 1,1-diphenylethylperoxy radicals and/or 1,1-diphenylethoxy radicals although it should be noted that the yields were significantly greater than were obtained from decomposition of tetraphenylbutane in the presence of oxygen.[13,14]

Rates of decomposition in the presence of oxygen were not influenced by the free-radical scavenger 2,6-di-*tert*-butyl-4-methylphenol. In this case the principal products were TMPO·, 1,1-diphenylethyl hydroperoxide, and 2,6-di-*tert*-butyl-4-methyl-4-(1,1-diphenylethylperoxy)-2,5-cyclohexadien-1-one, proving that $TMPOR_1$ does indeed decompose at the C–O bond to give TMPO· and 1,1-diphenylethyl. In the presence of oxygen the latter radicals were rapidly converted into 1,1-diphenylethylperoxy, which in the presence of a good hydrogen atom donor such as 2,6-di-*tert*-butyl-4-methylphenol was reduced to the hydroperoxide and trapped by the phenoxy radical according to reactions 5 and 6.[15]

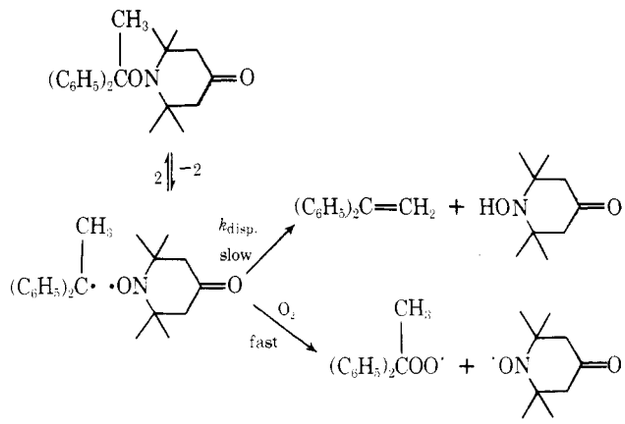


(5)



(6)

Scheme I



2,2,6,6-Tetramethyl-4-oxo-1-cumyloxypiperidine. The stability of *O*-alkyl hydroxylamines is quite sensitive to the nature of the alkyl moiety attached to oxygen as indicated by the fact that 2,2,6,6-tetramethyl-4-oxo-1-cumyloxypiperidine ($TMPOR_2$) is very much more stable than the *O*-1,1-diphenylethyl derivative. Thus the rate of disappearance of TMPO· in degassed *tert*-butylbenzene was equal to the rate of generation of cumyl radicals from thermolysis of azocumene at 50 °C. Furthermore, the reaction was zero order with respect to TMPO· and the nitroxide was completely destroyed by excess azocumene. An NMR study of the decomposition of $TMPOR_2$ indicated that it had a half-life of 1.3×10^4 s at 100 °C (cf. $\tau_{1/2}$ = 460 s for $TMPOR_1$ at 91.3 °C).

Decomposition of $TMPOR_2$ was much faster in the presence of oxygen. For instance, a 0.012 M solution in chlorobenzene absorbed oxygen (0.011 M) with an initial rate of 1.0×10^{-6} M s^{-1} at 60 °C to give TMPO· (0.012 M), acetophenone (0.006 M), and α-cumyl alcohol (0.005 M) as major reaction products. This ratio of acetophenone to cumyl alcohol (1.2) is similar to the ratio obtained from the decomposition of azocumene in oxygen saturated chlorobenzene[14] and is indicative of the intermediacy of cumylperoxy radicals.

The rate of oxidation of $TMPOR_2$ was not influenced by 2,6-di-*tert*-butyl-4-methylphenol. In this case α-cumyl hydroperoxide and 2,6-di-*tert*-butyl-4-methyl-4-cumylperoxy-2,5-cyclohexadien-1-one were the major reaction products.

Conclusions

It would appear that the kinetics and products for decomposition of 2,2,6,6-tetramethyl-4-oxo-1-(1,1-diphenylethoxy)piperidine in the absence and presence of oxygen can best be rationalized on the basis of the mechanism given in Scheme I.

The thermodynamic parameters for the equilibrium process (2) have been estimated to be $\Delta H°_2 = -21.4$ kcal mol^{-1} and $\Delta S°_2 = -36$ cal deg^{-1} mol^{-1}, which are not unreasonable when

Table III. Product and Kinetic Data for Decomposition of $TMPOR_1$ in Oxygen-Saturated Chlorobenzene

temp, °C	$[TMPOR_1]$, mM	$[O_2]_{abs}$,[a] mM	[TMPO·], mM	$[C_6H_5COCH_3]$, mM	$[(C_6H_5)_2CO]$, mM	$[(C_6H_5)_2CCH_3OH]$, mM	$10^3 k_{-2}$, s^{-1}
21	6.0	6.0	5.4	2.1	1.3	2.2	0.37
30	6.3	6.4	5.5	1.0	0.15	1.1	1.5
30	6.0[b]	4.1	3.6	—	—	1.8[c]	1.6
40	6.2	5.3	5.2	1.3	0.3	1.2	5.4
50	3.4	1.7	2.7	0.94	0.3	1.2	16
50	5.5[d]	12	—	1.5	0.2	0.3	—

[a] Concentrations of oxygen absorbed at the higher temperatures are low probably because of oxidation before the sample reached reaction temperature. [b] In the presence of 2,6-di-*tert*-butyl-4-methylphenol (0.09 M). [c] After reduction with Ph_3P (8 mM). [d] TPB (i.e., R_1–R_1).

compared with parameters for other radical–metastable dimer equilibria.[8,16-19] It should be pointed out, however, that the steady-state concentration of TMPO· may be influenced by reaction of TMPOH with 1,1-diphenylethyl or other reactive radicals in the system.

Decomposition is very fast in the presence of oxygen because 1,1-diphenylethyl radicals are efficiently scavenged by oxygen. The Arrhenius parameters for oxidation should be equal to the parameters for reaction −2; i.e., log (A_{-2}/s^{-1}) = 14.8 and E_{-2} = 24.5 kcal mol^{-1}. Now the thermodynamic parameters for 2 indicate that

$$\log \frac{k_2}{k_{-2}} = \log \frac{A_2}{A_{-2}} + \frac{E_{-2} - E_2}{2.303RT} = -7.87 + \frac{21\,400}{2.303RT}$$

from which we can calculate that log $(k_2/M^{-1}\,s^{-1})$ = 6.93 − 3100/2.303RT. This expression gives a rate constant for combination of TMPO· with 1,1-diphenylethyl = 5×10^4 M^{-1} s^{-1} at 30 °C, which is rather low when compared with the rate constants of ~10^8 M^{-1} s^{-1} reported by Ingold and Schmid[12] for addition of alkyl radicals to nitroxides. There may, however, be considerable steric hindrance to addition of 1,1-diphenylethyl to TMPO·.

The enthalpy change for reaction 2 (21.4 kcal mol^{-1}) is equivalent to the strength of the O–C bond in $TMPOR_1$ and is consistent with the activation energy for oxidation (24.5 kcal mol^{-1}) and a small activation energy for the radical recombination reaction.

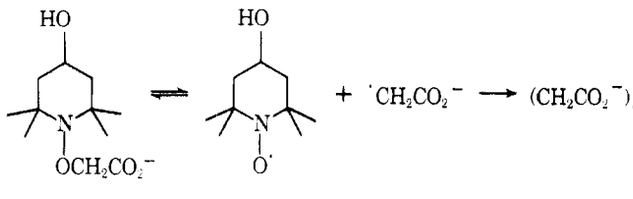
2,2,6,6-Tetramethyl-4-oxo-1-cumyloxypiperidine is ca. 10^{-3} times as reactive to oxidation at 60 °C as the *O*-1,1-diphenylethyl derivative, which means that the entropies of activation for reaction −2 must be very different because $\Delta\Delta H^{\ddagger}_{-2}$ should not be greater than about 2 kcal mol^{-1}.

Rate constants for the decomposition of $TMPOR_1$ in the absence of oxygen are described by log (k_3/s^{-1}) = 14.8 − 6425/T, which according to Scheme I is equivalent to $k_{disp.}/K_2$. We can therefore calculate log $(k_{disp.}/M^{-1}\,s^{-1})$ = 6.9 − 1746/T, which implies that the disproportionation reaction between TMPO· and 1,1-diphenylethyl is much slower than combination because of a substantial activation energy ($E_{disp.}$ = 8 kcal mol^{-1}).

Finally, we would like to comment on three reports in the literature concerning the chemistry of *O*-alkyl derivatives of TMPO· and related compounds. First we could find no evidence for reaction of alkylperoxy radicals ROO· with TMPOR via an S_H2 mechanism[20] to give TMPO· and ROOR.

Secondly, Hook and Saville[21] found that TMPO· had no effect on the amount of oxygen absorbed by TPB in the presence of 2,6-di-*tert*-butyl-4-methylphenol and concluded that the nitroxide, even in 50-fold excess, did not compete with oxygen for the 1,1-diphenylethyl radical. It is, however, clear from our work that even if reaction of TMPO· with 1,1-diphenylethyl in the presence of oxygen is very efficient, almost quantitative amounts of oxygen would be absorbed because of oxidation of $TMPOR_1$.

Thirdly, Sheats and McConnell[22] have noted that 2,2,6,6-tetramethyl-4-hydroxy-1-carboxymethoxypiperidine slowly decomposes to the nitroxide. In this case the carboxymethyl radicals probably undergo self-reaction.



Experimental Section

Materials. 2,2,3,3-Tetraphenylbutane (TPB) was generously provided by Dr. L. R. Mahoney (Ford Motor Co., Dearborn). Azocumene was prepared by the method of Bartlett and Nelsen.[23] 2,2,6,6-Tetramethyl-4-oxopiperidinyl-1-oxy was purified by sublimation: mp 40 °C.

2,2,6,6-Tetramethyl-4-oxo-1-(1,1-diphenylethoxy)piperidine. A mixture of 2,2,6,6-tetramethyl-4-oxopiperidinyl-1-oxy (0.138 g, 0.8 mmol) and 2,2,3,3-tetraphenylbutane (0.165 g, 0.45 mmol) was dissolved in hexane, thoroughly degassed, and heated for 10 h at 60 °C. The final reaction mixture was colorless and a white crystalline product crystallized out of solution upon cooling. These crystals were recrystallized from deoxygenated hexane: mp 112–114 °C; ^{1}H NMR δ (in CCl_4) 0.89 (6 H, ax CH_3), 1.29 (6 H, eq CH_3), 2.15 (3 H, CH_3C, A_2B_2 quartet, J = 12 Hz), 2.66, 2.47, 2.20, 1.97 (4 H, br m), 7–7.6 (10 H, $C(C_6H_5)_2$). Anal. Calcd for $C_{23}H_{29}O_2N$: C, 78.63; H, 8.26; N, 3.99. Found: C, 77.7; H, 8.06; N, 3.91. Interestingly catalytic reduction gave the hydroxylamine and 1,1-diphenylethane rather than the amine and carbinol.[3]

2,2,6,6-Tetramethyl-4-oxo-1-cumyloxypiperidine. A mixture of 2,2,6,6-tetramethyl-4-oxopiperidinyl-1-oxy (0.0414 g, 0.24 mmol) and azocumene (0.0363 g, 0.14 mmol) was heated at 60 °C in deoxygenated hexane for 10 h. A crude crystalline material was obtained when the solvent was removed. Recrystallization from oxygen-free hexane gave an analytically pure sample: mp 93–94 °C; ^{1}H NMR δ (in CCl_4) 0.99 (6 H, ax CH_3), 1.14 (6 H, eq CH_3), 1.67 (6 H, $(CH_3)_2CO$, A_2B_2 quartet, J = 12 Hz), 1.9, 2.1, 2.33, 2.53 (4 H, br m), 7–7.6 (5 H, $C(C_6H_5)$). Anal. Calcd for $C_{18}H_{27}O_2N$: C, 74.74; H, 9.34; N, 4.84. Found: C, 74.81; H, 9.53; N, 4.97. Both $TMPOR_1$ and $TMPOR_2$ contained traces of TMPO· which we were not able to remove by repeated recrystallization.

Kinetic Procedures. Rates of disappearance and appearance and absolute concentrations of TMPO· were determined by EPR spectroscopic techniques. Autoxidations were conducted in the automatic gas absorption apparatus described previously.[24] In a typical experiment $TMPOR_1$ (0.011 g, 6.3 mmol) in chlorobenzene (4 mL) was shaken with oxygen (720 torr) at 30 °C. The initial rate of oxygen absorption was 7.1×10^{-6} M s^{-1} and 6.4 mmol was absorbed. The yields of the principal reaction products were determined by standard GLC techniques using a Varian 2800 chromatograph equipped with a 12-ft 12% OV-101 on Chromosorb W column.

Rates of decomposition of $TMPOR_1$ and rates of formation of 1,1-diphenylethylene and TMPOH in the absence of oxygen were determined by NMR spectroscopy with a Varian XL 100 spectrometer. Relative concentrations of $TMPOR_1$, TMPOH, and $(C_6H_5)_2C{=}CH_2$ were determined from absorptions at δ 0.887, 1.223, 5.457, respectively. Oxidation of TMPOH to TMPO· was followed by ESR spectroscopy.

The products from oxidation of $TMPOR_1$ in the presence of 2,6-di-*tert*-butyl-4-methylphenol were identified and their approximate yields estimated by means of thin-layer chromatography on silica gel (Baker-flex 1B2-F). Authentic 1,1-diphenylethyl hydroperoxide and 2,6-di-*tert*-butyl-4-methyl-4-(1,1-diphenylethylperoxy)cyclohexa-1,4-dien-1-one were prepared from tetraphenylbutane by the method of Bickel and Kooyman.[15]

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Registry No.—2,2,6,6-Tetramethyl-4-oxo-1-(1,1-diphenylethoxy)piperidine, 67478-83-5; 2,2,6,6-tetramethyl-4-oxopiperidinyl-1-oxy, 2896-70-0; 2,2,3,3-tetraphenylbutane, 10496-82-9; 2,2,6,6-tetramethyl-4-oxo-1-cumyloxypiperidine, 67478-84-6; azocumene, 5676-79-9.

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Metal–Ammonia Reduction and Reductive Alkylation of Polycyclic Aromatic Compounds: Nature of the Anionic Intermediates

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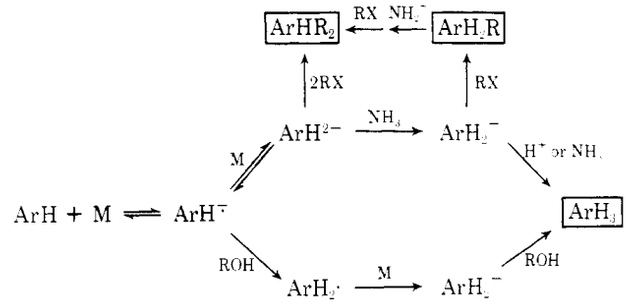
A scheme of metal–ammonia reduction is presented which categorizes the behavior of aromatic and polynuclear aromatic compounds according to the nature of the intermediate radical anions, monoanions, and dianions. It is found that the outcome of many reductions and reductive alkylations is, in fact, a result of secondary reactions that occur during the quenching process, and a dramatic difference is found in many cases by the introduction of an inverse quench procedure. That is, the ammonia solution is poured into the quenching agent, which may be a proton source (water, saturated ammonium chloride) or an alkyl halide solution. The results of a series of such experiments are presented and indicate that common hydrocarbons such as anthracene and naphthalene react with Li or Na in ammonia to form dianions which are quickly protonated by ammonia to form dianions which are quickly protonated by ammonia to form monoanions. The alkylation of these monoanions is studied under a variety of conditions, and both monoalkylation and dialkylation (via a subsequent reaction) can occur. This behavior is contrasted to dibenzocyclooctatetraene, which is shown to form a dianion resistant to protonation by ammonia.

The reduction of polycyclic aromatic compounds by solutions of alkali metals in liquid ammonia has received considerable attention,[1] and a wide variety of experimental procedures have been developed. For example, the metals employed are usually lithium or sodium, but also include potassium and calcium. Protonating agents range from moderately acidic, such as ammonium chloride and water, to weakly acidic, like ethanol and 2-methyl-2-propanol. A wide range of cosolvents is also employed (usually but not always ethers), and iron salts are sometimes added to limit reduction. In addition, polynuclear compounds often lead to stable anionic intermediates which can be alkylated by suitable alkylating agents, but once again the results are variable, leading to the incorporation of zero to three alkyl groups depending on the compound reduced as well as reaction conditions such as choice of metal and/or cosolvent.

Thus, it has become generally concluded that this reaction must be carried out with meticulous care, since it has been shown that the selection of reaction conditions can afford a wide range of results. For example, the reduction of anthracene[1c] can result in dihydro, tetrahydro, or further reduced products depending on the level of alkali metal employed, cosolvents, and the presence of iron impurities. To our surprise, however, we have found that anthracene can be reduced quantitatively to 9,10-dihydroanthracene (in 10 min) with no prior purification of ammonia or cosolvents, and with a wide variation in alkali metal concentration as well as stoichiometry (1.2–5 equiv of metal). These results were accomplished by inverse quenching (i.e., hydrocarbon/metal/ammonia solution poured into a large volume of water) and, although not applicable to all polycyclic hydrocarbons, should be useful in many cases. Of greater importance, however, are the mechanistic implications of this result and the fact that the quenching procedure is by far the most significant factor in this particular reaction.

Scheme I



Thus, a general understanding of the overall reaction mechanism should allow for predictions concerning which experimental variables should be of greatest importance. With this in mind, we would like to present Scheme I for reduction and reductive alkylation and catagorize aromatic compounds according to their particular position within this system.

a. Only Radical Anions Generated. In this case, the initial equilibrium usually lies to the left and $ArH^{-}\cdot$ is the only anionic species present. In order to effect reduction, a proton source must be added to shift the equilibrium by protonation of the radical anion, which then accepts another electron, resulting in a monoanion which is protonated to form the reduced product, ArH_3. It is important that the proton source not be too strong, or metal will be destroyed rapidly, shifting the equilibrium back to the left. Alcohols are most commonly used for this purpose, and this method represents the procedure known as the Birch reduction. Monobenzenoid compounds most frequently fall into this category, and reductive alkylation is not possible due to the low nucleophilicity of radical anions and the much more rapid electron-transfer reaction.[4]

b. Dianions Resistant to Protonation by Ammonia. In

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