adducts produced in the following competitive reactions

$$\mathrm{BuO\cdot} + \mathrm{trap} \longrightarrow \mathrm{BuO\text{-}trap} \qquad (2)$$

$$\mathrm{BuO\cdot} + \mathrm{RH} \longrightarrow \mathrm{R\cdot} + \mathrm{BuOH} \qquad (3)$$

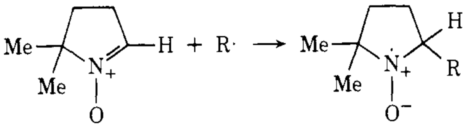
$$\mathrm{R\cdot} + \mathrm{trap} \longrightarrow \mathrm{R\text{-}trap} \qquad (4)$$

$$\mathrm{R\cdot} \longrightarrow \text{nontrappable products} \qquad (5)$$

Assuming steady-state conditions

$$\frac{d[\mathrm{BuO\text{-}trap}]/dt}{d[\mathrm{R\text{-}trap}]/dt} = \frac{k_2[\mathrm{trap}]}{k_3[\mathrm{RH}]} + \text{constant}$$

Such experiments appear to be successful with PBN using cyclohexane as the hydrocarbon but the overlap of the spin adduct spectra is serious. Because of this problem the cyclic spin trap, 5,5-dimethylpyrroline 1-oxide (DMPN, as in dimethylpyrrolidine "nitrone" which produces pyrrolidine nitroxide spin adducts), was chosen for these competition experiments. In general the oxy radical spin adduct spectra differ greatly from the alkyl radical spin adduct spectra.[5] Thus, for



DMPN R-DMPN

the *tert*-butoxy and cyclohexyl spin adducts of DMPN: BuO-DMPN, $a^N = 13.11$, $a_\beta{}^H = 7.93$, $a_\gamma{}^H = 1.97$ (1 H); cyclohexyl-DMPN, $a^N = 13.88$, $a_\beta{}^H = 20.86$ G. The same type of kinetics are observed with DBPO in cyclohexane with DMPN as found for PBN. Thus

$$\frac{d[\mathrm{BuO\text{-}DMPN}]/dt}{d[\mathrm{cyclohexyl\text{-}DMPN}]/dt} = \frac{k_2''[\mathrm{DMPN}]}{k_3[\mathrm{RH}]} + \text{constant}$$

The ratio of the rate constants k_2''/k_3 was found to be 4340 at [DMPN] = 0.0015 *M* at 25°. Assuming $k_3 = 1 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$ for cyclohexane,[6] the absolute rate constant of trapping *tert*-butoxy radicals by DMPN at 25° is $5 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$.

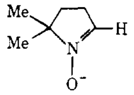
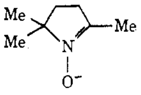
In order to obtain absolute rate constants for trapping *tert*-butoxy radicals by other traps a mixture of DMPN and some other trap was allowed to compete for *tert*-butoxy radicals and the ratio of the concentrations of the two spin adducts monitored as a function of time. Thus

$$\frac{d[\mathrm{BuO\text{-}trap}]/dt}{d[\mathrm{BuO\text{-}DMPN}]/dt} = \frac{k_2[\mathrm{trap}]}{k_2''[\mathrm{DMPN}]}$$

The rate constant ratios for a number of traps are given in Table I. Using the value $k_2'' = 5 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$ for trapping *tert*-butoxy radicals by DMPN absolute rate constants are estimated for a number of nitrones and *tert*-nitrosobutane.

The absolute rate constant for trapping *tert*-butoxy radicals by PBN is about 100× smaller than that found for the unsubstituted *N*-*tert*-butyl nitrone.[9] However, the absolute rate constant for the latter is comparable to that found for DMPN.[10] Substituents have a small effect on the rate of trapping *tert*-butoxy radicals by PBN. The substituent effect on the rate of addition of benzoyloxy radicals to PBN is larger ($\rho = 0.5$).[1]

Table I. Absolute Rate Constants for Spin Trapping *tert*-Butoxy Radicals by Various Spin Traps[a]

Trap	k_2/k_2''	$10^{-6}k_2$, $M^{-1}\ \mathrm{sec}^{-1}$
$CH_2{=}N^+(O^-)CMe_3$	0.5–1	300–500
$C_6H_5CH{=}N^+(O^-)CMe_3$ (PBN)	0.011	5.5
p-NO_2PBN	0.018	9.0
p-ClPBN	0.013	6.5
p-CH_3PBN	0.0068	3.4
p-CH_3OPBN	0.011	5.5
	1	500
	0.042	9
$Me_3CN{=}O$	0.0030	1.5

[a] In benzene at 25°.

Trapping of *tert*-butoxy radicals by *tert*-nitrosobutane is about $1.5 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$. Recently Perkins and Roberts[11] have reported the absolute rate constant for the addition of *tert*-butoxycarbonyl radicals to *tert*-nitrosobutane ($1.1 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$ in di-*tert*-butyl peroxide at 40°). These authors also estimate that the absolute rate constant for the addition of methyl radicals to nitrosobenzene is 10^6–$10^7\ M^{-1}\ \mathrm{sec}^{-1}$ at 65° based on Szwarc's methyl affinity data in the gas phase.[12] More recent absolute rate constants of radical additions to nitroso compounds are available in the gas phase.[13]

$$\mathrm{CD_3\cdot} + \mathrm{CD_3NO} \longrightarrow \mathrm{(CD_3)_2NO\cdot} \qquad 4 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$$

$$\mathrm{CH_3CH_2\cdot} + \mathrm{CH_3CH_2NO} \longrightarrow \mathrm{(CH_3CH_2)_2NO\cdot} \qquad 1.4 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$$

$$\mathrm{CF_3\cdot} + \mathrm{CF_3NO} \longrightarrow \mathrm{(CF_3)_2NO\cdot} \qquad 5.8 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$$

The absolute rate constants for spin trapping appear to fall between 1×10^6 and $5 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$ at room temperature depending on the trap used and to a lesser extent on the radical trapped.

---

(5) E. G. Janzen and J. I-P. Liu, *J. Magn. Resonance*, **9**, 510 (1973); E. G. Janzen, C. A. Evans, and J. I-P. Liu, *ibid.*, **9**, 513 (1973).

(6) Howard[4] has concluded that the hydrogen abstraction by *tert*-butoxy radicals from cyclohexane is close to the mean value estimated by Carlsson and Ingold[7] and by Walling and Kurkov,[8] namely $1 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$ at ambient temperatures.

(7) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **89**, 4885 (1967).

(8) C. Walling and V. P. Kurkov, *J. Amer. Chem. Soc.*, **89**, 4895 (1967).

(9) Spin trapping with *N*-*tert*-butyl nitrone was first reported by G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Amer. Chem. Soc.*, **90**, 7141 (1968).

(10) The absolute rate constant for trapping *tert*-butoxy by 2-phenyl-5,5-dimethylpyrroline *N*-oxide (2-phenyl-DMPN) is about 40× slower than for DMPN (results of Robert L. Eggers in these laboratories).

(11) M. J. Perkins and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 173 (1973).

(12) W. J. Heilman, A. Rembaum, and M. Szwarc, *J. Chem. Soc.*, 1127 (1957).

(13) A. Maschke, B. S. Shapiro, and F. W. Lampe, *J. Amer. Chem. Soc.*, **86**, 1929 (1964); H-S. Tan and F. W. Lampe, *J. Phys. Chem.*, **76**, 3303 (1972); **77**, 1335 (1973).

Edward G. Janzen,* C. Anderson Evans
Department of Chemistry, The University of Georgia
Athens, Georgia 30602

Received August 2, 1973

Pyrolysis of *N*,*N*,*N*-Trimethyl-3-homoadamantylammonium Hydroxide and *N*,*N*-Dimethyl-3-aminohomoadamantane *N*-Oxide. Evidence for Bridgehead Homoadamantene

Sir:

Since the pyrolysis[1] of aliphatic quaternary ammonium hydroxides[2] and amine oxides has been used

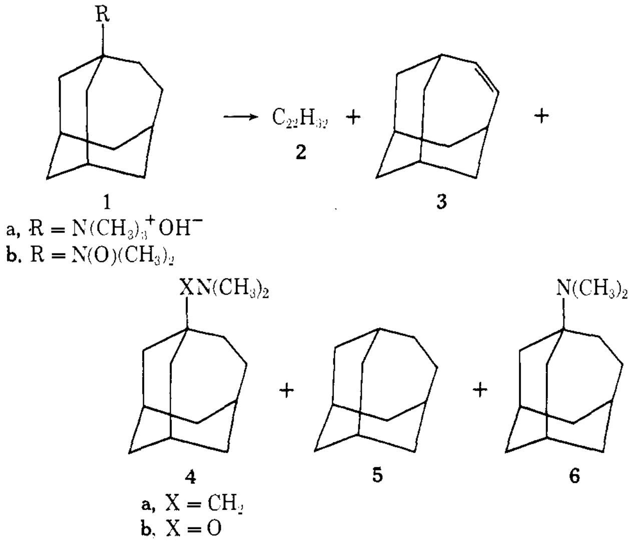
---

(1) A. C. Cope and E. R. Trumbull, *Org. React.*, **11**, 317 (1960).

(2) J. A. Chong and J. R. Wiseman, *J. Amer. Chem. Soc.*, **94**, 8627 (1972), and references cited therein.

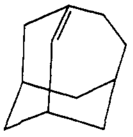
synthetically to yield unrearranged olefins, we decided to investigate this approach with the homoadamantyl system in connection with the question of the limits of Bredt's rule. This report presents evidence for formation of bridgehead homoadamantene, and subsequent dimerization, from pyrolysis of **1a**[3] and **1b**.[3]

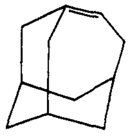
Decomposition of **1a** at 140–175° (1 mm) provided a mixture of bridgehead homoadamantene dimers (10%) (**2**), 4-homoadamantene[4] (0.3%) (**3**), *N*,*N*-dimethyl-3-aminomethylhomoadamantane[5] (43%) (**4a**), homoadamantane[4] (5%) (**5**), and *N*,*N*-dimethyl-3-aminohomoadamantane[3] (11%) (**6**).

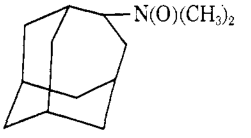


Under the same conditions, **1b** yielded an identical mixture of dimers (9%) (**2**), 4-homoadamantene (5%) (**3**), *N*,*N*-dimethyl-*O*-(3-homoadamantyl)hydroxylamine[5] (25%) (**4b**), homoadamantane (29%) (**5**), *N*,*N*-dimethyl-3-aminohomoadamantane (12%) (**6**), and unidentified material (about 2% of the product).

The dimer mixture (**2**) (mol wt, vapor pressure method: calcd for $C_{22}H_{32}$, 296.5; found, 298) was isolated as a white solid which had sublimed at the higher temperatures to cooler portions of the pyrolysis flask. Product **2**, from both pyrolyses, was found by glpc to consist of four components, a (29%), b (8%), c (3%), and d (60%). Preparative glpc provided material from the two major peaks (a and d), which gave satisfactory elemental analyses. The presence of a cyclobutane structure is supported by laser Raman spectral data for the solid dimers a and d (cyclobutane deformations at 970–980, 935–940, and 731–735 cm^{-1}, and cyclobutane ring puckering at 221–256 cm^{-1}). The Raman spectra compare favorably to that of adamantene dimer. The two investigated dimers displayed essentially identical Raman spectra and glpc retention times in comparison with the corresponding ones from 1-adamantylcarbene.[6] Both the 2- (**7**) and 3- (**8**) isomers are theoretically possible from these eliminations. Since the carbene route would be expected to provide only **8**, the similarity of the dimer mixtures suggests that reaction in our case occurs preferentially *via* **8** or else that **7** is favorably disposed toward rearrangement to **8**.


7


8



9

4-Homoadamantene (**3**) might be produced in Hofmann elimination by base-catalyzed isomerization or hydride shift,[7] and in the Cope pyrolysis by reverse[8] cycloelimination of **8** to **9** which can act as precursor. Note the tenfold increase in yield of **3** from **1b** *vs.* **1a**.

Compounds **4a** and **4b** are formed by Stevens[1,9] and Meisenheimer[1,10] rearrangements, respectively. Two similar mechanistic possibilities[9,10] have been advanced for the nature of the migrating group in the two cases, namely carbanion and radical. The radical[10] route appears to be favored in the Meisenheimer rearrangement. These represent unusual rearrangements since we have found no prior examples involving migration of a secondary or tertiary group. Compound **4a** was synthesized *via* an alternate route from 3-homoadamantanecarboxamide[3] by $LiAlH_4$ reduction followed by methylation with formaldehyde–formic acid.

Formation of **5** is analogous to the generation of neopentane as a by-product in the Stevens rearrangement of *N*,*N*,*N*-trimethylneopentylammonium iodide.[11] Apparently, the reactive intermediates can separate to some extent with subsequent abstraction of a proton[11] or a hydrogen atom.

Compound **6** is probably formed from **1a** *via* S$_N$2 attack by hydroxide ion. Recent evidence[8] indicates that *N*,*N*-dimethylhydroxylamine, formed from elimination, can reduce the amine oxide to the corresponding tertiary amine. This is a plausible rationalization for the formation of **6** from **1b**.

Another approach to bridgehead homoadamantene *via* ester pyrolysis is presented elsewhere.[12]

Acknowledgment. We thank the National Science Foundation for support of this work, Dr. K. L. Watters for assistance with laser Raman spectra, Dr. G. B. Gill and Dr. Z. Majerski for samples of 4-homoadamantene, and G. Karas for molecular weight determinations.

---

(3) E. I. du Pont de Nemours & Co., Neth. Appl. 6404755 (1964); *Chem. Abstr.*, **63**, 6887 (1965).

(4) R. M. Black and G. B. Gill, *J. Chem. Soc. C*, 671 (1970); Z. Majerski, S. H. Liggero, and P. v. R. Schleyer, *Chem. Commun.*, 949 (1970).

(5) Satisfactory elemental analysis and spectra were obtained for this compound.

(6) M. Fărcaşiu, D. Fărcaşiu, M. Jones, Jr., and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 8207 (1973).

(7) H. Gerlach, T. T. Huong, and W. Müller, *J. Chem. Soc., Chem. Commun.*, 1215 (1972).

(8) R. G. Laughlin, *J. Amer. Chem. Soc.*, **95**, 3295 (1973).

(9) S. H. Pine, *Org. React.*, **18**, 403 (1970).

(10) J. P. Lorand, R. W. Grant, P. A. Samuel, E. M. O'Connell, J. Zaro, J. Pilotte, and R. W Wallace, *J. Org. Chem.*, 38, 1813 (1973).

(11) S. H. Pine, B. A. Catto, and F. G. Yamagishi, *J. Org. Chem.*, **35**, 3663 (1970).

(12) B. L. Adams and P. Kovacic, *J. Chem. Soc., Chem. Commun.*, 1310 (1972).

Benjamin L. Adams, Peter Kovacic*
Department of Chemistry, University of Wisconsin—Milwaukee
Milwaukee, Wisconsin 53201

Received July 6, 1973

Fate of 1-Adamantylcarbene. Evidence for the Formation of the Bridgehead Olefin, 3-Homoadamantene

Sir:

We wish to describe a new method involving carbene ring expansion for the generation of "anti-Bredt" ole-