Mass Spectrometry of Cyclic Organic Peroxides

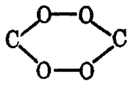
M. BERTRAND, S. FLISZÁR, AND Y. ROUSSEAU

Department of Chemistry, University of Montreal, Montreal, Quebec, Canada

Received September 20, 1967

The mass spectra of some cyclic peroxides are reported; in each case the mode of formation of the major fragment ions are tentatively described. It is concluded that, even in the absence of a molecular ion, peroxides of this type can be identified by mass spectrometry. The heterocycle comprising the four oxygen atoms appears to be less stable than the phenyl ring but more stable than the cyclohexyl ring toward electron impact.

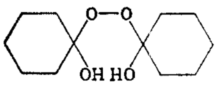
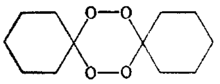
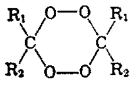
The present work has been undertaken to study the behavior toward electron impact of compounds containing the ring



and is a preliminary examination of the behavior of these compounds in the mass spectrometer. One can hope that such a common structural grouping will trigger similar modes of decomposition and that identification of these peroxides may be obtained by mass spectrometry. The compounds were chosen in order to establish the relative stability of cyclohexyl and phenyl rings as compared to the heterocycle. With aromatic rings in the molecule, a number of substitutions were made on these rings to investigate the influence of the substituted group on the mode of rupture of the oxygenated cycle. Finally, the spectrum of the 1,1′-dihydroxydicyclohexyl peroxide has been taken for comparison.

The peroxides studied are listed in Table I. They will be referred to as **1**–**7** throughout this paper.

TABLE I

1 	1,1′-Dihydroxydicyclohexyl peroxide
2 	Cyclohexanone diperoxide
	
3, $R_1 = R_2 = CH_3$	Acetone diperoxide
4, $R_1 = R_2 = C_6H_5$	Benzophenone diperoxide
5, $R_1 = H$; $R_2 = C_6H_5$	Benzaldehyde diperoxide
6, $R_1 = H$; $R_2 = p\text{-}CH_3C_6H_4$	*p*-Tolualdehyde diperoxide
7, $R_1 = H$; $R_2 = p\text{-}ClC_6H_4$	*p*-Chlorobenzaldehyde diperoxide

Experimental Section

All spectra were taken with a single focusing Hitachi RMU-6D mass spectrometer using the M/G-150 direct introduction system. The compounds, with the exception of compound **4**, which was heated to 80°, have a vapor pressure sufficiently high to eliminate the use of external heat on the sample holder. The ionization chamber was maintained at 220° and the ionizing electrons were accelerated by a 70-V potential.

Peroxides **1**–**5** were prepared and purified as described in the literature.[1–4] Molecular weight measurements of **2** using a Mechrolab osmometer support its structure (mol wt 224, calcd 228.3). Compound **7** (*p*-chlorobenzaldehyde diperoxide) was prepared in the following way.

A mixture of 46 ml of water, 50 ml of ethanol, and 100 ml of concentrated sulfuric acid was cooled to 0°. H_2O_2 (30%, 5 ml) and 10 g of *p*-chlorobenzaldehyde dissolved in 15 ml of ethanol were added to the mixture with vigorous stirring. The latter was kept at 0° overnight after which time 150 ml of cold ethanol was added. The fine needles formed were filtered and worked thoroughly with ethanol and methanol to eliminate all the *p*-chlorobenzoic acid. The white diperoxide obtained (6.8 g) was recrystallized in hot methanol (0.5 l./g): mp 236.5–237.5° dec.

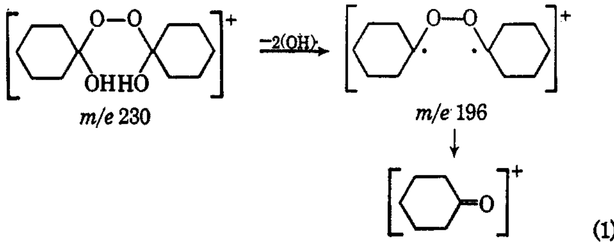
Anal. Calcd for $C_{14}H_{10}O_4Cl_2$: C, 53.69; H, 3.22; Cl, 22.64, active O, 10.2. Found: C, 53.94; H, 3.20; Cl ,22.23; active O, 9.0.

Compound **6** (*p*-tolualdehyde diperoxide) was prepared in a similar way: mp 230–230.5° dec.

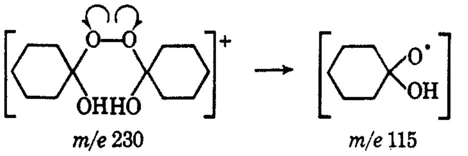
Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92; active O, 11.7. Found: C, 70.67; H, 6.06; active O, 10.9.

Results and Discussion

The spectra of compounds **1**–**7** are given in Figures 1–7, respectively. The spectrum of peroxide **1** (Figure 1) shows no molecular ion at *m/e* 230. Ions of *m/e* 196, the highest *m/e* observed, are believed to be formed by loss of two hydroxyl radicals from the molecular ion. The low intensity of the *m/e* 196 ion (0.16% Σ[5]) may indicate a further fragmentation[6] to yield a cyclohexanone molecule ion (eq 1). A second breakdown pattern consists of an homolytic scission of the O–O bond (eq 2). This process may also give rise to a cyclohexanone molecule ion by elimination of an hydroxyl radical (eq 3).



(1)



(2)

(3)

---

(1) M. Stoll and W. Sherer, *Helv. Chim. Acta*, **13**, 142 (1930).

(2) A. Baeyer and V. Villiger, *Chem. Ber.*, **33**, 858 (1900); **32**, 3632 (1899). We have preferred to dissolve the acetone in 12 volumes of ether before adding it to Caro's reagent dissolved in ether.

(3) C. S. Marvel and V. E. Nichols, *J. Org. Chem.*, **6**, 296 (1941); E. P. Køhler and N. K. Richtmyer, *J. Amer. Chem. Soc.*, **52**, 2038 (1930).

(4) A. Baeyer and V. Villiger, *Chem. Ber.*, **33**, 2484 (1900).

(5) %Σ = per cent of total ionic current recorded.

(6) Peaks of very low intensities have been omitted.

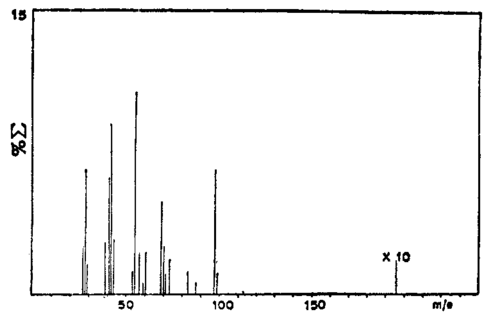


Figure 1.—Spectrum of 1,1′-dihydroxydicyclohexyl peroxide.

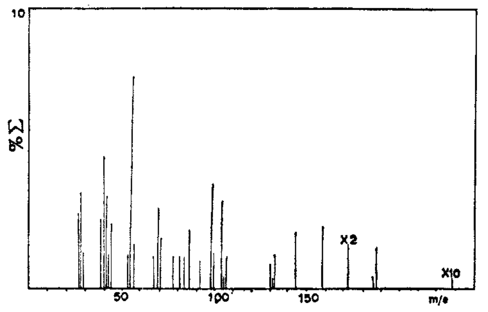
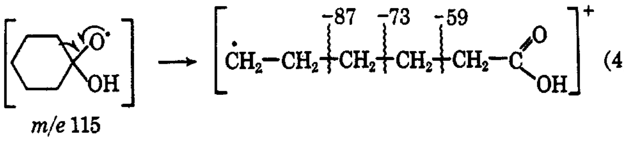


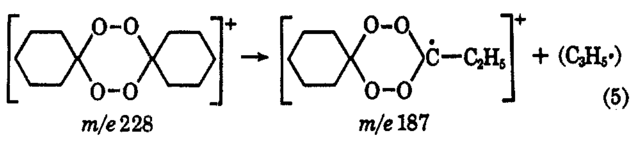
Figure 2.—Spectrum of diperoxide of cyclohexanone.

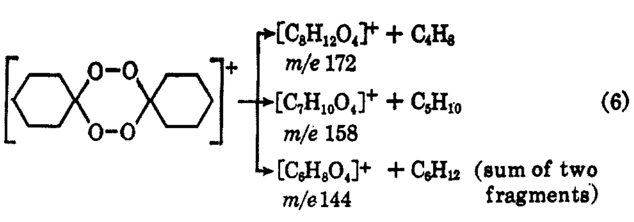
Fragments at *m/e* 83, 70, 69, 55, and 42 probably arise from the cyclohexanone molecule ion,[7] whereas those at *m/e* 45, 59, 60, 73, and 87 may be attributed to the opening of the cyclohexyl ring by an α cleavage to form an open chain (carboxylic acid ion) (eq 4). The



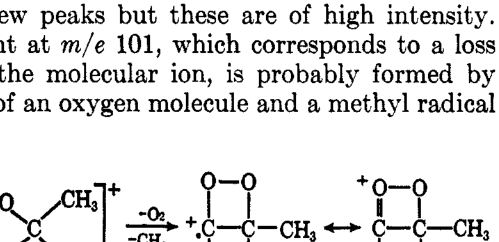
most abundant ion in this series, 3.2% Σ at *m/e* 60, is probably due to the formation of the acetic acid molecule ion, in a rearrangement process which has been postulated for the majority of open-chain carboxylic acids.[8] Furthermore, as in the spectrum of *n*-hexanoic acid, the *m/e* 115 ion is of very low intensity.[9] The molecular ion recorded for compound **2** (Figure 2) is ≈0.2% Σ.

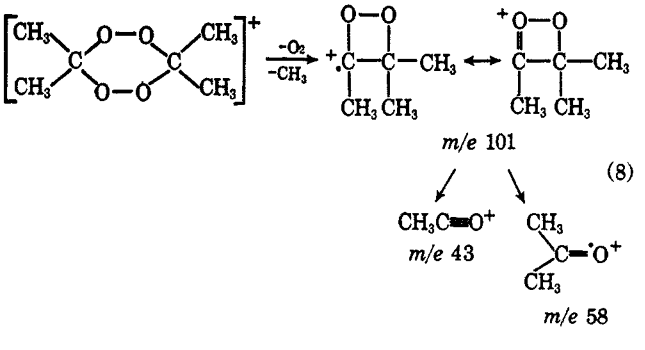
The loss of an allyl or cyclopropyl radical may produce the fragment at *m/e* 187 (eq 5) whereas the elimination of neutral molecules may be responsible for ions at *m/e* 172, 158 and 144 (eq 6). It is of special interest to note that the formation of a $(C_6H_8O_4)^+$ ion necessitates the opening of both cyclohexyl rings. The intensities of these ions are 2.17% Σ for *m/e* 158 and 2.07% Σ for *m/e* 144.





The other process observed would be a scission of the heterocycle itself to give oxygenated ions, of which *m/e* 98 and *m/e* 104 are the most abundant (eq 7). The mass spectrum of compound **3** (Figure 3) is quite different from those of compound **1** and **2** in that it contains very few peaks but these are of high intensity. The fragment at *m/e* 101, which corresponds to a loss of 47 from the molecular ion, is probably formed by elimination of an oxygen molecule and a methyl radical (eq 8).





A small number of high-intensity fragments are also found in the mass spectrum of the benzophenone diperoxide (Figure 4). These fragments have been identified as the benzophenone molecule ion at *m/e* 182, the

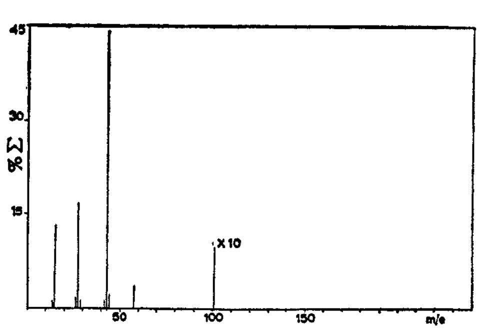


Figure 3.—Spectrum of diperoxide of acetone.

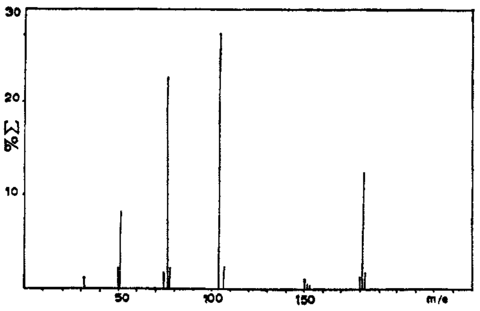


Figure 4.—Spectrum of diperoxide of benzophenone.

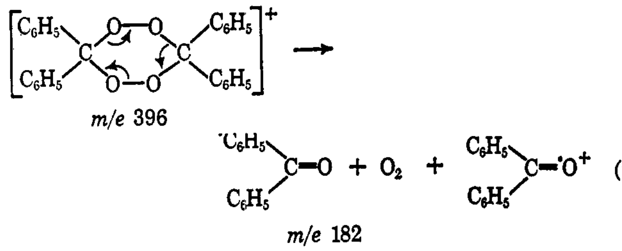
---

[7] J. H. Beynon, "Mass Spectrometry and its Application to Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960, pp 358–359.

[8] See ref 7, pp 372–373.

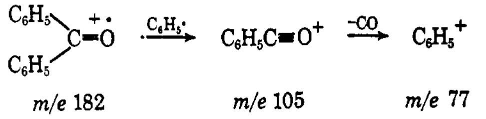
[9] American Petroleum Institute, Research Project 44, No. 664.

benzoylium ion at *m/e* 105, and the phenyl ion at *m/e* 77. The *m/e* 32 ion is attributed to O_2^+ which is probably formed by the cracking pattern in eq 9 with



(9)

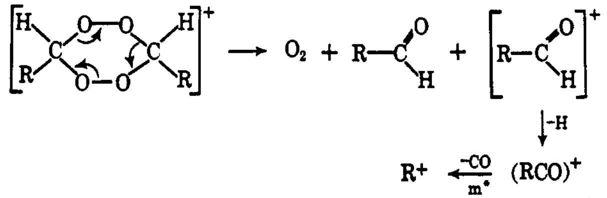
the positive charge remaining on any of these three fragments. This process of ring opening appears to predominate as the peaks at *m/e* 105, 77, and 51 are probably due to the further decomposition of the benzophenone molecule ion[10] (eq 10). In this compound, the



(10)

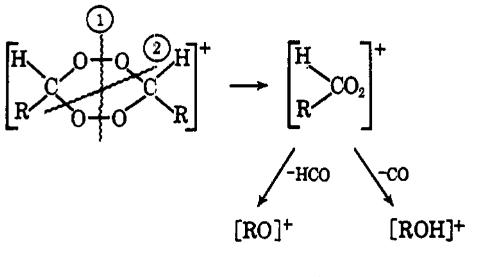
fragmentation pattern does not seem to involve an intermediate similar to the one proposed for compound **3**. Furthermore, it is interesting to note that the presence of an ion at *m/e* 32 coincides with the disappearance of an intermediate similar to the one recorded for compound **3**.

Compounds **5**, **6**, and **7** appear to decompose *via* two main reaction sequences. The first one proceeds by elimination of an oxygen molecule as indicated in eq 11.



(11)

The second path involves a rupture of the heterocycle to produce the half molecular ion (eq 12). R is, respectively, C_6H_5, $C_6H_4CH_3$, and C_6H_4Cl for compounds **5**, **6**, and **7**.



(12)

In eq 12, the initial splitting of the molecule can occur in one of two ways. Unfortunately, the method of preparation of these compounds does not permit useful isotopic labeling of the oxygen atoms within the molecule and hence further investigation of this initial split was not possible. The rearrangement process proposed for the formation of the phenol ion is similar to the one observed in solution.[11]

For peroxides **5**, **6**, and **7**, eq 11 seems to be predominant. The elimination of CO from the $[RCO]^+$ ion is indicated by the presence of metastable ions[12] at *m/e* 56.5, 69.5, and 88.7 for compounds **5**, **6**, and **7**, respectively.

For compound **5**, eq 11 explains peaks at *m/e* 106, 105, 77, 51, and 32 which may be attributed to $(C_6H_5CHO)^+$, $(C_6H_5CO)^+$, $(C_6H_5)^+$, $(C_4H_3)^+$, and $(O_2)^+$, respectively. With this compound the O_2 fragment may retain the charge. The $C_4H_3^+$ ion is formed by elimination of a C_2H_2 from $C_6H_5^+$, which is indicated by a metastable peak at *m/e* 33.8. Equation 12 explains peaks at *m/e* 122, 94, 93, 66, and 65. The $C_6H_5O^+$ ion is unlikely to be formed by elimination of an hydrogen atom from $C_6H_6O^+$ as phenol is known not to undergo this process to any large extent. In fact, the 93/94 peak ratio in the mass spectrum of phenol is very small,[13] whereas in this case it is approximately 1.0. It is therefore probable that the $C_6H_5O^+$ ion would form in a rearrangement process of the ion at *m/e* 122 by elimination of an HCO radical. Furthermore, there is little doubt as to the identity of the $C_6H_5O^+$ ion for the *m/e* 93 peak, as a metastable peak was observed at *m/e* 45.5, which can be attributed to the established transition[14]

$$\underset{m/e\ 93}{(C_6H_5O)^+} \longrightarrow \underset{m/e\ 65}{(C_5H_5)^+} + CO$$

Finally, the peaks at *m/e* 65 and 66 may also arise by elimination of HCO or CO from $(C_6H_6O)^+$.

For compound **6**, the intensity recorded for O_2^+ is of the same order of magnitude as those of compounds **4** and **5**. Equation 11 explains peaks at *m/e* 120, 119, 91, and 65, the latter arising by elimination of C_2H_2 from $(C_7H_7)^+$ as indicated by a metastable peak at *m/e* 46.5. Equation 12 would lead to peaks at *m/e* 136, 107, and 108. Loss of CO molecule from *m/e* 107 would then result in a peak at *m/e* 79. The presence of an *m/e* 79 fragment in the spectrum of methyl anisole has also been explained by the loss of a neutral CO molecule from $(CH_3C_6H_4O)^+$.[14a] The intensities of the major peaks found for this compound are similar to those found for the corresponding fragments in compound **5**. Figure 7 shows that the spectrum of the *p*-chlorobenzaldehyde diperoxide is similar to that of compounds **5** and **6**.

Equation 11 is suggested by the fragments at *m/e* 32, 140, 139, 111, and 75, the latter arising by elimination of HCl from $C_6H_4Cl^+$. Equation 12 can explain the ions at *m/e* 156, 128, and 127. That these ions contain one atom of chlorine is shown by the ratio of peaks at *m/e* 156 and 158, 128 and 130, 127 and 129.

Conclusion

Peroxides **1** and **3** have characteristic spectra and are therefore easily recognizable. The mass spectrum of compound **2** exhibits a larger number of peaks that may arise from any of a number of parallel processes. However, the presence of a molecular ion renders identification quite feasible. Compounds **4**–**7** have similar modes of fragmentation involving elimination of oxygen

---

[10] F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966, p 116.

[11] P. S. Bailey, *Chem. Rev.*, **58**, 952 (1958).

[12] R. I. Reed, "Applications of Mass Spectrometry to Organic Compounds," Academic Press Inc., London, 1966, p 196.

[13] See ref 7, p 382.

[14] (a) C. S. Barnes and J. L. Occolowitz, *Australian J. Chem.*, **16**, 219 (1963); (b) S. Meyerson, I. Puskas, and E. K. Fields, *J. Amer. Chem. Soc.*, **88**, 4974 (1966).

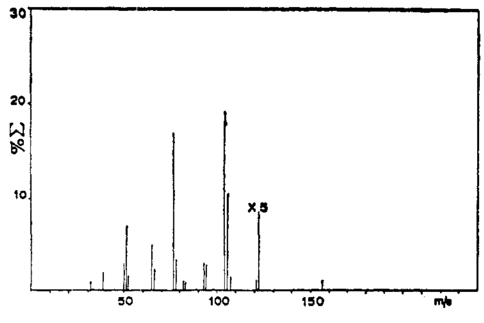


Figure 5.—Spectrum of diperoxide of benzaldehyde.

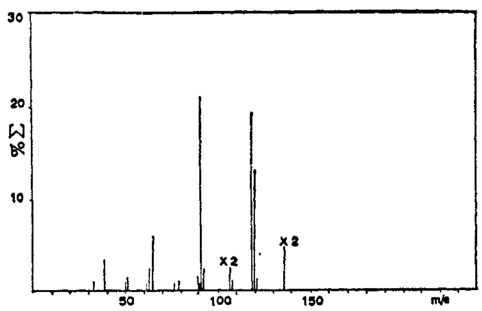


Figure 6.—Spectrum of diperoxide of *p*-tolualdehyde.

and, from the observed fragment ions, it is possible to build up the parent molecule. Furthermore, the spectra of compound **5**, **6**, and **7** exhibit fragment ions corresponding to half the molecular weight of the parent molecule. These three compounds all have hydrogen atoms attached directly to the two carbon atoms of the heterocycle. This implies that the hydrogen atom favors a competing process which leads to the formation of a half molecular ion.

The relative abundance of the half molecular ion expressed in $\%\ \Sigma$ in each case is 2.7, 2.5, and 0.72 for compounds **5**, **6**, and **7**, respectively. Thus the chlorinated phenyl group, by decreasing the electron density at the oxygen, appears to inhibit, to a certain extent, the hydrogen atom migration.

The deactivating effect of chlorine is also apparent from a consideration of the intensity of the O_2^+ ion in the spectra of compounds **4**–**7**. The abundance of the *m/e* 32 ion is 3.9% Σ for peroxide **7**, whereas it is about one-quarter of this value for peroxides **4**, **5**, and **6**. Accordingly the intensity of $(ClC_6H_4C{\equiv}O)^+$ in the spectrum of compound **7** is only 10.6% Σ as compared to 27.5% Σ, 18.7% Σ, and 19.3% Σ for the corresponding carbonyl fragments in the spectra of compounds **4**, **5**, and **6**. This is in agreement with McLafferty's conclusion that the chlorinated fragments retain the positive charge less readily than the unchlorinated fragments.[15]

Depending upon the particular process of decomposition, the aromatic ring in the peroxides which have been studied appears to be more stable toward electron impact than does the six-membered ring containing four oxygen atoms. This is illustrated in Figures 5–7. However, the interpretation of the spectrum of compound **2** leads to the conclusion that the cyclohexyl ring is less stable than the heterocycle toward electron bombardment. The proposed fragmentation process does involve the rupture of the cyclohexyl rings.

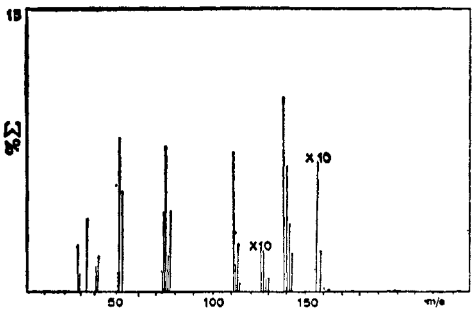


Figure 7.—Spectrum of diperoxide of *p*-chlorobenzaldehyde.

The unstable nature of these compounds raises the question as to whether the recorded spectra are really those of the peroxides and not the spectra of their decomposition products. One indication that thermal decomposition does not occur to any large extent is the presence of a molecular ion for compound **2**; especially since this peroxide is thermally less stable (mp 130–132°) than peroxides **4**–**7** which have melting points above 200°. A second indication for the nonoccurrence of thermal decomposition was obtained by the intentional decomposition of peroxide **4** on metal surfaces. In these experiments the compound was introduced into the mass spectrometer *via* the standard metal inlet system and the consecutive spectra were taken as the inlet was heated slowly. Carbon dioxide, benzene, and water were the only products detected, whereas these products do not contribute significantly to the spectrum of compound **4**.

Finally, it may be considered possible that the O_2^+ ion is indicative of an uncatalyzed decomposition as it is known that in a glass capillary apparatus, the decomposition of these cyclic peroxides yields O_2. Under the condition of uncatalyzed decomposition, the ratio of O_2 to carbonyl compounds formed should be 1:2. After applying approximate corrections for the relative sensitivity of O_2 to the carbonyl compounds, it can be calculated that the O_2^+ molecule ion would be at least five times more intense if it originated exclusively by thermal decomposition of the peroxide. Although this thermal decomposition cannot be ruled out completely, it is believed that it does not occur to any significant extent.

Registry No.—**1**, 2407-94-5; **2**, 183-84-6; **3**, 1073-91-2; **4**, 16204-36-7; **5**, 16204-37-8; **6**, 16204-38-9; **7**, 16204-39-0.

Acknowledgment.—We gratefully acknowledge the support of this research by the National Research Council of Canada, and by the Defence Research Board of Canada.

---

[15] M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 533 (1966).