value indicates that perhaps a carbon center radical might have been generated. Electron transfer in this type of system is not uncommon.[5] However, existence of a "diene–ammoniumyl radical" complex cannot be ruled out since positive assignment would require hyperfine splitting in both sets of ESR signals. We, therefore, took advantage of NMR contact shifts, arising from spin delocalization in the paramagnetic species, for positive identification. According to Pearson and Walter,[6] the ^{1}H NMR of **2** is out of the normal 10-ppm range.[7] Indeed, no signals due to the aromatic protons were detected when **2** was dissolved in CD_2Cl_2 and maintained at -65 °C with Me_4Si as internal reference while negligible shift (<10 Hz) was detected for internal cyclohexane and $CHDCl_2$. However, when 1 equiv of **1** was included in the solution, the signals (aromatic quartet centered at δ 7.19) due to tris(p-bromophenyl)amine (**3**) appeared. What is most revealing is that in the spectrum the diene protons on the B ring (quartet centered at δ 5.55) of **1** were missing while the olefinic protons on the side chain (multiplet centered at δ 5.26) of **1** remained. These results suggest that electron transfer had occurred from **1** to **2** and that the spin responsible for the contact shift in **2** was transferred to the diene moiety of **1**. Chemical shift data from ^{13}C NMR of the aromatic species formed in the mixture of **1** and **2** were found to be identical with those of amine **3** (δ 116.11 (C_1), 125.70 (C_2), 132.53 (C_3), 146.06 (C_4)), arguing against the formation of a charge-transfer complex or an ammonium salt (nitrogen addition on the diene) as being central to the oxygenation reaction. In addition, the signals of the carbons of the diene unit (originally[8] at δ 141.33 (C_5), 120.28 (C_6), 116.42 (C_7), 138.50 (C_8)) were not detected,[9] further confirming our contention that complete electron transfer had occurred with the formation of a four-center diene cation radical, **4**.

Although only "catalytic" quantities of **2** are required for the oxygenation, our results led us to question the "catalyst" function of **2** as suggested by Barton and co-workers.[1,2] Indeed the $\langle g \rangle = 2.004$ ESR signal of a solution of 2:1 ratio of **1:2** in CH_2Cl_2 under 1 atm of O_2, kept at -70 °C, persisted. The $\langle g \rangle = 2.009$ ESR signal of **2** was never regained. In this same experiment, roughly an equivalent quantity of **5** (based on **2**) was detected upon aqueous workup. We therefore proposed the mechanism shown in eq 1–3 for the oxygen–diene reaction as initiated by **2**.
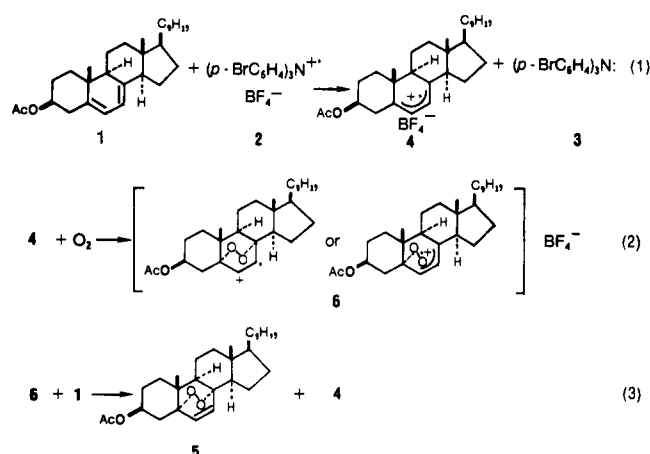
According to this mechanism, the chain-propagating species are **4** and its oxygen adduct **6**.[10,11] We subjected this to a test. Electrolytic oxidation[4b] of **3** is known to generate **2**. Under our conditions, cyclic voltammetry indicated a reversible oxidation wave at 0.3 V.[4b] The blue solution obtained exhibited the same ESR singal as the material prepared by chemical oxidation[1] and also was capable of effecting the "catalytic" oxygenation. Likewise, **1** was electrolytically oxidized[12,13] and the ESR spectrum was identical with that obtained above by electron

transfer, eq 1. A constant current oxidation ($i = 10$ μA cm^{-2}) of an equimolar solution of **1** and the amine **3**, at -78 °C, indicated that, of the two substrates, only **3** was first oxidized as judged by ESR. When this solution (with the current off) was slowly warmed to -70 °C, gradual $\langle g \rangle$ value shift from 2.009 to 2.004 in the ESR spectrum occurred and electron transfer with the formation of **4** was again indicated. Apparently, anodic oxidation of **1** on Pt electrode has considerably higher overpotential than that of **3**.[13] The diene **1** was then electrolytically oxidized at -70 °C in the absence of **3** at a potential of 0.9 V vs. 0.1 N Ag$^+$/Ag electrode. A total of 10.5 C were passed into the solution of **1** (2.23 mmol) in 75 mL of CH_2Cl_2 with 0.17 M $Bu_4N^+ClO_4^-$ as supporting electrolyte under 1 atm of O_2. After aqueous workup, the amount of endoperoxide **5** formed was determined by ^{1}H NMR to be 53% with the rest recovered as the diene **1**. This corresponds to a minimum chain length[14] of 10. These findings demonstrate that **2** is not necessary for the "catalytic" oxygenation except as an initiator and supports the cation-radical chain mechanism as proposed in eq 1–3. Preliminary results indicate that the mechanism (eq 1–3) valid for ammoniumyl radical initiated oxygenation is also representative for the Lewis acid "catalyzed" reactions.[i,2] These and other aspects of diene oxygenation are being investigated and are subjects of a future report.

References and Notes

(1) D. H. R. Barton, G. Leclerc, P. D. Magnus, and I. D. Menzies, *J. Chem. Soc., Chem. Commun.*, 447 (1972); D. H. R. Barton, R. K. Haynes, P. D. Magnus, and I. D. Menzies, *ibid.*, 511 (1974); D. H. R. Barton, R. K. Haynes, G. Leclerc, P. D. Magnus, and I. D. Menzies, *J. Chem. Soc., Perkin Trans. 1*, 2055 (1975).
(2) R. K. Haynes, *Aust. J. Chem.*, **31**, 121, 131 (1978).
(3) R. Tang and F. Mares, unpublished work.
(4) Details on the ESR of this species have never been published. See (a) F. A. Bell, A. Ledwith, and D. C. Sherrington, *J. Chem. Soc. C*, 2719 (1969); (b) E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, *J. Am. Chem. Soc.*, **88**, 3498 (1966).
(5) C. E. H. Bawn, F. A. Bell, and A. Ledwith, *Chem. Commun.*, 599 (1968).
(6) G. A. Pearson and R. I. Walter, *J. Am. Chem. Soc.*, **99**, 5262 (1977).
(7) Chemical shifts are reported in δ relative to internal Me_4Si for both ^{1}H and ^{13}C NMR.
(8) J. W. Blunt and J. B. Stothers, *Org. Magn. Reson.*, **9**, 439 (1977).
(9) Carbons adjacent to the diene unit were also not detected; details of ^{13}C NMR will be discussed in a separate report.
(10) For clarity, only two of the four structures for **6** are presented.
(11) According to this mechanism, the yield of product **5** is dictated by "the molar quantity of starting 1 minus that of **2**", since a molar equivalent of **1** (based on **2**) persists as **4** (or **6**). Therefore, the chain length or the product yield increases as the ratio of **1** to **2** increases. On the other hand, the yield of the product approaches zero as the ratio of **1** to **2** is ≤ 1.
(12) Electrolysis conditions: CH_2Cl_2 solution with 0.03 M substrate, 0.1 M $Bu_4N^+ClO_4^-$, -78 °C, Pt anode vs. 0.1 N Ag$^+$/Ag reference electrode.
(13) Cyclic voltammetry for **1** exhibited an irreversible oxidation wave at $\sim$0.6 V. Irreversible potential waves do not represent true chemical potentials and, therefore, the $E_{1/2}$ values obtained for **1** and **3** cannot be directly compared.
(14) A minimum average chain length of 15 was reported in ref 1.

Reginald Tang,* **Henry J. Yue**
J. Fredrick Wolf, Frank Mares
Chemical Research Center, Allied Chemical Corporation
*Morristown, New Jersey 07960*
Received May 1, 1978

Malonic Anhydride

Sir:

Malonic anhydride[1] is a classic unknown compound. Dehydration of malonic acid does not give the anhydride but leads

instead to carbon suboxide, C_3O_2.[2] Substituted malonic anhydrides may be obtained under dehydrating conditions, but these are polymeric.[3-6] Recently a monomeric diethylmalonic anhydride has been claimed,[7] on the basis of IR absorption at 1980 and 1900 cm^{-1}. However, a four-membered-ring anhydride ought to absorb near 1940 and 1830 cm^{-1}, according to extrapolation from glutaric anhydride (1802, 1761 cm^{-1} in CCl_4) and succinic anhydride (1872 and 1796 cm^{-1} in CCl_4).[8] (Frequencies for malonic imides[9] are in reasonable agreement with those extrapolated from glutarimides and succinimides.)

A preferable approach to malonic anhydrides would avoid dehydration methods and utilize an already formed four-membered ring. Such a method is the ozonolysis of the enol-lactone dimers of ketenes (eq 1). Opening of the molozonide

$$\text{(1)}$$
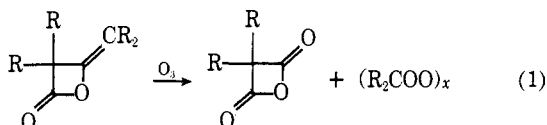
in the other sense—to produce R_2CO and the anhydride oxide—is less likely, since ozonolysis of dihydropyran[10] produces a formate ester and an aldehyde oxide. Indeed, formaldehyde and a small amount of malonic acid, as well as acetic acid, were obtained from ozonolysis of diketene.[11] Likewise, ozonolysis of substituted diketenes leads to aldehydes[11,12] and carboxylic acids[12] which might have arisen from decarboxylation of a malonic acid. However, there are no published reports of this ozonolytic method for synthesizing anhydrides, although anhydrides may have been produced in the ozonolysis of some enol acetates of cyclohexanone.[13,14] We therefore undertook to study the feasibility of this synthetic method.

Ozonolysis of isopropenyl acetate (Aldrich, 1% w/v in dry CH_2Cl_2) at −78 °C produced acetic anhydride, identified in the reaction mixture by its IR and ^1H NMR spectra. An additional ^1H NMR peak at δ 4.99 is attributed to $(CH_2OO)_x$. Ozonolysis of 6-phenyl-5-hydroxy-5-hexenoic acid δ-lactone[15] (10% in CH_2Cl_2), followed by reduction with methyl sulfide, produced benzaldehyde and glutaric anhydride, identified in the reaction mixture by their IR and ^1H NMR spectra. Evaporation of the solvent and recrystallization of the residue confirmed the presence of glutaric anhydride, mp 52.5–53.5 °C (lit.[16] mp 56–57 °C). When the ozonolysis was performed in the presence of an excess of methanol, the ^1H NMR spectrum indicated the presence of glutaric anhydride, but no benzaldehyde, which did appear on reduction with triphenylphosphine. We therefore conclude that ozonolysis of enol esters is a promising method for synthesis of anhydrides.

Ozonolysis of 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid β-lactone (Aldrich, 3% in dry CH_2Cl_2) at −78 °C produced acetone peroxide and dimethylmalonic anhydride, as judged by the following characteristics. The IR spectrum (precooled cells, kept cold with a stream of N_2) showed a strong absorption at 1820 cm^{-1}. This frequency is in good agreement with one of the extrapolated values. No absorption was seen between 1850 and 2000 cm^{-1}. However, the high-frequency mode is expected to be weak in malonic anhydrides since the carbonyls are opposed and the symmetric mode does not change the dipole moment appreciably. Indeed, tetramethyl-1,3-cyclobutanedione shows no high-frequency carbonyl absorption.[17] The ^1H NMR spectrum of the reaction mixture at −30 °C showed several singlets in the δ 1.3–2.1 region, attributed to acetone and acetone peroxide dimers, trimers, etc. There was also a singlet at δ 1.5 attributed to dimethylmalonic anhydride; on warming to ~10 °C, this was replaced by several peaks, including a doublet at δ 1.2 due to isobutyric acid or a derivative. The ^{13}C NMR spectrum at −30 °C showed strong absorption at δ 20.9 (broad, attributed to acetone peroxide) and 17.8, as

well as weaker ones at 59.2 and 169.1, attributed to the methyl, quaternary, and carbonyl carbons, respectively, of dimethylmalonic anhydride. For comparison, the corresponding ^{13}C NMR absorptions of tetramethyl-1,3-cyclobutanedione, the precursor β-lactone, and glutaric anhydride are at δ 18.8, 54.0, and 168.2, respectively.[18] The dimethylmalonic anhydride was further characterized by adding excess aniline, allowing the mixture to warm to room temperature, and isolating an 85% yield of dimethylmalonanilic acid, mp 135.5—137 °C (lit.[19] mp 133 °C). Likewise, reaction with ethanol produced 87% monoethyl dimethylmalonate (IR and ^1H NMR spectra as expected).

Ozonolysis of diketene (Aldrich, redistilled, 3% in CH_2Cl_2) at −78 °C produced formaldehyde peroxide and malonic anhydride, as judged by the following characteristics. The IR spectrum (cooled cells) showed a strong doublet at 1820 and 1830 cm^{-1} and no absorption in the 1850–2000-cm^{-1} region. The ^1H NMR spectrum at −30 °C showed singlets at δ 4.12 and 4.99; the latter, attributed to $(CH_2OO)_x$, was also observed in the ozonolysis of isopropenyl acetate. The ^{13}C NMR spectrum, in $CDCl_3$ at −30 °C, showed a broad peak at δ 100.9 (attributed to formaldehyde oxide), a strong peak at 45.4, and a weaker one at 160.3. These latter are assigned to CH_2 and carbonyl carbons of malonic anhydride; for comparison the corresponding absorptions of $CH_2(OCH_3)_2$, malonic acid, and glutaric anhydride are at δ 94.2, 41.4, and 168.2. The malonic anhydride was further characterized as the monoanilide (72% isolated yield, mp 127–130 °C (lit.[20] 132 °C dec), the monophenyl ester (56%; mp 66–67 °C (lit.[21] mp 65–66 °C), and the monoethyl ester (77%; IR and ^1H NMR as expected, n^{23}_D 1.4245 (lit.[22] n^{19}_D 1.4275)).

Over the course of an hour at −30 °C, the malonic anhydride underwent partial decomposition to CO_2 (δ 124.5 (lit.[18] δ 124.2), *m/e* 44) and ketene (δ 2.24, 193.66 (lit.[23] δ 2.5, 194.0)), which was apparently partially hydrolyzed to acetic anhydride (δ 22.3 (lit.[18] δ 21.9)). When the ozonolysis was performed at 0 °C, ketene could be demonstrated in the effluent O_2 by conversion to acetanilide. Similarly, isobutyranilide could be isolated following ozonolytic generation of dimethylmalonic anhydride. We conclude that a [2 + 2] cycloreversion to CO_2 and a ketene, rather than decarboxylation of malonic acid, is the origin of the carboxylic acids that had previously been observed.[11,12]

In summary, we have prepared the long-sought monomeric malonic and dimethylmalonic anhydrides. The spectral characteristics are in full accord with those expected for these structures. Moreover, *the facility of the decomposition to CO_2 and ketene is strong evidence that we have succeeded in preparing monomeric malonic anhydride, and that previous claims are erroneous.*

References and Notes

(1) *Chemical Abstracts* name: 2,4-oxetanedione.
(2) O. Diels and G. Meyerheim, *Ber.*, **40**, 355 (1907).
(3) A. Einhorn and H. von Diesbach, *Ber.*, **39**, 1222 (1906); A. Einhorn and H. von Diesbach, *Justus Liebigs Ann. Chem.*, **359**, 145 (1908).
(4) H. Staudinger and E. Ott, *Ber.*, **41**, 2208, 3829 (1908); H. Staudinger, F. Felix, and H. Harder, *Helv. Chim. Acta*, **8**, 306 (1925).
(5) A. C. Duckworth, *J. Org. Chem.*, **27**, 3146 (1962).
(6) W. Adam and J. W. Diehl, *J. Chem. Soc., Chem. Commun.*, 797 (1972).
(7) G. Resofszki, M. Huhn, B. Hegedüs, P. Dvortsák, and K. Kálóy, *Tetrahedron Lett.*, 3091 (1975).
(8) H. K. Hall, Jr., and R. Zbinden, *J. Am. Chem. Soc.*, **80**, 6428 (1958).
(9) A. Ebnöther et al., *Helv. Chim. Acta*, **42**, 918 (1959).
(10) Q. E. Thompson, *J. Org. Chem.*, **27**, 4498 (1962).
(11) C. D. Hurd and J. W. Williams, *J. Am. Chem. Soc.*, **58**, 962 (1936); C. D. Hurd and C. A. Blanchard, *ibid.*, **72**, 1461 (1950).

(12) C. M. Hill, M. E. Hill, H. I. Schofield, and L. Haynes, *J. Am. Chem. Soc.*, **74**, 166 (1952).
(13) U. Schmidt and P. Grafen, *Justus Liebigs Ann. Chem.*, **656**, 97 (1962).
(14) J. Champagne, H. Favre, D. Vocelle, and I. Zblkowski, *Can. J. Chem.*, **42**, 212 (1964).
(15) H. M. Walton, *J. Org. Chem.*, **22**, 1161 (1957).
(16) D. Mol, *Recl. Trav. Chim. Pays-Bas*, **26**, 373 (1907).
(17) Sadtler Standard Spectra No. 16350.
(18) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic, New York, N.Y., 1972; L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley-Interscience, New York, N.Y., 1972; G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972.
(19) W. H. Perkin, *J. Chem. Soc.*, **83**, 1217 (1903).
(20) L. Rüghelmer, *Ber.*, **17**, 736 (1884).
(21) N. S. Wulfson, *J. Gen. Chem. USSR*, **19**, a369 (1949).
(22) F. Marguery, *Bull. Soc. Chim. Fr.*, [3] **33**, 541 (1905).
(23) J. Firl and W. Runge, *Z. Naturforsch., B*, **29**, 393 (1974).

Charles L. Perrin,* Thomas Arrhenius

*Department of Chemistry
University of California, San Diego
La Jolla, California 92093*

Received June 13, 1977

Figure 1. Excitation spectrum of the $C_6F_6^+$ fluorescence. The 0-0 emission at 21 372 cm^{-1} was monitored.

Laser Fluorescence Spectra of the Hexafluorobenzene Cation in Solid Argon

Sir:

While an impressive array of unstable molecules and free radicals have been studied by the matrix isolation technique, the list of ions studied this way is rather restricted. Since the identification of C_2^- by Milligan and Jacox,[1] numerous small ions have been observed[2-9], mainly using infrared absorption spectroscopy. Particularly desirable would be studies of the electronic emission and excitation spectra of molecular ions. Since the totally symmetric modes are generally active in allowed electronic transitions, they should conveniently complement infrared observations and provide information about the ion's vibrational structures both in the ground and excited electronic states.

The fluorobenzene cations are an interesting group of polyatomic organic ions, which were recently observed in the gas phase emission using electron impact ionisation[10,11]. The first ionizing transitions in these species are conveniently located[12] near 9.5 eV, and are probably further red shifted in the solid.[13] They should thus easily be generated by the Lyman α radiation containing 10.2 eV of energy. In the present manuscript we report the observation of the emission and excitation spectra of $C_6F_6^+$ in solid argon. We deposited mixtures of the parent C_6F_6 with the Ar gas ($\approx$1:2000) on a sapphire substrate cooled to 4.2 K and photolyzed simultaneously with the 1216-Å radiation. Excitation of the photolyzed deposits with the N_2 pumped dye laser results in an intense $C_6F_6^+$ fluorescence. Its gas phase lifetime[11] of 48 ns is only moderately shortened in the solid to $\approx$20 ns, and the fluorescence probably again occurs with near-unity quantum efficiency. A typical excitation spectrum of the $C_6F_6^+$ fluorescence is shown in Figure 1. The appearance of the emission spectrum is independent of the vibrational level used for excitation and implies an efficient and complete vibrational relaxation in the upper electronic state.

Molecular ions are known to interact with the rare gas solids to a considerably larger degree than neutral species. Actually, solvation energies of a variety of cations in solid Ar were reported[13] to be of the order of 2 eV. It is gratifying that in spite of this strong interaction one can obtain mainly sharp zero phonon lines and a well-resolved vibronic structure. The line shapes of optical transitions in the solid environment are determined by the differences in the guest–host interaction potentials between the initial and final states. Apparently the interaction with the solid, while rather large in both the ground
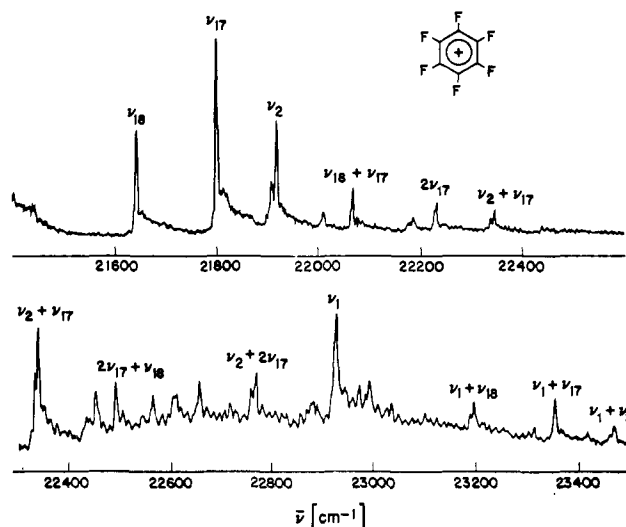
and excited electronic state, does not change appreciably during the electronic transition. In view of this strong interaction between ions and the solid host it is of particular interest to establish to what extent are the observed spectra representative of the free species. The recent observation of the gas phase $C_6F_6^+$ spectra[14] makes such a comparison possible. The electronic origin undergoes a moderate 234-cm^{-1} red shift from its gas phase position, and all the observed vibrational frequencies are within experimental error of the gas phase values. It appears that matrix isolation studies can provide useful spectroscopic information even for ionic species.

Vibrational analysis of the $C_6F_6^+$ data leads to conclusions similar to those derived from our recent $C_6F_3H_3^+$ gas phase work.[15] Some 30 vibronic bands are observed in our excitation spectrum and most of them can be interpreted in terms of vibrational frequencies of 270, 428, 547, and 1561 cm^{-1} and their overtones and combinations. The 1561-cm^{-1} frequency is clearly the totally symmetric C–F stretch, ν_1. As could be expected, it is shifted in the positively charged species upward from the 1498-cm^{-1} value in the neutral molecule.[16] The 547-cm^{-1} frequency can likely be attributed to the ring "breathing" mode, ν_2, which occurs at 558 cm^{-1} in the parent.[16]

If the molecule has the full D_{6h} symmetry in both states one might expect only the two totally symmetric vibrations to occur strongly. It is clear from the spectrum in Figure 1 that several other vibrational modes appear with comparable intensities. The $C_6F_6^+$ cation thus seems to be distorted and have symmetry lower than D_{6h} in at least one of the two electronic states, probably due to Jahn–Teller distortion of the degenerate $^2E_{1g}$ ground state[17]. The low-frequency 270-cm^{-1} vibration and the 428-cm^{-1} frequency are therefore tentatively assigned to the E_{2g} in plane deformation vibrations ν_{17} and ν_{18}, which occur at 445 and 272 cm^{-1}, respectively,[16] in the parent C_6F_6. The observed vibronic bands and their tentative assignments are summarized in Table I.

Less vibrational information is obtained from the study of the emission spectra. Besides the 0-0 band, only three other relatively weak and sharp bands superimposed upon a broad continuum are seen and give values of 300, 444, and 557 cm^{-1} for the ground-state vibrational frequencies. These are tentatively assigned to ν_{18}, ν_{17}, and ν_2, respectively. The broader appearance of the emission spectra may be due to the degeneracy of the ground electronic state and the resulting high density of states.

The work presented here clearly indicates that a considerable amount of useful information can be derived from the