formed on a Perkin-Elmer 240 elemental analyzer. The NMR spectra were taken with a Jeol C-60-XL recording spectrometer with tetramethylsilane as an internal standard and the chemical shifts are expressed in δ values. The ir spectra were taken with a Jasco Model IRA-1 grating infrared spectrophotometer.

Epoxidation of 1. A solution of **1** (200 mg) and *m*-chloroperbenzoic acid (170 mg) in chloroform (20 ml) was stirred for 24 hr at room temperature. Then chloroform (30 ml) was added to the reaction mixture and the solution was washed with a saturated sodium bicarbonate solution followed by water (20 ml). Drying over anhydrous sodium sulfate followed by evaporation of the chloroform solution gave **3** (100 mg): mp 209–211°; ir (KBr) 1860, 1840, and 1780 cm^{-1} (anhydride); NMR ($CDCl_3$) δ 6.30 (2 H, t, J = 4.5 Hz), 3.55 (2 H, d, J = 2.3 Hz), 3.35 (2 H, m), 3.04 (2 H, t, J = 1.5 Hz), and 2.43 (2 H, m).

Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.07; H, 4.72.

Epoxidation of 2. A solution of **2** (1.0 g) and *m*-chloroperbenzoic acid (700 mg) in chloroform (30 ml) was stirred for 24 hr at room temperature. Work-up as described above and evaporation of the solvent followed by silica gel chromatography using chloroform gave **4** (800 mg) and **5** (20 mg).

4: mp 83–84° (*n*-hexane); ir (KBr) 1740 and 1720 cm^{-1}; NMR ($CDCl_3$) δ 6.28 (2 H, t, J = 4.5 Hz), 3.55 (6 H, s, COOMe-2), 3.50 (2 H, m), 3.00 (2 H, m), 2.86 (2 H, s), and 2.30 (2 H, m); MS *m/e* 264 (M^+) and 233 (M − 31).

Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.62; H, 6.10. Found: C, 63.90; H, 6.04.

5: mp 263–265° (benzene–*n*-hexane); ir (KBr) 1740 cm^{-1}; NMR ($CDCl_3$) δ 6.50 (4 H, t), 3.60 (12 H, s), 3.18 (4 H, m), 3.02 (4 H, s), 2.68 (4 H, m), and 1.93 (4 H, m); MS *m/e* 528 (M^+) and 497 (M − 31).

Anal. Calcd for $C_{28}H_{32}O_{10}\cdot C_6H_6$: C, 67.31; H, 6.31. Found: C, 67.25; H, 6.24.

Acid-Catalyzed Reaction of 4. General Procedure. A solution of **4** in acidic condition was kept at 0° or room temperature for 2 days. After evaporation of the solvent, the residue was recrystallized from benzene to give **6**: mp 167–169°; ir (KBr) 3400 and 1740 cm^{-1}; NMR ($CDCl_3$) δ 4.75 (1 H, dd, J = 3.0 and 6.75 Hz), 4.06 (1 H, s), 3.68 (3 H, s, COOMe), 3.58 (1 H, m), 3.18 (1 H, dd, J = 4.5 and 6.75 Hz), 2.3–2.9 (6 H, m), 2.20 (broad s, 1 H, exchangeable by D_2O).

Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.62; H, 5.94.

The yields of **6** under various conditions are summarized in Table I.

Acetylation of 6. A. A solution of **6** (300 mg) in acetic anhydride (15 ml) was refluxed for 6 hr. After evaporation of the solvent, the residue was recrystallized from benzene–*n*-hexane to give **7** (345 mg); mp 158–159°; ir (KBr) 1790 and 1720 cm^{-1}; NMR ($CDCl_3$) δ 4.77 (1 H, dd, J = 3.0 and 8.0 Hz), 4.57 (1 H, s), 3.70 (3 H, s, COOMe), 3.40 (1 H, m), 3.20 (1 H, t, J = 5.0 Hz), 3.50–3.85 (6 H, m), and 2.10 (3 H, s, $COCH_3$).

Anal. Calcd for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 61.90; H, 5.52.

B. A solution of **6** (100 mg) in acetic anhydride (0.7 ml) and pyridine (2 ml) was kept at room temperature for 3 days. The reaction mixture was added with water and then extracted with chloroform. The extract was washed with dilute hydrochloric acid followed by aqueous sodium bicarbonate and finally with water. Evaporation of the solvent gave **7** (90 mg).

Reaction of 6 with *p*-Nitrobenzoyl Chloride. A solution of **6** (240 mg) and *p*-nitrobenzoyl chloride (360 mg) in pyridine (10 ml) was stirred for 2 hr at room temperature. Work-up as described above gave **8** (370 mg): mp 200–203° (benzene–chloroform); ir (KBr) 1765, 1750, 1720, 1530, and 1350 cm^{-1}; NMR ($CDCl_3$) δ 4.85 (1 H, s), 4.80 (1 H, dd, J = 3.0 and 8.0 Hz), 3.65 (3 H, s, COOMe), 3.50 (1 H, m), 3.23 (1 H, t, J = 5.0 Hz), 2.5–3.0 (6 H, m), 8.08 (2 H, d, J = 10.0 Hz), and 8.28 (2 H, d, J = 10.0 Hz).

Anal. Calcd for $C_{20}H_{17}O_8N$: C, 60.15; H, 4.29; N, 3.51. Found: C, 60.17; H, 4.32; N, 3.31.

Reaction of 6 with *p*-Nitrobenzenesulfonyl Chloride. A solution of **6** (250 mg) and *p*-nitrobenzenesulfonyl chloride (340 mg) in pyridine (10 ml) was stirred for 1 day at room temperature. Work-up gave **9** (401 mg): mp 202–203° (benzene–*n*-hexane); ir (KBr) 1770, 1730, 1540, 1370, and 1350 cm^{-1}.

Anal. Calcd for $C_{19}H_{17}O_9NS$: C, 52.52; H, 3.93; N, 3.21. Found: C, 52.47; H, 3.99; N, 3.12.

Reaction of 6 with Tosyl Chloride. A solution of **6** (80 mg) and tosyl chloride (100 mg) in pyridine (10 ml) was stirred for 2 days at room temperature. Work-up gave **10** (139 mg): mp 138–140° (benzene–*n*-hexane); ir (KBr) 1770, 1740, 1360, and 1180 cm^{-1}.

Anal. Calcd for $C_{20}H_{20}SO_7$: C, 59.39; H, 5.00. Found: C, 59.45; H, 5.08.

Hydrolysis of 6. A. A solution of **6** (300 mg) in 50% sulfuric acid (20 ml) was kept at 90° for 5 hr. After neutralization with 10% sodium hydroxide followed by acidification with 10% hydrochloric acid, the solvent was evaporated under reduced pressure. The resulting residue was extracted with hot acetone. Evaporation of the solvent gave **11** (178 mg); mp 220–222° (acetone–benzene); ir (KBr) 1775, 1710, and 3400 cm^{-1}.

Anal. Calcd for $C_{12}H_{12}O_5$: C, 61.01; H, 5.12. Found: C, 61.16; H, 5.17.

B. A suspension of **6** (970 mg) in 10% sodium hydroxide (20 ml) was stirred for 2 hr at room temperature. After acidification with hydrochloric acid followed by evaporation of the solvent, the resulting residue was extracted with acetone. Evaporation of the solvent gave **11** (806 mg).

Esterification of 11. A. A solution of **11** (400 mg) in methanol (10 ml) and a trace amount of sulfuric acid was refluxed for 4 hr. After evaporation of the solvent, the reaction mixture was added to water and the product was extracted with chloroform. Drying with sodium sulfate followed by evaporation of the solvent gave **6** (430 mg).

B. To a suspension of **11** (200 mg) in ether (20 ml), an excess of diazomethane in ether (50 ml) was added. The reaction mixture was stirred for 1 day. The resulting residue was recrystallized from benzene to give **6** (210 mg).

Registry No.—**1**, 51447-09-7; **2**, 35211-83-7; **3**, 54712-51-5; **4**, 54677-36-0; **5**, 54773-74-9; **6**, 54677-37-1; **7**, 54677-38-2; **8**, 54677-39-3; **9**, 54677-40-6; **10**, 54677-41-7; **11**, 54677-42-8; *m*-chloroperbenzoic acid, 937-14-4; *p*-nitrobenzoyl chloride, 122-04-3; *p*-nitrobenzenesulfonyl chloride, 98-74-8; tosyl chloride, 98-59-9.

References and Notes

(1) Molecular Design. XXII. Part XXI of this series: T. Sasaki, K. Kanematsu, and T. Kataoka, *J. Org. Chem.*, **40**, 1201 (1975).
(2) T. Sasaki, K. Kanematsu, and A. Kondo, *J. Org. Chem.*, **39**, 2246 (1974).
(3) T. Sasaki, K. Kanematsu, A. Kondo, and Y. Nishitani, *J. Org. Chem.*, **39**, 3569 (1974).
(4) T. Sasaki, K. Kanematsu, and A. Kondo, *Tetrahedron*, in press.
(5) Recently bromination of acid-catalyzed cleavage of epoxide was discussed from a point of intermediacy of cation: B. Giese, *Chem. Ber.*, **107**, 868 (1974).
(6) (a) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Justus Liebigs Ann. Chem.*, **560**, 1 (1948); (b) A. C. Cope, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **80**, 5504 (1958).
(7) J. G. Buchanan and H. Z. Sable in "Selective Organic Transformations", Vol. 2, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N.Y., 1972, p 8.

Specific Oxygen-18 Labeling and Mass Spectral Fragmentation of 2-Pyrone. CO vs. CS Loss on Fragmentation of Sulfur Analogs of 2-Pyrones

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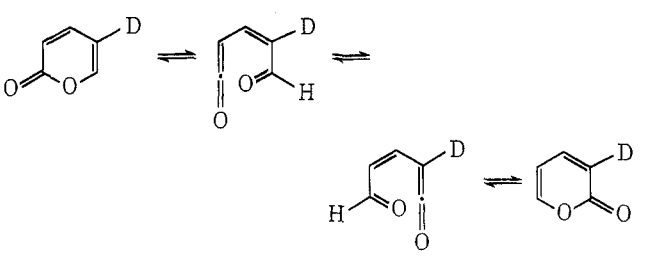
The discovery of a pyrolytic 2-pyrone (**1**) rearrangement[1] (Scheme I) which renders the 3 and 5 positions equivalent

Scheme I

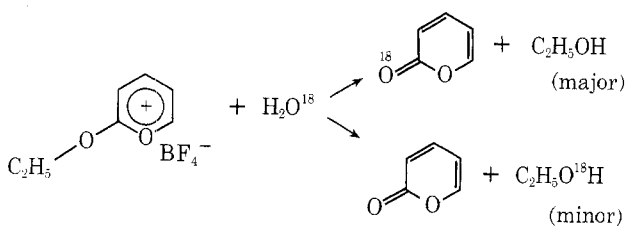


while maintaining the uniqueness of the 4 and 6 positions suggested a possible explanation for the previously observed[2] mass spectral deuterium distributions among the fragments from the four monodeuterated 2-pyrones. These distributions indicate that, at some stage, the 3 and 5 positions of **1** become equivalent, while the 4 and 6 positions remain unique. Whether the equivalence stems from ion symmetry or dynamic scrambling could not be ascertained, nor could it be determined whether it is attained in the $C_5H_4O_2$ molecular ion(s) or the C_4H_4O daughter ion(s). Because the thermal rearrangement scrambles the two oxygen atoms as well as the 3 and 5 positions of **1**,[3] it should be possible to learn whether a similar rearrangement is operative during electron impact induced fragmentation simply by noting the isotopic distribution among the fragments of 2-pyrone labeled specifically with oxygen-18.

Results and Discussion

Labeling of 2-pyrone with oxygen-18 was accomplished by hydrolysis of 2-ethoxypyrylium fluoroborate[4] with oxygen-18-enriched water (Scheme II). The extent of labeling

Scheme II



was determined by mass spectrometry. To minimize the possibility that thermal scrambling in the spectrometer inlet system might precede fragmentation, the labeled samples were adsorbed onto charcoal and directly loaded into the direct oven lock inlet system, which was maintained at 20°. The ion source temperature was 150°. Because M + 1 and M + 2 peaks were slightly larger in the spectrum of unlabeled 2-pyrone than was predicted on the basis of natural isotopic abundances, the oxygen-18 enrichment was found by subtracting the intensities of ions at *m/e* 98 and 100 in the spectrum of unlabeled 2-pyrone from those of labeled 2-pyrone.

Labeled 2-pyrone thus prepared with 30.0% oxygen-18-enriched water contains 24.5% oxygen-18 (Table I). No doubly labeled pyrone is observed. The oxygen-18 is incorporated selectively into the carbonyl group, since conversion of a portion of the labeled pyrone into pyran-2-thione (P_2S_5 in benzene)[5] removes at least 99.5% of the label (Table II). Incomplete labeling (i.e., 24.5/30.0) may be explained either by imperfect exclusion of atmospheric moisture or by partial hydrolysis of the ethyl group. Sib et al.[6] have recently shown that nucleophiles may attack alkoxypyryllium salts at either the ring or the alkyl group, as shown in the minor route of Scheme II.

Table I
Mass Spectra of 2-Pyrone and Oxygen-18-Labeled 2-Pyrone

m/e	Relative ion intensities: Labeled	Relative ion intensities: Unlabeled	Corrected ion intensities[a] (normalized)
	M⁺ Region[b]		
96	100	100	75.5
98	32.2 ± 0.5	0.68 ± 0.01	24.5 ± 0.3
100	0.21 ± 0.02	>0.01	
	M − CO Region[c]		
68	100	100	95.7
70	5.02 ± 0.07	0.65 ± 0.11	4.30 ± 0.09
72	0.09 ± 0.01	0.51 ± 0.03	

[a] Intensities of ions at *m/e* 98, 100, 70, and 72 for unlabeled 2-pyrone were subtracted from intensities of those ions for the labeled 2-pyrone. In addition, an isotropic correction at *m/e* 100 was based on the intensity of the ion at *m/e* 98. [b] Average of five scans at 10 eV. [c] Average of five scans at 70 eV.

Table II
Mass Spectra of 2-Pyran-2-thione

m/e	From labeled 2-pyrone[a]	Expected for C_5H_4OS
112	100	100
114	4.83 ± 0.03	4.78

[a] Containing ca. 25% oxygen-18. Average of three scans with 10-eV electrons.

To determine the extent of ^{18}O retention after decarbonylation of the molecular ion of labeled **1**, the ion intensities at *m/e* 68 of the labeled and unlabeled spectra were normalized to 100, and the intensities of the ions at *m/e* 70 and 72 of the latter were subtracted from the former. Under the same spectrometer conditions, which completely scramble the deuterium label in either 3- or 5-monodeuterated 2-pyrone, only 17.5% of the oxygen label is retained after decarbonylation of the molecular ion.[7] Hence, the two oxygens could have equilibrated in no more than 35% of the molecular ions and a rearrangement similar to that shown in Scheme I is thus ruled out as the principle source of deuterium scrambling. The actual extent of deuterium scrambling occurring via a Scheme I type mechanism may be considerably less; the molecular ion of ^{18}O-labeled **1** may lose unlabeled CO by some alternative process. However, in this regard, it should be noted that Johnstone et al.[8] examined the mass spectra of 4′-methyl-3,4,5′,6′-pyranocoumarin having both carbonyl carbons ^{13}C labeled and found that the first two (of four) sequential decarbonylations proceed with loss of the ^{13}C labels. No competing loss of unlabeled carbonyl was reported. In this instance, the presence of substituents in the 6 position of both pyrone rings presumably would prevent a Scheme I like rearrangement (see ref 3).

Mass spectra of several sulfur analogs of 2-pyrones suggest that a mechanism similar to that of Scheme I may play a role in fragmentation of their molecular ions. Table III shows the ratios of loss of CS to loss of CO for eight of these compounds. The numbers reflect intensities of the M − CS and M − CO ions and may, because of further frag-

Table III
Ratio of Loss of CS to Loss of CO in Sulfur Analogs of 2-Pyrones

Compd	M − CS/M − CO[a]
Thiapyran-2-one	0.01
4-Methylthiapyran-2-one	0.03
4,6-Dimethylpyran-2-thione	100
4-Methoxy-6-methylpyran-2-thione	>73[b]
Pyran-2-thione	0.69
5-Bromopyran-2-thione	0.40
3-Methylpyran-2-thione	0.37
4-Methylpyran-2-thione	0.95

[a] At 70 eV. [b] At 10 eV. Reference 10.

mentation, not represent the true ratios of loss of CS and CO. Nevertheless, the trend is obvious and invites the hypothesis that the more stable isomers,[9] thiapyran-2-one and 4-methylthiapyran-2-one, having sulfur in the ring, do not rearrange and lose solely CO. However, 4,6-dimethylpyran-2-thione, which cannot rearrange by the thermal mechanism because of the blocking methyl group in position 6 (see ref 3), loses CS almost exclusively. By analogy, 4-methoxy-6-methylpyran-2-thione is expected to lose only CS. This occurs predominately (98.6%).[10] Intermediate in behavior are the molecular ions of pyran-2-thione, 5-bromopyran-2-thione, 3-methylpyran-2-thione, and 4-methylpyran-2-thione, which, by this criterion, appear to rearrange substantially prior to fragmentation.

The simplest rationalization of the preceding results is that decarbonylation is several times faster than the rearrangement sequence for 2-pyrone molecular ions but several times slower for thio-2-pyrone molecular ions unless the rearrangement of the latter is blocked by a substituent in position 6. The failure of 2-pyrone to scramble the oxygen label requires the operation of some alternate process to scramble the 3 and 5 deuteriums. Whether this deuterium scrambling occurs before or after decarbonylation is unknown nor is it known whether it occurs via a symmetric ion or through dynamic scrambling. Hence, speculation on the source of the deuterium scrambling is presently unwarranted.

Experimental Section

Oxygen-18-Labeled 2-Pyrone. 2-Ethoxypyrylium fluoroborate[4] (0.17 g) was added to 0.07 g of water containing 30.0% oxygen-18 and 41.2% deuterium. After 3 hr at room temperature and 18 hr of storage at −20°, the sample was distilled at 80° (7 Torr). ^{1}H NMR showed the resulting pale yellow oil to be 2-pyrone, water, and ca. 1% of an ethoxyl-containing impurity. The sample was dissolved in methylene chloride and dried over anhydrous potassium carbonate. Vacuum evaporation of the solvent afforded 2-pyrone with an impurity with a significant ion at *m/e* 66. The impurity was removed by liquid chromatography on silica, eluting with 50:50 methylene chloride–pentane, to give 2-pyrone containing 24.5% oxygen-18 (Table I).

To assess the limits of acid-catalyzed exchange, an attempt was made to label 2-pyrone by HCl-catalyzed exchange with water containing 30.0% oxygen-18 (pH ca. 2). This experiment gave no oxygen-18 incorporation either after 32 days at room temperature or after 1 hr in a steam bath.

Acknowledgment. Mass spectrometric analyses were performed by Mr. J. Wrona on a Varian MAT CH-5 spectrometer. The mass spectral data processing equipment was provided by NIH Grants CA 11388 and GM 16864, from the National Cancer Institute and the National Institute of General Medical Sciences, respectively.

Registry No.—2-Pyrone, 504-31-4; 2-pyrone-2-thione, 23639-33-0.

References and Notes

(1) W. H. Pirkle, H. Seto, and W. V. Turner, *J. Am. Chem. Soc.*, **92**, 6984 (1970).
(2) W. H. Pirkle and M. Dines, *J. Am. Chem. Soc.*, **90**, 2318 (1968).
(3) W. H. Pirkle and W. V. Turner, *J. Org. Chem.*, **40**, 1617 (1975).
(4) M. Dines, Ph.D. Thesis, University of Illinois, 1968.
(5) R. Mayer and P. Fischer, *Chem. Ber.*, **95**, 139U (1962).
(6) S. Sib and M. Simalty, *Tetrahedron Lett.*, 3661 (1973).
(7) At lower ionization voltages, the extent of label loss is slightly greater (e.g., 85% at 10 eV). Mass spectra (70 eV) of similarly labeled 3-methyl-2-pyrone and 5-methyl-2-pyrone[3] indicate that as much as 71 and 66% rearrangement, respectively, may have taken place in these compounds prior to decarbonylation.
(8) R. A. Johnstone, B. J. Millard, F. M. Dean, and A. W. Hill, *J. Chem. Soc. C*, 1712 (1966).
(9) P. Beak, D. S. Mueller, and J. Lee, *J. Am. Chem. Soc.*, **96**, 3867 (1974).
(10) P. Beak, personal communication.

Methyl Hyponitrite

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Several of the lower molecular weight alkyl hyponitrites were synthesized by Partington and Shah,[1] Zorn,[2a] and Holden and Kutschke.[2b] The parent member of the series has been mentioned in the patent literature[3] but apparently has not been synthesized, probably because safety considerations outweighed the need. Methyl hyponitrite is an attractive, low-temperature source of methoxy radicals, and we were interested in the compound for use in connection with studies of gas-phase reactions leading to photochemical smog.

Reaction of silver hyponitrite[4] with excess methyl bromide at 0° according to Traylor's procedure[5] gave a solution that was fractionated at low pressure and temperature to remove methyl bromide. Methyl hyponitrite was obtained as a colorless, fragrant liquid at 25° that formed ice-like crystals when condensed from the gas phase onto the walls of a tube at −196°.

The ester was prepared twice without incident. A third preparation of ca. 1 g, however, exploded violently during a *second* bulb-to-bulb distillation from an 8-mm tube. The glass was pulverized into dust so fine that no damage was done to the vacuum system, although the operator sustained superficial cuts from particles that penetrated clothing.[6]

We suspected that "bumping" of the boiling liquid caused the detonation, but a 0.5-g sample in a wide, shallow-bottomed tube later exploded as it was being frozen in a Dewar flask containing liquid nitrogen. Since there was no obvious reason in this case, handling of the neat ester appears to be exceptionally unpredictable. Our experience is in accord with highly disparate accounts in the literature concerning the stability of lower alkyl hyponitrites.

A modified preparation with mineral oil as a diluent proceeded without incident. The ester was handled as a gas and cocondensed with excess 1,4-cyclohexadiene. The resulting solution was diluted with benzene-d_6. Portions were transferred to two NMR tubes for product study. The tubes were degassed and sealed off. One was placed in a bath at 100° for 5 min; a signal at δ 3.06 (CH_3OH) was the only resonance observed other than those from 1,4-cyclohexadiene (δ 2.6 and 5.8) and benzene (δ 7.2). The latter was initially present as an impurity, although it was also an expected product from H abstraction.

A second tube containing 0.9 ± 0.2 *M* hyponitrite was placed in a preheated ^{1}H NMR probe at 70°. The area of the resonance at δ 3.5 decreased 88% in 50 min, with $t_{1/2}$ 17 ± 5 min.

The area of the methanol product signal was only half of the original methyl area in the ester. We cannot account for the difference, since signals from dimethyl peroxide (δ 3.6) or low-field resonance from CH_2O were not observed. The absence of the former is consistent with a value of $k_{\text{disproportionation}}/k_{\text{recombination}} = 9.3$ reported in the gas phase,[7] and also with the small yield of di-*tert*-butyl peroxide observed from di-*tert*-butyl hyponitrite by Kiefer and Traylor[5] and by Neuman and Bussey.[8]

From group additivity[9] we estimate $\Delta H°_{f,g} \cong 70$ kcal/mol for the hyponitrite, and an enthalpy change for the reaction

$$CH_3ON{=}NOCH_3(l) \rightarrow N_2(g) + CH_3OH(g) + CH_2O(g)$$

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