viously. No reaction between the quinone and ammonium acetate was observed in this solvent, however; essentially quantitative conversion to 4 was observed when diphenaldehydic acid was added to the reaction mixture. We interpret this result not only as support for our proposed structure **4**, but also as an indication for an acid-catalyzed mechanism of formation.

It appears likely that spiro intermediate **3**, which is first formed, undergoes an acid-catalyzed stereoelectronically favored realignment involving the cleavage of the C_9–C_{10} bond and leading to the formation of **4**.

Experimental Section

All melting points were uncorrected. Unless otherwise stated, NMR, uv, and ir spectra were obtained in DMSO-d_6, absolute ethanol solutions, and Nujol mulls, respectively. Molecular formulae were arrived at by computer analysis of the high-resolution mass spectra. NMR positions are reported in τ units relative to Me_4Si standard.

2-Phenyl-1*H*-phenanthro[9,10-*d*]imidazole (2). Phenanthrenequinone (4.0 g, 0.02 mol), benzaldehyde (2.0 g, 0.02 mol), and ammonium acetate (15.0 g, 0.2 mol) were mixed with thorough stirring in DMSO (50 ml). The mixture was heated to 95° with continued stirring for 0.5 hr. The solution was cooled and diluted with water (250 ml), and the precipitate was filtered. Recrystallization of the solid from 2-butanone yielded 5.0 g of product, mp 318–320°; picrate mp 292–294° (lit.[2] mp 314, 289–290°, respectively); uv λ_{max} 362 nm (ϵ 12,500), 348 (13,500), 326 (23,000), 312 (22,000), 260 (56,000).

2′-(1*H*-Phenanthro[9,10-*d*]imidazol-2-yl)-2-biphenylcarboxylic Acid (4). Phenanthrenequinone (10.0 g, 0.045 mol) and ammonium acetate (75 g, 1.0 mol) were refluxed in glacial acetic acid (150 ml) for 1 hr. The solution was cooled and the crystalline precipitate was filtered and dried. Purification was effected by crystallization once from acetic acid and twice from cellosolve, giving 8.0 g of crystalline material, mp 320–322° (lit.[2] mp 290–292°; the crystalline compound obtained from acetic acid had mp 286–285°). Purification of material from other runs was accomplished by dissolving the crude compound in alcoholic potassium hydroxide solutions.

Anal. Calcd for $C_{28}N_{18}N_2O_2 \cdot H_2O$: C, 77.75; H, 4.66; N, 6.47. Found: C, 77.95; H, 4.98; N, 6.47.

The molecular water of crystallization could not be liberated by drying at 140° for 2.5 days at 6 mmHg pressure: picrate mp 307–309°; ir 3300–2800 (COO–H–N), 1660–1570 cm^{-1} (COO^- and NH, NH_2^+); hydrochloride 1670 cm^{-1} (CO); NMR 3.80 (s, D_2O exchanged), 1.10 (s, D_2O exchanged), 1.10–3.18 ppm (complex m, 16 H); uv 358 nm (ϵ 5,500), 340 (5,500), 306 (17,500), 286 (18,000), 258 (61,000).

The compound was also prepared by the following method. Phenanthrenequinone (1.0 g, 0.005 mol), diphenaldehydic acid[5] (1.10 g, 0.005 mol), and ammonium acetate (10 g, 0.13 mol) were heated in DMSO (25 ml) for 1 hr at 100°. The solution was allowed to cool and diluted with water to a final volume of 100 ml. After acidification of the solution with dilute hydrochloric acid, the precipitated compound was purified as above.

10H-Dibenzo[*f,h*]phenanthro[9,10-*b*]imidazo[1,2-*a*]azepin-10-one (6). Compound 4 (2 g, 0.005 mol) was dissolved in pyridine (25 ml) and the solution was cooled in an ice bath. Acetyl chloride (1.5 ml) was added and the solution was allowed to warm to ambient temperature. The reaction was allowed to proceed with stirring for an additional 2 hr and was diluted with water to 60 ml. The solid precipitate was collected and crystallized from 2-butanone, yielding 1.5 g of compound: mp 260–261°; ir 1710 cm^{-1} (CO); NMR 1.10–3.16 ppm (complex m); uv 360 nm (ϵ 11,250), 345 (12,2), 300 (35,000); MS *m/e* 396 ($C_{28}H_{16}N_2O$), 367 ($C_{27}H_{15}N_2$), 183 ($C_{11}H_7N_2O$), 163 ($C_{13}H_7$).

Anal. Calcd for $C_{28}H_{16}N_2O$: C, 84.83; H, 4.07; N, 7.07. Found: C, 84.38; H, 4.23; N, 7.25.

Ethyl 2′-(1*H*-Phenanthro[9,10-*d*]imidazo-2-yl)-2-biphenylcarboxylate (7). Compound 6 (0.5 g) was refluxed in a solution of ethanol (40 ml) and concentrated hydrochloric acid (10 ml) for 3 hr. The solution was cooled, diluted with water to 100 ml; and neutralized with Na_2CO_3. The product (0.25 g) was crystallized from ethanol: mp 185°; ir 1690 cm^{-1} (CO); NMR 1.17–3.0 (complex m, 16 H), 5.80 (q, J = 7 Hz, 2 H), 8.99 ppm (t, J = 7 Hz, 3 H); MS *m/e* 442 ($C_{30}H_{22}N_2O_2$), 396 (P – C_2H_5OH), 368 (P – $CO_2C_2H_5$), 184 ($C_{11}H_8N_2O$), 183 ($C_{11}H_7N_2O$); uv 358 nm (ϵ 6,000), 340 (7,000), 300 (17,000), 258 (56,700).

Methyl 2′-(1-Methyl-1*H*-phenanthro[9,10-*d*]imidazol-2-yl)-2-biphenylcarboxylate (5). Compound 4 (1 g) was refluxed with methyl iodide (2 ml) and potassium carbonate (1 g) in 50 ml of acetone and 2.5 ml of water for 20 hr, diluted with water to twice the original volume, and extracted with chloroform (3 × 50 ml). The organic extract was dried, evaporated to almost dryness, and crystallized from 1-butanol: mp 190–192°; ir 1705 cm^{-1} (CO); NMR 0.74–3.34 (complex m, 16 H), 6.05 (s, 3 H), 6.28 ppm (s, 3 H); uv 354 nm (ϵ 4500), 338 (4500), 306 (13,500), 284 (18,500), 254 (63,000); MS *m/e* 442 ($C_{30}H_{22}N_2O_2$), 383 (P – CO_2CH_3), 368 (P – CH_3, CO_2CH_3), 183 ($C_{11}H_7N_2O$).

Anal. Calcd for $C_{30}H_{22}N_2O_2$: C, 81.43; H, 5.01; N, 6.33. Found: C, 80.98; H, 4.82; N, 6.41.

Acknowledgment. The author wishes to express his gratitude to Drs. R. A. Coleman and R. K. Madison, and to his personal friend J. J. Leavitt for the many useful discussions and continued help. Thanks are extended to Dr. T. Mead for the mass spectra and to Dr. J. Gove for the NMR spectra.

Registry No.—**2**, 6931-31-3; **2** picrate, 54774-64-0; **4**, 54774-65-1; **4** picrate, 54774-66-2; **5**, 54774-67-3; **6**, 32005-25-7; **7**, 54774-68-4; ammonium acetate, 631-61-8; phenanthrenequinone 84-11-7.

References and Notes

(1) Address correspondence to Research and Development Division, Smith Kline & French Laboratories, Philadelphia, Pa. 19101.
(2) E. A. Steck and A. R. Day, *J. Am. Chem. Soc.*, **65**, 452 (1943).
(3) G. McCoy and A. R. Day, *J. Am. Chem. Soc.*, **65**, 2159 (1943).
(4) See Experimental Section for spectroscopic details.
(5) P. S. Bailey and R. E. Erickson, *Org. Syn.*, **41**, 46 (1961).

Acid-Catalyzed Epoxide Cleavage of 3,4-Epoxytricyclo[4.2.2.0^{2,5}]deca-7-ene[1]

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Received January 16, 1975

With a hope of providing a synthetic entry for new carbon-skeleton construction and further additional data for understanding the transannular reactions of tricyclo[4.2.2.0^{2,5}]deca-3,7-diene derivatives **1** and **2** (1:1 adducts of cyclooctatetraene with maleic anhydride and methyl maleate) with electrophiles,[2-4] we have investigated the reactions of **1** and **2** with *m*-chloroperbenzoic acid and the acid-catalyzed cleavage of the resulting epoxide derivatives.[5]

Reaction of **1** with *m*-chloroperbenzoic acid gave a monoepoxide product **3**.[6] Similar reaction of **2** gave **4**[6] together with a trace amount of unknown compound **5**. The NMR spectrum of **5** exhibits signals at δ 1.93 (4 H, m), 2.68 (4 H, m), 3.02 (4 H, s), 3.18 (4 H, m), 3.60 (12 H, s), and 6.50 (4 H, t) suggesting the presence of two cyclohexene moieties, and also the syn or anti dimer of **4** (Chart I).

Treatment of the epoxide **4** with hydrogen chloride in methanol at 0° gave compound **6** in an almost quantitative yield. The yields of **6** under various acidic conditions are summarized in Table I.

Similar treatment of **3** with the acid under various conditions gave a complex mixture, which we were unsuccessful in further purifying.

The NMR spectrum of **6** exhibits a methine proton at δ 4.75 (dd) adjacent to a lactone moiety, a sharp singlet at δ 4.06 (1 H) adjacent to a hydroxyl group, and one methoxyl group at δ 3.68 (3 H, s), but lack of olefinic protons. The

Chart I

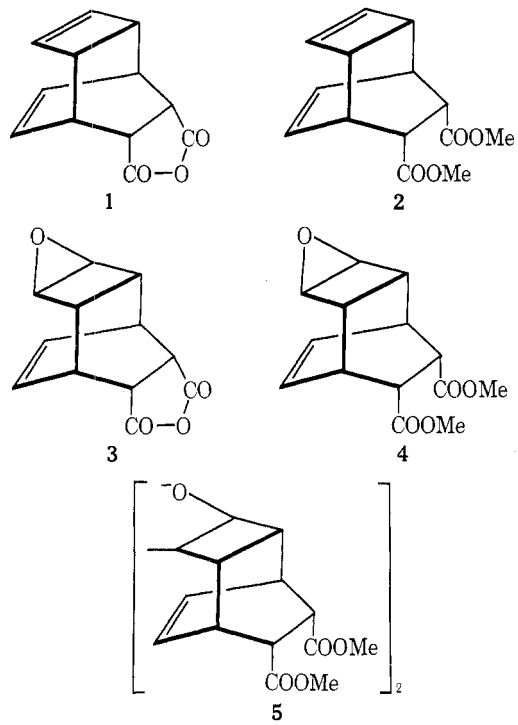


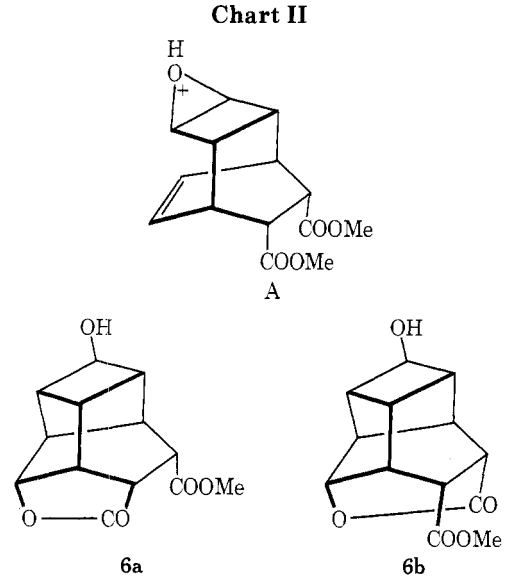
Table I
Acid-Catalyzed Cleavage Reaction of 4

Reagent	Solvent	Product 6 yield, %
HCl[a]	MeOH	Quantitative
Concd HCl	None	56.5
45% HBr	None	28
BF_3	AcOH	17.5

[a] In methanol saturated with dry hydrogen chloride.

spectral patterns of **6** are very similar to that of the halolactonization products.[2] Thus, the formation mechanism of **6** could be explained to proceed by an initial produced bridged protonated oxide (A) followed by ring opening to cause the transannular cross cyclization affording the lactonization product **6a** or **6b** (see Chart II). However, it is difficult to establish the structure of **6** from its ir data, since the spectrum in the solid state shows only one broad

Chart II



carbonyl band at 1740 cm^{-1}, but in chloroform two absorptions at 1775 and 1750 cm^{-1}. Therefore, the final determination of the structure was accomplished by the chemical transformations.

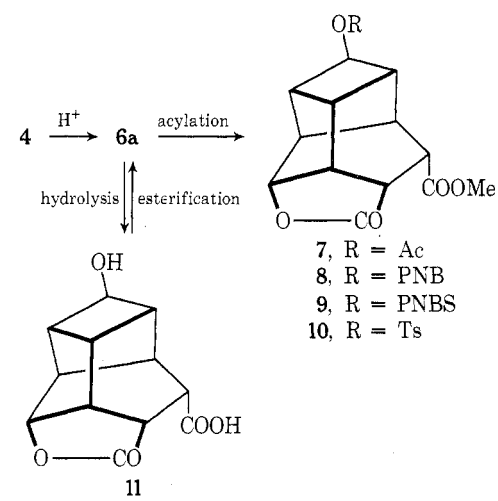
Acetylation of **6** with acetic anhydride in the presence or the absence of pyridine afforded compound **7**. The ir spectrum of **7** in the solid state shows carbonyl absorptions at 1790 cm^{-1} attributable to a five-membered lactone and at 1740 cm^{-1} due to acetoxyl and ester carbonyl groups. Similar treatments of **6** with *p*-nitrobenzoyl chloride, *p*-nitrobenzenesulfonyl chloride, and tosyl chloride in pyridine at room temperature gave the acylated compounds, **8**, **9**, and **10**, respectively. The ir spectra of these compounds in KBr exhibit lactone absorptions in the regions of 1770–1765 cm^{-1} as shown in Table II, suggesting the presence of a five-membered lactone moiety and at least the absence of a six-membered lactone group.

Table II
Carbonyl Absorptions of Acylated Compounds by Ir

Compd	Ir (KBr), C=O, cm^{-1}	
	Lactone	Ester
7	1790	1740
8	1765	1750, 1720
9	1770	1730
10	1770	1740

Furthermore, hydrolysis of **6** with 50% sulfuric acid or 10% aqueous sodium hydroxide at room temperature afforded compound **11** (Scheme I), which shows a lactone ab-

Scheme I



sorption at 1775 cm^{-1} suggesting the presence of a five-membered ring. Esterification of **11** with methanol in sulfuric acid or diazomethane in ether gave **6** exclusively. Thus, the structure **6** was established to be **6a**. From these data, it is pointed out that no skeletal rearrangement (relactonization) from the six-membered ring to the five-membered lactone moiety has occurred during the chemical conversions even under both acidic and basic conditions. By contrast, all attempted base-catlayzed cleavage of the epoxides **3** and **4** was unsuccessful, although many examples of the ring-opening reactions of epoxide derivatives with nucleophilic reagents have been reported.[7]

Experimental Section

The melting points were measured with Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were per-

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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Received January 3, 1975

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

Scheme I