Cyclopropanes. An Anti-Markovnikov Cleavage and Evidence for a σ-Complex Protonium Ion

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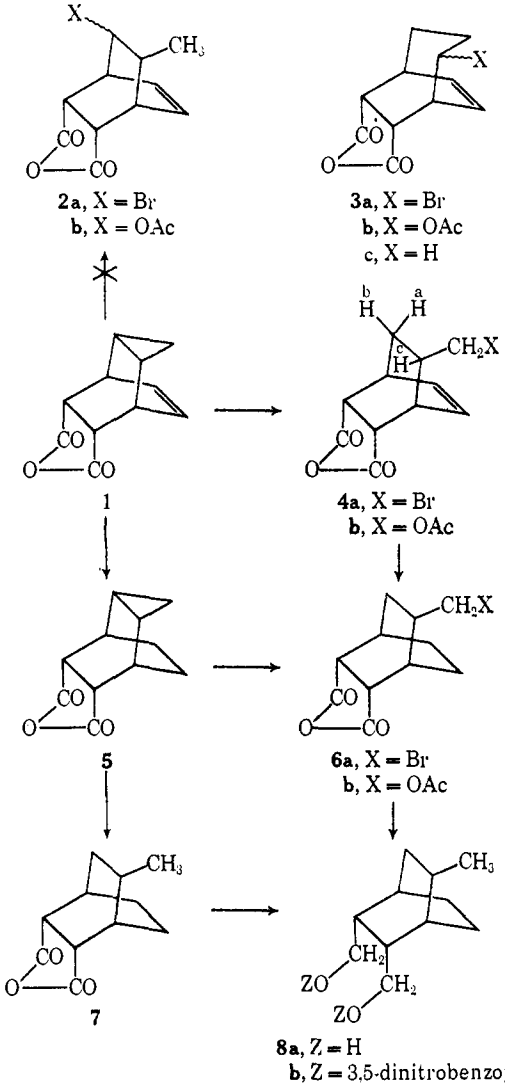
Abstract: The first example of anti-Markovnikov cleavage of a cyclopropane ring has been discovered in the acid-catalyzed reactions of the bicyclo[2.2.2]octane adduct (**1**). Cleavage of the cyclopropane ring by hydrobromic or acetic–sulfuric acids was shown to proceed in high yields to addition products without methyl groups, the reverse of electronic prediction. Use of deuterio acid allowed determination of the stereochemistry of proton attachment in the cleavage, which was shown to proceed exclusively *via* initial formation of a three-center protonium ion (σ complex). Steric inhibition to normal collapse of this ion by nucleophile attack is suggested as the cause of anti-Markovnikov cleavage in this instance.

In connection with some other synthetic work we had occasion to treat the adduct (**1**) of cycloheptatriene and maleic anhydride[2] with hydrogen bromide in glacial acetic acid. On electronic grounds and consistent with previous experience in acid-catalyzed cyclopropane additions[3] the predicted product should be **2a**, exhibiting bromide addition at the more substituted carbon, site of the better carbonium ion, *i.e.*, Markovnikov addition. Such addition leads to a methyl substituent.[3c-e] Less likely but still electronically acceptable is a pathway cleaving the ring-fusion bond, to **3a**. The crystalline bromide isolated in fact, in up to 65% yield, was characterized as the anti-Markovnikov addition product, **4a**. The other products were primarily acetates, formed in minor amounts, but *none of these possessed the methyl substituent* characteristic of the expected **2** as evidenced by the absence of any methyl doublet absorption in the nmr spectrum. The bromomethylene of the product (**4a**) was characterized by a doublet at τ 6.52, J = 6.5 cps, in the nmr spectrum, virtually unchanged in the dihydro derivative, **6a** (τ 6.58, J = 7 cps).

The proof of structure of **4a** was adduced in three sets of experiments, the first designed to show that the carbon skeleton was correct (as in **2** and **4**) and that no skeletal rearrangement has occurred, the second to demonstrate an *endo*-bromomethyl as in **4a**, ruling out **2a**, and the third to establish the orientation of the anhydride and cyclopropane as both *cis* to the olefin bridge in the initial bicyclooctene, **1**.

For the first set, the initial adduct (**1**) had been hydrogenated previously, first at the olefin, yielding **5**, then more slowly opening the cyclopropane to a methyl derivative, **7**.[2] This derivative (**7**) has a clear methyl doublet in the nmr spectrum (τ 8.92, J = 6 cps), indicating the common reductive cleavage of the fused cyclopropane. The other possible reduction product would be a bicyclononane and this is a known compound, from hydrogenation of the cycloheptadiene–maleic anhydride adduct, **3c**.[4] The latter saturated anhydride (mp 156–157°) is different from product **7** (mp 76–78°). Lithium aluminum hydride reduction of **7** yielded the diol **8a**, also produced by hydrogenation of **4a** to **6a**, followed by hydride reduction. The diols, **8a**, were converted to the 3,5-dinitrobenzoates, **8b**, mp



(1) NDEA Predoctoral Fellow.

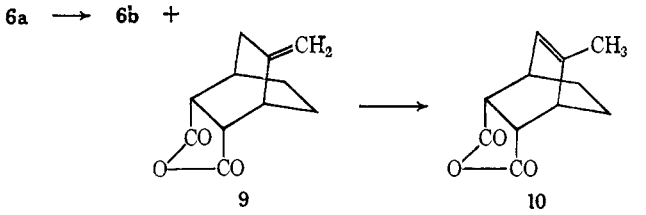
(2) K. Alder and J. Jacobs, *Ber.*, **86**, 1528 (1953).

(3) General discussion of acid-catalyzed cleavages of cyclopropane rings are to be found in: (a) R. T. La Londe and L. S. Forney, *J. Am. Chem. Soc.*, **85**, 3767 (1963); (b) R. L. Baird and A. Aboderin, *ibid.*, **86**, 252 (1963); (c) N. C. Deno, D. LaVietes, J. Moekus, P. C. Schiff, *ibid.*, **90**, 6457 (1968); cyclopropane fused to cyclohexane opens to give 2-methylcyclohexyl compounds, analogous to **2a**; (d) R. T. LaLonde and T. A. Tobias, *ibid.*, **85**, 3771 (1963); R. T. LaLonde and L. S. Forney, *ibid.*, **85**, 3767 (1963); (e) N. M. Kishner, *J. Russ. Phys. Chem. Soc.*, **92**, 1198 (1910).

(4) E. P. Kohler, M. Tishler, H. Potter, and H. T. Thompson, *J. Am. Chem. Soc.*, **61**, 1057 (1939).

184–185°, for comparison and were found identical from the two routes.

In the second set, proof of the bromomethyl structure was adduced by dehydrobromination of **6a** with sodium acetate in boiling dimethylformamide. The major product was the olefin **9**, with an unclean olefinic doublet (two protons) in the nmr spectrum at τ 5.05 (J = 10 cps) and strong ir bands at 6.05 and 11.0 μ. Minor amounts of the displacement product **6b** were also formed. That **9** was the less stable olefin and not produced by isomerization was shown by acid-catalyzed equilibration (in boiling benzene) of the exocyclic double bond to the endocyclic position, producing the



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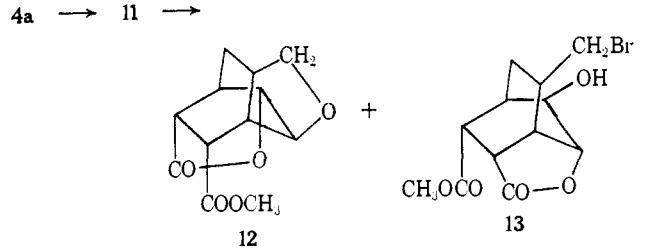
isomeric **10** in essentially quantitative yield and characterized by a rough one-proton doublet (J = 6 cps) at τ 3.95 and a three-proton doublet at τ 8.15 (J = 1.5 cps) in the nmr spectrum. If sodium acetate is not used in the hot dimethylformamide elimination reaction of **6a**, a mixture of **9** and **10** results. Structure **2a** would have produced **10** directly, and none of the less stable isomer, **9**.

One further structural question remained. While Alder and Jacobs[2] had shown that the anhydride grouping bore the *endo* orientation (*cis* to the double bond, shown by iodolactone formation), they inferred the orientation of the cyclopropane as shown (*cis* to the double bond) from analogy. In order to substantiate this stereochemistry we converted the original adduct, **4a**, to the corresponding dimethyl ester, **11**. Oxidation of this ester–olefin with *m*-chloroperbenzoic acid afforded an 88% crude yield of a mixture of two



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γ-lactone (ir band at 5.60 μ) products in a roughly 1:1 ratio; these were separated by thin layer chromatography. One of these corresponded to the expected lactone–ester (**13**) retaining bromine and a hydroxyl group (ir 2.79 μ). The other lactone–ester (**12**), mp 59–62°, corresponds to loss of HBr and exhibited no hydroxyl band in the ir spectrum. Both exhibited the assigned parent peaks in the mass spectrum and consistent nmr spectra. Product **12** also exhibited no methyl signal but showed a methylene as two self-coupled doublets (at τ 6.11 and 6.40, J = 8 cps). In addition the doublet at τ 6.11 is slightly coupled ($J \cong 1$ cps) to the adjacent methine proton whereas the doublet at τ 6.4 is not similarly coupled. These results confirm the structure **12** which serves at once to show that the anhydride as well as the cyclopropane in **1** are oriented, as shown, *cis* to the olefinic bridge. Furthermore, product **12** offers further confirmation of the bromomethyl structure of the HBr product, **4a**.

That the double bond was not involved in the cyclopropane cleavage was shown by the clean conversion of **5** to **6a** under the same conditions. In view of the occasional reversal of orientation exhibited by hydrogen bromide additions to olefins, we examined other cleavages of the cyclopropane derivative **5**. This compound was inert to hydrogen chloride and to bromine–silver acetate, both in glacial acetic acid at room temperature. However, sulfuric acid in glacial acetic acid at room temperature converted **5** to a mixture of four products separated by chromatography; the total crude product again showed in the nmr spectrum none of the methyl signal anticipated for the normal cleavage product (dihydro-**2b**).

Two products in the mixture were major; one of these (31% yield) was characterized as the analogous **6b** by its nmr spectrum (two-proton multiplet at τ 5.95) similar to **6a**. The second product (40% yield) was isomeric, differing spectrally chiefly in exhibiting a one-proton multiplet at τ 5.05 and was assigned the structure of dihydro-**3b**. The minor products, in very small yield, included an olefin and an acetate, both without methyl signals in the nmr spectrum. Therefore, the course of the reaction is the same—still abnormal—in this acidic medium as in the previous hydrobromic acid cleavage.

Discussion

The stereoelectronic circumstances implicit in acid-catalyzed cleavage of cyclopropanes have not been examined before in detail, but the present case can shed light on this because of its unique anti-Markovnikov orientation. In almost all cases examined previously the stereochemistry of the added proton cannot be ascertained since it is located on methyl in the product. In this case, however, the added proton is affixed to a rigid secondary carbon with two discernible stereoisomeric positions, so that the mode of its attachment may be deduced by using deuterium acid in the cleavage.

The approach of a proton may occur in one of the two stereoelectronic modes illustrated in Figure 1. The traditional representation might be path B with proton overlapping a minor σ-bond lobe at one carbon leaving the other carbon to bear the developing carbonium ion. In the alternative path A the proton may embed itself in the protruding center of the bent bond, between the carbons. This creates a three-center ion reminiscent of the three-center bonds in the similarly electron-deficient boranes. Following Mislow's calculation[5] the axes of the bonding orbitals of cyclopropane carbons are about 23° removed from the internuclear axis and their intersection is thus 0.83 Å from each carbon. This represents an estimate of the C–H distance in the three-center ion comparable to the internal B–H distance of 1.33 Å observed for diborane.[6]

The stereochemical consequences of the two modes of cleavage are shown in Figure 2 compared to proton-catalyzed addition to olefins. The three-center ion path A may be regarded as a σ complex, closely anal-

(5) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 20.
(6) F. A. Cotton and G. Wilkinson, *Advan. Inorg. Chem.*, 2, 276 (1966).

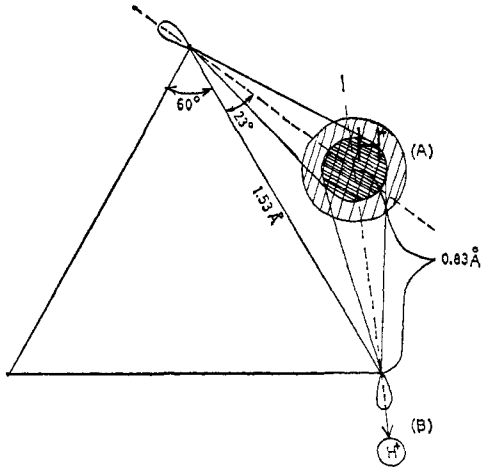


Figure 1. Two stereoelectronic modes for proton attack on cyclopropanes.

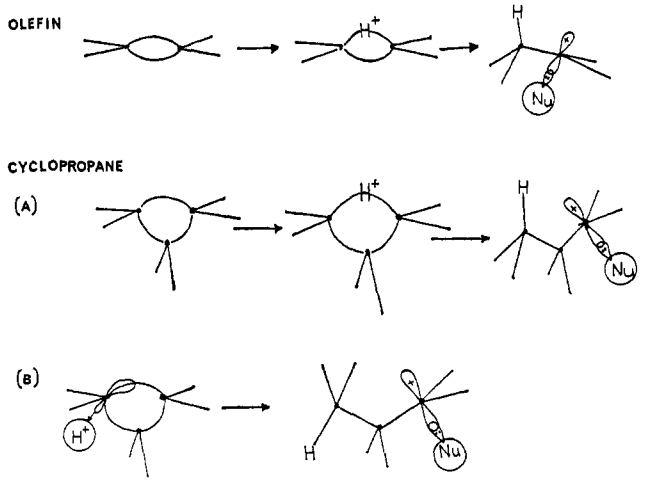


Figure 2. Stereochemistry of protonation.

ogous to the π complex commonly described for olefin protonation. This figure also shows that the two competitive modes of cyclopropane cleavage result in different product stereochemistry at the protonated carbon. Translated to the present case, in structure **4**, the added proton by path A must be a while that from path B will be b.

The highest field signal in the nmr spectrum of **4a** was a well-separated one-hydrogen multiplet (approximately a double doublet) at τ 9.05, tentatively assigned to proton a owing to its position over the olefinic π electrons. The two other protons, b and c, lay together as a multiplet around τ 8.00. When the cyclopropane **1** was opened with DBr in acetic acid, a deuterio-**4a** was obtained exhibiting a 4.6-μ band in the ir spectrum (C–D stretch) and a mass spectrum similar to that of **4a** except for parent ions one mass unit higher. The nmr spectrum now showed complete disappearance of the τ 9.05 band assigned to proton a as well as simplification of the patterns of the next two protons. The latter appeared, in a 100-Mc spectrum, as a quartet at τ 6.30 and a doublet at 6.80, each of one-proton intensity. Each proton showed one coupling of 9.5 cps, assigned to the 0° dihedral angle of *cis* protons, b and c,[7] as well as some blurring ($J \sim 2$ cps) owing to coupling with bridgehead protons. The quartet signal at τ 6.30 was further split ($J \sim 6$ cps) by the bromomethylene protons so that this quartet is assigned to proton c. Taken together these results show the deuterium to be attached at position a. Deuterium at b would have led to an a–c coupling (120° dihedral angle) of only ~4, not 10, cps.

This confirms the intermediacy of a three-centered protonium ion, or σ complex, as the initial step in opening this cyclopropane derivative (**1**). This three-centered ion has been invoked before[8b,c] to account for the mixing of deuterium label in deuterium acid-catalyzed cleavages of cyclopropane itself. It does not appear to be a mandatory conclusion. No mixing of label was observed on deuterium acid-catalyzed opening of methylcyclopropane,[8c] and indeed there is no evidence of label mixing in the present case.

(7) (a) The *cis* protons at the adjacent oxygen-bearing carbons in the symmetrical bis-γ-lactone prepared from **1** by hydrolysis and lead tetraacetate oxidation also showed $J \cong 10$ cps. (b) K. L. Williamson and W. S. Johnson, *J. Am. Chem. Soc.*, **83**, 9623 (1961).

Theoretical MO calculations[8] have recently been reported for the several possible forms of protonated cyclopropane. The results showed the σ complex invoked here to be the most stable of four possibilities considered by some 10 kcal/mol. The minimum-energy configuration calculated for the protonium ion was that of a more nearly equatorial triangle for the CHC three-center ion, with a C–H distance of 1.28 Å, closer to the boron–hydrogen bridge length. Both the present work and these calculations concur in favoring the σ-complex intermediate.

Following capture of the proton into a σ complex, the second step[9] involves the bonding of the nucleophile (bromide ion) to one of the two carbons of the protonium ion. The only effect likely to cause reversal here of the common experience of nucleophile attachment to the better carbonium site is a steric one. This possibility is most apparent in the interference created by the hydrogens α to the anhydride carbonyls, for they lie in the path of any solvent–nucleophile approaching to stabilize the opening σ complex from the rear. Furthermore, the rigidity of the bicyclooctane skeleton forbids these hydrogens any freedom to twist out of the way.

Assuming such approach of nucleophile (Nu:) along the axis of the bent bonding orbital of the cyclopropane (23° from the internuclear line of the cyclopropane; Figure 1), we made a geometric calculation[10] (see Figure 3) of the closest distance between such an approaching nucleophile and the α-hydrogen and found it to be only 1.09 Å, or indeed no more than bonding distance. This would represent an unacceptably severe nonbonded steric compression and seems adequate to destabilize seriously formation of the normal (solvated) secondary carbonium ion.

(8) H. Fischer, H. Kollmar, H. O. Smith, and K. Miller, *Tetrahedron Letters*, 5821 (1968).

(9) For convenience in this discussion the σ complex is regarded as an intermediate on the free energy diagram. This is arbitrary since no evidence is available. The subsequent carbonium ion (Figure 2) may be the only intermediate.

(10) We examined roughly first the most favored bicyclooctane ring CCC angles in terms of cumulative angle strain. As the six outer CCC angles are enlarged, the six bridgehead CCC angles diminish and little improvement in angle strain can be achieved. Hence we took the outer CCC angles to be the normal 112° for methylene, making the bridgehead angles 107°. This affords a distance of 2.72 Å from each α-hydrogen to its nearest cyclopropane carbon. The approach line for the nucleophile lies almost directly above the α-hydrogen by 1.09 Å.

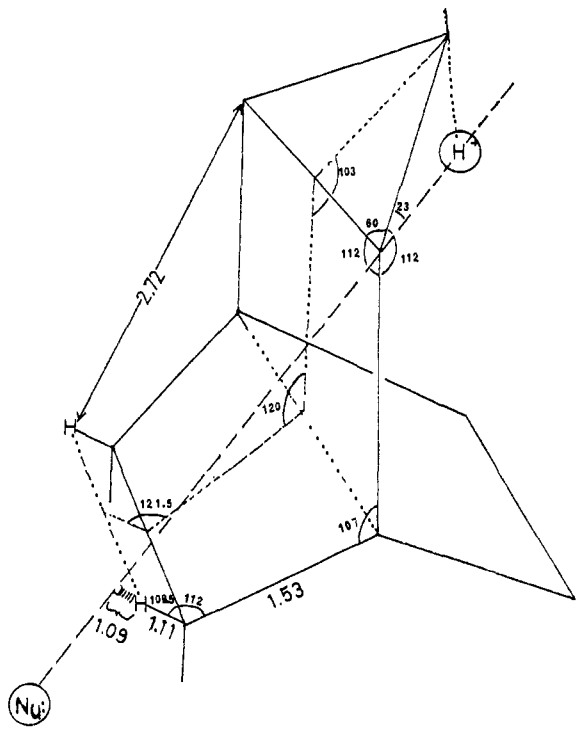
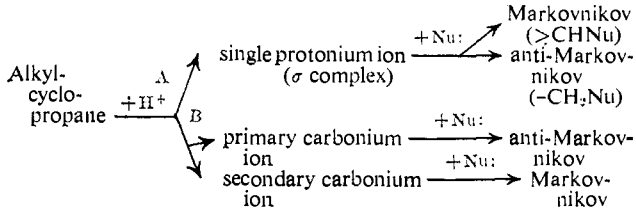
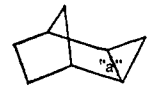


Figure 3. Geometry of nucleophile approach to adduct **1**.

Therefore, cyclopropane **1** opens abnormally (anti-Markovnikov) after initial protonation into the bent σ bond. This implies that the unique anti-Markovnikov opening in the present instance arises as a choice only after initial protonation to the σ complex. This argues in turn that the initial σ protonation is likely to be general for cyclopropanes since the special steric effect causing anti-Markovnikov cleavage in this molecule does not figure in the initial protonation step (protonation at the methylene for path B is not sterically hindered). We conclude that the general pathway for acid-catalyzed cleavage of unsymmetrical cyclopropanes is path A.



However, in special cases the approach of the solvated proton to the σ-bond center, in the cyclopropane plane, may be sterically hindered and so raise the activation energy of path A that path B becomes competitive. This appears to be the case in the cleavage of bond a in **14**, which was shown to occur by path B.[11]



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(11) R. T. LaLonde, J. Ding, and M. A. Tobias, *J. Am. Chem. Soc.*, **89**, 6651 (1967). A similar case with competing pathways was observed in methylnortricyclene by J. H. Hammons, E. K. Probasco, L. A. Sanders, and E. J. Whalen, *J. Org. Chem.*, **33**, 4493 (1968).

Experimental Section

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. All ir spectra were obtained on the Perkin Elmer 137 or Perkin Elmer DR-69 infrared spectrophotometers, and are reported in μ as potassium bromide dispersions unless otherwise noted. All nmr spectra were determined in deuteriochloroform on a Varian A-60 spectrometer and reported in τ (TMS internal standard) unless otherwise noted. The mass spectra were determined on an AEI MS-9 mass spectrometer. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Unsaturated Bromomethyl Anhydride. (4a). Diels–Alder adduct **1**[2] (1.407 g; 7.4 m*M*), was dissolved in glacial acetic acid (100 ml). After cooling the solution to 0–5° in ice, anhydrous hydrobromic acid was bubbled in with stirring. Addition was terminated after 30 min, and solvent evaporated to a yellow oil which crystallized on tituration with absolute ethanol. Recrystallization from absolute ethanol yielded 1.308 g (65%) of **4a**, mp 128–130°: ir 3.34, 5.39, 5.59, 8.12, 9.07, 9.17, 10.18, 10.90, 13.50, and 14.63; nmr 3.65 (m, 2), 6.52 (d, J = 6.5 cps, 2), 6.80–6.90 (m, 4), 7.60–8.40 (m, 2), 9.05 (d, 1); mass spectrum (70 eV) *m/e* 270 (parent), 272 (P + 2) equal intensities.

Anal. Calcd for $C_{11}H_{11}BrO_3$: C, 48.73; H, 4.09. Found: C, 48.68; H, 4.06.

The mother liquors contained an oily acetate which was not characterized; however, its structure was inferred to be **4b** because of similar spectra.

Saturated Bromomethyl Anhydride (6a). Unsaturated bromomethyl anhydride (**4a**) (200 mg; 0.74 m*M*) was dissolved in glacial acetic acid (10 ml). Platinum oxide (40 mg) was added and the system placed under a hydrogen atmosphere (1 atm). One equivalent was taken up in 19 hr. After dilution with water and extraction with ether, the extracts were washed with water, 5% sodium bicarbonate, and water (twice), dried, and evaporated to 172 mg of white crystalline solid. Recrystallization from absolute ethanol gave **6a**, mp 134–136°: ir 3.35, 5.37, 5.59, 8.25, and 10.99; nmr 6.58 (d, J = 7 cps, 2); 6.80 (m, 2), 7.50–8.20 (m, 3), 8.50 (m, 6); mass spectrum (70 eV) parent ion and p + 2 very weak; *m/e* 200, 202 (loss of -COOCO- from p and p + 2, intensities 1:1).

Anal. Calcd for $C_{11}H_{13}BrO_3$: C, 48.37; H. 4.80. Found: C, 48.51; H, 4.96.

Preparation of 6a from 5. Saturated cyclopropyl anhydride **5**[2] (1.0 g; 5.2 m*M*) was dissolved in glacial acetic acid (35 ml) and the solution was cooled to 0–5° in ice. Anhydrous hydrobromic acid was bubbled into the solution for 45 min with stirring; the mixture was poured into ice water and extracted with ether. The extracts were washed with water, 5% sodium bicarbonate, and saturated salt solution, dried, and evaporated to 1.36 g (80%) of **6a**. Recrystallization from absolute ethanol yielded white plates, mp 129–133°. This material was identical by ir, nmr, and tlc to **6a** obtained by the hydrogenation of **4a**.

Bisdinitrobenzoate 8b. Methyl diacid (or anhydride) **7**[2] (530 mg; 2.5 m*M*) was dissolved in dry ether–tetrahydrofuran (1:1, 25 ml), and added portionwise to 948 mg (25 m*M*) of lithium aluminum hydride suspended in 25 ml of dry ether. Additional tetrahydrofuran (5 ml) was added to aid solubility. The mixture was refluxed for 2 hr and excess hydride was decomposed by addition of water and 15% sodium hydroxide.[12] The granular salts were filtered, and the filtrate was washed with water, dried, and evaporated to 359 mg of crude diol **8a**. The diol without purification was dissolved in dry pyridine (10 ml) and 1.40 g (6 m*M*) of 3,5-dinitrobenzoyl chloride added. After refluxing 5 min, the mixture was poured into ice and water, the supernatant liquid decanted, and the residue washed twice with 10% sodium carbonate solution. Digestion with ethanol and recrystallization from benzene–petroleum ether (bp 60–110°) gave **8b** as off-white needles mp 184–185°: ir 3.20, 3.38, 5.78, 6.20, 6.28, 7.43, 7.85, 8.57, and 13.3 (doublet).

Anal. Calcd for $C_{25}H_{24}N_4O_{12}$: C, 52.45; H, 4.23. Found: C, 52.52; H, 4.43.

Preparation of 8b from 6a. Lithium aluminum hydride 627.5 mg (16.54 m*M*) was suspended in dry tetrahydrofuran (30 ml) with stirring, and cautiously 452 mg (1.66 m*M*) of **6a** in tetrahydrofuran (15 ml) was added. After 2 hr of reflux and dilution with ether, the excess hydride was decomposed as before. The ethereal solution was washed with water, dried, and evaporated to 225 mg of crude diol **8a**. Preparation of the bis-3,5-dinitrobenzoate as before

(12) V. M. Moćovic and M. LJ. Mihailović, *J. Org. Chem.*, 18, 1190 (1953).

gave 30 mg (after recrystallizations) of **8b**, mp 183–185°. The ir spectra (KBr and $CHCl_3$) and tlc behavior of this sample were identical in every way with that of **8b** prepared from **7**. Mixture melting point of the two samples was 182–184°.

Methylene Anhydride (9). Saturated bromomethyl anhydride (**6a**) (546 mg; 2.0 m*M*) was dissolved in N,N-dimethylformamide (15 ml) and 246.8 mg of anhydrous sodium acetate added. The mixture was heated at 150° for 9 hr, diluted with water (200 ml), and extracted with chloroform. The extracts were washed six times with water, dried, and evaporated to a yellow oil which on sublimation at 100° and 70 μ yielded 150 mg of **9**, mp 124–126°; ir 5.43, 5.58, 6.05, 11.05; nmr 5.05 (d, J = 10 cps, 2). 680 (s, 2), 7.20 (m, 1), 7.60 (m, 3), 8.30 (m, 4); mass spectrum (70 eV) *m/e* 192 (parent).

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.96; H, 6.00.

Unsaturated Methyl Anhydride (10). Methylene anhydride (**9**) (600 mg; 3.12 m*M*) was dissolved in benzene (25 ml) and 100 mg of *p*-toluene sulfonic acid was added. After a reflux period of 3 hr, the benzene solution was washed with water, dried, and evaporated to a yellow oil which was taken up in petroleum ether (bp 60–110°), treated with charcoal, and filtered. On cooling, the solution yielded crystalline (525 mg, 87%) which on recrystallization from hexane had mp 69–70°: ir 3.36, 5.38, 5.61, 8.25, 9.26, 9.35, 10.98, and 13.51; nmr 3.95 (d, J = 7 cps, 1), 6.92 (m, 2), 7.08 (m, 2), 8.15 (d, J = 1.5 cps, 3), 8.47 (q, J = 10 cps, 4); mass spectrum (70 eV), *m/e* 192 (parent).

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.64; H, 6.36.

Unsaturated Bromomethyl Dimethyl Ester (11). Unsaturated bromomethyl anhydride **4a** (1.08 g; 4.0 m*M*) was stirred with a solution of 1.6 g (15 m*M*) sodium carbonate and 15 ml of water for 12 hr, acidified to pH 1.0, and extracted with ethyl acetate which gave after drying and evaporation a white crystalline diacid. The diacid was not characterized but dissolved in 1:1 ether–tetrahydrofuran (50 ml) and treated with cold ethereal diazomethane until a distinct yellow color persisted. After 30 min, the solution was filtered and evaporated to yield **11** as a pale yellow oil 1.0939 g (86%) which crystallized under high vacuum, mp 53–56°. Recrystallization from benzene–petroleum ether (bp 20–40°) at −30° (rather inefficient) gave **11** as white prisms mp 65.5–67°: ir 3.33, 5.66, 5.72, 6.93, 8.24, and 13.85; nmr 3.71 (quintet, 2), 6.79 (m, 2), 6.93 (s, 2), 7.03 (m, 2), 7.93 (m, 1), 8.23 (double doublet, 1) 9.08 (double doublet, 1); mass spectrum (70 eV) *m/e* 316 (parent), 318 (p + 2) both of same intensity.

Anal. Calcd for $C_{13}H_{17}BrO_4$: C, 49.27; H, 5.40. Found: C, 49.47; H, 5.39.

Oxy Lactone Ester (12) and Bromo Hydroxy Lactone Ester (13). Unsaturated bromomethyl dimethyl ester **11** (1.12 g; 3.54 m*M*) was dissolved in chloroform (25–30 ml). *m*-Chloroperbenzoic acid (85%), 1.4368 g (7.08 m*M*), was added and the mixture refluxed for 24 hr (negative starch iodide test). The chloroform solution was washed with 5% sodium bicarbonate and saturated salt, dried, and evaporated to 1.202 g of a colorless oil. Careful separation on silica gel preparative tlc plates (1:1 chloroform–ethyl acetate) gave 419 mg of **12** and 400 mg of **13**. Lactone **12** crystallized from benzene–petroleum ether (bp 20–40°) mp 59–62°: ir 3.37, 3.45, 5.58, 5.78, 6.98, 7.38, 8.27, 8.78, 9.91, 10.37, 10.64, and 11.50; nmr 5.53–5.63 (m, 2), 6.12 (d, J = 7 cps, 1), 6.24 (s, 3), 6.41 (d, J = 7 cps, 1), 6.6–8.8 (m, 7); mass spectrum (70 eV) *m/e* 238 (parent).

Anal. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92. Found: C, 60.27; H, 5.94.

The bromo hydroxy lactone ester **13** could not be crystallized and was never obtained analytically pure. However, the structural assignment is clear from consideration of spectra: ir ($CHCl_3$) 2.80, 3.29, 3.35, 5.58, 5.73, 6.94, 7.32, 7.45, and 9.90; mass spectrum (70 eV) *m/e* 317 (parent), 319 (p + 2) equal intensities. This is the other expected product of the oxidation.

Acetoxymethyl Anhydride (4b) and Acetoxy Anhydride (3b). Cyclopropyl anhydride **5**[2] (960 mg; 5.0 m*M*) was dissolved in glacial acetic acid (35 ml). Concentrated sulfuric acid (5 ml) was added with stirring and cooling (water bath). After stirring at room temperature for 48 hr, the mixture was poured into water and extracted with chloroform; the extracts were washed with 5% sodium bicarbonate, dried, and evaporated to a colorless oil (899 mg), which was crystallized from benzene–petroleum ether (bp 20–40°) to 381 mg. After recrystallization from ethanol, **3b** had mp 124–127°: ir 3.34, 5.37, 5.63, 5.77, and 8.05; nmr 5.09 (m, 1), 6.70 (d, 2), 7.50 (m, 2), 7.95 (s, 3), and 8.00–8.50 (m, 4); mass spectrum (70 eV) *m/e* 252 (parent).

Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39; Found: C, 61.74; H, 6.61.

The nmr of the total crude mixture showed no methyl resonances at all which would have resulted from normal opening. A second major component was isolated fairly pure (~90%) by fractional distillation of the mother liquors above at 120° (bath temperature) and 100 μ. A viscous oil was obtained whose nmr spectrum was in accord with structure **4b**: nmr 5.90 (m, 2), 6.70–6.90 (m, 2), 7.94 (s, 3), 7.50–7.80 (m, 2), 8.00–9.00 (m, 5); multiplet at τ 5.90 attributed to $-CH_2OAc$ moiety. By a combination of nmr analysis and isolation, the total yield of acetates was ~71% with ~31% **4b** and ~40% **3b**.

Deuterio Unsaturated Bromomethyl Anhydride (4a). Acetic anhydride (dry), 13.62 g (133.5 m*M*), was cooled to 0° in ice and 48% deuterium bromide in deuterium oxide (5.13 g; 30 m*M*) was added portionwise with stirring, allowing hydrolysis to subside after each addition. Anhydride 1 (1.570 g; 3.0 m*M*) was added and the mixture allowed to warm to room temperature. After stirring for 12 hr (dry), the solution was poured into water and extracted with chloroform. The combined extracts were washed with water, 5% sodium bicarbonate (twice), dried, and evaporated to 893 mg of a clear oil which crystallized on tituration with absolute ethanol. Recrystallization from absolute ethanol gave **4a** (deuterio) mp 127–129°: ir 3.27, 4.59, 5.42, 5.62, 7.70, 8.13, 9.20, 9.99, 10.40, 10.75, 10.90, and 13.70; nmr 3.65 (quintet, 2), 6.53 (d, 2), 6.82–6.92 (m, 4), 7.57–8.27 (m, 2); nmr (100 MHz) 6.30 (quartet, J_{av} = 8.5 cps, 1), 6.80 (d, J = 9.5 cps, 1); mass spectrum (70 eV) *m/e* 291 (parent), 273 (p + 2); p and p + 2 are of equal intensity and the remainder of the cracking pattern is similar to **4a** (perhydrogenated) except displaced by one mass unit.

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