ation. A_0, B_0, and A_e = initial and equilibrium concentrations of reagents. The complete derivation, as tailored to the system under consideration, can be found in Hung's dissertation.[17]

Acknowledgment. This work was supported by a research grant (CA-06620) from the National Cancer Institute of the National Institutes of Health, Public Health Service. We are indebted to Dr. William F. Sager, Head, Department of Chemistry, The University of Illinois at Chicago Circle, for providing Mrs. Kanitkar with facilities to carry out most of her thesis research. We are also indebted to Dileep Kanitkar for his help in the derivation of the rate law for the reaction A + B $\rightleftharpoons$ X, where $A_0 \neq B_0$.

(17) William Mo-wei Hung, Doctoral Dissertation, University of Massachusetts, Aug 1970.

Cyclopropanes. II. An Electrophilic Addition with Nucleophile Retention[1]

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Abstract: The cyclopropane hydrocarbon **11** was synthesized as an analogy with the previous case **3**, to test the importance of polar *vs.* steric effects in cyclopropane cleavage. Unlike **3**, the major cleavage products of **11** with HBr exhibited Markovnikov direction. They also showed exclusive retention of nucleophile. These results are rationalized in terms of a unified picture of cyclopropane cleavages.

Electrophilic addition to cyclopropanes has aroused considerable interest in recent years, since it involves a nearly unique opportunity to study the stereoelectronic effects in σ-bond cleavage as well as an unusual system of strained bonding orbitals. Experimentally it is possible to discern not only the sites of electrophile and nucleophile attachment across a cleaved σ-bond but also their stereochemistry. Each may bond *via* retention or inversion of configuration (of a cyclopropane carbon) with respect to that of the bond cleaved. The four possible stereochemical results may be symbolized, with R = retention, I = inversion, as (RR), (RI), (IR), (II), the electrophile first followed by the nucleophile. These are shown in Figure 1 for a generalized cyclopropane.

Theoretical calculations on protonation of cyclopropanes implicate two kinds of initial species (intermediates?), arising from edge protonation and corner protonation, of roughly comparable energy[3] and presumably readily interconvertible by minor shifts in nuclear positions.[4a] These are summarized in Figure 1. Edge protonation of the bond cleaved leads to two possible products, reversed in site of attachment of electrophile–nucleophile but both exhibiting electrophile retention. Corner protonation can occur with H^+ oriented on either side and nucleophile attack at either of the other two cyclopropane carbons, opening either bond adjacent to the protonated corner carbon. Hence either retention or inversion of the electrophile (H^+) may be observed: the first case is the corner-protonated species nearest in geometry to (and interconvertible to) the edge-protonated species above; the second case is the corner-protonated species nearest in geometry to one edge-protonated at the bond *adjacent* to that which is finally cleaved. Thus if edge protonation precedes equilibration to a corner-protonated species electrophile inversion can proceed by edge protonation at one bond, equilibration to a corner-protonated species, and collapse with nucleophile to cleave the adjacent bond. The edge-protonated species is seen as a proton embedded in the σ-bond orbital, in the plane of the ring. The corner-protonated variant is essentially equivalent to the midpoint of a Wagner–Meerwein rearrangement, *i.e.*, of the corner-protonated carbon passing across the other two carbons; its two modes of collapse with nucleophile correspond to completion of a 1,2-shift in either direction.[4b]

Each species may collapse in two ways by nucleophile attack, the edge-protonated version at either end of the protonated bond, breaking only that bond in either case, the corner protonation by breaking either of the two adjacent bonds but nucleophile ultimately sited upon one of the other two carbons. The choice of mode is usually dictated by the residual preference in the complex cation for carbonium ion stabilization at one carbon site or the other (tertrary > secondary > primary; allylic > saturated; etc.), but the preference differential is presumably less in the complex cation than in "free" carbonium ions. Backside attack of nucleophile is the usual observation, leading to inversion at the nucleophile site, but the first clear case of

(1) Previous paper: J. B. Hendrickson and R. K. Boeckman, Jr., *J. Amer. Chem. Soc.*, **91**, 3269 (1969).

(2) National Institutes of Health Predoctoral Fellow, 1969–1970.

(3) (a) T. Yonezawa, K. Shimiza, and H. Kato, *Bull. Chem. Soc. Jap.*, **46**, 1302 (1967); (b) J. D. Petke and J. L. Whitten, *J. Amer. Chem. Soc.*, **90**, 3338 (1968); (c) H. Fischer, H. Kollmar, H. O. Smith, and K. Miller, *Tetrahedron Lett.*, 5821 (1968); (d) G. Klopman, *J. Amer. Chem. Soc.*, **91**, 89 (1969).

(4) (a) Since the distinction between the two species is geometrically small and the energy difference may indeed be only a few kilocalories per mole, the distinction may be unimportant. The electron-rich bent σ bond is the obvious place of attack, stereoelectronically, and subsequent passage through corner-protonated geometry can give observed products, as indicated in Figure 1. (b) The corner-protonated species may be envisioned as an sp^2 carbon bearing hydrogen, with its p orbital embedded in the midpoint of a π orbital between the other two carbons.

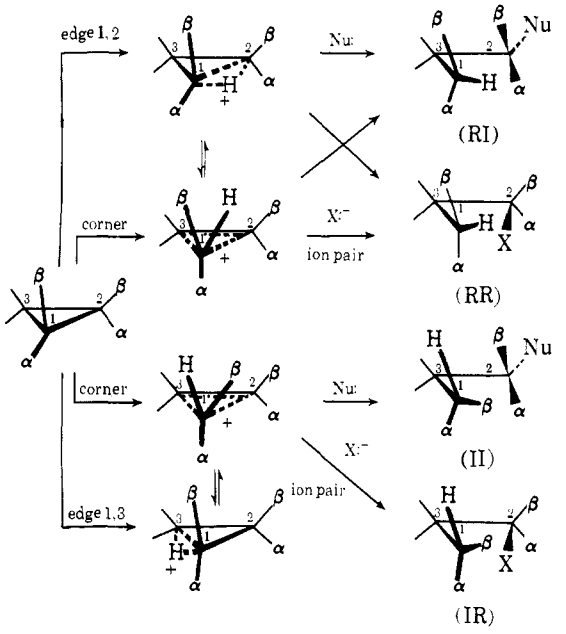
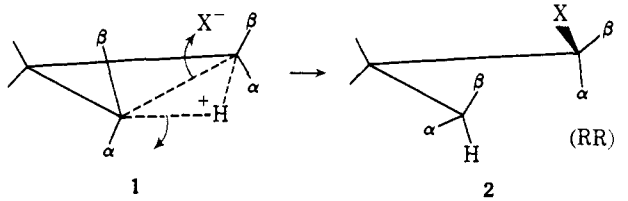


Figure 1. Cleavage of the 1,2 bond of a cyclopropane *via* edge protonation or corner protonation; edge protonation may be 1,2 (at the bond cleaved) or 1,3 (at a bond not ultimately cleaved).

nucleophile retention has recently been reported by Cristol.[5] Previous cases of minor nucleophile retention appear to have passed through a subsequent carbonium ion of adequate lifetime at the nucleophile site, with production of some of both epimers.[6] Cristol argued quite reasonably that retention as a major result probably occurred from collapse of an ion pair of the complex cation and nucleophilic anion.[5] Each kind of complex cation bears its positive charge distribution primarily in the cyclopropane ring plane so that the preferential positioning of the nucleophilic anion in the ion pair should be above (rather than in) that ring plane. This leads to a simple conrotatory collapse in the case of the edge-protonated ion pair (**1**) passing to the (RR) product (**2**) (the curved arrows are only meant to show the conrotatory direction of collapse of the ring orbitals). It should be noted that only when the nucleophile is an anion (*cf.* halide) can it take up this ion-pair situation and give retention; solvolysis should yield only inversion (*cf.* H_2SO_4–HOAc) and this has been most commonly studied system.[6]



1 **2**

Experimental evidence to date is consistent with this general picture although subsequent passage through other carbonium ions represents an occasional complication. With the exception of our previous example,[1] sites of nucleophile and electrophile attachment exhibit the predicted Markovnikov direction. Evidence for equilibration through corner-protonated species was offered by Baird[7] and others[8] in deuterium scrambling experiments on cyclopropane itself. Corner-protonated species were also shown by Nickon[9] and Hammons[10] to be the major source of products in cleavages of tricyclenes, and more stable by 6 kcal/mol than the edge-protonated species in that system in Olah's work.[11]

Stereochemical evidence, much of it by LaLonde,[6,12] has always shown inversion by nucleophile in acetic acid solvolyses, but until Cristol's recent study[5] showing nucleophilic retention by bromide, there were no stereochemical studies of nucleophile attack in hydrogen halide cleavages of cyclopropanes.[13] As to the electrophile, results showing inversion,[14] mixed inversion–retention,[9,10] and retention[1] of proton (studied as deuterium) have all been reported. These are all consistent with the routes of Figure 1 and appear to reflect the choice of the bond (or corner) which is protonated and the relative energies of the possible edge- and corner-protonated species in the particular molecule being examined.

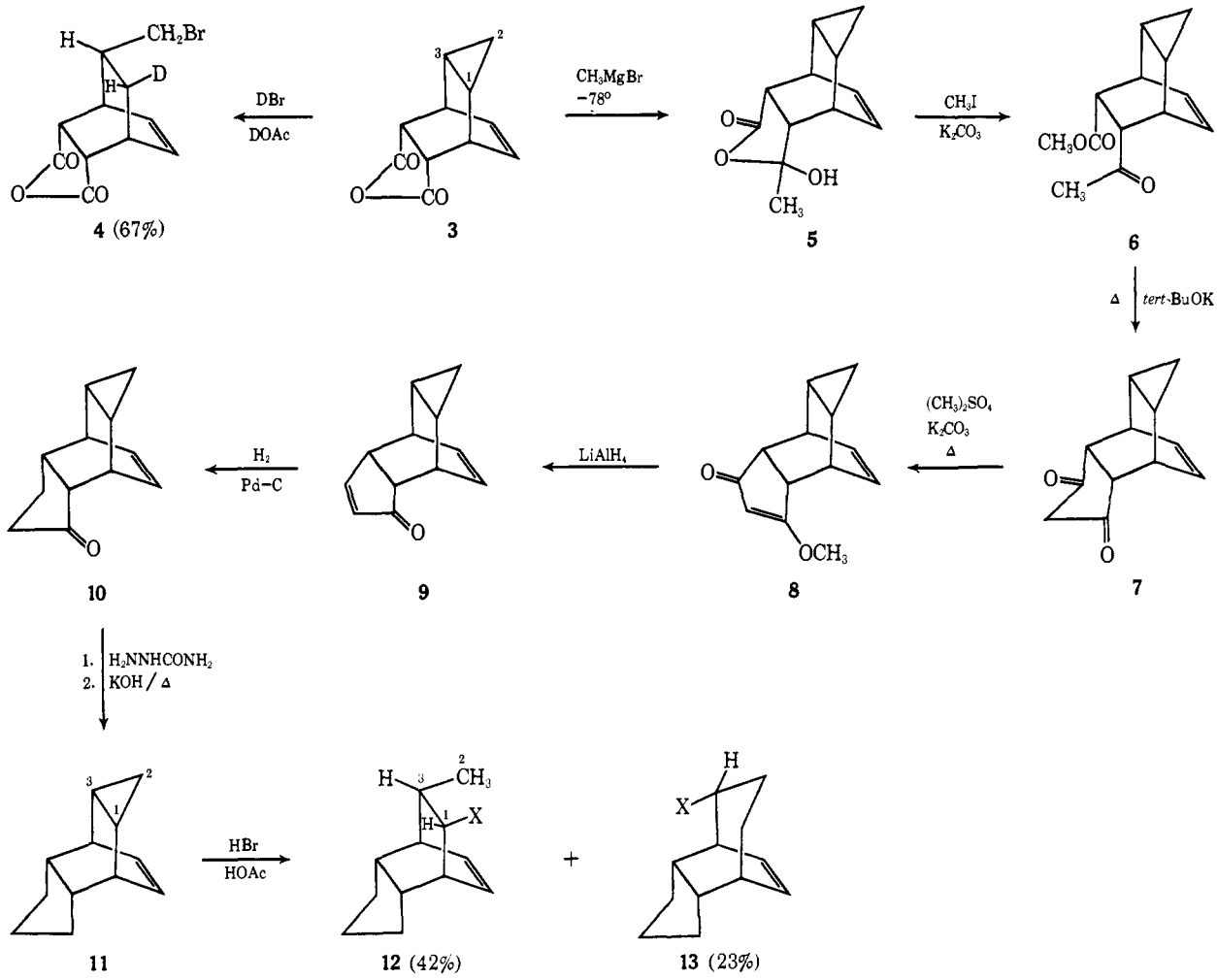
In our previous work we demonstrated a clear case of electrophile retention yielding only a single major product (**3** → **4**) (see Scheme I). The system chosen seems a good one since the reaction is clean and simple, uncomplicated by rearrangement, deuterium scrambling, or much opportunity for intervention of stabilized carbonium ion intermediates.[15] Besides clear electrophile retention we observed anti-Markovnikov direction of cleavage which we attributed to steric hindrance of nucleophile attack at the presumably favored secondary site. McManus has since commented that the reverse direction could arise from electronic imbalance in the σ-protonated cation, caused electrostatically by the nearby partially positive carbonyl carbons of the anhydride.[16]

In order to distinguish these causes we prepared the analogous hydrocarbon **11** to retain the rigid geometry and its intrinsic steric hindrance but eliminate the polar influence of the anhydride. The hydrocarbon **11** was prepared from **5** by the straightforward synthetic sequence shown (Scheme I).

Shorter syntheses, *via* cycloadditions of cycloheptatriene with cyclopentenes, were not successful with cyclopentadiene, cyclopentenone, or cyclopentenedione. Hence this longer but facile route was selected. The hydrocarbon **11** was characterized by its mode of preparation, analysis, and mass spectral parent ion, and by a symmetrical double doublet (J = 3.6, 4.8 Hz) of

(5) S. J. Cristol, W. Y. Lim, and A. R. Dahl, *J. Amer. Chem. Soc.*, **92**, 4013 (1970).
(6) R. T. LaLonde and M. A. Tobias, *ibid.*, **85**, 3771 (1963); **86**, 4068 (1964).
(7) R. L. Baird and A. Aborderin, *ibid.*, **86**, 252, 2300 (1964).
(8) (a) C. C. Lee and L. Gruber, *ibid.*, **90**, 3775, 3778 (1968); (b) N. C. Deno, *ibid.*, **90**, 6457 (1968).
(9) A. Nickon and J. H. Hammons, *ibid.*, **86**, 3322 (1964).
(10) J. H. Hammons, E. K. Probasco, L. A. Sanders, and E. J. Whalen, *J. Org. Chem.*, **33**, 4493 (1968).
(11) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3954, 3956 (1969).
(12) R. T. LaLonde and L. S. Forney, *ibid.*, **85**, 3767 (1963); *J. Org. Chem.*, **29**, 2911 (1964).
(13) Other cleavages of substituted cyclopropanes with Br_2 or with bases have shown nucleophilic inversion.
(14) R. T. LaLonde, J. Ding, and M. A. Tobias, *J. Amer. Chem. Soc.*, **89**, 6651 (1967).
(15) Furthermore, in a number of systems previously studied, the molecules exhibited considerable strain in the other parts of the molecule, thus rather obscuring what is due simply to opening of the cyclopropane part. In the system used here, the bicyclooctane is relatively strain free.
(16) L. D. McManus and N. A. J. Rogers, *Tetrahedron Lett.*, 4735 (1969).

Scheme I



two identical vinyl protons at τ 4.36, and two cyclopropane protons at τ 9.90.

Under the same conditions used previously (HBr/HOAc) cyclopropane **11** afforded, as the major product, **12** (X = Br). In this product the vinyl proton signal is similar to that in **11** (somewhat perturbed owing to dissymmetry) and the cyclopropane signal has been replaced by a methyl doublet at τ 8.98 (J = 6.6 Hz). A single-proton double doublet (J = 2.4, 8.7 Hz) at τ 5.61 is assigned to a secondary bromide site, and the large coupling constant is only consistent with the cis (eclipsed) orientation of hydrogens at carbons 1 and 3 in structure **12**; a similar assignment was made for the protons in structure **4**.[1] None of the lesser products, separated by thin layer chromatography, exhibited in the nmr spectrum either the methyl or $-CH_2X$ absorptions characteristic of opening the same bond in either direction. That no skeletal rearrangement had occurred was shown by hydrogenation of both **11** and **12** (X = Br) to the same hydrocarbon **12** (X = H; double bond saturated), which exhibited a single methyl doublet in the nmr spectrum.

Since the steric hindrance effects in **3** and **11** must be essentially equivalent, the observed reversal of the direction of cleavage must arise from the difference in polarity between **3** and **11**, as suggested by McManus.[16] The second effect which is clearly observable is that nucleophile attack has occurred exclusively with retention. The only previous case of hydrogen halide cleavage in which nucleophile stereochemistry was demonstrated was that of Cristol,[5] which also proceeded with retention and was ascribed to ion-pair collapse. The present observation suggests that with a nucleophilic counterion retention may be the usual event with its mechanistic presumption of ion-pair collapse. In the present case the steric hindrance to backside approach invoked in our previous paper[1] may still be the dominant influence, favoring the ion-pair collapse and retention only by default, but in Cristol's case this is apparently not a reasonable alternative explanation for the observed retention.

The main secondary product was presumed to be a bromide from its similar retention time to **12** (X = Br) in the gas chromatography directly after reaction. Two acetates, formed in lesser amounts, showed longer retention times and nmr spectra indicated that they possessed skeleton **13** and were not rearranged. Aqueous work-up of the reaction allowed isolation of bromide **12** and a crystalline alcohol, assigned structure **13** (X = OH), but no trace of the second bromide seen in the gas chromatogram. The chromatographic yield of the labile bromide before aqueous work-up was the same as that of the alcohol isolated, and the presumption was made that the alcohol arose by facile homoallylic solvolysis of the labile bromide in the aqueous work-up.[17] The stereoelectronic requirements of this

(17) Under the normal aqueous work-up conditions, acetates were never hydrolyzed in our previous series;[1] it seems unlikely that they could be the source of the alcohol isolated here. The very minor yield of acetates seen in the gas chromatogram before work-up here was also

solvolysis lead to assignment of both the labile bromide and the alcohol as **13** (X = Br or OH). The nmr spectrum of the alcohol **13** shows that no skeletal rearrangement has occurred, for the same nearly symmetrical vinyl pattern as that of **11** and **12** (and cases in the previous work,[1] *cf.* **3** and **4**) appears in the alcohol **13** and the lesser amounts of mixed acetates.[17] Had rearrangement occurred from the side opposite the cyclopropane, an allylic system (in a [3.2.1]bicyclooctene) would have appeared in the nmr spectrum, as discussed by Jefford and Ramey;[18] rearrangement from the same side as the cyclopropane is unlikely and has never been observed.[16]

The second product **13** then also shows retention of nucleophile (and presumably ion-pair collapse), as with the major product **12**, although in this case it is the internal (1–3) bond which is cleaved. These results can most simply be explained by initial edge protonation of **11** in the more sterically accessible (1–2) bond followed by internal collapse with retention of nucleophile to **12** as the major result. The minor result implicates equilibration to a 1-corner-protonated species (or on to edge protonation of 1–3) followed by internal collapse with retention of nucleophile to **13** (X = Br). Alternatively (and indistinguishably), corner protonation could occur first followed by collapse to both products. The same route characterizes the behavior of the polar anhydride **3** which differs only in a shift of the cationic center in the protonated species away from proximity with the carbonyl carbons so that more (1–2) cleavage occurs and this in the reverse, or anti-Markovnikov, direction. There remains no compelling reason to invoke steric hindrance to approach of either electrophile or nucleophile over the five-membered ring as a major influence, as we offered in the previous paper,[1] except to account for the predominance of cleavage of the external (1–2) bond over the internal one (1–3).

We did not carry out deuterium studies in the present series since in the major product electrophile stereochemistry cannot be determined in this way and in the minor product the experimental difficulties of determining deuterium stereochemistry (*cf.* ref 14) are excessive. We intend now to modify the ring system so as to allow clear stereochemical evaluation at all three carbons for both nucleophile and electrophile, since the basic ring system seems a good one for the several reasons advanced above.

Experimental Section

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. All ir spectra were obtained on a Perkin-Elmer 137 infrared spectrophotometer and absorption maxima are reported in microns as potassium bromide dispersions unless otherwise noted. All nmr spectra were obtained in CCl_4 on a Varian A-60-D spectrometer and are reported in τ (TMS) with multiplicity, coupling constants (if any), and integration appended. Mass spectra were determined on an AEI MS-12 mass spectrometer (purchased under National Science Foundation Research Instrument Grant GP-3644). Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Lactol (5). A solution of methylmagnesium bromide in ether prepared from 2.43 g (0.1 g-atom) of magnesium turnings and excess gaseous methyl bromide was added dropwise under nitrogen to a stirred solution of anhydride (**3**)[19] (19.0 g; 0.1 mol) in 500 ml of ether–pyridine (1:2) at −78°. The resulting milky suspension was stirred 8 hr at −78° and then poured into sufficient cold 20% sulfuric acid to neutralize the pyridine. The aqueous solution was partitioned with ether (three 200-ml portions). Combined ethereal layers were then extracted with two 100-ml portions of 10% sodium carbonate. The combined aqueous carbonate solutions were warmed to expel dissolved ether and acidified with concentrated hydrochloric acid to pH 1, and the resulting precipitate was filtered to yield crude crystalline lactol (**5**): 10.05 g (50%); ir λ_{max} (CH_2Cl_2) 2.95, 5.69, 7.72, 10.86 μ; nmr (τ) 3.98 (t, J = 3.6 Hz, 2), 5.96 (s,1), 6.66 (m,s), 7.26 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1), 8.36 (s,3), 8.96 (m,2), 9.80 (m,2).

The analytical sample recrystallized from benzene to mp 152.5–153° (sealed tube).

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.60; H, 6.93.

The yield was based on starting material consumed. Considerable amounts of unchanged anhydride were recovered by evaporation of the dried ethereal layers.

Acetyl Methyl Ester (6). Lactol (**5**), 25.09 g (0.12 mol), was dissolved in 1 l. of dry acetone; methyl iodide, 172 g (1.2 mol) and freshly fused anhydrous potassium carbonate (25 g) were added. After 72 hr at reflux, the solution was filtered and evaporated, and the residue was dissolved in methylene chloride. This solution was washed with water (two times), dried, and evaporated to afford crystalline keto ester (**6**): 22.4 g (84.5%); ir λ_{max} 5.77, 5.85, 8.42, 8.65, 10.73, 13.94; nmr τ 4.18 (m, 2), 6.48 (s, 3), 6.94 (m, 4), 7.98 (s, 3), 9.08 (m, 2), 9.88 (m, 2).

An analytical sample was recrystallized from benzene–petroleum ether (20–40°) at −78° after Norit treatment to mp 75–76°.

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.94; H, 7.30.

β-Diketone (7). Keto ester (**6**), 3.4 g (15.4 mmol), was refluxed in dry benzene under a nitrogen atmosphere with potassium *tert*-butoxide, 3.16 g (31 mmol), for 4 hr and then stirred overnight at room temperature. The resulting precipitate was filtered free of benzene and dissolved in water. The aqueous solution was boiled to remove traces of benzene, cooled, and acidified with glacial acetic acid. The resulting precipitate was filtered and air dried to yield β-diketone (**7**): 2.4 g (82%); ir λ_{max} 2.95 (broad), 6.80 (broad), 7.60, 8.03, 8.12, 8.53, 8.66, 11.76, 11.91, 13.50, 13.90 μ. β-Diketone (**7**) is readily soluble in aqueous sodium carbonate and insoluble in all common organic solvents; the ferric chloride test was negative. It was recrystallized from ethanol (sparingly soluble) to mp 225–230° dec. The crude material is sufficiently pure for further use.

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.51; H, 6.43. Found: C, 76.49; H, 6.68.

Dienone (9). β-Diketone (**7**), 188 mg (1.0 mmol), was suspended in 20 ml of dry dimethylformamide, 800 mg of anhydrous potassium carbonate was added, and the suspension was stirred until the solution clarified (~5 min). Dimethyl sulfate, 2.0 g (excess), was added and the mixture was warmed to 35–40° for 12 hr. The solution was poured into water, and the products were isolated by chloroform extraction (three times). Combined chloroform extracts were washed successively with water and 10% sodium hydroxide, and dried and evaporated to afford enol ether (**8**) as a pale yellow oil which crystallized on standing: 192.2 mg (95%); ir λ_{max} (methylene chloride) 5.98, 6.20, 7.42, 8.40, 8.59, 9.19, 9.51 9.86, 11.78, 12.02.

Enol ether (**8**), 192 mg (0.95 mmol), was dissolved in 10 ml of anhydrous ether and added dropwise to a suspension of lithium aluminum hydride, 40 mg (1.05 mmol), in 5 ml of anhydrous ether. The suspension was stirred overnight at room temperature; excess hydride was decomposed by cautious addition of water and the resulting slurry was poured into 25 ml of cold 10% sulfuric acid with vigorous stirring. The solution was stirred for 5 min and the ether layer separated. The aqueous layer was extracted with an additional 25 ml of ether, and the combined organic layers were washed with 5% sodium bicarbonate and water, dried over sodium sulfate, and evaporated to yield dienone (**9**) as a yellow oil, 138 mg (84%). Dienone (**9**) was purified by vacuum distillation (bp 92–93° (bath temp) (0.08 mm), and crystallized on cooling

isolated thereafter as a liquid mixture, apparently of skeleton **13** by nmr. The two acetates were present in small amounts and difficult to separate but are presumed to be epimers arising from minor amounts of free carbonium ion after 1–3 bond opening. This observation parallels that of certain minor products in LaLonde's studies.[6]

(18) Spectral discussion of rearranged and unrearranged skeletons is found in C. W. Jefford and K. C. Ramey, *Tetrahedron*, **24**, 2927 (1968).

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

to −78°: mp 35–37° (91 mg); ir λ_{max} (methylene chloride) 5.93, 6.30, 7.46, 8.22, 8.47, 9.61, 9.90, 11.34, 11.82 μ; nmr τ 2.65 (dd, J_1 = 5.7 Hz, J_2 = 2.1 Hz, 1), 4.02 (dd, J_1 = 5.7 Hz, J_2 = 2.1 Hz, 1), 4.55 (m, 2), 7.01 (m, 3), 7.58 (dd, J_1 = 6.0 Hz, J_2 = 3.0 Hz, 1), 8.92 (m, 2), 9.78 (m, 2).

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.57; H, 7.22.

Cyclopentanone (10). Dienone (**9**), 42 mg (0.244 mmol), was hydrogenated in 3.4 ml of ethanolic potassium hydroxide solution (200 mg/10 ml of ethanol) over 10 mg of 10% palladium on charcoal catalyst. The uptake was rapid, and ceased after 1 equiv of hydrogen had been absorbed. The catalyst was filtered, and the solvent was evaporated. Water was added and the product isolated by ether extraction (three times). Combined ethereal solutions were washed with water, dried over sodium sulfate, and evaporated to afford enone (**10**) as a pale yellow oil: 34 mg; 80%, which was pure (vpc 3% SE-30, 120°) as obtained; ir λ_{max} (methylene chloride) 5.81, 6.15 (wk), 8.54, 9.64, 11.85, 12.25 μ; nmr τ 4.28 (t, J = 3.9 Hz, 2), 6.60–9.30 (m, 10), 9.87 (m, 2).

Unsaturated Cyclopropane (11). Enone (**10**), 2.41 g (13.8 mmol), was converted to 3.0 g of crude crystalline semicarbazone in the usual way.[20] A mixture of the semicarbazone and 10 g of potassium hydroxide was fused in a short-path still under a regulated vacuum (150 mm). Both the distillate and residue were dissolved in water and extracted with hexane (three times); combined hexane solutions were washed with water, dried over sodium sulfate, and evaporated. The residue was taken up in hexane and filtered through a short alumina column (activity II) in hexane. The initial hexane eluates (200 ml) were evaporated to afford unsaturated cyclopropane (**11**) as a colorless oil, 1.22 g (60%), which analyzed >98% pure by vpc (3% SE-30 (135°): ir λ_{max} (neat) 3.33, 3.36, 3.44, 3.54, 6.06, 13.97 μ; nmr τ 4.36 (dd, J_1 = 4.8 Hz, J_2 = 3.6 Hz, 2), 7.33 (m, 2), 7.82 (m, 2), 8.00–9.34 (m, 8), 9.90 (m, 2).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 90.16; H, 10.16.

Reaction of Cyclopropane (11) with Hydrogen Bromide. Unsaturated cyclopropane (**11**), 74 mg (0.46 mmol), was dissolved in 2 ml of glacial acetic acid and cooled to ~10° in ice; a solution of 263 mg (3.24 mmol) of anhydrous hydrogen bromide in 2 ml of glacial acetic acid was added, and the solution was allowed to warm to room temperature and stirred for 7 hr. Vpc analysis (3% SE-30 (125°)) indicated four products present: two halides and two acetates (tlc (pentane and in carbon tetrachloride) confirmed this). The mixture was poured into water, and the products were isolated by methylene chloride extraction (three times). Combined extracts were washed with 5% sodium bicarbonate, dried over sodium sulfate, and evaporated to 95 mg of a yellow oil. Vpc analysis indicated almost complete disappearance of one halide.

Separation of this mixture by preparative tlc (SiO_2–chloroform) gave three major bands: I, bromide (**12**, X = Br), 40 mg (42%), a colorless oil (R_f 0.63); ir λ_{max} (methylene chloride) 3.27, 3.39, 6.90, 7.26, 8.36, 10.96, 13.89 μ; nmr τ 2.88 (m, 2), 5.61 (dd, J_1 = 8.7 Hz, J_2 = 2.4 Hz, 1), 6.78–9.20 (m, 11), 8.98 (d, J = 6.6 Hz, 3); mass spectrum (70 eV) *m/e* 242 (P + 2), 240 (P^+, intensity 1:1 (*Anal.* Calcd for $C_{12}H_{17}Br$: C, 59.76; H, 7.11. Found: C, 60.50; H, 7.52); II, a mixture (1:1) of acetates (**13**, X = OAc) which could not be resolved further (R_f = 0.39); ir λ_{max} (methylene chloride) 3.40, 5.80, 7.33, 8.07, 9.77 μ; nmr τ 2.98 (m, 2), 3.92 (m, 1), 7.30 (m, 1), 7.98 and 8.00 (s, 3); mass spectrum (70 eV) *m/e* 220 (P^+); III, unsaturated alcohol (**13**, X = OH), 25 mg (26%), recrystallized to mp 79.5–81.5° (petroleum ether 20–40°), R_f 0.18; ir λ_{max} (methylene chloride) 2.76, 2.90, 3.36, 9.61, 9.85, 9.96 μ; nmr τ 4.24 (m, 2), 6.10 (m, 1), 7.04–9.24 (m, 15); mass spectrum (70 eV) *m/e* 178 (P^+), 160 (P^+ − 18).

Hydrogenation of Unsaturated Cyclopropane (11) and Bromide (12, X = Br). Unsaturated cyclopropane (**11**), 41 mg (25.6 mmol), was dissolved in 1 ml of glacial acetic acid, 45 mg of platinum oxide catalyst was added, and the mixture was shaken under 60 psi of hydrogen in a Parr apparatus for 7 hr. The catalyst was filtered and the solvent evaporated to yield 40 mg (~100%) of saturated methyl hydrocarbon, homogeneous by vpc (3% SE-30 (125°)): ir λ_{max} (carbon tetrachloride) 3.42, 3.45, 6.94, 7.99 μ; nmr τ 7.82–9.12 (m, 17), 8.98 (d, J = 5.4 Hz, 3).

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.69; H, 12.31.

Unsaturated bromide (**12**, X = Br), 20 mg (0.083 mmol), which was ~90% pure, was dissolved in 2 ml of 1:1 methanol–ethyl acetate containing 60 mg of potassium hydroxide. Approximately 150 mg of 10% palladium on charcoal was added and the mixture was stirred under a hydrogen atmosphere (1 atm) for 12 hr at which time approximately the theoretical uptake had occurred. The catalyst was filtered, solvents were evaporated, the residue was taken up in water, and the product was isolated by thorough extraction with pentane. The extracts were dried over sodium sulfate and evaporated to 15 mg (73%) of an oil whose vpc retention time and ir spectrum were identical with the saturated methyl hydrocarbon (**12**, X = H and double bond saturated) prepared and characterized above. Peak enhancement on coinjection of an admixture of the two substances into the vpc (3% SE-30 (125°)) further verified the identity of the two compounds.

(20) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1964, p 253.