this band was the carbonyl stretching mode. The lower frequency absorptions of furotropone **2a** and benzotropone **1a** were also found to be solvent dependent.[4] By correlating the frequency of this absorption with calculated bond orders it was inferred[4] that **2a** was less aromatic than tropone or **1a**. Since the carbonyl in **3** does not have a similar geometric disposition[9] to that in **1a** and **2a**, we were unable to compare the infrared absorptions at 1620–1590 cm^{-1} in the same manner.

The ultraviolet absorption bands of **3** (methanol) at 215 nm (log ϵ 4.01) for the pyrazole ring, 252 (4.40) for the tropone ring, and 320 (3.81) for the conjugated keto group compare well with those for benzotropone **1a** [λ_{max}^{EtOH} 231 nm (log ϵ 4.50), 272 (4.69), 332 (3.64), and 348 (3.45)] and for furotropone **2a** [λ_{max}^{EtOH} 211 nm (log ϵ 4.08), 216 (4.05), 250 (4.57), 255 (4.55), 292 (3.67), and 301 (3.67)]. We had an opportunity here to compare the extent of delocalization of the ring electrons by comparing the long-wavelength absorptions. The shift in maxima of about 47 nm toward the blue from the band for benzotropone was attributed[4] to a decrease in delocalization in furotropone. By analogy, the blue shift of only 28 nm by pyrazolotropone indicates the order of aromaticity to be benzotropone > pyrazolotropone > furotropone. The dipolar structure **3d** must make a significant contribution to the resonance hybrid of **3**.

In Table I, pyrazolotropone is compared with the other pertinent tropones with regard to their nmr properties. It is apparent that the three bicyclic structures can sustain an induced ring current. A comparison with tropone, which shows only a broadened singlet, reveals the bicyclic tropones to be less aromatic. Benzotropone and furotropone show their symmetry in the very similar absorption pattern for the peripheral protons. The unsymmetrical distribution of heteroatoms in **3** produces four absorptions consisting of two singlets and two doublets.

TABLE I

CHEMICAL SHIFTS FOR TROPONES[a]

Compd	Assignment, δ ppm	
	Fused ring protons	Tropone ring doublets
Tropone[b]		6.95 (broad singlet)
1a[c]	7.47 (4 H, s)	7.27 (2 H), 6.65 (2 H), J = 12 Hz
2a[c]	8.08 (2 H, s)	7.37 (2 H), 6.52 (2 H), J = 12 Hz
3	8.24 (NH, 1 H, s) 7.80 (CH, 1 H, s)	7.60 (H_c, s),[d] 6.64 (H_d, s) 6.90 (H_a, d),[e] 6.40 (H_b, d)[e]

[a] The cross-conjugated 1,2,3,3a,8a-pentahydroazulen-6-one exhibited absorptions at δ 6.21 and 5.87 (J = 12.5 Hz) for the olefinic doublets: O. L. Chapman and T. H. Kock, *J. Org. Chem.*, **31**, 1042 (1966). [b] Data taken from D. J. Bertelli, C. Golino, and D. L. Dreyer, *J. Amer. Chem. Soc.*, **86**, 3329 (1964), solvent CCl_4. [c] Taken from ref 4, solvent not reported. [d] *Cf.* Scheme I for H symbols. [e] J = 2 Hz, solvent DMSO-d_6.

It was clear from the spectroscopic properties exhibited by pyrazolotropones **3** and **6** that they exist as keto tautomers, *e.g.*, **3a** and **3b**, rather than in the hydroxy form **3c**.

Experimental Section

All melting points, taken on a Mel-Temp apparatus, are uncorrected. Infrared spectra were measured on a Perkin-Elmer Infracord Model 137 using the potassium bromide pellet technique. Nuclear magnetic resonance spectra were recorded on a Varian A-60A using tetramethylsilane as an internal standard. Ultraviolet spectra were obtained with a Bausch and Lomb 505 spectrophotometer. Combustion analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and Childers Microanalytical Laboratory, Milford, N. J.

Materials.—Diazomethane was prepared by Eistert's procedure,[10] and assayed by the method of Fieser.[11] The acetylenedialdehyde bis(diethyl acetal) was prepared according to the procedure of Wohl[12] and used in the procedure described by Henkel and Weygand[13] for the preparation of pyrazole-3(5),4-dicarboxyaldehyde, yield 81.8%, mp 202–203° (lit. 203–205°).

2,7-Dicarbethoxy[4,5-*c*(*d*)]pyrazolotropone.—To 4.96 g. (0.039 mol) of pyrazole-3(5),4-dicarboxaldehyde suspended in 55 ml of benzene was added 7.95 g (0.0044 mol) of diethyl acetonedicarboxylate and 0.5 ml of piperidine. The suspension was refluxed for 2 hr and cooled, and the solid was filtered and recrystallized from chloroform–pentane to yield 8.7 g (76.5%) of **6** as a white powder, mp 159–161°. Five preparations gave yields ranging from 43 to 77%: nmr ($CDCl_3$) δ 1.33 (t, 6, CH_3, J = 7 Hz), 4.38 (q, 4, CH_2), 8.22 (s, 2, tropone ring), 8.40 (s, 1, pyrazole CH), 12.80 (br, 1, NH).

Anal. Calcd for $C_{14}H_{14}N_2O_5$: C, 57.93; H, 4.86; N, 9.65. Found: C, 57.77; H, 4.97; N, 9.58.

2,7-Dicarboxy[4,5-*c*(*d*)]pyrazolotropone.—A suspension of the above dicarbethoxypyrazolotropone (16 g, 0.055 mol) in 200 ml of 20% sulfuric acid was refluxed for 1.5 hr and then stirred for 2 hr at room temperature. The cooled suspension was filtered and the residue was dried overnight in a desiccator at 100°. Recrystallization from absolute ethanol afforded 10 g (78%) of **7** as a tan solid, mp 259–261°. Five preparations gave the acid in 73–78% yields: uv λ_{max}^{MeOH} 213 nm (log ϵ 3.97), 272 (4.43), 333 (3.78); ir λ_{max} (KBr) 3226 (NH), 1709 (COOH), 1590 cm^{-1} (C=O tropone); nmr (DMSO-d_6) δ 8.00 (s, 1 H, pyrazole CH), 8.24 (s, 2 H, tropone), 10.25 (broad absorption, 3 H, NH and two COOH).

Anal. Calcd for $C_{10}H_6N_2O_5$: C, 51.29; H, 2.58; N, 11.96. Found: C, 51.72; H, 2.92; N, 11.65.

[4,5-*c*(*d*)]Pyrazolotropone.—To 4.6 g (0.0197 mol) of the above dicarboxypyrazolotropone was added 0.7 g of copper powder and 25 ml of quinoline. The solution was heated in an oil bath at 205° for 3.5 hr. The black suspension was poured into 30 ml of an ice-cold solution of 50% hydrochloric acid and the suspension was filtered. The filtrate was extracted with five 60-ml portions of ethyl acetate, and the extracts were dried ($MgSO_4$) and evaporated to a yellow solid. Solution in ethyl acetate and addition of pentane to the cloud point yielded 1.02 g (35.5%) of **3** as a light yellow solid, mp 223.5–225°. Eight preparations gave yields ranging from 10 to 36%. The product did not react with 2,4-dinitrophenylhydrazine reagent.

Anal. Calcd for $C_8H_6N_2O$: C, 65.74; H, 4.14; N, 19.17. Found: C, 65.70; H, 4.17; N, 19.25.

Registry No.—**3a**, 33015-60-0; **3b**, 33015-61-1; **3c**, 33015-62-2; **6a**, 33015-63-3; **6b**, 33015-64-4; **7a**, 33015-65-5; **7b**, 33015-66-6.

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(9) O. L. Chapman and T. H. Kock, *J. Org. Chem.*, **31**, 1042 (1966).

(10) B. Eistert, "Organic Syntheses," Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1967, p 165.

(11) L. F. Feiser and M. Feiser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 191.

(12) A. Wohl, *Chem. Ber.*, **45**, 339 (1912).

(13) K. Henkel and F. Weygand, *Chem. Ber.*, **76**, 812 (1943).

The Electronic Effects of Oxygen in the 8-Oxabicyclo[4.3.0]non-3-ene Series

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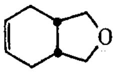
Replacement of a methylene group by an oxygen heteroatom has been shown to affect the chemistry of the molecule involved. A conformational effect has been noted by Paquette in the solvolysis of oxocan-3-yl brosylate.[1] A retarding field effect has been demonstrated by Tarbell in the solvolysis of 4-tetrahydropyranyl tosylate.[2] Increased reactivity due to resonance participation has been observed in the hydroboration of 2,3-dihydrofuran.[3] We wish to report here some of our work which suggests the possibility of long-range nonbonded electronic participation in a rigid system.

Rickborn[4] has questioned whether the heteroatom in *cis*-8-oxabicyclo[4.3.0]non-3-ene (**1**) might contribute to the chemistry of the alkene bond. As a consequence of our work trying to establish whether a directive effect might be observed in the chemistry of the 8-oxabicyclo[4.3.0]non-3-ene series,[5] we investigated the reactivity of these molecules. The phthalans **1** and **2** and Δ^5-*cis*-tetrahydroindan (**3**) were subjected to competition experiments in order to evaluate the relative reactivities of the alkene bond.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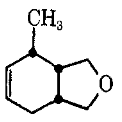

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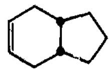
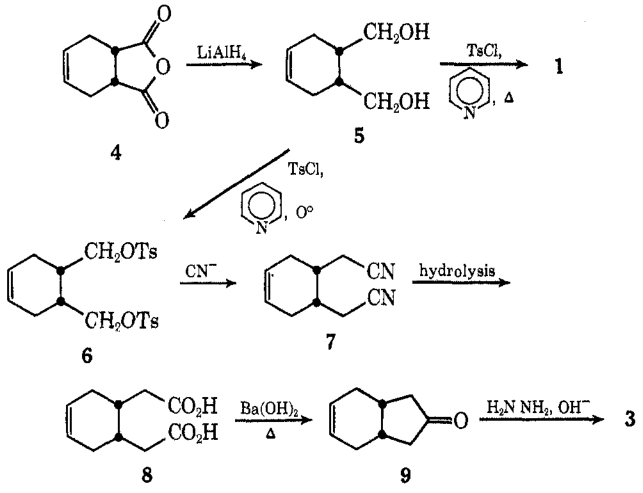


Results and Discussion

The synthesis of **1** and **3** are dilineated in Scheme I. The anhydride **4** was reduced to the 1,4-diol **5**, which in turn was readily cyclized to the tetrahydrofuranyl system by treating the diol with *p*-toluenesulfonyl chloride in refluxing pyridine. Formation of the ditosylate **6** was readily achieved by treating **5** with *p*-toluenesulfonyl chloride at 0°. The carbon chain lengthening was affected by a displacement of both tosylate functionalities with cyanide ion. The resulting dinitrile **7** was hydrolyzed to **8**, which under conditions of Ruzicka cyclization afforded the indanone derivative **9**. Wolff–Kischner reduction of **9** gave the desired Δ^5-*cis*-tetrahydroindan (**3**). The preparation of **2** has been reported.[5]

Scheme I



Each alkene was mixed with an equal molar amount of cyclohexene and was allowed to compete for a limited amount of mercuric acetate in THF–H_2O. The relative reactivities were ascertained by established methods[6] and are recorded in Table I.

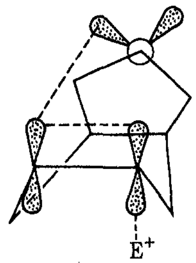
Table I

Results of Competition Studies

	Cyclohexene	1	2	3
Oxymercuration (K_{rel})	1.00	0.93	0.35	0.11
$AgNO_3$ equilibration (K_{eq})	0.018[a]	0.15	0.048	

[a] Reference 9.

The eightfold increase of reactivity of **1** as compared to **3** shows that the alkene bond is more reactive. Examination of various types of models suggests that the nonbonded electrons of the oxygen can stabilize any incipient charge which might result from electrophilic attack on the π system of the alkene. This interaction, as described by **10**, might be similar to the long-range oxygen participation reported by Paquette for **11**.[7]



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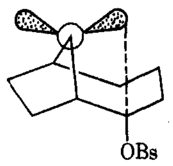

11

The decrease in reactivity of **2** must be attributed to a "steric effect" of the methyl group.[8] It is interesting to note that the relative reactivities of cyclohexene *vs.* 3-methylcyclohexene are 1.0–0.36. The remarkable similarities of rate retardation due to a methyl group are of interest, particularly since **2** is conformationally more homogeneous than 3-methylcyclohexene. The directive effects found in the chemistry of **2** and 3-methylcyclohexene are also quite similar.[5]

Comparison of the oxymercuration results with ease of silver nitrate complexing again suggests that the alkene bond of **1** is more susceptible to coordination with silver ion than cyclohexene (Table I). Distribution of **1** and **2** between carbon tetrachloride and aqueous silver nitrate[9] gave equilibrium constants whose ratio ($K_2/K_1 = 0.32$) is quite similar to the ratio of relative reactivities for oxymercuration.[10]

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(1) L. A. Paquette, R. W. Begland, and P. C. Storm, *J. Amer. Chem. Soc.*, **92**, 1971 (1970).

(2) D. S. Tarbell and J. R. Hazen, *ibid.*, **91**, 7657 (1969).

(3) G. Zweifel and J. Plamondon, *J. Org. Chem.*, **35**, 898 (1970).

(4) B. Rickborn and S. Y. Lwo, *ibid.*, **30**, 2212 (1965).

(5) B. P. Mundy, A. R. DeBernardis, and R. D. Otzenberger, *ibid.*, **36**, 3830 (1971).

(6) S. L. Friess and A. Weissberger, Ed., "Techniques of Organic Chemistry," Vol. VIII, Interscience, New York, N. Y., 1953, pp 101–108.

(7) L. A. Paquette and P. C. Storm, *J. Amer. Chem. Soc.*, **92**, 4295 (1970).

(8) D. J. Pasto and J. A. Gontarz, *ibid.*, **92**, 7480 (1970).

(9) J. G. Traynham and J. R. Olechowski, *ibid.*, **81**, 571 (1959).

(10) We realize that the partition of alkenes between organic and aqueous silver nitrate phases is not always a reliable measure of K_{eq}. However, the similarity of the ratios of K_{eq} for **1** and **2** with the ratio of oxymercuration relative rates is an interesting observation[11] worthy of recording for other research workers.

(11) The question of mercurinium ions has received some attention recently. Pasto argues for their existance on stereochemical grounds.[8] Olah[12] has reported a direct observation of the mercurinium ion. Based on the stereochemical course of oxymercuration of **1**, the effect of oxygen heteroatoms[13] and the similarity between the relative rates of oxymercuration of **1** and **2** and the relative ease of argentation, we also suggest that mercurinium ions exist. Further work to substantiate this is in progress.

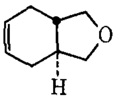
(12) G. A. Olah and P. R. Clifford, *J. Amer. Chem. Soc.*, **93**, 1261 (1971).

(13) (a) M. M. Jones, "Elementary Coordination Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1964, p 116; (b) R. W. Parry and R. N. Keller, "The Chemistry of the Coordination Compounds," J. C. Bailar, Jr., and D. H. Busch, Ed., Reinhold, New York, N. Y., 1956, p 123; (c) P. C. Chamberlain and G. H. Whitman, *J. Chem. Soc. B*, 1382 (1970).

This unexpected similarity leads us to at least consider the possibility that, in both oxymercuration and complexing with silver nitrate, *the reactive site is the alkene bond* rather than the ether osygen.[11] A recent discussion of electrophilic addition of Ag^+ and Hg^{2+} to ethylene suggests that their modes of addition may be quite similar.[14] Further evidence supporting the suggestion that the silver did not coordinate with oxygen may be seen in the nmr spectrum of the silver nitrate complex. Comparison of **1** in D_2O with the complex in D_2O shows clearly that the π bond is being influenced by silver ion, altering the vinyl hydrogens chemical shift from δ 5.7 to 6.7. This is the same shift observed for cyclohexene.[15] In general it has also been reported that silver ion does not coordinate strongly with oxygen.[13a,b]

Another argument that might be posed against oxygen participation is one of prior complexing of mercury ion with the oxygen, followed by a rapid transfer to the alkene bond (an entropy effect). Several arguments can be formulated against this possibility. In general, oxygen does not coordinate well with mercury ion, and particularly ether–oxygen functions.[13c] Also, since THF is the solvent for this reaction one must question why the phthalan oxygen would be *specifically* superior to the THF oxygen for complexing, and specific exchange would be necessary to account for the increased reactivity. A recent analysis of oxymercuration of substituted cyclohex-2-enols concludes that there is probably little direct interaction between mercury and the hydroxyl group.[13c]

Lastly, one can reasonably suggest that rate differences are merely a reflection of differences in ring strain or steric requirements of methylene *vs.* oxygen. We have tried to rule these out by analyzing the relative reactivities in the trans series, **12** and **13**.[16] Here we observe that **13** undergoes oxymercuration at about the same rate as **3** (k_{rel} = 0.15), while **12** oxymercurates about four times faster (k_{rel} = 0.4). Analysis of models demonstrates that **12** and **13** are conformationally similar and there is clearly little chance for participation by oxygen of **12**. At this time it is reasonable to suggest any increased reactivity as resulting from differences in strain. If we apply these arguments to the cis series, particularly **1** and **3**, it is not unreasonable to suggest that, *in the absence of participation by oxygen*, **1** and **3** should exhibit similar rates of oxymercuration. That **1** is considerably faster supports the concept of some sort of "oxygen-effect."[17]



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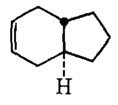
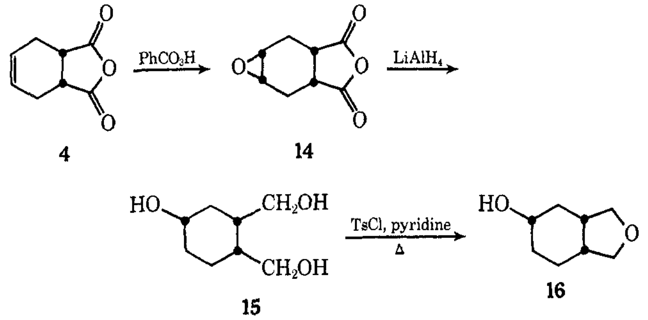


13

The major product resulting from oxymercuration of **1** is **16**. This was established by an unambiguous synthesis of **16**. Epoxidation of **4** with perbenzoic acid yielded the known epoxide **14**.[18] Reduction of **14** with lithium aluminum hydride afforded the triol **15**, which was immediately treated with 1 equiv of *p*-toluenesulfonyl chloride in pyridine at reflux. The product from this synthesis must have the stereochemistry of **16** based on the history of the reaction sequence. That the product did not arise from cis addition during the oxymercuration process was established by analyzing the organomercurial resulting from methoxymercuration of **1**.[19]



Although the increased reactivity is not overwhelming, it does lend some support for Rickborn's questioning the use of perhydrophthalans as models for the more difficultly obtained perhydroindans.

Experimental Section

The infrared spectra reported here were obtained on a Beckman IR-5, using polystyrene as an external standard. The nuclear magnetic resonance spectra were obtained on a Varian Model A-60 instrument, using tetramethylsilane as an internal standard. Melting and boiling points are uncorrected. The competition studies were measured by utilizing the product ratios as observed from an F & M Model analytical gas chromatograph and the peak areas integrated with a Disc integrater.

Cyclohexene-4-*cis*-1,2-dimethanol (5).—A solution containing 30.4 g of *cis*-1,2,3,6-tetrahydrophthalic anhydride in approximately 1 l. of anhydrous ether was added to 8.0 g of lithium aluminum hydride in 600 ml of anhydrous ether. Work-up gave the colorless cis diol (15.1 g, 53%) boiling at 167–170° (0.25 mm) [lit. bp 165–170° (12 mm),[20] mp 34.5°[21]].

Cyclohexene-4-*cis*-1,2-dimethanol Di-*p*-toluenesulfonate (6).—A solution of **5** (17.5 g) in 50 ml of pyridine was added dropwise to a cooled (0°) solution of *p*-toluenesulfonyl chloride (78.5 g) in 100 ml of pyridine. After completion of the addition, the mixture was stirred for an additional 3 hr. The reaction mixture was then poured into 200 ml of cold water, and within a few minutes the white crystalline ditosylate had formed. Filtration yielded 55 g (99% yield) of the ditosylate, mp 97.5°.[20,21]

Cyclohexene-4-*cis*-1,2-diacetonitrile (7).—A mixture of **6** (53 g), potassium cyanide (26 g), and ethanol (500 ml) was refluxed for approximatly 60 hr. After cooling, 20 ml of water was added to dissolve the salts, and the ethanol was removed. The residue was extracted with methylene chloride, and the combined extracts were reduced in volume. Distillation of the crude product yielded a clear, yellow dinitrile (11.9 g, 63%) boiling at 195° (8 mm). The dinitrile was crystallized from methanol–water, mp 45–46° (lit.[21] mp 50°).

Cyclohexene-4-*cis*-1,2-diacetic Acid (8).—A solution of **7**

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[14] R. D. Bach and H. F. Henneike, *J. Amer. Chem. Soc.*, **92**, 5589 (1970).

[15] F. A. Bovey, "Nmr Data Tables for Organic Compounds," Vol. I, Interscience, New York, N. Y., 1967, p 131.

[16] These compounds have been previously prepared by methods similar to those used for **1** and **3**.

[17] One might be concerned about differences in solubility as reflecting the rate differences. We have not analyzed the solubilities of the alkenes used in this study. However, we would expect **1** and **12** to have similar solubilities, as would **3** and **13**. If solubility were a major factor, we might expect **1** and **13** to exhibit similar reactivities, as we do observe. However, the greater reactivity of **3** than **12** again suggests some additional oxygen effect.

[18] See H. B. Henbest, *Proc. Chem. Soc.*, 159 (1963), for a concise report on some of the effects contributing to the course of epoxidation.

[19] W. Waters, *Tetrahedron Lett.*, 3769 (1969).

[20] E. Casadevall, C. Largeau, and P. Moreau, *Bull. Soc. Chim. Fr.*, 1514 (1968).

[21] D. C. Ayres and R. A. Raphael, *J. Chem. Soc.*, 1779 (1958).

(11.8 g) was refluxed until the evolution of ammonia ceased. After cooling the mixture was acidified with 87% phosphoric acid. The reaction yielded 10.0 g (68.5%) of white crystalline diacid (from acetonitrile) melting at 156–157° (lit.[21]. mp 157°).

***cis*-4,7,8,9-Tetrahydroindan-2-one** (9).—Cyclohexene-4-*cis*-1,-2-diacetic acid (5.0 g) was thoroughly mixed with iron powder (5.0 g) and barium hydroxide [0.6 g, $Ba(OH)_2 \cdot 8H_2O$]. This mixture was heated with an open flame while the ketone and water distilled. The crude ketone was separated from the water and redistilled to give 2.1 g (61.8%) of product boiling at 101° (11 mm). Spectral characteristics were consistant with the known product.[22]

Preparation of *cis*-4,7,8,9-Tetrahydroindan (10).—The Huang-Minlon modification of the Wolff–Kishner reduction was used.[23] A mixture of *cis*-4,7,8,9-tetrahydroindan-2-one (2.0 g), potassium hydroxide (2.8 g), 85% hydrazine (2.0 ml), and diethylene glycol (20 ml) was heated at 130° for 1.5 hr. The water and excess hydrazine were removed by distillation until the temperature reached 190–200°. The mixture was diluted with 200 ml of water and neutralized with 6 *N* hydrochloric acid. This mixture was extracted with methylene chloride, and the extracts were distilled to give the colorless hydrindan (1.0 g, 55.7%) boiling at 42–43° (9 mm). The infrared and nmr spectra were consistent with the structure.[22]

***cis*-8-Oxabicyclo[4.3.0]non-3-ene** (1).—A solution of **5** (7.1 g) in 10 ml of pyridine was heated to reflux and a solution of *p*-toluenesulfonyl chloride (14 g) in 10 ml of pyridine was added dropwise with stirring. After the addition was completed, the mixture was refluxed for 1 hr. This solution was cooled and poured into an ice–sulfuric acid bath to neutralize the pyridine. The aqueous mixture was extracted with ether, and the combined ether extracts were dried over anhydrous magnesium sulfate. Distillation yielded the colorless product (4.8 g, 77.5%) boiling at 58–64° (9 mm) [lit.[24] bp 63–64° (13 mm)].

Preparation of 12 and 13.—The trans series was prepared by methods similar to those outlined for **1** and **3**, except that cyclohexene-4-*trans*-1,2-dimethanol[20,21] was the starting material. Spectral and physical data for **12**[4] and **13**[25] were consistent with the reported values.

***cis*-1,3,6-Trihydro-8-oxabicyclo[4.3.0]non-3-ol** (16).—**4** (3 g) was mixed with an equivalent amount of perbenzoic acid[26] in 50 ml of chloroform and the reaction mixture was maintained at 0° for 3 days. The crystalline product **12** was collected and recrystallized from ethyl acetate, mp 201–202°.[27] The epoxide (0.5 g) was dissolved in 10 ml THF and reduced with 0.25 g of lithium aluminum hydride. The crude triol **13** from this sequence (400 mg) was mixed with 25 ml of pyridine and 0.47 g of *p*-toluenesulfonyl chloride and was heated at reflux for about 2 hr. Evaporation of excess pyridine yielded the alcohol **14**, which was identical by glc (20% Carbowax 20M on Chromosorb W, 200°) with the major product of oxymercuration. The 3,5-dinitrobenzoate was crystallized from ethanol, mp 150–152°. *Anal.* Calcd for $C_{15}H_{16}N_2O_7$: C, 53.6; H, 4.8; N, 8.3. Found: C, 53.6; H, 4.8; N, 8.1.

Competition Studies.—The competition studies were performed by allowing a mixture of cyclohexene (the standard, 1.5 mmol) and other alkene (1.5 mmol) to compete for a limiting amount of mercuric acetate (0.8 mmol) in THF-water (1:1). Generally, the reactions were complete (as evidenced by the loss of yellow color in the mercuric acetate–water–THF mixture) within 1 or 2 min. After sodium borohydride reduction of the oxymercurials[28] the crude product mixture was analyzed for both product and unreacted alkene. The relative rates were calculated by

$$\frac{k_A}{k_B} = \frac{\ln\ (\text{fraction of A remaining})}{\ln\ (\text{fraction of B remaining})}$$

Registry No.—**5**, 20141-17-7; **6**, 32970-96-0; **16** 3,5-dinitrobenzoate, 32970-97-1.

Acknowledgment.—We wish to express our appreciation to the Endowment and Research Foundation of Montana State University for its generous support of this work.

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(22) J. C. Jallageas and E. Casasevall, *C. R. Acad. Sci., Ser. C*, **268**, 449 (1969).

(23) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 431.

(24) E. L. Eliel and C. Pillar, *J. Amer. Chem. Soc.*, **77**, 3600 (1955).

(25) H. B. Henbest, W. R. Jackson, and B. C. G. Robb, *J. Chem. Soc. B*, 803 (1966).

(26) G. Braun, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 431.

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(28) The possibility of deoxymercuration accompanying reduction has not been eliminated. Future studies will attempt to analyze the problem.

Acid-Catalyzed Rearrangement of Laureatin to Isolaureatin and Related Reactions[1]

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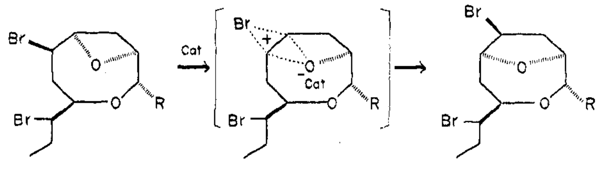
Laureatin (I) and isolaureatin (II) are naturally occurring bromo compounds containing oxetane and oxocane rings and oxolane and oxocane rings, respectively, from *Laurencia nipponica* Yamada.[2] In the course of studies aimed at selective cleavage of the oxetane ring of hexahydrolaureatin (III), we observed that on acid treatment (HBr-EtOH) III produced a trace of hexahydroisolaureatin (IV) besides a tribromo alcohol V, whose structure is discussed below. This finding prompted us to examine the reaction behavior of III and I under various acidic conditions. In this paper we report the rearrangement of these oxetane compounds (III and I) to the respective oxolane derivatives (IV and II) as well as related reactions.



I R = $-CH_2-CH{=}CH-C{\equiv}CH$
III R = $n\text{-}C_5H_{11}$

VII

II R = $-CH_2-CH{=}CH-C{\equiv}CH$
IV R = $n\text{-}C_5H_{11}$

Compounds III and I were treated with Lewis acids and afforded IV and II, respectively, in moderate yields (maximum 76%) depending on the reaction conditions, as summarized in Table I.[3]

The same type of rearrangement was also observed when III was treated with H_2 in the presence of Pd/C at room temperature for 40 hr. Compounds IV, V, and a new monobromo alcohol VI[4] were produced in 38, 13, and 21% yields, respectively. Heating (*in vacuo*) in a sealed tube at 130–220°[5] resulted in recovery of III.[6] We emphasize that this rearrangement is noteworthy from the biogenetical point of view, since

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(1) Part XVIII. Part XVII: M. Suzuki, E. Kurosawa, and T. Irie, *Tetrahedron Lett.*, 4995 (1970).

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(3) The products were identified by comparison of their optical rotations and ir, nmr, and mass spectra, as well as R_f values in tlc, with those of authentic specimens.[2] The optical rotation of IV has been observed as $[\alpha]_D$ +8° in $CHCl_3$.

(4) Upon treatment with Raney Ni, VI afforded XI (see Experimental Section).

(5) Upon being heated above 230°, III decomposed with evolution of HBr.

(6) *Cf.* D. H. R. Barton, *et al.*, *J. Amer. Chem. Soc.*, **72**, 1066 (1950); *J. Chem. Soc.*, 1048 (1951); 4284 (1954); 4398 (1958).