(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.

[27] A. P. Gray, D. E. Heitmeier and H. Kraus, *J. Amer. Chem. Soc.*, **84**, 89 (1962).

[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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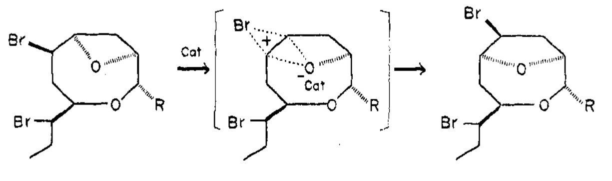
Received March 30, 1971

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).

[2] T. Irie, M. Izawa, and E. Kurosawa, *Tetrahedron*, **26**, 851 (1970).

[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).

TABLE I
REARRANGEMENT OF HEXAHYDROLAUREATIN (III) TO HEXAHYDROISOLAUREATIN (IV) AND OF LAUREATIN (I) TO ISOLAUREATIN (II)

Compd	Reagent	Reaction temp, °C	Reaction time, hr	Yield, % II	Yield, % IV	Yield, % V
III	HBr-EtOH	Reflux	24		10	51
III	KI-EtOH	Reflux	24		Trace	
III	KI-AcOH	Reflux	24		Trace	
III	KBr-AcOH	Reflux	21		39	
III	$ZnCl_2$-AcOH	80	17		42	
III	$ZnCl_2$-CF_3COOH-AcOH	40	53		76	
III	Br_2-CCl_4	Reflux	0.5		69	8
III	Br_2-EtOH	Reflux	0.5		13	65
I	$ZnCl_2$-AcOH	Reflux	24	19		
I	$ZnCl_2$-CF_3COOH-AcOH	40	48	33		

I and II have been isolated from the same alga.[2] The possibility was considered that II may have been formed by rearrangement of I during the isolation procedure. However, when an extraction procedure from alga was devised which rigorously excluded the conditions predicting rearrangement by heating or contacting with acid and alkali, I and II were isolated from the original extract in a ratio of 3:1 by neutral alumina chromatography. This fact supports the view that I and II are, indeed, naturally occurring compounds.

This rearrangement would certainly involve a synchronous shift of the Br atom and the oxido group oriented anti coplanar on adjacent carbon atoms, and relief of the oxetane ring strain in III or I would be, at least, a part of the driving force of this conversion.[7] A presumable structure VII for the intermediate, including an intimate ion pair, is favorable for this internal return.[8] This mechanistic pathway of the rearrangement is supported by the following evidence.

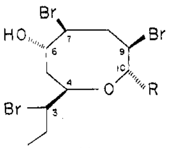
As shown in Table I, when III was refluxed with HBr or Br_2 in EtOH, compound IV in question was only a minor product (10–13%), and the main product (51–65%) proved to be a tribromo alcohol V (3,5-dinitrobenzoate, mp 162.5–163.5°). The structure of V, described later, suggests that both the relevant rearrangement and attack of the Br atom at C-9 leading to the formation of V would be concerted, probably *via* intermediate VII, because the oxolane ring of IV could not be cleaved under the conditions used.

The structure of V has been assigned on the basis of the spectral data (see Experimental Section) and the following evidence. (i) Treatment of V, its acetate, or its 3,5-dinitrobenzoate with 0.4 *N* NaOH-EtOH gave an epoxide (VIII) in a good yield, indicative of the trans disposition of the Br atom and the OH group on adjacent carbon atoms in V. (ii) Reduction of V with Raney Ni afforded a debromo alcohol (IX) which was oxidized with CrO_3-pyridine to yield the corresponding ketone (X). This alcohol IX was not identical with XI[2] and XII, the latter being prepared from hexahydrobisdebromolaureatin (XV)[2] *via* bromohydrin XVI (Br_2-EtOH, Raney Ni). Furthermore, ketone X proved to be different from XIII obtained by the oxidation of XI. The nmr spectral data of compounds IX-XIII are listed in Table II.

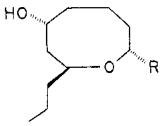
Contrary to expectation, oxidation of XII with CrO_3-pyridine gave no corresponding ketone XIV, yielding unidentified carboxylic acids. This anomalous behavior of XII could be explicable by the transannular effects, as shown below.[9]

TABLE II
NMR DATA (τ) OF COMPOUNDS IX-XIII (60 MHz, IN CCl_4)

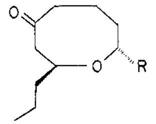
Compd	1-Me	15-Me	>CHOCH<	>CHOH	$-CH_2CO-$
IX	9.10 (br t)	9.10 (br t)	6.49 (2 H, m)	6.09 (1 H, m)	
X	9.05 (br t)	9.09 (br t)	6.52 (2 H, m)		7.78 (4 H, m)
XI	9.07 (br t)	9.07 (br t)	6.49 (2 H, m)	6.35 (1 H, m)	
XII	9.09 (br t)	9.09 (br t)	5.91 (2 H, m)	6.32 (1 H, m)	
XIII	9.07 (br t)	9.10 (br t)	6.39 (2 H, m)		7.21 (1 H, m)



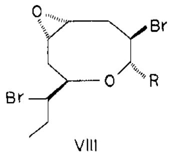
V



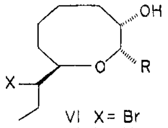
IX



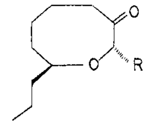
X



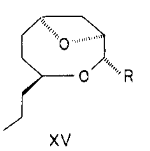
VIII



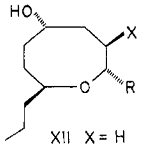
VI X= Br
XI X= H



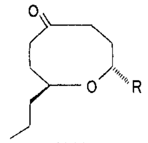
XIII



XV

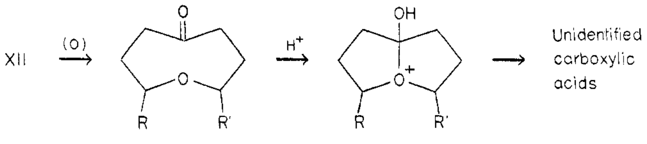


XII X= H
XVI X= Br



XIV

(R = n-C_5H_{11})



XIV XVII

Experimental Section[10]

General Procedure for the Rearrangement Reaction.—The sample (200–500 mg) was weighed in a tube, and a measured

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[7] *Cf.* R. Hirshmann, G. A. Bailey, G. I. Poos, R. Walker, and J. M. Chemerda, *J. Amer. Chem. Soc.*, **78**, 4814 (1956); J. E. Herz, J. Fried, P. Grabowich, and E. F. Sabo, *ibid.*, **78**, 4812 (1956).

[8] P. de Mayo, "Molecular Rearrangements," Interscience, London, 1963, pp 3, 111; *cf.* P. G. Gassman and R. L. Cryberg, *J. Amer. Chem. Soc.*, **91**, 2047 (1969); F. Kohen, G. Adelstein, and R. E. Counsell, *Chem. Commun.*, 770 (1970); K. N. Houk, *J. Amer. Chem. Soc.*, **92**, 4144 (1970).

[9] N. J. Leonard, T. W. Milligan, and T. L. Brown, *J. Amer. Chem. Soc.*, **82**, 4075 (1960).

[10] Melting points are uncorrected. The purity of each compound was always checked by tlc. Optical rotations were determined in $CHCl_3$ solution. Ir spectra were obtained from a Nihon-Bunko IR-S spectrophotometer. Nmr spectra were taken with a Hitachi H-6013 spectrometer using TMS as internal standard in CCl_4. Mass spectra were obtained with a Hitachi RMU-6E mass spectrometer.

weight (200–300 mg) of catalyst and a measured volume (2–5 ml) of solvent were added. After being heated at the appropriate temperature, the reaction mixture was filtered and poured into water (50 ml) or evaporated *in vacuo* (in the case of EtOH solution). To the product was added 2 *N* aqueous NaOH (100 ml) and the whole was extracted repeatedly with ether. The ether solution was washed two times with 50-ml portions of 2 *N* NaOH solution and three times with 50-ml portions of water, dried over Na_2SO_4, and then evaporated. The oily substance thus obtained was purified by column chromatography on silica gel.

Rearrangement of Hexahydrolaureatin (III) to Hexahydroisolaureatin (IV) by Treatment with Zinc Chloride.—The solution of III[2] (227 mg) and anhydrous $ZnCl_2$ (287 mg) in a mixture of AcOH (3.0 ml) and CF_3COOH (0.2 ml) was heated at 40–42° for 53 hr. After being worked up as mentioned above, colorless oil (173 mg) was obtained, $[\alpha]_D$ +8.3° (*c* 2.02, $CHCl_3$). The ir and nmr spectra were superimposable with those of an authentic sample of IV.[2]

Tribromo Alcohol V (3,7,9-Tribromo-4,10-epoxypentadecan-6-ol).—To a solution of III (2.69 g) in 99.5% EtOH (20 ml) was added Br_2 (1.0 ml) and the mixture was refluxed for 30 min. After being cooled, the solution was evaporated *in vacuo* and the residual oil was percolated with ether (*ca.* 100 ml). The ether solution was shaken successively with water, 10% $Na_2S_2O_3$ solution, and water and dried over Na_2SO_4. After removal of the solvent, the oily residue was purified by column chromatography on silica gel to give V (2.09 g) as a colorless oil: $[\alpha]_D$ +14.8° (*c* 2.10, $CHCl_3$); ir (neat) 3450, 1041 cm^{-1}; nmr τ 9.09 (br t, 3), 8.91 (t, 3, J = 7 Hz), 8.71 (br m, 7), *ca.* 8.4–7.8 (br m, 4), 7.44 (br m, 4), 6.80 (br m, 1), 6.01 (br m, 5); mass spectrum *m/e* 359, 357, 355 ($M^+ - C_3H_6Br$), 329, 327, 325 ($M^+ - C_5H_{11} - HBr$), 301, 299, 297 ($M^+ - C_6H_{11}O - HBr$).

Acetate of V was obtained as a colorless oil: ir (neat) 1746, 1227, 1025 cm^{-1}; nmr τ 9.09 (br t, 3), 8.93 (t, 3, J = 7 Hz), 8.69 (br m, 6), *ca.* 8.4–8.0 (br m, 4), 7.98 (s, 3), 7.43 (br m, 4), 6.12 (br m, 4), 5.83 (m, 1), 4.77 (m, 1); mass spectrum *m/e* 401, 399, 397 ($M^+ - C_3H_6Br$).

3,5-Dinitrobenzoate of V was obtained as fine needles: mp 162.5–163.5°; ir ($CHCl_3$) 3100, 1745, 1630, 1602, 1551, 1463, 1347, 1273, 1165, 1076, 922 cm^{-1}; nmr τ 9.09 (br t, 3), 8.90 (t, 3, J = 7 Hz), 8.75 (br m, 6), *ca.* 8.4–7.8 (br m, 4), 7.28 (br m, 4), 5.09 (br m, 4), 4.60 (m, 1), 4.25 (m, 1), 0.83 (s, 3).

Anal. Calcd for $C_{22}H_{29}O_7N_2Br_3$: C, 39.25; H, 4.34; N, 4.16. Found: C, 39.51; H, 4.35; N, 4.34.

Epoxide VIII. A.—Compound V (746 mg) was eluted with benzene through a column packed with alumina (45 g), which was freshly shaken with 2 *N* NaOH and dried at 110°. The benzene eluate was evaporated *in vacuo* to give VIII (606 mg, 98%) as a colorless oil: $[\alpha]_D$ −42.2° (*c* 2.25, $CHCl_3$); ir (neat) 1151, 1134, 1102, 1065, 964, 926, 905, 801, 762 cm^{-1}; nmr τ 9.10 (br t, 3), 8.95 (t, 3, J = 7 Hz), 8.75 (br m, 6), *ca.* 8.5–7.9 (m, 4), 7.69 (br m, 3), 7.35 (br m, 1), 6.90 (br m, 2), 3.86 (br m, 4); mass spectrum *m/e* 329, 327, 325 ($M^+ - C_5H_{11}$), 277, 275 ($M^+ - C_3H_6Br$), 235, 233, 219, 195 ($M^+ - C_3H_6Br - HBr$).

B.—Hydrolysis of the acetate of V (274 mg) with 0.4 *N* NaOH–EtOH for 15 hr afforded VIII (157 mg) along with a small amount of unidentified by-product.

Alcohol IX (4,10-Epoxypentadecan-6-ol).—To a cold solution of V (194 mg) in EtOH (3 ml) was added freshly prepared W-7 Raney Ni (from 4 g of Al–Ni alloy). After being set aside for 3 hr, the reaction mixture was filtered and evaporated. The residual oil thus obtained was purified by column chromatography on silica gel to yield IX (85 mg) as colorless needles: mp 46.0–46.5° (from *n*-hexane); $[\alpha]_D$ −20.6° (*c* 1.99, $CHCl_3$); ir ($CHCl_3$) 3350, 1130, 1080, 1054, 1033, 1009 cm^{-1}; nmr τ 9.10 (br t, 6), 8.70 (br m, 10), *ca.* 8.6–8.2 (br m, 10), 7.06 (br m, 1), 6.49 (br m, 2), 6.09 (br m, 1); mass spectrum *m/e* (rel intensity) 242 (0.2, M^+), 224 (3, $M^+ - H_2O$), 199 (17, $M^+ - C_3H_7$), 181 (11, $M^+ - C_3H_7 - H_2O$), 171 (19, $M^+ - C_5H_{11}$), 163 (17), 153 (13, $M^+ - C_5H_{11} - H_2O$), 141 (47), 123 (38), 113 (72), 95 (75), 83 (73), 81 (71), 69 (88), 55 (100), 43 (99).

Ketone X (4,10-Epoxypentadecan-6-one).—The alcohol IX (57 mg) was oxidized with CrO_3 (182 mg) in pyridine (1 ml) at room temperature for 4 days. After being worked up in the usual manner, the product was purified by chromatography on silica gel to yield X (52 mg) as colorless crystals: mp 35–37°; $[\alpha]_D$ +32.6° (*c* 1.99 $CHCl_3$); ir ($CHCl_3$) 1700, 1128, 1071, 1038 cm^{-1}; nmr τ 9.09 (br t, 3), 9.05 (br t, 3), 8.68 (br m, 12), *ca.* 8.4–7.9 (m, 4), 7.78 (m, 4), 6.52 (br m, 2); mass spectrum *m/e* 240 (M^+), 197 ($M^+ - C_3H_7$), 169 ($M^+ - C_5H_{11}$), 157, 139, 129, 111, 85, 69, 55, 42.

Alcohol XI (4,10-Epoxypentadecan-9-ol).—This alcohol was prepared from III by treatment with Raney Ni in EtOH:[2] ir (neat) 3460, 1132, 1082, 1060 cm^{-1}; nmr τ 9.07 (br t, 6), *ca.* 6.5 (m, 3); mass spectrum *m/e* 242 (M^+).

Ketone XIII (4,10-Epoxypentadecan-9-one).—The alcohol XI (92 mg) was oxidized with CrO_3 (340 mg) in pyridine (2 ml) to give XIII (61 mg) as a colorless oil: ir (neat) 1710, 1129, 1085 cm^{-1}; nmr τ 9.10 (br t, 3), 9.07 (br t, 3), 8.63 (br m, 13), *ca.* 8.4–7.8 (br m, 6), 7.21 (m, 1), 6.39 (m, 2).

Bromohydrin XVI (9-Bromo-4,10-epoxypentadecan-7-ol).—To a solution of hexahydrobisdebromolaureatin (XV)[2] (250 mg) in EtOH (2 ml), Br_2 (0.2 ml) was added. After the mixture was allowed to stand for 2 days at room temperature, the solvent was removed *in vacuo* and the residue was percolated with ether. The ether solution was washed with 10% aqueous $Na_2S_2O_3$ and then with water, and dried. Removal of the ether followed by purification by silica gel chromatography afforded XVI (218 mg) as a colorless oil: ir (neat) 3400, 1085, 1025 cm^{-1}; nmr τ 9.09 (br t, 3), 9.06 (br t, 3), 8.63 (br m, 10), *ca.* 8.5–7.9 (m, 8), 7.73 (s, 1, OH), 6.30 (m, 1), 5.88 (m, 3).

The 3,5-dinitrobenzoate had mp 60.5–62.5°; ir (Nujol) 1737, 1629, 1600, 1549, 1274, 1168, 734, 725 cm^{-1}.

Anal. Calcd for $C_{22}H_{31}O_7N_2Br$: C, 51.27; H, 6.06; N, 5.44. Found: C, 51.20; H, 5.81; N, 5.27.

Alcohol XII (4,10-Epoxypentadecan-7-ol).—To a solution of XVI (125 mg) in EtOH (3 ml) was added freshly prepared W-7 Raney Ni (from 1 g of Al–Ni alloy). After being allowed to stand at room temperature for 3 hr, the catalyst and the solvent were removed and the residue was purified by column chromatography on silica gel to afford XII (80 mg) as colorless crystals: mp *ca.* 25°; ir (neat) 3350, 1085, 1055, 1030 cm^{-1}; nmr τ 9.09 (br t, 6), 8.69 (br m, 15), *ca.* 8.5–7.8 (br m, 5), 7.52 (s, 1, OH), 6.32 (m, 1), 5.91 (m, 2); mass spectrum *m/e* 242 (M^+), 224 ($M^+ - H_2O$), 199 ($M^+ - C_3H_7$), 171 ($M^+ - C_5N_{11}$).

Treatment of III with H_2 over Pd/C Catalyst.—In a hydrogenation vessel, III (668 mg) in AcOH (15 ml) was treated with H_2 over Pd/C catalyst at room temperature for 40 hr. After removal of the catalyst, the solution was neutralized and extracted with ether. The ether solution was dried and evaporated to yield a colorless oil. The product (672 mg) thus obtained was purified by column chromatography on silica gel to give IX (250 mg), V (107 mg), and VI (114 mg). Compound VI, colorless oil, $[\alpha]_D$ + 14.3° (*c* 2.02, $CHCl_3$), showed ir spectrum 3450, 1123, 1110, 1085, 1050, 961, 803 cm^{-1}; nmr τ 9.09 (br t, 3), 8.95 (t, 3, J = 7 Hz), 6.54 (br m, 1), 6.24 (br m, 3); mass spectrum *m/e* 322, 320 (M^+), 241 ($M^+ - Br$), 224, 221 ($M^+ - C_6H_{12}O$), 199 ($M^+ - C_3H_6Br$).

Debromination of VI.—To a solution of VI (14 mg) in EtOH (0.5 mol) was added freshly prepared W-7 Raney Ni (from 0.5 g of Al–Ni alloy). After being worked up in the usual manner, colorless oil (8 mg) was obtained and identified as XI by a comparison of R_f value in tlc and ir spectrum with those of an authentic sample.[2]

Registry No.—I, 33122-30-4; II, 19897-64-4; III, 18762-31-7; IV, 19897-65-5; V, 33069-32-8; V acetate, 33069-33-9; V 3,5-dinitrobenzoate, 33069-34-0; VI, 33069-35-1; VIII, 33069-36-2; IX, 33069-37-3; X, 33069-38-4; XI, 33069-39-5; XII, 33069-40-8; XIII, 33069-41-9; XVI, 33069-42-0; XVI 3,5-dinitrobenzoate, 33069-43-1.

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