0.2 g. (4%) of a white substance believed to be 6-[tri(4-methylphenoxy)methyl]purine (VIII); m.p. 214–215° dec., R_f 0.92.

Anal. Calcd. for $C_{27}H_{24}O_3N_4$: C, 71.4; H, 5.3; N, 12.7. Found: C, 71.9; H, 5.5; N, 12.2.

Compound VIII gave no color reaction with ferric chloride and could not be converted into VII by treatment with 1 *N* hydrochloric acid for 30 min. at 60–70°.

Catalytic Reduction of VII.—A solution of VII (0.55 g.) in 5% aqueous ammonia (50 ml.) containing 5% palladium on carbon (50 mg.) was shaken for 4 hr. under hydrogen at atmospheric pressure and room temperature. The total volume of hydrogen absorbed was about 62 ml. The solution was filtered and evaporated to dryness under reduced pressure. The residue (0.5 g., 91%) was recrystallized from methanol to yield pure (purin-6-yl)(2-hydroxy-5-methylphenyl)carbinol (X); m.p. 233–234° dec., R_f 0.70. The carbinol gave an intense blue coloration with a trace of ferric chloride in methanol.

Anal. Calcd. for $C_{13}H_{12}O_2N_4$: C, 60.9; H, 4.7; N, 21.9. Found: C, 60.8; H, 5.2; N, 21.8.

Acknowledgment.—The authors wish to thank Dr. G. B. Brown for his interest and help.

Notes

Preparation of 4,5-Dihydroöxepine and 1,2-Divinylethylene Oxide

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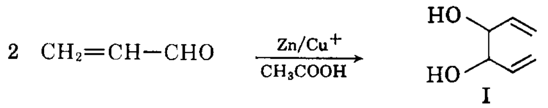
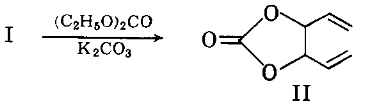
In recent years several examples of unsaturated derivatives of seven-membered heterocyclic systems have been reported[1–6] and have been of interest because of the possibility of planarity and aromatic stability. We wish to report a three-step synthesis of the new compounds, 4,5-dihydroöxepine (III) and 1,2-divinylethylene oxide (3-epoxy-1,5-hexadiene) (IV), as well as a new example of valence isomerism of a strained ring compound.[7] 1,5-Hexadiene-3,4-diol (I) is conveniently prepared by the bimolecular reduction of acrolein through the influence of a zinc–copper couple. *sym*-divinylethylene carbonate (II) was obtained in high yield from the reaction of (I) with diethyl carbonate using potassium carbonate as catalyst.



I

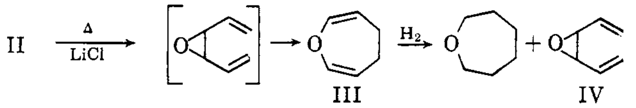


II

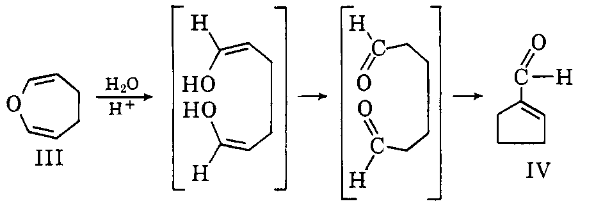
The lithium chloride-catalyzed pyrolysis of II at 200° was expected to give one or both isomers of 1,2-divinylethylene oxide. The constant boiling pyrolysate was separated into two fractions by preparative scale vapor phase chromatography.

The first fraction was shown to be one of two steric forms of 1,2-divinylethylene oxide (IV) and, on the basis of known relative stabilities of *cis*- and *trans*-divinylcyclopropanes,[8,9] we believe the *trans* form was isolated. The other fraction was identified as 4,5-dihydrooxepine (III) and presumably resulted from the Cope rearrangement of the less stable *cis* isomer 1,2-divinylethylene oxide.

The infrared, near-infrared, ultraviolet, and nuclear magnetic resonance spectra of III are consistent with the structure assigned. Hydrogenation of 4,5-dihydrooxepine resulted in the uptake of two moles of hydrogen, and reaction of (III) with aqueous acetic acid and 2,4-dinitrophenylhydrazine reagent results in the formation of the corresponding hydrazine derivative of 1-cyclopentene carboxaldehyde (V).



III IV



1-Cyclopentene carboxaldehyde presumably results from the acid-catalyzed hydrolysis of III to adipaldehyde which readily undergoes an internal Aldol condensation to give V.[10]

Experimental

1,5-Hexadiene-3,4-diol (I).—Compound I is obtained by the bimolecular reduction of acrolein with zinc–copper couple and acetic acid using the method described previously for the reduction of crotonaldehyde.[11] Compound I is a colorless liquid, b.p. 55° (0.2 mm.), $n^{25}{}_D$, 1.4739, $d^{25}{}_4$ 1.0097, which has been prepared previously only in 20–30% yields.[12] The yield can be improved to above 90% by using an ether such as tetrahydrofuran or dioxane as solvent instead of water.

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sym-**Divinylethylene Carbonate (II).**—A mixture of 57 g. (0.5 mole) of 1,5-hexadiene-3,4-diol, 71 g. (0.6 mole) of diethyl carbonate and 0.2 g. of anhydrous potassium carbonate was slowly heated to 110°. At this temperature reaction occurred and ethyl alcohol was distilled from the reaction mixture through a packed column. After 1 hr. the theoretical amount of ethyl alcohol was recovered. The residue was filtered and fractionated to give 51.8 g. (74%) of compound IV, b.p. 64° (0.2 mm.), $n^{25}{}_{\mathrm{D}}$ 1.4598, $d^{25}{}_{4}$ 1.0650. The infrared spectrum is consistent with the proposed structure.

Anal. Calcd. for $C_7H_8O_3$: C, 60.00; H, 5.75. Found: C, 60.27; H, 5.94.

Compound IV does not have to be isolated before proceeding to the pyrolysis step.

Pyrolysis of *sym*-Divinylethylene Carbonate, 1,2-Divinylethylene Oxide, and 2,3-Dihydroöxepine.—A slurry of *sym*-divinylethylene carbonate (140 g., 1.0 mole) and 5.0 g. of lithium chloride powder[13] was heated slowly to 200–210°, and the distillate was collected in a Dry Ice trap. The distillate was washed twice with cold water and dried over magnesium sulfate to give 49.7 g. of crude product. Distillation through a 20-in., helices-packed column gave a constant boiling fraction, b.p. 108° (760 mm.), with a refractive index ranging from $n^{25}{}_{\mathrm{D}}$ 1.4541 to 1.4561. A 10.7 g. sample of the distilled product was separated into two fractions by vapor phase chromatography using a 6-ft. column with 3-methyl-3-nitro-1,5-dicyanopentane on firebrick as the stationary phase. The first fraction (retention time, 12 min., column temp., 90°; flow rate, 500 ml./min.) (3.3 g.) was 4,5-dihydroöxepine (I); and the second fraction (retention time, 18 min., (6.1 g.) was 1,2-divinylethylene oxide (II).

4,5-Dihydroöxepine.—B.p. 108° (760 mm.), $n^{25}{}_{\mathrm{D}}$ 1.4632. The infrared spectrum was consistent with the proposed structure: 3055 cm.$^{-1}$ (CH stretching of *cis*-CH═CH—), 2940 and 2860 cm.$^{-1}$ (CH stretching of CH_2), 1650 cm.$^{-1}$ (nonconjugated C═C), 1448 cm.$^{-1}$ (CH_2 deformation frequency of —CH═C—CH_2), 1238 cm.$^{-1}$ (*cis*-C═C adjacent to oxygen). The near-infrared spectrum showed that terminal epoxide or terminal methylene groups were absent and the ultraviolet spectrum indicated the absence of conjugated unsaturation. The proton resonance indicated three different protons in the expected ratio of 2:1:1; peaks occurring at 7.3 τ, assigned to the hydrogens at the 4 and 5 position; 5.3 τ, hydrogens at the 3 and 6 positions; 3.42 τ, hydrogens at 2 and 7 positions (split).[14]

Anal. Calcd. for C_6H_8O: C, 74.97; H, 8.38; O, 16.65; mol. wt., 96. Found: C, 74.89; H, 8.26; O, 17.12 (Unterzaucher method); mol. wt. (f.p. benzene), 100.

Hydrogenation of 4,5-dihydroöxepine over platinum oxide resulted in a 101% uptake of 2 moles of hydrogen. The 4,5-dihydroöxepine was hydrolyzed by warming with aqueous acetic acid for 10 min. to give a solution which reduced ammoniacal silver nitrate (suggesting a rearrangement to an aldehyde). Freshly prepared 2,4-dinitrophenylhydrazine reagent was added to the hydrolyzed 4,5-dihydroöxepine. The crude derivative was purified by chromatographing it on neutral alumina and eluting with chloroform. The pure derivative was brilliant red, m.p. 215–216° (lit.,[15] m.p. for 2,4-DNP of 1-cyclopentene carboxaldehyde, 215–216°).

Anal. Calcd. for $C_{12}H_{12}N_4O_4$: N, 20.28. Found: N, 20.18.

sym-**Divinylethylene Oxide.**—B.p. 108° (760 mm.), m.p. 35°, $n^{25}{}_{\mathrm{D}}$ 1.4474. The infrared spectrum was consistent with the proposed structure: 3125 cm.$^{-1}$ (C—H), 3030 cm.$^{-1}$ (saturated C—H with low frequency due to strained ring configuration), 1887 cm.$^{-1}$ (C═C overtone), and bands at 993, 927, and 869 cm.$^{-1}$ (epoxide). The compound gave a positive periodic acid test indicating the presence of an epoxide group. The nuclear magnetic resonance spectrum indicated two different protons in the ratio 3:1; 4.97 τ, vinyl protons overlapped and 6.58 τ, protons on epoxide ring.

Anal. Calcd. for C_6H_8O: C, 74.97; H, 8.39; O, 16.67; mol. wt., 96. Found: C, 74.99; H, 8.38; O, 17.32 (Unterzaucher method); mol. wt., 95.

Acknowledgment.—The author expresses his appreciation to Dr. Anthony J. Papa, John W. Robson, and Charles B. Matthews for helpful discussions and to Dr. Heinz F. Reinhardt who first prepared compound II.

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[13] Lithium chloride is a much more effective catalyst for the pyrolysis than other salts used previously for the pyrolysis of carbonate; U. S. Patent 2,856,413.

[14] The n.m.r. spectrum rules out the possible alternative structure, 2,3-dihydroöxepine.[2]

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A General Synthesis of 3-Indolealkanoic Acids

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3-Indolealkanoic acids are very active plant growth substances. 3-Indoleacetic and 3-indolebutyric acids are used commercially by nursuries to promote growth of plant cuttings, and many other interesting biological properties have been reported for these acids and their derivatives. 3-Indolecaproic acid and its amide also have excellent biological properties.[1,2] A simple one-step synthesis for the preparation of 3-indolealkanoic acids is described which involves the direct base-catalyzed reaction of lactones with indole or its derivatives.

3-Indolealkanoic acids have been prepared previously by the reaction of lactones with indole, but these syntheses generally involved several steps, or gave low yields. The reaction of butyrolactone with the potassium salt of indole at 200° has given 1-indolebutyric acid,[3] while with the magnesium iodide salt of indole at 120–130° has given 3-indolebutyric acid.[4] These syntheses required the prior preparation of the respective salts *via* involved procedures. The noncatalytic reaction of propiolactone with indole at 120° is reported to give 3-indolepropionic acid in 40–50% yield.[5] An attempt was made to duplicate this result, but only starting material was recovered in 90% yield. A reaction did occur when the temperature was raised to 245°, but the product was a nitrogen-containing polymeric acid which was not investigated further.

The reaction of lactones with indole, in the presence of base, takes place at 200–300° to give high yields of 3-indolealkanoic acids (Table I). The acids described in Table I were prepared at 250° using a reaction mixture comprising 1.0 mole of indole, 1.05 moles of lactone and 1.1 moles of base. The base used was potassium hydroxide, but sodium hydroxide or sodium methoxide also gave satisfactory results. Some skatole was produced when sodium methoxide was used.[6] No solvent was used in these preparations, but solvents, such as tetralin, methylnaphthalene, or diethylbenzene, can be used. When the reactions were run in the presence of a solvent the yields were generally lower. The purity of the crude acids, which were isolated by the

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