was added to an aliquot of the reaction mixture before chromatography, the peak was enhanced without the appearance of an inflection or an additional peak, and, furthermore, when benzene was substituted for Ia and the experiment carried out as above, a peak with the same retention time resulted.

The yield of benzene was determined from the area of the peak by reference to a calibration curve constructed as follows. Appropriate, known amounts of benzene were substituted for Ia in reaction mixtures, chromatography was carried out as above, and the areas of the peaks due to benzene were plotted against the concentration of benzene in the mixture. Pertinent data are summarized in Table I; the yield of benzene is given in Table II.

Phenol and Phenyl Acetate, Detection and Yield.—The procedures used for the detection of these products and the determination of their yields were the same as those used for benzene with the exception that the column was kept at a constant temperature of 175°. Under these conditions the retention time for phenol was 5.55 min. and, for phenol acetate, it was 1.96 min. (both relative to toluene). Because of the slow rate of extraction of these products into toluene, due probably to adsorption onto solids in the reaction mixture, the yields were determined 5 hr. after the start of the reaction. Pertinent data are given in Table I and the yields in Table II.

Substitution of Benzenediazonium Ion for Ia.—A solution of 0.0396 mmole of aniline in 0.65 ml. of cold glacial acetic acid was treated with 0.35 ml. of cold, aqueous 0.11 *M* sodium nitrite solution and 31.47 mg. of activated manganese dioxide.[7] The mixture was agitated in a stoppered flask at room temperature for 40 min. It was then analyzed for aromatic products by gas chromatography as described above. Both phenol and phenyl acetate were found, but no benzene could be detected.

Valence Tautomerism of Vinyl-Substituted Three-Membered Heterocycles. I. Conversion of 1,2-Divinylethylene Oxide to 4,5-Dihydrooxepine

E. L. Stogryn, M. H. Gianni, and A. J. Passannante

The Special Projects Unit, Esso Research and Engineering Company, Linden, New Jersey

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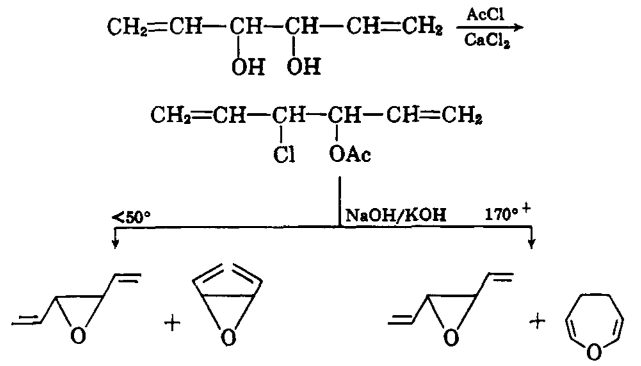
In recent years there has been considerable interest in the valence tautomerism of strained ring systems.[1-5] Until the work of Braun,[6] ring expansion of strained heterocyclic rings by a mechanism analogous to alicyclic systems had not been demonstrated. During the preparation of 1,2-divinylethylene oxide by the pyrolysis of *sym*-divinylethylene carbonate, Braun isolated its valence tautomer, 4,5-dihydrooxepine. Temperature requirements of cyclic carbonate pyrolysis precluded the isolation of *cis*- or *trans*-1,2-divinylethylene oxide free of 4,5-dihydrooxepine. We wish to report a convenient synthesis of *cis*- and *trans*-1,2-divinylethylene oxide together with the thermal requirements for conversion of each isomer to 4,5-dihydrooxepine.

The preparation of *cis–trans*-1,2-divinylethylene oxide and *trans*-1,2-divinylethylene oxide–4,5-dihydrooxepine was realized by the procedure shown.



$$CH_2{=}CH{-}\underset{OH}{CH}{-}\underset{OH}{CH}{-}CH{=}CH_2 \xrightarrow[CaCl_2]{AcCl} CH_2{=}CH{-}\underset{Cl}{CH}{-}\underset{OAc}{CH}{-}CH{=}CH_2$$

In the absence of solvent, 1,5-hexadiene-3,4-diol was converted to 3-chloro-4-acetoxy-1,5-hexadiene in yields of 40–50%. Infrared spectra of the chloro ester exhibited C–Cl (12.7 μ), acetate (5.78, 8.15 μ), and terminal olefin absorption (6.1, 10.12, 10.7 μ)

Both high and low temperatures were used to accomplish ring formation from the chloro ester. The isomer distribution and ring size is a function of the ring closure temperature. At 170°+, only *trans*-1,2-divinylethylene oxide and 4,5-dihydrooxepine were formed in a ratio of 2:1. However, if the temperature was maintained at less than 50°, the *cis* and *trans* oxides were isolated in a ratio of 1:2. Under the latter conditions, only trace amounts (1–2%) of 4,5-dihydrooxepine were formed.

Neither the *trans*-1,2-divinylethylene oxide–4,5-dihydrooxepine nor *cis–trans*-1,2-divinylethylene oxide mixtures could be fractionated by distillation through a 75-plate concentric tube column. Pure *trans* and *cis–trans* oxides and 4,5-dihydrooxepine, for structural determination and thermal isomerization studies, were obtained by preparative g.c. separation.

Braun was unable to establish definitely the structure of the 1,2-divinylethylene oxide he isolated. Since we were able to isolate the *cis* and *trans* epoxide, structural assignment could be made on the basis of infrared and n.m.r. The infrared spectra of *trans*-1,2-divinylethylene oxide exhibits intense absorption at 11.51 μ.[7] In the *cis–trans* mixture, the presence of the *cis* isomer is indicated by a band at 12.1 μ and a decrease in intensity of the 11.51-μ absorption. 1,2-Divinylethylene oxide, *cis* and *trans*, give τ values of 6.85 and 7.15, respectively, for the methine protons. The chemical shifts[8] for the *cis* and *trans*-2-butene oxides exhibit this pattern; *i.e.*, the *cis* protons have a smaller τ value than the *trans* protons. The spin–spin splitting pattern of the oxide ring protons[8] also distinguishes between the *cis* and *trans* isomers.

Unequivocal evidence for the origin of 4,5-dihydrooxepine during high temperature 1,2-divinylethylene oxide preparation was obtained by the thermal isomerization of *trans*- and *cis–trans*-1,2-divinylethylene oxide. The *trans* oxide of 93% purity was heated in a sealed tube for 17 hr. at 230°. The composition after this heating period was 48.3% *trans*-1,2-divinylethylene oxide and 42.9% 4,5-dihydrooxepine. Under identical conditions, the 4,5-dihydrooxepine was recovered unchanged. However, a *cis–trans*-1,2-divinylethylene

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[1] T. Nozoe, "Progress in Organic Chemistry, Vol. 5, J. W. Cook and W. Carruthers, Butterworth, Inc., Washington, D. C., 1961, pp. 132-165.

[2] W. E. Parham, *et al.*, *J. Am. Chem. Soc.*, **82**, 4085 (1960).

[3] (a) E. Vogel, Abstracts, 141st National Meeting of the American Society, Washington, D. C., April, 1962, p. 20; (b) E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **1**, 53 (1962).

[4] A. Cope, *et al.*, *J. Am. Chem. Soc.*, **74**, 4867 (1952).

[5] W. E. Doering and M. J. Goldstein, *Tetrahedron*, **5**, 53 (1959).

[6] R. A. Braun, *J. Org. Chem.*, **28**, 1383 (1963).

[7] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, New York, N. Y., **1959**, pp. 118-119.

[8] M. H. Gianni, E. L. Stogryn, and C. M. Orlando, Jr., *J. Phys. Chem.*, **67**, 1385 (1963).

oxide mixture (64.4% *trans*, 27.8% *cis*, and 7.8% 4,5-dihydrooxepine) heated on a steam bath overnight resulted in the disappearance of *cis*-1,2-divinylethylene oxide. The composition after the heating period was 61.8% *trans* oxide and 38.2% 4,5-dihydrooxepine.

The thermal requirements for ring expansion of 1,2-divinylethylene oxide and 1,2-divinylcyclopropane[8] are apparently analogous. In both cases, ring expansion of the *cis* isomer requires about 200° less than the corresponding *trans* isomer. Extension of valence tautomerism to other small ring heterocycles is currently under investigation in our laboratories.

Experimental

3-Chloro-4-acetoxy-1,5-hexadiene.—The procedure used for the preparation of 3-chloro-4-acetoxy-1,5-hexadiene was an adaptation of Searles[9] technique for preparation of chloro esters from 1,3-diols.

Acetyl chloride, 190 g. (2.44 moles), was added to a stirred suspension of 41.6 g. (0.38 mole) of calcium chloride and 228 g. (2.0 moles) of 1,5-hexadiene-3,4-diol over a period of 45 min. During the addition, the temperature was maintained below 10°. The reaction mixture then was stirred for 40 hr. at room temperature and then 1 hr. at 50°. The dark brown viscous product was poured into ice, neutralized with cold aqueous sodium bicarbonate extracted with ether, and dried over anhydrous potassium carbonate. After filtration and removal of ether, there remained 269 g. of crude chloro ester.

The crude chloro ester was distilled through a spinning band column to give a water-white, sweet-smelling liquid, b.p. 88–93° (19 mm.).

Anal. Calcd. for $C_8H_{11}ClO_2$: C, 55.17; H, 6.32; Cl, 20.11. Found: C, 54.53; H, 6.26; Cl, 20.00.

1,2-Divinylethylene Oxide. High Temperature Ring Closure.—Crude 3-chloro-4-acetoxy-1,5-hexadiene, 257 g., was slowly added to a reactor containing 362 g. (9.05 moles) of sodium hydroxide 362 g. (6.46 moles) of potassium hydroxide, and 36.2 g. (2.01 moles) of water at 170°. The addition of the chloro ester caused a rapid rise in temperature. During the addition, the pressure in the reactor was decreased so that an overhead temperature of 90–100° was maintained. If the pressure were too low, the overhead temperature dropped and the caustic foamed up into the distillation head causing it to plug. Approximately 80 ml. of product–water mixture was collected in a receiver cooled to −78°. Separation of the crude product from water, drying over anhydrous magnesium sulfate, and atmospheric distillation yielded 40 g. of *trans*-1,2-divinylethylene oxide–4,5-dihydrooxepine mixture, b.p. 105–113° (760 mm.), in a ratio of 2:1.

The composition of this mixture was determined on a Perkin-Elmer g.c. 2-m. column (Dow-Corning silicone oil no. 200 on firebrick) at 75°. The relative retention times of *trans*-1,2-divinylethylene oxide to benzene was 1.83 and 2.81 for 4,5-dihydrooxepine. Separation of the epoxide–oxepine mixture was not effective by distillation through a 75-plate concentric tube column. Pure *trans*-1,2-divinylethylene oxide and 4,5-dihydrooxepine for structural determination and subsequent reactions were obtained with an Autochrome preparatory g.c. unit. A Carbowax-Chromosorb column operated at 175° was utilized.

trans-1,2-Divinylethylene oxide (93% pure by g.c.) gave the following physical constants: b.p. 108° (760 mm.)[10]; n^{25}_D 1.4470; d^{20}_4 0.870; infrared maxima (neat) 3.35 (m), 6.10 (m), 7.03 (m), 10.17 (s), 10.82 (vs), 11.38 (s), 11.50 (vs), and 14.79 (s)μ. 4,5-Dihydrooxepine (93% pure by g.c.) had b.p. 113° (760 mm.)[10]; n^{25}_D 1.4735; d^{20}_4 0.978; infrared maxima (neat) 3.45 (m), 6.05 (s), 6.10 (s), 7.46 (m), 7.70 (vs), 8.99 (vs), and 13.35 (s) μ.

Anal. Calcd. for C_6H_8O (*trans* epoxide): C, 75.01; H, 8.33. Found: C, 74.68; H, 8.46.

Low Temperature Ring Closure.—The apparatus and quantities used in this procedure were identical with that used in the high temperature ring closure except that 700 ml. of ethylene glycol was used in addition to the caustic and water. The reactor temperature was maintained at 40–50° and the pressure at 10–15 mm. during the addition of the chloro ester. In this way, 241 g. of crude chloro ester yielded 101 ml. of *cis–trans* 1,2-divinylethylene oxide in ratio of 1:2 (composition determined by g.c.). This product showed only trace quantities (1–2%) of 4,5-dihydrooxepine. Distillation of the *cis–trans* mixture through a 75-plate concentric tube column at 45 mm. failed to separate the isomeric oxides. The *cis–trans* epoxide mixture (ratio 1:2) gave the following physical constants: b.p. 107° (760 mm.)[10]; n^{25}_D 1.4520; d^{20}_4 0.899; infrared maxima (neat) 3.35 (m), 6.10 (m), 7.03 (m), 10.17 (s), 10.82 (vs), 11.50 (s), 12.10 (w), and 14.79 (s) μ.

Anal. Calcd. for C_6H_8O: C, 75.01; H, 8.33. Found: C, 74.88; H, 8.03.

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[9] S. Searles, K. A. Pollart, and F. Block, *J. Am. Chem. Soc.*, **79**, 952 (1957).

[10] Determined by the inverted capillary tube technique.

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cis–trans Isomerism of Exocyclic α,β-Unsaturated Indanones and Tetralones

DENNIS N. KEVILL, ERNEST D. WEILER, AND
NORMAN H. CROMWELL[1]

Avery Laboratory, University of Nebraska, Lincoln 8, Nebraska

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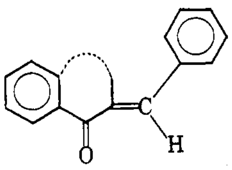
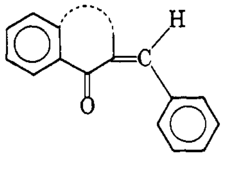
Exocyclic α,β-unsaturated ketones have a fixed *sym-cis* conformation of the C=C with respect to the C=O. Assignments of the *cis* and *trans* isomers of three such compounds by proton magnetic resonance spectroscopy are reported.



trans



cis

The deshielding effect resulting from the diamagnetic anisotropy of the carbonyl group leads to the vinyl proton in the *trans* isomer (with the proton *cis* to the carbonyl group) giving a signal at a greater chemical shift than in the *cis* isomer.

2-Benzal derivatives of 4,4-dimethyl-1-tetralone,[2] 1-indanone,[2] and 3,3-dimethyl-1-indanone,[3] as prepared by condensation with benzaldehyde in the presence of base, were isolated as sharp melting solids having the *trans* arrangement of phenyl and carbonyl groups (see Table I).

In methanol these *trans* isomers were largely converted by ultraviolet irradiation into the corresponding *cis* isomers. Chromatography of the crude irradiation products gave pure specimens of each of these *cis* iso-

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[1] To whom communications concerning this paper should be addressed.

[2] A. Hassner and N. H. Cromwell, *J. Am. Chem. Soc.*, **80**, 893 (1958).

[3] B. D. Pearson, R. P. Ayer, and N. H. Cromwell, *J. Org. Chem.*, **27**, 3038 (1962).