CONCLUSIONS

In addition to the relevant points already discussed this section will briefly comment on some of the salient factors derived from this study, especially in respect to fluorene. The ionization constants, reflecting conditions in the molecule in the ground state, suggest that interactions between rings are considerably less than might be expected on the basis of the profound alterations, as a function of structural changes, in the ultraviolet (and visible) spectra, which serve as indicators of molecules in the excited state.[30]

The substituent groups vary greatly in their ability to alter the ionization constants. The following order, arranged in decreasing proton-releasing power was observed, over-all, in the series of fluorene compounds studied: $-NO_2$, $-9-SO_2$, $9-CO$, $9-SO$, $-NH_3^+$, $9=O$, $-F$, $-I$, $-Cl$, $-Br$, $-NHCOCH_3$, $-H$, $-OCH_3$, $-OH$, $-NH_2$. A substituent in an *ortho* position exhibits, generally, a considerably larger effect than the same group in another position. Substituents in the same ring, even in a *meta* relationship for the most part are more effective than when they are located in different rings.

The ionization constants of the isomeric 1-, 2-, 3-, and 4-fluorenamines, 3.57, 4.27, 4.39, and 3.15, respectively, bear no relation to the carcinogenicity of these compounds in rats. Thus, the 2-isomer is carcinogenic, the 1- and 3-derivatives are considerably weaker, and 4-fluorenamine is inactive, according to the presently available data.[31,cf. 6] This lack of a correlation may mean that (1) the compounds examined themselves are not the substances directly involved in eliciting the carcinogenic action, (2) the differences in ionization constants play no role in allowing the penetration of the compounds at the physiological *p*H into the cells where metabolism and tumorigenesis take place. The latter point is quite likely since at *p*H of 7.4 all of the above compounds would be almost completely nonionized. Hence it would appear that point (1) is also a true statement. Other studies[cf. 6,27] suggest the same conclusion, namely that metabolism of the amines is required to elicit the carcinogenic intermediate.

BETHESDA 14, MD.

(28) However, an excellent study by E. Berliner and E. H. Winicov, *J. Am. Chem. Soc.*, **81**, 1630 (1959), suggests that factors other than hydrogen bonding may play a role in the relatively weak acid character of the 5-nitrofluorene-4-carboxylic acid. They noted that 7-nitro-1-naphthoic acid and the 8-nitro-2-isomer were the weakest of the respective nitronaphthoic acids, even though the substituents were in conjugated positions (as they are in our fluorene derivative). In the two exceptional acids of Berliner and Winicov, intramolecular hydrogen bonding cannot be implicated.

(29) For example, whereas 4-fluorenamine diazotizes in the normal manner, the yields of compounds resulting from the replacement of the diazonium derivative by hydroxy or bromine are as a rule quite poor. Likewise, the 4-substituted fluorenes are usually the lowest melting of any of the isomeric derivatives.

(30) R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, Wiley, New York, 1957; R. A. Friedel, *Appl. Spectroscopy*, **2**, 13 (1956).

(31) H. R. Schinz, H. Fritz-Niggli, T. W. Campbell, and H. Schmid, *Oncologia*, **8**, 233 (1955); H. P. Morris, C. A. Velat, B. P. Wagner, M. Dahlgard, and F. E. Ray, *J. Natl. Cancer Inst.*, **24**, 149 (1960).

[CONTRIBUTION FROM THE FOOD MACHINERY AND CHEMICAL CORPORATION
CHEMICAL RESEARCH AND DEVELOPMENT CENTER]

Reaction of (4,5), (8,9)-Diepoxytricyclo[5.2.1.0^{2,6}]decane with Hydrogen Bromide in Glacial Acetic Acid[1]

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Dicyclopentadiene dioxide was shown to react with hydrogen bromide in glacial acetic acid to give 5-bromotricyclo-[5.2.1.0^{2,6}]decane-4,9-dihydroxy-8-acetate[2] instead of the corresponding dibromohydrin. The structure of the product was inferred from infrared spectra and the formation of corresponding derivatives.

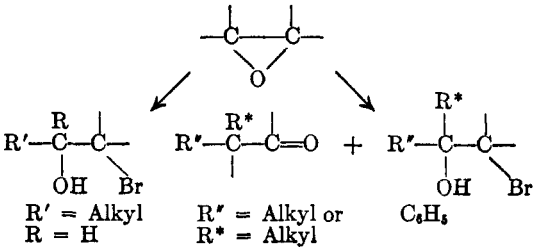
A series of epoxy derivatives with the tricyclo[5.2.1.0.^{2,6}]decane skeletal structure were synthesized and the characteristic position of bands attributable to the oxirane oxygen functional groups were studied. No absorption peaks in the 11.8 μ region were observed for compounds that had no epoxy group on the bicyclo [2.2.1.] heptane ring. Likewise, bands in the 12 μ region were absent for compounds with no oxirane oxygen on the cyclopentane ring. According to these results, assignment of the 852 cm.$^{-1}$ and 834 cm.$^{-1}$ bands of dicyclopentadiene dioxide to the oxirane oxygen of the bicyclo-[2.2.1.]heptane and the cyclopentane ring respectively was made.

The synthesis of dicyclopentadiene dioxide was first reported by Wieland and Bergel.[3] Recent commercial availability of this compound has focused attention on the reactivity of the oxirane oxygen groups and its corresponding assay by means of hydrohalogenation methods.[4,5]

When most epoxides are treated with hydro-

(1) This was presented before the 136th meeting of the American Chemical Society in Atlantic City, N. J., September 13, 1959.

halogen acids in glacial acetic acid, the corresponding halohydrins are formed rapidly and quantitatively. Certain epoxides which contain a tertiary carbon atom in the oxirane ring and other compounds which isomerize readily in acid media (*e.g.* styrene oxide), give the corresponding aldehyde or ketone with this reagent.[6] All hydrocarbon epoxides observed to date had given one of these two reactions. Therefore, we were surprised



to observe that the reaction of dicyclopentadiene dioxide with hydrogen bromide in glacial acetic acid consumed only one instead of two moles of hydrogen bromide per mole of compound.

This observation might be explained in several ways: (1) The possible isomerization of one epoxy group; (2) no reaction of one oxirane oxygen; (3) acetylation of one epoxy group of the dicyclopentadiene dioxide.

The infrared spectrum of dicyclopentadiene dioxide gives strong absorption bands related to the oxirane oxygen ring in the form of a doublet.[7] Since the two epoxy bands could be due to the respective oxirane oxygen of the dicyclopentadiene dioxide, it was felt that differentiation and specific assignment of frequencies will aid in the characterization of the reaction products and explanation of the observed reaction. With this in mind a series of epoxy derivatives with one epoxy group at one of the two possible positions on the tricyclo[5.2.1.$0^{2,6}$]decane skeletal structure were prepared according to the procedures described in the experimental section and the characteristic position of bands attributable to the oxirane oxygen functional groups were studied. The frequencies of the oxirane oxygen ring bands are given in Table I.[8,9]

Compounds with oxirane oxygen on the bicyclo[2.2.1]heptane ring gave a strong absorption in the 11.8 μ region. Compounds with oxirane oxygen on the cyclopentane ring gave strong absorption bands in the 12.0 μ region. In view of these results, the 852 cm.$^{-1}$ and 834 cm.$^{-1}$ bands of the dicyclopentadiene dioxide were assigned to the oxirane oxygen of the bicyclo[2.2.1]heptane and the cyclopentane ring, respectively.

TABLE I

FREQUENCY OF OXIRANE OXYGEN BANDS IN CM.$^{-1}$

Correlation of frequencies of oxirane oxygen bands of compounds with tricyclo[5.2.1.$0^{2,6}$]decane skeletal structure, bicyclo[2.2.1]-2,3-epoxyheptane, and 6-oxabicyclo[3.1.0]-hexane

Compound	Oxirane Oxygen at Bicyclo-[2.2.1]-heptane Ring	Oxirane Oxygen at Cyclo-pentane Ring
(8,9)-Epoxy-*endo*-tricyclo[5.2.1.$0^{2,6}$]-dec-4-ene	850	
(4,5),(8,9)-Diepoxy-*endo*-tricyclo-[5.2.1.$0^{2,6}$]decane	852	834
(4,5)-Epoxy-*endo*-tricyclo[5.2.1.$0^{2,6}$]-decane		838
(4,5)-Epoxy-*exo*-tricyclo[5.2.1.$0^{2,6}$]-decane-8-formate		838
(4,5)-Epoxy-*exo*-tricyclo[5.2.1.$0^{2,6}$]-decan-8-ol		837
(4,5)-Epoxy-*endo*-tricyclo[5.2.1.$0^{2,6}$]-decane-8,9-diol		837
(2,3)-Epoxybicyclo[2.2.1]heptane	854	
6-Oxabicyclo[3.1.0]hexane		838

Dicyclopentadiene dioxide was allowed to react with hydrogen bromide in glacial acetic acid reagent at room temperature. The product formed was isolated after removal of the excess hydrogen bromide and acetic acid under vacuum at 0°. Infrared, functional group, and elemental analysis of the isolated product indicated the formation of the corresponding bromohydrin-hydroxyacetate (II).[2]

Alkaline hydrolysis of II with aqueous sodium carbonate resulted in the formation of III with an absorption band at 837 cm.$^{-1}$. The dihydroxy epoxide, III, reacted readily with hydrogen bromide in acetic acid to give V. The above experimental results established with no doubt that acetylation of the oxirane oxygen of the bicyclo[2.2.1]heptane ring occurs readily when dicyclopentadiene dioxide is allowed to react with hydrogen bromide in acetic acid. Attempts to treat I with acetic acid alone, under the same conditions utilized in the reaction with acetic acid–hydrogen bromide reagent, resulted in the quantitative recovery of I. The latter reaction suggested an acid catalyzed acetylation of the relatively basic epoxy group. This was substantiated by the fact that acetylation of the oxirane oxygen of the bicyclo[2.2.1]heptane ring proceeded readily and quantitatively in excess glacial acetic acid in the presence of catalytic amounts of perchloric acid. The isolated product after hydrolysis with aqueous sodium hydroxide had the same structure as III.

The acid catalyzed hydrolysis of I and III gave IV which reacted quantitatively with periodic

(2) For convenience only one of the two possible isomers is indicated throughout this paper. No experimental work to differentiate between 5-bromotricyclo[5.2.1.$0^{2,6}$]decane-4,9-dihydroxy-8-acetate and 5-bromotricyclo[5.2.1.$0^{2,6}$]decane-4,8-dihydroxy-9-acetate was undertaken.

(3) H. Wieland and F. Bergel, *Ann.*, **446**, 13 (1925).

(4) A. J. Durbetaki, *Anal. Chem.*, **28**, 2000 (1956).

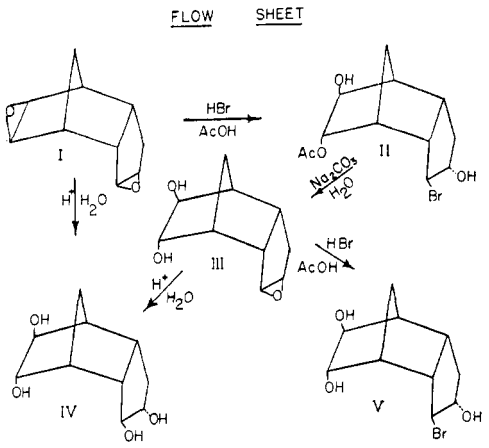
(5) A. J. Durbetaki, *Anal. Chem.*, **30**, 2024 (1958).

(6) A. J. Durbetaki, *Anal. Chem.*, **29**, 1666 (1957).

(7) J. Bomstein, *Anal. Chem.*, **30**, 544 (1958).

(8) Determined in carbon disulfide solution.

(9) Determined as 1.5% solution.



acid according to the method of Pohle *et al.* for vicinal diols.[10] No apparent rearrangement of the type found for bicyclo[2.2.1]-2,3-epoxyheptane[11] was observed in the hydrolysis of I as is apparent from the positive periodic acid test.

The difference in reactivity between the oxirane oxygen of the bicyclo[2.2.1]heptane and that of the cyclopentane rings could not be readily explained by differences in group substituents and the donating or attracting nature of such groups. Flett[12] has shown that in some cases there is a correlation between the position of a characteristic absorption band and the reactivity of the group. The effect of steric strain on frequencies has been clearly demonstrated in small rings.[13–15] It is generally observed that analogous group structures with greater strain absorb about 20–35 cm.$^{-1}$ higher than those with lesser steric strain. The frequency of oxirane oxygen of the bicyclo[2.2.1]heptane ring appears 18 cm.$^{-1}$ higher than that of the corresponding epoxy of the cyclopentane ring (Table I). The behavior of dicyclopentadiene dioxide, resulting in the ring opening of one epoxy group by a weak acid while the other oxirane oxygen remains unaffected by it could therefore be attributed to steric strain.[16]

No apparent shift in oxirane band frequency was observed when the cyclopentane ring was *endo* or *exo* to the bicyclo[2.2.1]heptane ring (Table I). Furthermore, reaction with hydrogen bromide in acetic acid was quantitative in both isomeric forms as shown in the experimental section.

(10) W. D. Pohle, V. C. Mehlenbacker, and J. H. Cook, *Oil and Soap*, **22**, 115 (1945); *J. Am. Oil Chemists' Soc.*, **27**, 54 (1950).

(11) H. W. Kwart and W. G. Vosbrugh, *J. Am. Chem. Soc.*, **76**, 5400 (1954).

(12) M. St. C. Flett, *Trans. Faraday Soc.*, **44**, 767 (1948).

(13) J. LeComte, *J. phys. Radium*, **6**, 127 (1945); **6**, 257 (1945).

(14) S. L. Friess and P. E. Frankenburg, *J. Am. Chem. Soc.*, **74**, 2679 (1952).

(15) C. D. Gutsche, *J. Am. Chem. Soc.*, **73**, 786 (1951).

(16) It might be pointed out here that epoxides in general do not readily react with acetic acid under the experimental conditions described.[4,5]

EXPERIMENTAL

The dicyclopentadiene used in the preparation of the compounds described below was the *endo*-isomer, fractionally distilled, m.p. 33.6°. The *endo*-dicyclopentadiene dioxide was Food Machinery and Chemical Corporation Commercial product, recrystallized, m.p. 189.5–190.5°.

5-Bromotricyclo[5.2.1.0^{2,6}]decane-(4,9)-dihydroxy-8-acetate (II).[2] To dicyclopentadiene dioxide (0.5 g., 0.003 mole) dissolved in 5 ml. of chlorobenzene was added 0.006 mole of anhydrous hydrogen bromide in 50 ml. of glacial acetic acid. Upon complete addition of the reagent the solution was evaporated to dryness at 0–10° *in vacuo*. The residue was crystallized from acetonitrile to yield 0.89 g. (96%) of product. The infrared spectrum[17] of the product has bands at 3584 cm.$^{-1}$ (free —OH stretching), 3424 cm.$^{-1}$ (associated —OH stretching), 1724 cm.$^{-1}$ (ester C=O), 1245 cm.$^{-1}$ (acetate C=O) and 1076 cm.$^{-1}$ (—OH deformation). No bands at 834 and 852 cm.$^{-1}$ characteristic of oxirane oxygen are present.

Anal. Calcd. for $C_{12}H_{17}O_4Br$: C, 47.2; H, 5.7; Br, 26.2; CH_3COO, 19.3; OH, 11.2 Found: C, 47.0; H, 5.6; Br, 26.5; CH_3COO, 19.3; OH, 11.2.

Hydrolysis of II *to the (4,5)-epoxy-endo-tricyclo[5.2.1.0^{2,6}]-decane-8,9-diol* III. Compound II (0.7 g., 0.002 mole) was treated with 100 ml. of sodium carbonate solution (21.2 g. sodium carbonate in 100 ml. of distilled water) for 1.5 hr. while maintaining the temperature at about 98°. The alkaline solution was then extracted with chloroform. The chloroform extract was dried over anhydrous sodium sulfate and the solvent was removed *in vacuo*. The residue was crystallized from petroleum ether (b.p. 30–60°) to yield 0.4 g. (95.4%) of III, m.p. 122–123°. The infrared spectrum of the crude product has bands at 3424 cm.$^{-1}$ (—OH stretching), 1080 cm.$^{-1}$ (—OH deformation), 837 cm.$^{-1}$ (C_6, oxirane oxygen). This material titrated with acetic acid–hydrobromic acid reagent and gave a positive periodic acid test for vicinal diol.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.9; H, 7.7; OH, 18.6; O(oxirane), 8.78. Found: C, 65.9; H, 7.6; OH, 18.7; O(oxirane), 8.6.

Hydrobromination of III *to 5-bromo-endo-tricyclo[5.2.1.0^{2,6}]-decane-4,8,9-triol* (V). To (4,5)-epoxy-*endo*-tricyclo[5.2.1.0^{2,6}] decane-8,9-diol (0.5 g., 0.003 mole) dissolved in 5 ml. of chlorobenzene was added 0.003 mole of anhydrous hydrogen bromide in 50 ml. of glacial acetic acid. Upon complete addition of the reagent the solution was evaporated to dryness at 0–10° *in vacuo*. The infrared spectrum of the product has bands at 3584 cm.$^{-1}$ (free —OH stretching), 3424 cm.$^{-1}$ (associated hydroxyl stretching), and 1076 cm.$^{-1}$ (—OH deformation). No bands at 837 cm.$^{-1}$ (C_6, oxirane oxygen) or 1724 cm.$^{-1}$ (ester C=O) are present.

Anal. Calcd. for $C_{10}H_{15}O_3Br$; C, 45.6; H, 5.7; Br, 30.4. Found: C, 45.5; H, 5.7; Br, 30.3.

endo-tricyclo[5.2.1.0^{2,6}]dec-4-ene.[18] To a solution of dicyclopentadiene (13.5 g., 0.10 mole) in 100 ml. of cyclohexane was added 2.2 g. of 5% palladium on barium sulfate. The mixture was shaken for 6 min. under 60 lbs. of hydrogen pressure in a Parr apparatus. After removal of the catalyst the solution was fractionally distilled *in vacuo* to yield 12.9 g. (94.3%) of a camphor-like crystalline solid m.p. 52–53° (lit.,[18] m.p. 52–53°). The infrared spectrum of the product has bands at 1613 cm.$^{-1}$ (C=C cyclopentane ring)[19]. No band at 992 cm.$^{-1}$ (C=C of the bicyclo[2.2.1] heptane ring[19]) is present.

Anal. Calcd. for $C_{10}H_{14}$: C, 89.5, H, 10.5. Found: C, 89.4; H, 10.3.

(4,5)-Epoxy-endo-tricyclo[5.2.1.0^{2,6}]decane. To a solution of 10.2 g. (0.076 mole) of dihydrocyclopentadiene in 50 ml.

(17) Determined in chloroform solution.

(18) K. Alder and G. Stein, *Ann.*, **485**, 223 (1931).

(19) K. W. F. Kohlrausch and R. Seka, *Ber.*, **69**, 729 (1936).

of chloroform was added 16 g. of 41% peracetic acid and 2 g. of sodium acetate. During the addition of peracetic acid the temperature was not allowed to rise above 25°, and this temperature was maintained for 3 hr. after the addition had been completed. The reaction mixture was neutralized with 5% sodium hydroxide. The chloroform layer was separated, washed with water, and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue sublimed to yield 10.5 g. (92.3%) of product, m.p. 97–98° (lit.,[19] m.p. 98°). This material reacted with acetic acid–hydrobromic acid reagent. A discussion of the infrared spectra can be found in another section of this paper.

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.0; H, 9.4; O(oxirane), 10.65. Found: C, 79.8; H, 9.4; O(oxirane), 10.65. Found, C, 79.8; H, 9.3; O(oxirane), 10.6.

(8,9)-Epoxy-endo-tricyclo[5.2.1.0^{2,6}]dec-4-ene. This compound, m.p. 79.5–80° (lit.,[18] m.p. 79–80°), was prepared as previously described.[18] The infrared spectrum of the product has bands at 992 cm.$^{-1}$ (C=C of the cyclopentane ring[19]) and 850 cm.$^{-1}$ (oxirane oxygen).

exo-tricyclo[5.2.1.0^{2,6}]dec-4-ene 8-formate (VI). This compound b.p. 136°/25 mm. (lit.[20] b.p. 136°/25 mm.) was prepared as previously described.[20] The infrared spectrum of the product has bands at 1721 cm.$^{-1}$ (ester C=O), 1179 cm.$^{-1}$ (formate C=O) and 1613 cm.$^{-1}$ (C=C of the cyclopentane ring[19]).

Epoxydation of VI to the (4,5)-Epoxy-exo-tricyclo[5.2.1.0^{2,6}]-decan 8-formate VII. To a solution of VI (36 g., 0.20 mole) in 150 ml. of chloroform was added 5 g. of sodium acetate and 52 g. of 41% peracetic acid. During the addition of peracetic acid the temperature was not allowed to rise above 25° and this temperature was maintained for 3 hr. after the addition had been completed. The reaction mixture was neutralized with 5% sodium bicarbonate. The chloroform layer was separated, washed with water, and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo*. The residual oil was distilled to yield 38.1 g. (97.1%) of the epoxide, b.p. 111° (1 mm.), n^{21} 1.5042. The infrared spectrum of the product has bands at 1720 cm.$^{-1}$ (ester C=O), 1179 cm.$^{-1}$ (formate C=O), and 838 cm.$^{-1}$ (oxirane oxygen).

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.3; O(oxirane), 8.2. Found: C, 68.0; H, 7.2; O(oxirane), 8.1.

Hydrolysis of VII to the (4,5)-epoxy-exo-tricyclo[5.2.1.0^{2,6}]-decan-8-ol VIII. Compound VII (3.0 g., 0.015 mole) was treated with 100 ml. of sodium carbonate solution (21.2 g. sodium carbonate in 100 ml. of distilled water) for 1.5 hr. while maintaining the temperature at about 98°. The alkaline solution was extracted with chloroform. The chloroform extract was dried over anhydrous sodium sulfate and the solvent was removed *in vacuo*. The highly viscous oil residue was crystallized from petroleum ether (b.p. 30–60°) to yield 2.4 g. (96.1%) of pure product. The infrared spectrum of the oily product has bands at 3380 cm.$^{-1}$ (—OH stretching) 1080 cm.$^{-1}$ (—OH deformation), 838 cm.$^{-1}$ (cyclopentane ring oxirane oxygen).

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.3; H, 8.5; O(oxirane), 9.6. Found: C, 72.2; H, 8.4; O(oxirane), 9.5.

Acetylation of I *to* III. To dicyclopentadiene dioxide (1 g.) dissolved in 50 ml. of glacial acetic acid was added 2 drops of 72% perchloric acid. The solution was kept at 50° for 15 min. The acetic acid solution was made alkaline with 25% sodium hydroxide. The alkaline solution was extracted with chloroform. The chloroform extract was dried over anhydrous sodium sulfate and the solvent was removed *in vacuo*. The residue was crystallized from petroleum ether to yield 1.09 g. (98.4%) of glycol, m.p. 122–123°. The infrared spectrum of the crude product was identical with that obtained from the alkaline hydrolysis of II.

Acetylation of I. To a solution of I, 0.5 g. in chloroform, was added 50 ml. of glacial acetic acid. The acetic acid was removed *in vacuo* at 10°. The residue, m.p. 189.5–190.5°, had an infrared spectrum identical with I and gave a negative periodic acid test for vicinal diol.

Hydrolysis of I.[21] Dicyclopentadiene dioxide 1 g. and 100 ml. of distilled water containing 2 drops of 72% perchloric acid was maintained at 85° for 8 hrs. The water solution was extracted with chloroform. The chloroform extract dried over anhydrous sodium sulfate and the solvent removed *in vacuo*. The residue was a hygroscopic resin and could not be recrystallized.[18] The infrared spectrum was characteristic of that of a glycol and 1 mole of the compound reacted quantitatively with 2 moles of periodic acid as expected for a tetrol.

6-Oxabicyclo[3.1.0]hexane. To a solution of 10.2 g. (0.015 mole) of cyclopentene in 50 ml. of chloroform was added 24 g. of 40% peracetic acid and 2 g. of sodium acetate. During the addition of peracetic acid the temperature was not allowed to rise above 25°, and this temperature was maintained for 3 hr. after the addition had been completed. The reaction mixture was neutralized with 5% sodium hydroxide. The chloroform layer was separated, washed with water, and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residual liquid was distilled to yield 12.2 g. (97%) of the epoxide, b.p. 99–100° (lit.,[22] b.p. 98.5–100°). The infrared spectrum of the product has a band at 838 cm.$^{-1}$ (C_5, oxirane oxygen). No bands at 904 cm.$^{-1}$ and 1619 cm.$^{-1}$ (C=C of the cyclopentene ring) are present.

(2,3)-Epoxybicyclo[2.2.1]heptane. This compound m.p. 125–126° (lit.,[23] m.p. 125–127°) was prepared as previously described. The infrared spectrum of the product has a band at 854 cm.$^{-1}$.

Analytical methods. 1. Acetoxy: E. P. Clark, *Ind. Eng. Chem. Anal. Ed.*, **8**, 487 (1936). 2. Hydroxyl (lithium aluminum hydride method): R. E. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 1197 (1947). 3. Oxirane oxygen (acetic acid–hydrobromic acid method).[3] 4. Glycol (periodic acid).[9]

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PRINCETON, N. J.

(20) P. D. Bartlett and A. Schneider, *J. Am. Chem. Soc.*, **68**, 6 (1946).

(21) The hydrolysis of I on a micro scale followed by an *in situ* periodic acid oxidation in chloroform–acetic solution was adapted for the quantitative analysis of dicyclopentadiene dioxide by the author (unpublished data).

(22) J. Böeseken, *Rec. Trav. Chim.*, **47**, 689 (1928).

(23) H. M. Walborsky and D. F. Loncrini, *J. Am. Chem. Soc.*, **76**, 5396 (1954).