# **40.** *Aspects of Stereochemistry. Part XI.* Epoxide Formation in the* cyclo*Hexene and* bicyclo*Heptene Series.*

By H. B. HENBEST and B. NICHOLLS.

On reaction with *cyclo*hexenes with $CH_2$·OH, $CH_2$·OAc, or $CO_2Me$ substituents at the 4-position, approach of perbenzoic acid is preferentially *trans* to the substituent. In the *bicyclo*heptene series the usual direction of attack of peracids (on the same side as the methylene bridge) is not altered by substituents (OH, OAc, $CH_2$·OAc, $CO_2H$, or $CO_2Me$) on the other side of the ring. However, in the case of a hydroxymethyl substituent the isolation of a tetrahydrofuran derivative and a high reaction velocity indicate that the primary alcohol group is rendering intramolecular nucleophilic assistance to the olefin–peracid reaction. The epoxide from " *endo*-dehydronorborneol " is isomerized by alkali to an oxetan derivative, the reaction confirming the accepted configuration of the initial olefinic alcohol.

PREVIOUS studies have shown that some positive directing effect is involved in the reaction of *cyclo*hex-2-enol with peracids, as a *cis*-hydroxy-epoxide is obtained as the major product.[1,2] In contrast, *cyclo*hex-3-enol gave a mixture of the *cis*- and *trans*-isomers.[2] This work has now been extended to some compounds related to *cyclo*hex-3-enol in which the hydroxyl group has been replaced by bulkier groups, as in (I; R = $CH_2$·OH, $CH_2$·OAc, or $CO_2Me$). Each of these *cyclo*alkenes gave a liquid epoxide, homogeneous on distillation and reduced by lithium aluminium hydride to the known [3] *trans*-diol (III). The formation of this 1 : 3-compound by hydride reduction may be visualized as proceeding from conformations (IIA) (bulky aluminohydride complex equatorial), opening of the epoxide ring giving the axial 3-alcohol. The lower homologue of the epoxy-alcohol (II; $CH_2$·OH), with hydroxyl in place of the hydroxymethyl group, gave the 1 : 4-product on hydride reduction by an intramolecular mechanism involving a six-ring transition state.[2] The similar reduction of the higher homologue (II; $CH_2$·OH) would involve an unlikely seven-ring transition state, and the more usual reaction (cf. IIA) therefore takes place.

Recent work [4] has shown that the *trans*-isomer is the major product from the reaction

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* Part X, *J.*, 1958, 3293.

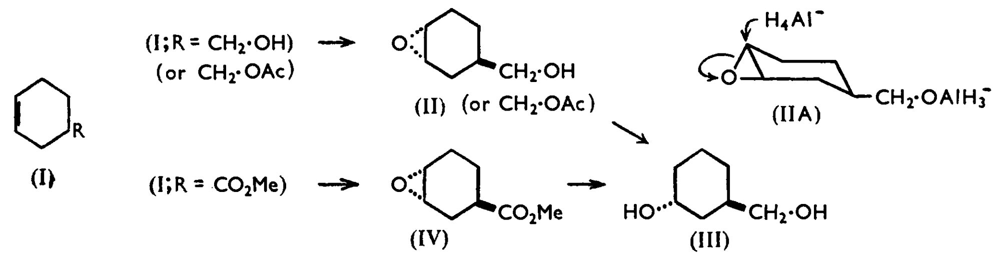
[1] Henbest and Wilson, *J.*, 1957, 1958.

[2] Henbest and Nicholls, *J.*, 1957, 4608.

[3] Clarke and Owen, *J.*, 1950, 2108.

[4] Hopff and Hoffmann, *Helv. Chim. Acta*, 1957, **40**, 1585.

of 4-phenyl*cyclo*hexene (I; R = Ph) with peracetic acid. On the other hand our own preliminary observations have shown that a mixture of epoxides results from the reaction of the nitrile (I; R = CN) with perbenzoic acid. So far, the results in the *cyclo*hexene series seem to suggest that *trans*-isomers tend to be formed when the 4-substituent is relatively bulky ($CH_2$·OH, $CH_2$·OAc, $CO_2Me$, Ph), whereas mixtures are produced from *cyclo*alkenes with smaller 4-substituents (OH, CN). If further work should establish that *trans*-approach is caused by steric factors, the effectiveness of the moderately remote groups at the 4-position is noteworthy since in the preferred conformation the substituent lies approximately in the plane of the ring in an equatorial or slightly distorted equatorial position.



bicyclo*Heptene Series.*—*Nomenclature.* The convenient αβ-prefix system has been used [5] in bicyclic compounds to denote the configurations of substituents relative to a bridge. In continuity with this usage and with our own usage of these prefixes in other alicyclic compounds,[6] the configurations of substituents in the *bicyclo*heptane series will be denoted by α and β (the latter signifying a group *cis* to the methylene bridge) instead of the *endo*- and *exo*-terms. The latter terms have recently been used in a somewhat different sense to denote the direction of reagent approach towards trigonal carbon in the *cyclo*hexane series.[7, 8]

*Results.* The first compound studied in the bicyclic series was the unsaturated alcohol (V), which may be regarded as a methylene-bridged analogue of the *cyclo*hex-3-enol that was investigated earlier. In the *bicyclo*heptene series, reagents normally approach the double bond on the less hindered β-side, and the reaction of the olefinic alcohol (V) was no exception to this rule, isolation of the crystalline *trans*-hydroxy-epoxide (VI) in high yield showing that the hydroxyl group was exerting no detectable directing effect of the kind observed with cyclic allylic alcohols.[1]

The *trans*-configuration of the new epoxide (VI) was established by the following reactions. Treatment with potassium *tert.*-butoxide in *tert.*-butyl alcohol gave an isomeric hydroxy-epoxide (VII) that exhibited a strong infrared band at 940 $cm.^{-1}$, analogous to that given at 950 $cm.^{-1}$ by 2 : 2-dimethyloxetane. [All the *vic.*-epoxides of the *bicyclo*heptane series (*e.g.*, VI and X) gave a strong band near 850 $cm.^{-1}$ (cf. ref. 9).] Both epoxides (VI and VII) were reduced by lithium aluminium hydride to the same diol, formulated as (VIII). The unidirectional opening of the epoxide ring in each case may be due to the *trans*-disposition of the groups which would cause the reactions to proceed *via* cyclic transition states (VIA and VIIA) similar to those proposed for the monocyclic series.[1, 2] Acetylation of the initial hydroxy-epoxide (VI) gave the epoxy-acetate (X), also obtained directly in high yield from the unsaturated acetate (IX) and perbenzoic acid.

It may be noted that these reactions, particularly the isomerization, (VI ⟶ VII),

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[5] *Inter alia*, Fodor and Nádor, *J.*, 1953, 721; Cookson, *J.*, 1954, 282.

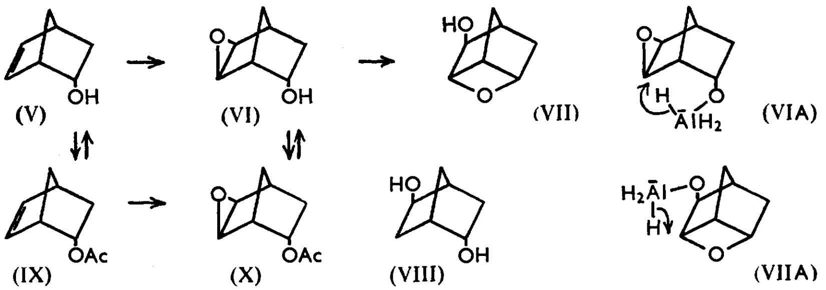
[6] Henbest, Smith, and Thomas, *J.*, 1958, 3293; see also following paper.

[7] Zimmerman, *J. Amer. Chem. Soc.*, 1956, **78**, 1168.

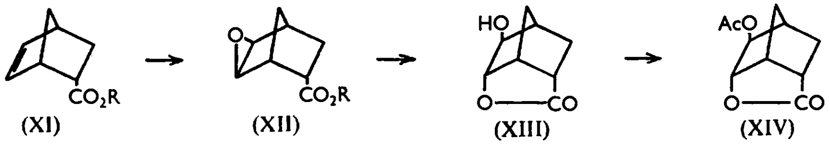
[8] Bordwell and Hewett, *ibid.*, 1957, **79**, 3493.

[9] Meinwald, Nozaki, and Wiley, *ibid.*, p. 5580.

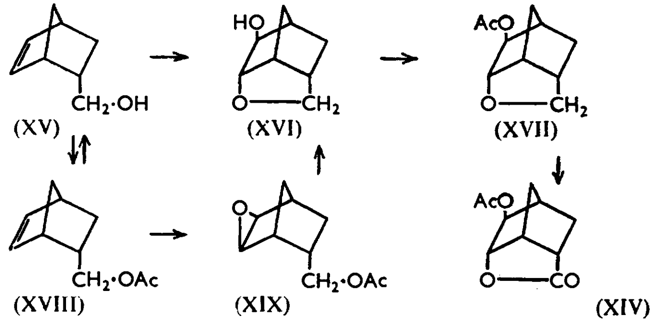
provide rather direct proof for the accepted α-configuration of the unsaturated alcohol (V) and the acetate (IX; a Diels–Alder adduct) from which it is prepared.[10]



The reaction of perbenzoic acid with the unsaturated ester (XI; R = Me) (equivalent to I; R = $CO_2Me$ with an extra methylene bridge) gave a homogeneous product formulated as the β-epoxide (XII; R = Me). On treatment with aqueous formic acid this epoxide yielded the hydroxy-lactone (XIII) (carbonyl band at 1750 $cm.^{-1}$), also isolated when the unsaturated ester (XI; R = Me) was treated with a formic acid–hydrogen peroxide mixture. The acetate (XIV) was obtained on acetylation and also by another route (below). The infrared absorption of the crude product from the reaction of perbenzoic acid with the unsaturated acid (XI; R = H) indicated that the epoxy-acid (XII; R = H) had been formed, but attempts to separate it from benzoic acid by crystallization were frustrated by its ready isomerization to the hydroxy-lactone (XIII).



Reactions of the unsaturated alcohol (XV) (structurally related to I; R = $CH_2{\cdot}OH$) and some of its derivatives with peracid have also been examined. The methyl ether of (XV) and the acetate (XVIII) reacted with perbenzoic acid at normal rates and in a preparative experiment the acetate gave a good yield of an epoxide which had a strong absorption band at 850 $cm.^{-1}$ and may therefore be formulated as the β-epoxide (XIX).



However, the parent alcohol (XV) reacted with the peracid at an abnormally rapid rate to give a product formulated as (XVI). This structure is suggested because the compound (*a*) was recovered unchanged after treatment with lithium aluminium hydride and (*b*) gave a crystalline acetate (XVII) different from the previously obtained epoxy-acetate (XIX), and (*c*), because the alcohol and its acetate each exhibited a strong ether band near 1150 $cm.^{-1}$, also shown by the corresponding compound lacking the hydroxyl (or acetoxyl)

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[10] Alder and his co-workers, *Annalen*, 1936, **525**, 183, 201; 1939, **543** 1.

group (following paper). The ease of formation of the tetrahydrofuran ring structure was also shown by the formation of the hydroxy-ether (XVI) from the epoxy-acetate (XIX) on treatment with alkali or even with lithium aluminium hydride.

Clearly the proximity of the α-hydroxymethyl grouping to the double bond in (XV) causes its participation in the peracid reaction; in the related monocyclic alcohol (I; $R = CH_2{\cdot}OH$) normal vicinal epoxide formation occurs as the hydroxymethyl group is presumably equatorial and well separated in space from the double bond. In bicyclic compounds, analogous participation probably takes place in the conversion of the α-carboxylic acid (XI; R = H) into an iodo-lactone under conditions where the isomeric β-carboxylic acid is unaffected,[11] and also in the mercuration of the alcohol (XV) (following paper). For reactions with perbenzoic acid, the present results indicate that participation by an α-hydroxymethyl group is more powerful than that by an α-carboxylic acid group, in line with their relative nucleophilic strengths.

As the position adjacent to an ether group is often susceptible to oxidation, the preparation of the acetoxy-lactone (XIV) from the acetoxy-ether (XVII) was thought possible. This conversion was effected in good yield by use of chromic acid in acetone.

## EXPERIMENTAL

M. p.s in this and the following paper were determined on a Kofler hot stage. The peracid reactions were performed at 0° and were followed by titration. When reaction was complete, acids were removed by means of calcium hydroxide.[2] Alumina was deactivated with dilute acetic acid. Light petroleum refers to the fraction of b. p. 60—80° unless otherwise stated. The infrared spectra of all compounds were consistent with the structures assigned. As stated on p. 222 the αβ-system of nomenclature is used for denoting relative configuration in racemic compounds.[6] As none of these was resolved, the (±)-prefix has been omitted throughout the two papers.

*Reactions of* cyclo*Hex-3-enylmethanol* (I; $R = CH_2{\cdot}OH$) *and its Acetate with Perbenzoic Acid.*—The reaction mixture from the unsaturated alcohol (5·55 g.) and perbenzoic acid in ether (100 c.c.; 0·64M) was shaken with calcium hydroxide (25 g.) until neutral. Isolation in the usual way gave 3α : 4α-*epoxy*-1β-cyclo*hexylmethanol* (II) (5·93 g., 90%), b. p. 64°/0·3 mm., $n_D^{21}$ 1·4828 (identical for six fractions) (Found: C, 65·5; H, 9·3. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4%). The α-*naphthylurethane*, formed in high yield, separated from light petroleum (b. p. 80—100°) as needles, m. p. 112—114° (Found: C, 72·9; H, 6·3. $C_{18}H_{19}O_3N$ requires C, 72·7; H, 6·4%).

The epoxy-alcohol (2·8 g.) was reduced with lithium aluminium hydride (1·01 g.) in ether (70 c.c.) in the usual way.[2] Distillation gave 3α-hydroxy-1β-*cyclo*hexylmethanol (III) (2·66 g.), b. p. (bath-temp.) 122—125°/0·03 mm. The bisphenylurethane, formed in good yield, had m. p. and mixed m. p. 118—120° (sample kindly provided by Dr. L. N. Owen of Imperial College).

A similar reaction between the unsaturated acetate (7·74 g.) and perbenzoic acid in ether (100 c.c.; 0·64M) afforded 3α : 4α-*epoxy*-1β-cyclo*hexylmethyl acetate* (8·12 g., 95%), b. p. 57°/0·25 mm., $n_D^{21}$ 1·4625 (identical for five fractions) (Found: C, 63·5; H, 8·3. $C_9H_{14}O_3$ requires C, 63·5; H, 8·3%). Hydrolysis of the epoxy-ester (2·46 g.) with potassium hydroxide (1·04 g.) in methanol (30 c.c.) and water (2 c.c.) yielded the foregoing epoxy-alcohol (1·73 g., 90%), b. p. (bath-temp.) 85—94°/0·05 mm., $n_D^{20}$ 1·4840 (α-naphthylurethane, m. p. and mixed m. p. 112—114°).

Reduction of the epoxy-acetate (3·7 g.) with lithium aluminium hydride (1·7 g.) in ether (100 c.c.) yielded 3α-hydroxy-1β-*cyclo*hexylmethanol (2·49 g., 88%), b. p. (bath-temp.) 120—125°/0·04 mm. (bisphenylurethane, m. p. and mixed m. p. 117·5—120°).

*Reaction of Methyl* cyclo*Hex-3-ene-1-carboxylate with Perbenzoic Acid.*—The reaction between the unsaturated ester (7·07 g.) and perbenzoic acid in ether (93 c.c., 0·65M) gave *methyl* 3α : 4α-*epoxy*cyclo*hexane-1β-carboxylate* (IV) (7·49 g., 95%), b. p. 50—51°/0·5 mm., $n_D^{21}$ 1·4630 (six fractions) (Found: C, 61·35; H, 7·75. $C_8H_{12}O_3$ requires C, 61·5; H, 7·75%).

The epoxy-ester (3·43 g.) was reduced with lithium aluminium hydride (2 g.) in ether (100 c.c.) in the usual way to 3α-*hydroxy*-1β-cyclo*hexylmethanol* (III) (2·8 g.), b. p. (bath-temp.) 125—130°/0·05 mm. (bisphenylurethane, m. p. and mixed m. p. 118—120°).

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[11] Rondestvedt and Ver Nooy, *J. Amer. Chem. Soc.*, 1955, **77**, 4878.

*Reactions of* bicyclo[2 : 2 : 1]*Hept*-5-*en*-2α-*ol* (V) *and its Acetate* (XI) *with Perbenzoic Acid.*—The reaction mixture from the alcohol (3·76 g.) and perbenzoic acid in ether (100 c.c. of a 0·43M-solution) was shaken with calcium hydroxide (20 g.) until neutral. One crystallization of the product from ether–pentane gave material (4·01 g., 93%), m. p. 155—161° (sublimes). The pure 5β : 6β-*epoxy*bicyclo[2 : 2 : 1]*heptan*-2α-*ol* (VI) had m. p. 160—162° (sublimes) (Found: C, 66·7; H, 7·9. $C_7H_{10}O_2$ requires C, 66·65; H, 8·0%). Its α-*naphthylurethane* had m. p. 143·5—145° (from light petroleum) (Found: C, 72·9; H, 6·0. $C_{18}H_{17}O_3N$ requires C, 73·2; H, 5·8%). Acetylation gave the *epoxy-acetate* (X), b. p. 114—115°/14 mm., m. p. 52·5—54° (from pentane) (Found: C, 64·55; H, 7·05. $C_9H_{12}O_3$ requires C, 64·3; H, 7·1%).

The reaction mixture from the unsaturated acetate (10 g.) and perbenzoic acid in ether (125 c.c. of a 0·59M-solution) was shaken with calcium hydroxide (28 g.) until neutral. Distillation gave the epoxy-acetate which solidified. Crystallization from pentane gave the epoxy-acetate (9·75 g., 88%), m. p. and mixed m. p. with the foregoing compound, 53—54°. For hydrolysis, the epoxy-acetate (3·76 g.) and potassium hydroxide (1·2 g.) in methanol (40 c.c.) and water (5 c.c.) were kept at 20° for 24 hr. Isolation with ether gave the epoxy-alcohol (2·66 g.), m. p. and mixed m. p. 159—162° (sublimes) (α-naphthylurethane, m. p. and mixed m. p. 143—145°).

*Reduction of the Epoxy-alcohol* (VI).—The epoxy-alcohol (2·46 g.) was added to lithium aluminium hydride in ether (50 c.c.; 0·4M) and heated under reflux for 3 hr. Decomposition with ethyl acetate and dilute acid, followed by continuous extraction with ether, gave a solid (2·49 g.), m. p. 162—210°. Crystallization from benzene gave a sparingly soluble compound (0·24 g.), m. p. 223—227°, probably a triol. The remainder was chromatographed on deactivated alumina (200 g.). Elution with benzene–ether (1 : 1) gave starting material (0·18 g.). Elution with ether gave bicyclo[2 : 2 : 1]*heptane*-2β : 5α-*diol* (VIII) (1·77 g.), m. p. 191—192·5° (from benzene–*iso*propyl ether) (Found: C, 65·5; H, 9·3. $C_9H_{12}O_2$ requires C, 65·6; H, 9·4%). Its *di*-p-*bromobenzenesulphonate* had m. p. 151·5—154° (from ethyl acetate–*iso*propyl ether) (Found: C, 40·0; H, 3·5. $C_{19}H_{18}O_6Br_2S_2$ requires C, 40·6; H, 3·25%).

*Isomerization of the Epoxy-alcohol* (VI).—Solutions of the epoxy-alcohol (3·02 g.) in *tert.*-butyl alcohol (75 c.c.) and potassium *tert.*-butoxide in *tert.*-butyl alcohol (10 c.c.; M) were mixed and kept at 20° for 4 days, previous small-scale experiments having shown that this time was necessary for complete isomerization (disappearance of *vic.*-epoxide band at 850 cm.$^{-1}$). The solution was filtered through deactivated alumina (100 g.), and the solvent removed through a Fenske column. Recrystallization from ethyl acetate–light petroleum followed by sublimation gave 3α : 5α-*epoxy*bicyclo[2 : 2 : 1]*heptan*-2β-*ol* (VII) (2·47 g., 82%), m. p. 173—176° (Found: C, 66·7; H, 8·1. $C_7H_{10}O_2$ requires C, 66·65; H, 8·0%).

The 3α : 5α-epoxide (0·816 g.) and lithium aluminium hydride (0·4 g.) in dry dioxan (10 c.c.) were heated under reflux for 36 hr. After decomposition of the excess of hydride, the diol was isolated by continuous ether-extraction. Recrystallization from ether acetate–*iso*propyl ether and sublimation in a short-path still at 130°/0·2 mm. gave *bicyclo*[2 : 2 : 1]heptane-2β : 5α-diol (VIII) (0·753 g., 90%), m. p. and mixed m. p. 192—194°.

*Reactions of* bicyclo[2 : 2 : 1]*Hept*-5-*en*-2α-*ylmethanol* (XV) *and its Acetate* (XVIII) *with Perbenzoic Acid.*—The reaction mixture from the alcohol (10·02 g.) in ether (50 c.c.) and perbenzoic acid in ether (161 c.c.; 0·59M) was shaken with calcium hydroxide (40 g.). Distillation at 110° (bath-temp.)/0·1 mm. gave the crude product (10·83 g.) as a hygroscopic solid, m. p. 115—130°. The pure 6-*oxa*tricyclo[3 : 2 : 1 : $1^{3:8}$]*nonan*-4β-*ol* (XVI) had m. p. 147—150° (from benzene–light petroleum) (Found: C, 68·3; H, 8·6. $C_8H_{12}O_2$ requires C, 68·55; H, 8·65%). Acetylation with acetic anhydride and pyridine at 20° yielded the *acetate* (XVII), m. p. 50—52° (from pentane) (Found: C, 66·0; H, 7·9. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·75%). The hydroxy-ether (XVI) was unchanged after treatment with lithium aluminium hydride in boiling ether for 3 hr.

The reaction mixture from the unsaturated acetate (XVIII) (10·01 g.) and perbenzoic acid in ether (120 c.c.; 0·58M) was shaken with calcium hydroxide (40 g.). Distillation yielded 5β : 6β-*epoxy*bicyclo*hept*[2 : 2 : 1]-2α-*ylmethyl acetate* (XIX) (10·59 g., 95%), b. p. 129—130°/12 mm., $n_D^{23}$ 1·4813 (constant for 5 fractions) (Found: C, 65·8; H, 7·35. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·75%). Part of the epoxy-acetate (4·01 g.) was treated with potassium hydroxide (1·51 g.) in methanol (45 c.c.) and water (5 c.c.). Isolation with ether gave a wax (3·04 g.), m. p. 111—127°, which on sublimation (120°/0·2 mm.) and crystallization from benzene–light petroleum gave the hydroxy-ether (XVI) identified as its acetate, m. p. and mixed m. p.

50—52°. This hydroxy-ether was also obtained on treating the *vic.*-epoxy-ester (3·58 g.) with lithium aluminium hydride (2 g.) in ether (200 c.c.).

The starting *acetate* (XVIII) was prepared from the alcohol (XV) in the usual way; it had b. p. 89·5—90°/13 mm., $n_D^{15}$ 1·4733 (Found: C, 70·85; H, 8·45. $C_{10}H_{14}O_2$ requires C, 71·1; H, 8·4%).

*Reaction of Methyl* bicyclo[2 : 2 : 1]*Hept-5-ene-2α-carboxylate* (XI; R = Me) *with Perbenzoic Acid.*—The reaction solution from the ester (15 g.) and perbenzoic acid in ether (250 c.c.; 0·43M) was neutralized with calcium hydroxide (70 g.). Distillation gave *methyl* 5β : 6β-*epoxy*bicyclo[2 : 2 : 1]*heptane-2α-carboxylate* (XII; R = Me) (16·45 g., 98%), b. p. 122·5—124°/17 mm., $n_D^{23}$ 1·4812 (constant for 5 fractions) (Found: C, 64·5; H, 7·0. $C_9H_{12}O_3$ requires C, 64·25; H, 7·2%).

*Formation of the Acetoxy-lactone* (XIV).—(*a*) The unsaturated acid (XI; R = H) (2·51 g.) [or its methyl ester (2·73 g.)] was dissolved in 98% formic acid (5·8 g.) at 45° and hydrogen peroxide (2·3 g.; 100-vol.) was added during 5 min. while the temperature was kept at 45—50°. The mixture was stirred at 50° for 1 hr. during which it became homogeneous. It was then steam-distilled until no more formic acid came over, and the residue was extracted continuously with ethyl acetate to give 5β : 6α-*dihydroxy*bicyclo[2 : 2 : 1]*heptane-2α-carboxylic* 6α-*lactone* (XIII) (2·47 g., 88% from the acid; 2·02 g., 72% from the ester), m. p. 160° (Found: C, 62·4; H, 6·6. $C_8H_{10}O_3$ requires C, 62·3; H, 6·55%). Acetylation with acetic anhydride and pyridine gave 5β-*acetoxy*-6α-*hydroxy*bicyclo[2 : 2 : 1]*heptane-2α-carboxylic* 6α-*lactone* (XIV), m. p. 95—96° (from *iso*propyl ether) (Found: C, 61·45; H, 6·0. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·1%).

The hydroxy-lactone (XIII), m. p. and mixed m. p. 160°, was also obtained in high yield from the β-epoxide (XII; R = Me) by treatment with formic acid followed by isolation by the above procedure.

(*b*) A solution of the acetoxy-ether (XVII) (2·21 g.) in acetone (15 c.c.) was cooled to 5° and treated dropwise with 8N-chromic acid (15 c.c.) at <10°. It was then kept overnight at 20°, treated with sulphur dioxide and, after the addition of water, extracted with ether. Crystallisation from *iso*propyl ether gave the acetoxy-lactone (2·05 g., 89%), m. p. and mixed m. p. 95—96·5°.

*Preparation of Methyl Ethers.*—A solution of the unsaturated alcohol (V) (15 g.) in dry benzene (150 c.c.) containing potassium (20 g.) was stirred vigorously at 70—80° during 1·5 hr. while methyl iodide (50 g.) was added dropwise. The mixture was heated and stirred for a further 2 hr., then it was cooled to 0° and methanol (40 c.c.) was added cautiously to decompose the excess of potassium. Isolation with ether afforded 6α-*methoxy*bicyclo[2 : 2 : 1]*hept-2-ene* (14·1 g.), b. p. 76°/18 mm., $n_D^{18}$ 1·4667 (Found: C, 77·2; H, 9·8. $C_8H_{12}O$ requires C, 77·4; H, 9·8%).

The alcohol (XV) (16 g.) was methylated similarly, to give bicyclo[2 : 2 : 1]*hept-5-en-2α-ylmethyl methyl ether* (15·1 g.), b. p. 138—140°/400 mm., $n_D^{19}$ 1·4687 (Found: C, 78·0; H, 10·0. $C_9H_{14}O$ requires C, 78·2; H, 10·2%). These two ethers were used for some preliminary kinetic work (below).

*Reaction Rates.*—Bimolecular rate constants at 5° in benzene solution were determined for several of the unsaturated bicyclic compounds.

| Compound | Initial concn. of compound (mole/l.) | Initial concn. of of $BzO_2H$ (mole/l.) | *k* (mole$^{-1}$ l. min.$^{-1}$) |
|---|---|---|---|
| (V) | 0·0342 | 0·0707 | 0·121 |
| (V; Me ether) | 0·0352 | 0·07075 | 0·285 |
| (V; acetate) | 0·0345 | 0·07075 | 0·0592 |
| (XV) | 0·0365 | 0·0707 | 5·7 * |
| (XV; Me ether) | 0·0349 | 0·07075 | 0·173 |
| (XV; acetate) | 0·0350 | 0·0708 | 0·127 |

* This relatively rapid reaction did not exactly follow a bimolecular law, the value of *k* decreasing with time. The value given is an approximate one computed after a reaction time of 2 min.

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THE UNIVERSITY, MANCHESTER, 13.
KING'S COLLEGE, LONDON, W.C.2.
THE QUEEN'S UNIVERSITY OF BELFAST.

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