was recovered. The yield of 2,3-dihydro-6-chloroöxepine (III) obtained was 6.49 g. (83%), b.p. 103–107° (78 mm.), $n^{25}D$ 1.5167–1.5178.

A redistilled sample had b.p. 75° (25 mm.), $n^{25}D$ 1.5166; infrared spectrum (neat): 3019w, 2980m, 2940m, 2895m, 2820w, 1687w, 1633m, 1605s, 1465m, 1425m. 1357m, 1342m, 1292s, 1238s, 1187s, 1067m, 1040m, 973s, 923s, 885m, 851m, 802m, 734m, 642w.

The nuclear magnetic resonance spectrum, run as 10% in carbon tetrachloride with 1% tetramethylsilane as reference, gave the following: 3.36 τ, a singlet, weight 1, designated as the C-7 hydrogen; 4.23 τ, multiple, weight 1.9, C-4 and 5 hydrogens; 5.89 τ, triplet, weight 2.1, C-2 hydrogens; 7.44 τ, pseudoquad, weight 1.8, C-3 hydrogens.

Anal. Calcd. for C_6H_7ClO: C, 55.19; H, 5.40. Found: C, 54.90; H, 5.53.

Hydrogenation of 2,3-dihydro-6-chloroöxepine (III), with platinum oxide catalyst in anhydrous ether resulted in the uptake of 102% of four moles of hydrogen, and afforded a 63% yield of 1-hexanol, b.p. 80–82° (36 mm.), $n^{25}D$ 1.4163. The ethereal solution gave a chlorine test with silver nitrate and was acid to wet litmus. The infrared spectrum of the alcohol and that of an authentic sample were identical. The 3,5-dinitrobenzoates were prepared and their melting points and mixed melting points were the same.

2-Oxa-7-chloronorcarane (XIII).—Commercial butyllithium (3.54 moles) in heptane was added dropwise over a period of 4 hr. to a cold (−10 to −20°) mixture of dry dihydropyran (IV) (378 g., 4.5 moles) and dry methylene chloride (382 g., 4.5 moles). The mixture was allowed to warm to room temperature overnight. Water (600 ml.) was added, the mixture was filtered, and the organic layer was separated; the aqueous layer was extracted three times with 400-ml. portions of petroleum ether (30–60°). The organic layers were combined, dried ($MgSO_4$), and distilled. There was obtained 134 g. (28% yield) of a mixture of the racemic isomers XIIIa and XIIIb, b.p. 45° (3 mm.) to 48° (1.5 mm.), $n^{25}D$ 1.4798–1.4879. This mixture was separated by fractional distillation into the two racemates.

endo-**2-Oxa-7-chloronorcarane** (**XIIIa**) had b.p. 34.0° (1.1 mm.), $n^{25}D$ 1.4765; infrared spectrum (neat): shoulder 3050m, shoulder 3010m, 2950vs, 2875s, 2735vw, 1472m, 1460m. 1450m, 1404m. 1380w, 1350m, 1317w, 1285m. 1238vs. 1215vs, shoulder 1200m. 1137vs, 1115vs, 1072s, 1036s, 1015s, 990s, 955m, 938m, 883s, 848s, shoulder 827w, 812vw, shoulder 782m, 773s, 642m.

Anal. Calcd. for C_6H_9ClO: C, 54.35; H, 6.84. Found: C, 54.60; H, 7.04.

This lower boiling isomer XIIIa was distilled unchanged at atmospheric pressure (b.p. 175.5–176.5° (739 mm.), $n^{25}D$ 1.4765) in the presence and absence of quinoline.

exo-**2-Oxa-7-chloronorcarane** (**XIIIb**) had b.p. 48° (1.5 mm). $n^{25}D$ 1.4873; infrared spectrum (neat): 2935–45vs, 2875vs. 2740w, shoulder 1465–1470m, 1457s, 1444s, 1394s. shoulder 1378–1382m. 1357s, 1338m, 1321m, 1287vs, 1243vs, 1220vs. 1145vs, 1110vs, 1075vs, 1047vs. 990m, 973vs, 915s, 878s. 847m, 792s, 756m. 733vs, 701vs, 672s.

Anal. Calcd. for C_6H_9ClO: C, 54.35; H, 6.84. Found: C, 54.45; H, 6.84.

This isomer XIIIb decomposed upon attempted distillation at atmospheric pressure, and afforded a high yield of 2,3-dihydroöxepine (XIV) when distilled from quinoline.

The composition of the original mixture XIII was calculated to be composed of approximately 40% *endo*-2-oxa-7-chloronorcarane (XIIIa) and 60% *exo*-2-oxa-7-chloronorcarane (XIIIb) by use of refractive index data.

2-Oxanorcarane (**VI**) **from** *endo*-**2-oxa-7-chloronorcarane** (**XIIIa**) was obtained from a sample (4 g.) of the *endo*-racemic mixture XIIIa, b.p. 34.0° (1.1 mm.), $n^{25}D$ 1.4768. The procedure was essentially the same as that described for the conversion of V to VI except that 1.2 g. of sodium was employed in approximately 25 ml. of anhydrous liquid ammonia. The crude product weighed 2.15 g. (b.p. 121–122°, $n^{25}D$ 1.4200–1.4450) and was shown to be 82% 2-oxanorcarane (VI) by vapor phase chromatographic analyses. Thus 1.76 g. (60%) of 2-oxanorcarane (VI) was present. A redistilled sample of this product had b.p. 122°, $n^{25}D$ 1.4486 (lit.[6] b.p. 121°, $n^{25}D$ 1.4488), and its infrared spectrum was identical with that of an authentic sample of 2-oxanorcarane (VI).[6]

2-Oxanorcarane (**VI**) **from** *exo*-**2-oxa-7-chloronorcarane** (**XIIIb**) was obtained from a sample (4.2 g.) of the *exo*-racemic mixture XIIIb, b.p. 47–48° (1.6–1.7 mm.), $n^{25}D$ 1.4861. The procedure was essentially the same as that described above (1.8 g. of sodium was employed). The crude product weighed 2.40 g. (b.p. 120–122°, $n^{25}D$ 1.4457–1.4487) and was shown to be 91% 2-oxanorcarane (VI) by vapor phase chromatographic analyses. Thus 2.18 g. (70%) of 2-oxanorcarane (VI) was present. A redistilled sample of this product had b.p. 122°, $n^{25}D$ 1.4487 (lit. b.p. 121°, $n^{25}D$ 1.4488), and its infrared spectrum was identical with that of an authentic sample of 2-oxanorcarane (VI).[6]

2,3-Dihydroöxepine (**XIV**).—To 20 g. of distilled quinoline was added 10 g. (0.075 mole) of *exo*-2-oxa-7-chloronorcarane (XIIIb racemates). The flask was attached to a semi-micro spiral wire column and the system was evacuated to a pressure of 156 mm. The flask was immersed in an oil-bath set at 150°. Distillation of the 2,3-dihydroöxepine (XIV) as it was formed yielded 5.4 g. (74%), b.p. 94–62° (150–156 mm.), $n^{25}D$ 1.4940–1.4950. A redistilled sample had b.p. 61° (100 mm.), $n^{25}D$ 1.4965; infrared spectrum (neat): 3040m, 2985w, 2940m, 2915m, 2830ww, 1641m, 1611s, 1467w, 1433w, 1403w, 1370vw, 1341w, 1302s, 1232w, 1203w, 1120s, 1063vw, 1037vw, 979w, 920m, 882w, 773w, 718s, 635w.

The nuclear magnetic resonance spectrum, run the same as the chloroöxepine III, had: at 3.69 τ, doublet, weight 1.35, assigned to the hydrogen at the 7-position; 4.32 τ, pseudo-doublet, wt. 2.4. 4- and 5-hydrogens; 5.23 τ, triplet, wt. 1, 6-hydrogen; 5.89 τ, intense triplet, wt. 1.86, 2-hydrogen; 7.47 τ, pseudoquadruplet, 7-hydrogen.

Anal. Calcd. for C_6H_8O: C, 74.97; H, 8.39. Found: C, 74.71; H. 8.58.

Hydrogenation of 2,3-dihydroöxepine (**XIV**) over platinum oxide resulted in a 97% uptake of two moles of hydrogen. An 89% yield of oxepane XV was obtained: b.p. 119–120.5° (740 mm.), $n^{25}D$ 1.4351. The pure material had b.p. 121° (741 mm.), $n^{25}D$ 1.4365 (lit.[12] b.p. 119–120°, $n^{25}D$ 1.4393; lit.[3] $n^{24}D$ 1.4361).

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Seven-Membered Heterocyclic Systems. II. The Synthesis of 2,3-Dihydroöxepine[1]

BY JERROLD MEINWALD,[2] DAVID W. DICKER AND NAFTALI DANIELI

RECEIVED FEBRUARY 3, 1960

Two routes to a cyclic diene from 2,3,6,7-tetrahydroöxepine are described. This diene is shown to be 2,3-dihydroöxepine, rather than the expected 2,7-dihydroöxepine, on the basis of its physical properties and its acid lability.

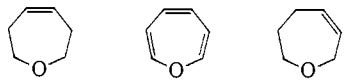
Introduction.—The synthesis of 2,3,6,7-tetrahydroöxepine (I) has been described in a recent publication from this Laboratory.[3] Interest in this compound stemmed from its possible utilization as an intermediate in the synthesis of the as

(1) This research was supported by a Research Grant from the National Institutes of Health. This support is gratefully acknowledged.

(2) Fellow of the Alfred P. Sloan Foundation.

(3) For the previous paper in this series, see J. Meinwald and H. Nozaki, THIS JOURNAL, **80**, 3132 (1958).

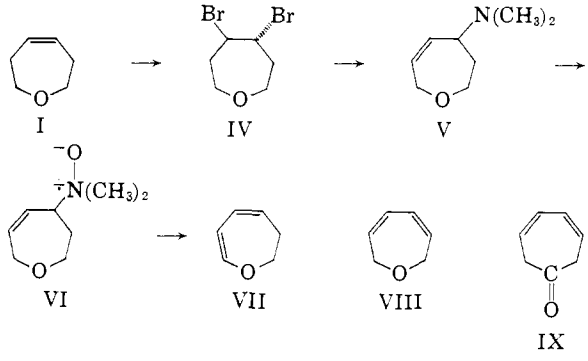
yet unknown heterocycle, oxepine (II). As part of our work directed toward the ultimate synthesis of oxepine, we wish now to describe the conversion of I into a dihydroöxepine (VII) by two independent routes.



I II III

Discussion.—At about the same time our synthesis of I was reported, an independent synthesis of 2,3,4,7-tetrahydroöxepine (III) from 4-acetoxy-2,3,4,5,6,7-hexahydroöxepine was described by Olsen and Bredoch.[4] Although the selectivity of the elimination involved seemed surprising, the route to III appeared especially convenient, and we examined the possibility of using III as a point of departure for the introduction of further unsaturation into the seven-membered ring. Unfortunately, vapor-phase chromatography of the Olsen–Bredoch product revealed it to be a *mixture* of I (about 70%) and a second component (presumably III, about 30%), so that the use of this material appeared unattractive.

2,3,6,7-Tetrahydroöxepine (I) was prepared essentially as described previously, but with improvement of the yields in several of the steps.[5] Addition of bromine to I gave the *trans*-dibromide IV as a low-melting, crystalline solid. Treatment of IV with excess dimethylamine gave the unsaturated tertiary amine V.[6] The amine was smoothly converted into the corresponding N-oxide VI by hydrogen peroxide. Finally, pyrolysis of VI at 80–110° gave the diene VII. This diene was at first considered to possess structure VIII, the product to be expected from a normal *cis* elimination



of this type.[6] However, several observations served to exclude this possibility.

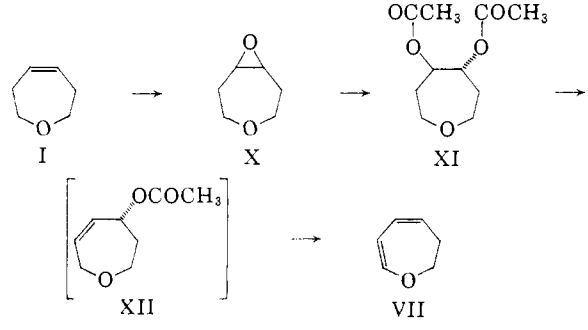
The presence of a *conjugated* grouping in this diene was obvious from its ultraviolet absorption spectrum ($\lambda_{max}^{isooctane}$ 260 mμ, log ε 3.95). The position of this maximum would seem to favor structure VII, with the oxygen atom extending conjugation (*cf.* 1,3-cycloheptadiene shows maximal absorption at 248 mμ).[7] However, in view of the unexpectedly abnormal ultraviolet absorption of the cycloheptadienone IX (λ_{max} 214 mμ),[8] a confident prediction for VIII does not appear possible at this time. The formation of a crystalline Diels–Alder adduct from the diene with tetracyanoethylene confirms the presence of the conjugated diene system, but does not serve to distinguish between the two possibilities.

The nuclear magnetic resonance spectrum of VII provided the most convincing physical evidence for its structure. The observed spectrum showed a complexity beyond what would be expected for the relatively symmetrical formula VIII. In particular, the absorption for the unique olefinic proton at C_7, at lower field than any proton in I, and split into a doublet by the single C_6 proton, serves to make a clear-cut distinction between the two possibilities. (For additional details see the Experimental section.)

Treatment of VII with dilute hydrochloric acid at room temperature resulted in ready cleavage to give complex carbonyl-containing products. This observation serves to confirm structure VII, an enol ether, and to eliminate VIII, which should not be so readily hydrolyzed by acids.

It should be pointed out that the exact stage at which rearrangement occurred in this reaction sequence has not been rigorously established. However, since no clear reason can be discerned for rearrangement in going from the dibromide IV to the unsaturated amine, the only other ambiguous step, we tentatively postulate a 1,4-elimination in the final pyrolysis. The alternative possibility that diene VIII was formed first and then rearranged to VII can be excluded on the basis of Cope's studies of amine oxide pyrolysis, in which such rearrangements are found not to occur.[6]

In an attempt to achieve a synthesis of the symmetrical olefin VIII, an alternate reaction sequence was investigated. Epoxidation of I with perbenzoic acid gave the expected epoxide X. This epoxide reacted readily with a mixture of acetic acid, acetic anhydride and *p*-toluenesulfonic acid



to give the diacetate XI, which gave rise to a diene on pyrolysis at 525°. Since this diene was found to be identical to that obtained earlier *via* N-oxide pyrolysis, it appears that the intermediate XII, analogous to the amine oxide VI, also suffers

(4) S. Olsen and R. Bredoch, *Chem. Ber.*, **91**, 1589 (1958).

(5) All relevant changes are recorded in detail in the Experimental section.

(6) These steps are essentially those used by R. Willstätter, *Ann.*, **317**, 223 (1901), for the synthesis of cycloheptadiene from cycloheptene. See also E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, THIS JOURNAL, **61**, 1057 (1939). Amine oxide pyrolysis (see A. C. Cope, E. Ciganek and N. A. LeBel, *ibid.*, **81**, 2799 (1959), for a leading reference) was used in the last step in place of Hofmann elimination.

(7) E. Pesch and S. L. Friess, *ibid.*, **72**, 5756 (1950).

(8) J. Meinwald, S. L. Emerman, N. C. Yang and G. Büchi, *ibid.*, **77**, 4401 (1955).

preferential 1,4-elimination.[9] Examination of models of XII and of VI does not reveal any obvious steric factor favoring 1,4- over 1,2-eliminations for these pyrolyses. However, to the extent that double bond character between the carbon atoms about to become olefinic enters into the corresponding transition states,[6] it may be that the product formed is controlled largely by the greater stability of VII, compared to VIII, derived from the presence of a more extended conjugated system in the former diene.

A few preliminary experiments aimed at extending the conjugation in VII to give I have so far been unrewarding. However, we hope to study this problem more intensively when a larger supply of diene is available.[9a] Should these attempts fail, the synthesis of the symmetrical diene VIII would take on renewed importance.

Experimental

4-(2-Tetrahydropyranyloxy)-1-butyne.—The procedure as described was found convenient for large-scale work. An equimolar mixture of 3-butyn-1-ol and dihydropyran was cooled to −30° and stirred during the addition of 1 ml. of concentrated hydrochloric acid. When the exothermic reaction had subsided, the reaction mixture was distilled directly under nitrogen in the presence of solid potassium carbonate to give the desired tetrahydropyranyl ether, b.p. 44–45° (0.1 mm.), 63–67° (1.9–2.7 mm.), $n^{25}D$ 1.4542–1.4552 (lit.[10] b.p. 92–95° (18 mm.), $n^{18}D$ 1.4589), in 87–93% yield.

6-(2-Tetrahydropyranyloxy)-3-hexyn-1-ol.—The alkylation of the lithium derivative of 4-(2-tetrahydropyranyl oxy)-1-butyne with ethylene oxide in liquid ammonia was readily carried out on a 2–3 molar scale as previously described[11] to give an 84–90% yield of the desired product, b.p. 111–114° (0.4 mm.), $n^{25}D$ 1.4811–1.4819 (lit.[11] 77% yield of product, b.p. 116° (0.4 mm.), $n^{21}D$ 1.4828).

***cis*-6-(2-Tetrahydropyranyloxy-3-hexen-1-ol.**—Semihydrogenation of 6-(2-tetrahydropyranyloxy)-3-hexyn-1-ol proceeded smoothly on a one molar scale in ethyl acetate over 10% palladium-on-charcoal. This procedure was found somewhat more convenient than our earlier one[3] using Lindlar catalyst.

***cis*-6-Hydroxy-3-hexen-1-yl *p*-toluenesulfonate** was prepared as described previously.[3] The crude material, shown below to contain *cis*-6-chloro-3-hexen-1-ol, was used directly in the Finkelstein reaction. Since the chlorohydrin is also converted into the desired iodohydrin, careful purification at this stage was unnecessary.

***cis*-6-Iodo-3-hexen-1-ol.**—The tosylate displacement was carried out as described in Part I,[3] except that 100% excess of sodium iodide was used, and the reaction mixture was allowed to reflux for 48 hours. Under these conditions the iodohydrin, b.p. 96–100° (1.3 mm.), $n^{25.5}D$ 1.5512–1.5532 (*cf.* ref. 3; b.p. 89–95° (1 mm.), $n^{25}D$ 1.5354) was obtained in 98–116% "apparent yield."

In one experiment in which the reaction was carried out at room temperature overnight, repeated fractionation gave the iodohydrin in only 53% yield. Accompanying this was a low-boiling component (b.p. 61–63° (0.7 mm.), $n^{25}D$ 1.4738–1.4772; 63 g. from 493 g. of hydroxy tosylate) which contained chlorine and was identified as *cis*-6-chloro-3-hexen-1-ol on the basis of spectral evidence (showing typical hydroxylic absorption in the 2.9 μ region and olefinic stretching at 5.99 μ), hydrogenation and elementary analysis. A redistilled analytical sample had b.p. 63° (0.5 mm.), $n^{26}D$ 1.4742.

Anal. Calcd. for $C_6H_{11}OCl$: C, 53.54; H, 8.23. Found: C, 53.56; H, 8.46.

Hydrogenation of this chlorohydrin in ethyl acetate over platinum catalyst in the presence of a trace of acid was very slow, and was accompanied by transesterification. The product was identified as *n*-6-chlorohexyl acetate, b.p. 88–90° (3.4 mm.), $n^{23}D$ 1.4388 (lit.[12] b.p. 113–116° (17 mm.), $n^{20}D$ 1.4416).

2,3,6,7-Tetrahydroöxepine.—The cyclization of the above iodohydrin was carried out essentially as described earlier.[3] One of the high-boiling by-products, designated as "fraction B" in Part I, was probably the *cis*-6-chloro-3-hexen-1-ol described above. This product was not observed when pure iodohydrin was used.

The nuclear magnetic resonance spectrum of this olefin, run on the neat liquid at 40 mc., gave the following results (with reference to benzene = 0); triplet at +43 c.p.s., weight 2, assigned to olefinic hydrogens at C_4 and C_5, split by adjacent methylenes; triplet at +123 c.p.s., weight 4, assigned to C_2 and C_7-methylene hydrogens, split by adjacent methylenes; complex multiplet at +169 c.p.s., weight 4, assigned to C_3- and C_6-methylene hydrogens.

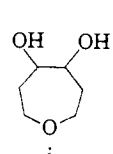
Elimination of Acetic Acid from 4-Acetoxy-2,3,4,5,6,7-hexahydroöxepine.—A sample of the saturated acetate, prepared as described by Olsen and Bredoch,[4] was treated with *p*-toluenesulfonic acid to give the reported olefin. The infrared spectrum of the product was very similar to that of 2,3,6,7-tetrahydroöxepine, with a few additional peaks. Vapor-phase chromatography at 109°, using helium gas and silicone oil as absorbent, resolved this mixture into two clearly defined peaks, one (about 70%) corresponding to the 2,3,6,7-tetrahydro compound and the other (about 30%) attributable to the 2,3,4,7-tetrahydro isomer. Boric acid dehydration of the corresponding alcohol gave a somewhat better yield of olefin mixture with a similar isomer distribution.

***trans*-4,5-Dibromo-2,3,4,5,6,7-hexahydroöxepine.**—A solution of 2,3,6,7-tetrahydroöxepine (5.0 g., 0.051 mole) in 10 ml. of carbon tetrachloride was cooled to 0° and stirred while a solution of 8.15 g. (0.051 mole) of bromine in 10 ml. of carbon tetrachloride was added dropwise. Removal of the solvent under reduced pressure gave 13.05 g. of an oil, which was treated with Norite in 30 ml. of pentane. The solution was filtered and stored overnight at −78°, when crystallization which began at 0° was complete. The mother liquor was removed by means of a fine pipet, and the crystals were washed twice with cold pentane. The last traces of solvent were finally removed under reduced pressure to give the crystalline dibromide (12.2 g., 93%), m.p. 29°. An analytical sample crystallized from pentane at −25° as clusters of prisms, m.p. 29°.

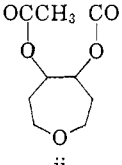
Anal. Calcd. for $C_6H_{10}OBr_2$: C, 27.96; H, 3.91; Br, 62.00. Found: C, 28.09; H, 3.98; Br, 61.72.

4-N,N-Dimethylamino-2,3,4,7-tetrahydroöxepine.—A solution of 26.6 g. (0.103 mole) of the above dibromide in 100 ml. of dry benzene was introduced into a thick-walled Pyrex tube which was then cooled in a Dry Ice-bath. A cold solution of 41 ml. (0.618 mole) of dimethylamine in 50 ml. of dry benzene was added, and the tube was flushed out with nitrogen and carefully sealed. After warming up to room temperature, the sealed tube was heated in an oil-bath at 95–100° for 6 hours, when crystals of dimethylamine hydrobromide were observed to separate. The tube was cooled and cautiously opened. The reaction mixture was extracted with 10% hydrochloric acid, and the acid extract was washed with ether and made strongly alkaline with 20%

(9) Before the *trans*-diacetate was prepared and pyrolyzed, osmium tetroxide oxidation of I was used to convert I into the *cis*-glycol i, from which the *cis*-diacetate ii was prepared. Since pyrolysis of ii should also proceed through intermediate XII, this more expensive route was not pursued further.



i



ii

(9a) A much more direct synthesis of VII has been accomplished recently by Schweizer and Parham, THIS JOURNAL, **82**, 4085 (1960). The properties of VII, as obtained in the present work, are in excellent agreement with those described by the Minnesota group. We are most grateful to Professor Parham for making his results available to us before publication.

(10) E. R. H. Jones, T. Y. Shen and M. C. Whiting, *J. Chem. Soc.*, 230 (1950).

(11) R. A. Raphael and C. M. Roxburgh, *ibid.*, 3875 (1952).

(12) G. M. Bennett and A. N. Masses, *ibid.*, 1697 (1931).

aqueous potassium hydroxide. The basic solution was extracted with ether, and the ethereal layer was washed with a little water, dried over sodium sulfate, and evaporated. Distillation of the residue gave the unsaturated, tertiary amine (8.52 g., 59%), b.p. 42–43° (1.4 mm.), $n^{25.5}D$ 1.4754–1.4756; infrared maxima at 3.44, 3.56, 3.63, 6.04, 6.85, 7.21, 7.87, 8.49, 8.85, 9.63, 11.26, 12.24 μ.

Anal. Calcd. for C_8H_5ON: C, 68.05; H, 10.72; N, 9.91. Found: C, 68.11; H, 10.70; N, 9.79.

A solution of 100 mg. of this amine was treated with 5 ml. of a saturated solution of picric acid in absolute ethanol. After several hours at room temperature, a crop of 160 mg. of yellow needles of the corresponding picrate, m.p. 138–140°, had formed. An analytical sample, m.p. 136–138°, was obtained by recrystallization from 95% ethanol.

Anal. Calcd. for $C_{14}H_{18}O_8N_4$: C, 45.41; H, 4.90; N, 15.14. Found: C, 45.02; H, 5.06; N, 15.24.

4-N,N-Dimethylamino-2,3,4,7-tetrahydroöxepine N-Oxide.—A solution of 8.52 g. (0.06 mole) of amine in 20 ml. of methanol was cooled to −10° and stirred while 20.5 g. (0.18 mole) of 30–35% hydrogen peroxide solution was added over a 20-minute period. After standing overnight, the reaction mixture was cooled to 0° and a methanolic suspension of 100 mg. of platinum was added. The vigorous decomposition of the excess hydrogen peroxide was complete in two hours, as indicated by lead sulfide test paper. The platinum was removed by filtration and the solvent removed at 40° under reduced pressure to give the desired N-oxide (11.0 g.) as a colorless sirup, which was used directly for the subsequent pyrolysis reaction.

A 100-mg. sample of this N-oxide gave 170 mg. of picrate, m.p. 159–162°, from ethanol solution. Recrystallization from ethanol gave an analytical sample as light yellow needles, m.p. 164–166°.

Anal. Calcd. for $C_{14}H_{18}O_9N_4$: C, 43.53; H, 4.69; N, 14.51. Found: C, 43.94; H, 4.80; N, 14.61.

2,3-Dihydroöxepine.—A 17.6-g. portion of crude N-oxide was heated in a flask packed with glass wool and connected to a receiver cooled in an acetone–Dry Ice-bath. The pressure was reduced to *ca.* 5 mm., and decomposition occurred over a 1.5-hour period while the bath temperature was raised from 80 to 110°. The distillate was allowed to warm to room temperature and was then acidified with dilute hydrochloric acid. The lower layer was carefully removed by means of a fine pipet, and the upper layer (6.4 g.) was dried over anhydrous sodium sulfate. This crude product was distilled in the presence of a small amount of hydroquinone to give 2,3-dihydroöxepine (5.42 g., 55% based on *amine* used), b.p. 119–122°, $n^{25.5}D$ 1.4956–1.4960. Redrying and redistillation over sodium gave an analytical sample, b.p. 118–120°, $n^{25.5}D$ 1.4949–1.4950; infrared maxima (neat): 3.37(m), 3.42(m), 3.46(m), 3.55(w), 6.05(s), 6.17(vs), 6.80(m), 6.98(m), 7.10(w), 7.30(vw), 7.44(w), 7.69(vs), 8.10(m), 8.30(m), 8.91(vs), 9.40(vw), 9.64(vw), 10.18(w), 10.87(s), 11.20(m), 11.30(m), 12.9(m), 13.9(vs)μ; ultraviolet spectrum: $\lambda_{max}^{isooctane}$ 260 mμ, log ϵ 3.95.

The nuclear magnetic resonance spectrum showed the peaks: +18 c.p.s., a doublet assigned to the unique C_7-hydrogen split by the single proton on C_6; +42 c.p.s., a complex group assigned to protons at C_4, C_5 and C_6; +70 c.p.s., weak band, unassigned; +98 c.p.s., a triplet assigned to methylene hydrogens at C_2 split by C_3-methylene; +149 c.p.s., complex multiplet assigned to methylene hydrogens on C_3. These assignments are in accord with those found for 2,3,6,7-tetrahydroöxepine, as discussed above.

Gas chromatography of this material on a dinonyl phthalate column at 117° using helium as carrier gas resulted in a single peak.

Anal. Calcd. for C_6H_8O: C, 74.95; H, 8.38. Found: 74.62; H, 8.38.

Acid Hydrolysis of 2,3-Dihydroöxepine.—A mixture of 200 mg. of 2,3-dihydroöxepine and 10 ml. of 2% aqueous hydrochloric acid was allowed to stand at room temperature for 30 minutes, with occasional shaking. The mixture was diluted to 50 ml. and extracted with ether and methylene chloride. After washing and drying the organic extract in the usual way, it was evaporated at 40° under reduced pressure to give 35 mg. of an oily residue showing new infrared absorption bands at 5.80, 5.92 and 6.08 μ. The ultraviolet spectrum showed no maximum in the 224–300 mμ region, but rising end absorption. Treatment with 2,4-dinitrophenylhydrazine gave a dark red precipitate, m.p. 150–160°, after a few minutes. This product was not investigated further because of the small amount available.

8,8,9,9-Tetracyano-2-oxa-bicyclo[3,2,2]non-6-ene.—To a solution of 260 mg. of tetracyanoethylene in 10 ml. of dry benzene was added 170 mg. of 2,3-dihydroöxepine. The mixture was kept under nitrogen. A transient dark brown color appeared, after which the adduct (297 mg., 75%) separated as fine prisms, m.p. 208–210° (sublimation). This product was recrystallized from 95% ethanol and from methylene chloride–methanol to give an analytical sample, m.p. 208–209° (subl.).

Anal. Calcd. for $C_{12}H_8ON_4$: C, 64.28; H, 3.60; N, 25.00. Found: C, 64.14; H, 3.74; N, 25.03.

***cis*-2,3,4,5,6,7-Hexahydroöxepine-4,5-diol.**—To a solution of osmium tetroxide (8.0 g., 31.5 mmoles) in dry dioxane (90 ml.) was added 2,3,6,7-tetrahydroöxepine (3.43 g., 35 mmoles) in dioxane (10 ml.). The mixture rapidly became dark and a black precipitate was formed. The mixture was allowed to stand at room temperature in the dark for 5 days, and it was then saturated with hydrogen sulfide during 2 hours and filtered. The filtrate was clarified by the addition of a suspension of Celite in dioxane followed by centrifugation. It was then evaporated to give a sirup of the crude diol (3.13 g., 75% based on OsO_4). The infrared spectrum of this material indicated the presence of impurities absorbing in the carbonyl region (5.77 μ).

The material could be sublimed at 60° (0.05 mm.) onto a cold finger cooled with Dry Ice, as a partially crystalline mass, m.p. 42–45°.

Anal. Calcd. for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.45; H, 9.13.

***cis*-4,5-Diacetoxy-2,3,4,5,6,7-hexahydroöxepine.**—The crude diol (3.44 g.) obtained from an osmium tetroxide hydroxylation was added to a mixture of pyridine (25 ml.) and acetic anhydride (26.5 g.) and allowed to stand at room temperature for 5 days. The mixture was then dissolved in ether (250 ml.), washed successively with water, 10% aqueous sulfuric acid, 10% sodium bicarbonate solution, and water, and dried over anhydrous magnesium sulfate.

The ethereal solution was evaporated and the residue distilled to give the diacetate (2.68 g., 48% based on diol) b.p. 80–83° (0.2 mm.), $n^{25.5}D$ 1.4535.

Anal. Calcd. for $C_{10}H_{16}O_5$: C, 55.54; H, 7.44. Found: C, 55.90; H, 7.41.

The yield of diacetate obtained by the action of iodine and silver acetate on tetrahydroöxepine in wet glacial acetic acid[13] was only 16%.

4,5-Epoxy-2,3,4,5,6,7-hexahydroöxepine.—To 5 g. of 2,3,6,7-tetrahydroöxepine in 20 ml. of chloroform was added *ca.* 1.5 equivalents of perbenzoic acid in 300 ml. of chloroform. The mixture was allowed to stand at room temperature for 40 hours. After washing the solution with 10% sodium bicarbonate and drying, the chloroform was distilled off and the residue was distilled at reduced pressure. The desired epoxide (3.2 g.) was redistilled to give an analytical sample, b.p. 77.5–78° (30 mm.), $n^{25.5}D$ 1.4600.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.13; H, 8.83. Found: C, 63.35; H, 8.69.

***trans*-4,5-Diacetoxy-2,3,4,5,6,7-hexahydroöxepine.**—The above epoxide (3.0 g.) was dissolved in a mixture of 12.5 ml. of acetic anhydride and 2.5 ml. of glacial acetic acid. After the addition of 150 mg. of *p*-toluenesulfonic acid, the mixture was refluxed for one hour. After standing overnight, the resultant solution was poured onto chipped ice and allowed to stand for one hour. Extraction and isolation in the usual way gave 3.50 g. of colorless product, b.p. 87–91° (0.35 mm.). Redistillation gave an analytical sample, b.p. 91–91.5° (0.40 mm.), $n^{26}D$ 1.4521.

Anal. Calcd. for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.82; H, 7.48.

Pyrolysis of *trans*-4,5-Diacetoxy-2,3,4,5,6,7-hexahydroöxepine.—A mixture of 3.2 g. of diacetate and 2 ml. of glacial acetic acid was dropped at a rate of 1 drop per minute through a vertical tube, packed with carborundum chips and held at 525°, in a slow stream of nitrogen. The products

(13) R. B. Woodward and F. V. Brutcher, Jr., THIS JOURNAL, **80**, 209 (1958); K. B. Wiberg and K. A. Saegebarth, *ibid.*, **79**, 6256 (1957).

were collected in a receiver cooled to −78°. When the pyrolysis was complete, the tube was flushed with an additional 2 ml. of acetic acid. The trapped products were diluted with ether and worked up in the usual way to give 1.7 g. of neutral pyrolysate. Upon distillation at atmospheric pressure, 0.2 g. of a colorless liquid boiling between 100 and 130° was collected. Continued distillation at reduced pressure gave only unchanged starting material. The low-boiling product had an infrared spectrum very similar to that of 2,3-dihydroöxepine, and showed λ_{max}^{EtOH} 260 mμ, $\epsilon \cong 6500$. This product readily yielded an adduct, m.p. 204–206°, with tetracyanoethylene. A mixture melting point with the authentic adduct derived from 2,3-dihydrooxepine (m.p. 206–209°) gave no depression (204–208°), and infrared spectra of the two samples were superimposable.

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[CONTRIBUTION NO. 2492 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

The Peroxidation of Bicyclo[2.2.1]heptadiene

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RECEIVED NOVEMBER 21, 1959

The peroxidation of bicyclo[2.2.1]heptadiene has been found to give a mixture of 3-*exo*-hydroxy-5-*exo*-tricyclo[2.2.1.$0^{2,6}$]-heptyl formate, 3-*exo*-hydroxy-5-*endo*-tricyclo[2.2.1.$0^{2,6}$]heptyl formate, tricyclo[2.2.1.$0^{2,6}$]heptanone and 3-hydroxy-3-tricyclo[2.2.1.$0^{2,6}$]heptyl formate. A procedure for the preparation of tricyclo[2.2.1.$0^{2,6}$]heptanone from the corresponding alcohol is described.

In connection with other investigations which we are pursuing related to the chemistry of bicyclic systems, it became necessary to prepare a substantial quantity of *exo*-3-hydroxy-*exo*-5-hydroxytricyclo[2.2.1,$0^{2,6}$]heptane[3] (I). This compound was first reported to have been isolated in low yield by Roberts and his co-workers[5] from the solvolysis of 2,3-*trans*-dichlorobicyclo[2.2.1]-5-heptene.

Alder[6] has subsequently reported the preparation of the corresponding diacetate from the reaction of bicyclo[2.2.1]heptadiene (II) with lead tetraacetate and obtained what presumably is I (*vide infra*) on saponification. Although the yields for these reactions were high, the necessity of working with large quantities of lead tetraacetate presents a distinct disadvantage.

More recently, Wilder[7] has claimed that compound I could be obtained in small amounts from the oxidation of II with performic acid followed by saponification of the resulting formate ester. Due to the availability of these starting materials, we chose to investigate this reaction further in an attempt to develop a practical and convenient synthesis of I.

Reactions which involve the addition of various substances to II have been the subject of numerous papers in recent years.[8] The products which arise can be accounted for on the basis of: (a) simple 1,2-addition, (b) addition followed by skeletal rearrangement and (c) addition followed by homoallylic rearrangement.[9] In the bromination of II, products are formed which can be attributed mechanistically to all three of these reaction paths.

Oxidation of II with performic acid at 40–50° with ethyl acetate as a solvent gave a complex mixture of products from which we were able to isolate 3-*exo*-hydroxy-5-*exo*-tricyclo-[2.2.1.$0^{2,6}$]heptyl formate (III), 3-*exo*-hydroxy-5-*endo*-tricyclo[2.2.1.-$0^{2,6}$]heptyl formate (IV), tricyclo[2.2.1.$0^{2,6}$]heptanone (3-keto-nortricyclene) (V) and 3-hydroxy-3-tricyclo[2.2.1.$0^{2,6}$]heptyl formate (VI). The formation of 3-keto-nortricyclene as one of the reaction products is of special interest since it represents a new mode of reaction for II; *i.e.*, one in which a 1,3-hydride shift has occurred after homoallylic rearrangement has taken place. The reaction and a mechanistic rationalization of the products is depicted in formula Fig. 1.

The major portion of the reaction products consisted of the hydroxy-formate fraction (III and IV) which was isolated in a total yield of 40%. The ratio of the low boiling to the high boiling isomer was estimated by vapor phase chromatography (v.p.c.) analysis to be about 5:1, a figure which varied slightly with experimental conditions. Due to the similarity of the boiling points of the two isomers, separation by distillation was impractical and purification was deferred until a crystalline mixture of diols was obtained.

Saponification of the hydroxy-formate mixture with aqueous potassium hydroxide gave a mixture of the two diols in 86% yield. Careful fractional crystallization from acetonitrile yielded two pure diols, m.p. 157.5–158.8° (A) and m.p. 167.8–168.6° (B). Diol A was obtained in much greater quantity than B and therefore must be related to the low boiling hydroxy formate. That the two diols in question were geometrically isomeric nortricyclene diols was supported by elemental analysis and the infrared spectrum which showed characteristic absorption peaks at 3490 (hydroxyl group) and 812 cm.$^{-1}$ (nortricyclene ring system) in carbon tetrachloride. The absence of any unsaturated diols was indicated by a negative reaction of the diols with bromine and by the absence of any olefinic absorption in the infrared region of the spectrum. It

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(3) The system of nomenclature suggested by Cristol and LaLonde (ref. 4) for the naming of nortricyclene derivatives will be used in this paper.

(4) S. J. Cristol and R. T. LaLonde, THIS JOURNAL, **80**, 4355 (1958).

(5) J. D. Roberts, F. O. Johnson and R. A. Carboni, *ibid.*, **76**, 5692 (1954).

(6) K. Alder, F. H. Flock and H. Wirtz, *Ber.*, **91**, 609 (1958).

(7) G. T. Youngblood, C. D. Trivette and P. Wilder, *J. Org. Chem.*, **23**, 684 (1958).

(8) Reference 6 contains a list of the pertinent papers on the chemistry of bicyclo[2.2.1]heptadiene.

(9) S. Winstein and M. Shatavsky, *Chemistry & Industry*, 56 (1956).