TABLE II

HOMOCOMPETITIVE RATE DATA

Paracyclophanes	Weight in mg.				Solvent	T, °C.	Time, hr.	k_b/k_a[a]	$\delta(k_b/k_a)$[b]
	A_0[a]	A[a]	B_0[a]	B[a]					
[6.6] and [4.4]	800	392	1320	408	CS_2	25	1.5	1.6	±0.37
[4.4] and [3.4]	161	136	216	69	CS_2	25	1.0	7.0	± .76
[3.4] and [2.2]	242	194	198	111	$C_2H_2Cl_4$	−20	0.5	2.6	± .39
[4.4] and [2.2]	1003	1000	823	212	$C_2H_2Cl_4$	−20	0.5	100	....

[a] Defined in equation 1. [b] Defined in equation 5.

the procedure employed was identical to that employed with the [3.4]- and [2.2]-cycles. The [4.4]-cycle was recovered almost quantitatively. An assumed 5% error in isolation of hydrocarbon and 5% in analysis requires $\delta(k_b/k_a)$ to be larger than k_b/k_a. Therefore this experiment serves only for qualitative purposes.

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Seven-membered Heterocyclic Systems. I. The Synthesis of 2,3,6,7-Tetrahydroöxepine

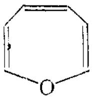
BY JERROLD MEINWALD AND HITOSI NOZAKI[1]

RECEIVED JANUARY 22, 1958

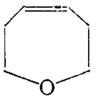
A seven-step synthesis of 2,3,6,7-tetrahydroöxepine (III) starting from 3-butyn-1-ol (IV) is described. The cyclization of *cis*-6-iodo-3-hexen-1-ol (X), brought about by the use of silver oxide in ether, gives III in *ca.* 25% yield, accompanied by some elimination product, *cis*-3,5-hexadien-1-ol (XI). Attempts to prepare oxepine itself by more direct routes are described briefly.

Introduction.—Interest in the chemistry of seven-membered ring compounds has grown apace in recent times. The principal recent advances have been confined largely to the field of carbocyclic compounds related to tropolones or azulenes. The simple heterocyclic compounds, such as oxepine (I), would also be of considerable theoretical interest, however, since they bear the same electronic relationship to cycloöctatetraene as furan and pyrrole do to benzene. This comparison is especially intriguing, since models reveal that the seven-membered heterocycles, in contrast to cycloöctatetraene, can attain planarity with a relatively small amount of steric strain.

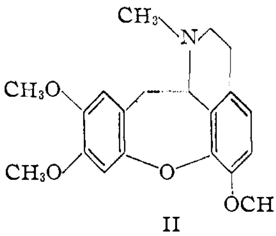
Several groups of workers are actively pursuing the chemistry of the benzo-derivatives of seven-membered heterocycles.[2] This work has been motivated in part by the discovery that the alkaloid cularine (II) has a dibenzdihydroöxepine skeleton.[3] In spite of this activity, the synthesis of oxepine, or of the other parent systems (with nitrogen or sulfur as the heteroatom) has yet to be achieved. It is the purpose of this paper to describe the synthesis of a promising intermediate, 2,3,6,7-tetrahydroöxepine (III), as well as to outline several attempts to prepare oxepine itself *via* more direct routes.[3a]



I

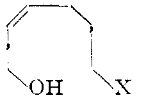


III

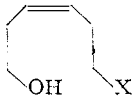


II

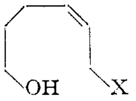
Synthesis of 2,3,6,7-Tetrahydroöxepine (III).—The successful synthesis of III was carried out in a series of seven steps starting from commercially available 3-butyn-1-ol. The over-all scheme is summarized in Chart I. The general idea for this reaction sequence stemmed from the hope that an intramolecular nucleophilic substitution could be encouraged to lead to a seven-membered ring by the inclusion of a *cis*-double bond in a suitable 1,6-disubstituted hexane derivative. This idea led to the consideration of three potential types of intermediate, shown as A, B and C. Of these possibilities, B seemed preferable to the others since in it neither the –OH nor the –X group is allylic. It was therefore decided to utilize a compound of type B as the immediate precursor of the seven-membered heterocyclic system.



A



B



C

3-Butyn-1-ol (IV) was converted into its tetrahydropyranyl ether V and alkylated to give VI, using ethylene oxide and lithium amide in liquid ammonia, as previously described.[4] Partial catalytic

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[1] On leave from the Department of Industrial Chemistry, Kyôto University, Kyôto, Japan.

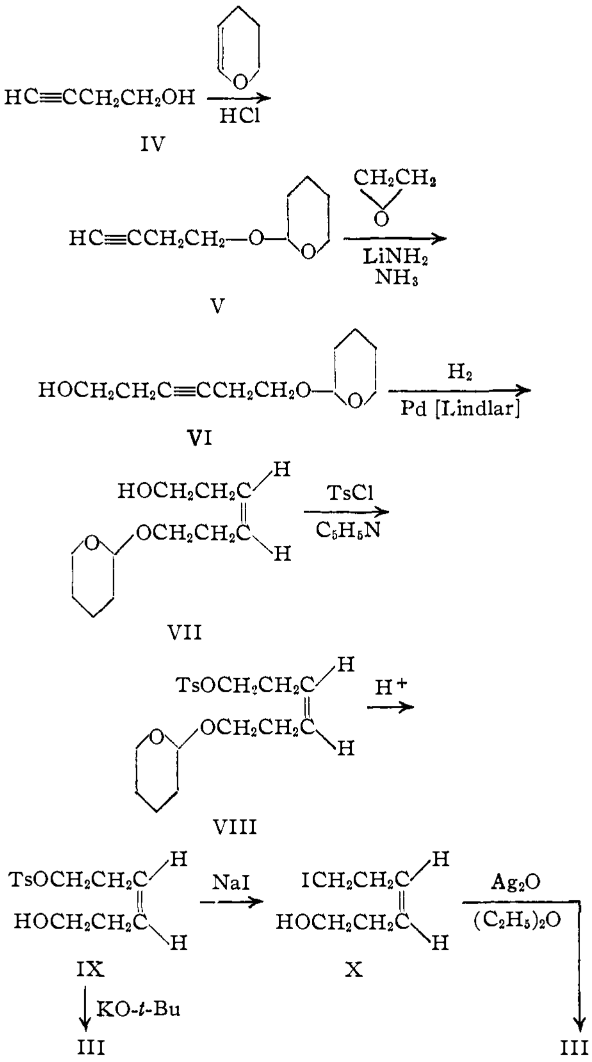
[2] See, for example, J. T. Braunholtz and F. G. Mann, *J. Chem. Soc.*, 4174 (1957); J. D. Louden and L. A. Summers, *ibid.*, 3809 (1957); K. Dimroth and H. Freyschlag, *Chem. Ber.*, **90**, 1628 (1957).

[3] R. H. F. Manske, THIS JOURNAL, **72**, 55 (1950).

[3a] NOTE ADDED IN PROOF.—Since the submission of this manuscript, some valuable, unpublished work of H. J. Dauben, Jr., and S. B. Maerov in the field of seven-membered heterocyclic compounds has come to our attention (S. B. Maerov, Doctoral Thesis, University of Washington, 1954). These authors have prepared a tetrahydroöxepine (or mixture of isomeric tetrahydroöxepines) by the acid-catalyzed dehydration of oxepin-4-ol. However, neither the homogeneity of this product nor the double bond position(s) appear to have been established.

[4] R. A. Raphael and C. M. Roxburgh, *J. Chem. Soc.*, 3875 (1952).

CHART I



hydrogenation of VI gave the desired *cis*-olefin VII in quantitative yield; VII was characterized by analysis, infrared spectrum and hydrolysis as well as conversion to the known bisphenylurethan of *cis*-3-hexen-1,6-diol.

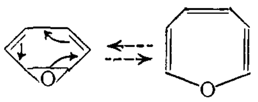
To continue the route to III, *cis*-6-(2-tetrahydropyranyloxy)-3-hexen-1-ol (VII) was converted into its toluenesulfonate ester VIII in 80% yield. Removal of the tetrahydropyranyl group gave the half-tosylate IX, which upon treatment with potassium *t*-butoxide in diethylene glycol diethyl ether could be converted into a product, b.p. 118–120°, whose infrared spectrum and lack of ultraviolet absorption were compatible with structure III. Because of experimental difficulties in obtaining this product in pure form by this technique, it was decided to introduce a better leaving group in B and the half-tosylate IX was therefore converted into the corresponding iodohydrin X, by treatment with sodium iodide in acetone. Slow addition of an ethereal solution of X to a refluxing suspension of silver oxide in ether resulted in a quantitative elimination of the elements of hydriodic acid, isolated as silver iodide. After careful working up of the organic product, 2,3,6,7-tetrahydroöxepine (III), b.p. 118–119°, could be isolated in about 25% yield. The redistilled product showed the same infrared spectrum as the material of similar boiling point obtained directly from the half-tosylate IX. This product gave a single peak upon vapor-phase chromatography, and took up one mole of hydrogen over Adams catalyst.

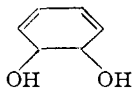
A large amount of high-boiling material was formed along with III in the silver oxide reaction. From this mixture, one by-product has been tentatively identified as *cis*-3,5-hexadien-1-ol (XI) on the basis of elementary analysis and spectral data. It showed ultraviolet absorption (λ_{max} 226 mμ, ϵ 30,900) in accord with this structure, and took up two moles of hydrogen over Adams catalyst to give *n*-hexyl alcohol, identified as its phenylcarbamate. The formation of *cis*-3,5-hexadien-1-ol (XI) along with III is not surprising, since it is to be anticipated that the desired displacement reaction might well be accompanied by a competitive elimination[5] leading, in this case, to a conjugated diene.

The problem of introducing further unsaturation into III is in some ways analogous to the problem of preparing cycloheptatriene from cycloheptene, whose classical solution by Willstätter is well known.[6] We hope to report the results of attempts to prepare oxepine from its symmetrical tetrahydro derivative in a future publication.

Appendix.—Before the above work was carried out, a number of other possible routes to oxepine were explored without success. It is hoped that the following outline may help in avoiding duplication of effort on the part of other investigators.

The direct approaches to oxepine were based on the feeling that if the epoxy diene XII could be prepared, it should be thermally convertible into oxepine, of which it is a "valence tautomer."[7]


XII I



XIII

Although XII is an epoxide of benzene and an isomer of phenol, it is not unreasonable to consider it capable of existence, particularly in view of the successful synthesis of the closely related compound XIII by Takei, *et al.*[8] The results of four attempts to prepare XII are presented below.

(1) Attempted Epoxidation and Dechlorination of α-Benzene Tetrachloride (XIV).—The sequence shown in equation 1 was abandoned when it was found that XIV was unattacked by either peracetic acid or perfluoroperacetic acid.

(2) Pyrolysis of 1,2-Epoxy-4,5-cyclohexanediol Diacetate (XVII).—Compound XVI was prepared in about 40% yield by treatment of 1,4-cyclohexa-

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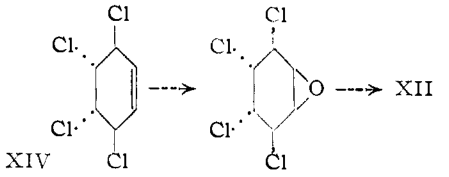
(5) It is also possible that the elimination and substitution products arise from a common intermediate; *cf.* S. Winstein, D. Darwish and N. J. Holness, THIS JOURNAL, **78**, 2915 (1956).

(6) R. Willstätter, *Ann.*, **317**, 223 (1901); E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, THIS JOURNAL, **61**, 1057 (1939).

(7) In the closely related case of cycloheptatriene ⇄ norcaradiene, present evidence shows that the seven-membered triene is the preferred form. See E. J. Corey, H. J. Burke and W. A. Remers, *ibid.*, **77**, 4941 (1955); *cf.* footnote 30 in the recent paper by R. B. Turner, W. R. Meador, W. von E. Doering, L. H. Knox, J. R. Mayer and D. W. Wiley, *ibid.*, **79**, 4127 (1957).

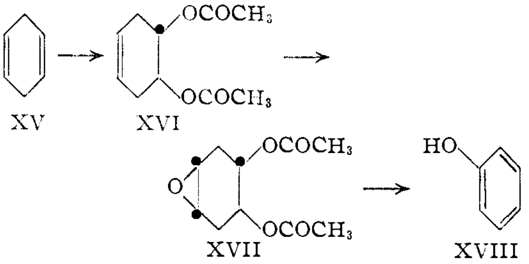
(8) M. Nakijama, I. Tomida, A. Hashizume and S. Takei, *Chem. Ber.*, **89**, 2224 (1956).

diene (XV) with peracetic acid followed by acetic anhydride. The corresponding epoxide XVII was obtained using perbenzoic acid in chloroform, in



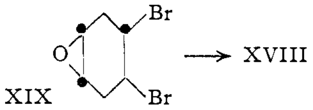
(1)

about 75% yield. Pyrolysis of XVII at 505° gave phenol XVIII, in about 30% yield, as the only characterizable product. This sequence is summarized in equation 2.



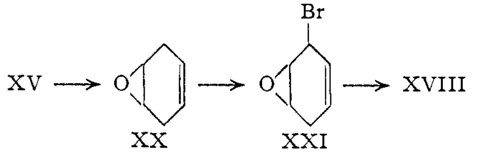
(2)

(3) **Dehydrobromination of 1,2-Epoxy-4,5-dibromocyclohexane (XIX).**—Compound XIX, prepared as described previously,[9] gave phenol as the only volatile product when treated with either hot γ-collidine or the sodium salt of ethylene glycol in excess ethylene glycol (see equation 3). It is interesting that in the latter case, *added phenol did not distil from the reaction mixture* under the reaction conditions. This seems to indicate that the desired epoxide was formed, but that it rearranged to phenol after leaving the basic medium.



(3)

(4) **Allylic Bromination and Dehydrobromination of 4,5-Epoxycyclohexene (XXI).**—Oxidation of 1,4-cyclohexadiene (XV) with monoperphthalic acid gave 4,5-epoxycyclohexene (XX) in 50% yield. Treatment of XX with N-bromosuccinimide gave a monobromo derivative (arbitrarily assigned structure XXI, although the allylic isomer is another possibility). This bromoepoxide gave only phenol on being treated with silver oxide in ether (equation 4).



(4)

Acknowledgment.—The authors wish to express their gratitude to the National Institutes of Health for the award of a research grant which has made this work possible.

Experimental

cis-**6-(2-Tetrahydropyranyloxy)-3-hexen-1-ol** (VII).—A mixture of 79.2 g. (0.4 mole) of 6-(2-tetrahydropiranyloxy)-3-hexyn-1-ol,[4] 1.5 g. of the Lindlar catalyst,[10] 0.5 ml. of quinoline and 300 ml. of ethyl acetate was shaken with hydrogen at room temperature. After about two hours shaking the calculated amount of hydrogen was absorbed and the reaction slowed down. The catalyst was removed by filtration and the filtrate concentrated and distilled under reduced pressure to give 79 g. (quantitative) of a colorless oil, b.p. 103–106° at 0.5 mm., $n^{24.0}\mathrm{D}$ 1.4750; infrared spectrum (NaCl plates): 2.95, 3.43, 3.50, 6.02, 6.80, 6.93, 7.21, 7.31, 7.39, 7.55, 7.93, 8.32, 8.46, 8.63, 8.79, 8.91, 9.32, 9.68, 10.10, 10.81, 11.03, 11.50 and 12.29 μ.

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.95; H, 10.18.

cis-**6-(2-Tetrahydropyranyloxy)-3-hexenyl** *p*-**Tosylate** (VIII).—A warm solution of 105 g. (0.55 mole) of *p*-tosyl chloride in 50.7 g. (0.638 mole) of pyridine was cooled rapidly in an ice-bath with stirring. When the temperature was below 10°, 100 g. (0.5 mole) of VII was added dropwise with continued stirring, keeping the reaction temperature at 10–15° for one hour.[11] The mixture was stirred at 20–25° for an additional 20 hours and treated with water and ether. The ethereal extract was washed with iced 10% sulfuric acid, water, saturated sodium bicarbonate solution and finally with water. After drying over calcium sulfate, the solvent was removed under reduced pressure. The residue weighed 142 g. (80%). A small sample was purified by chromatography on alumina and analyzed, $n^{26.7}\mathrm{D}$ 1.4799. The infrared spectra (NaCl plates) of the crude product and of the purified material were quite similar: 3.42, 3.52, 6.25, 6.95, 7.37, 7.57, 7.84, 7.95, 8.35, 8.42, 8.51, 8.60, 8.93, 9.11, 9.32, 9.71, 10.21–10.40, 11.05, 11.50, 12.29, 12.93, 14.15 and 14.57 μ.

Anal. Calcd. for $C_{18}H_{26}O_5S$: C, 60.99; H, 7.39. Found: C, 60.92; H, 7.74.

Attempted distillation caused serious decomposition; the crude product was used for the subsequent step without purification.

cis-**6-Hydroxy-3-hexen-1-yl** *p*-**Tosylate** (IX).—To a mixture of 142 g. of crude VIII, 500 ml. of methanol and 450 ml. of water, 44 ml. of concentrated sulfuric acid was added dropwise under stirring and with ice-bath cooling. The stirring was continued for 20 hours and then the mixture was neutralized with 85 g. of sodium carbonate, added in small portions. Enough water was then added to dissolve the solid, methanol was removed under reduced pressure and the residue extracted with methylene chloride. The extract was washed with saturated sodium bicarbonate solution, dried over anhydrous calcium sulfate and concentrated under reduced pressure. The residue formed a viscous oil which weighed 75 g. (55% based on VII). A small sample was purified by chromatography on alumina; the infrared spectrum remained the same as that of the crude material: 2.98, 3.42, 3.53, 6.24, 6.94, 7.39, 7.65, 7.75, 8.27, 8.42, 8.52, 8.98, 9.12, 9.65, 9.77, 10.40, 10.95, 12.27 and 12.96 μ. The analysis was unsatisfactory, since III was unstable toward heat.

cis-**6-Iodo-3-hexen-1-ol** (X).—A solution of 75.0 g. (0.278 mole) of III and 41.7 g. (0.278 mole) of sodium iodide in 310 ml. of dry acetone was stirred for 14 hours at room temperature and then refluxed for two hours. The solid was removed by filtration, the filtrate was concentrated under reduced pressure and the residue was treated with water and methylene chloride. The organic layer was washed with sodium thiosulfate solution and water, dried over calcium sulfate, concentrated, and distilled under reduced pressure. A pale orange oil distilled at 89–95° (1 mm.) and weighed 50 g. (80% based on IX or 44% based on VII), $n^{25.0}\mathrm{D}$ 1.5354; infrared spectrum (NaCl plates): 3.03, 3.35, 3.43, 3.50, 6.05, 7.05, 8.07, 8.57, 9.57, 10.93, 11.50 and 14.02–14.18 μ.

Anal. Calcd. for $C_6H_{11}IO$: C, 31.88; H, 4.90; I, 56.14. Found: C, 32.47; H, 5.03; I, 54.26.

2,3,6,7-Tetrahydroöxepine (V).—To a mixture of 92 g. (0.39 mole) of silver oxide[12] and 500 ml. of anhydrous ether, a solution of 43 g. (0.19 mole) of X in 350 ml. of anhydrous ether was added dropwise with rapid stirring. The addition required 8 hours and the mixture was refluxed for an additional 15 hours. The inorganic solids were removed by filtration and the filtrate was concentrated carefully. Upon distillation of the residue, a colorless, mobile liquid (7.2 g.) boiling at 118–120° was obtained. Another run

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(9) E. E. van Tamelen, THIS JOURNAL, **77**, 1704 (1955).

(10) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(11) *Cf.* G. Eglinton and M. C. Whiting, *J. Chem. Soc.*, 3650 (1950).

(12) D. Stein and H. Schinz, *Helv. Chim. Acta*, **34**, 1176 (1951).

was made, using 75 g. of 6-iodo-3-hexen-1-ol and 157.5 g. of silver oxide in 1350 ml. of anhydrous ether, in which 13.4 g. of a distillate, b.p. 118–120° was obtained.

Fractional distillation of the combined 118–120° product gave 13.3 g. (23%) of the tetrahydroöxepine, b.p. 118–119°, besides 2.8 g. of a fore-run which showed the same infrared spectrum as the main product. Gas chromatography of the former fraction gave a single peak, while that of the latter one gave two peaks, one of which was definitely ascribed to ether, the other to III, $n^{25.5}_{D}$ 1.4548; infrared spectrum (NaCl plates): 3.33, 3.44, 3.51, 3.64, 5.02(w), 5.31(w), 6.02, 6.83, 7.01, 7.19, 7.45, 7.65, 7.80, 8.04(w), 8.26, 8.86, 9.48, 9.67, 10.52, 11.50, 13.12 and 14.15 μ.

Anal. Calcd. for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.27; H, 10.54.

Bromine titration of the olefinic double bond[13] gave 93.6% absorption of the calculated amount, while quantitative hydrogenation in 95% ethanol in the presence of 10% palladium–charcoal gave 98.2% absorption of the calculated amount of hydrogen.

Hexamethylene oxide[14] was isolated from the hydrogenation mixture, $n^{24.0}_{D}$ 1.4361; infrared spectrum: 3.44, 3.51, 5.71, 6.78, 6.89, 7.20, 7.28, 7.35, 7.79, 7.88, 8.05, 8.45, 8.76, 9.01, 9.66, 9.81, 10.01, 10.22, 11.90, 12.10, 12.42, 13.20 and 13.58 μ.

Fractional distillation of the higher boiling by-products using a Podbielniak column gave the following three fractions: fraction A, b.p. 59–61° (4 mm.), weighed 1.3 g.; ultraviolet absorption: λ_{max} 226 mμ, ε 30,900; infrared spectrum: 2.99, 3.25, 3.34, 3.43, 3.50, 5.77, 6.00, 6.25, 6.95, 7.25, 7.91, 8.39, 9.21, 9.54, 9.77, 9.95, 10.36, 11.03, 11.41, 12.30 and 12.71 μ.

Anal. Calcd. for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.24; H, 10.15.

This fraction was identified as (possibly *cis*-) 3,5-hexadien-1-ol, since quantitative hydrogenation resulted in the uptake of 97.6% of two molar equivalents of hydrogen. Isolation of the hydrogenation product, followed by the treatment with phenyl isocyanate gave *n*-hexyl phenylcarbamate, m.p. 41–42° (lit.[15] 42°).

The next higher boiling fraction B came over at about 53–63° (0.4 mm.), weighing 5.7 g., $n^{25.0}_{D}$ 1.4747–1.4754; infrared spectrum: 2.99, 3.35, 3.43, 3.50, 5.76, 6.00, 6.90, 6.99, 7.09, 7.22, 7.70, 8.05, 8.45, 8.99, 9.50, 10.28, 11.50 and 13.52–14.23 μ. This spectrum was compared to that of *cis*-3-hexene-1,6-diol prepared by the method of Raphael and Roxburgh,[4] b.p. 107–112° (0.4 mm.), $n^{25.6}_{D}$ 1.4742; infrared spectrum: 3.03, 3.35, 3.44, 3.50, 6.04, 7.04, 7.12, 7.30, 8.48, 8.96, 9.54, 11.46 and 13.90–14.60 μ. Almost all of the main absorptions showed a good agreement, but treatment of the fraction B with phenyl isocyanate did not give the crystalline bisphenylurethan, m.p. 107–108°, which was obtained easily from authentic hexenediol.

The highest boiling fraction C came over at 120–130° (0.6 mm.), and appeared to be a mixture. It was not characterized.

An attempted cyclization of X with silver oxide in acetone did not give III, but a product which showed a strong carbonyl absorption at 5.83 μ, whose structure was not determined.

Treatment of IX with potassium *t*-butoxide in diethylene glycol–diethyl ether gave a small amount of III.

Attempted Epoxidation of α-Benzene Tetrachloride (XIV).[16]—Compound XIV was found to be recoverable unchanged from treatment with either peracetic acid or perfluoroperacetic acid. Although the desired epoxide has been described by Takei, *et al.*,[8] the yield using chromic acid oxidation of XIV was too low to allow it to be a useful synthetic intermediate.

***trans*-Cyclohexen-4,5-diol Diacetate (XVI).**—1,4-Cyclohexadiene[17] was treated with 40% peracetic acid in excess acetic acid in the usual way. The crude product was isolated and acetylated by treatment with excess acetic anhydride and pyridine on the steam-bath for one hour. A 38% yield of XVI, b.p. 76–79° (0.35 mm.), n^{25}_{D} 1.4587, was obtained.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.79; H, 7.14.

1,2-Epoxy-4,5-cyclohexane Diol Diacetate (XVII).—Compound XVI was epoxidized in the usual way with perbenzoic acid in chloroform. The desired epoxide, b.p. 115–122° (0.9 mm.), n^{25}_{D} 1.4619, was obtained in 74% yield. The structure of XVII was confirmed by acid hydrolysis and acetylation to give a product identical with authentic tetraacetate of 1,2,4,5-cyclohexanetetraol.[18]

Anal. Calcd. for $C_{10}H_{14}O_6$: C, 56.07; H, 6.59. Found: C, 56.19; H, 6.38.

Allylic Bromination of 4,5-Epoxycyclohexene.—Compound XX[19] was allowed to react with N-bromosuccinimide in carbon tetrachloride solution, with a trace of benzoyl peroxide as catalyst. The crude product, containing some succinimide, was purified by chromatography on Magnesol: Celite (1:1). The eluted product was distilled (b.p. 60–70° (bath) (0.9 mm.)) to give an analytical sample.

Anal. Calcd. for C_6H_7OBr: C, 41.17; H, 4.03; Br, 45.66. Found: C, 41.35; H, 4.21; Br, 45.54.

ITHACA, N. Y.

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(13) H. J. Lucas and D. Pressman, *Ind. Eng. Chem., Anal. Ed.*, **10**, 140 (1938).

(14) A. Müller and W. Vanc, *Ber.*, **77B**, 669 (1944).

(15) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 446.

(16) The authors are indebted to Dr. H. D. Orloff, Ethyl Corporation, for a generous supply of this material.

(17) J. P. Wibaut and F. A. Haak, *Rec. trav. chim.*, **67**, 85 (1948).

(18) G. E. McCasland and E. C. Horswill, THIS JOURNAL, **76**, 1658 (1954).

(19) M. Tiffeneau and B. Tchoubar, *Compt. rend.*, **212**, 581 (1941); *cf.* ref. 9.

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY]

4- and 5-Phenylazulenes

BY ERNST D. BERGMANN AND RAPHAEL IKAN

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5-Phenylazulene has been prepared from bicyclo[5.3.0]decan-5-one (VIII) by reaction with phenylmagnesium bromide, dehydration and dehydrogenation. It is different from a previously described phenylazulene for which thus, indirectly, the 6-position of the phenyl group has been confirmed. The known liquid 4-phenylazulene has also been synthesized by a new route, in which 4-phenylbicyclo[5.3.0]decan-6-one (XVII) is the key substance. Whilst 4-phenylazulene absorbs at the same wave length as azulene itself, a bathochromic shift is observed for the 5- and 6-isomers, which have practically identical absorption spectra. This statement refers to the longest wave length band in the spectrum.

In a recent communication,[1] a synthesis of 6-phenylazulene (I) has been described, and it has been reported that the introduction of the phenyl group at C_6 causes a bathochromic shift in the spectrum of azulene, whilst the theory[2] predicted a hypsochromic effect. It seemed not impossible that in the preparation of 6-phenylazulene a migra-

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(1) E. D. Bergmann and R. Ikan, THIS JOURNAL, **78**, 1482 (1956).

(2) B. Pullman, J. Berthier and J. Baudet, *J. chim. phys.*, **50**, 69 (1953); *J. Chem. Phys.*, **21**, 187 (1953).