be planar there is no way in which such close interaction can be relieved in the *cis* configuration. The *cis*-1,2-cyclobutanedicarboxylic acid on the other hand shows a much smaller K_1/K_2 ratio which is of the same order as that found in the cyclopentane analog. Simple geometrical considerations would suggest that if the cyclobutyl system were planar one would observe a K_1/K_2 ratio of the same order of magnitude as found in the cyclopropyl case.

Further studies of the conformational factors involved in the chemistry of cyclobutane systems and the general stereochemistry of the small ring systems are being undertaken.

Experimental

Vapor phase chromatographic analytical data were obtained with both a Beckman GC-2A gas chromatographic instrument using a 6-ft. column of May-Baker silicone oil on C-22 firebrick and with an F and M flame ionization gas chromatograph, Model 609 using a 6-ft. Carbowax packed column. All the starting diesters used in equilibrations runs were shown to contain less than 1% of the other isomer as a contaminant. All the ester mixtures obtained from equilibrations were completely resolved and analysis of standard reference mixtures showed that no significant correction factors were needed for the analytical procedure. Component peak areas were measured with an automatic disk integrator. A minimum of three equilibrations of each ester gave equilibrium compositions which varied by not more than 1%.

Cyclopentane-1,2-dicarboxylic Acid.—The *trans* isomer was prepared by the method of Fuson and Cole.[6] The *cis* isomer was prepared by converting the *trans* acid to the *cis* anhydride by prolonged reflux with acetyl chloride and hydrolysis of the anhydride with water. The *trans* acid had m.p. 160–161° (lit.[6a] m.p. 161°); the anhydride had m.p. 72–73° (lit.[6a] m.p. 74.5–75°); and the *cis* acid had m.p. 140–141° (lit.[6] m.p. 139°).

Cyclobutane-1,2-dicarboxylic Acids.—The *cis* acid was prepared by the method described by Buchman[6b] and afforded material m.p. 136–138° (lit.[6b] m.p. 139–140°). The *trans* acid was prepared by equilibration of the dimethyl ester of the *cis* acid followed by hydrolysis of the mixed esters with hydrochloric acid. The crude acid was recrystallized repeatedly to afford a 70% yield of *trans* acid, m.p. 129–130° (lit.[6b] m.p. 130–131°).

Cyclopropane-1,2-dicarboxylic Acids.—The *cis* and *trans* acids were prepared by the method described by McCoy.[7] The *trans* acid had m.p. 178° (lit.[7] m.p. 177–177.5°). The acid could be isolated in two crystalline modifications, prisms which change to needles at about 165° and the needle form, m.p. 178°. The *cis* acid had m.p. 140–142° (lit.[7] m.p. 139–142°).

Cyclohexane-1,2-dicarboxylic Acids.—The *cis* acid was prepared by hydrolysis of the anhydride[8] in water and had m.p. 192–193° (lit.[8] m.p. 192°). The *trans* acid was prepared by equilibration of the *cis* dimethyl ester followed by hydrolysis with hydrochloric acid. Repeated recrystallization of the acid mixture thus obtained afforded an 80% yield of pure *trans* diacid m.p. 223° (lit.[9] m.p. 221°).

Preparation of Methyl Esters.—The dimethyl esters were prepared from the pure diacids by reaction with diazomethane according to the following general procedure.

A solution of diazomethane in ether was prepared from N-nitrosomethylurea[10] and added to a slurry of the dicarboxylic acid in ether. When no further consumption of diazomethane was apparent the solution was evaporated and the residual diester was distilled. All the diesters thus prepared were found to be free of contaminating materials by v.p.c. analysis.

Equilibration of Dimethyl Esters.—The equilibrations of the pure isomeric diesters were conducted according to the following general procedure.

About 0.01 mole of pure ester was added to a freshly prepared solution of about 0.08 g.-atom of sodium metal dissolved in 100 ml. of anhydrous methanol. The solution was refluxed for a period of 2 to 14 hr. (Runs of various times were made in each case to assure attainment of equilibrium.) All cases studied had reached essential equilibrium in 2 hr. though a 4-hr. reflux period was needed for the cyclopropyl system. The cooled equilibration solution was poured into 1 l. of ice–water containing 10 ml. of concentrated hydrochloric acid. The ester was isolated by ether extraction and simple transfer distillation of the ether extract to separate the solvent from the ester and the ester from traces of high-boiling colored substances. A wide boiling cut was taken in each case to assure that no fractionation of esters had taken place. The yield of recovered equilibrated ester averaged 90% or more after such transfer distillation indicating little loss of material through condensation or hydrolysis reactions in the course of equilibration. V.p.c. analysis of both the crude equilibration product and the distilled ester mixture gave identical results. The equilibration compositions are indicated in Table I.

(6) (a) R. C. Fuson and W. Cole, *J. Am. Chem. Soc.*, **60**, 1237 (1938); (b) E. R. Buchman, A. O. Reims, T. Skei, and M. Schlatter, *ibid.*, **64**, 2696 (1942).

(7) L. McCoy, *ibid.*, **80**, 6568 (1958).

(8) C. C. Price and M. Schwarcz, *ibid.*, **62**, 2733 (1940).

(9) W. Huchel and E. Goth, *Ber.*, **58**, 449 (1925).

(10) W. E. Beckman and W. S. Struve, "Organic Syntheses," Coll. Vol. I, John Wiley and Son, Inc., New York, N. Y., 1942, p. 50.

The Free-Radical Chemistry of Cyclic Ethers. V. β-Hydrogen Atom Abstraction from Epoxides and a Thioepoxide

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Further studies in the *t*-butyl peroxide-induced free-radical reactions of epoxides have shown that, in the absence of olefin, abstraction of a hydrogen atom beta to the oxygen atom occurs in addition to the previously reported abstraction of a hydrogen atom alpha to the oxygen atom. The intermediate formed from this β-hydrogen atom abstraction rearranges by the opening of the epoxide ring to form an unsaturated alkoxy radical. Various chain termination steps, which can lead to the observed products, are outlined. The same reaction with propylene sulfide resulted in the formation of products similar to those observed for propylene oxide.

Previously it was reported that in the free-radical chemistry of cyclic ethers, the chain transfer atom is the hydrogen atom alpha to the oxygen atom.[2] The epoxy radicals formed from this α-abstraction were found to rearrange to α-keto radicals which yielded ketonic products. The abstraction and rearrangement steps, as suggested for propylene oxide, are shown (p. 3438, col. 1).

The first objective of the present work was to ascertain whether a free radical would abstract a hydrogen atom beta to the oxygen atom (allylic to the epoxide ring) and to determine the products formed from such

(1) Abstracted from the Ph.D. thesis (1963) of E. C. S., M. W. Kellogg Co., Jersey City, N. J.

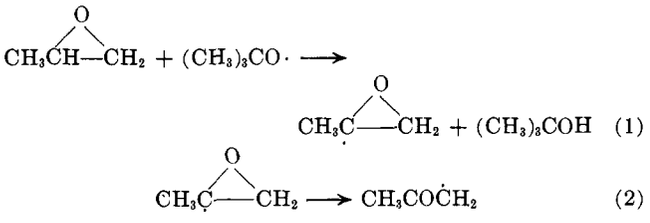
(2) T. J. Wallace and R. J. Gritter, *Tetrahedron*, **19**, 657 (1963).

TABLE I

REACTION CONDITIONS USED AND PRODUCTS IDENTIFIED FROM THE FREE-RADICAL REACTIONS

Reactants (mole)	*t*-Butyl peroxide, mole	Temp., time, °C. (hr.)	Product (% yield[a])	Origin of product
Cyclohexene oxide (0.005)	0.0005	150 (3)	Cyclohexanone (32)	α-Hydrogen abstraction
			2-Cyclohexenone (9.0)	β-Hydrogen abstraction
			2-Cyclohexenol (7.0)	β-Hydrogen abstraction
1,2-Butylene oxide (0.10)	0.05	150 (2)	2-Butanone (0.12)	α-Hydrogen abstraction
			Crotonaldehyde (0.18)	β-Hydrogen abstraction
			Crotyl alcohol (0.14)	β-Hydrogen abstraction
Propylene oxide (1.0)	0.01	150 (2)	Allyl alcohol (2.0)	β-Hydrogen abstraction
Propylene sulfide (0.50)	0.10	150 (2)	Thioacetone (0.15)	α-Hydrogen abstraction
			Allyl mercaptan (0.30)	β-Hydrogen abstraction
			Allyl disulfide (0.84)	β-Hydrogen abstraction

[a] Based on the amount of peroxide.



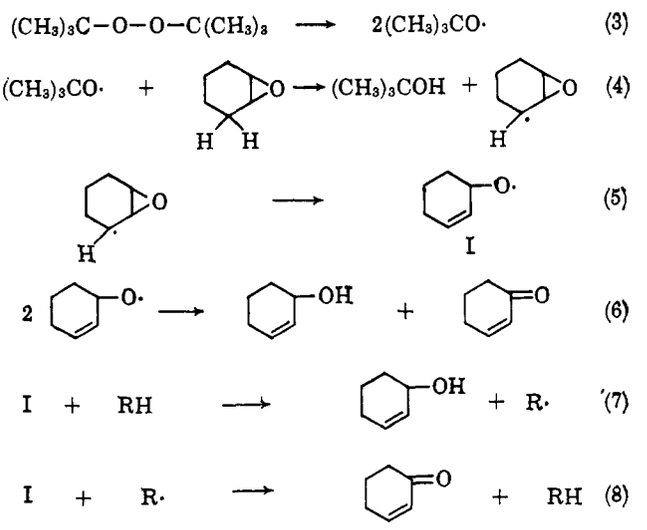
an abstraction. Also, since it is known that sulfur-containing radicals have different stability characteristics from those of their oxygen-containing analogs,[3] the second objective of this work was to determine whether a thiirane would undergo the same abstraction reactions as the oxiranes and whether similar products would be formed.

Results

The *t*-butyl peroxide-initiated free-radical reaction of cyclohexene oxide has resulted in the formation of cyclohexanone, 2-cyclohexenone, and 2-cyclohexenol. The cyclohexanone undoubtedly arises by a mechanism similar to that previously advanced, while the initial step in the formation of the unsaturated products is considered to be the β-abstraction of a hydrogen atom. Other representative epoxides that gave products arising from this β-abstraction and rearrangement were 1,2-butylene oxide, which afforded crotonaldehyde and crotyl alcohol, and propylene oxide, which afforded allyl alcohol. No attempt was made to identify acrolein in the latter reaction. In a comparable, way, propylene sulfide gave thioacetone from α-abstraction and allyl mercaptan and allyl disulfide from β-abstraction. The results of representative reactions are summarized in Table I. Functional group identification was made by infrared analysis and the product identities were established by gas chromatography.

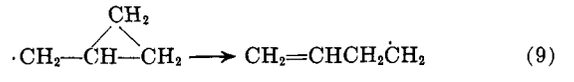
Discussion

It has been substantiated that in the free-radical reactions of epoxides, one of the chain transfer atoms is the hydrogen atom alpha to the oxygen atom.[2,4] In the present work, the intermediate epoxy radical formed from cyclohexene oxide was found to form the expected product, cyclohexanone. The novel formation of 2-cyclohexenone and 2-cyclohexenol is postulated to occur by the following reaction sequence.



The abstraction of a hydrogen atom beta to the oxygen atom, as indicted in step 4, is readily explicable if the epoxide ring is considered to act as a pseudoolefin. Thus, this position of abstraction can be considered an allylic position. Farmer and Moore[5] have reported that *t*-butoxy radicals attack alkenes at the allylic position and Walling[3] has reviewed in detail the susceptibility of the allylic position to radical attack. It must be pointed out, however, that the activation of the α-position due to the epoxide ring is less than that given by the unsaturation. Thus, it would appear that the α-position of an olefin is more susceptable to radical attack than the corresponding position in an epoxide.

The novel decyclization of the α-epoxy radical, as shown in step 5, has hitherto not been reported, although similar type rearrangements are found in the chemistry of the cyclopropylmethyl radical.[6,7] The decyclization step, first discovered by Roberts and Mazur,[6] is shown.



Since the unsaturated products are formed in small

(3) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

(4) C. Walling and P. S. Fredricks, *J. Am. Chem. Soc.*, **84**, 3326 (1962).

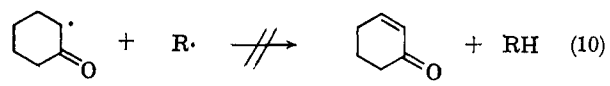
(5) E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, 131 (1951).

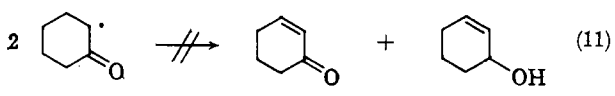
(6) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

(7) D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *ibid.*, **82**, 2368 (1960).

but approximately equal quantities, the disproportionation of the unsaturated alkoxy radical is thought to be the main reaction path of this intermediate radical. Thus, a chain reaction step which favors formation of the unsaturated alcohol, as shown in step 7, cannot occur to any great extent. This can be attributed to the inactivity of the beta C–H bond. It also is felt that more data must be obtained before a strict correlation can be made for the reactivity of the alpha and beta C–H bonds in epoxides in this type of radical reaction.

The proposed mechanism, β-abstraction followed by electron isomerization with opening of the epoxide ring, was substantiated by the following experiments. First, it was shown that 2-cyclohexenone was not formed from an intermediate α-keto radical, as indicated by reactions 10 and 11. This was done by generating the α-keto





radical from the reaction of cyclohexanone and *t*-butoxy radicals[8] and showing that unsaturated products were not produced. Secondly, the conversion of cyclohexene oxide to the said products was shown to be peroxide induced, since heat alone (150°) did not decompose the epoxide.

The products obtained from the free-radical reactions of propylene sulfide showed that the same hydrogen atoms were abstracted and the same rearrangements were observed as in the reaction of propylene oxide. Chain termination steps are similar to those indicated previously, except for step 12, which leads to the di-

$$2CH_2{=}CHCH_2S\cdot \longrightarrow CH_2{=}CHCH_2S{-}SCH_2CH{=}CH_2 \quad (12)$$

sulfide. The disulfide is thought to form because the thiyl radical is quite stable compared to an alkoxy radical and the disulfide is a more stable product than the corresponding peroxide.[3]

Although the same free-radical chain sequence has been suggested for propylene sulfide as for propylene oxide, the over-all reactions are quite different. In the reaction of propylene oxide, a large quantity of the epoxide is recovered and only a small amount of residue remains. In contrast, very little propylene sulfide is recovered and a large amount of black residue is obtained. Propylene sulfide apparently undergoes extensive decomposition, which was not investigated further.

Experimental

Reagents.—*t*-Butyl peroxide (b.p. 45° at 68 mm., $n^{20}D$ 1.3892), cyclohexene, cyclohexanone, crotonaldehyde, acetone, allyl bromide, and allyl chloride were distilled through a 14-in. or an 18-in. silvered column equipped with a tantalum wire spiral. Propylene oxide (Matheson Coleman and Bell, b.p. 34°, $n^{20}D$ 1.3662) and 1,2-butylene oxide (Dow Chemical Co., b.p. 60.5°, $n^{20}D$ 1.3831) were purified by distillation through an 80-plate concentric tube Podbielniak column (Model 2208).

Preparation of Cyclohexene Oxide.—2-Bromocyclohexanol was prepared by the reaction of cyclohexene and N-bromosuccinimide according to the method of Guss and Rosenthal.[9] The unpurified bromohydrin ($n^{20}D$ 1.5162, lit.[9] $n^{20}D$ 1.5180) was treated with aqueous sodium hydroxide[9] and the cyclohexene oxide was purified by distillation through a 6-in. silvered column equipped with a tantalum wire spiral (b.p. 132°, $n^{20}D$ 1.4522; lit.[9] b.p. 129–130°, $n^{20}D$ 1.4528).

Preparation of Propylene Sulfide.—Propylene sulfide was prepared from a sulfuric acid solution of propylene oxide and thiourea, as described by Bordwell and Andersen.[10] On completion of the reaction, a sodium sulfate solution was added. Separation and distillation of the resulting oil yielded pure propylene sulfide (b.p. 76°, $n^{15}D$ 1.4780; lit.[10] b.p. 72–75°, lit.[11] $n^{15}D$ 1.4780).

Infrared analyses and gas chromatography showed that the epoxides and thioepoxide were free from all impurities. The free radical reactions reported subsequently are representative of the many reactions carried out. Yields were based on the initial amount of peroxide and were measured by gas chromatography from among the following columns: column A, 10-ft. 1,3-butanediol phthalate; column B, 10-ft. di-*n*-decyl phthalate; column C, 10-ft. Carbowax 3%, 400 m.; column D, 10-ft. Ucon, polar; and column E, 10-ft. silicone. The gas chromatographic unit, Aerograph Master A-100, Wilkens Instrument and Research Inc., was equipped with a Speedomax graphic recorder, Model S, Leeds and Northrup Co. The recorder was equipped with a disk integragor, Model K3-1, Disc Instrument Co.

Free-Radical Reaction of Cyclohexene Oxide.—Cyclohexene oxide (0.005 mole, 0.490 g.) and 0.0005 mole of *t*-butyl peroxide (0.073 g.) were heated in a deaerated glass bomb at 150° for 3 hr. Product identifications were as follows: cyclohexanone (32%; column A, 130°, 5 lb., 13.2 min.; column B, 167°, 8 lb. 19.2 min.); 2-cyclohexenone (9.0%; column A, 130°, 5 lb., 26.3 min.; column B, 167° 8 lb., 26.3 min.); and 2-cyclohexenol (7.0%; column A, 130°, 5 lb., 1.5 min.; column B, 167°, 8 lb., 4.3 min.).

Preparation of 2-Cyclohexenone.—2-Bromocyclohexanone was prepared by the reaction of cyclohexanone, bromine, chloroform, water, and calcium carbonate according to the procedure of Braude and Evans.[12] The bromo ketone was found to be very unstable and had to be dehydrohalogenated immediately. The dehydrohalogenation was effected with 2-collidine,[12] the 2-cyclohexenone being purified by distillation (b.p. 46° at 5 mm., $n^{22}D$ 1.4860; lit.[12] b.p. 61–62° at 10 mm., $n^{22}D$ 1.4897). It formed a 2,4-dinitrophenylhydrazone, m.p. 171–171.5°, lit.[12] m.p. 168°.

Preparation of 2-Cyclohexenol.—3-Bromocyclohexene was prepared by the reaction of cyclohexene and N-bromosuccinimide in carbon tetrachloride according to the method of Buckles, Johnson, and Probst.[13] The purified 3-bromocyclohexene (0.10 mole, 16.10 g.) was hydrolyzed to the alcohol by heating at 60° for 5 hr. with 10 moles of distilled water. 2-Cyclohexenol (2.15 g., 21%) was purified by distillation through a 6-in. tantalum wire spiral column, b.p. 70° at 10 mm., and formed a phenylurethane, m.p. 106–106.5°, lit.[14] m.p. 107°, and a 2-naphthylurethane, m.p. 157–157.5°, lit.[14] m.p. 156°.

Heating of Cyclohexene Oxide.—Cyclohexene oxide (0.10 mole, 9.81 g.) was heated as described previously for 4 hr. at 150°. The infrared spectrum and the gas chromatogram of the heated cyclohexene oxide compared exactly with those of the unheated oxide.

Free-Radical Reaction of 1,2-Butylene Oxide.—1,2-Butylene oxide (0.10 mole, 7.21 g.) and 0.05 mole of *t*-butyl peroxide (7.30 g.) were heated in a deaerated glass-lined stainless steel bomb at 150° for 2 hr. The low-boiling material was removed by distillation and a Kuger–Rohr tube distillation of the remaining material (oven temp., 100°, 70 mm.) yielded 0.75 g. of product-containing material. Product identifications were as follows: 2-butanone (0.12%; column B, 90°, 10 lb., 8.4 min.); crotonaldehyde (0.18%; column B, 90°, 10 lb., 16 min.); and crotyl alcohol (0.14%; column B, 90°, 10 lb., 22 min., and column C, 89°, 10 lb., 8 min.).

Preparation of Crotyl Alcohol.—Crotonaldehyde was reduced by sodium borohydride according to the method of Chaikin and

(8) M. S. Kharasch, J. Kuderna, and W. Nudenberg, *J. Org. Chem.*, **18**, 1225 (1953).

(9) C. O. Guss and R. Rosenthal, *J. Am. Chem. Soc.*, **77**, 2549 (1955).

(10) F. G. Bordwell and H. M. Andersen, *ibid.*, **75**, 4959 (1953).

(11) C. J. Culvenor, W. Davies, and K. H. Pausacker, *J. Chem. Soc.*, 1050 (1946).

(12) E. A. Braude and E. A. Evans, *ibid.*, 607 (1954).

(13) R. E. Buckles, R. C. Johnson, and W. J. Probst, *J. Org. Chem.*, **22**, 55 (1957).

(14) J. Heilbron and H. Bunbury, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953.

Brown[15] to yield crotyl alcohol, which was isolated by distillation (b.p. 118–119°, $n^{20}D$ 1.4263; lit.[15] b.p. 118°, $n^{20}D$ 1.4249). It formed a 3,5-dinitrobenzoate, m.p. 69.7–70°, lit.[14] m.p. 70°.

Free-Radical Reaction of Propylene Oxide.—One mole of propylene oxide (58.08 g.) and 0.01 mole of *t*-butyl peroxide (1.46 g.) were heated for 2 hr. as mentioned before. The unchanged propylene oxide was removed and allyl alcohol was identified in the remaining material by gas chromatography (2.0%; column A, 100°, 10 lb., 7.2 min.; and column C, 92°, 5 lb., 7.1 min.).

Free-Radical Reaction of Propylene Sulfide.—Propylene sulfide (0.50 mole, 37 g.) and 0.10 mole of *t*-butyl peroxide (14.6 g.) reacted for 2 hr. in a glass bomb as described previously. The black reaction mixture was distilled to remove the low-boiling material. Vacuum distillation (30–40° at 0.15 mm.) yielded 1.7 g. of higher boiling material and a large polymeric residue (approximately 20 g.). Product identifications were made as follows: thioacetone (0.15%; column D, 158°, 10 lb., 12 min.; and column E, 150°, 10 lb., 14.7 min.); allyl mercaptan (0.3%; column C, 87°, 8 lb., 6.5 min.; and column D, 74°, 6 lb., 3.3 min.); and allyl disulfide (0.84%; column D, 115°, 10 lb., 11.6 min.; and column E, 107°, 5 lb., 7 min.).

Preparation of Thioacetone.—Thioacetone was prepared by treating a solution of acetone and hydrochloric acid with hydrogen sulfide according to the method of Fromm and Baumann.[16] A yellow oil was obtained from steam distillation of the reaction mixture from which thioacetone trimer was obtained by distillation (b.p. 120–125 at 11 mm.; lit.[16] b.p. 130° at 13 mm.).

Preparation of Allyl Mercaptan.—Allyl mercaptan was prepared from an aqueous solution of allyl bromide and thiourea according to the method of Backer and Kramer.[17] It was purified by distillation (b.p. 66–68°, lit.[17] b.p. 67–69°).

Preparation of Allyl Disulfide.—Allyl chloride and sodium thiosulfate were caused to react to form the Bunte salt as repored by Westlake and Dougherty.[18] The Bunte salt was decomposed with hydrogen peroxide as described by Twiss.[19] Allyl disulfide was purified by distillation (b.p. 58–60° at 3.5 mm. lit.[20] b.p. 58–59° at 5 mm.).

Acknowledgment.—The authors wish to thank the National Institutes of Health, Public Health Service (CY-3691), and the Quartermaster Corps, U. S. Army (DA19-129-QM-1708), for their support of this work.

(15) S. W. Chaikin and W. G. Brown, *J. Am. Chem. Soc.*, **71**, 122 (1949).

(16) E. Fromm and E. Baumann, *Ber.*, **22**, 1035 (1889).

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(18) H. E. Westlake, Jr., and G. Dougherty, *J. Am. Chem. Soc.*, **63**, 658 (1941).

(19) D. F. Twiss, *J. Chem. Soc.*, **105**, 36 (1914).

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The Syntheses of Tricyclic Systems with Nitrogen at a Bridgehead[1]

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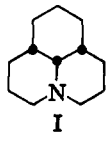
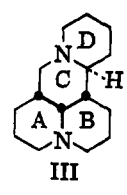
A facile synthesis of the all-*cis* isomer of hexahydrojulolidine is presented as well as its application to the preparation of other similar ring systems.

We have investigated the preparation of the all *cis* isomer of hexahydrojulolidine (I) as a model for the A, B, and C rings in the development of syntheses for matrine (II)[3] and matridine (III).[4]



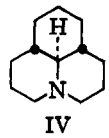
I

II

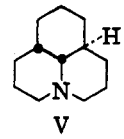


III

The three possible stereoisomers of hexahydrojulolidine, I, IV, and V, have been synthesized and characterized by Bohlmann[5] on the basis of their relative



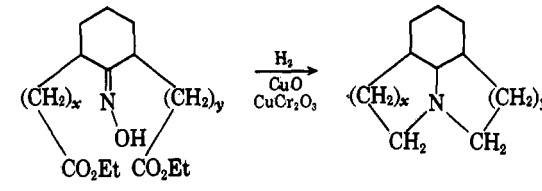
IV



V

rates of dehydrogenation as catalyzed by mercuric acetate, their very characteristic infrared spectral differences, and their behavior during chromatography.

We chose the work of Leonard and Middleton[6] as a pattern for the syntheses of these substances. Their approach involved the reductive cyclization of oximino diesters, as shown.



VI

Bohlmann demonstrated that in the case where $x = y = 2$ (hexahydrojulolidine) Leonard had incorrectly assigned the stereochemistry of his product as V and in fact the material prepared *via* this procedure was IV. Although this stereochemical consequence would appear to negate the application of Leonard's method of the synthesis of I, we felt that appropriate modification of the reduction conditions would allow formation of the all-*cis* product. An additional modification would be necessary for this approach to be applicable to a synthesis of matrine, II; namely, the reduction should not proceed *via* amide intermediates, as is probably the case in the reductive cyclization of oximino esters, for then the survival of the ring D lactam of matrine during reduction would be problematical.

Both of these requirements, milder reducing conditions and reduction intermediates not involving amides,

(1) First presented at the 138th National Meeting of the American Chemical Society, New York, N. Y., September, 1960. We wish to acknowledge the support of this research by the National Institutes of Health through Research Grant RG-7902.

(2) This work is taken in part from the Ph.D. dissertations of J. U. P. and K. P. S.

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