fluxing benzene, with sampling at 16, 24, and 40 hr. The spectra of the reaction mixture showed carbonyl, λ_{max} 5.87 μ, which was about one-half as intense as that for A and remained unchanged from 16 to 40 hr. The isocyanate content was high (λ_{max} 4.44 μ) being only about half consumed at 16 hr. At 24 and 40 hr., this had decreased slightly, and simultaneously a shoulder appeared at 5.65 μ, which could have been due to traces (possibly 5–10%) of the cyclic trimethylene allophanate. On evaporation, a pungent (isocyanate) pale yellow oil, 1.653 g., was obtained, which did not crystallize: $\lambda_{max}^{CHCl_3}$ (infrared) 2.93, (3.06), 3.42, 4.42, (5.65), 5.85, 6.58, 6.75, 7.85 to 8.25, 8.75 and 9.6 μ. The figures in parentheses could belong to the allophanate (X), whereas all the others are found in the bisurethan (IX) but also possible in X.

Authentic Trimethylene Bisethylurethan.—The procedure for IVa was repeated using, however, 3.7 g. of trimethylene diamine with 5.5 g. of ethyl chloroformate. The crude (oil) product obtained on evaporation of the filtrate slowly crystallized. It was distilled, b.p. 136° (0.1 mm.), affording 4.5 g. (80%) of a soft crystalline solid: m.p. 39–42° (lit.[3] m.p. 42°); b.p. 210° (30 mm.); $\lambda_{max}^{CHCl_3}$ (infrared) 2.94, 3.42, 5.87, 6.60, 8.05–8.25, 8.75, and 9.6 μ.

Conversion of a 1,2-Glycol Monocarbamate into Two Isomeric 1-Piperidinecarboxylates

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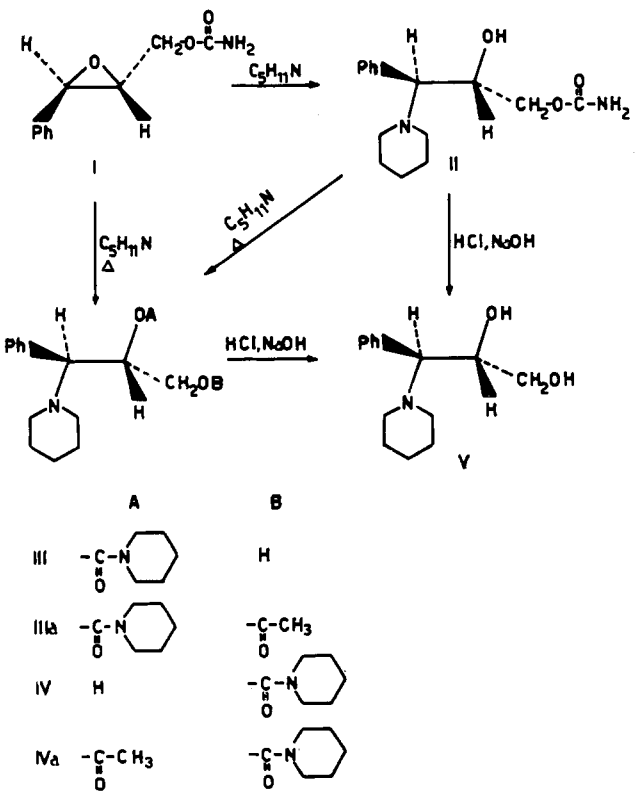
Interaction between piperidine and 2-hydroxy-3-phenyl-3-piperidinopropyl carbamate results in the formation of the two structurally isomeric 1-piperidinecarboxylates of 3-phenyl-3-piperidino-1,2-propanediol. Both isomers react with $SOCl_2$ to give the same 1-chloro-3-phenyl-3-piperidino-2-propyl 1-piperidinecarboxylate. The structures of these compounds were proved by unequivocal synthetic routes.

An investigation still underway in our laboratories dealt with the synthesis of several 3-amino-2-hydroxy-3-phenylpropyl carbamates, which were obtained by the action of primary and secondary amines on *trans*-2,3-epoxy-3-phenylpropyl carbamate (I, Chart I).

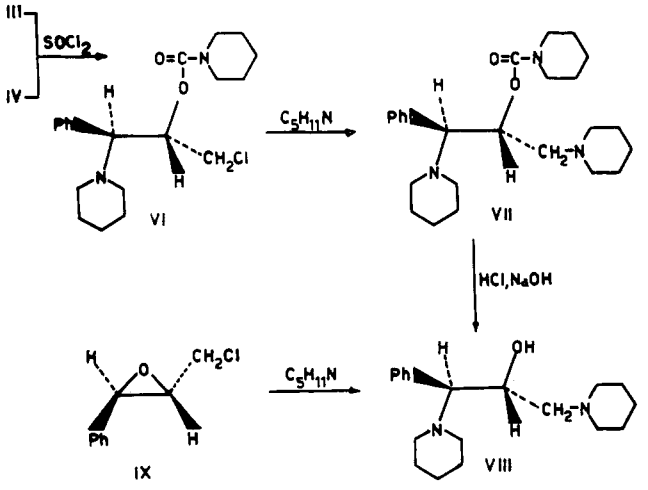
CHART I



Interaction between I and piperidine at room temperature gave the expected *erythro*-2-hydroxy-3-phenyl-3-piperidinopropyl carbamate[1] (II), no other reaction occurring than the opening of the epoxide ring. However, when the reaction was carried out at higher temperature no II could be detected in the reaction mixture, the isomeric *erythro*-1-piperidinecarboxylates III and IV being the only reaction products. These were formed also from II and piperidine at reflux temperature. Compounds III and IV had different melting points and infrared spectra, and were transformed by acetic anhydride into the acetates IIIa and IVa.

Structural Investigation.—Hydrolysis of II, III, and IV yielded the known *erythro*-3-phenyl-3-piperidino-1,2-propanediol[2] (V), m.p. 93–95°, thus indicating III and IV to differ only with respect to the position of the esterifying group. Furthermore, both III and IV gave upon treatment with $SOCl_2$ the same chlorinated derivative, *erythro*-1-chloro-3-phenyl-3-piperidino-2-propyl 1-piperidinecarboxylate (VI), whose structure was proved as shown in Chart II. Reaction of VI with piper-

CHART II



(1) *trans* epoxides are known to react with amines with inversion of configuration at the point of attack to yield the *erythro* isomers [*cf.* R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959)]. We have therefore assigned the products of ring opening of I (which, being derived from *trans*-cinnamyl alcohol, is a *trans* epoxide) and their derivatives the *erythro* configuration.

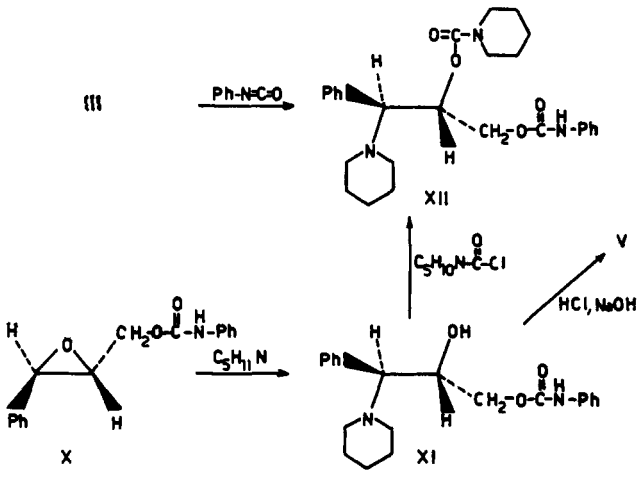
(2) K. C. Tsou and N. H. Cromwell, *J. Org. Chem.*, **15**, 1293 (1950). Another 3-phenyl-3-piperidino-1,2-propanediol, m.p. 126°, described in the literature [*cf.* K. Bodendorf and B. Binder, *Arch. Pharm.*, **287**, 453 (1954)], is probably the *threo* isomer. Investigation is under way to clarify this point.

idine resulted in the formation of VII, which was hydrolyzed to the corresponding alcohol VIII, also prepared by an independent synthesis from the known 1-chloro-2,3-epoxy-3-phenylpropane[3] (IX) and piperidine.

Structurally isomeric β-hydroxyethyl carbamates have been shown[4] to react with $SOCl_2$ to give, through a common intermediate, the same chloro carbamate with the chlorine attached to the primary carbon atom. Our results appear to corroborate these findings, and to extend their validity to isomeric 1,2-glycol N,N-disubstituted monocarbamates.

The structure of III was proved by the sequence of Chart III.

CHART III

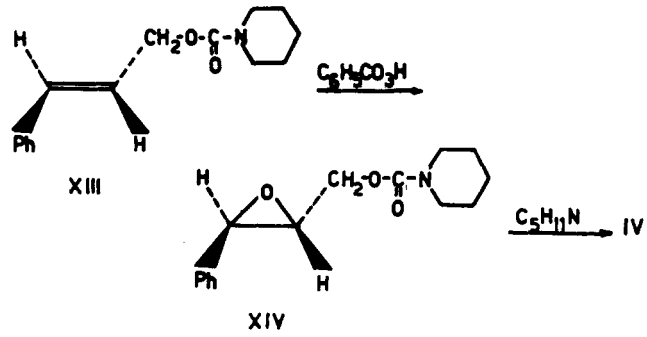


trans-2,3-Epoxy-3-phenylpropyl carbanilate[5] (X) reacted with piperidine to give XI, whose structure was confirmed through hydrolysis to V. Condensation of XI with 1-piperidinecarbonyl chloride gave the 1-piperidinecarboxylate XII, which was identical with the compound obtained from the reaction of III with phenyl isocyanate.

The rule[6] which assigns the secondary carbamate structure to the higher melting member of an isomeric pair of 3-substituted 1,2-propanediol monocarbamates appears therefore to be followed also in the case of 3-substituted 1,2-propanediol 1-piperidinecarboxylates.

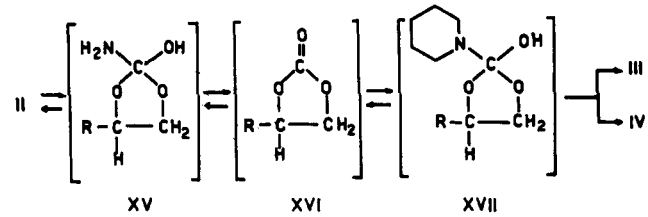
The structure of IV was proved through the following sequence. Condensation of the sodium derivative of cinnamyl alcohol with 1-piperidinecarbonyl chloride gave the ester XIII, which, on treatment with peroxybenzoic acid, produced the epoxide XIV. This was treated with piperidine to yield a compound which was identical with IV (see col. 2, top).

The formation of II as the only product of the reaction between 2,3-epoxy-3-phenylpropyl carbamate (I) and piperidine under mild conditions, and the reaction of II with piperidine to yield the same couple of isomers originating from I and piperidine under more severe conditions, clearly indicates the reaction to proceed *via* formation of II from I, and subsequent interaction



between II and piperidine to yield III and IV. That III does not arise by isomerization of initially formed IV was shown by the fact that IV was recovered unchanged after a 5-hr. reflux in piperidine.[7]

The cyclic carbonate of 3-phenyl-3-piperidino-1,3-propanediol (XVI) appears as the most likely key intermediate in the path leading from II to III and IV. The full sequence could involve XV (cyclic tautomer of II), XVI, and XVII. 1,2-Glycol monocarbamates are in-



deed known to yield the respective cyclic carbonates under various experimental conditions.[6a] The cyclic carbonates are known, on the other hand, to react with ammonia or amines to yield carbamates.[8]

The compound XVI is probably very unstable, since several attempts at preparing it by ester interchange between V and diethyl carbonate (*cf.* ref. 6a) gave negative results. All attempts at cyclizing II to the same dioxolone, even under the influence of acid and basic catalysts, also failed. The particular structure of XVI can account for its instability. Esters bearing an amino group in the β-position are known to hydrolyze very rapidly through intramolecular facilitation.[9]

Pharmacological data for some of the compounds described herein will be reported elsewhere.

Experimental[10]

***trans*-2,3-Epoxy-3-phenylpropyl Carbamate (I).**—A cold solution of 11 g. (0.062 mole) of *trans*-cinnamyl carbamate[11] in 200 ml. of chloroform was treated with 9.3 g. (0.067 mole) of peroxy-

(3) J. P. Fourneau and S. Chantalou, *Bull. soc. chim. France*, **12**, 845 (1945).

(4) J. R. Clark and M. Pugliese, *J. Org. Chem.*, **24**, 1088 (1959).

(5) M. Darmon and P. Weill, *Bull. soc. chim. France*, **8**, 405 (1941).

(6) (a) M. M. Baizer, J. R. Clark, and J. Swidinsky, *J. Org. Chem.*, **22**, 1596 (1957); (b) J. Swidinsky, J. Kervenski, and B. B. Brown, *J. Pharm. Sci.*, **52**, 955 (1963).

(7) Conversely, III under the same conditions was isomerized to IV to the extent of *ca.* 13%. This is in agreement with the findings of Baizer, Clark, and Swidinsky (ref. 6a) and of O. Schmid and D. Voak [*Monatsh. Chem.*, **94**, 339 (1963)] on the more facile isomerization of a secondary to primary carbamate than *vice versa*.

(8) (a) H. Najer, P. Chabrier, and R. Giudicelli, *Compt. rend.*, **238**, 690 (1954); (b) *Bull. soc. chim. France*, 1142 (1954).

(9) (a) W. Davis and W. C. J. Ross, *J. Chem. Soc.*, 3056 (1950); 2706 (1951); (b) G. Berti, G. Moretti, and D. Segnini, *Farmaco* (Pavia), *Ed. sci.*, **15**, 414 (1960); (c) J. A. Zaslowsky and E. Fisher, *J. Phys. Chem.*, **67**, 959 (1963).

(10) Melting points (Kofler apparatus) are uncorrected. Infrared spectra were recorded on a Perkin-Elmer "Infracord" Model 137 spectrophotometer. Microanalyses were carried out by Alfred Bernhardt Microanalytical Laboratory, Mülheim, Germany. Identity of compounds was verified by mixture melting point and comparison of infrared spectra.

(11) This was prepared in 40% yield from *trans*-cinnamyl alcohol and urea, m.p. 122–124° [lit. m.p. 120–121°; *cf.* J. R. Boissier, *Compt. rend. soc. biol.*, **155**, 27 (1961)]. *Anal.* Calcd. for $C_{10}H_{11}NO_2$: N, 7.91. Found: N, 7.80.

benzoic acid in 150 ml. of chloroform. After 24 hr. at room temperature, the solution was washed with 10% sodium carbonate and water, dried (magnesium sulfate), and evaporated to yield 11 g. (92%) of crude I, m.p. 83–85°. Recrystallization from benzene gave the analytical sample, m.p. 90–92°.

Anal. Calcd. for $C_{10}H_{11}NO_3$: C, 62.16; H, 5.74; N, 7.25. Found: C, 62.31; H, 5.84; N, 7.32.

***erythro*-2-Hydroxy-3-phenyl-3-piperidinopropyl Carbamate (II).**—A solution of 2 g. (0.01 mole) of I in 4.25 g. (0.05 mole) of piperidine was allowed to stand at room temperature for 3 days. Elimination of excess piperidine *in vacuo* followed by crystallization of the oily residue from aqueous ethanol gave 2.15 g. (75%) of II, m.p. 153–154° (after recrystallization from ethanol).

Anal. Calcd. for $C_{15}H_{22}N_2O_3$: C, 64.72; H, 7.97; N, 10.07. Found: C, 64.69; H, 7.92; N, 10.06.

***erythro*-1-Hydroxy-3-phenyl-3-piperidino-2-propyl 1-Piperidinecarboxylate (III) and *erythro*-2-Hydroxy-3-phenyl-3-piperidinopropyl 1-Piperidinecarboxylate (IV). A. From I.**—A solution of 5 g. of crude I in 8.5 g. of piperidine and 6 ml. of methanol was refluxed for 5 hr. Removal of methanol and excess piperidine *in vacuo* followed by crystallization of the oily residue from aqueous ethanol gave 6.1 g. of a mixture of III and IV.[12] Fractional crystallization of the crude mixture from ethyl acetate afforded 1 g. (11%) of the less soluble III, m.p. 126–128°, λ_{OH} 3.10 μ, λ_{CO} 5.91 μ (Nujol), and 1 g. (11%) of IV, m.p. 108–109°, λ_{OH} 2.93 μ, λ_{CO} 5.99 μ (Nujol).

B. From II.—A solution of 1 g. of II in 2 g. of piperidine and 1 ml. of methanol was refluxed for 2 hr. Removal of methanol and excess piperidine *in vacuo* gave 500 mg. of a crude mixture of III and IV, whose components were separated as described under A.

Anal. Calcd. for $C_{20}H_{30}N_2O_3$: C, 69.33; H, 8.73; N, 8.09. Found III: C, 69.52; H, 8.90; N, 8.05. IV: C, 69.23; H, 8.75; N, 7.85.

Synthesis of IV from *trans*-Cinnamyl Alcohol.—Sodium (0.46 g., 0.02 g.-atom) was added in small portions to a stirred solution of *trans*-cinnamyl alcohol (3 g., 0.022 mole) in 5 ml. of anhydrous ether. Stirring at room temperature was continued overnight; then 1.5 g. (0.01 mole) of 1-piperidinecarbonyl chloride[13] was added and the mixture was heated at 50° for 1 hr. and filtered. Elimination of ether and excess cinnamyl alcohol *in vacuo* gave *trans*-cinnamyl 1-piperidinecarboxylate (XIII) as a viscous, dark oil (infrared spectrum, no hydroxyl absorption, strong bands at 5.9, 7.0, 7.95, 8.15, 8.7, and 10.3 μ) which was used without purification. To a solution of 1.2 g. (5 mmoles) of crude XIII in 3 ml. of chloroform was added 0.8 g. (5.8 mmoles) of peroxybenzoic acid in 15 ml. of chloroform. The mixture was allowed to stand at room temperature for 24 hr., washed with sodium carbonate and water, and dried (magnesium sulfate). Evaporation of solvent gave crude, oily *trans*-1,2-epoxy-3-phenylpropyl 1-piperidinecarboxylate (XIV, infrared spectrum, no *trans*-ethylenic absorption at 10.3 μ, epoxy band at 11.25 μ), which was directly dissolved in excess (4 g.) piperidine. The mixture was allowed to stand at room temperature for 48 hr., the excess piperidine was removed *in vacuo*, and the oily residue was dissolved in 10% hydrochloric acid. The acid solution was washed with ether, made alkaline with 10% sodium hydroxide, and extracted with ether. Evaporation of the dried (magnesium sulfate), ethereal extract gave a residue which was triturated with a small amount of ether to yield crystalline IV, m.p. 108–109°.

***erythro*-1-Acetoxy-3-phenyl-3-piperidino-2-propyl 1-Piperidinecarboxylate (IIIa) and *erythro*-2-Acetoxy-3-phenyl-3-piperidinopropyl 1-Piperidinecarboxylate (IVa).**—The acetates IIIa, m.p. 122–124°, and IVa, m.p. 91–92°, were prepared in *ca.* 80% yield by heating a solution of the parent compound in acetic anhydride at 110° for 3 hr., evaporation *in vacuo* of the excess acetic anhydride, and crystallization of the residue from ethanol.

Anal. Calcd. for $C_{22}H_{32}N_2O_4$: N, 7.21. Found for IIIa: N, 7.21. Found for IVa: N, 7.44.

***erythro*-3-Phenyl-3-piperidino-1,2-propanediol (V). A. From II.**—A solution of 1.6 g. (5.8 mmoles) of II in 4.5 ml. of concentrated hydrochloric acid and 1.5 ml. of acetic acid was refluxed for 7 hr. The cooled solution was filtered and the filtrate was made alkaline with 10% sodium hydroxide and extracted with ether. Evaporation of the dried (magnesium sulfate), ethereal solution gave a residue which afforded upon crystallization from ethyl acetate–petroleum ether (b.p. 60–80°) 1 g. (74%) of pure V, m.p. 93–95°.

B. From III, IV, and XI. Acid hydrolysis of III, IV, and XI as described above afforded V in *ca.* 70% yield. This material was identical with a sample prepared according to Tsou and Cromwell.[2]

***erythro*-1-Chloro-3-phenyl-3-piperidino-2-propyl 1-Piperidinecarboxylate (VI). A. From III.**—Thionyl chloride (0.2 g., 1.7 mmoles) was added to a solution of 500 mg. (1.45 mmoles) of III in 1 ml. of anhydrous toluene. The mixture was heated under reflux for 1 hr., diluted with ether, washed with sodium carbonate and water, and dried (magnesium sulfate). Removal of the solvent and crystallization of the residue from ethanol yielded 270 mg. (51%) of VI, m.p. 129–131°, λ_{CO} 5.91 μ (Nujol).

B. From IV.—Treatment of IV with thionyl chloride as described for III gave VI in 17% yield.

Anal. Calcd. for $C_{20}H_{29}ClN_2O_2$: C, 65.85; H, 7.95; N, 7.68. Found: C, 65.64; H, 8.15; N, 8.06.

***erythro*-3-Phenyl-1,3-dipiperidino-2-propyl 1-Piperidinecarboxylate (VII).**—Piperidine (340 mg., 4 mmoles) was added to a solution of 364 mg. (1 mmole) of VI in 2 ml. of absolute methanol. After a 2-hr. reflux, water was added to the cooled reaction mixture. The crude product was filtered and crystallized from ethanol to give 360 mg. (87%) of VII, m.p. 144–146°.

Anal. Calcd. for $C_{25}H_{39}N_3O_2$: C, 72.60; H, 9.51; N, 10.16. Found: C, 72.48; H, 9.46; N, 10.31.

***erythro*-2-Hydroxy-3-phenyl-1,3-dipiperidinopropane (VIII). A. From VII.**—A solution of 200 mg. of VII in 2 ml. of concentrated hydrochloric acid and 1 ml. of acetic acid was refluxed for 7 hr. The cooled solution was made alkaline with 10% sodium hydroxide and extracted with ether. Evaporation of the dried (magnesium sulfate), ethereal extract yielded 100 mg. (68%) of VIII, m.p. 92–93° (after recrystallization from petroleum ether).

B. From IX.—A solution of 1.68 g. (0.01 mole) of 1-chloro-2,3-epoxy-3-phenylpropane[3] (IX) in 3.4 g. (0.04 mole) of piperidine was allowed to stand at room temperature for 3 days. Removal of excess piperidine *in vacuo* followed by crystallization of the residue from ethanol afforded 800 mg. (27%) of VIII.

Anal. Calcd. for $C_{19}H_{30}N_2O$: C, 75.45; H, 10.00; N, 9.26. Found: C, 75.59; H, 10.01; N, 9.10.

***erythro*-2-Hydroxy-3-phenyl-3-piperidinopropyl Carbanilate (XI).**—A solution of 3 g. (0.011 mole) of *trans*-2,3-epoxy-3-phenylpropyl carbanilate (X) m.p. 87–89° (lit.[5] m.p. 88.5°), in 1.7 g. (0.02 mole) of piperidine and 5 ml. of methanol was allowed to stand at room temperature for 3 days. The crystalline solid which separated (3.3 g., 83%) had m.p. 129–131° after recrystallization from ethanol, λ_{OH} 2.94 μ, λ_{NH} 3.00 μ, and λ_{CO} 5.86 μ (Nujol).

Anal. Calcd. for $C_{21}H_{26}N_2O_3$: C, 71.16; H, 7.39; N, 7.90. Found: C, 71.42; H, 7.27; N, 8.03.

***erythro*-1-Carbaniloxy-3-phenyl-3-piperidino-2-propyl 1-Piperidinecarboxylate (XII). A. From III.**—Phenyl isocyanate (70 mg., 0.59 mmole) was added to a solution of 200 mg. (0.58 mmole) of III in anhydrous benzene (3 ml.), the solvent was distilled and the residue was crystallized from ethanol to yield 240 mg. (89%) of pure XII, m.p. 167–169°, λ_{NH} 3.00 μ, λ_{CO} 5.80 and 5.97 μ (Nujol).

B. From XI.—A solution of 200 mg. (0.56 mmole) of XI in 1 g. of 1-piperidinecarbonyl chloride was heated at 100° for 1 hr. The resulting viscous oil was dissolved in 10% hydrochloric acid, the acid solution was washed with ether, made alkaline with 10% sodium hydroxide, and extracted with ether. Evaporation of the dried (magnesium sulfate), ethereal extract gave a residue which was triturated with ethanol to give 100 mg. (38%) of crystals, m.p. 167–169° after recrystallization from ethanol.

Anal. Calcd. for $C_{27}H_{35}N_3O_4$: C, 69.65; H, 7.58; N, 9.03. Found: C, 69.50; H, 7.42; N, 8.70.

Attempts at Preparation of 4-(α-Piperidinobenzyl)-2-dioxolone (XVI).—The reaction between V, diethyl carbonate, and sodium methylate gave consistently negative results. Styrene glycol, under the same conditions, afforded 4-phenyl-2-dioxolone[4,14] in excellent yield. Treatment of II with hydrogen chloride in chloroform, hydrogen chloride in 2-propanol, sodium ethoxide in ethanol, and sodium isopropoxide in 2-propanol resulted in formation of decomposition products and partial recovery of the starting material.

(12) Comparison of the infrared spectrum of this mixture with spectra of mixtures containing known amounts of III and IV showed its components to be present in approximately equal proportions.

(13) Prepared according to W. J. Rost, *J. Am. Pharm. Assoc. Sci. Ed.*, **46**, 290 (1957).

(14) J. I. Jones, *J. Chem. Soc.*, 2735 (1957).

Rearrangement of III to IV.—A solution of 300 mg. (0.87 mmole) of III in 1 g. of piperidine and 1.5 ml. of methanol was refluxed for 5 hr. Elimination of piperidine and methanol *in vacuo* followed by fractional crystallization of the oily residue from ethyl acetate afforded 40 mg. (13%) of IV.

Analogous treatment of IV resulted in total recovery of the starting material.

Acknowledgment.—We take pleasure in thanking Professor G. Berti for many helpful discussions.

Some Observations on Allylic Oxidation[1]

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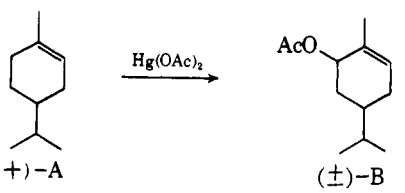
Received May 4, 1964

Allylic oxidation by mercuric acetate, lead tetraacetate, chromic acid, and selenium dioxide have been studied. The oxidation by the first two reagents involves a symmetrical intermediate which is probably formed *via* the decomposition of an allylmercuric or an allyllead intermediate. The oxidation by chromic acid also leads to a symmetrical intermediate. However, the difference in position of attack between this reagent and the other two suggests that it is the initial attack by chromic acid which forms the symmetrical intermediate. The oxidation by selenium dioxide differs from that of the other reagents in that asymmetry is retained during the reaction. The oxidation of (+)-carvomenthene in aqueous ethanol gave carvotanacetone with 45–55% retention of configuration (*i.e.*, attack at the allylic carbon), but the oxidation of cyclohexene-C^{13} gave 90% reaction at the olefinic carbon. The mechanisms of the reactions are discussed.

Allylic oxidation by N-bromosuccinimide and related N-halo compounds has been extensively studied. The kinetics of the reaction with cyclohexene have been examined in detail,[4] the stereochemistry[5] and effect of substituents[6] have been studied, and other aspects of the reaction have also been investigated.[7] As a result, the nature of the reaction is fairly well understood. However, allylic oxidation by other reagents such as selenium dioxide,[8] chromic acid,[9] lead tetraacetate,[10] and mercuric acetate[11] have received relatively little attention. Some experiments designed to give information on the nature of the intermediates involved are described below.

Mercuric Acetate.—The oxidation of (+)-carvomenthene (A) by mercuric acetate has been investigated by Treibs and Bast[10] and by Kergomard.[12] The product was (±)-carvotanacetol acetate (B), which on hydrolysis and oxidation gave (±)-carvotanacetone. From this it was concluded that a symmetrical intermediate, presumably the allyl radical or cation, was involved as an intermediate.



(+)-A (±)-B

It had not been established that the reactant and product are configurationally stable under the reaction conditions. In order to settle this point, in one experiment, we employed a 100% excess of (+)-carvomenthene and found that the recovered hydrocarbon had 99% of its original rotation. In a second run, a sample of (+)-carvotanacetol acetate was heated with mercuric acetate and acetic acid under the reaction conditions. The recovered acetate had 96% of its original rotation. To check the possibility that some intermediate catalyzed the racemization of the product, an amount of carvotanacetol acetate (α_D 34.6°) equivalent to that expected as the product was added to the reactants, and the reaction was carried out as usual. The product had a rotation of α_D 16.7° indicating no significant racemization of the product once it is formed.

It was possible to separate the two epimeric carvotanacetol acetates by gas chromatography. The ratio of *trans* to *cis* was 72:28.[13]

In order to be sure that the reaction would proceed on the same course with a less substituted alkene, we examined the oxidation of cyclohexene-C^{13}. Starting with material having 1.442 ● 0.004% C^{13} at each end of the double bond, the reaction was carried out to give 3-acetoxycyclohexene. Hydrogenation, hydrolysis and oxidation gave cyclohexanone, which was degraded by the method of Loftfield[14] to give the carbonyl carbon in the form of carbon dioxide. Analysis of the latter indicated that the carbon attached to the acetoxy group had 1.268 ± 0.018% C^{13} (average of duplicate determinations) which is very close to that expected for a symmetrical intermediate (1.276%).[15] These data confirm that a symmetrical intermediate is involved in the reaction.

The oxidation of 1-methylcyclohexene proceeds under the same conditions as for cyclohexene, and gives about

(1) This work was supported by a grant from the National Science Foundation.

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(3) Taken from part of a thesis submitted to the University of Washington in partial fulfillment of the requirements for the Ph.D. degree, 1962; Allied Chemical Corp. Fellow, 1960–1961.

(4) H. J. Dauben, Jr., and E. A. Youngman, unpublished results, quoted in C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 382.

(5) H. J. Dauben, Jr., and L. L. McCoy, *J. Am. Chem. Soc.*, **81**, 5404 (1959).

(6) R. E. Pearson and J. C. Martin, *ibid.*, **85**, 354 (1963); G. A. Russell, C. De Boer, and K. M. Desmond, *ibid.*, **85**, 365 (1963).

(7) C. Walling, ref. 4, p. 381; H. J. Dauben, Jr., and L. L. McCoy, *J. Am. Chem. Soc.*, **81**, 4863 (1959).

(8) *Cf.* G. R. Waitkins and C. W. Clark, *Chem. Rev.*, **36**, 235 (1945).

(9) F. C. Whitmore and G. W. Pedlow, *J. Am. Chem. Soc.*, **63**, 758 (1941).

(10) R. Criegee, *Ann.*, **481**, 263 (1930).

(11) W. Treibs and H. Bast, *ibid.*, **561**, 165 (1949); W. Treibs, G. Lucius, H. Kögler and H. Breslauer, *ibid.*, **581**, 59 (1953).

(12) A. Kergomard, *Ann. chim.* (Paris), **8**, 153 (1953).

(13) The assignment of configuration of the carvotanacetols was based on the work of H. G. Kuivila and O. F. Beumell, Jr., *J. Am. Chem. Soc.*, **83**, 1246 (1961).

(14) R. B. Loftfield, *ibid.*, **73**, 4707 (1951).

(15) The normal abundance of carbon-13 was taken as 1.110% and all data were normalized to this value.