

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA, AND NAVAL STORES STATION¹]***p*-Menthane Hydroperoxide²**

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The oxidation of *cis*- and *trans*-*p*-menthane with oxygen to give *p*-menthane hydroperoxides has been studied. Both oxidized at the same rate to give similar mixtures containing the 1- and 8-monohydroperoxides and the 1,8 dihydroperoxide. In each case the 8-isomer obtained corresponded to the starting material and the 1-hydroperoxide was a mixture of the *cis* and *trans* isomers. The proportion of 1-hydroperoxides was greater in the case of *cis*-*p*-menthane which has an equatorial hydrogen in the 1- position. The maximum peroxide content obtainable in the oxidate under the conditions used was 25–35%. Elevated temperatures were required for rapid peroxidation and 130° was used for preparative work. For identification, the hydroperoxides were reduced to the corresponding alcohols. Except for *cis*-terpin, which was obtained pure, identification was based on infrared spectral data. *p*-Menthane hydroperoxide was found to undergo a first order thermal decomposition with an activation energy of 27 kcal. per mole.

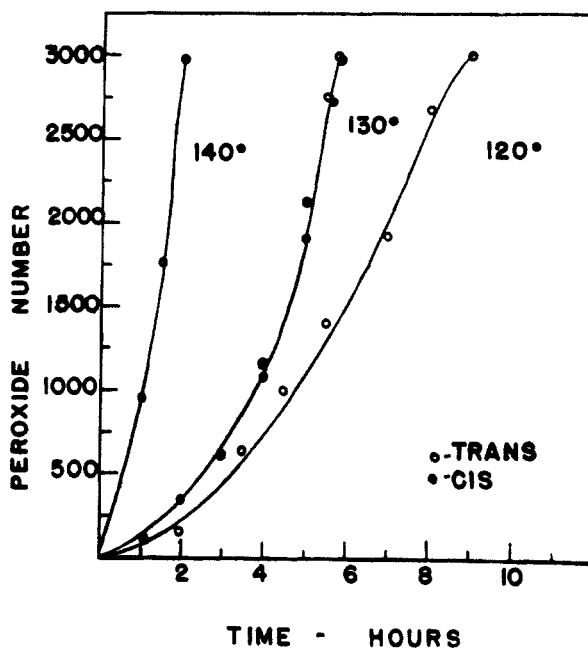
For some time it has been known that *p*-menthane can be oxidized to a hydroperoxidic product which is an excellent initiator for low temperature copolymerization of butadiene-styrene.^{3,4} Substantial quantities are now being manufactured and used in the production of synthetic rubber.

There is, however, no published data on the production, structure and properties of *p*-menthane hydroperoxide comparable in scope to the data on pinane-2-hydroperoxide.^{5–7} The present investigation was undertaken to supply such information.

Discussion. Commercial limonene from citrus peel oil is a readily available material and is easily fractionated to give pure limonene, which yields a mixture of *cis*- and *trans*-*p*-menthanes which can be separated by fractional distillation.

In contrast to the marked difference in rates of oxidation of *cis*- and *trans*-pinane,⁵ the rate of peroxide accumulation at 130° was essentially the same for *cis*- and *trans*-*p*-menthane. Both forms were much more resistant to oxidation than *cis*-pinane.⁵ At 120° *trans*-*p*-menthane oxidized about one tenth as rapidly as *cis*-pinane.

The effect of temperature on peroxidation was studied using *trans*-*p*-menthane. As shown in Fig. 1, increasing the oxidation temperature makes a marked increase in the rate of peroxidation. Al-

Fig. 1. Oxidation of *p*-menthane

though the peroxide content obtained at 140° with *trans*-*p*-menthane was considerably higher than that obtained at the same temperature with pinane, reduction in oxidation temperature made only a small increase in the maximum peroxide content that could be obtained. The maximum peroxide content obtainable was about 25–30% in the temperature range of 120–140°. This figure dropped off to about 20% at 150° and increased only to about 35% even at 80°. The use of higher oxidation temperatures led to the production of larger amounts of acidic by-products. Thus, in the oxidations shown in Fig. 1, the acid numbers were 26 for the oxidate obtained at 140°, 17 for the oxidate obtained at 130°, and 14 for that obtained at 120°. It should be noted that at 140° the oxidation conditions used in this investigation led to very rapid decomposition of the peroxide after the maximum peroxide content was obtained.

(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) Taken in part from a thesis presented by J. S. Stinson to the graduate council of the University of Florida in partial fulfillment of the requirements for the degree of Master of Science. Presented at the Southeast Regional Meeting of the American Chemical Society, Gainesville, Fla., Dec. 11–13, 1958. Present address of J. S. S.: Newport Industries, Pensacola, Fla.

(3) G. S. Fisher, L. A. Glodblatt, I. Kneil, and A. D. Snyder, *Ind. Eng. Chem.*, **43**, 671 (1951).

(4) G. S. Fisher and L. A. Goldblatt (to Secretary of Agriculture), U. S. Patent 2,775,578 (1956).

(5) G. S. Fisher, J. S. Stinson, and L. A. Goldblatt, *J. Am. Chem. Soc.*, **75**, 3675 (1953).

(6) G. A. Schmidt and G. S. Fisher, *J. Am. Chem. Soc.*, **76**, 5426 (1954).

(7) G. S. Fisher, J. S. Stinson, R. N. Moore, and L. A. Goldblatt, *Ind. Eng. Chem.*, **47**, 1368 (1955).

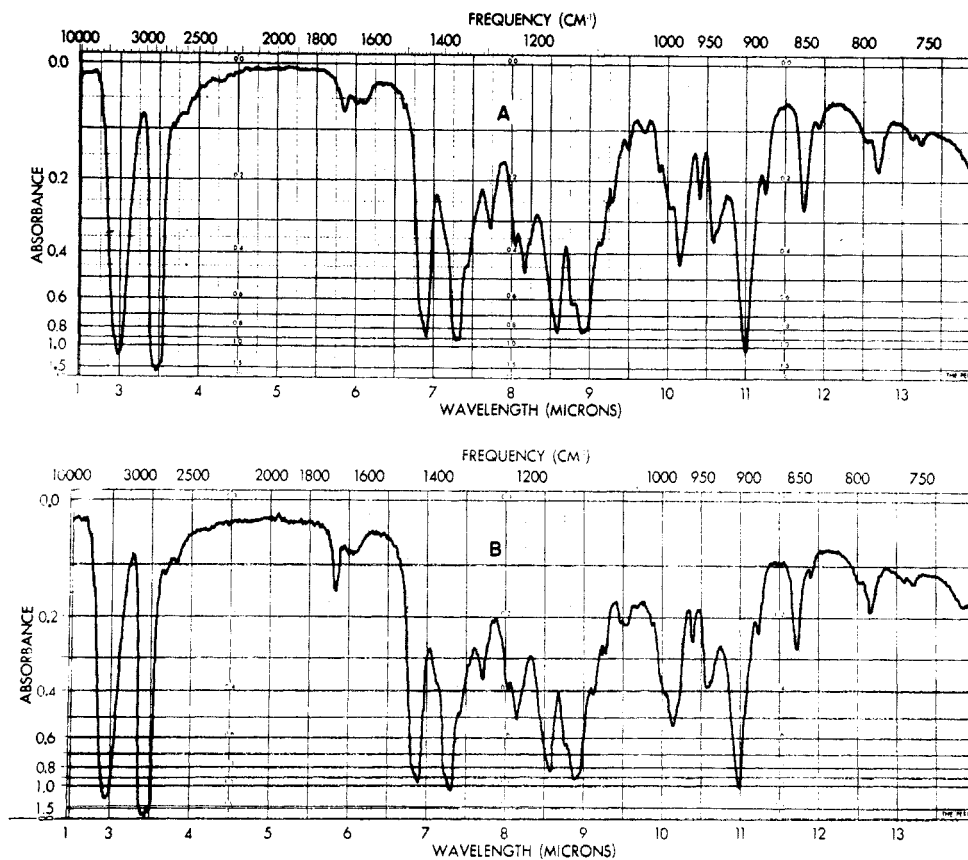


Fig. 2. Infrared spectra of mixed *p*-menthanols: A. 50% *trans-p*-Menthan-8-ol, 25% *cis-p*-menthan-1-ol, 25% *trans-p*-menthan-1-ol. B. Mixed *p*-menthanols from reduction of *trans-p*-menthane hydroperoxide

The most of the preparative portion of the present investigation, an operating temperature of 130° was selected as providing the best compromise between rapid oxidation and minimum amount of peroxide decomposition. Since the rate of peroxidation of the *p*-menthane is rather low until the peroxide number reaches about 500, the time required to prepare a batch of *p*-menthane hydroperoxide can be reduced by adding enough peroxide from a previous run to give an initial peroxide number of 500, or by initiating the oxidation at a higher temperature.⁸

Although direct oxidation failed to yield peroxide contents comparable to those obtained with pinane, high concentrations of *p*-menthane hydroperoxide were readily obtained by vacuum stripping using water vapor as a carrier gas. It was found advisable to wash the oxidate with sodium carbonate prior to concentration of the peroxide to remove acids formed during oxidation. These acidic products tended to catalyze decomposition of the hydroperoxide. *p*-Menthane oxidates containing about 25% of hydroperoxide yielded a concentrate containing about 84% of *p*-menthane hydroperoxide when stripped. These peroxide concentrates could be distilled at low pressures but satisfactory frac-

tionation could not be obtained and there was considerable decomposition. The best method found for preparing *p*-menthane hydroperoxide of very high purity was the precipitation of the sodium salt from pentane solutions of either the concentrate or the distilled hydroperoxide followed by regeneration of the hydroperoxide with carbon dioxide. However, the yields by this process were poor. Hence, peroxide concentrates containing 80–85% or *p*-menthane hydroperoxide were used for reduction to alcohol.

In order to determine whether the peroxidation occurred predominantly at one of the three tertiary positions, as it does in the case of pinane, the hydroperoxides were reduced to the corresponding alcohols for comparison with known compounds. Liquid products were obtained in all cases. Attempts to separate solid alcohols by low temperature crystallization from pentane yielded about 6% by weight of *cis*-terpin in the case of the hydroperoxide from *trans-p*-menthane and a small amount of what appeared to be a mixture of terpins in the case of the hydroperoxide from *cis-p*-menthane. The amount of this latter alcohol was too small for purification and identification. Attempts to purify the crude alcohols by distillation removed small amounts of a ketonic impurity but the alcohols distilled over about a 3° range without any signifi-

(8) G. S. Fisher and L. A. Goldblatt (to Secretary of Agriculture), U. S. Patent 2,735,870 (1956).

cant fractionation. Attempts to prepare phenyl urethanes from the mixed alcohols were also unsuccessful.

Inasmuch as *cis*-terpin which has the same configuration as *trans-p*-menthane was isolated and identified, it was reasonable to assume that both the 1 and the 8 positions in the *p*-menthane molecule were peroxidized and that *trans-p*-menthan-1-ol and *trans-p*-menthan-8-ol⁹ were the major components of the mixture of alcohols. The *cis* and *trans* forms of *p*-menthan-1-ol were available¹⁰ as was *trans-p*-menthan-8-ol.¹¹ The infrared spectra of these compounds were compared with that of the reduced *trans-p*-menthane hydroperoxide. Most of the stronger bands were common to all four spectra but bands at 13.2, 13.1, 12.65, 11.25, 10.40 microns characteristic of *trans-p*-menthan-8-ol were obvious in the spectrum of the unknown and a broad, strong band at 8.9 microns suggested the presence of *cis-p*-menthan-1-ol as did a weak band at 7.75 microns.

The spectrum of a 50:50 mixture of these two alcohols was determined and found to be similar to that of the unknown but the bands at 7.75 and 8.9 microns were too strong and the general separation of bands was too good. The bands characteristic of *trans-p*-menthan-8-ol were of about the correct magnitude. Hence, the spectra of mixtures, containing 50:25:25 and 40:35:25 ratios of *trans-p*-menthan-8-ol, *cis-p*-menthan-1-ol, and *trans-p*-menthan-1-ol, respectively, were determined. The spectra of the 50:25:25 mixture is compared with that of the unknown alcohol in Fig. 2. The two are nearly identical but the *trans-p*-menthan-8-ol bands are a little strong and the *cis-p*-menthan-1-ol ones are a little weak. This situation was reversed in the other mixture. Hence, the monohydric alcohol from reduced *trans-p*-menthane hydroperoxide appears to be a mixture of about 45% *trans-p*-menthan-8-ol, 30% *cis-p*-menthan-1-ol, and 25% *trans-p*-menthan-1-ol. These figures should be regarded as only semiquantitative, particularly since the known mixtures all show less absorption than the unknown in the 9.4 to 10.3 micron region, and the possibility of some *p*-menthan-4-ol being present cannot be excluded.

Inasmuch as the hydrogenation conditions used were mild it seems safe to assume that the corresponding hydroperoxides were present in the same ratio. Hence, the 1 and 8 positions of *trans-p*-menthane are attacked at about equal rates and the addition of oxygen to the *p*-menthan-1-yl free radical is not very stereospecific. This is in contrast to the high degree of stereospecificity in the oxidation of pinane.⁵

The infrared spectrum of the alcohol from *cis-p*-menthane hydroperoxide was similar to that of the

trans-alcohols. This mixture would be expected to contain *cis-p*-menthan-8-ol as well as the *cis*- and *trans-p*-menthan-1-ols. Attempts to prepare pure *cis-p*-menthan-8-ol, by hydrogenation of α -terpineol, for use in estimating the composition of the mixture gave only mixtures of the two isomers. Some idea of the spectrum of the *cis*-isomer was obtained by suitable compensation with the *trans*-isomer. The major bands in this spectrum corresponded to major bands in the spectrum obtained by similar compensation of the crude alcohols with a 6:5 mixture of *cis*- and *trans-p*-menthan-1-ols. The crude alcohol contained some additional bands due to a carbonyl impurity. A very rough approximation indicated that only about 30% of *cis*-8-ol was present. This predominance of the 1-isomers is reasonable because the equatorial 1-hydrogen of *cis-p*-menthane should be attacked more readily than the axial hydrogen of the *trans*-isomer while the ease of attack at the 8 position should be the same for both isomers.

In view of the difficulty experienced in obtaining high concentrations of *p*-menthane hydroperoxide by direct oxidation, it seemed desirable to make a brief study of the decomposition of an oxidate containing about 25% of the hydroperoxide. The oxidate used was prepared in the usual manner at 130° and the decomposition was followed iodometrically at 120° and 130°. The results are presented in Fig. 3. The first order reaction rate constants are 0.22 and 0.53 hr.⁻¹ corresponding to an activation energy 27 kcal./mole. Although the activation energy is the same as that observed for the decomposition of pinane hydroperoxide, the individual rates are much higher, than were obtained for pure pinane

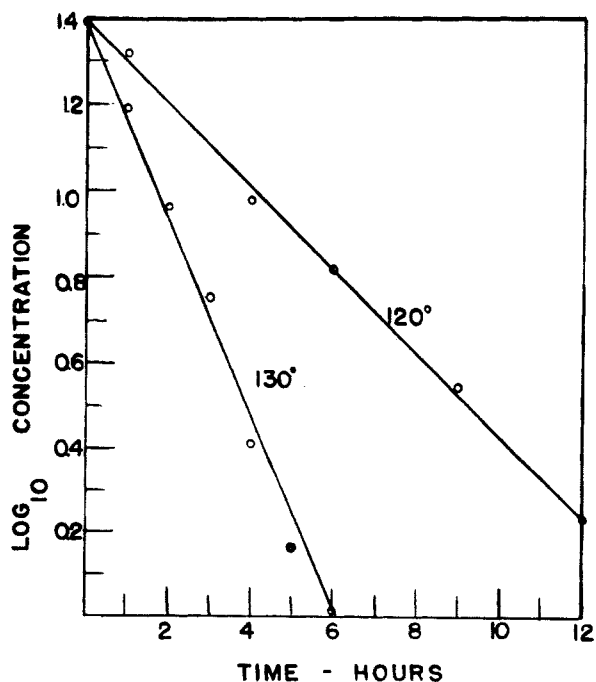


Fig. 3. Decomposition of *p*-menthane hydroperoxide from *trans-p*-menthane

(9) *cis*-Terpin is *trans-p*-menthan-1,8-diol.

(10) Prepared by Dr. G. A. Schmidt from β -terpineols kindly supplied by Dr. J. P. Bain of the Glidden Co.

(11) Kindly supplied by the Hercules Powder Co.

hydroperoxide.¹² The slower rate of oxidation of *p*-menthane and equal or greater rate of decomposition of the hydroperoxide at a given temperature is in accord with the low maximum peroxide content obtainable with *p*-menthane.

EXPERIMENTAL

p-Menthane. The *p*-menthane used in this work was prepared by hydrogenation of a commercial limonene using a nickel on filter aid catalyst at 100 atm. and 130°. The crude *p*-menthane, n_D^{20} 1.4422, d_4^{20} 0.8010, was subjected to a preliminary distillation at 20 mm. to remove low and high boiling impurities. The heart cut was then passed through a column of activated silica gel to remove small amounts of residual unsaturated compounds. The product purified in this manner was substantially pure *p*-methane (n_D^{20} 1.4409, d_4^{20} 0.8011), but was a mixture of *cis* and *trans* isomers.

This mixture was separated by fractional distillation at 20 mm. through a column rated at 100 plates. A reflux ratio of 100:1 was used for removal of the lower boiling *trans* form and this was decreased to 30:1 for the *cis* form. The physical constants of both the *trans*-*p*-menthane (b.p.₂₀ mm. 64°, d_4^{20} 0.7930, n_D^{20} 1.4369) and *cis*-*p*-menthane (b.p.₂₀ mm. 66°, d_4^{20} 0.8086, n_D^{20} 1.4433) were in excellent agreement with those reported by O'Connor and Goldblatt.¹³ The assignment of configuration is based on the Auwers-Skita rule.

p-Menthane hydroperoxide. Samples of *p*-menthane, usually 100–250 ml., were oxidized in the conventional manner using reactors having a fritted-glass false bottom. The oxygen flow rate was varied within the range of 15–80 per hour and the temperature was varied within the range of 120–150°. During a given oxidation the temperature was held constant by immersing the reactor in a suitable liquid constant temperature bath and if necessary by use of a thermostatically controlled internal cooling coil.⁷ Progress of the peroxidation was followed by determining the peroxide number of small samples withdrawn intermittently using the Wheeler method¹⁴ as modified for terpenes.⁵ To avoid excessive decomposition, preparative oxidations were stopped when the oxidate contained 20–25% hydroperoxide. In calculating percentage of *p*-menthane hydroperoxide present in the oxidates it was assumed that only the monohydroperoxide (peroxide number 11,620, 9.3% active oxygen) was formed.

In a typical preparation, oxidation of *cis*-*p*-menthane for 5.5 hr. at 130° gave an oxidate having a peroxide number of 3000. This product was washed with small portions of 3% aqueous sodium carbonate solution until free of acid. Vacuum steam stripping at a pressure of 0.3 mm. to a maximum pot temperature of 60° gave a peroxide concentrate having a peroxide number of 9800 (84%). The recovered *p*-menthane contained about 1% of peroxide and could be re-used without further purification.

The physical properties of typical peroxide concentrates (84%) prepared for the isomeric *p*-menthanes were: *cis* n_D^{20} 1.4686, d_4^{20} 0.966; *trans* n_D^{20} 1.4679, d_4^{20} 0.965.

A portion (20 g.) of the concentrated hydroperoxide from *cis*-*p*-menthane was dissolved in about 100 ml. of pentane. After cooling this solution in an ice bath, 8 g. of 50% sodium hydroxide was added dropwise with shaking, keeping the temperature below 5°. The precipitated salt of the hydroperoxide was filtered off, washed with pentane and with benzene, and suspended in benzene. This suspension was stirred vigorously with distilled water while a stream of

carbon dioxide was passed through the mixture. After 30 min. the two layers were separated and the benzene layer was dried. After removal of the benzene under vacuum, 4.7 g. of *p*-menthane hydroperoxide, peroxide number 11,420, n_D^{20} 1.4689, d_4^{20} 0.967, was obtained. Treatment of the filtrate with additional sodium hydroxide yielded more precipitate but the peroxide regenerated from the second and third crops was less pure than the starting material.

A commercial sample of "pure" *p*-menthane was found to contain appreciable amounts of unsaturated compounds. These were removed by adsorption on silica gel. A 200-ml. sample of this was oxidized in a manner similar to that described above, but the oxidation was started at 145° to avoid or reduce the induction period. The oxidation temperature was reduced as the oxidation progressed.

Time, Min.	Peroxide No.	Temp. Reduced to
30	200	140
60	600	135
90	1100	130
150	2200	125
180	2600	120
240	3000	115
270	3200	—

The final oxidate was yellow and had an acid number of 13. A stripping distillation to a pot temperature of 85° at 0.3 mm. yielded 42 g. of yellow residue, peroxide number 9300, acid number 45. This product was dissolved in heptane, washed with base to remove the acids and recovered by stripping off the heptane. This treatment gave 34 g. of light yellow peroxide concentrate, peroxide number 9800. Distillation at 0.2–0.3 mm. gave 29 g. b.r. 68–80°. Neither the distillate or the residue had as high a peroxide number as the charge. The distillate was dissolved in 2 volumes of pentane and cooled in an ice bath and treated with half the stoichiometric amount of 50% sodium hydroxide solution. The precipitated sodium salt was washed with pentane and ether, suspended in ether, and stirred with a little water and solid carbon dioxide. From the ether layer 2 g. of product was isolated in the usual manner, n_D^{20} 1.4659, d_4^{20} 0.961, peroxide number 11,600.

Reduction of p-menthane hydroperoxide from trans-p-menthane. The method of reduction was essentially that of Lorand.¹⁵ A concentrated, purified peroxide (47.7 g.) prepared from *trans*-*p*-menthane in the usual manner, peroxide number 9600 (83%), was added dropwise, over a 45-min. period, to a solution of 33 g. of sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) and 3.6 g. of 50% sodium hydroxide in approximately 70 ml. of water. The temperature was maintained between 50–60° for 2 hr., and at 70–80° until a final peroxide number of 400 was obtained. This required about 3 hr. The aqueous layer was separated from the alcohol layer after cooling, and the alcohol layer was washed with 50 ml. of water. Thirty-six g. of crude alcohol (n_D^{20} 1.4611) was obtained.

An additional 4.2 g. of terpene alcohol, n_D^{20} 1.4610, was obtained by extracting the aqueous layers with ether. Numerous attempts to separate crystals of the alcohol which formed in an ice bath were unsuccessful. When pentane was used as a solvent crystals were obtained which, after drying on a porous plate, melted 79–93°. Recrystallization gave 0.20 g. of alcohol, m.p. 97–103°. After drying by heating the capillary tube at 125–130° for 20 min., the alcohol recrystallized, m.p. 103.5–105°. Authentic *cis*-terpin melted at 104–105°. A mixed sample melted at 103–105°. This confirmed the presence of *cis*-terpin to the extent of about 6% in the reduction product.

(12) It should be noted that less pure samples of pinane hydroperoxide decomposed more rapidly.

(13) R. T. O'Connor and L. A. Goldblatt, *Anal. Chem.*, **26**, 1726 (1954).

(14) D. H. Wheeler, *Oil & Soap*, **9**, 89 (1932).

(15) E. J. Lorand (to Hercules Powder Co.), U. S. Patent 2,484,841 (1949).

Catalytic hydrogenation⁵ of the hydroperoxide in ethyl acetate, using PtO_2 catalyst, produced a crude alcohol n_D^{20} 1.4612, which was similar to that obtained by sodium sulfide reduction. The hydroperoxide absorbed 1.01 moles of hydrogen per mole.

A portion of the alcohol mixture remaining after crystallization of *cis*-terpin was distilled at a pressure of 0.9 mm. of mercury. The first fraction (about 5%) had b.p. 48–54°, n_D^{20} 1.4561. This was primarily ketonic material and was discarded. The main fraction (about 72%) had b.p. 54–57°/0.9 mm. 207–209°/approximately 760 mm., n_D^{20} 1.4610. Infrared spectral data¹⁶ (Fig. 2) indicated that this product was a mixture of *p*-menthanols with a trace of ketone (5.8 micron band). Attempts to obtain solid derivatives from it were unsuccessful.

Reduction of p-menthane hydroperoxide from cis-p-menthane. Preparation and reduction were carried out as described for the *trans* isomer. The crude reduction product was steam distilled to give a product having n_D^{20} 1.462, d_4^{20} 0.910 and an infrared spectrum quite similar to that of the product from *trans*-*p*-menthane. A small amount of non-

(16) All spectra were obtained on the neat liquids using a Perkin-Elmer 21 spectrophotometer with NaCl optics and an 0.025 mm. cell.

steam volatile matter was recovered by ether extraction. After removal of the ether and addition of pentane, crystals melting at 115–130° were obtained. Recrystallization reduced the melting range to 122–124°. The amount was too small for further purification and identification.

Acidic oxidation products Acidification of the sodium carbonate extracts obtained during preparation of the hydroperoxide and extraction with chloroform yielded a liquid product, neut. equiv. 208. Partition chromatographic analysis¹⁷ of this material indicated the presence of both mono- and dicarboxylic acids. On the basis of a quantitative hypoiodite oxidation, only 60% of the monocarboxylic acid fraction was the methyl keto acid which would be expected as a decomposition product of *p*-menthane-1-hydroperoxide.

Thermal decomposition of p-menthane hydroperoxide. Thermal decomposition was carried out in the same manner as previously described for pinane hydroperoxide.⁵ In the present case 0.3 g. samples of a *p*-menthane oxidate containing 25% of hydroperoxide by weight were used.

OLUSTEE, FLA.

(17) D. E. Baldwin, V. M. Loeblich, and R. V. Lawrence. *Anal. Chem.*, **26**, 760 (1954).

[CONTRIBUTION FROM RESEARCH LABORATORIES OF S. B. PENICK AND COMPANY]

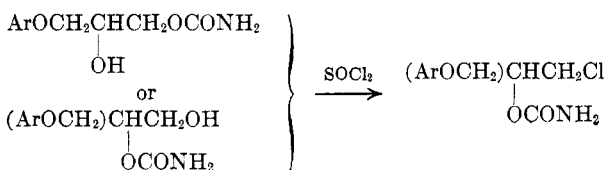
Rearrangement of Substituted 1,2-Glycol Monocarbamates and Related Reactions

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The influence of substituents on the rearrangement of β -hydroxyethylcarbamates in the presence of thionyl chloride is discussed. Analogous reactions of epoxides in strongly acid media are related.

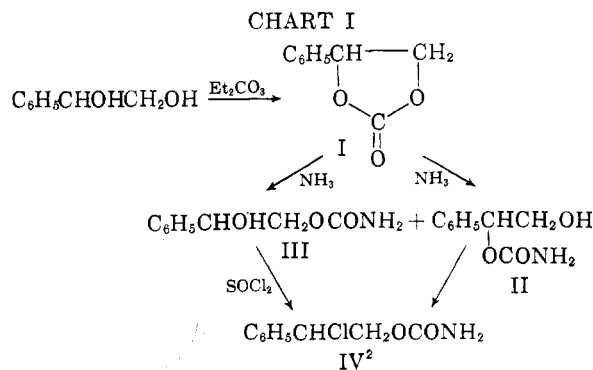
It was recently shown that structurally isomeric β -hydroxyethylcarbamates react with SOCl_2 to give the same β -chloroethylcarbamate through rearrangement of one of the isomers.¹ This rearrangement has now been confirmed by several more examples. (Table I)



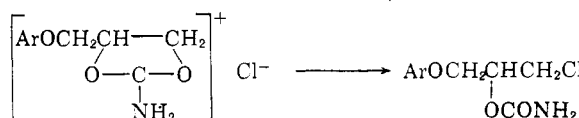
Further investigation of the generality of this process, however, revealed that the nature of the substituent in β -hydroxyethylcarbamates determined the position of the chloro group formed by reaction with thionyl chloride. When the substituent was phenyl, the rearrangement occurred to give the chlorocarbamate in which the chlorine was attached to a secondary carbon atom.

The synthetic method was the same as was previously described.¹

(1) M. M. Baizer, J. R. Clark and J. Swidinsky, *J. Org. Chem.*, **22**, 1595 (1957).



The importance of the substituent in β -hydroxyethylcarbamates, as shown in Chart I, was emphasized by contrast with our previous experience.¹ In that case, rearrangement of the primary carbamate occurred and was assumed to result from addition of the chloride ion to the primary carbon atom of a carbonium ion intermediate, but in both in-



stances a chlorosulfite intermediate is presumably decomposed to give the carbonium ion.¹