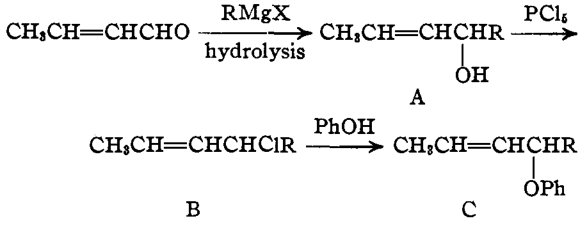
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Rearrangements of α-Propylcrotyl Chloride and α-Propylcrotyl Phenyl Ether

BY CHARLES D. HURD AND JONATHAN W. WILLIAMS

The rearrangement of several α-alkylcrotyl phenyl ethers was studied by Hurd and Cohen.[1] The ethers were synthesized from crotonaldehyde by the following series of steps.



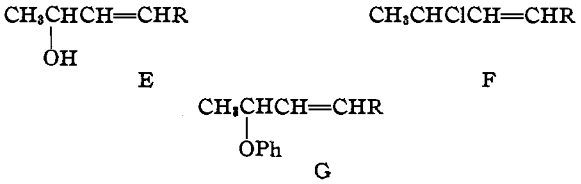
$$CH_3CH{=}CHCHO \xrightarrow[\text{hydrolysis}]{RMgX} \underset{OH}{CH_3CH{=}CHCHR} \xrightarrow{PCl_5}$$

A

$$CH_3CH{=}CHCHClR \xrightarrow{PhOH} \underset{OPh}{CH_3CH{=}CHCHR}$$

B C

Rearrangement of (C) by heating at 230° yielded the phenol (D), $C_6H_4\begin{smallmatrix}OH\\ CH(CH_3)CH{=}CHR\end{smallmatrix}$. It was not established whether or not A, B and C were free from allylic isomers E, F and G, respectively.



$$\underset{OH}{CH_3CHCH{=}CHR} \qquad CH_3CHClCH{=}CHR$$

E F

$$\underset{OPh}{CH_3CHCH{=}CHR}$$

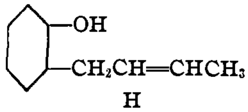
G

This question was significant since an allylic rearrangement of α-alkylallyl alcohols, $CH_2{=}CHCHOHR$, does occur during reaction with halogen acids. Until recently it was thought that the rearrangement into $CH_2XCH{=}CHR$ was complete. In the case of α-methylallyl alcohol, it has been established[2] that the related bromide is an equilibrium mixture of 1-bromo-2-butene and 3-bromo-1-butene, the former predominating. It would be reasonable to assume, therefore, that B (as prepared) would be a mixture of B and F, in which case C would be admixed with G.

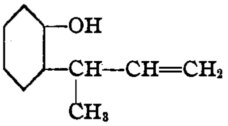
The R-groups in the α-alkylcrotyl compounds of Hurd and Cohen were methyl, ethyl and propyl. It was decided to study the last of these, although the second would have been equally appropriate. The first was inapplicable (since B = F). It was planned to test for the presence of isomeric pairs by ozonolysis. Compounds A to C would yield acetaldehyde or acetic acid, whereas E to G would produce butyraldehyde or butyric acid. Mixtures of isomeric pairs would produce corresponding mixtures of acetic and butyric acids.

It was found by this means that the propylcrotyl alcohol was practically pure A. Conversion to the chloride did cause some isomerization, but B predominated over F. About the same ratio (80:20) was observed in the case of the phenyl ether, showing that the latter was a mixture of C + G, with C in considerable excess.

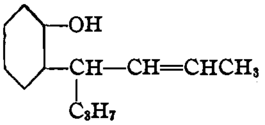
The rearrangement of C into D involves an inversion of the propylcrotyl group. Claisen[3] was the first to call attention to such an effect. He demonstrated that (H), which may be formed from phenol by direct crotylation, differs from I, the chief product formed on pyrolysis of phenyl crotyl ether. Evidence in support of Claisen's viewpoint was obtained in the present work. Rearrangement of propylcrotyl phenyl ether (the mixture of C + G) yielded a mixture of phenols (D + J). Analysis showed that the ratio of phenols in the (D + J)-mixture corresponded within limits of experimental error to the ratio in (C + G).



H



I



J

Experimental Part

2-Heptene-4-ol, 4-chloro-2-heptene, α-propylcrotyl phenyl ether and α-methyl-δ-ethylcrotylphenol were prepared as described by Hurd and Cohen.[1] The boiling points taken, respectively, were 60–65° (23 mm.), 140–145°, 170–173° (35 mm.) and 190–195° (18 mm.). For ozonizations, 2 to 3 g. was dissolved in 150–250 cc. of carbon tetrachloride and a stream of ozonized oxygen was conducted through the solution. The solvent was then distilled off and 100 cc. of water added to the residue of oily ozonide. After ten hours, 0.5–1 g. of sodium hydroxide and silver oxide (from 10 g. of silver nitrate) were added and the mixture refluxed for three hours. It was then filtered, acidified with dilute sulfuric acid and the volatile acid distilled. The moist silver oxide served not only to oxidize the aldehydes to acids, but also to convert the α-chloroaldehydes (from B or F) to non-volatile α-hydroxy

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[1] Hurd and Cohen, THIS JOURNAL, 53, 1917 (1931).

[2] Winstein and Young, *ibid.*, 58, 104 (1936).

[3] Claisen and Tietze, *Ber.*, 58, 275 (1925); 59, 2344 (1926).

acids. Analysis of the volatile acids was by Duclaux determinations[4] on 100-cc. specimens.

Duclaux values of 6.4, 6.9, 7.3 were obtained for the first three 10-cc. portions of distillate collected from the volatile acids from 2-heptene-4-ol. This represents nearly pure acetic acid. The slight deviation may be due to the presence of α-hydroxyvaleric acid, whose influence in this determination is unknown. Confirmation that the volatile acid was acetic was the conversion of 0.5 g. of the sodium salts to 0.5 g. of *p*-bromophenacyl acetate, m. p. 84–85°, by reaction in 50% alcohol with *p*-bromophenacyl bromide.

The volatile acids from the 4-chloro-2-heptene gave a Duclaux value of 23.3 for the first 30 cc. of distillate. From this, these simultaneous equations are applicable: $\text{Ac} + \text{Bu} = 100\%$; $0.197\ \text{Ac} + 0.448\ \text{Bu} = 23.3\%$. Solving, Ac (for acetic) = 86%; Bu (for butyric) = 14%. Hydrolysis of the chloride (3 g.) to the alcohol (1.6 g.; 62% yield), b. p. 60–65° at 23 mm. and subsequent ozonolysis of the alcohol as before gave confirmatory evidence that a mixture was involved. The value for 30 cc. of Duclaux distillate was 22.2, indicative of 90% Ac and 10% Bu.

Duclaux analysis of the volatile acids from α-propylcrotyl phenyl ether (after ozonolysis, etc.) gave 24.7 as the value for 30 cc. of distillate. This represents 80% Ac, 20% Bu and indicates that the ether is a mixture of C and G possibly in the ratio of 80:20. The assumption that the volatile acids are exclusively acetic and butyric may not be entirely correct in this case since a small portion of the volatile acid may come from the aromatic part of the molecule. The figures, however, seem fairly reliable.

The product of rearrangement, namely, α-methyl-δ-ethylcrotylphenol, was treated analogously. The Duclaux value for 30 cc. of distillate was 40.3. Calculation gives 18% Ac, 82% Bu, which indicates that the phenol is chiefly D together with a smaller amount of J. The preponderance of butyric acid in the volatile acids was witnessed by converting the acids to dry sodium salts (0.5 g.) and treating the latter with *p*-bromophenacyl bromide. *p*-Bromophenacyl butyrate, m. p. 63°, was formed abundantly.

Summary

Partial allylic rearrangement of 4-chloro-2-heptene into 2-chloro-3-heptene is encountered during synthesis of the former from 2-heptene-4-ol (α-propylcrotyl alcohol). α-Propylcrotyl phenyl ether and its rearrangement product were prepared and their structures determined by ozonolysis. The evidence obtained supports the contention that the allyl group undergoes inversion during rearrangement of allyl phenyl ether into *o*-allylphenol.

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[4] Virtanen and Pulkki, THIS JOURNAL., **50**, 3143 (1928); McNair, *ibid.*, **55**, 1471 (1933).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Adsorption by Dehydrated Chabasite as a Function of the Water Content

BY ARTHUR B. LAMB AND JOHN C. WOODHOUSE

Vom Rath[1] in 1876 demonstrated that crystals of chabasite, a hydrated calcium, sodium, aluminum silicate, on dehydration retain their original form and clarity unchanged even when the loss of water amounts to nearly one-fifth of their original weight and a still larger fraction of their original volume. Friedel[2] in 1896 found that these dehydrated crystals adsorb gases with marked avidity. Especially interesting is the more recent discovery made independently by several investigators[3] that such an adsorption does not take place with gases whose molecules are larger than a certain definite limiting size and so cannot enter the pores of uniform and atomic dimensions characteristic of this adsorbent.

Impressed by the interesting potentialities of these "crystallogenetic"[4] adsorbents as we have called them, we have now made a careful study of the development of the adsorptive activity of chabasite as it is progressively dehydrated. As a criterion of this activity we have used the adsorptions of hydrogen, oxygen and carbon dioxide upon it, since they represent gases which are, respectively, very slightly, moderately and largely adsorbed.

No similar study, so far as we are aware, has been made.

Apparatus

The samples of chabasite were dehydrated and the adsorption of the resultant product measured in the apparatus shown in Fig. 1.

The manometer C was of the constant-level type. The mercury level on the adsorbent side was kept exactly at (1) by the use of the mercury reservoir B, placed under any de-

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[1] G. vom Rath, *Pogg. Ann.*, **158**, 396 (1876).

[2] Friedel, *Bull. Soc. franc. mineral*, **19**, 93–118, 363–384 (1896).

[3] Lamb, U. S. Patent 1,813,174 (Applied for September 25, 1925); McBain, *Colloid Sym. Mon.*, **4**, 1 (1926); *Kolloid Z.*, **40**, 1 (1926); Schmidt, *Z. physik. Chem.*, **133**, 280 (1928).

[4] That is, adsorbents which owe their adsorptive activity to the crystal structure of the parent substance from which they have been prepared.