they were exposed (the nitriles distil at about 120° below 1.0 mm.). In the case of oximes A, D and H much black, amorphous matter was formed in the reaction. Some of this was separated from the ether extract; the rest appeared as residue in the distilling vessel. The residue is not formed by decomposition during distillation, as can be seen by the small residues from oximes B and G. The results are given in tabular form.

Summary

The structures of seven mixed benzoins, obtained by the usual potassium cyanide condensation, have been determined by means of a second-type Beckmann reaction. The results, interpreted according to Werner's views of the Beckmann rearrangement, give structures in agreement with those determined by independent methods.

TUCKAHOE, NEW YORK

CROTYL ETHERS OF PHENOL

BY CHARLES D. HURD AND FRANK L. COHEN

When allyl aryl ethers are heated, rearrangement into o-allylphenols usually occurs with ease. The same has been shown to be true in some cases when substituted allyl aryl ethers undergo pyrolysis. Only the following groups seem to have received study in this connection: (1) crotyl, $CH_3CH=CHCH_2$—, with phenol,[1,2] β-naphthol,[2] and hydroxynaphthoquinone;[3] (2) cinnamyl, $C_6H_5CH=CHCH_2$—, with phenol;[4] (3) α-methylcrotyl, $CH_3CH=CH—CH(CH_3)$—, with phenol;[5] (4) γ-methylcrotyl, $(CH_3)_2C=CHCH_2$—, with phenol;[6] (5) α,α-dimethylallyl, $CH_2=CH—C(CH_3)_2$—, with phenol;[7] (6) geranyl, $CH_2=C(CH_3)—(CH_2)_3—C(CH_3)=CHCH_2$—, with catechol.[8]

The first four groups undergo rearrangement of the type exemplified in the equation

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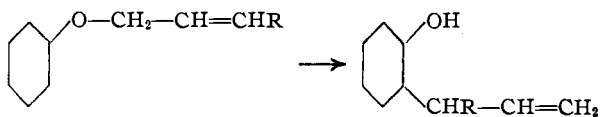
[1] Claisen and Tietze, *Ber.*, **59**, 2350 (1926).

[2] Von Braun and Schirmacher, *ibid.*, **56**, 544–5 (1923).

[3] Fieser, THIS JOURNAL, **48**, 3205 (1926).

[4] Claisen, Kremers, Roth and Tietze, *Ann.*, **442**, 233 (1925).

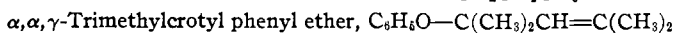[5] Claisen and Tietze, *Ber.*, **58**, 277 (1925); Claisen, Kremers, Roth and Tietze, *Ann.*, **442**, 226 (1925).

[6] Claisen and Tietze, Ref. 5; the reference by these authors in *Ber.*, **59**, 2349 (1926), gives a conflicting notation and evidently refers to $CH_2=CH—C(CH_3)_2—O—C_6H_5$.

[7] Claisen, Kremers, Roth and Tietze, *J. prakt. Chem.*, **105**, 67 (1922).

[8] Kawai, *Sci. Papers Inst. Phys. Chem. Research*, **6**, 53 (1927).

With C_6H_5—O—$C(CH_3)_2CH$=CH_2, however, the pyrolysis leads to iso-prene and phenol.

In the case of α-methylcrotyl phenyl ether, we corroborated the results of Claisen[4] in all essential details. To extend this study, the following substituted allyl ethers of phenol were investigated

α-Ethylcrotyl phenyl ether C_6H_5O—CH—CH=CHCH$_3$
                                                                                                           |
                                                                                                          CH$_2$CH$_3$

α-n-Propylcrotyl phenyl ether C_6H_5O—CH—CH=CHCH$_3$
                                                                                                                        |
                                                                                                                       CH$_2$CH$_2$CH$_3$

α,α,γ-Trimethylcrotyl phenyl ether, C_6H_5O—$C(CH_3)_2CH$=$C(CH_3)_2$

α-n-Propylallyl phenyl ether, C_6H_5O—CH($C_3H_7(n)$)—CH=CH$_2$, was also synthesized and studied. This will be reported in a later paper.
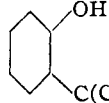
Synthesis of these ethers was effected by refluxing phenol, potassium carbonate and the corresponding crotyl chloride in an ether–acetone solution for several hours. The α-ethyl- and α-propylcrotyl ethers could be purified by vacuum distillation but the trimethylcrotyl ether underwent pyrolysis with such treatment. All of these ethers were liquids.

Pyrolysis.—Normal rearrangements of α-methyl-, α-ethyl- and α-n-propylcrotyl phenyl ethers occurred when they were heated. A temperature of 200° sufficed for the first two, and with the third an exothermic reaction was noticed at 228°. The products formed in the three cases, respectively, were o-α-methylcrotylphenol (I), o-α,δ-dimethylcrotylphenol (II), and o-α-methyl-δ-ethylcrotylphenol (III). The yields in the three
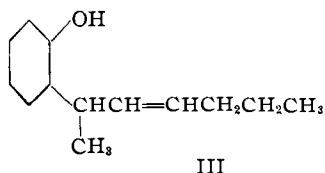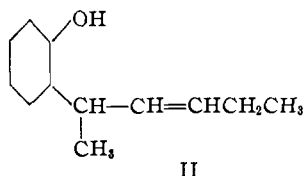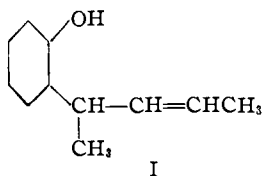

cases were 83, 75 and 52%. All of these phenols were very viscous oils and were alkali-soluble.

For a similar type of rearrangement, trimethylcrotyl phenyl ether should have given rise to o-α,α,γ-trimethylcrotylphenol,

but none was found. Instead, the reaction followed an entirely different

course, yielding phenol, 2,4-dimethylpentadiene-1,3 and tar. The yield of the diene was about 33%.

The course of pyrolysis of these crotyl ethers is sufficiently analogous to the course of pyrolysis of similar allyl and propargyl ethers which have already been studied that two generalizations may be made. (1) Rearrangement into an ortho or para substituted phenol is the chief effect in the heating of allyl or crotyl aryl ethers, and the same holds if the allyl or crotyl groups contain one alpha substituent. Thus, compounds of the types $Ar-O-CH_2CH=CH_2$, $Ar-O-CH_2CH=CHR$, $Ar-O-CHRCH=CH_2$ and $Ar-O-CHRCH=CHR$ may be expected to rearrange if there is an available o- or p-position in the aromatic nucleus. (2) When α,α-disubstituted allyl, crotyl or propargyl aryl ethers are heated, they undergo scission into a phenol and a hydrocarbon. These ethers of phenol have been studied: α,α-dimethylallyl,[7] trimethylcrotyl (this paper), and trimethylpropargyl.[9] All of these contain the grouping $Ph-O-C(CH_3)_2-z$ and all pyrolyze into $PhOH + CH_2=C(CH_3)-z$. It might be argued that the reason for hydrocarbon formation in these cases is the presence of the hydrogens on the α-methyl substituent, thereby making it easy for the phenol to be detached, thus

$$PhO-\!\!\!\!\!\mid-C(CH_3)-z$$
$$H-\!\!\!\!\!\mid-CH_2$$
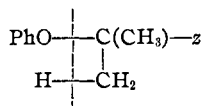
However, the alpha monosubstituted allyl and crotyl ethers with a similar structure fail to give this scission into phenol and hydrocarbon. Furthermore, triphenylpropargyl phenyl ether,[9] with no structure of the $\begin{matrix} PhO-C= \\ H-C= \end{matrix}$ type, also yields phenol and a hydrocarbon on pyrolysis.

The rearrangement of aryl crotyl ethers is a special case of the "three-carbon system": $xCH_2-CH=CHR \longrightarrow CH_2=CH-CHxR$. Undoubtedly the mechanisms of both[10] are similar. In turn, the three-carbon system is but a special case of the general formulation: $xE-E=E' \longrightarrow E=E-E'x$, wherein E represents any element such as C, N, O or S. The union between E and x is a loose one. Applied to the phenyl crotyl ethers, the products of the reaction seem to be most readily explained by assuming an initial scission at the position of weakness, $PhO-\!\!\!\mid-crotyl$, into radicals which immediately readjust themselves. With a primary or secondary crotyl radical, the PhO— radical rearranges to [structure with OH] before attaching

[9] Hurd and Cohen, THIS JOURNAL, 53, 1068 (1931).

[10] For a survey of the three-carbon system, see "Annual Reports on the Progress of Chemistry," 25, 119–130 (1929).

itself to the γ-crotyl carbon. If the crotyl group is tertiary, the PhO-radical selects a hydrogen from the crotyl radical, giving phenol and a hydrocarbon.

The triphenylmethyl alkyl ethers[11] resemble the crotyl (or allyl) aryl ethers in being far less stable than most other ethers. With them, heat induces a rupture of the carbon-to-oxygen bond on the side of the radical with low electron attraction, namely, the triphenylmethyl radical. Evidence for this is the isolation of triphenylmethane and an aldehyde (or ketone) as pyrolytic products. Undoubtedly, the initial effect of heat with both series of ethers (Ar—O—crotyl and R—O—CPh₃) is very similar, if not identical.

Experimental Part

The β-unsaturated alcohols were synthesized by literature methods. Pentene-3-ol-2,[12] hexene-2-ol-4[13] and heptene-2-ol-4 were prepared by the interaction of crotonaldehyde in the cold with a Grignard reagent (Me-, Et- and *n*-Pr-MgBr, respectively). The yields of the three alcohols were 47, 60 and 68%. 2,4-Dimethylpentene-3-ol-2 was prepared in 30% yield[14] from mesityl oxide and methylmagnesium iodide. Simultaneously, a 57% yield of 2,4-dimethylpentadiene-1,3 was realized.

Chlorides from the Alcohols.—2-Chloropentene-3 was synthesized[15] by interaction of the alcohol (in absolute ether) with phosphorus trichloride. The reaction was left for three days at room temperature, whereupon a 37% yield was realized. In the preparation[13,16] of 4-chlorohexene-2 and 4-chloroheptene-2, phosphorus pentachloride was used instead of the trichloride. The yields were 54 and 73%, respectively.

Trimethylcrotyl chloride (2,4-dimethyl-2-chloropentene-3) was too unstable for purification by distillation. It was prepared in solution as follows. To 5.0 g. of 2,4-dimethylbutene-3-ol-2 dissolved in 25 cc. of dry ether was added 2.0 g. of phosphorus trichloride. The reaction mixture was kept at ice temperature for an hour and then it was left for two days at room temperature. The ether solution was decanted from the phosphorus acid layer, after which it was washed with water and dried over sodium sulfate. This solution of trimethylcrotyl chloride was used in subsequent reactions with no further purification, since all attempts to distil it gave almost quantitative yields of 2,4-dimethylpentadiene-1,3.

Synthesis of the Phenyl Ethers

α-Methylcrotyl phenyl ether was prepared by Claisen's method.[5] Our yield of the ether from 2-chloropentene-3 was only 30% instead of 40%, and our boiling point at 12 mm. was 103–104° instead of 96–98°. A weight of tarry material was formed which was equal to the weight of the desired ether.

α-Ethylcrotyl Phenyl Ether.—To a solution of 10 g. of 4-chlorohexene-2 (0.08 mole) in 100 cc. of dry ether was added 10 g. of anhydrous potassium carbonate, 40 cc. of pure

[11] Norris and Young, THIS JOURNAL, **52**, 754 (1930).

[12] Courtot, *Bull. soc. chim.*, [3] **35**, 657 (1906). See also, Baudrenghien, *Bull. sci. acad. roy. Belg.*, **15**, 53 (1929).

[13] Reif, *Ber.*, **39**, 1603 (1906).

[14] Grignard, *Compt. rend.*, **130**, 1324 (1898); von Fellenberg, *Ber.*, **37**, 3578 (1904); Kohler, *Am. Chem. J.*, **31**, 647 (1904); **38**, 514 (1907).

[15] Reif, *Ber.*, **41**, 2741 (1908).

[16] Reif, Ref. 15, p. 2742.

acetone and 7.6 g. of phenol (0.09 mole). The reaction mixture was refluxed vigorously for eleven hours. Water was then added to dissolve the salts and to remove some of the acetone and excess phenol. The ether solution was washed with dilute alkali until it was free from phenol. After drying over calcium chloride, the solution was distilled at reduced pressure. Four grams of the unreacted chloride, b. p. 50–53° at 15 mm., 4.2 g. of α-ethylcrotyl phenyl ether, b. p. 116–118° at 15 mm., and 1.8 g. of o-α,δ-dimethyl-crotylphenol, b. p. 140–143° at 15 mm., were obtained. The 4.2 g. yield of the ether is a 30% yield.

Anal. Subs., 0.1512, 0.1413: CO_2, 0.4525, 0.4216; H_2O, 0.1240, 0.1157. Calcd. for $C_{12}H_{16}O$: C, 81.75; H, 9.15. Found: C, 81.4, 81.5; H, 9.11, 9.10.

α-*n*-Propylcrotyl Phenyl Ether.—A mixture of 20 g. of 4-chloroheptene-2 (0.14 mole), 40 cc. of pure acetone, 26 g. of potassium carbonate (0.2 mole), 100 cc. of dry ether and 16.8 g. of phenol (0.2 mole) was placed in a liter round-bottomed flask and refluxed vigorously for six hours. Water was then added, the ether layer separated and washed with small portions of normal alkali, dried over calcium chloride and fractionated. Propylcrotyl phenyl ether, b. p. 153–154° at 23 mm., was obtained as a colorless viscid oil, which almost immediately turned to a dark red on cooling. The tarry residue decomposed on further heating. The yield was 17.4 g., or 65%.

Anal. Subs., 0.1408: CO_2, 0.4219; H_2O, 0.1197. Calcd. for $C_{13}H_{18}O$: C, 82.04; H, 9.54. Found: C, 81.8; H, 9.44.

α,α,γ-Trimethylcrotyl Phenyl Ether.—To the ether solution which contained the trimethylcrotyl chloride (see above) was added 25 cc. of acetone, 5.0 g. of potassium carbonate and 3.7 g. of phenol. This was refluxed for several hours and 50 cc. of ether was added. The ether solution was then washed with dilute sodium hydroxide and water, dried over sodium sulfate and carefully distilled. After removing the ether and the 2,4-dimethylpentadiene-1,3 which was formed simultaneously, an almost colorless but quite viscous oil remained. Its index of refraction n_D^{20} was 1.3047. The oil did not distil at 150° and 1.5 mm., whereas above 150° decomposition ensued.

Mol. wt. Subs., 0.2114; benzene, 21.96 g.; freezing point lowering, 0.240°. Calcd. for $C_{13}H_{18}O$: mol. wt., 190.1. Found: 189.0.

Pyrolysis of the Ethers

From 2 to 10 g. of the ether specimens was placed in a side-arm test-tube or in a small distilling flask which was connected with a small condenser. In turn, this was attached to a receiver which was immersed in an ice–salt bath. A thermometer was extended into the ether, and the reaction tube was heated by immersion in an oil-bath.

With α-methylcrotyl phenyl ether, a temperature of 200° was maintained for one hour. The pyrolytic mixture was then cooled, dissolved in ether and the alkali-soluble material washed out with 5% sodium hydroxide. The alkali-soluble material was then obtained fairly pure by acidifying the alkaline solution. The yellowish oil which resulted was ether-extracted, dried and distilled. o-α-Methylcrotylphenol was a colorless, viscous oil with a strong phenolic odor. The boiling point of 120–121° at 11 mm. corresponded to that given by Claisen.[5] The yield from 4 g. was 3.3 g., which is 83% of the theoretical.

α-Ethylcrotyl Phenyl Ether.—Four grams of this ether was heated slowly until the temperature was 200–205°. At this point the ether darkened appreciably and seemed to reflux slightly. No volatile material was evolved. The temperature was maintained for thirty minutes without any further apparent change. After cooling, the reaction product was dissolved in 50 cc. of ether and washed with dilute alkali. The alkaline solution was acidified and a red oil separated. The reaction product was then ex-

tracted with more alkali until no more alkali-soluble material remained. Four extractions with 10-cc. portions of normal sodium hydroxide solution were sufficient. The alkali-soluble material, which was obtained as an oil when acid was added, was extracted with ether, dried, and the solution distilled.

o-α,δ-Dimethylcrotylphenol was obtained as a red oil. At 15 mm. it boiled at 143–145°. The yield was 3.1 g., or 75%.

Anal. Subs., 0.1030, 0.1650: CO_2, 0.3090, 0.4958; H_2O, 0.0843, 0.1343. Calcd. for $C_{12}H_{16}O$: C, 81.75; H, 9.10. Found: C, 81.9, 81.8; H, 9.10, 8.98.

α-n-Propylcrotyl Phenyl Ether.—A 9.5-g. sample of this ether was pyrolyzed. At 228–230° rearrangement occurred exothermically. No volatile distillate was observed. After continued heating for one-half hour, the pyrolyzed mixture was fractionally distilled and 5.2 g. of alkali-soluble material, b. p. 154–155° at 14 mm., was obtained. Also, 2.1 g. of unchanged ether, b. p. 143–145° at 14 mm., was recovered. The pyrolyzed material, α-methyl-δ-ethylcrotylphenol, $HO—C_6H_4—CH(CH_3)—CH=CHCH_2CH_2CH_3$ was completely alkali-soluble. It was light yellow in color and very viscous. The yield was 54% of the theoretical value.

Anal. Subs., 0.1614, 0.1531: CO_2, 0.4853, 0.4595; H_2O, 0.1375, 0.1309. Calcd. for $C_{13}H_{18}O$: C, 82.04; H, 9.54. Found: C, 82.0, 81.9; H, 9.46, 9.49.

α,α,γ-Trimethylcrotyl Phenyl Ether.—Two grams of α,α,γ-trimethylcrotyl phenyl ether was heated at such a rate that the difference in temperature between the bath and the ether did not exceed 5°. At 150° the ether showed an appreciable darkening. At 160–170° there was an evolution of vapor which was condensed and collected in a small receiving flask. The material in the test-tube reaction flask rapidly became darker. The temperature of 160–170° was maintained for half an hour until evolution of the volatile material ceased. The residual material in the reaction tube was a thick black tar after it had cooled.

The volatile distillate was shown to be 2,4-dimethylpentadiene-1,3.[17] Its boiling point was 92–93°. The yield of this material was 0.3 g., or 33% of the theoretical. The tarry residue was extracted with small portions of normal alkali, the alkaline extract acidified and treated with bromine water until no more bromine was absorbed. Half a gram of tribromophenol was obtained, which corresponded to 0.2 g. of phenol. No other alkali-soluble material was isolated.

Summary

The following ethers of phenol have been synthesized and studied: α-methylcrotyl, α-ethylcrotyl, α-n-propylcrotyl and α,α,γ-trimethylcrotyl. The first three of these ethers rearranged into phenolic isomers on heating, namely, into o-α-methylcrotylphenol, o-α,δ-dimethylcrotylphenol, and o-α-methyl-δ-ethylcrotylphenol. The trimethylcrotyl ether was less stable than the others and it pyrolyzed into phenol and 2,4-dimethylpentadiene-1,3.

It was pointed out that the substituted allyl aryl ethers with the grouping $Ar—O—CH_2—C=C$ or $Ar—O—CHR—C=C$ may be expected to rearrange on heating, whereas with a grouping such as $Ar—O—CR_2—C=C$ pyrolysis leads to phenol (ArOH) and a hydrocarbon.

EVANSTON, ILLINOIS

[17] Von Fellenberg, *Ber.*, **37**, 3578 (1904).