Notes A departmemt for short papers of immediate interest.

The Mechanism of Pyrolysis of β-Hydroxyolefins

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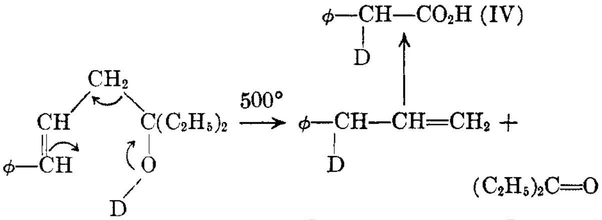
In a previous publication[1] it was demonstrated that the pyrolytic degradation of β-hydroxyolefins at 500° to form new olefinic substances and aldehydes (or ketones) is a general reaction, and that the well known decomposition of ricinoleic acid into heptaldehyde and undecylenic acid is merely a specific example of this transformation.

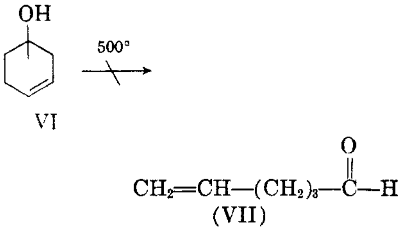
Two pieces of evidence have now been found to support the proposal[1] that this thermal degradation occurs *via* a six-membered cyclic transition state. The first of these follows from results of a study of the pyrolysis of 1-phenyl-4-ethylhexen-1-ol-4-*d* (I) to give 3-phenylpropen-1-3-*d* (II) and pentanone-3 (III).



(I) (II) (III)

$C_6H_{13}-CH=CHD$

(V)



$CH_2=CH-(CH_2)_3-\overset{O}{\overset{\|}{C}}-H$

VI (VII)

No evidence for the presence of excess deuterium in III was found by careful examination of its infrared spectrum.[2] The —C—D stretching frequency at 4.7μ as well as other differences characteristic of the presence of deuterium[3,4] were, however, found in II and IV. That the deuterium atom in II was located at C_3 and not at C_1 was clearly indicated by the fact that the intensity of the =CH_2 deformation bands at 10.04μ and 10.91μ in II and in an authentic sample of allylbenzene were indistinguishable. The presence of any appreciable amount of =CHD should markedly reduce the absorption intensities in the 10–11μ region.[5] Further experimental evidence in support of this view was found by an examination of the infrared spectrum of octene-1-1-*d* (V) which showed the normal —C—D stretching frequency (4.5μ), but the intensity of the deformation bands at 10.1μ and 10.9μ were approximately one half of those observed in an undeuterated sample of octene-1 when measured under identical conditions.

The second piece of evidence in favor of a cyclic mechanism follows from geometric considerations. This mechanism requires the β-hydroxyolefin to have at least one readily attainable conformation in which the hydrogen atom of the hydroxyl group can come into close proximity with the π-electrons of the carbon-carbon double bond. An examination of molecular models indicated that such a conformation is not favorable in cyclohexen-3-ol-1 (VI), and it was predicted that VI upon pyrolysis would not be transformed into its "normal" product VII. This, in fact, proved to be the case. When VI was subjected to the usual conditions for the pyrolytic decomposition of β-hydroxyolefins (*i.e.* 500°), there was obtained a condensate whose infrared spectrum showed the absence of carbonyl compounds. Fractionation of this crude product led to a recovery of starting material (73%) plus a low-boiling component (9%) which we regard as a mixture of cyclohexadienes formed by thermal dehydration. Dehydration has been observed invariably as a side reaction during the pyrolytic decomposition of β-hydroxyolefins.

EXPERIMENTAL

Pyrolysis of 1-phenyl-4-ethylhexen-1-ol-4-d (I). The undeuterated alcohol[1] (17 g.) was dissolved in dry ether (25 ml.) and shaken successively with four portions (1 g. each) of essentially pure deuterium oxide. The etheral solution was dried (sodium sulfate) and distilled to give a quantitative yield of product, b.p. 115–117°/1 mm. This material showed extremely weak absorption in the hydroxyl region, but strong absorption in the 3.7–3.9μ region expected for the —O—D stretching vibration.[6] From the ratio of intensities of the absorption bands, it was estimated that the exchange reaction had occurred to the extent of 90–95%. This material was pyrolyzed (500°), as described earlier, for the undeuterated alcohol[1] to give allylbenzene (b.p. 156°) and pentanone-3 (b.p. 101–102°) in 72% yield. The infrared spectrum of the pentanone-3 was identical with that of

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[1] R. T. Arnold and G. Smolinsky, *J. Am. Chem. Soc., in press.*

[2] All infrared spectra reported in this paper were measured on CCl_4 solutions.

[3] A. Streitwieser and J. R. Wolfe, *J. Am. Chem. Soc.*, **79**, 904 (1957).

[4] R. D. Shutz and F. W. Millard, *J. Org. Chem.*, **24**, 297 (1959).

[5] R. Breslow, *J. Am. Chem. Soc.*, **80**, 3722 (1958).

[6] A. Weissberger, *Technique of Organic Chemistry*, Interscience Publishers, Inc., New York, Vol. IX, p. 333.

an authentic sample, and no bands attributable to deuterium could be detected. The allylbenzene fraction, however, showed —C—D stretching bands at 4.7μ as well as differences in the 7–13μ region[3,4] when compared with an authentic undeuterated sample of allylbenzene. The strong absorption bands at 10.04μ and 10.91μ[7] were identical in the deuterated and undeuterated samples of allylbenzene indicating the absence of any appreciable =CHD in the former compound. Oxidative degradation of the deuterated allylbenzene (630 mg.) with ozone in ethyl acetate afforded phenylacetic acid (m.p. 74–76°) whose infrared spectrum—compared with authentic undeuterated phenylacetic acid—exhibited differences in the 7–12μ region characteristic of deuterium containing analogs.

Octene-1-1-d (V). Lithium metal (1.38 g.) and 1-bromooctene[8] (20 g.) were allowed to react in ether solution as previously described.[1] The resulting lithium octenyl solution was decomposed with deuterium oxide (4 ml.). The ether solution was dried (sodium sulfate) and fractionated to give octen-1-1-*d*. Yield 7 g. (60%); b.p. 121°; n_{D}^{25} 1.4078. Reported[9] for 1-octene, b.p. 121–122°; n_{D}^{19} 1.4085. The intensity of the out-of-plane bending vibrations at 10.1μ and 10.9μ for octen-1-1-*d* were approximately one half of those found in 1-octene. Our sample of octen-1-1-*d* showed the expected —C—D stretching band at 4.5μ.[3]

Pyrolysis of cyclohexen-3-ol-1 (*VI*). The procedure of Owen and Robins[10] was used in the preparation of this unsaturated alcohol. Cyclohexen-3-ol-1 (7.5 g.) was added dropwise to the pyrolysis tube at 500° in an atmosphere of nitrogen using the procedure normally employed.[1] The infrared spectrum of the condensate showed no carbonyl bands. Fractionation of this material gave a small forerun (0.6 g., 9%)—presumably a mixture of cyclohexadienes and starting material (5.45 g., 73%, b.p. 160–163°, n_{D}^{25} 1.4840). The nonvolatile residue weighed 0.45 g.

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(7) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, 1954, p. 39.

(8) G. B. Bachman, *J. Am. Chem. Soc.*, **55**, 4279 (1933).

(9) M. A. Kirrmann, *Bull. soc. chim. France*, [4] **39**, 990 (1926).

(10) L. N. Owen and P. A. Robins, *J. Chem. Soc.*, 320 (1949).

An Attempt to Synthesize 3,5-Diphenylbenzocyclopentatriene, a Cyclic Allene

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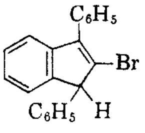
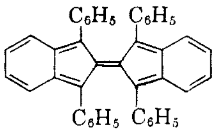
1,2-Cycloheptadiene has been prepared, but attempts to obtain 1,2-cyclohexadiene have led only to polymers.[1]

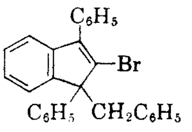
Considerable distortion, both bending and twisting, would be involved if the allenic system were present in the still smaller five-membered ring. In spite of this, it was considered of interest to discover what would happen if the sodio derivative of 2-bromo-1,3-diphenylindene (I) were prepared, for the heavy substitution might inhibit polymerization of the expected cyclic allene. If the allene could not be isolated, it was considered possible that a dimer (II) might be isolated, and this would be of interest since such a dimer has the structure originally proposed for rubrene,[2] and unsuccessful attempts to synthesize a compound having this structure have been reported.[3]



I



II



III

Surprisingly, it has now been found that the anion of 2-bromo-1,3-diphenylindene shows no tendency to eliminate a bromide anion. When the indene was added to sodium *iso*-propoxide in *iso*-propyl alcohol, a bright yellow solution resulted, and no sodium bromide was formed when this solution was boiled for thirty minutes. That the anion was present was shown by addition of benzyl chloride. This caused immediate disappearance of the yellow color and formation of 1-benzyl-2-bromo-1,3-diphenylindene (III) in nearly quantitative yield. The benzyl derivative was identical with the product of bromination of 1-benzyl-1,3-diphenylindene.

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EXPERIMENTAL

2-Bromo-1,3-diphenylindene (I). Bromination of 1,3-diphenylindene has been investigated previously[4] but the 2-bromo derivative has not been reported. It was obtained easily in nearly quantitative yield by adding 3.2 g. of bromine in 5 ml. of carbon tetrachloride to a cooled solution of 5.3 g. of 1,3-diphenylindene in 20 ml. of carbon tetrachloride. The solvent was then removed by distillation and the residue was heated at 100° under reduced pressure for a few minutes. Solution in hexane and chromatography over alumina gave 6.55 g. of colorless oil which solidified completely when it was rubbed with ether-hexane at −70°. Recrystallization from hexane furnished prisms, m.p. 66–68°.

Anal. Calcd. for $C_{21}H_{15}Br$: C, 72.6; H, 4.3. Found: C, 72.5; H, 4.5.

Oxidation of the bromo compound with chromic acid in acetic acid gave *o*-dibenzoylbenzene identified by mixed melting point and infrared spectrum.

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(1) A. Favorsky and N. A. Domnin, *Bull. Soc. Chim.*, (4) **3**, 1727 (1936); N. A. Domnin, *J. Gen. Chem.* (*U.S.S.R.*), **15**, 461 (1945); *Chem. Abstr.*, **40**, 4682 (1946); *Vestnik Leningrad Univ.*, **I**, No. 3, 103 (1946); *Chem. Abstr.*, **42**, 3337 (1948).

(2) C. Moureu, C. Dufraisse, and A. Willemart, *Compt. rend.*, **187**, 266 (1928); Dufraisse and Loury, *Compt. rend.*, **194**, 1832 (1932).

(3) J. C. Eck and C. S. Marvel, *J. Am. Chem. Soc.*, **57**, 1898 (1935); C. F. Koelsch and H. J. Richter, *J. Am. Chem. Soc.*, **57**, 2010 (1935).

(4) R. Weiss and S. Luft, *Monatsh.* **48**, 337 (1927); C. Dufraisse and L. Enderlin, *Bull. Soc. Chim.* (5) **1**, 267 (1934).