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## Thermal Rearrangement of Tetrachloro-2*H*-pyran-2-one to Trichloro-2-furoyl Chloride

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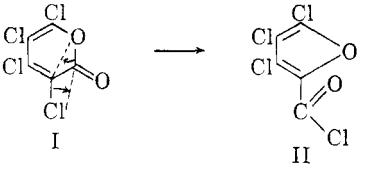
Prolonged heating of tetrachloro-2*H*-pyran-2-one (I)[1] was observed to yield a lower boiling product of the same empirical formula ($C_5Cl_4O_2$). This product has been proved to be the hitherto unreported trichloro-2-furoyl chloride (II). The structure was established by hydrolysis to the known acid, ammonolysis to the known amide, and alcoholysis to the known ethyl ester. Since these compounds have previously been accessible only in poor yield *via* chlorination of ethyl furoate,[2] the present method offers an advantageous route to trichloro-2-furoic acid and its derivatives.

The reaction, which does not require a catalyst, may be viewed as an intramolecular rearrangement favored by the formation of the aromatic furan ring. No evidence could be found (by infrared



I II

examination) for the reverse reaction in the temperature range used for the rearrangement.

### EXPERIMENTAL

The reaction was carried out in a 3-l. flask fitted with a 4-ft. fractionating column packed with glass helices and fitted with a still head having provision for control of the reflux ratio. In this apparatus, 3150 g. of tetrachloro-2*H*-pyran-2-one[1] (13.5 moles) was heated at reflux temperature for 1 hr. until the still head temperature dropped to about 177°. The reaction mixture was then distilled at 20:1 reflux ratio and the product taken off over the course of 36 hr. Except for a small foreshot distilling at 177°–228°, the vapor temperature was 228–234°. The distillation was stopped when the pot temperature reached 340°.

The colorless distillate, amounting to 2240 g., was found to contain 82% trichloro-2-furoyl chloride by comparison of its infrared spectrum with that of a purified specimen. Purification was effected by repeated recrystallizations from chilled hexane. The recrystallized trichloro-2-furoyl chloride melted at 34°.

*Anal.* Calcd. for $C_5Cl_4O_2$: C, 25.68; H, 0.00; Cl, 60.6. Found: C, 25.56; H, 0.11; Cl, 60.2.

*Infrared bands (positions given in microns).* Tetrachloro-2*H*-pyran-2-one (I): 5.59 (s), 5.66 (vs), 7.80 (w), 8.14 (s), 9.10 (w), 9.15 (w), 9.47 (w), 10.77 (m), 11.84 (m), 13.44 (m), 13.74 (m) in carbon disulfide; double bond stretching bands at 6.29 (m), 6.64 (m) in carbon tetrachloride.

Trichloro-2-furoyl chloride (II): 5.68 (s), 5.76 (m), 5.82 (m), 7.40 (s), 7.95 (m), 8.07 (w), 9.15 (m), 9.69 (w), 9.87 (w), 11.38 (w), 11.64 (vs), 14.49 (w), 14.89 (m) in carbon disulfide; double bond stretching bands at 6.30 (m), 6.42 (shoulder), 6.16 (shoulder) in potassium bromide disc.

*Characterization of the acid chloride* (II). The purified acid chloride was dissolved in aqueous acetone followed by partial evaporation of the acetone, to obtain a substantially quantitative yield of trichloro-2-furoic acid, m.p. 174–175°. By dissolving the acid chloride in excess ethanol followed by evaporation to dryness, there was obtained a nearly quantitative yield of ethyl trichloro-2-furoate, m.p. 63°. By passage of dry ammonia through a solution of the acid chloride in benzene for 1 hr. at room temperature, filtration of the precipitated solids, extraction of the ammonium chloride therefrom by water, and recrystallization of the remaining solid from ethanol, there was obtained a nearly quantitative yield of trichloro-2-furamide, m.p. 161°. These products were shown by infrared and mixed melting points to be identical to trichloro-2-furoic acid, ethyl trichloro-2-furoate, and trichloro-2-furamide prepared by the procedures of Hill and Jackson.[2]

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(1) A. Roedig and G. Märkl, *Ann.*, **636**, 1–18 (1960); H. M. Hill (to Eastman Kodak Co.), U. S. Patent **2,629,681** (1949); *Chem. Abstr.*, **47**, 5066 (1953).

(2) H. B. Hill and L. L. Jackson, *Am. Chem. J.*, **12**, 112–130 (1890).

## Pyrolysis of β-Hydroxy Olefins. IV. The Synthesis of Long-Chain Unsaturated Ketones

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Previous publications[5–7] from this laboratory have demonstrated that β-unsaturated secondary alcohols can be pyrolyzed at temperatures in the range of 500° to yield olefinic substances and aldehydes. Cyclic alcohols yield ω-olefinic aldehydes. The cyclic transition state mechanism[6] invoked to rationalize these transformations predicts that β-unsaturated tertiary alcohols should yield ketones when pyrolyzed.

Specifically, 2-(1′-cyclohexenyl)cyclohexanone

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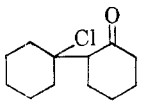
(5) R. T. Arnold and G. Smolinsky, *J. Am. Chem. Soc.*, **81**, 6443 (1959).

(6) R. T. Arnold and G. Smolinsky, *J. Org. Chem.*, **25**, 129 (1960).

(7) R. T. Arnold and G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 4918 (1960).

(II) was prepared by dehydrohalogenating[8] the hydrogen chloride condensate (I) of cyclohexanone.[9] Compounds III and IV were prepared by treating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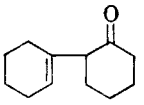
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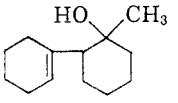
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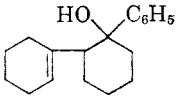
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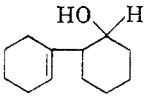
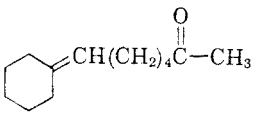

V

II with methylmagnesium iodide and phenylmagnesium bromide, respectively. Compound V was prepared by reducing II with sodium borohydride. No adduct alcohol was obtained when *n*-butylmagnesium bromide or *n*-butyllithium was treated with II. The pyrolyses of compounds III and IV proceeded smoothly to yield VI and VII and were essentially complete (infrared) under previously described conditions.[5] The pyrolysis of V, however,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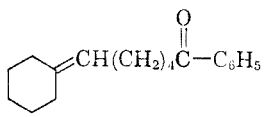
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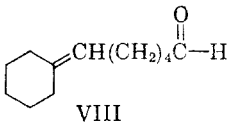
VIII

was incomplete (infrared) under these conditions, and even at 520–530°, the conversion to the aldehyde VIII was only to the extent of 56%, as indicated by vapor phase chromatography (Perkin-Elmer 154, Tide column). Compound VIII reacted with bisulfite quite readily.

The most significant aspect of this work is the fact that it has been demonstrated that β-unsaturated tertiary carbinols can be pyrolyzed to their corresponding ketones. The oxidation of any convenient β-hydroxyolefin to its corresponding ketone and subsequent reaction with various Grignard reagents followed by the pyrolysis of the resulting tertiary alcohols affords a method of preparation of a wide variety of long-chain ketones.

## EXPERIMENTAL

*Preparation and pyrolysis of 2-(1′-cyclohexenyl)cyclohexanol.* 2-(1′-Cyclohexenyl)cyclohexanone (35.2 g.) was dissolved in 70 ml. of 95% ethanol. The solution was cooled in an ice bath and 23 g. of sodium borohydride was added with stirring. The solution was removed from the ice bath and when the initial yellow color disappeared, 70 ml. of water was added. The reaction mixture was then placed on a steam bath for 1 hr. in order to hydrolyze the excess borohydride and boil off some of the ethanol.

The reaction mixture was allowed to cool and was extracted with two 25-ml. portions of ethyl ether. After drying over sodium sulfate and evaporation of the ether, 35.5 g. of product was obtained. Infrared analysis indicated that the carbonyl-carbinol conversion was essentially complete. The product was distilled on a spinning band column (b.p. 90° at 1 mm.) and vapor phase analysis indicated that it was essentially a mixture of the two *cis-trans* isomeric alcohols in the ratio of 11:1.

*Pyrolysis.* 2-(1′-Cyclohexenyl)cyclohexanol (32.5 g.) was pyrolyzed at 520°–530°; 27.5 g. of product was recovered and carefully fractionated on a spinning-band column. After 1 g. of forerun, 22.5 g. of product (b.p. 90° at 1 mm.) was collected, leaving behind 4 g. of residue. The infrared analysis of the main fraction indicated that pyrolysis was not complete. A dinitrophenylhydrazone was prepared and recrystallized from methanol three times (m.p. 31°).

*Anal.* Calcd.: C, 59.98; H, 6.71. Found: C, 59.98; H, 6.55.

Its analysis substantiated expectation that the pyrolysis of 2-(1′-cyclohexenyl)cyclohexanol would result in 6-cyclohexylidene hexaldehyde.

Two grams of the dinitrophenylhydrazone was treated with a large excess of levulinic acid.[10] After the work-up and distillation, .65 g. of pure 6-cyclohexylidene hexaldehyde was isolated ($n_D^{25}$ 1.4247).

*Preparation and Pyrolysis of 1-methyl-2-(1′-cyclohexenyl)-cyclohexanol to 7-cyclohexylidene heptane-2-one.* Methyl iodide (14.2 g.) was dissolved in three times its volume of ethyl ether. Magnesium turnings (3.2 g.) were then added and after the reaction subsided, 17.8 g. of 2-(1-cyclohexenyl)-cyclohexanone dissolved in an equivalent volume of ether was added slowly with stirring. After 0.5 hr., water was added slowly with stirring and then dilute hydrochloric acid until all the magnesium salts had dissolved. The mixture was extracted with ethyl ether, the ethyl ether extracts were dried over sodium sulfate, and the ether was evaporated. The residue gave upon spinning-band distillation 13.5 g. (64% based on the ketone) of a fraction boiling at 80° at 4 mm., $n_D^{25}$ 1.5058. The material did afford satisfactory analytical data.

*Anal.* Calcd.: C, 81.2; H, 10.5. Found: C, 79.8; H, 11.2.

*Pyrolysis.* The alcohol (12 g.) was pyrolyzed at 500°. A product (11 g.) boiling at 85° at 4 mm. was obtained, $n_D^{24}$ 1.4797.

*Anal.* Calcd.: C, 81.2; H, 11.5. Found: C, 80.6; H, 11.3.

The infrared indicated that the carbonyl-carbinol conversion was essentially complete. The product gave a positive iodoform test. A semicarbazone derivative was prepared, m.p. 147°, from which an analytical sample was made up (recrystallized from ethanol three times).

*Anal.* Calcd.: C, 66.89; H, 10.02. Found: C, 66.97, H, 10.00.

*Preparation and pyrolysis of 1-phenyl-2-(1′-cyclohexenyl) cyclohexanol to 6-cyclohexylidene-1-phenylhexan-1-one.* The synthesis of this compound has been described by Rapson.[8] Five grams of this substance was pyrolyzed in the usual manner. Three and one-half grams of a ketone (infrared), b.p. 114° at 15 mm, was obtained after careful distillation employing a spinning band column ($n_D^{24}$ 1.5381).

*Anal.* Calcd.: C, 84.32; H, 9.31. Found: C, 84.46; H, 9.36.

A dinitrophenylhydrazone was prepared and recrystallized three times. It melted sharply at 111°.

*Anal.* Calcd.: C, 65.88; H, 6.7. Found: C, 65.78; C, 6.23.

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(8) W. S. Rapson, *J. Chem. Soc.*, 16 (1941).
(9) O. Wallach, *Ber*, 40, 70 (1907).
(10) C. H. DePuy and B. W. Ponder, *J. Am. Chem. Soc.*, 81, 4629 (1959).