G31) and the Research Corp. for mutual support of this work and to the National Institutes of Health for a graduate fellowship (GF 11801).

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

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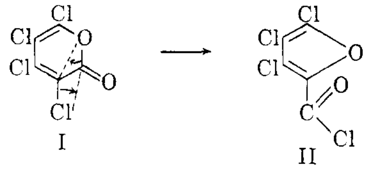
*Received July 17, 1961*

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



I II

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

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*Received May 29, 1961*

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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