2,4-Bis(pentafluorophenyl)-3-chlorofuran

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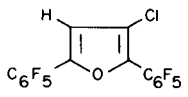
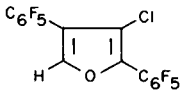
We have been interested in the preparation of some thermally stable heterocyclic compounds containing polyhalogenated groups. One approach is through polyhalogenated acetophenones, of which we have prepared 2-chloro-2′,3′,4′,5′,6′-pentafluoroacetophenone and 2,2′,3′,4′,5′,6′-hexachloroacetophenone *via* polyhaloaryl copper compounds (2-4).

Pentafluorophenylcopper or its complex was prepared by the reaction of pentafluorophenyllithium and copper (I) chloride. Treatment of pentafluorophenylcopper with chloroacetyl chloride afforded 2-chloro-2′,3′,4′,5′,6′-pentafluoroacetophenone in 48% yield. In this reaction we have also isolated a small quantity of a neutral compound (containing chlorine), m.p. 129°, whose IR spectrum did not show any strong band corresponding to the carbonyl group. The NMR spectrum in carbon tetrachloride showed a singlet at 2.22 τ which could be assigned to the α-proton of a furan. The UV spectrum in ethyl alcohol showed absorptions at 214 mμ (log ϵ, 4.23) and 261 mμ (log ϵ, 4.14). It has been reported (5) that 2,5-bis(pentafluorophenyl)furan shows UV absorption at 310 mμ (log ϵ, 4.482). It has also been reported (6) that 2,5-diphenylfuran shows UV absorptions at 226 and 324 mμ, while 2,4-diphenylfuran shows UV absorptions at 242 and 277 mμ. The mass spectrum indicated the molecular weight to be 435 (calcd. 434.4). Of the two isomeric structures I and II, the spectral data is consistent with structure II.



I



II

Treatment of pentachlorophenylcopper with chloroacetyl chloride afforded only 2,2′,3′,4′,5′,6′-hexachloroacetophenone. No 2,4-bis(pentachlorophenyl)-3-chlorofuran could be isolated.

The formation of 2,4-bis(pentafluorophenyl)-3-chlorofuran is a novel reaction in which the α-haloketone is undergoing a self condensation probably in the presence of copper salts and ammonia. In the preparation of 2-chloro-2′,3′,4′,5′,6′-pentafluoroacetophenone when ammonia was not used in the work-up the furan (II) could not be isolated. In the above preparation, a pyrrole could not be isolated when ammonia had been used in the work-up.

The Feist-Benary (7-8) synthesis of furans involves the base-catalysed condensation of an α-haloketone with a β-ketoester. Sodium hydroxide, pyridine or ammonia can be used as the basic catalyst (9-10), but if ammonia is used, the conditions approximate those of the Hantzsch pyrrole synthesis (11) and both furans and pyrroles can be formed. In some condensations (chloroacetone, acetonedicarboxylic ester and ammonia), a furan derivative seems to be the major product (12-13).

We were not able to convert 2-chloro-2′,3′,4′,5′,6′-pentafluoroacetophenone into the furan (II) by using the basic catalysts generally used in the Feist-Benary synthesis of furans such as aqueous sodium hydroxide, pyridine or ammonia. Simple heating of 2-chloro-2′,3′,4′,5′,6′-pentafluoroacetophenone did not give the furan (II).

It is interesting to note that α-haloketones are very sensitive towards bases (14-15). In particular, reactions of 2-chloroacetophenone with sodium hydroxide, pyridine and ammonia may be noted (16-20).

The furan (II) shows promising thermal stability.

EXPERIMENTAL

Preparation of 2-chloro-2′,3′,4′,5′,6′-pentafluoroacetophenone.

Pentafluorophenyllithium (0.1 mole) was prepared from pentafluorobenzene and *n*-butyllithium at -78° in THF. Copper (I) chloride was added and the mixture was stirred for sixteen hours to give pentafluorophenylcopper or its complex. Chloroacetyl chloride (11.6 g., 0.11 mole) in ether (30 ml.) was slowly added at -10° and stirring was continued for six hours. The reaction mixture was hydrolyzed with water, and copper salts were removed by treatment with aqueous ammonium chloride and ammonium hydroxide solution. Drying of the ether layer over anhydrous

sodium sulphate and removal of volatile material left an amber colored liquid (15.5 g.) which upon distillation under reduced pressure gave 2-chloro-2′,3′,4′,5′,6′-pentafluoroacetophenone (11.5 g., 48%), b.p. 46-47°/1 mm. Infrared cm^{-1} (liquid film), 1000 (C-F), 1500 and 1520 (aromatic ring), and 1720 (C=O in α-haloketones).

Anal. Calcd. for $C_8H_2ClF_5O$: C, 39.22; H, 0.8. Found: C, 39.72; H, 0.76.

Isolation of 2,4-Bis(pentafluorophenyl)-3-chlorofuran.

The residue, left after distillation of 2-chloro-2′,3′,4′,5′,6′-pentafluoroacetophenone, upon crystallization from ethyl alcohol afforded a solid (0.5 g., 2%), m.p. 129°. This has been identified as 2,4-bis(pentafluorophenyl)-3-chlorofuran. UV λ max (ethanol), 214 (log ε, 4.23) and 261 mμ (log ε, 4.14); infrared cm^{-1} (carbon tetrachloride), 1000 (C-F), 1510 and 1520 (aromatic ring); NMR (carbon tetrachloride), singlet at 2.22 τ.

Anal. Calcd. for $C_{16}HClF_{10}O$: C, 44.2; H, 0.23. Found: C, 44.6; H, 0.85.

Screening of the furan (II) for thermal stability.

The initial melting point in a small (1″) sealed capillary tube was 128-129°. No gas bubbles were observed until 230°, but liquid condensed in the upper parts of the capillary. At 278°, the liquid became pale yellow and at 320° was dark brown. The furan (II), upon heating to 265° and allowing to cool until the liquid solidified, remelted at 129°.

Preparation of 2,2′,3′,4′,5′,6′-hexachloroacetophenone.

Pentachlorophenylcopper or its complex (0.1 mole) was prepared from pentachlorophenyllithium and copper (I) chloride in THF. Chloroacetyl chloride (11.6 g., 0.11 mole) in ether (30 ml.) was added slowly at -10° and stirring was continued for six hours. The reaction mixture was hydrolyzed with water, and copper salts were removed by treatment with ammonium hydroxide and ammonium chloride. Drying the ether layer and removal of volatiles afforded 2,2′,3′,4′,5′,6′-hexachloroacetophenone (25.5 g., 78%), m.p. 140-142°. Crystallization from ethanol gave the pure compound (14.5 g., 44%), m.p. 143-144°. Infrared cm^{-1} (nujol), 1740 (C=O group of α-haloketone); NMR (deuteriochloroform), a singlet at 5.42 τ.

Anal. Calcd. for $C_8H_2Cl_6O$: C, 29.3; H, 0.61. Found: C, 29.78; H, 0.89.

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