The Degradation of Resorcinol

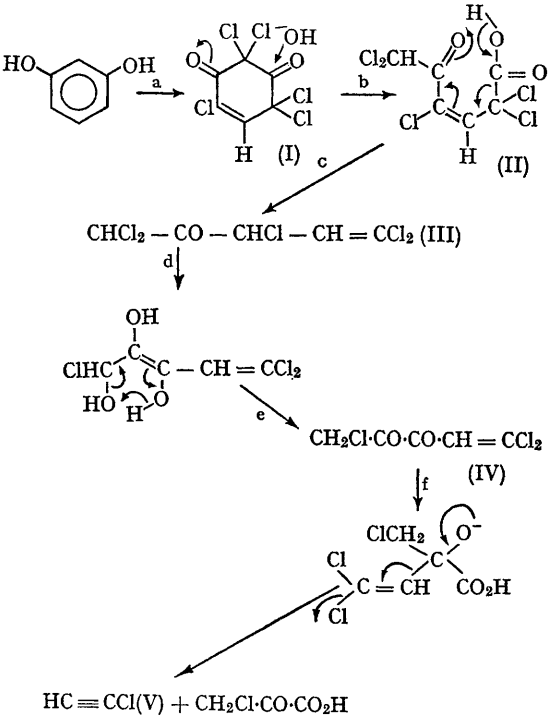
By C. J. MOYE

(*Riker Research Laboratories, P.O. Box* 122, *Hornsby, Sydney, Australia*)

PENTACHLORORESORCINOL (2,2,4,6,6-pentachlorocyclohex-4-ene-1,3-dione), (I), m.p. 92°, *m/e* 280 (5 chlorines) and single ^{1}H n.m.r. signal* at 449 c./sec., may be obtained in 90% yield by the chlorination of resorcinol in chloroform. It is unstable in aqueous media, and here we report the results of a re-investigation of Zincke's[1] original work on this decomposition.

Cold water rapidly transforms pentachlororesorcinol into a dihydrate (*cf.*, chloral hydrate), and then slowly into an acid, m.p. 122°, which decarboxylates very readily and shows uncoupled protons at 373 c./sec. ($-CHCl_2$) and 405 c./sec. (vinylic proton). The mass spectrum has a base peak at *m/e* 44 and a major peak at *m/e* 254 ($M^+ - CO_2$). The molecular ion is absent, but the presence of five chlorines is confirmed in the decarboxylation peak, and the cracking pattern is in accord with the acid being 2,2,4,6,6-pentachloro-5-oxohex-3-enoic acid (II); in particular the fragments at *m/e* 171 and 111 which would result from cleavage on either side of the carbonyl group, are obtained.

Compounds (I) and (II) decompose rapidly in boiling water to give a steam-volatile oil which may be readily separated into two products which we have formulated as 1,1,3,5,5-pentachloropent-4-en-2-one (III) and 1,5,5-trichloropent-4-ene-2,3-dione (IV); m.p. 85°, λ_{max} 251 mμ, ϵ 11,150. That compound (III) is the decarboxylation product of (II), is confirmed by mass spectrometry [M^+ at *m/e* 254; 5 chlorines, and main peaks at *m/e* 171; 254 $-$ 83 ($CHCl_2$) and *m/e* 108 ($-\overset{+}{C}H-CH=CCl_2$)], a ^{1}H n.m.r. spectrum due to three protons, two of which are coupled (H_A, 378 c./sec.; H_B, 341 c./sec.; J_{AB} = 9·8 c./sec.; and H_X, 383 c./sec.) and lack of significant absorption in the ultraviolet above



a; Cl_2,$CHCl_3$. b; OH^-,H_2O, Tautomerise. c; $-CO_2$, Tautomerise. d; $+2OH^-$, $-2Cl^-$. e; $-H_2O$, Tautomerise. f; Benzylic acid rearrangement.

* N.m.r. spectra recorded on a Varian A60 instrument with tetramethylsilane as internal reference.

220 mμ. Structure (IV) follows from the compounds ready formation of a quinozaline (which has a characteristic mass spectral fragmentation pattern[2]) and its transformation by strong base[1] into chloroacetylene. It possesses a ^1H n.m.r. spectrum consisting of two uncoupled signals [proton ratio 2 : 1; J_A = 281 c./sec.; (−CH_2Cl) and J_B = 451 c./sec. (=C=CH—)] and a mass spectrum having (besides other less important features) a M^+ at m/e 200 (3 chlorines) and peaks at m/e 123 and 77, corresponding to direct cleavage of the α-diketone.

Since compound (III) is transformed slowly into (IV) in boiling water and more rapidly if trichloroacetic acid is added, it would appear that (III) is an intermediate in the transformation of (II)→ (IV). The mechanism suggested for this transformation has some precedent in the literature,[3] but loss of HCl instead of H_2O would give the same result.

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[3] C. Neuberg and E. Kansky, *Biochem. Z.*, 1909, **20**, 461.