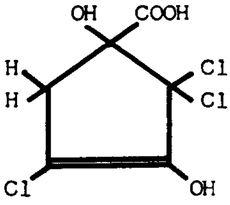
Tetrahedron Letters No.35, pp. 2411-2417, 1964. Pergamon Press Ltd.
Printed in Great Britain.

THE DEGRADATION OF AROMATIC RINGS:
THE ACTION OF HYPOCHLORITE ON PHENOL.

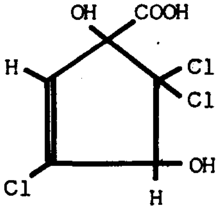
C.J. Moye,
C.S.R. Research Laboratories, Box 39 P.O., Roseville,
and S. Sternhell,
Department of Organic Chemistry, The University of Sydney,
Sydney, N.S.W., Australia.

(Received 7 July 1964)

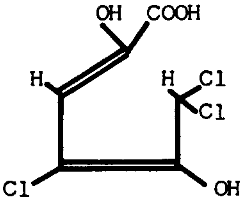
The reaction of phenol with alkaline hypochlorite, and various transformations of the resulting product were investigated by Hantzsch,[1.] but certain of the structures Ia, b or c, II and III assigned to the series of compounds appeared to be unlikely on mechanistic grounds.



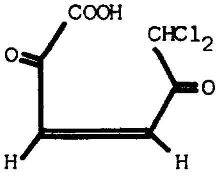
Ia



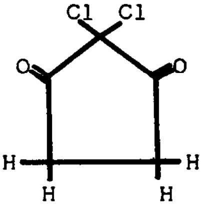
Ib



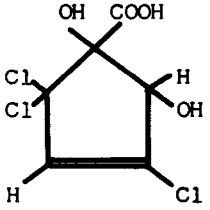
Ic



II



III



IV

In view of the industrial importance of chlorinated phenolics, as well as the potential usefulness of the reaction as a degradative tool in biosynthetic studies,[2.] we decided to re-investigate this work.

Treatment of phenol with strongly alkaline hypochlorite solution gave varying yields (up to 35%) of an acid which was isolated as its ammonium salt. The free acid (m.p. 175-6°C), identical with the product obtained by Hantzsch,[1.] analysed for $C_6H_5O_4Cl_3$ and was further characterised as its methyl ester and diacetate. Neither the acid nor its methyl ester showed any characteristic absorption above 220 mu in the Ultra-violet and the infra-red spectrum of the acid in nujol mull showed strong absorption at 810, 840, 855, 900, 1,060, 1,100sh, 1,130, 1,190, 1,240, 1,275, 1,300, 1,625, 1,725 and 3,350 (doublet) cm^{-1}. The p.m.r. spectrum of the ester[a] ($CDCl_3$) showed two doublets at 352 and 292 c/s (J - 1.3 c/s) of one proton intensity each, a singlet at 231 c/s of 3 protons intensity and a broad signal due to two labile protons[3.] near 250 c/s. The p.m.r. spectrum of the acid (in D_2O) showed the presence of an AB system similar to that present in the ester with signals at 367 c/s and 313 c/s (J - 1.8 c/s).

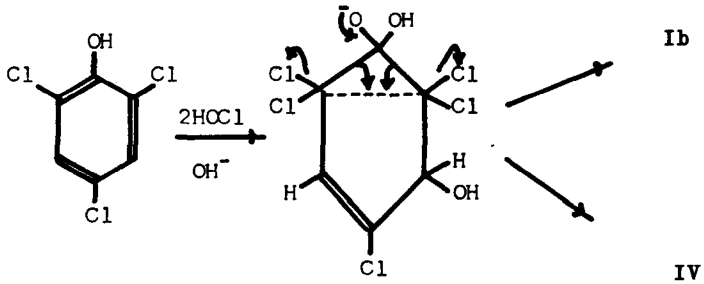
---

[a] The p.m.r. spectra were recorded on an A60 spectrometer in deuteriochloroform or deuterated water with tetramethylsilane or sodium trimethylsilylpropiosulphonate as internal reference.

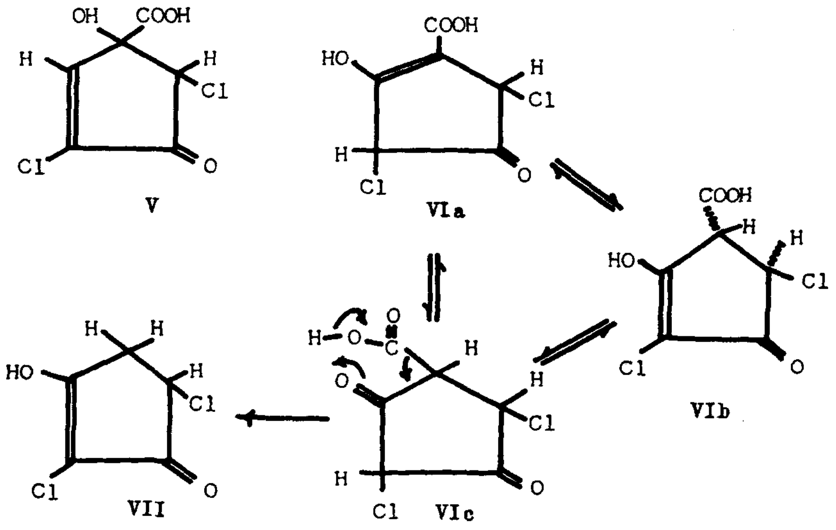
Hantzsch found that 2,4,6-trichlorophenol was an intermediate to the formation of the acid, and assigned structure Ia to it, with Ib and Ic as less likely alternatives. The p.m.r. evidence excludes structure Ia which does not possess allylic-coupled protons,[4] while structure Ic is incompatible with the U.V. spectrum.

We believe that structure Ib is the correct structure for the acid, but in attempting to formulate a mechanism for its formation, had also to consider a further alternative structure IV

Compounds Ib and IV could arise from 2,4,6-trichlorophenol by the addition of hypochlorous acid (or its equivalent) to two double bonds of the trichlorophenol, followed by ring contraction via a mechanism related to the benzylic acid rearrangement. This mechanism is also in accord with products of the degradation of chloranilic acid[5] and catechol[6]. Grounds



for rejecting structure IV will be fully presented elsewhere, but depend partly on subsequent transformation products obtained by Hantzsch. Hantzsch obtained a compound (assigned structure II) by reaction of the acid Ib with concentrated sulphuric acid at room temperature, and a further compound (assigned structure III) by pyrolysis of Compound II. Compound Ib is transformed slowly into Compound II (30 minutes) and we observed the formation of an intermediate by p.m.r. spectroscopy. It had signals (in D_2O) corresponding to two uncoupled protons at 422 c/s and 304 c/s and labile protons ($CDCl_3$) at 360 c/s. This evidence is compatible with structure V which could result from Compound Ib by loss of hydrogen chloride. The intermediate isomerised in sulphuric acid to Compound II, which we obtained in 80% crude yield (m.p. 151-2°C) by prolonged treatment of Compound Ib with concentrated sulphuric acid. Hantzsch assigned the structure II to this compound, but its U.V. spectrum (λmax : 276 mu; ϵ - 8,700) excluded this structure. A more likely structure is VI, resulting from protonation of the carbonyl of V, double bond migration and a 1,2-oxotropic shift via a protonated epoxide. The product would thus contain a beta-diketone system capable of enolising in a variety of ways, and further evidence to support this structure was obtained by p.m.r. and I.R. spectroscopy. The p.m.r. spectrum of the acid (in D_2O) showed an AB system of two protons at 291 c/s and 242 c/s coupled with J - 2.7 c/s. This coupling is far too small for the vinylic system present in II but would be accomodated by the system present in the tautomer VIb. Although the beta-diketone system can enolise in a large number of ways, the preferred direction would be one of the two ways leading to an -OH beta to the carboxylic acid group and subsequent H-bonding. The I.R. spectrum in chloroform solution shows two carbonyl bands at 1730 (aliphatic acid) and 1655cm^{-1} (enolic beta-diketone in 5-membered ring), while the I.R. spectrum in nujol mull has an additional carbonyl band at 1705 cm^{-1} (α-β unsaturated acid). This suggests that in solution the compound exists as VIb, while in the solid form it exists as a tautomeric mixture of VIa and VIb. The observed[1]. stability of this "beta" keto-acid to decarboxylation is also in accord with structures VIa and b as decarboxylation of beta-keto acids proceeds through the beta-carbonyl (VIc) and not the beta-enol form[7].



We obtained the decarboxylation product (m.p. 118°C) by sublimation of VI under reduced pressure with heating. Hantzsch[1.] assigned structure III to this compound, but this was excluded by its characteristic absorption in the U.V. at 272 mu (ε- 11,750). It would seem most likely that the chromophore of compound VI had been preserved during pyrolysis. The p.m.r. spectrum of the material (in $CDCl_3$) consisted of a signal due to one labile proton (broad at approximately 400 c/s) and a simple 3 proton ABX system with H_X : 267 c/s, H_A : 223 c/s, H_B : 175 c/s, J_{AB} : 17 c/s, J_{AX} : 6.3 c/s, J_{BX} : 2.5 c/s. This also clearly excluded structure III. From the above evidence however, we propose that the structure of this compound is VII, which is an isomer of III, and could be generated from VI by the mechanism shown. Further confirmatory evidence was obtained by mass spectrometry. The mass spectrum showed the molecular ion (m/e 166), with isotope peaks at (M+2) and (M+4)[8], which confirms the presence of two chlorine substituents, one of which is readily lost to give the base peak at m/e 131.

The structures of an analogous series of compounds obtained from the reduction product of I by Hantzsch[1.] may readily be deduced by their direct relationship to VI and VII.

Full details of this work and mechanistic implications will be described in the Australian Journal of Chemistry.

Acknowledgements

The authors wish to thank the Management of the Colonial Sugar Refining Co. Ltd. for permission to publish this work, R. Goldsack for technical assistance, and Dr. Gillis of The Defence Standards Laboratories, Melbourne for Mass Spectra.

References

1. A. Hantzsch, Ber. **20**, 2780, (1887)
   Ber. **22**, 1238, (1889).
2. C.J. Moye, Ph.D. Thesis (Manchester Uni.) 96-122, (1958).
3. a. L.M. Jackman, "Applications of N.M.R. to Organic Chemistry". Pergamon Press, London, (1959).
   b. H.M. Fales and A.V. Robertson, Tetrahedron Letters III, (1962).
4. D.J. Collins, J.J. Hobbs, and S. Sternhell, Aust. J. Chem. **16**, 1030, (1963)
5. A. Hantzsch, Ber, **21**, 2421, (1888)
   Ber, **25**, 827, (1892).
6. Th. Zincke and Fr. Küster, Ber. **21**, 2719, (1888)
   Ber. **23**, 2200, (1890).
7. E.S. Gould, "Mechanism and Structure in Organic Chemistry" Holt, Rinehart and Winston, New York, 346 ff. (1959).
8. J.H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry" Elsevier, Amsterdam, (1960), 298.