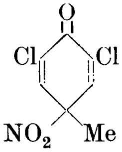
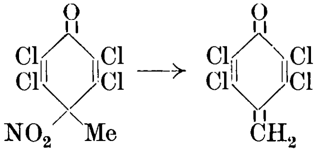
CCLXV.—*The Interaction of 2 : 6-Dichloro-4-methylquinitrol with Methyl and Ethyl Alcohols.*

By Edward Charles Snell Jones and James Kenner.

In a recent paper dealing with the decomposition of 2 : 6-diphenyl-6-nitrophenol (this vol., p. 1842), it was shown, on the one hand, that a substance of high molecular weight accompanied 2 : 6-diphenyl-*p*-benzoquinone as a product of the reaction, and on the other, that the reaction was comparable with the decomposition of quinitrols. Our interest was, therefore, aroused by a well-crystallised compound, $C_{15}H_9O_3Cl_3$, described by Zincke (*Annalen*, 1903, **328**, 261) as resulting from the decomposition of 2 : 6-dichloro-4-methylquinitrol (I) in boiling methyl-alcoholic solution, and which separated when the solution was allowed to cool. Not only had the nitrogen been entirely removed from the quinitrol in the form of methyl nitrite, but also two molecules of the quinitrol had been concerned in the formation of the new substance. A closer examination by Suhl (*Diss.*, Marburg, 1906; compare Zincke, *Ber.*, 1911, **44**, 186) revealed the presence of a methoxyl group, which apparently had taken the place of one of the four chlorine atoms originally present in the two molecules of the quinitrol. Taking into account Zincke's preparation of what was regarded as a tetrachloromethylene-*p*-benzoquinone (III) from (II), also by treatment with methyl alcohol, Suhl therefore concluded that the product represented a bimolecular compound in some way derived from (III).

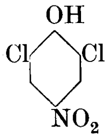


(I.)

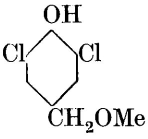


(II.) (III.)

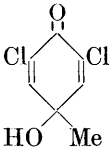
A repetition of Zincke's preparation enabled us to isolate, in addition to the compound in question, no fewer than four other products which remained in solution in the methyl alcohol, and could be separated owing to their different acidities. The first remained unidentified—it was a strongly acidic substance, which yielded purple solutions with the weakest alkali. The second was soluble in sodium bicarbonate solution, and was easily identified as 2 : 6-dichloro-4-nitrophenol (IV). The third, soluble in sodium carbonate, was 3 : 5-dichloro-4-hydroxybenzyl methyl ether (V), whilst the fourth, extracted by sodium hydroxide, was identical with the quinol (VI) prepared in the usual manner from the original quinitrol. From the neutral residue a further small quantity of Zincke's compound could then be isolated.



(IV.)

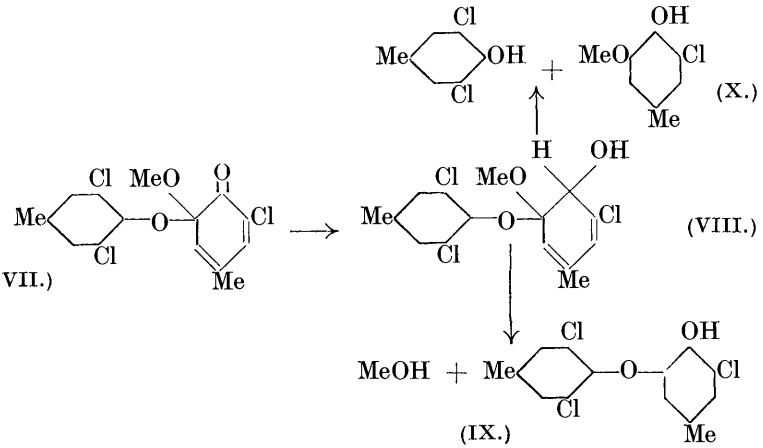


(V.)



(VI.)

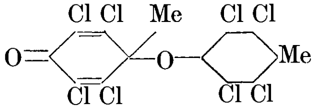
Analysis indicated that the molecule of this last compound contained two more hydrogen atoms than Zincke and Suhl had suggested, and, indeed, Zincke's own analyses favour the same conclusion. Furthermore, when Zincke's compound was treated with concentrated hydriodic or hydrobromic acid, iodine or bromine, respectively, was liberated at temperatures below 100°. This indicated the presence of a quinonoid oxygen atom, since not merely can quinone itself be determined quantitatively by means of dilute hydriodic acid (compare Willstätter and Majima, *Ber.*, 1910, **43**, 1172), but quinols also, *e.g.*, (VI), are reduced by both hydriodic and hydrobromic acid (Auwers, *Ber.*, 1912, **35**, 443). Further treatment with hydriodic acid yielded a small amount of 3 : 5-dichloro-*p*-cresol, and as main product a phenolic compound which was further characterised by its benzoyl derivative. These facts led us to regard Zincke's compound as 3′ : 5′ : 6-*trichloro*-2-p-*tolyloxy*-2-*methoxy*-4-*methyl*cyclo*hexa*-3 : 5-*dienone* (VII), which would pass on reduction in the first place to (VIII). From this, either 3 : 5-dichloro-*p*-cresol or methyl alcohol could be eliminated, and in the latter case 3 : 3′ : 5′-*trichloro*-5-p-*tolyloxy*-p-*cresol* (IX) would be produced. The elementary composition of our phenol and of its *benzoyl* derivative were in agreement with this formula.


(VII.) (VIII.) (IX.) (X.)

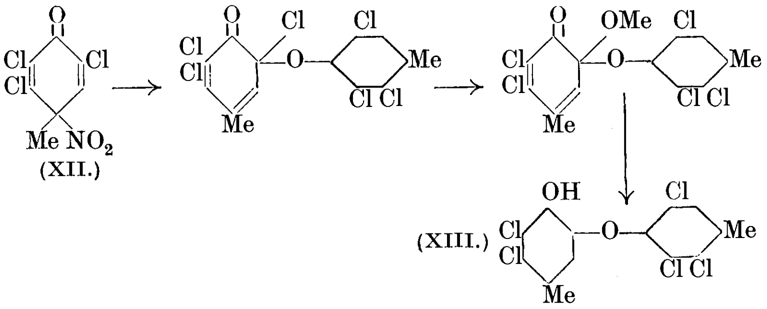
The only product unaccounted for in this scheme is (X), which would be produced in only small amount corresponding to that of the dichloro-*p*-cresol, and then undergo demethylation to a chloromethylcatechol, and so not be readily isolated from the mixture.

Zincke also studied the action of ethyl alcohol on his quinitrol, but merely recorded the formation of an oil in place of the crystalline product derived from methyl alcohol. A repetition of his experiment, however, has shown that an exactly parallel series of compounds is formed, the two methyl ethers being represented by the corresponding ethyl ethers. Of these, one agreed in properties and composition with those recorded for 3 : 5-dichloro-4-hydroxybenzyl ethyl ether by Mettler, who obtained it by electrolytic reduction of 3 : 5-dichloro-4-hydroxybenzoic acid in alcoholic solution (*Ber.*, 1906, **39**, 2940). The composition of the second compound agreed with that of the ethyl ether corresponding to (VIII), and this constitution followed from the isolation of 3 : 5-dichloro-*p*-cresol, together with (IX), after treating the compound with hydriodic acid.

Our conclusion agrees with that recorded by Pummerer and Cherbuliez (*Ber.*, 1914, **47**, 2964; 1919, **52**, 1395) in regard to Zincke's compound. The fact that its oxidising power is only half that required by the formula (III), and its agreement in properties with those of the dehydrophenols prepared by them by direct oxidation of phenols, led them to regard this compound as dehydrotetrachloro-*p*-cresol (XI).


(XI.)

The behaviour of the di- and tetra-chloroquinitrols is, therefore, initially the same, and the results only differ in the points of attachment selected by the respective radicals. The comparison shows that when a choice is possible, an ortho-quinolic is preferred to a para-quinolic structure, and this conclusion is further illustrated by the behaviour of 2 : 3 : 6-trichloroquinitrol (XII), from which Zincke (*loc. cit.*) obtained a crystalline product; Suhl (*loc. cit.*) assigned a molecular formula $C_{15}H_9Cl_5O_3$ to this product, and converted it by treatment with hydriodic acid into a phenol, $C_{14}H_9Cl_5O_2$. Allowance being made for the addition of two hydrogen atoms to the molecular formula of the initial product, as was shown to be necessary in the case of the dichloro-derivative, the results accord with the scheme :


(XII.)

(XIII.)

It should be added that Suhl characterised his phenol, to which we assign the formula (XIII), by its acetyl derivative.

Since these three products, obtained directly from quinitrols, are dehydrophenols, it is highly probable that, just as the usual mode of formation of such compounds depends on the generation of a residue with an odd electron from phenols by loss of a hydrogen atom, so in the present instances the initial reaction is one of dissociation into nitrogen peroxide and a similar residue (compare also Pummerer, *Ber.*, 1914, **47**, 2964). The marked difference of the products in orientation and type from the quinones derived from nitrophenols, therefore, indicates that decomposition of these last does not proceed by direct dissociation.

The formation of 2 : 6-dichloro-4-nitrophenol (IV) represents an exchange of hydrogen for methyl, and this, so far as we are aware, has not previously been observed as a mode of transition from the quinonoid to the aromatic condition. We regard the methyl ether (V) as arising from 2 : 6-dichloro-4-methylenequinone, and since (VII) does not exhibit the same tendency to dissociation as Pummerer and Cherbuliez observed in the case of (XI), it would seem that the methylenequinone must then be formed directly from the quinitrol in the manner contemplated by Zincke (II ⟶ III).

EXPERIMENTAL.

Decomposition of 2 : 6-*Dichloro*-4-*methylquinitrol in Methyl-alcoholic Solution.*—A mixture of the quinitrol (67·9 g.) with methyl alcohol (670 c.c.) was boiled for 2 hours in a reflux apparatus. By conducting the vapours evolved through a receiver at —40°, methyl nitrite (8 c.c.) was collected (compare Zincke, *loc. cit.*), and identified by its odour and b. p., — 12°. The cooled solution gradually deposited the compound described by Zincke (11·2 g., m. p. 155°), and a further quantity (6 g.) was isolated after concentrating the solution. Methyl alcohol and hydrogen chloride having been removed as completely as possible from the liquor by distillation on the steam-bath, the ethereal solution of the residue was washed with water, and then treated with dilute aqueous disodium hydrogen phosphate solution. The purple extract thus obtained became straw-coloured on acidification, and on extraction with ether provided a material which has not been closely examined, owing to the small quantities obtained. It may be remarked, however, that the purple colour characteristic of its alkaline solutions also developed when the material was shaken with ordinary distilled water. When the ethereal solution was successively extracted after this treatment with dilute aqueous sodium bicarbonate, sodium carbonate, and sodium hydroxide solutions (the last in an atmosphere of hydrogen), products of decreasing acidity were isolated. In order to make the separation sharper, each alkaline extract was acidified and shaken with ether, the ethereal solution so obtained again being then treated with the alkali appropriate to removal of any more strongly acidic material.

The material extracted by sodium bicarbonate in this manner (5 g.) melted at 127° (decomp.) after crystallisation from ligroin, and did not depress the m. p. of an authentic specimen of 2 : 6-dichloro-4-nitrophenol.

The product soluble in aqueous sodium carbonate (14·0 g.) was purified by repeated crystallisation, and so obtained from ligroin in oblique, creamy-white plates, m. p. 68—71°, free from nitrogen, but containing chlorine. Its composition agreed with that of 3 : 5-*dichloro*-4-*hydroxybenzyl methyl ether* (Found : C, 46·4; H, 3·9. $C_8H_8O_2Cl_2$ requires C, 46·4; H, 3·9%). Its constitution follows by analogy with that of the ethyl ether, isolated from a corresponding experiment with ethyl alcohol. The material soluble in aqueous sodium hydroxide melted at 123° after crystallisation from ligroin, and did not depress the m. p. of an authentic specimen of 2 : 6-dichloro-4-methyl-ψ-quinol. The ethereal solution remaining after removal of these various products yielded a residue (7·0 g.) on evaporation, from which a further quantity of the compound, m. p. 155°, could be isolated by treatment with methyl alcohol.

It should be mentioned that whilst the operation just described is representative, the actual yields depend very much on the conditions under which the original decomposition is carried out. As indicated by Suhl (*loc. cit.*), the proportion of the material, m. p. 155°, is greater under mild conditions of reaction. The most favourable yield (17 g.) was obtained when the quinitrol (38 g.) was warmed with methyl alcohol (190 c.c.) at the lowest temperature necessary to maintain evolution of methyl nitrite, and finally boiled for one hour. Solution was not complete at any stage of this experiment. Pummerer and Cherbuliez (*loc. cit.*) record a similar experience in the case of the reaction with tetrachloromethylquinitrol.

Investigation of Zincke's Compound.—The material obtained from the preceding experiment melted at 157° after repeated crystallisation from methyl alcohol, and did not decompose or darken in the manner described by Zincke, but evolved gas when heated to 250° [Found : C, 51·4; H, 3·8; Cl, 30·6; OMe, 9·25, 8·9. $C_{14}H_8O_2Cl_3(OMe)$ requires C, 51·8; H, 3·8; Cl, 30·6; OMe, 8·9%]. The data recorded by Suhl (*loc. cit.*) are C, 51·8, 52·1; H, 3·8, 3·8; Cl, 30·7, 30·6; OMe, 8·8, 8·9%.

When the compound (2 g.) was boiled in a stream of carbon dioxide with hydrobromic acid (b. p. 125°; 10 c.c.), bromine was at once liberated, and a crystalline material was deposited in a reflux condenser attached to the flask. This melted at 35—40°, and furnished a benzoyl derivative, m. p. 91°, and both were identified by direct comparison respectively with authentic 3 : 5-dichloro-*p*-cresol and its benzoyl derivative. The acid solution, however, darkened considerably on boiling, and the other products of the decomposition were more satisfactorily obtained when the original compound (5 g.) was heated with hydriodic acid (*d* 1·7; 20 c.c.) in a stream of carbon dioxide at 80° until evolution of methyl iodide was complete. As in the previous experiment, 3 : 5-dichloro-*p*-cresol volatilised into the condenser together with iodine. After decantation of the acid from the gummy residue, the latter was dissolved in ether and treated successively with aqueous sodium thiosulphate solution and then with just sufficient aqueous sodium hydroxide to discharge the colour of the ethereal solution. When this was dried and evaporated, the residue (4·2 g.) crystallised. It separated from methyl alcohol in well-formed colourless prisms, which melted at 78—80° with loss of methyl alcohol, and then at 98—100° (Found, after the attainment of constant weight: C, 52·7; H, 3·5. $C_{14}H_{11}O_2Cl_3$ requires C, 52·9; H, 3·5%). This 3 : 3′ : 5′-*trichloro*-5-p-*tolyloxy*-p-*cresol* was very easily soluble in organic solvents, but with difficulty in aqueous sodium hydroxide owing to the sparing solubility of its sodium salt. It gave no colour with ferric chloride, and was characterised by its *benzoyl* derivative, which crystallised from alcohol in transparent well-formed prisms, m. p. 173° (Found: C, 59·8; H, 3·7. $C_{21}H_{15}O_3Cl_3$ requires C, 59·8; H, 3·6%).

Decomposition of 2 : 6-*Dichloro*-4-*methylquinitrol in Ethyl-alcoholic Solution.*—A mixture of the quinitrol (5 g.) with ethyl alcohol (50 c.c.) was boiled for one hour in a reflux apparatus. Ethyl nitrite was collected as a product of the reaction, and identified by its b. p. 18·5°, and odour. In agreement with Zincke's observation (*loc. cit.*), no solid material separated from the resulting solution, and this was worked up in the manner described in the case of the reaction in methyl-alcoholic solution. A similar strongly acid material having been removed, 2 : 6-dichloro-4-nitrophenol (0·6 g., m. p. 127°) was isolated. The product soluble in sodium carbonate (1·3 g.) crystallised from ligroin in well-formed plates, m. p. 86° (Found: C, 48·9; H, 4·6. Calc. for $C_9H_{10}O_2Cl_2$: C, 48·9; H, 4·55%). Its composition was therefore that of 3 : 5-dichloro-4-hydroxybenzyl ethyl ether, and a sample of this material prepared according to the directions of Mettler (*loc. cit.*) agreed with our product in crystalline form, and did not depress its m. p. 2 : 6-Dichloro-4-methyl-*ψ*-quinol (1·2 g., m. p. 123°) was then isolated as before, and finally the neutral residue (0·9 g.) was purified by crystallisation from ligroin. In this manner, well-formed oblique plates, m. p. 125°, were obtained (Found: C, 53·15; H, 4·2. $C_{16}H_{15}O_3Cl_3$ requires C, 53·1; H, 4·2). The yield of this product was not improved when the proportion of ethyl alcohol used was halved, and the reaction carried out at the lowest possible temperature.

In order to establish the constitution of this 3′ : 5′ : 6-*trichloro*-2-p-*tolyloxy*-2-*ethoxy*-4-*methyl*cyclo*hexa*-3 : 5-*dienone*, it (4 g.) was heated with hydriodic acid (*d* 1·7; 20 c.c.) in a stream of carbon dioxide at 110° until the evolution of ethyl iodide was complete. As in the other instance, iodine and 3 : 5-dichloro-*p*-cresol were volatilised, whilst the residue in the flask yielded the same phenol (3 g.) as the parallel compound derived from methyl alcohol. As before, the m. p.'s, 78—80° and 98—100°, were observed after crystallisation from methyl alcohol, and identity of the two products was established in the usual manner.

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