[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

THE ALUMINUM CHLORIDE-CATALYZED REACTION OF BENZOTRICHLORIDE WITH *p*-CRESOL

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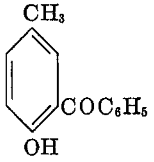
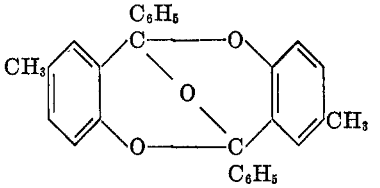
In continuation of studies on the Zincke and Suhl reaction (1), the reaction of benzotrichloride and *p*-cresol was investigated. The products of this reaction consisted of 2-hydroxy-5-methylbenzophenone (I) (40.4% yield), a high-melting white compound (II) (29.4%), and a dark polymer. In spite of a careful search no trace of a substituted cyclohexadieneone similar to those formed in the Zincke and Suhl reaction (2) was found.

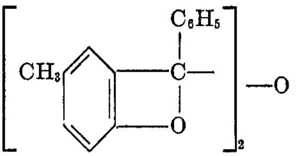
Analyses and molecular weight determinations indicated a formula of $C_{28}H_{22}O_3$ for II. Infrared analysis showed the absence of hydroxyl and carbonyl groups. The compound gave no color with ferric chloride solution and was inert to acetyl chloride and to potassium hydroxide in boiling ethylene glycol for 24 hours. When a solution of II in concentrated sulfuric acid was poured into water I, $C_{14}H_{12}O_2$, was obtained in almost quantitative yield. On the basis of these facts we propose that II is 6,12-diphenyl-2,8-dimethyl-6,12-epoxy-6*H*,12*H*-dibenzo[*b*,*f*][1,5] dioxocin, as indicated in the formula.



I



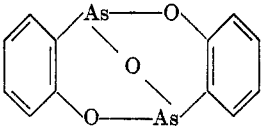
II



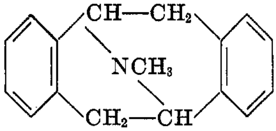
IIa

The structure of II indicated is preferred over the alternate possible structure IIa for the reason that compounds containing the heterocyclic 1,3,3-bicyclononane system in the center are fairly common. The following examples have been found in the literature (3).

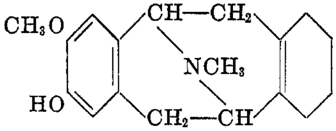
On the other hand a careful review (12a) of the literature covering compounds allegedly containing a four membered ring fused to an aromatic nucleus (such as in IIa) reveals that there is insufficient evidence to establish firmly this structure in any case (12b). The structure of diphenylene (IX) however, is firmly established (13). It should also be pointed out that structures such as X and XI



III(4)

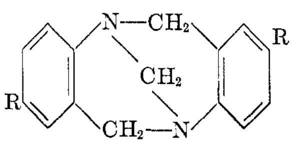


IV(5)

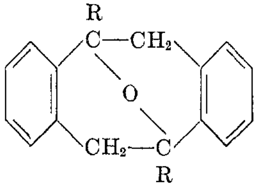


V(6)

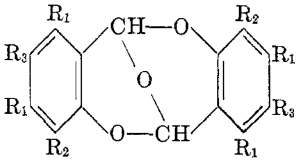
are well established (3) but in these the six membered ring is non-aromatic and the carbon atoms at the points of fusion are not doubly bonded.



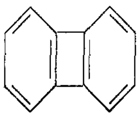
VI A (R = CH_3) (7)
VI B (R = OCH_3, OC_2H_5) (8)



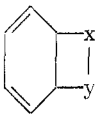
VII (R = CH_3, OH) (9)



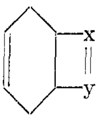
VIII (10, 11)



IX



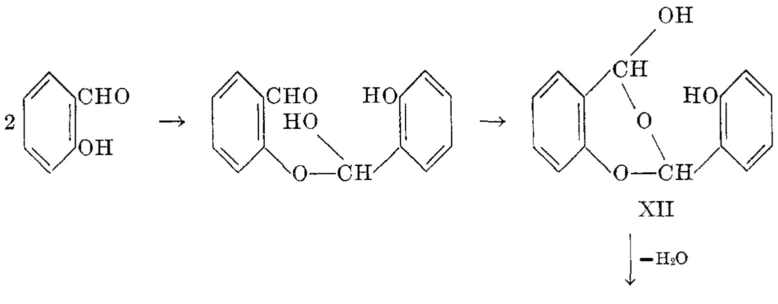
X

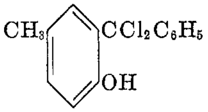


XI

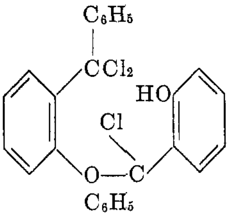
A further argument in favor of structures of type II as opposed to IIa is the fact that only one form of these compounds has ever been found. Models show that only a *cis* structure for compounds of type II–VIII is possible whereas structures of type IIa permit racemic and meso forms.

The structure we propose for II is similar to that proposed for "disalicylaldehyde" (XIII) and the chemical behavior (14) of the latter and II is quite comparable. A mechanism involving the stepwise formation of the bicyclic ring system through a six member ring intermediate (XII) was proposed (14). The chlorinated intermediate (XIV), which would be formed if the mechanism (see below) of condensation of benzotrichloride with *p*-cresol is similar to that postulated for the Zincke and Suhl reaction in the accompanying paper (2), would be expected to yield I on direct hydrolysis. On stepwise reaction of the phenolic group of one molecule of XIV with the CCl_2 group of another molecule of XIV an intermediate XIVa would be formed. Hydrolysis of the tertiary chlorine, ring closure with the remaining CCl_2 group, and cyclization of the latter tertiary chloride with the remaining OH group would yield II. The analogy with the formation of XIII is apparent.

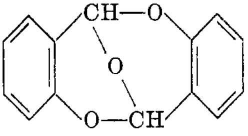




XIV



XIVa

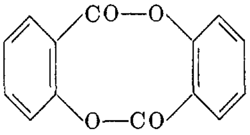


XIII

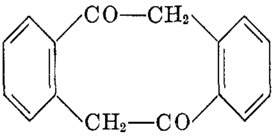
Several attempts were made to isolate the postulated intermediate (XIV), but these were unsuccessful. When the reaction mixture was treated with dry methanol, in an attempt to obtain the ketal corresponding to I, the only products obtained (in addition to the dark polymer) were I (78%) and a small amount of 2,6-dibenzoyl-*p*-cresol (see accompanying paper (15)). When the hydrolysis of the reaction mixture was carried out in the cold in the presence of calcium carbonate, only I (75.6% yield) was obtained, no II being detectable. Evidently acid catalysis is necessary for the formation of the dioxocin (II) from the intermediate.

However, several attempts to convert I into II with acidic reagents failed completely. Furthermore, II is quite resistant to acidic hydrolysis, the only effective method found for accomplishing this step being the dissolution of II in concentrated sulfuric acid followed by quenching of this solution in water. It is interesting to note that the solution of I in sulfuric acid is yellow whereas that of II in sulfuric acid is deep red. When the solution of II in sulfuric acid was poured into methanol only I was obtained. A dichloro compound similar to XIV has been obtained from 2-hydroxy-3,5-dibromo-4,6-dimethylbenzaldehyde by treatment with phosphorus pentachloride (10), the corresponding dioxocin (VIII) being a by-product. Hydrolysis of this 2-hydroxy-3,5-dibromo-4,6-dimethylbenzal chloride yielded the starting aldehyde.

Several attempts were made to synthesize a compound analogous to II from disalicylide (XV) (16) by reaction with phenylmagnesium bromide and phenyllithium. Since these were unsuccessful no attempt was made with di-*p*-cresotide (16). It has been shown that *sym*-dibenzocycloöctanedione-5,11 (XVI) reacts with only one equivalent of methylmagnesium iodide (9).



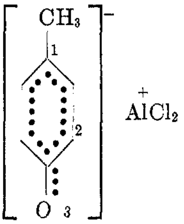
XV



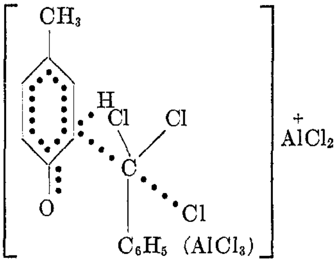
XVI

When phenol replaced *p*-cresol in the condensation with benzotrichloride only *p*-hydroxybenzophenone (90%) was obtained. When chlorinated benzotrichlorides were used in place of benzotrichloride, compounds similar to I and II were obtained, together with other compounds which are described in an accompanying paper (17).

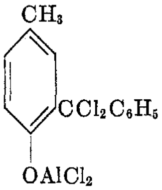
The formation of the products, I and II, may be accounted for by a mechanism similar to that previously postulated for the formation of 4-methyl-4-trichloromethyl-2,5-cyclohexadieneone (2) from *p*-cresol and carbon tetrachloride. The ion pair (XVII) produced by the reaction of *p*-cresol with aluminum chloride, is susceptible to attack at positions 1, 2, and 3. In the case of the Zincke and Suhl reaction, condensation takes place mainly at position 1. In the case of reaction with benzotrichloride the increased steric requirements in the transition state involving benzotrichloride effectively prevent condensation from taking place at position 1. Accordingly reaction occurs at position 2 as pictured in the formula for the transition state, XVIII. The chloride ion displaced combines with the proton which is lost to yield hydrogen chloride. It is noteworthy that in this reaction the product is a chloroaluminum salt (XIX) containing an aromatic ring whereas in the Zincke and Suhl reaction the reaction product is a complex formed from aluminum chloride and a 4,4-disubstituted-2,5-cyclohexadieneone system (2).



XVII



XVIII



XIX

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EXPERIMENTAL

General. Melting points have been taken with Anschütz total immersion thermometers on the purest samples obtained. Boiling points are uncorrected. All solvents used have been redistilled in addition to further purification wherever noted. The analysis is by Clark Microanalytical Laboratories, Urbana, Illinois. Infrared absorption curves were taken on a Baird double beam recording spectrophotometer using sodium chloride prisms.

Aluminum chloride-catalyzed reaction of benzotrichloride and p-cresol. The procedure used was similar to that in the previous paper (2) using 8.33 g. (0.0625 mole) of aluminum chloride, 5.41 g. (0.050 mole) of purified *p*-cresol, 9.77 g. (0.050 mole) of redistilled benzotrichloride, and 20 ml. of carbon disulfide. The *p*-cresol and aluminum chloride were first reacted as before and then the benzotrichloride was added dropwise over 5–10 minutes to the mixture which was cooled by an ice-bath.

On addition of the benzotrichloride, the mixture turned black immediately with hydrogen chloride evolution. After two hours of stirring and cooling, the solvent was removed *in vacuo*, and the mixture was decomposed by the cautious addition of water. (No difference in results was noted when dilute hydrochloric acid was used for the decomposition.) The product was taken up in benzene-ether and the layers were separated. The organic layer was washed in turn with water and a saturated sodium chloride solution and then filtered through anhydrous sodium sulfate. Most of the solvent was removed by distillation and petroleum ether, b.p. 65–70°, (Skellysolve B) was added gradually to the solution until the formation of crystals was noted. The mixture was then allowed to stand for 2–3 hours and then heated and filtered (see below for filtrate). After washing with Skellysolve B and drying 2.99 g. (29.4%) of II, m.p. 236.0–236.5°, was obtained. Recrystallization from dioxane-water gave colorless crystals, m.p. 236.5–236.7°.

Anal. Calc'd for $C_{28}H_{22}O_3$: C, 82.7; H. 5.5; Mol. wt., 406.

Found: C, 82.6; H, 5.5; Mol. wt., 405 (ebullioscopic method in benzene using a differential water thermometer).

The Skellysolve filtrate from the dioxocin above was distilled to yield 4.57 g. of 2-hydroxy-5-methylbenzophenone (I) as a yellow solid, m.p. 76–83°, b.p. 119–122° at 1–2 mm. Recrystallization from Skellysolve B gave 4.30 g. (40.4%) of I as yellow leaflets, m.p. 82–83.0°. A further recrystallization raised the melting point to 83.6–84.0°, reported (18) 84°. The presence of benzotrichloride in the original mother liquor was confirmed by a color test (19). In alcohol solution, the hydroxybenzophenone gave a dark-greenish-blue color with ferric chloride. A mixture melting point with a sample of 2-hydroxy-5-methylbenzophenone prepared by a Fries rearrangement of the benzoate of *p*-cresol (18) was not depressed. The residue from the distillation above consisted of a dark polymer which gave a deep purple color when dissolved in acetone. This probably consists of a triphenylmethane dye of the type mentioned in the preceding paper (2).

The infrared spectrum of I in mineral oil (Nujol) and also in methylene chloride exhibited a strong carbonyl absorption band at 6.11 μ, an absorption band at 6.22 μ in the double bond region, and no absorption in the region assigned to phenolic hydroxyl band fundamentals. Compounds which have similar groupings such as *o*-hydroxyacetophenone and salicylaldehyde also show no hydroxyl band in this region. This phenomenon has been ascribed to hydrogen bonding (20).

An infrared curve of II in Nujol mull showed no absorption in the hydroxyl or carbonyl regions and evidenced four absorption bands in the region ascribed to unsaturation: 6.13, 6.17, 6.22, and 6.25 μ, the first and third being of corresponding intensity and the second and fourth being somewhat weaker. An infrared curve of "disalicylaldehyde" (XIII) showed two absorption bands in the same region *i.e.*, 6.15 and 6.23 μ, which probably correspond to the two *benzo* groupings in this molecule.

In further experiments it was found that reactions run at room temperature and higher yielded larger amounts of dark polymer, whereas at temperatures lower than 0° reaction was incomplete after two hours. In a further search for other products, a benzene-Skellysolve B solution of the reaction mixture was extracted with Claisen's alkali (21) but no alkali-insoluble compounds were found besides the dioxocin and the dark polymer.

Attempted reaction of the dioxocin (II) *with potassium hydroxide.* Following a general procedure (22) the dioxocin in diethylene glycol solution was heated with potassium hydroxide for 24 hours. Dilution with water and filtration gave back unchanged starting material.

Hydrolysis of the dioxocin (II) *with sulfuric acid.* A 0.037-g. sample of finely powdered dioxocin was dissolved in 2 ml. of concentrated sulfuric acid at room temperature to form a blood-red solution. Dilution with water returned I in 91% yield. When sulfuric acid solutions of II were poured into methanol or methanol solutions of excess sodium methoxide in attempts to obtain methoxylated compounds only I was found (compare 23).

Attempted syntheses of II. A solution of 0.038 g. (0.00390 mole) of disalicylide, m.p. 233–234° (16) in 60 ml. of pure tetrahydrofuran was treated with a solution of 0.0078 mole of phenylmagnesium bromide in the usual apparatus for one hour at room temperature after which time a negative test for Grignard reagent (24) was obtained. After hydrolysis of the reaction mixture we were unable to find any trace of II. No II was formed in the reaction of phenyllithium with disalicylide.

Attempts to convert 2-hydroxy-5-methylbenzophenone (I) *into the dioxocin* (II). The methods tried were: heating at the melting point for two hours; heating with aluminum chloride at 85° for 11 hours; heating with phosphorus pentoxide in benzene for 3 hours and treatment with acetyl chloride and sulfuric acid under conditions used in the preparation of "disalicylaldehyde" (14). An orange-colored solid was formed with aluminum chloride and also with phosphorus pentoxide, but on decomposition with water, I was recovered in all cases except the last one in which the acetate (m.p. 63–64°) [reported (25) 64–65°] was found. When I or II were treated under the conditions used in the original reaction, they were recovered unchanged.

Attempted isolation of the dichloro intermediate (XIV). 1. *Directly from the reaction mixture.* At the completion of a typical reaction involving 8.33 g. of aluminum chloride, 5.41 g. of *p*-cresol, and 9.77 g. of benzotrichloride, the solvent was removed from the reaction solids through a sintered glass filter-stick. Evaporation of solvent under reduced pressure left no residue.

2. *Decomposition with limited amounts of water.* At the completion of a typical reaction, 0.90 g. (0.050 mole) of water was added dropwise and the mixture was stirred at 0° for 15 minutes. The solution was then siphoned off with the aid of a filter stick and evaporated to dryness under reduced pressure. A small quantity of a dark polymeric residue was obtained. In another experiment 3.25 g. (0.203 mole) of water was added to the reaction mixture. Removal of solvent from the filtered solution and washing the residue with dry ether left 2.9 g. (28.7%) of colorless crystals of dioxocin, m.p. 236.0–236.5°.

3. *Decomposition in the presence of calcium carbonate.* At the completion of a typical reaction, 6.24 g. (0.0625 mole) of finely powdered calcium carbonate was added and the mixture was decomposed by the dropwise addition of water. The product was taken up in benzene-ether and worked up in the usual manner. The residue obtained after removal of solvent was completely soluble in hot Skellysolve B, indicating the absence of II. On cooling the solution, I was obtained in two crops, 5.45 g., m.p. 82–83.5°; and 2.54 g., m.p. 80–81.5°, 75.6% yield. The mother liquors, on evaporation yielded a dark polymeric residue.

Aluminum chloride-catalyzed reaction of phenol and benzotrichloride. A procedure similar to the original one was used with 4.71 g. (0.050 mole) of phenol dissolved in 10 ml. of carbon disulfide, 9.77 g. (0.50 mole) of benzotrichloride, 8.33 g. (0.063 mole) of aluminum chloride, and 30 ml. of carbon bisulfide. The reaction was run at 0°. After working up in the usual manner a white solid was obtained by a vacuum-distillation. On recrystallization from Skellysolve B, 8.66 g. (90.2% yield) of *p*-hydroxybenzophenone, m.p. 132.0–133.0° was obtained as colorless crystals. Recrystallization of a small sample raised the melting point to 133.5–134.5°, reported 134–135° (26). The compound dissolved to give a colorless alkaline solution and a light pink color in aqueous alcohol with ferric chloride as observed previously (26).

SUMMARY

1. The aluminum chloride-catalyzed reaction of benzotrichloride and *p*-cresol in carbon disulfide produces a complex which on hydrolysis yields mixtures of 2-hydroxy-5-methylbenzophenone (I) and 6,12-di-phenyl-2,8-dimethyl-6,12-epoxy-6*H*,12*H*-dibenzo[*b*, *f*][1,5]dioxocin (II).

2. A mechanism consistent with the facts has been proposed.

3. The dioxocin (II) on hydrolysis with concentrated sulfuric acid yields 2-hydroxy-5-methylbenzophenone (I).

4. The aluminum chloride-catalyzed reaction of benzotrichloride and phenol in carbon disulfide produces a 90% yield of *p*-hydroxybenzophenone.

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REFERENCES

(1) ZINCKE AND SUHL, *Ber.*, **39**, 4148 (1906).

(2) NEWMAN AND PINKUS, *J. Org. Chem.*, **19**, preceding paper (June 1954).

(3) CRAIG, *Chem. Revs.*, **49**, 103 (1951).

(4) KALB, *Ann.*, **423**, 70 (1921).

(5) WITTIG, *et al.*, *Ann.*, **572**, 1 (1951).

(6) GREWE, MORDON, AND NOLTE, *Ann.*, **464**, 161 (1949).

(7) TROEGER, *J. prakt. Chem.*, **36**, 227 (1887).

(8) MILLER AND WAGNER, *J. Am. Chem. Soc.*, **63**, 832 (1941).

(9) WAWZONEK, *J. Am. Chem. Soc.*, **62**, 745 (1940).

(10) LINDEMAN AND FORTH, *Ann.*, **435**, 219 (1924).

(11) TAMAKI AND ENDO, *J. Chem. Soc. Japan*, **61**, 231 (1940).

(12a) SCHROETER AND EISLEB, *Ann.*, **367**, 101 (1909); RODINOV AND FEDOROVA, *Bull. soc. chim.*, **6**, 478 (1939); DROSDOW AND DROSDOW, *J. Gen. Chem. U.S.S.R.*, **4**, 1 (1934) [*Chem. Abstr.*, **28**, 5456 (1934)] [*Chem. Zentr.*, 3762 (1934)]; ALBERT AND MINNEL, *J. Chem. Soc.*, 22 (1938); JOURDAN, *Ber.*, **18**, 1444 (1885); MOSER AND GOMPF, *J. Org. Chem.*, **15**, 583 (1950); SCHIFF, *Ann.*, **178**, 187 (1875); LIEB AND WINTERSTEINER, *Ber.*, **56**, 1283 (1923); RUDDY AND BURT, *J. Am. Pharm. Assoc.*, **28**, 286 (1939); BOREDIANU, *Ann. Sci. Univ. Jassy*, **Pt. I, 23**, 212 (1937); *Bull. Soc. Stunte Farm. Romania*, **2**, 39 (1937) [*Chem. Abstr.*, **32**, 5802 (1938)]; HELLER, *Ber.*, **49**, 2757 (1916); CLAAZ, *Ber.*, **50**, 511 (1917); ALLEN AND GATES, *J. Am Chem. Soc.*, **65**, 1230 (1943); COHN, *Monatsh.*, **16**, 271 (1895); DARAPSKY, BERGER, AND NEUHAUS, *J. prakt. Chem.*, **147**, 145 (1936); SHAH AND ALIMCHANDANI, *J. Indian Chem. Soc.*, **8**, 261 (1931); ILLARI AND GIUSEPPETTI, *Gazz. chim. ital.*, **78**, 913 (1948) [*Chem. Abstr.*, **43**, 5770 (1949)]; LAGIDZE AND PETROV, *Doklady Akad. Nauk U.S.S.R.*, **83**, 235 (1952) [*Chem. Abstr.*, **47**, (1953)]; BERGMANN AND VON LIPPMANN, *Ann.*, **452**, 135 (1927).

(12b) ZENTMYER AND WAGNER, *J. Org. Chem.*, **14**, 967 (1949); CLEMO, PERKIN, AND ROBINSON, *J. Chem. Soc.*, 1779 (1924); RASCHIG, *Z. angew. Chem.*, **25**, 1944 (1912); ANSCHÜTZ, *Ber.*, **45**, 2378 (1912); ANSCHÜTZ, *Ann.*, **415**, 65 (1918); SCHOEPFLE, VAN NATTA, AND CLARKSON, *J. Am. Chem. Soc.*, **50**, 1171 (1928); BAKER, *J. Chem. Soc.*, 258 (1945); FUSON in *Advanced Organic Chemistry*, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 114.

(13) LOTHROP, *J. Am. Chem. Soc.*, **63**, 1187 (1941); **64**, 1698 (1942). WASER AND LIU, *J. Am. Chem. Soc.*, **66**, 2035 (1944).

(14) ADAMS, FOGLER, AND KRIEGER, *J. Am. Chem. Soc.*, **44**, 1126 (1922).

(15) NEWMAN AND PINKUS, *J. Org. Chem.*, **19**, following paper (June 1954).

(16) BAKER, OLLIS, AND ZEALLEY, *J. Chem. Soc.*, **202**, 210 (1951).

(17) NEWMAN AND PINKUS, *J. Org. Chem.*, **19**, paper 4 of this group (June 1954).

(18) VON AUWERS AND BETTERIDGE, *Z. physik. Chem.*, **32**, 39 (1900).

(19) WARE, *Chemist and Druggist*, **123**, 282 (1935).

(20) GORDY, *J. Chem. Phys.*, **8**, 516 (1940); BADGER AND BAUER, *J. Chem. Phys.*, **5**, 839 (1937) and references therein.

(21) CLAISEN, *Ann.*, **418**, 96 (1919); *Ann.*, **442**, 224 (1924).

(22) SHRINER AND FUSON, *The Systematic Identification of Organic Compounds*, 3rd edition, John Wiley and Sons, Inc., New York, 1948, p. 133.

(23) NEWMAN AND DENO, *J. Am. Chem. Soc.*, **73**, 3644 (1951).

(24) GILMAN AND SCHULZE, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(25) WITTIG AND SCHULZE, *J. prakt. chem.*, **130**, 81 (1931).