[Contribution from the McPherson Chemical Laboratory, the Ohio State University]

ALUMINUM CHLORIDE-CATALYZED REACTIONS OF CHLORINATED BENZOTRICHLORIDES WITH *p*-CRESOL

MELVIN S. NEWMAN and A. G. PINKUS

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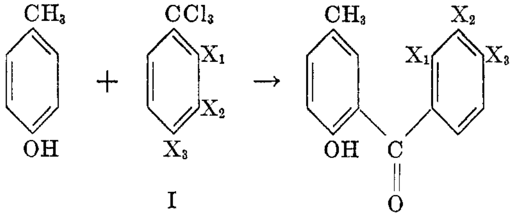
In view of the interesting results obtained in the condensation of benzotrichloride with *p*-cresol in the presence of aluminum chloride (1, 2) the behavior of commercially available chlorinated benzotrichlorides (I) was examined. When 2-chloro-, 4-chloro-, 2,4-dichloro-, and 3,4-dichloro-benzotrichlorides were reacted with *p*-cresol, the corresponding chlorinated hydroxybenzophenones (II) and dioxocins (III) (1) were obtained. In addition, two other types of compounds were isolated in small yields, xanthones (IV) and 2,6-diaroylcresols (V) (2). The results are summarized in Table I.

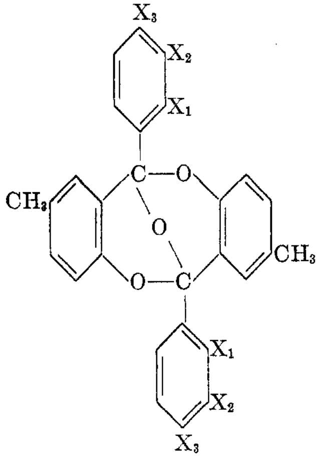


I

A, B, C, D, E

II

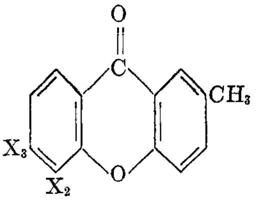
A, B, C, D, E



III

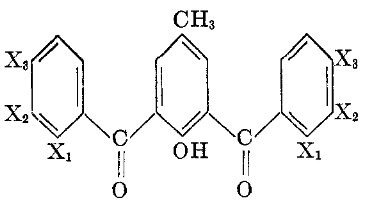
A, B, C, D, E

	X_1	X_2	X_3
A	H	H	H
B	H	H	Cl
C	Cl	H	H
D	Cl	H	Cl
E	H	Cl	Cl



IV

C, D



V

A, E

The proportion of products isolated depended somewhat upon the method used in decomposing the reaction mixture. For example, in the reactions involving

TABLE I

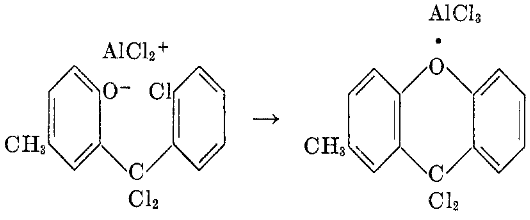
YIELDS[a] OBTAINED IN THE ALUMINUM CHLORIDE-CATALYZED REACTIONS OF BENZOTRICHLORIDE(S) AND *p*-CRESOL

	HYDROXY-BENZOPHENONE, % (II)	DIOXOCIN, % (III)	XANTHONE, % (V)	2,6-DIBENZOYL-*p*-CRESOL, % (IV)
A	(1) 40.4	29.4	—	—
	78.0	—	—	4.2[b]
	75.6[c]	—	—	—
B	28.7	30.0	—	—
C	34.9[d]	16.7[d]	19.3[d]	—
	57.3[e]	14.0[e]	—	—
D	22.1[d]	32.0[d]	10.6[d]	—
	31.8[e]	29.8[e]	—	—
E	56.7	8.8	—	14.4

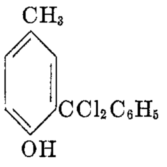
[a] Yields are based on the benzotrichloride. [b] Absolute methanol used in decomposition before addition of water. [c] Calcium carbonate added before decomposition with water. [d] Ether or alcohol used in working up reaction products before addition of water. [e] Benzene and hydrocarbons used in working up reaction products in conjunction with slow addition of water.

2-chloro- and 2,4-dichloro-benzotrichloride, hydroxybenzophenones (II-C and D), dioxocins (III-C and D), and xanthones (IV-C and D), were obtained if ether or alcohol were used in decomposition of the aluminum chloride complex. When benzene or petroleum ether was used, in conjunction with water, only mixtures of hydroxybenzophenones (II-C and D), and dioxocins (III-C and D), were obtained. Therefore, the xanthones were formed during the treatment of the reaction complex with ether or alcohol prior to the addition of water. The xanthones (IV-C and D), were prepared by heating the corresponding hydroxybenzophenones (II-C and D), with potassium hydroxide in ethylene glycol (3). The use of potassium hydroxide instead of sodium hydroxide (3) allows for completion of the reaction in 10 minutes at 50–60° instead of 5.5 hours at reflux (3). 2-Methylxanthone has been prepared before (3, 4) and was identical to our compound IV-C. 2-Methyl-6-chloroxanthone (IV-D) is a new compound.

According to the mechanism previously proposed (1) the reaction mixture, obtained when equimolar amounts of 2-chlorobenzotrichloride and *p*-cresol are condensed with the aid of aluminum chloride, contains the dichloroaluminum salt (VI) present as an insoluble complex in the carbon disulfide. When methanol or ether is used in decomposing the complex the anion formed by removing the $AlCl_2^+$ as a complex ($AlCl_2 \cdot S^+$ where S is the basic solvent) evidently has a long enough life to undergo an intramolecular reaction involving the displacement of an *ortho* chlorine to yield VII which on hydrolysis yields a xanthone. When water is involved the anion picks up a proton too rapidly to undergo the cyclization and the chlorinated intermediate (VIII) is formed. On hydrolysis of VIII hydroxybenzophenones (II), or dioxocins (III), are obtained.

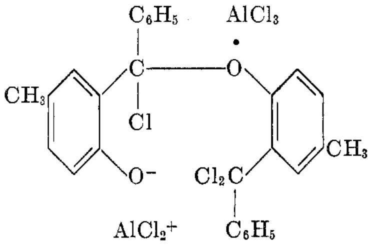


VI VII

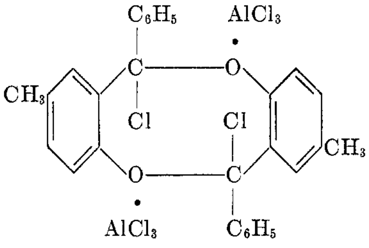


VIII

The absence of the dioxocin (III-A) from the reaction products when the reaction mixture of benzotrichloride and *p*-cresol was treated with calcium carbonate prior to decomposition with water has been discussed (1). In the cases of 2-chloro- and 2,4-dichloro-benzotrichloride, the corresponding dioxocins (III-C and D) were formed in about the same yields (see Table I) when water or more basic solvents, ether and alcohol, were used to decompose the reaction mixture. Therefore, we believe, in these cases at least, the dioxocins are formed from a complex such as IX. The elaboration of the dioxocin structure must occur during the hydrolysis as we believe it unlikely that an eight membered ring complex such as X would be formed. The internal bridging oxygen atom in the dioxocin structure (III) is the key to any mechanism involving the elaboration of the dioxocin structure by means of the stepwise formation of two six membered rings [see ref. (1) for this mechanism and note ref. (14) therein]. This oxygen can only be supplied during hydrolysis. The structures of the dioxocins are based mainly on the analogy with III-A (1) and on hydrolysis to the corresponding hydroxybenzophenones, II (see experimental).



IX



X

In the condensation of 3,4-dichlorobenzotrichloride with *p*-cresol an appreciable amount of 2,6-di(3,4-dichlorobenzoyl)-*p*-cresol (V-E) was obtained. The formation of V-E did not depend upon the method used in working up the reaction products as was the case in the formation V-A (2). V-E was synthesized by treating the dichloroaluminum salt of II-E with I-E in carbon disulfide solution. The synthesis of V-A by this method was unsuccessful in carbon disulfide but successful in nitrobenzene. Hence it is apparent that the solubilities of the complex salts formed are of importance in determining the ratio of products formed.

TABLE II

ANALYSES AND PROPERTIES OF BENZOPHENONES (II) AND DIOXOCINS (III)

COMP.	MOLECULAR FORMULA	M.P., °C.	ANALYSES					
			C		H		Cl	
			Calc'd	Found	Calc'd	Found	Calc'd	Found
III[a]	A $C_{28}H_{22}O_3$	236.5–236.7	82.7	82.6	5.5	5.5		
	B $C_{28}H_{20}Cl_2O_3$	254.2–255.0					14.9	14.9
	C $C_{28}H_{20}Cl_2O_3$	287.0–287.5					14.9	14.7
	D $C_{28}H_{18}Cl_4O_3$	273.5–274.0	61.8	61.6[w]	3.3	3.5[w]		
	E $C_{28}H_{18}Cl_4O_3$	252.7–253.0					26.1	25.8
II[b]	A	83.6–84.0						
	B	66.4–67.2						
	C	76.0–77.0						
	D	92.1–92.8					25.2	25.3
	E	90.2–90.6	59.8	59.8[w]	3.6	3.6[w]	25.2	24.7

[a] All recrystallized from dioxane-water mixtures. [b] All recrystallized from Skellysolve B except E which was recrystallized from an acetone-water mixture. All of these compounds are yellow. [w] Analyses by R. C. Warfel, Ohio State University.

Acknowledgement. We should like to take this opportunity to thank the Heyden Chemical Corporation for gifts of the benzotrichlorides used in this work.

EXPERIMENTAL

General. Melting points below 240° were taken with Anschütz total immersion thermometers. Melting points above 240° were taken on an electrically heated Fisher block with the finely powdered sample between two glass slides and are corrected to correspond with the immersion temperatures. All liquids were redistilled in addition to further purification wherever noted. Analyses by the Clark Microanalytical Laboratories, Urbana, Illinois are unmarked while those by Robert C. Warfel of The Ohio State University Chemistry Department are marked "w". We wish to thank Robert Lieberman and Albert C. Antoine for many of the infrared absorption curves which were taken on a Baird double beam recording instrument using sodium chloride prisms.

The procedure for the reactions of the chlorinated benzotrichlorides and *p*-cresol was the same as that used in the original reaction (1) with benzotrichloride and is not repeated. Since the methods used in the separation of the reaction products differ these are described. In Table II are listed the analytical data and properties for the dioxocins and benzophenones. In Table III are listed the significant infrared absorption bands for the dioxocins in the unsaturated region and also the carbonyl and unsaturated bands for the benzophenones.

Reaction with 4-chlorobenzotrichloride. 4-Chlorobenzotrichloride had the following properties: b.p. 99–102° at 1–2 mm., n_{D}^{25} 1.5704. The reaction mixture was treated in the same way as that involving benzotrichloride (1). 4′-Chloro-2-hydroxy-5-methylbenzophenone (II-B) was obtained by distillation, b.p. 143–145° at 1–2 mm. Attempted recrystallizations were unsuccessful in separating II-B from a dark-red polymeric residue.

Reaction with 2-chlorobenzotrichloride. 2-Chlorobenzotrichloride had the following properties: b.p. 102–108° at 1–2 mm.; n_{D}^{25} 1.5788. When benzene was used in taking up the reaction products, the dioxocin and hydroxybenzophenone were obtained in a manner similar to that used with benzotrichloride (1). 2′-Chloro-2-hydroxy-5-methylbenzophenone (II-C) was obtained by distillation, b.p. 141–145° at 1–2 mm. The dioxocin (III-C) was

TABLE III

INFRARED ABSORPTION DATA[a] FOR DIOXOCINS (III) AND BENZOPHENONES (II)

DIOXOCIN[b, d] (III)	Unsaturated region			
A (1)	6.13	6.17	6.22	6.25
C	6.13		6.22	6.27
D	6.12		6.23	
E	6.13		6.22	
F (1)	6.15		6.23	

BENZOPHENONE (II)	Carbonyl	Unsaturated region	
A (1)	6.12[c]	6.22[c]	
	6.08[b]	6.19[b]	
B[e]	6.11	6.20	6.29
D[c]	6.08	6.15[f]	6.27
E[b]	6.09		6.26

[a] Wave length in μ. [b] In Nujol suspension. [c] Approximately 10% carbon disulfide solution. [d] The absorption peaks were not well resolved for compound III B. [e] Disalicylaldehyde. [f] Shoulder.

obtained from the residue by extraction with warm ether to dissolve the dark red polymer. The remaining dioxocin was then recrystallized from dioxane-water. In other experiments when benzene-ether was used in taking up the reaction products, a mixture of the benzophenone (II-C) and 2-methylxanthone (IV-C) was obtained on vacuum-distillation. This mixture could be partly separated by fractional crystallization using Skellysolve B. The xanthone was recrystallized from methanol, m.p. 122.8–123.2°, [reported (4) 125.5°]. A sample of II-C was converted into IV-C in 66.2% yield by the reported method (3). The xanthone gave a yellowish-green fluorescence in sulfuric acid solution. When this solution was diluted with water, the xanthone was recovered unchanged. Attempts to prepare a 2,4-dinitrophenylhydrazone by the usual methods (5) were unsuccessful. A suspension of IV-C in mineral oil (Nujol) showed a carbonyl absorption band at 6.00 μ which corresponds with 6.03 μ reported (6) for xanthone in chloroform solution.

Reaction with 2,4-dichlorobenzotrichloride. 2,4-Dichlorobenzotrichloride had the following properties: b.p. 96–102° at 1–2 mm.; m.p. 47.0–48.2° [reported (7) 47–48°]. Attempts at recrystallization were unsuccessful due to the high solubility in all solvents tried. The reaction products were separated as in the case of 2-chlorobenzotrichloride except that 6-chloro-2-methylxanthone (IV-D) was recrystallized from Skellysolve B, m.p. 148.2–148.4°.

Anal. Calc'd for $C_{14}H_9ClO_2$: Cl, 14.5. Found: Cl, 14.8.

The *xanthone* gave a yellowish-green fluorescence in sulfuric acid solution. When this solution was diluted with water, IV-D was recovered unchanged. Attempts to prepare a 2,4-dinitrophenylhydrazone or a phenylhydrazone by the usual (5) methods were unsuccessful. A Nujol suspension of IV-D showed a carbonyl absorption band at 5.98 μ.

Synthesis of 6-chloro-2-methylxanthone (IV-D). In a small flask, 0.191 g. of 2,4-dichloro-2′-hydroxy-5′-methylbenzophenone was dissolved in 5 ml. of diethylene glycol with the aid of heat. About 0.1 g. of crushed potassium hydroxide was added and the mixture was heated at 50–60° with occasional shaking. A heavy precipitate formed in about ten minutes. The mixture was heated ten minutes longer, diluted with water and filtered, washing well with water. After drying, and recrystallization from Skellysolve B, 0.139 g. (83.3%) of IV-D, m.p. 148.0–148.5° was obtained. The aqueous filtrate from the reaction mixture had a bright yellow color indicating the presence of unreacted hydroxybenzophenone as the potassium salt. In the published method (3) in which sodium hydroxide is used, a reaction period of 5.5 hours at reflux temperatures is required in this type of reaction.

TABLE IV

SULFURIC ACID HYDROLYSES OF THE DIOXOCINS (III)

DIOXOCIN (III)	COLOR IN 100% SULFURIC ACID	YIELD OF II OBTAINED, %	M.P. of II, °C.
A (1)	Blood-red	90.7	82.0–82.5
B	Blood-red	93.3	65.5–66.0
C	Orange	74.4	76.0–77.0
D	Orange	56.7	91.5–92.5
E	Yellow	76.4	89.5–90.5

Reaction with 3,4-dichlorobenzotrichloride. 3,4-Dichlorobenzotrichloride had the following properties: b.p. 80–85° at 1–2 mm.; n_D^{25} 1.5868. (This compound could not be found in the literature.) The reaction products were best separated in the following manner. The dioxocin (III-E) was insoluble in hot Skellysolve B and was filtered off. Skellysolve was removed from the filtrate and the residue was taken up in acetone. Water was added to incipient crystallization. After standing for about 30 minutes the dibenzoyl-*p*-cresol (V-E) was collected. Further addition of water precipitated the hydroxybenzophenone (II-E). By repetition of this method of fractional precipitation V-E and II-E were more completely separated. The analytical sample of V-E was obtained by recrystallization from benzene-cyclohexane and melted at 173.6–174.0°.

Anal. Calc'd for $C_{21}H_{12}Cl_4O_3$: C, 55.5; H. 2.7.

Found^{w}: C, 55.6; H, 2.6.

In alcohol solution, V-E gave no color with ferric chloride. In Nujol suspension, V-E showed a carbonyl band at 6.02 μ (5.97 μ in carbon disulfide), which corresponds with that previously (2) observed for 2,6-dibenzoyl-*p*-cresol (V-A) at 5.99 μ. For the synthesis of V-E see (2).

Sulfuric acid hydrolyses of the dioxocins (III). The procedure followed was essentially the same as that described (1) for the non-chlorinated dioxocin (III-A), except that in some cases, heat was needed in order to effect complete solution, a larger quantity of sulfuric acid also being used. In these cases the lower yields are probably due to increasing sulfonation. The results are in Table IV.

SUMMARY

1. The aluminum chloride-catalyzed reactions of four chlorinated benzotrichlorides and *p*-cresol were investigated and were found to yield the corresponding 2-hydroxy-5-methylbenzophenones and dioxocins. In addition, xanthones were obtained from the reactions involving benzotrichlorides bearing a chlorine in the 2-position. 2,6-Bis(3,4-dichlorobenzoyl)-*p*-cresol was obtained from the reaction involving 3,4-dichlorobenzotrichloride.

2. 6-Chloro-2-methylxanthone was prepared in 83% yield from 2,4-dichloro-2′-hydroxy-5′-methylbenzophenone.

3. 2,6-Bis(3,4-dichlorobenzoyl)-*p*-cresol was prepared in 93% yield by the aluminum chloride-catalyzed reaction of 3′,4′-dichloro-2-hydroxy-5-methylbenzophenone and 3,4-dichlorobenzotrichloride in carbon disulfide.

4. The dioxocins were each converted into the corresponding hydroxybenzophenones by sulfuric acid hydrolysis.

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