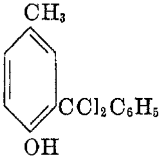
[Contribution from the McPherson Chemical Laboratory, the
Ohio State University]

2,6-DIBENZOYL-*p*-CRESOL

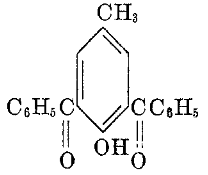
MELVIN S. NEWMAN and A. G. PINKUS

Received January 18, 1954

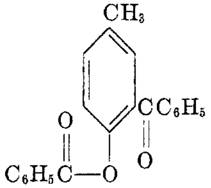
In an accompanying paper (1) the aluminum chloride-catalyzed condensation of benzotrichloride with *p*-cresol to yield 2-hydroxy-5-methylbenzophenone (I) and 6,12-diphenyl-2,8-dimethyl-6,12-epoxy-6*H*,12*H*-dibenzo[*b*,*f*][1,5]dioxocin, II,[1] was discussed. Several unsuccessful attempts to isolate the supposed chlorinated intermediate (III) were also described. In one case the reaction mixture, resulting from the condensation of equimolar amounts of *p*-cresol and benzotrichloride with a 25% excess of aluminum chloride in carbon disulfide, was carefully treated with dry methanol. A careful examination of the reaction products revealed that no dioxocin (II) was present. A 78% yield of I was obtained together with 4% of a new compound (IV), which we believe to be 2,6-dibenzoyl-*p*-cresol, on the basis of the evidence cited below.



III



IV



V

Analysis and molecular weight determination establish the formula $C_{21}H_{16}O_3$. The infrared absorption curve was quite similar to that of I (1) the salient features of which were the lack of absorption in the hydroxyl region (characteristic for *o*-hydroxy carbonyl groups) and the peak at 6.11μ. In addition, IV showed a strong peak at 5.99μ, characteristic of the carbonyl group in conjugated ketones such as acetophenone, 5.93μ, and benzophenone, 6.04μ (2, 3). It was not possible to prepare a phenylhydrazone or a 2,4-dinitrophenylhydrazone from IV nor did it yield a color with ferric chloride.

IV is slightly soluble in aqueous sodium hydroxide and forms a sodium salt (soluble in benzene) when shaken in benzene with sodium at room temperature. On treatment of this yellow solution with acetyl chloride the colorless acetyl derivative of IV was obtained in quantitative yield. This reaction rules out structure V for our compound. Furthermore, the benzoate (V) has been described previously (4) and has different properties. It is noteworthy that the Fries rearrangement of *p*-cresyl benzoate is quite sluggish (5), and also the Fries rearrangement is interfered with if the phenolic moiety carries a nitro or benzoyl group (6). However, the acetate of I has been rearranged to 2-acetyl-6-benzoyl-4-methylphenol (5). The formation of tribenzoylphoroglucinol in 30% yield by

---

[1] The structures I and II in this paper are the same as those designated I and II in the accompanying paper, ref. (1).

heating the tribenzoate of phloroglucinol at 130–140° with aluminum chloride for 30 minutes has been reported (7) but no chemical evidence supporting the structure of the compound obtained was given. The same compound has been obtained by reaction of phenylmagnesium bromide with carbon suboxide (8).

We have synthesized 2,6-dibenzoyl-*p*-cresol (IV) in 59% yield by condensing 2-benzoyl-4-methylphenol (I) with benzotrichloride in nitrobenzene solution but the reaction failed in carbon disulfide, probably because of the insolubility of the dichloroaluminum ($AlCl_2^+$) salt of I.

In a similar way 2,6-bis(3,4-dichlorobenzoyl)-*p*-cresol was synthesized in 93% yield from 2-(3,4-dichlorobenzoyl)-*p*-cresol and 3,4-dichlorobenzotrichloride (9). These syntheses are the first examples of what may be a general method for the direct synthesis of 2,6-diaroylphenols. It is noteworthy that the use of benzotrichlorides appears to be highly preferable to that of the corresponding benzoyl chlorides.

Under the conditions we used in condensing *p*-cresol with benzotrichloride (1) in carbon disulfide, 2,6-dibenzoyl-*p*-cresol (IV) was not formed. Only when the reaction complex was treated with methanol was it possible to isolate a small amount of IV. When the reaction complex was treated with water, no IV was formed. However, in the case of 3,4-dichlorobenzotrichloride a chlorinated analog of IV was formed directly (9). The formation of IV when the reaction complex is treated with methanol is undoubtedly due to the further condensation of unreacted benzotrichloride with some partly decomposed complex. We have always found that unreacted benzotrichloride was present after condensations involving equimolar amounts of *p*-cresol and benzotrichloride, but never any *p*-cresol. The dark resins formed in small amounts in all of these condensations undoubtedly arise from condensation of the 1:1 condensation complex with *p*-cresol. If some solvent, *e.g.* nitrobenzene, were used in which the complex formed was soluble, other results would probably be obtained. We hope to study this and other aspects of this problem.

The fact that 2,6-dibenzoyl-*p*-cresol (IV) is slightly soluble in aqueous sodium hydroxide but forms a sodium salt when shaken with sodium in benzene at room temperature indicates that the benzoyl group has an effect intermediate between that of secondary alkyl and tertiary alkyl groups with regard to the behavior of 2,6-disubstituted phenols towards various alkaline reagents (10).

EXPERIMENTAL

General. Melting points were taken with Anschütz total immersion thermometers. All liquids were redistilled in addition to further purification wherever noted. The molecular weight determination was by an ebullioscopic method in benzene using differential water thermometers. The authors are indebted to Walter Edwards for the ebullioscopic molecular weight determination and to Robert Lieberman for the infrared curve taken on a Baird double beam recording spectrophotometer using sodium chloride prisms.

Isolation of 2,6-dibenzoyl-p-cresol (IV). A reaction involving 5.41 g. of *p*-cresol, 8.33 g. of aluminum chloride, and 9.77 g. of benzotrichloride was carried out as previously described (1). At the completion of the reaction (2 hours), 40 ml. of anhydrous methanol was added dropwise to the reaction mixture at 0°. A vigorous reaction occurred with the initial formation of a yellow-orange color followed by solidification of the mixture and then subsequent dissolution in the excess methanol. The solution was blood-red in color. After the cautious addition of water the products were isolated in the usual manner (1). On removal of solvent, 10.9 g. of a dark solid remained. Extraction with methanol removed the dark color and left 7.54 g. of a yellow residue (see below). Evaporation of part of the methanol from the extract yielded 1.06 g. of I, m.p. 78–81° as discolored yellow crystals. On heating the yellow residue from above with petroleum ether (b.p. 65–70°, Skellysolve B), an insoluble residue remained. It was collected, washed with hot Skellysolve B, and dried *in vacuo*, 0.35 g., m.p. 162–164° (see below). The filtrate, on cooling, yielded I in two crops, 5.89 g. and 1.23 g.; m.p. 79–81° and 82–83° resp. The total yield of I was 78%. The high-melting residue from above was recrystallized from methanol to yield 0.33 g. (4.2% yield based on benzotrichloride) of IV, m.p. 164.8–165.0°. In the preparation of an analytical sample, the material was taken up in benzene-ether and extracted with 10% sodium hydroxide (see below for extract) to remove any traces of I which was much more soluble in alkali than IV. The solvent was removed and the residue was recrystallized from ethanol to yield yellow crystals, m.p. 166.4–166.6°.

Anal. Calc'd for $C_{21}H_{16}O_3$: C, 79.7; H, 5.1; Mol. wt., 316.
Found: C, 79.7; H, 5.2; Mol. wt., 321.

The sodium hydroxide extract from above, on acidification, yielded a small amount of IV, m.p. 165.0–165.5°. This shows that very little, if any, of I was present and that IV is slightly soluble in alkali. Pure IV in alcohol solution gave no color with ferric chloride. Attempts to prepare the phenylhydrazone and the 2,4-dinitrophenylhydrazone were unsuccessful.

Synthesis of 2,6-dibenzoyl-p-cresol (IV). To a stirred suspension of 3.0 g. (0.023 mole) of aluminum chloride in nitrobenzene was added 2.12 g. (0.01 mole) of I. After stirring for 15 minutes, during which time hydrogen chloride was evolved and a homogeneous solution was formed, 1.95 g. (0.10 mole) of benzotrichloride was added. The stirred mixture was heated at 70° for two hours during which time a dark green complex separated. The mixture was treated with ice and the nitrobenzene and unreacted benzotrichloride were removed by steaming. The steam-distillation was stopped when unreacted I was observed as a yellow solid in the condenser. The residue was collected, dried, and recrystallized from alcohol-benzene. Pure IV, m.p. 166.0–166.5°, was obtained in 59% yield (1.87 g.). A mixture melting point with a sample of IV isolated as described above from the reaction of *p*-cresol with benzotrichloride showed no depression.

An attempt to prepare IV by condensing *p*-cresol with two moles of benzotrichloride in nitrobenzene failed. It is noteworthy that nitrobenzene proved to be an unsatisfactory solvent for the condensation of carbon tetrachloride with *p*-cresol (11). The attempted condensation of I with benzotrichloride in carbon disulfide also failed, probably because of the insolubility of the dichloroaluminum salt of I in the solvent.

2,6-Bis(3,4-dichlorobenzoyl)-p-cresol. To a stirred suspension of 2.70 g. (0.02 mole) of aluminum chloride in 20 ml. of carbon disulfide was added a solution of 2.52 g. (0.009 mole) of 3,4-dichlorobenzoyl-*p*-cresol [see (9) for preparation]. Hydrogen chloride was evolved and an orange complex, partly soluble, separated. On addition of 2.38 g. (0.009 mole) of 3,4-dichlorobenzotrichloride the mixture turned very dark at room temperature but no hydrogen chloride evolution occurred until the mixture was warmed to 35°. After two hours at 35° the solvent was removed under reduced pressure and the residue was treated cautiously with cold water. The organic matter was taken into benzene-ether and after the usual washings, there was obtained by crystallization from benzene-Skellysolve V, 3.77 g. (92.8%) of 2,6-bis(3,4-dichlorobenzoyl)-*p*-cresol, m.p. 172.5–174.0°, in three crops. The melting point was not depressed by admixture with a sample isolated from the reaction of *p*-cresol with 3,4-dichlorobenzotrichloride (9).

Preparation of the acetate of IV. A solution of 0.325 g. (0.0011 mole) of IV in 10 ml. of dry benzene was treated with small pieces of clean sodium at room temperature with occasional shaking over a period of two hours with gentle heating at the end to ensure complete reaction. The solution was decanted from the excess sodium and the flask and sodium were washed with benzene until the washings were no longer colored yellow. The washings were combined with the solution. Acetyl chloride was then added dropwise to the yellow solution until decolorization was effected by one drop, six drops being used. The solution was filtered from the sodium chloride formed. On removal of solvent, 0.399 g. (99.7%) of the acetate of IV, m.p. 118–119.5° was obtained. An analytical sample was obtained by recrystallization from Skellysolve B as colorless plates, m.p. 119.4–120.0°.

Anal. Calc'd for $C_{23}H_{18}O_4$: C, 77.1; H, 5.1.
Found: C, 77.3; 77.3; H, 5.5, 5.4.

This acetate could not be prepared by acetylation in the usual way.

SUMMARY

1. 2,6-Dibenzoyl-*p*-cresol is formed on treating with methanol the complex resulting from the aluminum chloride-catalyzed reaction of *p*-cresol with benzotrichloride in carbon disulfide solution.

2. The synthesis of 2,6-dibenzoyl-*p*-cresol and 2,6-bis(3,4-dichlorobenzoyl)-*p*-cresol has been accomplished for the first time by a new synthesis involving the condensation of a 2-aroyl-*p*-cresol with a benzotrichloride.

COLUMBUS 10, OHIO

REFERENCES

(1) NEWMAN AND PINKUS, *J. Org. Chem.*, **19**, preceding paper (June 1954).
(2) HERGERT AND KURTH, *J. Am. Chem. Soc.*, **75**, 1622 (1953) and references therein.
(3) RASMUSSEN, TUNNICLIFF, AND BRATTAIN, *J. Am. Chem. Soc.*, **71**, 1068 (1949).
(4) HANTZSCH, *Ber.*, **39**, 3095 (1906).
(5) ROSENMUND AND SCHNURR, *Ann.*, **460**, 56 (1928).
(6) BLATT in *Org. Reactions*, **1**, 347 (1942).
(7) ROSENMUND AND LOHFERT, *Ber.*, **61**, 2601 (1928).
(8) CRAM AND ZIMMERMAN, *J. Am. Chem. Soc.*, **74**, 2646 (1952).
(9) NEWMAN AND PINKUS, *J. Org. Chem.*, **19**, following paper (June 1954).
(10) See STILLSON, SAWYER, AND HUNT, *J. Am. Chem. Soc.*, **67**, 303 (1945).
(11) NEWMAN AND PINKUS, *J. Org. Chem.*, **19**, paper 1 of this group (June 1954).