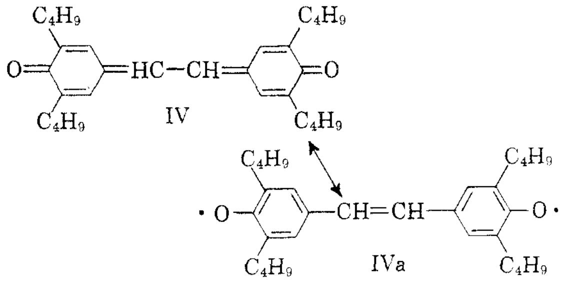
state (IV ⟷ IVa) for the molecule, which would be favored by steric effects.



IV

IVa

It is interesting to note that IV can be copolymerized with styrene in small amounts (~10%) to give what is probably a polyether.

### EXPERIMENTAL

*Tetra-t-butylstilbenequinone.* 2,6-Di-*t*-butyl-*p*-cresol was treated with one mole of bromine in acetic acid to give the bromo compound I, m.p. 91°,[1,2] which did not react with tertiary amines. It was rearranged to II by distillation, b.p. 124–6/0.5 mm. Treatment of II in benzene with pyridine or triethylamine gave an immediate precipitation of amine hydrobromide. The supernatant liquid became pale lemon yellow, indicating the possible presence of III. During the work-up of the reaction mixture, the solution acquired a darker orange color; the product finally isolated consisted of dark orange crystals. These were recrystallized from acetone, to give a product melting at 315°,[4] with partial volatilization to a yellow vapor, but without appearance of decomposition.

*Anal.* Calcd. for $C_{30}H_{44}O_2$: C, 82.55; H, 10.15. Found: C, 82.80, 82.56; H, 9.73, 9.55.

*4,4'-Dihydroxy-3,3',5,5'-tetra-t-butyldiphenylethylene.* One g. of the stilbene quinone (IV) was boiled with zinc dust and acetic acid until a colorless solution resulted. The diphenol melted at 240° after recrystallization from hexane.[4]

*4,4'-Dihydroxy-3,3',5,5'-tetra-t-butyldiphenylethane.* The stilbene quinone (1.63 g.) was dissolved in 50 ml. of tetrahydrofuran. Pulverized lithium aluminum hydride was added until the color was discharged. The solution was filtered, and diluted with dilute aqueous hydrochloric acid. The product was recrystallized from methanol, m.p. 172°.[4]

*Anal.* Calcd. for $C_{30}H_{46}O_2$: C, 82.18; H, 10.58. Found: C, 81.96, 81.76; H, 10.42, 10.49.

*Copolymer of styrene and tetra-t-butylstilbenequinone.* About 500 mg. of the quinone was dissolved in 5 g. of styrene (purified) and a trace of benzoyl peroxide was added. The mixture was heated on the steam bath under nitrogen in a sealed tube. As polymerization took place and the mixture became viscous, the color of the stilbene quinone was discharged. When the contents of the tube had solidified, it was dissolved in methylene chloride, and reprecipitated with large volumes of methanol several times. Analysis of the polymer indicated that the quinone was incorporated as an integral part of the polymer.

*Anal.* Found: C, 89.53, 89.72; H, 6.76, 7.07.

*Infrared spectra.* Tracings of the IR spectra of IV, V, and VI will be found in Figures 1–3. Concentrations were respectively 0.151 g., 0.150 g., and 0.157 g. per 4 cc. of $CHCl_3$. A differential technique was used to cancel the chloroform contribution to the spectra; however "dead" regions still exist which correspond to the blank portions of the curves.

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(4) C. D. Cook, *J. Org. Chem.*, **18**, 261 (1953).

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## Acid Cleavage of Some Substituted Tribenzoylmethanes

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During the course of an investigation of the multiple benzoylation of methyl ketones by benzoyl chloride in the presence of bromomagnesium-*t*-alkoxides,[2] it was observed that tribenzoylmethane is cleaved readily to dibenzoylmethane and benzoic acid by heating with acetic or formic acid.

There appears to be no recorded study of the hydrolysis of triacylmethanes with the exception of a brief mention by Hassall[3] that dibenzoylmethane was obtained by the action of cold concentrated sulfuric acid on dibenzoylacetylmethane. However, the cleavage of β-diketones by both acids and bases has been studied quite extensively.[4]

The present report describes a brief investigation of the effect of *para*-substituents on the direction of acid cleavage of monosubstituted tribenzoylmethanes. *p*-Nitro-, *p*-chloro- and *p*-methoxytribenzoylmethane were hydrolyzed by refluxing with acetic acid, and the products of the reactions were separated fairly quantitatively. The results of these experiments are summarized in Table I.

TABLE I

PERCENTAGE YIELDS OF PRODUCTS FROM CLEAVAGE OF $p$-$ZC_6H_4COCH(COC_6H_5)_2$

| Substituent (Z) | $C_6H_5$-$CO_2H$ | $p$-$ZC_6H_4$-$CO_2H$ | $(C_6H_5$-$CO)_2$-$CH_2$ | $p$-$ZC_6$-$H_4CO$-$CH_2CO$-$C_6H_5$ |
|---|---|---|---|---|
| $—NO_2$ | 14 | 83 | 80 | 16 |
| —Cl | 57 | 39 | 35 | 60 |
| $—OCH_3$ | 81 | 18 | 16 | 81 |

Formic acid hydrolysis of the above substituted tribenzoylmethanes gave variable results depending upon the source of the acid. Some samples behaved in a fashion similar to acetic acid, whereas others led to mixtures of 1,1,3,3-tetrabenzoylpropanes instead of the expected dibenzoylmethanes. They apparently arose from a Knoevenagel type reaction between the dibenzoylmethanes and formaldehyde which was either present in, or formed from, the formic acid during the course of the reactions.

### EXPERIMENTAL

*Tribenzoylmethanes.* These materials were prepared according to the method of Claisen[5] by causing the appropri-

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(1) Abstracted in part from the Ph.D. thesis of J. L. Guthrie, 1956.

(2) Guthrie and Rabjohn, *J. Org. Chem.*, **22**, 176 (1957).

(3) Hassall, *J. Chem. Soc.*, 50 (1948).

(4) For leading references see Hauser, Swamer, and Ringler, *J. Am. Chem. Soc.*, **70**, 4023 (1948).

(5) Claisen, *Ann.*, **291**, 90 (1896).

ately substituted benzoyl chloride to react with dibenzoylmethane in the presence of sodium ethoxide. The *p*-nitro- and *p*-methoxytribenzoylmethane have been reported by Curtin and Russell[6] and their results were repeated. The *p*-chlorotribenzoylmethane seems to be new, and it apparently was obtained as a mixture of the enol and keto forms. Its melting point (uncorrected) remained at 189–204° after five recrystallizations from benzene–petroleum ether (b.p. 60–68°).

*Anal.* Calcd. for $C_{22}H_{15}ClO_3$: C, 72.83; H, 4.17. Found: C, 72.77; H, 4.35.

*Hydrolysis of the tribenzoylmethanes.* A mixture of 150 ml. of glacial acetic acid, to which a few milliliters of water had been added, and approximately 0.015 mole of the tribenzoylmethane was heated at reflux for 2 hr. The resulting solution was poured into 1 l. of water and the precipitate was removed by filtration. The solid was stirred with sodium bicarbonate solution to dissolve acidic materials, and the mixture of dibenzoylmethanes was removed by filtration. The combined filtrates, which were still acidic, were extracted ten times with ether and the crude acids were obtained by evaporation of the ethereal solutions under reduced pressure.

The mixtures of dibenzoylmethanes were separated by fractional crystallization from methanol. The mixed benzoic acids were dissolved in sodium carbonate solution and the solution was washed with petroleum ether (b.p. 60–68°). The acids were reprecipitated with hydrochloric acid and separated by fractional crystallization from water.

The melting points of the substituted dibenzoylmethanes and benzoic acids corresponded with those recorded in the literature. The percentage yields of the various cleavage products obtained are given in Table I.

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[6] Curtin and Russell, *J. Am. Chem. Soc.*, **73**, 5160 (1951).

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# Synthesis of DL-Threoninol

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*Received October 26, 1956*

During the course of an investigation of the anticoagulant activity[1] of synthetic sphingosine[2] and its derivatives we became interested in studying the behavior of both diastereoisomers of threoninol which is the lowest homologue of dihydrosphingosine.

Carter and coworkers[3] obtained the pure oxalate of allothreoninol by hydrogenation of allothreonine methyl ester with Raney nickel under high pressure. However, an attempt to prepare threoninol similarly resulted in a mixture of the epimers. Recently threoninol has been prepared by reduction of threonine ethyl ester with lithium aluminum hydride,[4] and by hydrolysis of *N*-benzoylthreoninol obtained by treatment of *N*-benzoylthreonine ethyl ester with lithium borohydride.[5] In both cases, however, the raw products were converted directly into the dinitrophenyl derivatives without specification of yields. We wish now to report a convenient synthesis of threoninol.

When the benzamido esters of allothreonine and threonine were reduced with lithium aluminum hydride and the resulting benzylaminodiols were debenzylated with palladium-on-charcoal the pure oxalates of both allothreoninol and threoninol were obtained in excellent yields. The benzamido esters were prepared by selective reduction of ethyl $\alpha$-benzamidoacetoacetate with sodium borohydride.[2]

## EXPERIMENTAL

*Reduction of ethyl $\alpha$-benzamidoacetoacetate with sodium borohydride.* Ten g. of 2-phenyl-4-(1-hydroxyethylidene)-oxazolone-5[6] were refluxed for 2 hr. with 100 cc. of absolute alcohol. The dark red solution was decolorized with charcoal and cooled to 20°. A solution of 0.8 g. sodium borohydride in 20 cc. of methanol (stabilized with a few drops of normal sodium hydroxide) was added dropwise and the mixture left for 30 min. Twenty ml. of water were then added and a few drops of acetic acid to bring the solution to *p*H 6. It was then evaporated *in vacuo* and the oil extracted with 60 cc. of hot chloroform. After evaporation of the solvent the residue was taken up with 15 cc. of ether and left overnight at 0°. A crystalline precipitate (3.5 g.) of m.p. 75–91° was collected which, after three crystallizations from ethyl acetate and petroleum ether (2:3) gave 2.5 g. of *N*-benzoylallothreonine ethyl ester, m.p. 101–102°. From the collected mother liquors the threonine ester was obtained following the procedure of Elliott.[7]

*N-benzyl-*DL*-allothreoninol.* To a stirred suspension of 2 g. of lithium aluminum hydride in 50 cc. of tetrahydrofuran (distilled over lithium aluminum hydride) was added slowly a solution of 4 g. of *N*-benzoylallothreonine ethyl ester in 50 cc. of tetrahydrofuran and the mixture was refluxed for 2 hr. After cooling in an ice bath 3 cc. of water was added followed by 3 cc. of 20% sodium hydroxide and 6 cc. of water. The precipitated inorganic salts were filtered off and washed with ether. The combined filtrates were washed with saturated sodium chloride solution and dried over sodium sulfate. Evaporation of the solvent left an oil which was dissolved in 20 cc. of hot benzene and precipitated with 40 cc. of petroleum ether. There was obtained 3.1 g. (99%) of crystals m.p. 56–60°. Crystallization from benzene–petroleum ether (2:3) yielded 2.3 g. of m.p. 62–63°.

*Anal.* Calcd. for $C_{11}H_{17}O_2N$: C, 67.6; H, 8.8; N, 7.1. Found: C, 67.0; H, 8.7; N, 6.6.

*N-benzyl-*DL*-threoninol*, prepared as above, was obtained in a 90% yield as an oil which could not be induced to crystallize and was used directly for debenzylation.

DL*-Allothreoninol.* 2.3 g. of *N*-benzylallothreoninol dissolved in 50 cc. of alcohol was hydrogenated with 1 g. palladium-on-charcoal (10%) at 50 p.s.i. and 40° for 15 hr. The oil obtained after evaporation of the filtrate was dissolved in 30 cc. absolute alcohol and converted into the

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[1] E. Hecht and D. Shapiro, forthcoming publication.

[2] D. Shapiro and K. H. Segal, *J. Am. Chem. Soc.*, **76**, 5894 (1954).

[3] H. E. Carter, W. P. Norris, and H. E. Rockwell, *J. Biol. Chem.*, **170**, 295 (1947).

[4] Marian Jutisz, Michel Privat de Garilhe, Michel Suquet, and Claude Fromageot, *Bull. soc. chim. biol.*, **36**, 117 (1954).

[5] J. C. Crawhall and D. F. Elliott, *Biochem. J.*, **61**, 264 (1955).

[6] J. Attenburrow, D. F. Elliott, and G. F. Penny, *J. Chem. Soc.*, 310 (1948).

[7] D. F. Elliott, *J. Chem. Soc.*, 589 (1949).