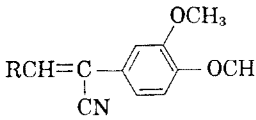
TABLE I

SUBSTITUTED ACRYLONITRILES



R	Formula	Yield, %[a]	M.P., °C.[b]	Color	Analyses: Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
3-Pyridyl[c]	$C_{16}H_{14}N_2O_2$	69	142 -143.5	Light yellow	72.16	72.40	5.29	5.28
4-Pyridyl[d]	$C_{16}H_{14}N_2O_2$	18	141 -142	White	72.16	72.09	5.29	5.51
2-Quinolyl[e]	$C_{20}H_{16}N_2O_2$	63	139- 140	Light yellow	75.93	76.00	5.10	5.16
4-Quinolyl[f]	$C_{20}H_{16}N_2O_2$	41	180 -181.5	Yellow	75.93	75.85	5.10	5.29
3-Isoquinolyl[g]	$C_{20}H_{16}N_2O_2$	81	147 -148	Yellow	75.93	75.90	5.10	5.14
2-Furyl	$C_{15}H_{13}NO_3$	81	99 -100	Yellow-orange	70.57	70.57	5.13	5.24
3-Indolyl	$C_{19}H_{16}N_2O_2$	46	196 -197	Yellow	74.98	74.87	5.30	5.49
9-Julolidyl	$C_{23}H_{24}N_2O_2$	76	157.5-158.5	Yellow	76.64	76.60	6.71	6.84
2-Thienyl	$C_{15}H_{13}NO_2S$	91	122 -123.5	Yellow	66.41	66.37	4.83	4.68

[a] Yield of recrystallized product. [b] All melting points are uncorrected. [c] Literature m.p. 141–142° (Ref. 1). Hydrochloride salt, recrystallized from ethanol-water, yellow crystals, m.p. 220–222° dec. *Anal.* Calcd. for $C_{16}H_{14}N_2O_2 \cdot HCl$: C, 63.47; H, 4.99. Found: C, 63.68; H, 5.07. [d] Literature m.p. 138.5–139.5° (Ref. 1). [e] Hydrochloride salt, recrystallized from ethanol, red crystals, m.p. 229–231° dec. Anal. Calcd. for $C_{20}H_{16}N_2O_2 \cdot HCl$: C, 68.08; H, 4.86. Found: C, 68.27; H, 4.92. [f] Hydrochloride salt, recrystallized from ethanol-water, red crystals, m.p. 233–235° dec. *Anal.* Calcd. for $C_{20}H_{16}N_2O_2 \cdot HCl$: C, 68.08; H, 4.86. Found: C, 67.83; H, 4.84. [g] Hydrochloride salt, recrystallized from ethanol, light green crystals, m.p. 105–107° dec. *Anal.* Calcd. for $C_{20}H_{16}N_2O_2 \cdot HCl$: C, 68.08; H, 4.86. Found: C, 68.42; H, 4.67.

sulting solution was made basic with sodium carbonate solution. The white crystals which appeared were filtered and recrystallized from Methyl Cellosolve.

α-3,4-Dimethoxyphenyl-β(3-indolyl)acrylonitrile. A mixture of 8.9 g. (0.05 mole) of 3,4-dimethoxyphenylacetonitrile and 7.3 g. (0.05 mole) of indole-3-aldehyde was refluxed in 200 ml. of absolute ethanol in the presence of 10 ml. of piperidine for 18 hr. On cooling, a precipitate appeared which was filtered and recrystallized from Methyl Cellosolve.

α-3,4-Dimethoxyphenyl-β(9-julolidyl)acrylonitrile. A mixture of 20.1 g. (0.1 mole) of julolidine-9-carboxaldehyde,[2] 17.7 g. (0.1 mole) of 3,4-dimethoxyphenylacetonitrile and 5.6 g. (0.1 mole) of potassium hydroxide in 200 ml. of absolute ethanol was refluxed. Crystals of the product began appearing in 5 min. and after 0.5 hr. the heating was stopped, 100 ml. of water was added and the flask cooled in an ice bath. The yellow product was filtered and recrystallized from Methyl Cellosolve-water.

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Infrared Spectrum of Tetra-*t*-Butylstilbenequinone

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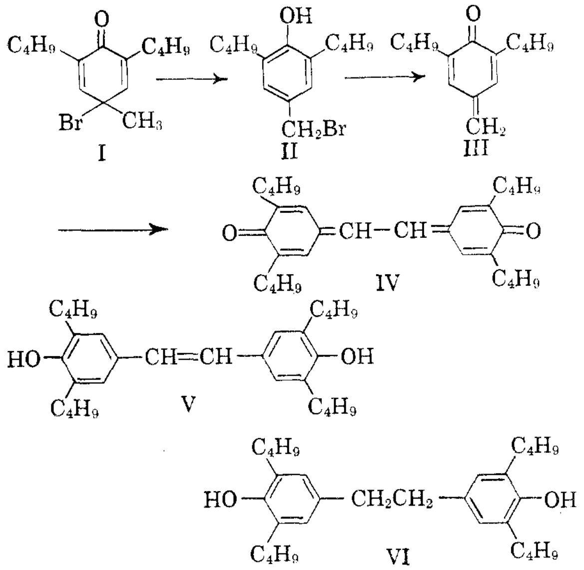
2,6-Di-*t*-butyl-*p*-cresol reacted with bromine to give I, a cyclohexadienone derivative[1] which rearranged on distillation[1,2] to the benzyl bromide II. Compound II was treated with tertiary amines which removed the elements of HX to give the presumed intermediate III, which was isolated as tetra-*t*-butylstilbenequinone.



This bright orange quinone was reduced to the corresponding diphenols (V) and (VI) by zinc-acetic acid, and lithium aluminum hydride, respectively.

The infrared absorption spectra of V and VI show a sharp "free" hydroxyl band at 2.75μ with no indication of any hydrogen-bonded hydroxyl even at relatively high concentrations. This results from the very effective steric hindrance provided by the adjacent *t*-butyl groups. The infrared spectrum of IV in $CHCl_3$ solution shows a remarkably large shift of the carbonyl band to 6.22 μ. For comparison, the carbonyl absorption in a $CHCl_3$ solution of 3,5,3′,5′-tetra-*t*-butyldipheno-

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(1) G. M. Coppinger and T. W. Campbell, *J. Am. Chem. Soc.*, **75**, 734 (1953).

(2) C. D. Cook, N. G. Nash, and H. R. Flanagan, *J. Am. Chem. Soc.*, **77**, 1783 (1955).

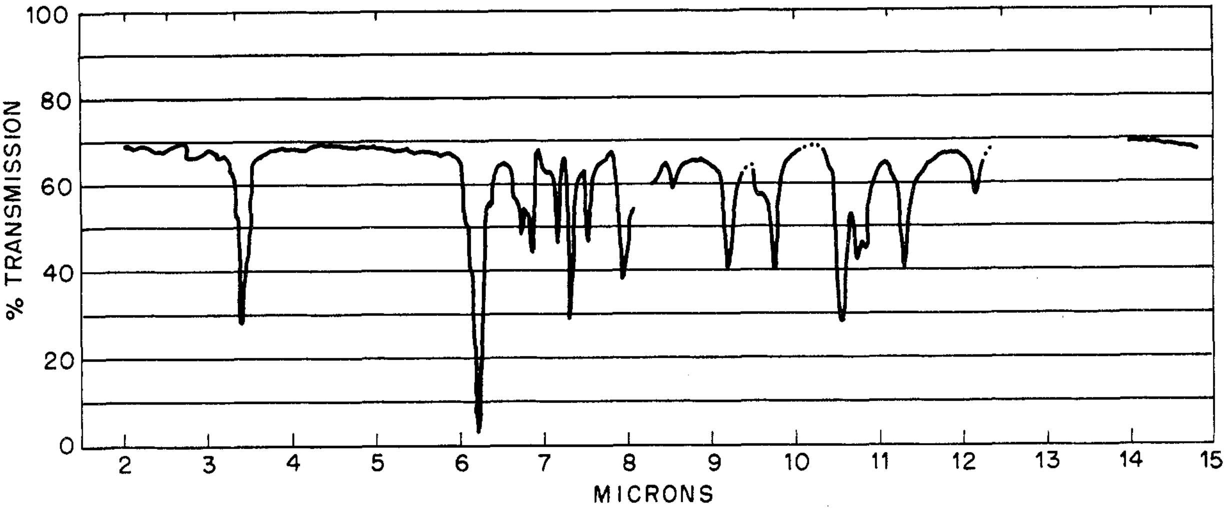

FIG. 1. Tetra-*t*-butylstilbenequinone (IV)

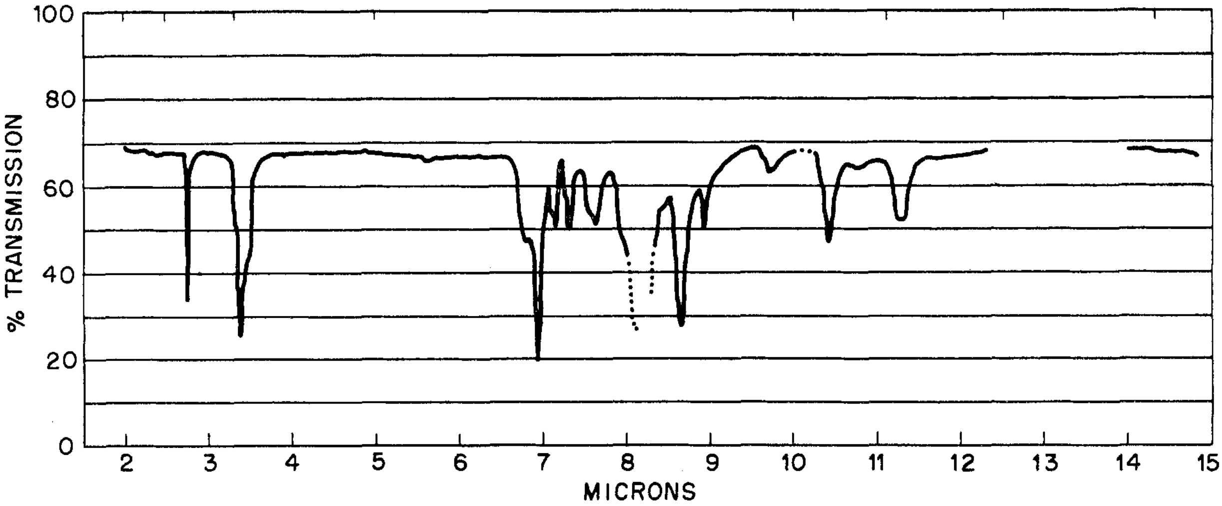

FIG. 2. 4,4′-Dihydroxy-3,3′,5,5′-tetra-*t*-butyldiphenylethylene. (V)

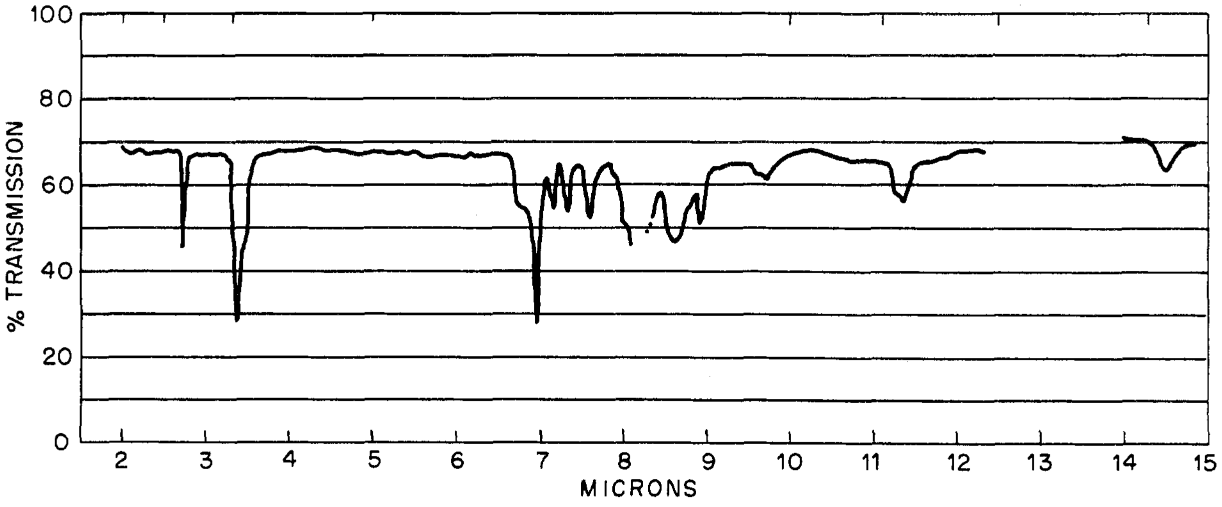

FIG. 3. 4,4′-Dihydroxy-3,3′,5,5′-tetra-*t*-butyldiphenylethane (VI)

quinone occurs at 6.12 μ.[3] Compound IV is the only compound to the authors' knowledge in which straight conjugation is effective enough to cause such a large shift. This unusual band position is also evidence of an abnormally weak C=O bond, and it is felt that a molecular orbital calculation would probably show a low-lying diradical

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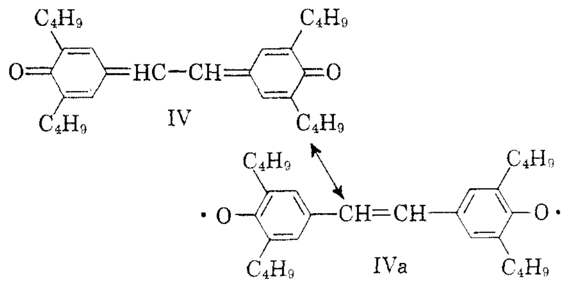
(3) N. Fuson, M. L. Josien, and E. M. Shelton, *J. Am. Chem. Soc.*, 76, 2526 (1954).

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).

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 $p\text{-}ZC_6H_4COCH(COC_6H_5)_2$

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).