181-183° (yield 84%). *Anal.* Calcd. for $C_{14}H_{18}O_4$: C, 67.16; H, 7.24; neut. equiv., 125. Found: C, 67.47; H, 7.26; neut. equiv., 124.

2-Hydroxy-2,5-dimethyl-5-phenylhexanone-3 (IV).—Aluminum chloride (114 g., 0.86 mole) was added gradually during the course of 0.5 hour to a stirred solution of 40.5 g. (0.28 mole) of 2,2,5,5-tetramethyltetrahydrofuranone (11) and 250 cc. of dry benzene, while maintaining the reaction mixture at 30-40° with occasional cooling. Stirring was continued at 40° for 20 hours. The cooled reaction mixture was poured into 1 liter of an ice and water mixture, the benzene solution was separated, washed with soda solution and water, dried and evaporated to give 55 g. of a dark, reddish sirup. A 4.7-g. aliquot of this material was chromatographed on an alumina column. The non-hydroxylic products were entirely eluted off with petroleum ether and benzene. Elution with diethyl ether then yielded 1.2 g. of the desired hydroxy ketone, b.p. 86–87° (0.3 mm.) as a colorless liquid, $n^{25}D$ 1.5073. This corresponds to a 23% yield. *Anal.* Calcd. for $C_{14}H_{20}O_2$: C, 76.31; H, 9.14. Found: C, 76.06; H, 8.94.

Oxidation of IV to β,β-Dimethyl-β-phenylpropionic Acid.—A mixture of 5 g. of chromic oxide, 5 cc. of water, 50 g. of glacial acetic acid and 2 g. of the hydroxy ketone IV was allowed to stand for 20 hours at room temperature. Excess chromic oxide was decomposed with methanol, the mixture poured into water extracted with ether and the ether extract concentrated under reduced pressure to a thick sirup. This was purified *via* its cyclohexylamine salt (m.p. 166–167°) to yield the crystalline acid, m.p. 56–57° (from petroleum ether); yield 90%; neut. equiv. calcd. 178, found 179.

For comparison purposes a sample of pure β,β-dimethyl-β-phenylpropionic acid was prepared in 70% yield by treating 30 g. of chloro-*t*-butylbenzene[8] (neophyl chloride) in 100 cc. of dry ether with 4.3 g. of magnesium turnings. When formation of the Grignard reagent was complete, it was decomposed by adding powdered solid CO_2 followed by decomposition with water and dil. HCl, and extraction of the desired acid with ether. It melted at 56–57° and gave no melting point depression on admixture with the acid obtained above from the chromic acid oxidation.

Cyclization of IV to 1,1,4,4-Tetramethyltetralone-2 (III).—To a stirred solution of 11 g. of the hydroxyketone IV and 200 cc. of carbon disulfide, there was gradually added 13.3 g. of powdered anhydrous $AlCl_3$ at 10°. The temperature was then raised slowly to the refluxing point (46°) and held there 4 hours. The cooled product was decomposed with ice-water, and the product (10.2 g. of oil) recovered by evaporation of the carbon disulfide. A 2.2-g. aliquot of this oil was chromatographed on a column of alumina and eluted with benzene. Evaporation of the benzene gave 0.2 g. of the crystalline tetralone III, corresponding to a 10% conversion of IV to III. Further elution with ether gave 1.9 g. of non-crystalline sirup.

Ketone (V).—Aluminum chloride (333 g., 2.5 moles) was added portionwise to a stirred solution of 142 g. (1 mole) of 2,2,5,5-tetramethyltetrahydrofuranone (II) in 500 cc. of dry benzene, while maintaining the reaction mixture at 40–50°. The mixture was then boiled under reflux (75–80°) for 4 hours. The cooled product was poured into ice and water, the benzene layer separated and the aqueous phase extracted with ether. The combined organic layers were washed with soda solution and water, dried and evaporated to a sirup. Fractional distillation of this sirup under vacuum at 1 mm. gave: (a) 15 g., 82-96°; (b) 52 g., 96–103°; (c) 49 g., 103–105°; (d) 5 g., 105–112°; (e) 23 g. of residual tar. Upon cooling to −15° for 24 hours, fraction d yielded 1.4 g. of the solid tetralone III. None of the other fractions showed any crystalline separation. Fraction b was a colorless liquid, the infrared analysis of which showed it to be an *o*-substituted benzene containing unstrained carbonyl and free from unsaturation or hydroxy groups. The analytical sample boiled at 99-101° (1 mm.). Calcd. for $C_{14}H_{18}O$: C, 83.14; H, 8.95. Found: C, 82.85; H, 9.25. Fraction c also contains a considerable amount of this compound (V).

Oxidation of Ketone V to Monocarboxylic Acid XII.—A mixture of 10 g. of V, 50 g. of $KMnO_4$ in 800 cc. of water and 1 g. of sodium hydroxide was boiled under reflux for 20 hours, then cooled and the manganese dioxide decomposed with sodium bisulfite. The solution was then filtered and the filtrate acidified with sulfuric acid. The white crystalline product (1.0 g.) was filtered off and recrystallized from petroleum ether to give colorless crystals, m.p. 131-132°. *Anal.* Calcd. for $C_{13}H_{16}O_2$: C, 76.42; H, 7.89; neut. equiv., 204. Found: C, 76.35; H, 7.85; neut. equiv., 206.

Attempts to esterify the carboxyl group of the acid XII by refluxing with ethyl alcohol and sulfuric acid as a catalyst for three hours were completely unsuccessful. The acid was recovered unchanged, which is consistent with the behavior of a tertiary carboxylic acid.

Reduction of Ketone V to Corresponding Alcohol XIII.—This was carried out as described for the preparation of X except that 1 g. of ketone V and 1 g. of lithium aluminum hydride in dry ether was used. The alcohol obtained was a crystalline solid, m.p. 76-77°. *Anal.* Calcd. for $C_{14}H_{20}O$: C, 82.28; H, 9.87. Found: C, 82.26; H, 9.94.

NEW HAVEN, CONNECTICUT

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[8] F. C. Whitmore, C. A. Weisgerber and A. C. Shabica, THIS JOURNAL, **65**, 1469 (1943).

[CONTRIBUTION NO. 448 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Syntheses by Free Radical Reactions. VI. The Addition of Stable Aryloxy Radicals to Unsaturates

BY W. R. HATCHARD, R. D. LIPSCOMB AND F. W. STACEY

RECEIVED JANUARY 20, 1958

Stable aryloxy radicals derived from 2,4,6-tri-*t*-butylphenol and 2,6-di-*t*-butyl-4-phenylphenol reacted with butadiene, chloroprene, 2,5-dimethylene-2,5-dihydrofuran, vinyl chloride and acrylonitrile at 25–80° to form crystalline products in which two aryloxy radicals were combined with one unsaturate molecule. These products are postulated to be mixtures of isomeric alkylene-bis-trisubstituted cyclohexadienones with the preponderant isomers being 4,4'-alkylenebis-(2,4,6-trisubstituted-2,5-cyclohexadienones). Much higher yields were obtained with chloroprene and butadiene than with monounsaturates. Maleic anhydride reacted with 2,4,6-tri-*t*-butylphenol under oxidizing conditions to give a mixture of products.

Free radical reactions of 2,4,6-trialkylphenols under mild oxidizing conditions have been shown to lead to derivatives of trialkylcyclohexadienones. Thus, with nitric acid,[1] benzoyl peroxide[2] and alkylperoxy radicals,[3,4] 2,4,6-trialkylphenols yielded the 4-substituted-2,4,6-trialkylcyclohexa-2,5-dien-1-ones. "Hindered phenols"[5] substituted in

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[1] D. G. Jones, British Patent 699,125 (1953).

[2] S. L. Cosgrove and W. A. Waters, *J. Chem. Soc.*, 388 (1951).

[3] T. W. Campbell and G. M. Coppinger, THIS JOURNAL, **74**, 1469 (1952).

[4] A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 3211 (1953).

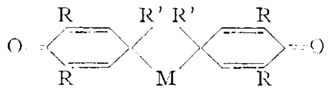
[5] (a) W. C. Sears and L. J. Kitchen, THIS JOURNAL, **71**, 4110 (1949); (b) G. H. Stillson, D. W. Sawyer and C. K. Hunt, *ibid.*, **67**, 303 (1945); (c) N. D. Coggeshall, *ibid.*, **69**, 1620 (1947).

the 2,4,6-positions with bulky groups lacking hydrogen atoms on the atom adjacent to the ring undergo reaction stepwise with initial formation of a stable free radical[6,7] and subsequent reaction to form tetrasubstituted cyclohexadienones. In this way, bromine, oxygen and nitrogen dioxide reacted with a solution of 2,4,6-tri-*t*-butylphenoxy radical to form the corresponding 4-substituted-2,4,6-tri-*t*-butylcyclohexa-2,5-dien-1-ones.[8]

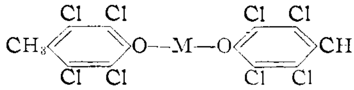
The present paper describes the reaction of stable aryloxy radicals derived from 2,4,6-tri-*t*-butylphenol and 2,6-di-*t*-butyl-4-phenylphenol with butadiene, chloroprene, 2,5-dimethylene-2,5-dihydrofuran, vinyl chloride, acrylonitrile and maleic anhydride. Reaction of the aryloxy radicals with the dienes gave good yields of yellow, crystalline solids in which two aryloxy radicals were combined with one unsaturate molecule. Similar products were obtained in low yield from vinyl chloride, acrylonitrile and maleic anhydride.

The new products were prepared by the reaction at 25–80° of the unsaturate in a neutral solvent either with a mixture of hindered phenol and oxidizing agent or with a solution of aryloxy radical preformed by oxidation of the phenol. The dienes reacted more rapidly than the monoölefins. In addition to the solids, yellow oils, which could not be induced to crystallize, were obtained.

The 2:1 adducts have been assigned the structure I, where M represents the unsaturate molecule.



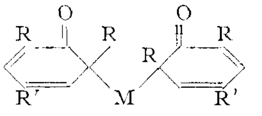
I, R = $C(CH_3)_3$
R' = $C(CH_3)_3$ or C_6H_5



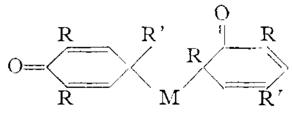
II

These 4,4'-alkylenebis-(2,4,6-trisubstituted-2,5-cyclohexadien-1-ones) thus are different in structure from the alkylene diethers (II, M = unsaturate) prepared by Pummerer, *et al.*,[9] by the oxidation of tetrachloro-*p*-cresol and subsequent reaction of the oxidation product with dimethylbutadiene or cyclopentadiene. Structural assignment was based on elemental analysis, molecular weight determination, and infrared and ultraviolet absorption spectra which showed (1) quinone-type carbonyl absorption in the 6.0 μ region of the infrared, (2) the absence of hindered phenol ether absorption in the 8.0 μ region and (3) strong absorption at 244 mμ characteristic of 4-substituted-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-ones.[8] Quantitative catalytic hydrogenation of the butadiene adduct in ethanol with platinum oxide catalyst resulted in the absorption of two moles of hydrogen, which is more likely for structure I than for a structure similar to II. No evidence was found for phenolic ether compounds analogous to II in infrared spectra taken on the non-crystallizable, oily residues also obtained in these reactions.

Ultraviolet spectra of most of the crystalline adducts show additional absorption at 317 mμ of lower intensity than the absorption at 244 mμ. This absorption suggests the presence of the 6,6-disubstituted-2,4-cyclohexadiene-1-one moiety.[4] Although elemental analyses of the 2:1 adducts were in excellent accord with theoretical values, the melting points were raised by repeated recrystallizations and could not be brought to constant values. It is very likely that some of the adducts contain minor amounts of isomers having the structures III and/or IV, which are gradually eliminated by successive recrystallizations. This would account for the rise in extinction coefficient at about 245 mμ and the decrease at 317 mμ.



III, R = $C(CH_3)_3$
R' = $C(CH_3)_3$ or C_6H_6

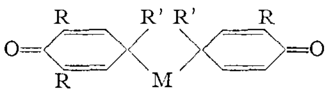


IV, R = $C(CH_3)_3$
R' = $C(CH_3)_3$ or C_6H_6

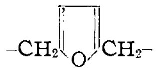
In the case of the dienes, addition apparently occurs in the 1,4-manner, since the products show infrared absorption at 10.35 μ for a *trans* internal double bond and do not show the absorption bands at 10.1 and 11.0 μ expected for a vinyl group.

Proposed structures for the 2:1 adducts along with yields and melting points are given in Table I.

TABLE I



R = $C(CH_3)_3$

Compound	R'	M	Yield, %	M.p., °C.
V	$C(CH_3)_3$	$-CH_2CH{=}CHCH_2-$	61	167–168.5
VI	$C(CH_3)_3$	$-CH_2CH{=}CClCH_2-$	79	163–170
VII	$C(CH_3)_3$	$-CH_2C(CN)H-$	*ca.* 1	195.5–197
VIII	$C(CH_3)_3$	$-CH_2CHCl-$	11	168–172
IX	$C(CH_3)_3$		100[a]	143.5–144.5
X	C_6H_5	$-CH_2CH{=}CHCH_2-$	*ca.* 2	169–170
XI	C_6H_5	$-CH_2CH{=}CClCH_2-$	8	179–180

[a] Before purification, m.p. 107–112°.

An attempt to form 2:2 adducts of the additive dimer type described by Coffman and Jenner[10] by the slow addition of 2,4,6-tri-*t*-butylphenol to a hot mixture of chloroprene, lead dioxide and benzene was unsuccessful, but gave the 2:1 adduct in 74% yield.

Oxidation of 2,4,6-tri-*t*-butylphenol with lead dioxide, in the presence of maleic anhydride, gave several different crystalline products. The major product was a relatively insoluble solid which melted with sublimation at 299–300°. It dissolved slowly in refluxing alkali solution and could be recovered unchanged by acidification, indicating that it was probably an anhydride or lactone. Analytical data indicate a molecular formula

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

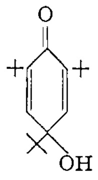
(7) E. Müller and K. Ley, *Chem. Ber.*, **87**, 922 (1954).

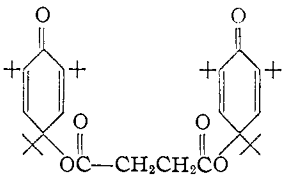
(8) C. D. Cook and R. C. Woodworth, THIS JOURNAL, **75**, 6242 (1953).

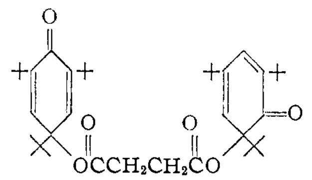
(9) R. Pummerer, G. Schmidutz and H. Seifert, *Chem. Ber.*, **85**, 535 (1952).

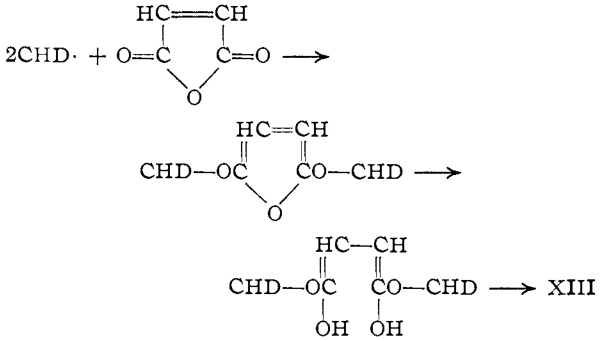
(10) D. D. Coffman and E. L. Jenner, THIS JOURNAL, **80**, 2872 (1958).

$C_{26}H_{38}O_6$, for which no corresponding structural formula is apparent. Maxima for the cyclohexadienone structure are absent from its ultraviolet absorption spectra. Three other compounds were isolated in low yield. One, m.p. 135–135.5°, was found to be 2,4,6-tri-*t*-butyl-4-hydroxy-2,5-cyclohexadien-1-one (XII).[11] The other two, m.p. 234–235° (A) and m.p. 173–174° (B), had the same composition, $C_{40}H_{62}O_6$, but differed in their ultraviolet absorption spectra. Both showed strong absorption in the 245 mμ region at 246 and 243 mμ, respectively. Compound B showed infrared absorption bands for quinone carbonyl at 5.98 and 6.05 μ and for other carbonyl at 5.56 and 5.70 μ. The infrared spectrum of A was not measured. On the basis of elemental analyses, molecular weight and absorption spectra, it is postulated that these compounds are isomeric tri-*t*-butyloxocyclohexadienyl succinates of possible structures XIIIa and XIIIb. Compounds of this structure could arise from 1,6-addition of cyclohexadienone radicals to the carbonyl functions of maleic anhydride followed by hydrolysis to an unstable enediol which would ketonize to give the ester.

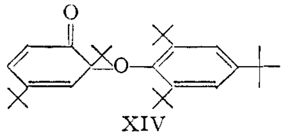

XII


XIIIa

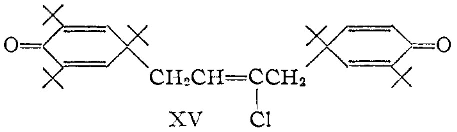

XIIIb


CHD· = tri-*t*-butyloxo-cyclohexadienyl

In some preparations, degradation products of the aryloxy radicals were isolated in low yield. One of these, a yellow solid melting at 145–146°, is apparently a dimer of the 2,4,6-tri-*t*-butylphenoxy radical minus the elements of isobutylene. This compound is probably identical to that described by Cook, Kuhn and Fianu,[12] but ultraviolet absorption spectra suggest a structure different from that proposed by these authors. This dimer does not exhibit the strong absorption at 244 mμ found to be characteristic of 4,4-disubstituted-2,5-cyclohexadien-1-ones, but instead shows absorption bands at 277, 286 and 308 mμ. The first two bands are characteristic of phenol ethers, and the third is most likely due to a 6,6-disubstituted-2,4-cyclohexadienone structure. A proposed structure is XIV, although it should be noted that loss of the *t*-butyl group from the indicated position is arbitrary.


XIV

That the aryloxy–unsaturate adducts were thermally unstable also was demonstrated by their behavior on melting. Melting points taken by slow heating covered a wider range than those taken rapidly and, at least in some cases, melting was accompanied by gas evolution. Heating the 2,4,6-tri-*t*-butylphenol–chloroprene adduct VI at 150–200° was found to cause evolution of isobutylene and formation of an oil from which a crystalline solid, m.p. 210–210.5°, was isolated. Elemental analysis and absorption spectra showed that this product still had a structure similar to that of the starting adduct, but had lost the elements of isobutylene. A possible structure is XV.


XV

Experimental

All melting points are uncorrected.

Preparation of Adducts.[13]—Two methods were used to prepare the adducts. In method A, the unsaturate was caused to react with a hydrocarbon solution of stable aryloxy radical which had been prepared by oxidation either with lead dioxide or with an alkaline potassium ferricyanide solution according to the method of Cook.[8] In method B, the phenol, oxidizing agent and unsaturate were mixed together, oxidation taking place in the presence of the unsaturate. Reaction mixtures were allowed to react at 25–80° until the characteristic color of the aryloxy radical had disappeared. Reaction usually was complete in 18 hours at 50° or several days at 25°.

4,4′-(2-Butenylene)-bis-(2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one) (V). Method A.—A 500-ml., three necked flask was fitted with a water-cooled condenser, a gas inlet tube which extended to the bottom of the flask, and a column packed with a mixture of 110 g. of lead dioxide and about 15 g. of Celite to which nitrogen pressure could be applied at the top. The system was flushed with nitrogen, and then 80 ml. of benzene was passed down the column followed by a solution of 22 g. (0.084 mole) of 2,4,6-tri-*t*-butylphenol in 60 ml. of benzene and a rinse of 100 ml. of benzene. A slow stream of butadiene gas was then passed through the dark blue solution at 10–20°. After 30 hours, the color of the solution had changed to yellow. Evaporation of the benzene gave a yellow, pasty solid from which was obtained by recrystallization from alcohol 10.2 g. (42%) of pale yellow crystals, m.p. 169–172°; ultraviolet $\lambda_{\max}^{\text{isooctane}}$ 244 mμ (ε 8900) and 317 mμ (ε 3500); infrared bands at 6.03 and 6.08 μ (quinone-type carbonyl).

Anal. Calcd. for $C_{40}H_{64}O_2$: C, 83.27; H, 11.18; mol. wt., 577. Found: C, 83.27; H, 11.28; mol. wt. (cryoscopic, benzene), 563.

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[11] K. Ley and E. Muller, *Chem. Ber.*, **89**, 1402 (1956).

[12] C. D. Cook, D. A. Kuhn and P. Fianu, THIS JOURNAL, **78**, 2002 (1956).

[13] R. D. Lipscomb, U. S. Patent 2,794,051 (May 28, 1957).

Method B.—A mixture of 20 g. (0.076 mole) of 2,4,6-tri-*t*-butylphenol, 30 g. (0.55 mole) of butadiene and 50 g. (0.21 mole) of lead dioxide in 100 ml. of benzene was sealed in a pressure bottle and mixed by tumbling at 50° for 20 hours. Filtration and evaporation gave 25 g. of oily, yellow crystals. After recrystallization from alcohol, the product weighed 14.6 g. (61%) and melted at 167–168.5°. A sample recrystallized once from chloroform and three times from benzene melted at 206–208°; mol. wt., 554, 557; $\lambda_{\max}^{\text{isoöctane}}$ 246 mμ (ε 19,000), 317 mμ (ε 1100).

4,4'-(2-Chloro-2-butenylene)-bis-(2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one) (VI).—A solution of aryloxy radical in benzene prepared by the ferricyanide oxidation of 12.5 g. (0.048 mole) of 2,4,6-tri-*t*-butylphenol was mixed with 48 g. (0.54 mole) of freshly-distilled chloroprene in a pressure bottle. The pressure bottle was sealed and allowed to stand at 25° for 5 days until the color had changed from blue to yellow. Evaporation of the solvent gave 14.2 g. of yellow crystals, which after recrystallization from alcohol melted at 163–170° (11.5 g., 79%); $\lambda_{\max}^{\text{isoöctane}}$ 244 mμ (ε 14,000) and 316 mμ (ε 2200).

Anal. Calcd. for $C_{40}H_{63}ClO_2$: C, 78.58; H, 10.39; Cl, 5.80; mol. wt., 611. Found: C, 78.36; H, 10.38; Cl, 5.48; mol. wt. (cryoscopic in benzene), 560, 570.

In a second preparation at 40°, reaction was complete in 18 hours, as judged by color change.

An attempt was made to form a 2:2 adduct by the following procedure. A solution of 7.0 g. (0.027 mole) of 2,4,6-tri-*t*-butylphenol in 100 ml. of benzene was added dropwise over 3 hours to a stirred mixture of 88 g. (1.0 mole) of chloroprene, 96 g. (0.38 mole) of lead dioxide and 100 ml. of benzene maintained under nitrogen at 65 ± 5° in a 500-ml., four-necked flask. Addition was made so slowly that the blue color formed by one drop was dispelled before the next drop was added. The reaction mixture was filtered and the filter cake was washed with ether. The filtrate and washings were combined and subjected to steam distillation. Extraction of the distillation residue with ether and then drying and evaporating the extract gave 7.2 g. of solid residue. Trituration in methanol gave 6.0 g. (74%) of yellow crystals, m.p. 169–172°. The melting point of a mixture with VI was not depressed.

Degradation Product of VI.—Five grams of VI heated at 150–200° for 20 minutes evolved a gas identified by mass spectrometry as isobutylene. The residue was a mixture of crystals and oil. Trituration in methanol followed by filtering gave 1.07 g. of tan solid, m.p. 208–210°. Further recrystallization from benzene after treatment with decolorizing charcoal yielded white crystals, m.p. 210–210.5°. $\lambda_{\max}^{\text{isoöctane}}$ 244 (ε 19,500).

Anal. Calcd. for $C_{36}H_{55}O_2Cl$: C, 77.87; H, 9.98; Cl, 6.39; mol. wt., 555. Found: C, 78.05, 78.09; H, 10.23, 10.29; Cl, 6.36; mol. wt., 524, 524.

4,4'-(Cyanoethylene)-bis-(2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one) (VII).—Into a three-necked flask fitted with a stirrer, condenser and addition funnel was placed 26 g. (0.10 mole) of tri-*t*-butylphenol, 113 g. (0.42 mole) of lead dioxide and 100 ml. of benzene. The mixture was stirred on the steam-bath for 5 minutes; then 100 g. (1.8 mole) of freshly-distilled acrylonitrile was added, and the mixture was stirred under reflux for 18 hours. The reaction mixture was then filtered to give an amber filtrate, the concentration of which gave 26.5 g. of amber oil. Trituration with methanol resulted in the formation of crystalline material which after separation and recrystallization from methanol melted at 195.5–197°, 0.37 g., $\lambda_{\max}^{\text{isoöctane}}$ 244 mμ (ε 24,000).

Anal. Calcd. for $C_{39}H_{61}O_2N$: N, 2.44; mol. wt., 575. Found: N, 2.69, 2.68; mol. wt., 585, 580.

Most of the product isolated was a red oil which was not further identified. Its nitrogen content, however, indicated the presence of materials richer in acrylonitrile residues. Found: N, 3.28, 3.26.

4,4'-(Chloroethylene)-bis-(2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one) (VIII).—A mixture of 10 g. (0.038 mole) of 2,4,6-tri-*t*-butylphenol, 50 ml. of benzene, 50 g. (0.21 mole) of lead dioxide and 50 g. (0.81 mole) of vinyl chloride was sealed in a pressure bottle and heated at 40° for 48 hours. Since the reaction mixture was still blue, the bottle was allowed to stand for a month at room temperature with occasional shaking until the color was yellow. Filtration and evaporation of the filtrate yielded 7.0 g. of a viscous, orange resin which was taken up in methanol and allowed to stand. Eventually 1.26 g. (11%) of yellow solid, m.p. 168–172°, was isolated. Recrystallization from benzene and alcohol gave a product which melted at 168–182°; $\lambda_{\max}^{\text{isoöctane}}$ 244 mμ (ε 14,900) and 316 mμ (ε 870).

Anal. Calcd. for $C_{38}H_{61}O_2Cl$: C, 77.97; H, 10.49; Cl, 6.05; mol. wt., 585. Found: C, 78.40, 78.19; H, 10.09, 10.11; Cl, 5.98; mol. wt., 640, 610.

2,5-Bis-[1,3,5-tri-*t*-butyl-4-oxo-2,5-cyclohexadienylmethyl]-furan (IX).[14]—To a benzene solution of aryloxy radical prepared by the lead dioxide oxidation of 15 g. (0.058 mole) of 2,4,6-tri-*t*-butylphenol was added 60 ml. of an ethereal solution containing 3.6 g. (0.038 mole) of 2,5-dimethylenedihydrofuran.[15] The mixture was allowed to stand 16 hours at room temperature during which time the color changed from blue to yellow. Evaporation of the solvent under reduced pressure gave 18 g. of yellow oil which subsequently crystallized. After recrystallization from acetonitrile, methanol and alcohol, the light yellow product melted at 143.5–144.5°.

Anal. Calcd. for $C_{42}H_{64}O_3$: C, 81.76; H, 10.46; mol. wt., 614. Found: C, 81.44, 81.72; H, 10.50, 10.54; mol. wt., 665.

4,4'-(2-Butenylene)-bis-(2,6-di-*t*-butyl-4-phenyl-2,5-cyclohexadien-1-one) (X).—A mixture of 2.8 g. (0.010 mole) of 2,6-di-*t*-butyl-4-phenylphenol, 15 ml. (9.3 g., 0.17 mole) of butadiene, 10 g. (0.042 mole) of lead dioxide and 50 ml. of benzene was sealed in a pressure bottle at room temperature for 14 days. The product obtained on evaporation of the filtered reaction mixture was a yellow, viscous oil. Solution in methanol and cooling gave 0.5 g. of pale yellow crystals. The melting point after further recrystallization was 169–170°.

Anal. Calcd. for $C_{44}H_{56}O_2$: C, 85.65; H, 9.15; mol. wt., 617. Found: C, 85.16; H, 9.18; mol. wt., 650, 645.

4,4'-(2-Chloro-2-butenylene)-bis-(2,6-di-*t*-butyl-4-phenyl-2,5-cyclohexadien-1-one) (XI).—A mixture of 0.5 g. (1.8 mmoles) of 2,6-di-*t*-butyl-4-phenylphenol, 24 ml. (23 g., 0.26 mole) of distilled chloroprene, 10 ml. of petroleum ether and 8.0 g. (0.033 mole) of lead dioxide was allowed to stand for 3 days at room temperature and was then filtered. Evaporation of the filtrate gave 0.47 g. of oily residue which crystallized after standing for 10 days. Recrystallization from alcohol gave 0.03 g. of yellow needles, m.p. 179–180°.

Anal. Calcd. for $C_{44}H_{55}O_2Cl$: C, 81.13; H, 8.52. Found: C, 80.52, 80.51; H, 8.55, 8.39.

Reaction of 2,4,6-Tri-*t*-butylphenoxy Radical with Maleic Anhydride.—A mixture of 10 g. (0.039 mole) of 2,4,6-tri-*t*-butylphenol, 40 g. (0.18 mole) of lead dioxide, 10 g. (0.10 mole) of maleic anhydride and 100 ml. of benzene was heated in a sealed pressure bottle at 80° for 18 hours. The yellow reaction mixture was filtered, and the filter cake was washed with benzene and chloroform and then dried, wt. 51 g. The cake was extracted for 18 hours with acetone. Evaporation of the extracts yielded 5.7 g. of tan solid, which was triturated in ether to give 4.49 g. of white solid, m.p. 294.5–297°. An analytical sample recrystallized from acetone melted at 299–300° with sublimation; $\lambda_{\max}^{\text{EtOH}}$ 216 mμ (ε 4500) and 334 mμ (ε 130); infrared bands at 3.7, 3.8 and 5.8 μ (COOH); 5.73 μ (ester carbonyl) and 5.6 μ (five-membered ring carbonyl).

Anal. Calcd. for $C_{26}H_{38}O_6$: C, 69.93; H, 8.58; mol. wt., 447. Found: C, 70.29, 70.19; H, 8.63, 8.55; mol. wt., 430, 435; sapn. equiv., 195.

The elemental analysis was not changed by recrystallization from alcohol (C, 70.01, 69.95; H, 8.56, 8.55; sapn. equiv., 193) or by sublimation (C, 70.12; H, 8.63). The solid dissolved in warm 5% aqueous sodium hydroxide solution. Acidification of the alkaline solution reprecipitated the original compound.

The original benzene filtrate was washed five times with 100-ml. portions of distilled water and two times with 100-ml. portions of 10% sodium hydroxide solution, dried over sodium sulfate, and evaporated. The residue was 7

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[14] This preparation was carried out by Dr. W. S. Friedlander.

[15] The preparation of this compound will be described in a forthcoming publication from these laboratories.

g. of oil which, on trituration in petroleum ether, gave 0.12 g. of white crystals which melted at 135–135.5°. This product had the same elemental analysis and ultraviolet absorption as a sample of 4-hydroxy-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one (XII) prepared by the decomposition of 2,4,6-tri-*t*-butyl-4-nitro-2,5-cyclohexadien-1-one.[11] The mixture melting point was not depressed. Evaporation of the petroleum ether and recrystallization of the residual crystals from petroleum ether and from alcohol ultimately yielded 0.5 g. of an additional white crystalline product, m.p. 234–235°; $\lambda_{max}^{CHCl_3}$ 246 mμ (ε 11,000) and 319 mμ (ε 420); infrared bands at 5.98 and 6.05 μ (quinone carbonyl); 5.56 and 5.70 μ (other carbonyl bands).

Anal. Calcd. for $C_{40}H_{62}O_6$: C, 75.19; H, 9.78. Found: C, 75.04; H, 9.60.

In a similar experiment using double the amount of maleic anhydride and the same quantities of other reactants, an additional compound was isolated from the neutral fraction by crystallization from methanol, 0.2 g., m.p. 173–174°; $\lambda_{max}^{isooctane}$ 243 mμ (ε 22,000) and 375 mμ (ε 64).

Anal. Calcd. for $C_{40}H_{62}O_6$: C, 75.19; H, 9.78; mol. wt., 639. Found: C, 75.18; H, 9.50; mol. wt., 600, 605.

Acidification of the alkaline extracts did not produce a water-insoluble solid. Maleic acid was recovered by ether extraction of the acidified extracts.

Dimer of 2,4,6-Tri-*t*-butylphenoxy Radical (XIV).—In the preparation of VII, 0.55 g. of a yellow crystalline solid, m.p. 145–146°, was isolated by crystallization from the mother liquors; $\lambda_{max}^{isooctane}$ 277 mμ (ε 370), 286 mμ (ε 420) and 308 mμ (ε 3,501); λ_{min} 293 mμ (ε 280). The same product was prepared in 50% yield by heating solid 2,4,6-tri-*t*-butylphenoxy radical at 80° for a week in the absence of air. Isobutylene was identified in the evolved gas.

Anal. Calcd. for $C_{32}H_{50}O_2$: C, 82.34; H, 10.80; mol. wt., 466. Found: C, 81.93; H, 10.60; mol. wt., 466, 455.

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[CONTRIBUTION NO. 449 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Syntheses by Free-radical Reactions. VII. The Reaction of 2,6-Di-*t*-butyl-4-methylphenol and 2,6-Di-*t*-butyl-4-isopropylphenol with Chloroprene

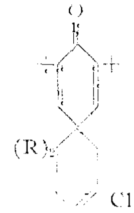
BY W. R. HATCHARD

RECEIVED JANUARY 20, 1958

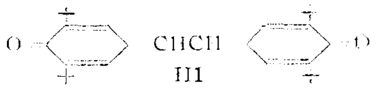
The oxidation of 2,6-di-*t*-butyl-4-methylphenol and of 2,6-di-*t*-butyl-4-isopropylphenol in the presence of chloroprene yielded crystalline 1:1 adducts which are postulated to be spiro[5.5]undeca-1,4,8-trien-3-one derivatives. A mechanism for their formation is proposed.

In an earlier paper[1] it was shown that stable aryloxy radicals add to unsaturates to form 4,4′-alkene- and 4,4′-alkenylene-bis-(2,4,6-trisubstituted-2,5-cyclohexadienone) derivatives. Stable radicals investigated were those formed by the oxidation of hindered 2,4,6-trisubstituted phenols which did not contain hydrogen on the α-carbon atoms. Chloroprene was found to be the most active unsaturate examined. The present paper describes the reaction of chloroprene under oxidizing conditions with 2,6-di-*t*-butyl-4-methylphenol and 2,6-di-*t*-butyl-4-isopropylphenol, neither of which forms an aryloxy radical of high stability. Oxidations of these phenols have been studied by a number of investigators[2–8] and shown to proceed through free radical intermediates.

In the present work, these phenols were found to react with chloroprene to form crystalline, 1:1 adducts which have the probable structures I and II. Reactions were carried out most conveniently by mixing a benzene solution of the phenol with an excess of lead dioxide and chloroprene in a pressure vessel and shaking at 50° for 16 hours. Under these conditions 2,6-di-*t*-butyl-4-methylphenol gave a 75% yield of the adduct. At 25°, the adduct was obtained in 34% yield along with a 32% yield of the stilbenequinone, 4,4′-acetylene-bis-[2,6-di-*t*-butyl-2,5-cyclohexadienone] (III).[3]



I, R = H
II, R = CH_3



III

When the phenol and a stoichiometric amount of aqueous alkaline potassium ferricyanide were added simultaneously to a solution of chloroprene in benzene at 55°, the adduct was formed in 46% yield. About 3% of 4,4′-ethylene-bis-[2,6-di-*t*-butylphenol][3] also was obtained. There was no evidence for the formation of 2:1 phenol–chloroprene adducts of the type described previously[1] or 2:2 adducts of the additive dimer type described by Coffman and Jenner.[9]

The structure proposed for the 2,6-di-*t*-butyl-4-methylphenol adduct (I) is based upon elemental composition, molecular weight and absorption spectra data and upon the properties of its hydrogenation products. Elemental analysis and molecular weight agree for the composition $C_{19}H_{27}OCl$. The infrared absorption spectrum shows bands in

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