Sterically Blocked Ketones, Alcohols and Acids

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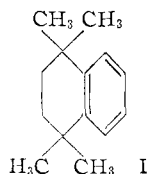
The condensation of benzene in the presence of anhydrous aluminum chloride with 2,2,5,5-tetramethyltetrahydrofuranone yields 1,1,4,4-tetramethyltetralone, an α-ketol $C_6H_5C(CH_3)_2CH_2COC(CH_3)_2OH$, and a third ketone $C_{14}H_{18}O$, not yet completely identified but believed to be 1-acetyl-1,3,3-trimethylindane. Oxidation of 1,1,4,4-tetramethyltetralone with *alkaline* permanganate solution gives 2-hydroxy-1,1,3,3-tetramethylidane-2-carboxylic acid; whereas oxidation with *neutral* permanganate cleaves the ring to yield o-phenylenedi-isobutyric acid. Sterically-hindered products derived from these intermediates for use in studies on radiation resistant polymers and plasticizers are described.

It is generally recognized that one of the weak linkages in certain industrial organic products, notably, coatings, plasticizers and plastics which are derived from alcohols, glycols and polycarboxylic acids, is the hydrogen-bearing α-carbon atom in these compounds. Such products often show a greater tendency to undergo decomposition induced by hydrolysis, heat, light, oxidation or γ-radiation, than those in which the hydrogen atoms on the α-carbon atom are absent or are replaced by bulky substituents.

The present paper reports the synthesis of some new types of sterically blocked compounds and their behavior toward various reagents.

Some time ago, it was shown that benzene, phenol and many other aromatics undergo a cyclialkylation reaction[1] when treated with certain 1,4-ditertiary glycols or their internal ethers, namely, the 2,2,5,5-tetraalkyltetrahydrofuranes, to yield naphthalene derivatives (I) possessing two sets of *gem*-dialkyl groups.
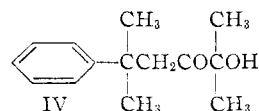
This easy method of introducing a plurality of *gem*-dialkyl groups into organic compounds induced us to study the condensation of benzene with 2,2,5,5-tetramethyltetrahydrofuranone (II) in the presence of aluminum chloride with the hope of obtaining the cyclic ketone, 1,1,4,4-tetramethyltetralone (III) which could serve as a starting
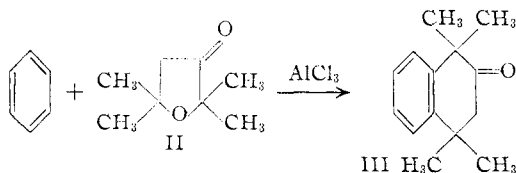
material for the preparation of mono- and dicarboxylic acids, substituted caprolactams, alcohols, glycols and other sterically hindered functional derivatives.

Actually, III was obtained in about 30% yield, but two other ketones also were isolated. One of these was identified as the α-ketol IV, obtained in about 23% yield.

The α-ketol IV upon further treatment with AlCl$_3$, cyclizes in part to III. The infrared spec-

trum of IV showed it to be a monosubstituted benzene derivative containing hydroxyl, carbonyl and *gem*-dimethyl groups with no olefinic unsaturation. A possible alternative β-ketol formula (IVa) was ruled out by the fact that upon chromic
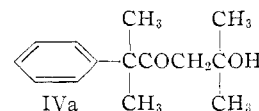
acid oxidation, the substance cleaved to yield β,β-dimethyl-β-phenylpropionic acid $C_6H_5C(CH_3)_2CH_2$-COOH, instead of α,α-dimethylphenylacetic acid.

The tetralone III is a crystalline solid possessing a sweet camphoraceous odor. Its structure was shown by the following considerations:

Its infrared spectrum indicated the presence of o-disubstituted benzene[2] and *gem*-dimethyl groups. The usual unsaturation tests with permanganate in acetone and bromine in CCl$_4$ were negative. The carbonyl absorption at 5.86 μ eliminated the possibility that the material was an indanone derivative since such strained five-membered ring compounds absorb considerably lower.

In an effort to show that III was a tetralin derivative, several dehydrogenation reactions were attempted with the hope that an easily identifiable naphthalene compound could be isolated. Dehydrogenations with selenium at 250–320° were all unsuccessful. However, palladium-on-charcoal under very vigorous conditions effected a dehydrogenation which yielded 1,2,3,4-tetramethylnaphthalene instead of the anticipated 1,4-dimethylnaphthalene. It is known that *gem*-dimethyl groups are not always eliminated as methane in such reactions but often migrate to adjacent positions.[3]

A number of other reactions of III were attempted, but the steric hindrance about the carbonyl group and its adjacent methylene group caused by the two sets of *gem*-dimethyl groups lowers the reactivity of this system very considerably. For example attempts to form a benzylidene derivative of III by reaction with benzaldehyde, a cyanoethylation product with acrylonitrile or a nitroso derivative with amyl nitrite, were all un-

(1) H. A. Bruson and J. W. Kroeger, THIS JOURNAL, **62**, 36 (1940).

(2) C. W. Young, R. B. DuVall and N. Wright, *Anal. Chem.*, **23** 709 (1951).

(3) R. P. Linstead, *Ann. Reports*, **33**, 294 (1936).

successful. Likewise futile were the attempts made to form an enol-acetate of III or to cleave the ring with peracetic acid. Furthermore, vigorous chromic acid or nitric acid oxidation failed to yield recognizable fragments.

The vigorous oxidation of the tetralone III with basic potassium permanganate solution gave an unexpected crystalline product. Its infrared spectrum and analysis showed it to be a hydroxy mono-carboxylic acid, containing an o-disubstituted benzene ring. No light was shed on the structure of this hydroxy acid until its further oxidation with chromic acid was attempted. Under very mild conditions, CO_2 was eliminated and a crystalline neutral ketone was isolated. A carbonyl absorption band at 5.78 μ indicated that the carbonyl group was present in a strained five-membered ring system and suggested that this product was an indanone derivative. From these facts the transformation is postulated
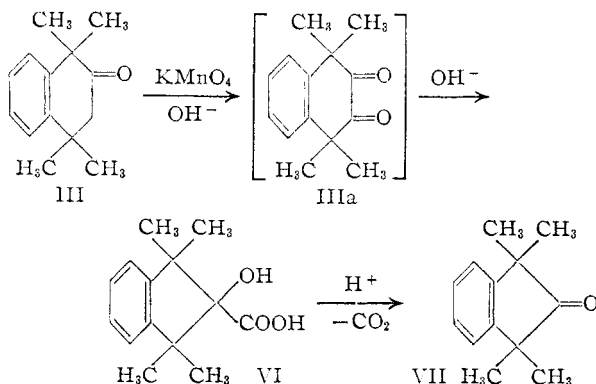

The formation of an α-diketone intermediate IIIa is not inconsistent with what is known about the mechanism of basic permanganate oxidations. The benzilic acid rearrangement[4] which follows under alkaline conditions takes place in preference to the cleavage reaction, yielding the hydroxy acid VI. A similar resistance to α-diketone cleavage in permanganate oxidations has been reported by others.[5] The acid-catalyzed elimination of CO_2 from VI to 1,1,3,3-tetramethylindanone (VII) is easy and straightforward.

When the permanganate oxidation of III was carried out in the presence of a magnesium sulfate buffer to prevent the formation of strong base, during the oxidation, the ring cleavage of III readily occurred giving an excellent yield of o-phenylene-di-isobutyric acid (VIII)
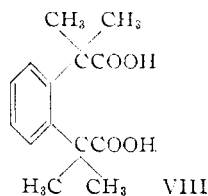
Although the methylene group of the tetralone III is unreactive, the carbonyl group slowly forms an oxime and a hydrazone. The oxime undergoes the Beckmann rearrangement in hot polyphos-

(4) O. Wallach, Ann., 414, 300 (1918); 437, 166 (1924).
(5) A. Y. Drummond and W. A. Waters, J. Chem. Soc., 435 (1953).

phoric acid to yield a crystalline substituted caprolactam derivative of the probable formula IX.
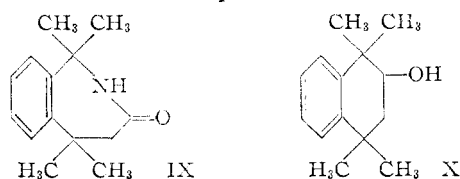

The carbonyl group of III is readily reduced by means of lithium aluminum hydride in ether to the corresponding 1,1,4,4-tetramethyltetralol-2 (X). This alcohol is also quite unreactive. In the course of an attempted dehydrogenation with selenium, it was recovered unchanged after heating at 300–320° for 40 hours.

Attempts, however, to reduce the carbonyl group of III directly to the parent hydrocarbon I by various modifications of the Clemmensen procedure were all unsuccessful. The results from the usual Wolff–Kishner reduction of III were equally poor when decomposition of its hydrazone XI was attempted in situ. By employing the hydrazone XI in purified crystalline form, the Wolff–Kishner reduction to the parent hydrocarbon I was carried out successfully, thus establishing the structure of III without question.

As regards the third ketone V isolated from the condensation of benzene and the furanone II, an infrared analysis showed the presence of an o-disubstituted benzene ring, a normal, unstrained carbonyl group and freedom from olefinic unsaturation. Its formula $C_{14}H_{18}O$ is isomeric with III. Upon reduction with lithium aluminum hydride, it gives a corresponding alcohol, (XIII) different from X. Upon alkaline permanganate oxidation, it loses one carbon atom as CO_2 and yields a tertiary mono-carboxylic acid having the formula $C_{13}H_{16}O_2$ (XII).

Such properties agree with those of a ketone having formula V, which might be formed by ring closure from the pinacol–pinacoline type rearrangement of the α-ketol IV under the influence of the strongly acidic $AlCl_3$.
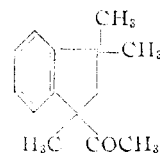
A number of experiments were carried out to determine the best conditions for obtaining each of the three ketones:

Ketone IV.—From 0.1 to 5.0 moles of $AlCl_3$ were used per mole of the furanone at temperatures ranging from 0 to 100°. Optimum yields (25%) were obtained using 0.1–2.0 moles of $AlCl_3$ per mole of the furanone at 30–100° or 2.0–5.0 moles of $AlCl_3$ per mole of the furanone at 0–30°.

Ketone III.—From 1 to 3 moles of $AlCl_3$ per mole of the furanone were used. Optimum yields (29–30%) were obtained using 1.7–1.8 moles of $AlCl_3$ per mole of the furanone at 70–100°.

Ketone V.—From 1.5 to 5.0 moles of $AlCl_3$ per mole of the furanone were used at temperatures from 50° to the refluxing temperature of the

solution (70–100°). Optimum yields (50–55%) were obtained at 70–120° using 1.9–2.5 moles of $AlCl_3$ per mole of the furanone.

The following catalysts were tried in place of $AlCl_3$ and found to be completely ineffective in obtaining the ketones: concentrated sulfuric acid, BF_3, BF_3 etherate, $SnCl_4$ and polyphosphoric acid.

Experimental Part

2,2,5,5-Tetramethyltetrahydrofuranone[6] (II).—2,5-Dihydroxy-2,5-dimethylhexyne-3 (700 g.) (from the Air Reduction Co.) was placed in a 5-liter, 2-necked flask containing 35 g. of mercuric acetate and 35 cc. of concentrated sulfuric acid in 3500 cc. of water. The apparatus was equipped for steam distillation with a steam inlet tube and a long efficient condenser with a Kjeldahl trap. The contents were heated to 80° and steam was passed in cautiously. The reaction is quite exothermic in its early phase and it is often necessary to stop the flow of steam and remove external heat. Steam is passed through until no more oil separates in the distillate. The organic layer in the steam distillate is separated, dried over anhydrous sodium sulfate and distilled under reduced pressure; yield 665 g. (95% of theor.), b.p. 80–82° (93–96 mm.).

1,1,4,4-Tetramethyltetralone-2 (III).—To a stirred mixture of dry 2,2,5,5-tetramethyltetrahydrofuranone (128 g., 0.9 mole) in 500 cc. of dry benzene, there was added gradually anhydrous, powdered aluminum chloride (226 g., 1.7 moles) while maintaining the mixture between 40 and 50° by external cooling. The solution was then heated at reflux (75–80°) for 4 hours. The cooled solution was poured into one liter of ice and water containing 100 cc. of concentrated hydrochloric acid. Ether (200 cc.) was added and the organic layer separated. The aqueous layer was washed twice with 200-cc. portions of ether. The combined organic layers were washed with water, saturated sodium bicarbonate solution and then water, dried over sodium sulfate and evaporated to a dark sirup. This material was taken up in twice its volume of petroleum ether (b.p. 30–60°) and set aside at −15° to crystallize; 22 g. of a light yellow crystalline product was obtained. The mother liquor was evaporated to a sirup and distilled through a $^3/_4'' \times 18''$ Vigreux column at 0.5–1.0 mm. pressure. Fraction 1, light yellow liquid (7 g.) boiling at 41–92°, was discarded. Fraction 2, yellow sirup (46 g.) boiling at 92–96°, and fraction 3, orange-yellow sirup (23 g.) boiling at 96–100°, were collected. A 45-g. still pot tar was discarded. Fractions 2 and 3 were taken up in twice their volume of petroleum ether and set aside at −15° to crystallize; 20.7 and 14.7 g. of the crystalline crude product, respectively, were obtained. The total of the crude product (57.4 g.) represents a 31.5% yield. It was purified by recrystallization from petroleum ether with the aid of decolorizing charcoal, and separated as colorless, stout prisms, m.p. 75°. *Anal.* Calcd. for $C_{14}H_{18}O$: C, 83.14; H, 8.95. Found: C, 83.0; H, 8.9.

1,1,4,4-Tetramethyltetralone Oxime.—A mixture of 20 cc. of alcohol, 4 g. of potassium hydroxide, 1 g. of hydroxylamine hydrochloride and 1 g. of the tetralone III was boiled under reflux for 2.5 hours, cooled and poured into cold water. The crude oxime (1 g.) was filtered off and recrystallized from alcohol to m.p. 191–193°. *Anal.* Calcd. for $C_{14}H_{19}ON$: N, 6.45. Found: N, 6.43.

Conversion to Lactam IX.—A mixture of 1,1,4,4-tetramethyltetralone oxime (4 g.) and 140 g. of polyphosphoric acid was heated with stirring at 140° for 20 minutes. The product was cooled, poured into water, extracted with ether and the ether extract washed with water, sodium bicarbonate solution and water. After drying over sodium sulfate and removing the ether, a yellowish sirup was obtained which gradually crystallized; yield 1.0 g. (24%). Upon recrystallization from petroleum ether, it formed colorless crystals, m.p. 144–145°. Its infrared spectrum confirmed the presence of a lactam structure. *Anal.* Calcd. for $C_{14}H_{19}ON$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.06; H, 8.80; N, 6.30.

1,1,4,4-Tetramethyltetralone Hydrazone (XI).—A mixture of 50 cc. of alcohol, 1 cc. of acetic acid, 3 g. of hydrazine hydrate (85%) and 5 g. of III was boiled under reflux for 72 hours. On cooling, white crystals of the azine (0.8 g.) separated, m.p. 171–172°. The filtrate upon concentration,

deposited another crop of crystals (1.8 g.) which upon recrystallization from a little alcohol proved to be the hydrazone XI, m.p. 117–118°. *Anal.* Calcd. for $C_{14}H_{20}N_2$: N, 12.96. Found: N, 12.91.

Wolff–Kishner Reduction of 1,1,4,4-Tetramethyltetralone Hydrazone.—A mixture of 1.6 g. of the above purified hydrazone XI and 0.16 g. of powdered potassium hydroxide was heated in a thick walled test-tube for 5 hours at 200–250°. Water and ether were added to the cooled product and the ether layer extracted with dilute hydrochloric acid. After washing the ether layer with water, the ether was removed and the residual oil fractionally distilled in a micro Claisen flask. The first few drops of distillate were collected and an infrared analysis was taken on this material. A slight odor similar to that of the tetralone III was noted. The infrared spectrum showed all of the major peaks characteristic of 1,1,4,4-tetramethyltetralin (I). However, a slight carbonyl bond indicated contamination with ketone. The oil was purified by chromatography on alumina and yielded the hydrocarbon I in purified form, possessing the same infrared spectrum as a pure specimen.

Dehydrogenation of 1,1,4,4-Tetramethyltetralone.—A mixture of 12.6 g. of III and 6.3 g. of 5% palladium-on-charcoal was heated at 350° for 92 hours. The cooled residue was taken up in ether, filtered and the filtrate evaporated to a thick sirup. The sirup was dissolved in methanol and set aside at −10° to crystallize. Several crops of the unchanged tetralone were obtained. The mother liquor was treated with a saturated solution of picric acid in methanol. The crude, crystalline picrate was decomposed on a column of alumina. The crystalline product (0.2 g.) obtained melted at 105–106° after recrystallization from methanol; and its picrate after recrystallization from methanol melted at 178–180°, in agreement with the properties of 1,2,3,4-tetramethylnaphthalene.[7] *Anal.* Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 90.95; H, 8.78.

1,1,4,4-Tetramethyltetralol-2 (X).—To a concentrated solution of 1 g. of lithium aluminum hydride in dry ether there was added a solution of 1 g. of III in dry ether with stirring. The mixture was warmed under reflux for a half-hour and any excess $LiAlH_4$ was decomposed with methanol and finally with water. The ether solution was decanted and the residue was repeatedly extracted with ether. The combined ether extracts upon evaporation gave a sirup which upon recrystallization from ethyl alcohol gave colorless crystals, m.p. 86–87°. *Anal.* Calcd. for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.26; H, 9.94.

2-Hydroxy-1,1,3,3-tetramethylindane-2-carboxylic Acid (VI).—A mixture of 255 cc. of water, 13 g. of potassium permanganate, 0.5 g. of sodium hydroxide and 3.3 g. of the tetralone III was boiled under reflux for 3 hours with stirring. The product was then acidified with dilute sulfuric acid and decolorized with sodium bisulfite. The white crystalline product (2.5 g.) was recrystallized from benzene. It formed long, water-soluble prisms, m.p. 188–189°. *Anal.* Calcd. for $C_{14}H_{18}O_3$: C, 71.75; H, 7.74; neut. equiv., 234. Found: C, 71.73; H, 7.56; neut. equiv., 235.

1,1,3,3-Tetramethylindanone-2 (VII).—A mixture of 20 cc. of aqueous 25% acetic acid, 2 g. of chromic oxide, and 1 g. of the hydroxy acid VI was allowed to stand for 4 hours at room temperature. Evolution of CO_2 was noted. Water and ether were then added, and the ether solution separated, washed thoroughly with water, and the ether layer evaporated to dryness. The residue was taken up in methanol, diluted with water to slight turbidity and set aside to crystallize. The white crystalline product melted at 76–77° after recrystallization from dilute methanol; yield 90%. *Anal.* Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.56; neut. equiv., 0. Found: C, 82.85; H, 8.74; neut. equiv., 0.

o-Phenylene-di-isobutyric Acid (VIII).—A mixture of 400 cc. of water, 40 g. of magnesium sulfate (anhydrous), 18 g. of potassium permanganate and 4.5 g. of the tetralone III was boiled under reflux for 40 hours with stirring. The MnO_2 was then removed by adding sodium bisulfite and the solution acidified with sulfuric acid, and repeatedly extracted with ether. The ether solution was then extracted with sodium bicarbonate solution, and the aqueous bicarbonate extract acidified and evaporated slowly under an air jet. The flocculent crystalline product which settled out was filtered off, dried and recrystallized from benzene to m.p.

(6) H. Richet, *Ann. chim.*, [12] **3**, 317 (1948).

(7) C. L. Hewett, *J. Chem. Soc.*, 302 (1940).

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 (II) 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) re-

covered 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 $C_{13}H_{18}O_2$: C, 76.42; H, 7.89; neut. equiv., 204. Found: C, 76.35; H, 7.83; 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.

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(8) F. C. Whitmore, C. A. Weisgerber and A. C. Shabica, This Journal, **65**, 1469 (1943).

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

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

(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**, 1490 (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).