mm. column of carbon and Celite (1:1), and the column was developed with 2 l. each of water, 2 and 4% ethanol. The ethanol effluents were collected in separate 200-ml. volume each of which was concentrated to dryness, dissolved in a few drops of water and placed as successive spots along the base of a paper chromatogram. The separation was highly satisfactory with only a little overlapping, which was later remedied by increasing the amount of 2% ethanol developer.

Using the automatic fraction collector[14] fitted with a 75 × 780 mm. column of carbon–Celite (2:3), 7.80 g. of the disaccharide mixture was completely separated into its components with 2 and 4% ethanol as developers. To ensure the preparation of pure materials, each of the effluents was concentrated separately to a small volume *in vacuo* and analyzed by paper chromatography.[16] The proper solutions were combined and dried. The yields were 5.65 g. of 2% effluent and 2.11 g. of 4% effluent.

Characterization of 2% Effluent.—The chromatographically pure amorphous solid was dissolved in a minimum of water and a large volume of methanol was added. The solution was heated and filtered. To the cool filtrate was added a volume of butanol-1 equal to that of methanol. The solution was evaporated on a steam-bath to slight turbidity. Upon cooling, the sugar crystallized as tufts of long thin needles. After two recrystallizations from the same solvent mixture, m.p. was 193.2–194.0° and $[\alpha]^{25}\text{D}$ −7.7 → −2.3 in 20 hours (*c* 2.5, water). The equivalent weight by iodimetric titration was 175 and indicated the sugar was a disaccharide. The physical constants were identical with those reported for the mannobiose isolated from an enzymatic hydrolysate of guaran.[2,7] The mixed melting point with a specimen of the known sugar showed no depression, 192–193°. In addition, the X-ray diffraction patterns of the two samples were identical. These data established the structure of the disaccharide as being 4-(β-D-mannopyranosyl)-β-D-mannopyranose. The yield was 3.2% of the weight of guaran used.

Anal. Calcd. for $C_{12}H_{22}O_{11}$: C, 42.10; H, 6.48. Found: C, 42.1; H, 6.5.

Characterization of 4% Effluent.—The amorphous solid, chromatographically pure, was crystallized from the same solvents as used for the mannobiose and with the same technique. The sugar appeared to crystallize in the form of cubes. The equivalent weight by iodimetric titration was 176.5 and indicated that this material was a disaccharide. Mannose[12] and galactose determinations[12] indicated the presence of one mannose and one galactose unit. After three recrystallizations from the methanol–butanol mixture, the m.p. was 201.0–201.5° and $[\alpha]^{25}\text{D}$ +120.9 → +124.6, 36 hours, (*c* 2.15, water). The yield was 2.2% of the weight of guaran used.

Anal. Calcd. for $C_{12}H_{22}O_{11}$: C, 42.10: H, 6.48. Found: C, 42.1; H, 6.5.

The structure of this disaccharide was established through periodate oxidation and by comparison of its osazone with melibiosazone.[17] Periodate oxidation[18] was carried out on approximately 100-mg. samples, and the periodate consumption and formic acid production were determined. Its mode of reaction was identical with that of melibiose and the data indicated the presence of 1,6′ linkage.[19]

The osazone was prepared by dissolving 0.77 g. of the crystalline sugar, 1.46 g. of phenylhydrazine hydrochloride and 2.10 g. of sodium acetate hydrate in 10 ml. of water and heating for 1 hour on a boiling water-bath. Upon cooling, a yellow crystalline precipitate was obtained. This was recrystallized from 50% aqueous ethanol and then from 95% ethanol. The yield was 0.26 g. The m.p. was 175.0–176.0° and $[\alpha]^{25}\text{D}$ +43.1 (*c* 1.3, pyridine). This osazone in admixture with an authentic specimen of melibiosazone gave no depression in m.p., 174.5–175.5.[20] In addition the X-ray diffraction patterns of the two osazones were identical.

Anal. Calcd. for $C_{24}H_{32}O_9N_4$: C, 54.4; H, 6.2; N, 10.76. Found: C, 54.3; H, 6.3; N, 10.74.

These data indicate that the disaccharide is 6-(α-D-galactopyranosyl)-β-D-mannopyranose.

Acknowledgment.—The authors wish to thank the General Mills, Inc., for supplying the guar flour used in this work.

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(17) Suggestion of C. S. Hudson before the Division of Sugar Chemistry at the 117th Meeting of the American Chemical Society at Detroit, April, 1950.

(18) T. G. Halsall, E. L. Hirst and J. K. N. Jones, *J. Chem. Soc.*, 1427 (1947).

(19) K. Ahlborg, *Chem. Zentr.*, **114**, I, 279 (1943).

(20) C. Scheibler and H. Mittelmeier, *Ber.*, **23**, 1438 (1890); B. Helferich and H. Rauch, *ibid.*, **59**, 2655 (1926).

LAFAYETTE, INDIANA RECEIVED MARCH 5, 1951

[CONTRIBUTION FROM THE WESTERN REGIONAL RESEARCH LABORATORY[1]]

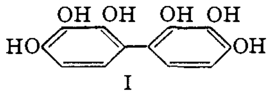
The Oxidation of Di-t-Butylpyrogallol by Oxygen in Alkaline Solution

BY TOD W. CAMPBELL

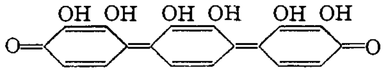
The autoxidation of di-*t*-butylpyrogallol in alkaline media with air gives an orthoquinone, which is partially cleaved to α-hydroxy-β, Δ-di-*t*-butylmuconic acid, and partially rearranged and oxidized to 2,4-di-*t*-butylcyclopentanedione-1,3 and 2,4-di-*t*-butylcyclopentanetrione-1,3,5.

The reaction of oxygen with polyphenolic antioxidants, especially in alkaline media, gives rise to extremely complex mixtures of poorly defined compounds. Pyrogallol in alkaline solution has been used for many years to remove oxygen from gaseous systems, since it reacts with oxygen so avidly. The oxidized solution of pyrogallol, however, is not amenable to a careful investigation, since the principal product is a black, intractable tar of complex nature. A number of small molecules are also formed.[2]

However, Harries[3] was able to isolate hexahydroxy-biphenyl (I) by oxidizing pyrogallol under mild alkaline conditions, while Nierenstein[4] was able to isolate a compound which he formulated as hexahydroxyterphenoquinone (II).



I



II

Erdtmann,[5] using conditions prescribed by Harries,[3] converted 4-ethylpyrogallol to diethylhexahydroxybiphenyl. However, he obtained only unidentifiable resins from 4,6-diethylpyrogallol. He

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(1) Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Beilstein, "Handbuch," Vol. 6, p. 1071.

(3) C. Harries, *Ber.*, **35**, 2957 (1902).

(4) M. Nierenstein, *J. Chem. Soc.*, **107**, 1217 (1915).

(5) H. Erdtmann, *Ann.*, **513**, 240 (1944).

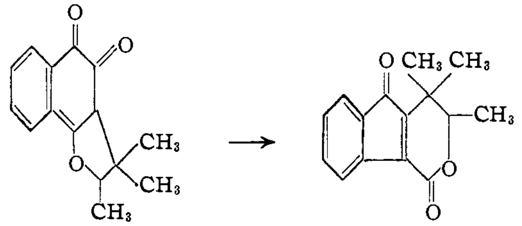
assumed a reactive intermediate stage of oxidation in each case, which in the latter case presumably could not couple to give a biphenyl, since the 4- and 6-positions, through which coupling occurs, are blocked. The "reactive intermediates" thus had to deteriorate *via* less clean-cut paths.

In a previous publication,[6] it was reported that the oxidation of 4,6-di-*t*-butylpyrogallol (III) appeared to be much less complex than that of pyrogallol itself. These observations are now elaborated in the present communication.

Di-*t*-butylpyrogallol is a white, nicely crystalline compound, which in the solid state appears to be stable indefinitely. In solutions, however, it is partially converted to a brilliant purple substance. This is particularly noticeable when an inert solvent, *e.g.*, isoöctane, is used for recrystallization. An originally pure white compound dissolved in isoöctane yields a solution that becomes too deeply colored to see through if allowed to stand overnight exposed to the air. In solvents such as methanol, the color does not become so pronounced, although partial decomposition does occur.

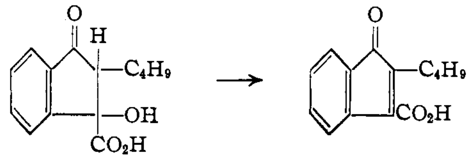
In alkaline solution, di-*t*-butylpyrogallol absorbs oxygen very rapidly from the air, and the solution becomes colored a very intense purple. The color, however, is transient, and on continued standing the purple color fades and the solution again becomes colorless. From this latter solution four crystalline compounds, IV, V, VI and VII, can be isolated. These account for virtually all of the starting material.

Superficially similar rearrangements of orthoquinones have been observed previously. Thus it is well known that phenanthraquinone rearranges in alkali to 9-hydroxy-fluorene-9-carboxylic acid.[7] More recently, Price and Robinson[8] have noted that dunnione (VIII), an *ortho* naphthoquinone derivative, is converted by alkali to allodunnione and proposed the structure IX for the latter. This structure has since been confirmed by Cooke and Somers[9] and by Fieser and Bader,[10] who have shown that 2-hydroxy-3-*t*-butylnaphthoquinone gives in alkali X, which dehydrates easily to XI.



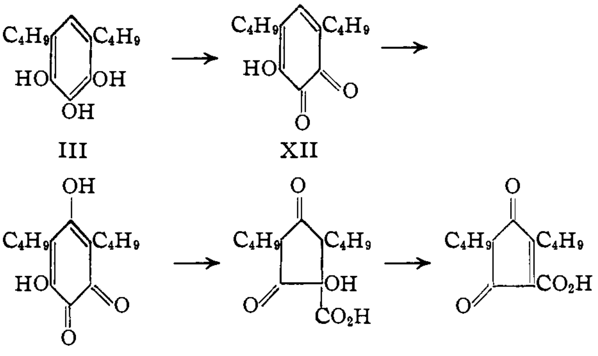
VIII IX

It was noted that substitution of the tertiary alkyl group for other alkyl groups in alkylhydroxynaphthoquinones causes the rearrangement to occur much more cleanly and easily.



X XI

Compounds IV and V, obtained from di-*t*-butylpyrogallol are closely related; indeed IV is converted to V very readily by removal of the elements of water. It was at first thought attractive to formulate IV as XIV and V as XV, using the further assumption that the intermediate *o*-quinone, XII, was hydroxylated during the course of the reaction to XIII, which then rearranged to XIV

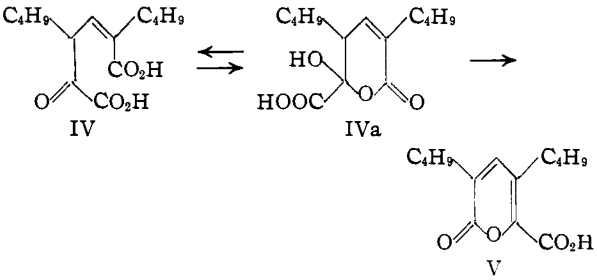


III XII

XIII XIV XV

However, compound IV and V have ultraviolet absorption spectra which are not compatible with these structures. Thus XIV, an enolizable β-diketone, should absorb in the neighborhood of 255 mμ,[11] while XV, an α,β-unsaturated ketone, should not absorb beyond 260 mμ.[12] Furthermore, compound V is easily reconverted to IV by the action of dilute alkali. Neither IV nor V is enolic; V is a monobasic acid, pK 4.1, while IV is dibasic, pK_1 4.3, pK_2 7.2, in aqueous methanol.

On the basis of the above observations, it now appears more reasonable to consider IV to be α-hydroxy-β, Δ-di-*t*-butylmuconic acid,[13] or its lactol IVa while V is the lactone of this acid, 3,5-di-*t*-butylcoumalic acid, or 3,5-di-*t*-butyl-α-pyrone-6-carboxylic acid



IV IVa

V

Compound V can be decarboxylated by heating to $C_{13}H_{20}O_3$, which is presumably 3,5-di-*t*-butylcoumalin (3,5-di-*t*-butyl-α-pyrone) (XVI). The spectra observed for V and XVI are essentially in agree-

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(6) T. W. Campbell and G. M. Coppinger, This Journal, 73, 2708 (1951).

(7) H. Baeyer, *Ber.*, 10, 125 (1877); P. Friedlander, *ibid.*, 10, 534 (1877).

(8) J. R. Price and Sir R. Robinson, *J. Chem. Soc.*, 1522 (1939); 1943 (1940).

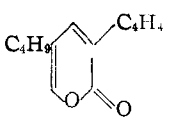
(9) R. G. Cooke and T. C. Somers, *Nature*, 165, 314 (1950).

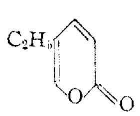
(10) L. F. Fieser and A. R. Bader, This Journal, 73, 681 (1951), and paper presented at 118th Meeting of the American Chemical Society at Chicago, September, 1950.

(11) R. B. Woodward and E. R. Blout, *ibid.*, 65, 562 (1943).

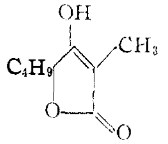
(12) R. B. Woodward, *ibid.*, 64, 76 (1942).

(13) *Chemical Abstracts* naming. The compound is non-enolic, so should perhaps better be named 3,5-di-*t*-butyl-2-ketohexene-4-dioic acid.


XVI

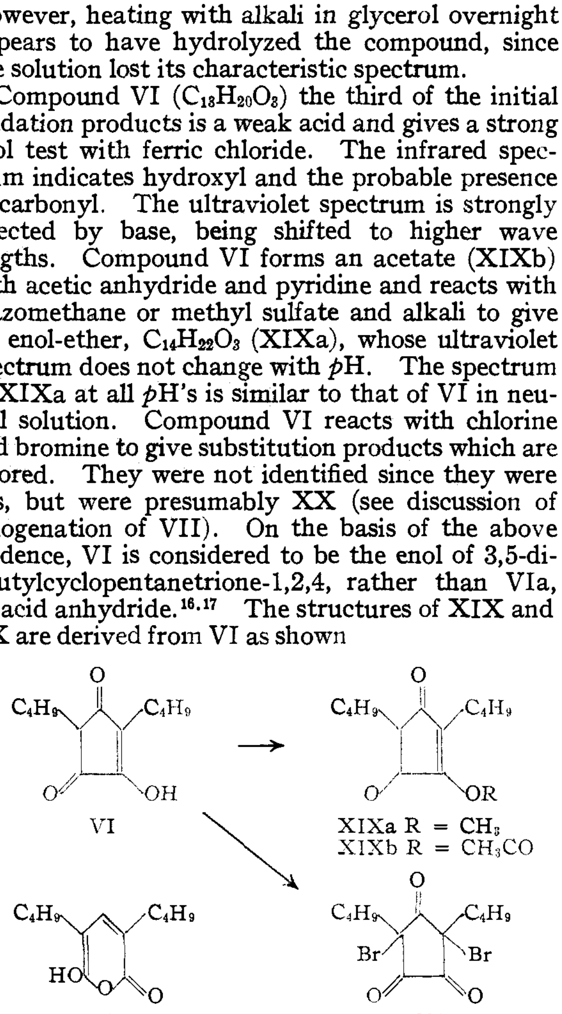

XVII

ment with those observed by Fried and Elderfield for the analogous compound XVII, and its 6-carboxylic acid.[14] Compound XVI is non-enolic and rather resistant to hydrolysis with strong alkali.[15]


XVIII

However, heating with alkali in glycerol overnight appears to have hydrolyzed the compound, since the solution lost its characteristic spectrum.

Compound VI ($C_{13}H_{20}O_3$) the third of the initial oxidation products is a weak acid and gives a strong enol test with ferric chloride. The infrared spectrum indicates hydroxyl and the probable presence of carbonyl. The ultraviolet spectrum is strongly affected by base, being shifted to higher wave lengths. Compound VI forms an acetate (XIXb) with acetic anhydride and pyridine and reacts with diazomethane or methyl sulfate and alkali to give an enol-ether, $C_{14}H_{22}O_3$ (XIXa), whose ultraviolet spectrum does not change with *p*H. The spectrum of XIXa at all *p*H's is similar to that of VI in neutral solution. Compound VI reacts with chlorine and bromine to give substitution products which are colored. They were not identified since they were oils, but were presumably XX (see discussion of halogenation of VII). On the basis of the above evidence, VI is considered to be the enol of 3,5-di-*t*-butylcyclopentanetrione-1,2,4, rather than VIa, an acid anhydride.[16,17] The structures of XIX and XX are derived from VI as shown



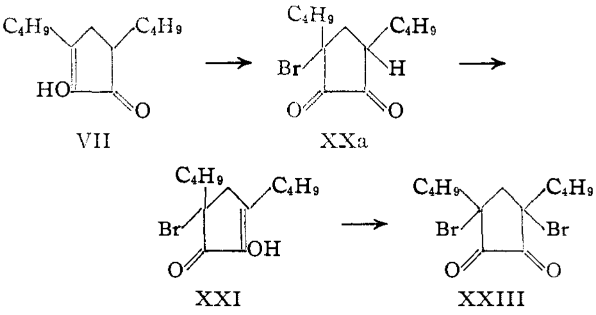
Compound VI, on heating with strong alkali, gives a bicarbonate soluble product, which on distillation is converted to a solid crystalline material which analyzes for $C_{12}H_{20}O_2$. This material was not investigated further.

The proposed identity of VII, $C_{13}H_{22}O_2$, with the enol of 3,5-di-*t*-butylcyclopentanedione-1,2 may be seen from the following considerations. It gives a strong enol test with ferric chloride, although it is non-acidic, does not react with diazomethane, nor with methyl sulfate, though it can be acetylated to an oil which was not characterized, but which no longer gives an enol test. The ultraviolet maximum (262 mμ) is not shifted radically by alkali.[18] Treatment of one mole of VII with one mole of bromine gives a reaction mixture from which an unstable pink compound XXa can be isolated. This compound reverts to the colorless substance XXI on standing or on treatment with weakly basic substances, as pyridine. Both XXa and XXI have the same empirical formula, $C_{13}H_{21}O_2Br$. Action of excess alkali converts XXI to $C_{13}H_{22}O_3$ (XXII), by replacement of halogen by hydroxyl.

Treatment of VII with two moles of bromine or of either XXa or XXI with one mole of bromine gives XXIII, a substance which occurs in two modifications, a pink metastable form (different from XXa) which reverts on standing to an orange, stable form. Crystallographic examination indicates that the two forms are not polymorphs, but different entities, probably *cis–trans* isomers. Compound XXIII does not appear to exist in a colorless form. It is reconverted to XXI by the action of *o*-phenylenediamine.

Infrared spectra indicate that both VII and XXI have –OH groups, and probably carbonyl. (Compound XXa could not be obtained pure enough for spectral measurements.) Compound XXIII, however, shows no hydroxyl, only an indication of carbonyl.

On the basis of the above physical and chemical evidence, we feel that VII and its derivatives are best represented as



Since XXIII can no longer enolize, it must remain as the colored cyclic α-diketone, while XXa, also a colored cyclic α-diketone, can enolize to the colorless XXI.

A number of similar conversions of colorless cyclic enols of α-diketones to colored compounds which can no longer enolize have been recorded. Thus, colorless diosphenol (buchucamphor XXIV)

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[14] J. Fried and R. C. Elderfield, *J. Org. Chem.*, **6**, 566 (1941).

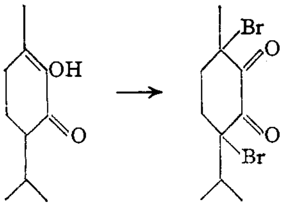
[15] A similar observation has been recorded recently by E. B. Reid and R. B. Fortenbaugh, *ibid.*, **16**, 16 (1951), who observed that the tetronic acid (XVIII) was extremely stable toward hydrolysis.

[16] N. Brand and J. F. Thorpe, *J. Chem. Soc.*, 856 (1912).

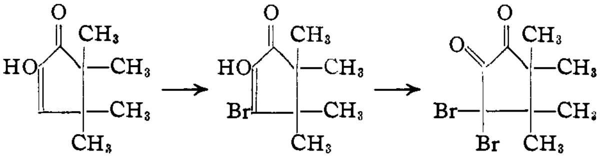
[17] The referee has pointed out additional evidence for rejecting VIa. Thus the anion of glutacondialdehyde has an absorption maximum at 365 mμ (Schwarzenbach, *et al.*, *Helv. Chim. Acta*, **27**, 576 (1944)) while VI in alkali absorbs at 328 mμ. Further, the spectral shift for VI (23 mμ) is comparable to that for β diketones (25 mμ) (Blout, Eager and Silverman, THIS JOURNAL, **68**, 566 (1946)), when the *p*H is shifted from alkaline to acid. The corresponding change with glutacondialdehyde is *ca.* 75 mμ.

[18] The non-acidic character of this enol is reminiscent of other highly hindered enols. See for example R. C. Fuson, J. Corse and C. H. McKeever, *ibid.*, **62**, 3250 (1940).

is converted to the golden-yellow dibromide[19] XXV, while 3,3,4,4-tetramethylcyclopentanedione-1,2 (XXVI) (colorless) gives a colorless monobromide (XXVII) or chloride but a bright orange dibromide (XXVIII) or dichloride,[20,21] where enolization can no longer occur.

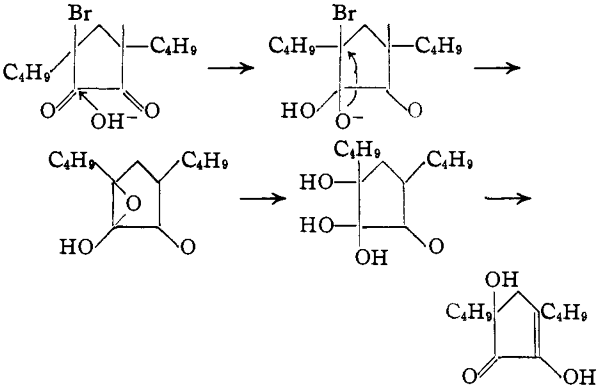


XXIV XXV



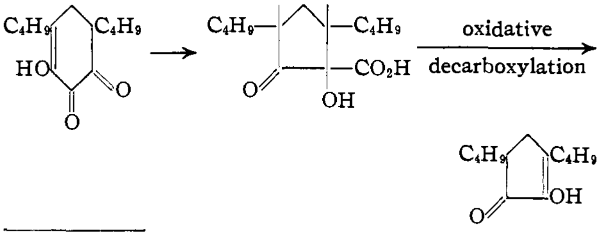
XXVI XXVII XXVIII

The relatively facile displacement of halogen from XXI, a neopentyl halide, by base is at first surprising but can be considered to go *via* an hydroxyethylene oxide.[22]



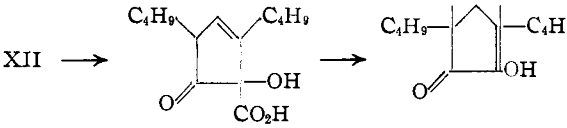
XXII

Furthermore, the reduction of XXIII to XXI by *o*-phenylenediamine is somewhat surprising, since it would indicate that one halogen has positive character with respect to its reaction with amines,[23,24] while the other does not. This is at least partially confirmed by the fact that hydrazine is oxidized[23] by XXIII to nitrogen, with production of XXI, which is not further reduced to VII.



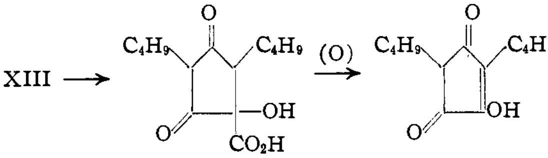
The mechanism of formation of VII from III is not immediately apparent. The possibility that III might rearrange without benefit of oxygen was considered. However, di-*t*-butylpyrogallol is unchanged on long standing in strong alkali in the absence of oxygen.

A more likely source of VII is the rearrangement of the *o*-quinone XII to give XXIX, which then decarboxylates with shift of proton to VII.



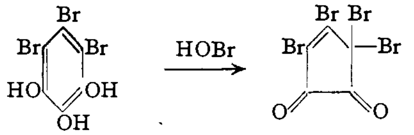
XXIX VII

The formation of VI requires an additional stage of oxidation, and may involve intermediates such as XIII and XIV.



XIV VI

It should be noted that the conversion of 4,5,6-tribromopyrogallol (XXX) to xanthogallol (XXXI) by the action of aqueous bromine appears to be accompanied by a similar oxidative ring contraction with elimination of one carbon atom.[25]



XXX XXXI

Similar decarbonylations of polyketones[26] have been discussed recently by Roberts, Smith and Lee.[27] It has been observed repeatedly that carbon monoxide is a product of the autoxidation of pyrogallol in alkaline media,[28] however, none of the gaseous products of the autoxidation of di-*t*-butylpyrogallol have been examined.

Experimental Part

Preparation of Di-*t*-butylpyrogallol (III).—A modification of the method of Rozycki[29] was employed. Pyrogallol (252 g., 2 moles) was dissolved in 500 ml. of glacial acetic acid. *t*-Butyl chloride (250 ml.) and ferric chloride (0.05 g.) were added and the mixture was refluxed for three hours, with addition of a 250-ml. portion of *t*-butyl at the end of the first hour. The total volume of the solution was reduced to about 400 ml. by vacuum distillation, and then water was added to the cooled solution until it became cloudy. Crystallization was induced by seeding, and then the solution was diluted to three liters and set aside to crystallize. Next day the crystalline mass was sucked as dry as possible on a Buchner funnel, and recrystallized from dilute acetic acid. The yield of product melting at 120° was about 100 g. (21%).

In view of the simplicity of this procedure and the high quality of the product, no attempt was made to improve the rather low yield.

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(19) O. Wallach and E. Grote, *Ann.*, **418**, 36 (1919); *C. A.*, **13**, 2339 (1919).

(20) F. Francis and F. G. Willson, *J. Chem. Soc.*, **103**, 2238 (1913).

(21) C. K. Ingold and C. W. Shoppee, *ibid.*, 365 (1928).

(22) C. L. Stevens, W. Malik and R. Pratt, THIS JOURNAL, **72**, 4758 (1950). We are indebted to Dr. L. L. Ingraham for suggesting this explanation.

(23) B. W. Howk and S. M. McElvain, *ibid.*, **54**, 282 (1932).

(24) E. C. Hirst and A. K. Macbeth, *J. Chem. Soc.*, **121**, 904 (1922).

(25) F. T. Moore and R. M. Thomas, THIS JOURNAL, **39**, 974 (1917).

(26) Note that XII is a cyclohexenetrione-1,2,3, while XIII is a 1,2,3,5-cyclohexanetetron.

(27) J. D. Roberts, D. R. Smith and C. C. Lee, THIS JOURNAL, **73**, 618 (1951).

(28) "Beilstein," Vol. II, p. 1072.

(29) L. Rozycki, *Ber.*, **32**, 2428 (1899).

Anal. Calcd. for $C_{14}H_{22}O_3$: C, 70.6; H, 9.32. Found: C. 70.7; H, 9.34.

Di-*t*-butylpyrogallol reacts with diazomethane. and dimethyl sulfate to give a series of methyl ethers, which have not been fully investigated.

However, it does not show many of the usual reactions of phenols. For example, no azo dye is produced with *p*-nitrobenzenediazonium chloride, and it is oxidized. rather than substituted. by bromine.

Oxidation of Di-*t*-butylpyrogallol by Air.—Solutions of this phenol in various solvents turned purple when exposed to oxygen, presumably with formation of an *o*-quinone. The rate appeared to be dependent on *p*H; in alkaline methanol. the reaction was extremely rapid, one mole of oxygen reacting with one mole of the phenol. During the course of the reaction. the initially colorless solution became deep purple, and then faded back to colorless in a matter of a few minutes when intimate contact was maintained between solution and oxygen.

Products of Autoxidation of Di-*t*-butylpyrogallol.—Ninety grams of di-*t*-butylpyrogallol was dissolved in four liters of methanol, and 200 ml. of 7 *N* sodium hydroxide was added. Air was bubbled through the solution until the initial purple had faded to colorless. The solution was diluted to ten liters with water, acidified with sulfuric acid and extracted with three liters of ether. The ethereal layer was concentrated to 500 ml., and extracted thoroughly with aqueous potassium bicarbonate. The bicarbonate layer, on acidification, yielded 41 g. of white crystalline powder, a mixture of IV and V. The ethereal layer, on evaporation, yielded 39 g. of crystalline material, a mixture of VI and VII. This crystalline cake was dissolved in boiling isoöctane (150 ml.) and the solution was cooled in ice. The crystalline material was filtered off, and recrystallized twice from isoöctane. to give pure VI (6.5 g.). The mother liquor from VI was cooled in a Dry Ice–acetone-bath, and filtered rapidly. The crystalline material so obtained was rich in VII; it was sublimed at atmospheric pressure and 110°, and the needle-like sublimate separated manually from some compact, crystalline agglomerates which also sublimed. The needle-like crystals were recrystallized twice from aqueous methanol to give pure VII.

A less tedious method for obtaining VII was discovered later. Thus 15 g. of crude VII containing 10–20% VI was heated at 150° for 30 minutes with 7 g. of potassium hydroxide and 50 ml. of glycerol. The solution was poured into water, acidified, and the Compound VII taken up in ether, together with a product which resulted from VI. The latter was removed with potassium bicarbonate, and the pure VII recrystallized from aqueous methanol.

The bicarbonate soluble compound was separated and distilled. The distillate (VIa) was recrystallized from aqueous methanol, m.p. 91–91.2°.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.4; H, 10.3. Found: C, 73.2; H, 10.3.

Spectrophotometric examination of the original crystalline cake indicated that it was composed of about 45% of VII and 55% of VI.

Preliminary Examination of IV, V, VI and VII.—Compound IV obtained as above, was a white, microcrystalline powder. It was found to be somewhat unstable to recrystallization, dehydrating easily to give V (*vide infra*). It had no definite melting point. It titrated as a dibasic acid, with *pK* 4.3, and *pK* 7.2, determined potentiometrically by titrating a methanolic solution with aqueous base. Its ultraviolet absorption spectrum[30] showed strong absorption in the region 2100–2200 Å., but no other bands in the region characteristic of benzene derivatives. It gave no color with ferric chloride.

Anal. Calcd. for $C_{14}H_{22}O_5$: C, 62.2; H, 8.20. Found: C. 62.5; H, 8.32.

Compound VI was a nicely crystalline solid with a melting point of 122.5–123°. It was weakly acidic and gave a bright green color with ferric chloride. It showed strong absorption in the ultraviolet, with maxima at 3050 Å. (ϵ 7700). The spectrum was shifted toward the visible in alkali, maxima appearing at 3280 Å. (ϵ 8400) and 2610 Å. (ϵ 4500). In the infrared, strong indications of OH, and probable presence of carbonyl were detected.

Anal. Calcd. for $C_{13}H_{20}O_3$: C. 69.6; H, 8.98. Found: C, 69.8; H, 9.10.

Compound VII was a non-acidic white crystalline solid which gave a green color with ferric chloride. It melted at 108–108.5°, and absorbed in the ultraviolet. Its spectrum showed a maximum at 2630 Å. (ϵ 11.900) which in alkali was shifted to 2650 Å. (ϵ 8800). A molecular weight determination by isothermal distillation showed that VII was definitely monomeric. Its infrared spectrum shows OH (definite) and carbonyl (probable).

Anal. Calcd. for $C_{13}H_{22}O_2$: C. 74.2; H, 10.5. Found: C, 74.2; H, 10.6.

Detailed Study of IV. Conversion to 3,5-Di-*t*-butylcoumalic Acid.—Treatment of IV with a variety of acidic reagents. as acetic anhydride, acetyl chloride. hydrogen bromide in acetic acid, etc., resulted in the production of a crystalline compound (V). Thus 1.0 g. of IV was heated with 5 ml. of acetyl chloride until solution was complete. This solution was poured into water to give a quantitative yield of V. This compound sublimed readily at about 200°. In a sealed tube it melted at 203–205°. Compound V was separated from the original bicarbonate-soluble reaction mixture fractional crystallization from isoöctane.

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.6; H, 8.01; mol. wt., 252. Found: C, 66.7; H, 8.07; mol. wt. by isothermal distillation, 230.

Potentiometric titration showed V to be a monobasic acid, with *pK* 4.1. Its ultraviolet absorption spectrum showed a maximum at 2970 Å. (ϵ 14,000) which was shifted to 3050 Å. (ϵ 15.200) in basic solution.

Hydrolysis of 2,5-Di-*t*-butylcoumalic Acid.—One gram of this α-lactone acid was dissolved in 15 ml. of 1 *N* potassium hydroxide solution, and refluxed 15 minutes. On acidification, a compound was recovered in quantitative yield, which was identified as IV by direct crystallographic comparison.

Anal. Calcd. for $C_{14}H_{22}O_5$: C, 62.2; H, 8.20. Found: C, 62.5; H. 8.18.

Decarboxylation of V to 3,5-Di-*t*-butylcoumalin (XVI).—Compound V was easily decarboxylated to XVI. Thus 33 g. of V was heated at its boiling point for 30 minutes, whence carbon dioxide was smoothly and nearly quantitatively liberated. The residue was distilled at reduced pressure. b.p. 152° (25 mm.). The distillate solidified in the receiver to a crystalline mass, which was recrystallized from isoöctane, in which it is moderately soluble. 3,5-Di-*t*-butylcoumalin crystallizes in thick needles, m.p. 67.5–68°. It has a pleasant, camphoraceous odor, and is non-acidic. It will not react with bromine at room temperature although substitution occurs slowly in boiling acetic acid to give an unidentified oil. The ultraviolet spectrum of XVI shows a strong maximum at 2930 Å. (ϵ 13,500) which is not affected by base. The infrared spectrum shows no OH band, and a band at 5.8 and 6.1 μ, probably due to carbonyl.

Anal. Calcd. for $C_{13}H_{20}O_2$: C, 74.9; H, 9.69. Found: C, 74.9.

Hydrolysis of 3,5-Di-*t*-butylcoumalin.—This compound was extremely resistant to hydrolysis. However, 100 mg. of it was heated overnight at 150° in a 10% solution of potassium hydroxide in glycerol. It was apparently hydrolyzed, since the characteristic maximum at 2930 Å. disappeared. No product was isolated.

Attempts to prepare an oxime of XVI by refluxing 24 hours with pyridine and hydroxylamine hydrochloride failed. Refluxing for 36 hours with amalgamated zinc and hydrochloric acid caused no change. In presence of massive amounts of platinum oxide, two moles of hydrogen was absorbed. Thus, 0.1746 g. of XVI absorbed 41.8 ml. of hydrogen at 26° and 757 mm. in the presence of 0.235 g. of platinum oxide. while theory calls for 41.0 ml.

Detailed Examination of VI—Methylation.—Treatment of 100 mg. of VI in 2 ml. of methanol with excess methyl sulfate and alkali gave a good yield of a new compound, XIXa, needles, m.p. 101.5–103°. Its spectra had maxima at 3030 and 2350 Å., which were not displaced by changing *p*H. Its infrared spectrum shows no OH band.

Anal. Calcd. for $C_{14}H_{22}O_3$: C, 70.5, H. 9.30. Found: C, 70.6; H, 9.31.

The same enol-ether was produced by the action of diazomethane on VI. It gave no color with ferric chloride.

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[30] All spectra reported were taken in absolute methanol.

Acetylation of VI.—Three hundred mg. of VI was dissolved in a mixture of 1 ml. of pyridine and 1 ml. of acetic anhydride. After standing overnight, it was poured into water, and crystallized on standing. The acetate (XIXb) recrystallized from isoöctane in large cubes, similar in appearance to potassium chloride.

Anal. Calcd. for $C_{15}H_{22}O_4$: C, 67.7; H, 8.33. Found: C, 67.8; H, 8.35.

Attempted Reaction of VI with Aniline.—Two hundred mg. of VI was heated at 100° with 0.5 ml. of aniline for one hour. Compound VI was recovered unchanged.

Reaction of VI with Halogen.—Treatment of VI with one or more moles of bromine or chlorine in glacial acetic acid gave orange colored oils which were not further identified.

Acetylation of VII.—Compound VII was acetylated in the same manner as VI. The only product could not be induced to crystallize, so could not be obtained analytically pure. However, the oil no longer gave an enol test, so was presumably an enol-acetate.

Halogenation of VII.—Bromination of compound VII (1.2 g.) in acetic acid was accomplished in good yield by adding an excess 30% bromine in acetic acid to a solution of VII. The product (XXIII) was obtained by addition of water. It was recrystallized from dilute acetic acid in two modifications. The stable form consisted of long, bright orange spears, while the metastable form occurred as garnet colored prisms. The stable form melted at 110–111.5°.

Anal. Calcd. for $C_{13}H_{20}O_2Br_2$: C, 42.5; H, 5.48. Found: C, 42.4; H, 5.65.

The two forms were not polymorphic crystal modification; rather they were two different chemical species, probably *cis–trans* isomers, since the two forms when melted under a cover glass showed a distinct line of demarcation on cooling. On standing the pink form changes slowly to the orange form. The ultraviolet absorption spectrum showed a shoulder at 2400 Å. but no maxima or minima. No hydroxyl band could be detected in the infrared.

The orange compound XXIII was quantitatively reconverted to VII by warming with zinc dust in acetic acid and by hydrogenation on platinum. A solution of XXIII in propanol reacted with hydrazine hydrate to give nitrogen and XXI.

Chlorination of compound VII likewise gave an orange crystalline compound, m.p. 82–83°, very similar in appearance to the bromo compound.

Anal. Calcd. for $C_{13}H_{20}O_2Cl_2$: C, 56.0; H, 7.23. Found: C, 55.8; H, 7.30.

Reaction of VII with One Mole of Bromine.—Treatment of 0.4618 millimole of compound VII in 20 ml. of glacial acetic acid with 1 ml. of bromate–bromide solution equivalent to 0.4618 millimole of bromine gave a pink solution which deposited pink needles (XXa) on dilution with water. The pink compound was taken up in ether, dried and evaporated on the steam-bath. The pink color gradually faded and a white solid remained after the ether had evaporated. This was recrystallized from dilute acetic acid to give (XXI) feathery leaflets, m.p. 131–131.2°.

Anal. Calcd. for $C_{13}H_{21}O_2Br$: C, 54.0; H, 7.32. Found: C, 54.0; H, 7.30.

The pink compound, in another experiment, was filtered out after precipitation, dried and examined under the microscope. It consisted of pink needles (XXa) admixed with some (XXI). It was analyzed without further purification.

Anal. Calcd. for $C_{13}H_{21}O_2Br$: C, 54.0; H, 7.32. Found: C, 53.4; H, 7.35.

This compound XXI had an absorption spectrum with a strong maximum at 2850 Å. in neutral and acid solutions. In alkali, the spectrum showed maxima at 3255, 2780 and 2440 Å. The spectrum in alkali changed with time. Acidification of the alkaline solution gave a compound (XXII) with a maximum at 2740 Å. Compound XXI gives a strong OH band in the infrared.

Compound (XXII) was isolated and purified, m.p. 154.5–155°.

Anal. Calcd. for $C_{13}H_{22}O_3$: C, 69.1; H, 9.81. Found: C, 69.1; H, 9.97.

Compound XXI was obtained by treating the dibromo compound (XVIII) with *o*-phenylenediamine.

Treatment of XXI or XX with bromine in acetic acid gave the identical bromo compound obtained previously, while reduction of XX or XXI with zinc and acetic acid gave (VII).

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Transesterification. I. β-Keto Esters

BY ALFRED R. BADER, LOWELL O. CUMMINGS AND HENRY A. VOGEL

A series of β-keto esters of higher alcohols has been prepared in essentially quantitative yields by transesterification with methyl and ethyl β-keto esters under mild conditions in the absence of catalysts. The generality of this reaction and its usefulness is discussed.

As part of a more extensive study of ester interchanges we have investigated the transesterification of methyl and ethyl acetoacetate with a series of alcohols. Such transesterifications of acetoacetic esters have been previously studied, mostly at high temperatures and with basic catalysts with the lower alcohols,[1] *l*-menthol,[2] allylic alcohols,[3] and glycerol,[4] but it has not been realized that these reactions differ from conventional transesterifications and can proceed without catalyst and at steam-bath temperatures. We have prepared the acetoacetates of a series of alcohols in essentially quantitative yields and believe that most primary and secondary alcohols can be esterified in this manner provided that they dissolve in methyl and ethyl acetoacetate and do not, as may some benzylic alcohols,[5] C-alkylate the β-keto ester. Tertiary alcohols react more sluggishly, and we have ob-

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