201. *An Anomalous Barbier–Wieland Degradation.*

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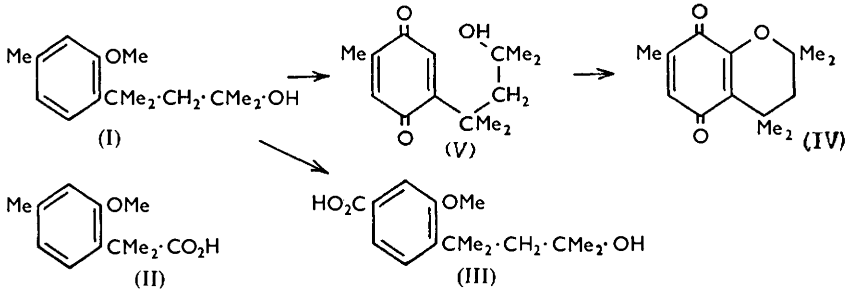
The tertiary alcohol (I) does not yield the normal Barbier–Wieland degradation product (II), but the acid (III) and the quinone (IV). The related tertiary alcohol (VI) gives a small yield of the expected acid (IX) and a little acetophenone, but the major reaction product is the ketone (VIII).

It was reported by Baker, Curtis, and McOmie[1] that when the tertiary alcohol (I) was oxidised with chromic acid, the usual Barbier–Wieland degradation to the acid (II) did not occur, and they reserved further details and comment on this abnormal behaviour in a widely used degradative process.



When the alcohol (I) was oxidised with chromic acid in acetic acid–water, two products were isolated. The first (11·8%) was a carboxylic acid with the same number of carbon atoms as the alcohol (I), which could only arise by oxidation of a methyl group and must in consequence be regarded as 4-(4-carboxy-2-methoxyphenyl)-2 : 4-dimethylpentan-2-ol (III). The second product (9·0%) was a bright yellow, neutral, quinonoid substance which proved to be 2 : 2 : 4 : 4 : 7-pentamethylchroman-5 : 8-quinone (IV), this structure being based on the following facts. Reductive acetylation gave a colourless diacetyldihydro-compound, and a Zeisel estimation showed the absence of a methoxyl group, which must have been replaced by one of the quinonoid oxygen atoms. The infrared spectrum proved the absence of an alcoholic hydroxyl group and was compatible with the spectrum of a *p*-benzoquinone;[2,3] the spectrum is too complex to prove the existence of the ether linkage, though it is consistent with its presence. The colour suggests that the

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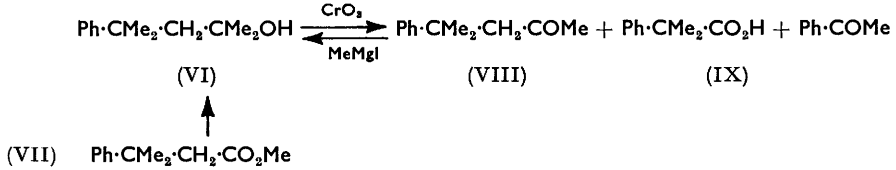
[1] Baker, Curtis, and McOmie, *J.*, 1951, 77.
[2] Yates, Ardao, and Fieser, *J. Amer. Chem. Soc.*, 1956, **78**, 650.
[3] Otting and Staiger, *Chem. Ber.*, 1955, **88**, 828.

compound is a *para*-quinone rather than the possible isomeric *ortho*-quinone; the latter may also be excluded because *para*- but not *ortho*-quinones are formed by chromic acid oxidation of anisoles having free *ortho*- and *para*-positions.



$$\begin{tikzcd} \underset{\text{(VI)}}{\mathrm{Ph{\cdot}CMe_2{\cdot}CH_2{\cdot}CMe_2OH}} \arrow[r, shift left, "\mathrm{CrO_3}"] & \underset{\text{(VIII)}}{\mathrm{Ph{\cdot}CMe_2{\cdot}CH_2{\cdot}COMe}} + \underset{\text{(IX)}}{\mathrm{Ph{\cdot}CMe_2{\cdot}CO_2H}} + \mathrm{Ph{\cdot}COMe} \arrow[l, shift left, "\mathrm{MeMgI}"] \\ \text{(VII)}\ \mathrm{Ph{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2Me} \arrow[u] & \end{tikzcd}$$

It was considered of interest to study, under the same conditions, the Barbier–Wieland degradation of the simpler tertiary alcohol 2 : 4-dimethyl-4-phenylpentan-2-ol (VI), which possesses the same aliphatic chain but is without other substituents in the aromatic nucleus. The alcohol (VI) was prepared by reaction of methylmagnesium iodide with methyl β-methyl-β-phenylbutyrate (VII) or, more conveniently, with 4-methyl-4-phenylpentan-2-one (VIII). Oxidation of this alcohol with chromic acid in acetic acid–water at 60° gave three products: the normal degradation product, α-methyl-α-phenylpropionic acid (IX) (19%); 4-methyl-4-phenylpentan-2-one (VIII) (39%); and acetophenone (8%); the yields quoted are those before final purification. A similar oxidation at room temperature gave α-methyl-α-phenylpropionic acid (IX) (5%), 4-methyl-4-phenylpentan-2-one (60%), and acetophenone (2%). It is thus established that the failure of the tertiary alcohol (I) to undergo the usual degradation to the acid (II) cannot be ascribed solely to the steric effect of the groups attached to the quaternary carbon atom, but that it is primarily due to the presence of the methoxyl group which allows an oxidative attack on the aromatic nucleus, to give, first, the quinone (V) which undergoes reductive cyclisation with the tertiary hydroxyl group and then further oxidation to the quinone (IV).

Oxidation of *tert.*-butylbenzene with chromic acid in acetic acid–water gives trimethylacetic acid rather than benzoic acid, but the hydrocarbon is not readily oxidised.

EXPERIMENTAL

Oxidation of 4-(2-*Methoxy*-4-*methylphenyl*)-2 : 4-*dimethylpentan*-2-*ol* (I).—The alcohol (I) (1·4 g.) in acetic acid (10 ml.) was treated with chromic acid (3·0 g.) in water (5 ml.) and acetic acid (10 ml.) at such a rate that the temperature remained at 30—40°. Next day the mixture was diluted with water and extracted with ether (3 × 50 ml.), the bright yellow ethereal solution shaken with excess of aqueous sodium carbonate, and the alkaline layer acidified. The resulting precipitate was collected (0·186 g., 11·8%; m. p. 200°), sublimed under diminished pressure (200°/11 mm.), and crystallised from benzene–light petroleum (b. p. 60—80°), giving 4-(4-*carboxy*-2-*methoxyphenyl*)-2 : 4-*dimethylpentan*-2-*ol* (III) as rhombs, m. p. 205° (Found: C, 68·1; H, 7·6; OMe, 11·5%; equiv., 261. $C_{15}H_{22}O_4$ requires C, 67·7; H, 8·3; OMe, 11·7%; equiv., 266).

The yellow ethereal solution was dried ($MgSO_4$) and yielded an oil from which bright yellow needles separated. These were collected, washed with ice-cold methanol, and crystallised from aqueous methanol, giving 2 : 2 : 4 : 4 : 7-*pentamethylchroman*-5 : 8-*quinone* (IV) as yellow needles (0·125 g., 9·0%), m. p. 111°; after recrystallisation from light petroleum (b. p. 40—60°) it had m. p. 112° (Found: C, 71·7; H, 7·7. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%).

Reductive acetylation of this quinone (IV) (0·100 g.) was carried out in acetic anhydride (5 ml.) and glacial acetic acid (1 ml.) under reflux by gradual addition of zinc dust until the yellow colour was discharged. After boiling for a further 2 hr., the whole was poured into water, the solid was collected and extracted with hot methanol (4 × 5 ml.), the extracts were concentrated and diluted with water, and the solid (0·109 g.) recrystallised from light petroleum (b. p. 40—60°), giving 5 : 8-*diacetoxy*-2 : 2 : 4 : 4 : 7-*pentamethylchroman* as colourless prisms, m. p. 95° (Found: C, 67·4; H, 7·6. $C_{18}H_{24}O_5$ requires C, 67·5; H, 7·5%).

2 : 4-*Dimethyl*-4-*phenylpentan*-2-*ol* (VI).—(*a*) Methyl β-methyl-β-phenylpropionate, b. p. 116—125°/11 mm., was prepared by esterification of the acid[4] by the Fischer–Speier method.

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[4] Bergmann, Taubadel, and Weiss, *Ber.*, 1931, **64**, 1493.

This ester (6 g.; 1 mol.) in dry ether (30 ml.) was added slowly to an ethereal solution of methylmagnesium iodide (3 mols.) prepared from magnesium (2·25 g.), methyl iodide (13·2 g.), and ether (75 ml.), and the mixture was boiled for 12 hr., then poured into dilute hydrochloric acid and ice. The ethereal layer was shaken with aqueous sodium sulphite, the ether removed, and the residual oil boiled for 4 hr. with sodium hydroxide (1·5 g.) in water (7·5 ml.) and ethanol (30 ml.) to hydrolyse unchanged ester. Ether-extraction then yielded an oil, b. p. 74—79°/0·2 mm., b. p. 90—92°/0·5 mm. (4·7 g., 78%). At 0° this 2 : *4-dimethyl-4-phenylpentan-2-ol* (VI) crystallised in plates, m. p. 24—26° (Found: C, 81·0; H, 10·1. $C_{13}H_{20}O$ requires C, 81·3; H, 10·4%).

(*b*) A solution of 4-methyl-4-phenylpentan-2-one (VIII) (30 g.) (prepared by condensation of benzene with mesityl oxide [5]) [the 2 : *4-dinitrophenylhydrazone* separates from ethanol in yellow plates, m. p. 98·5° (Found: C, 60·5; H, 5·6; N, 16·0. $C_{18}H_{20}O_4N_4$ requires C, 60·7; H, 5·6; N, 15·7%)] in anhydrous ether (120 ml.) was slowly added under nitrogen to a stirred solution of methylmagnesium iodide prepared from magnesium (9·1 g.) and methyl iodide (53 g.) in ether (100 ml.). The mixture was boiled under reflux for 6 hr., kept at room temperature for 12 hr., then worked up as before, giving the pentanol (VI) in 72% yield.

Oxidation of 2 : *4-Dimethyl-4-phenylpentan-2-ol* (VI).—A solution of chromium trioxide (42 g.) in water (70 ml.) and acetic acid (140 ml.) was added to 2 : 4-dimethyl-4-phenylpentan-2-ol (VI) (15·0 g.) (free from 4-methyl-4-phenylpentan-2-one) in acetic acid (70 ml.), and the mixture was stirred for 6 hr. at 60°, and poured into water (1 l.) and extracted with ether (4 × 450 ml.). The extracts were concentrated, shaken repeatedly with water to remove acetic acid, then twice with 10% aqueous sodium hydrogen carbonate (80 ml.), the solvent removed, and the residual oil (7·6 g.) steam-distilled. The distillate (100 ml.) yielded liquid fractions, b. p. 85—115°/18 mm. (0·91 g.) and b. p. 115—125°/18 mm. (0·78 g.); the first proved to be essentially acetophenone [2 : 4-dinitrophenylhydrazone from benzene–alcohol (Found: C, 55·2; H, 3·8; N, 18·7. Calc. for $C_{14}H_{12}O_4N_4$: C, 56·0; H, 4·0; N, 18·7%), m. p. and mixed m. p. 246°], and the second was characterised as 4-methyl-4-phenylpentan-2-one (VIII) (2 : 4-dinitrophenylhydrazone m. p. and mixed m. p. 97—97·5°). The residue from the steam-distillation yielded a further quantity (4·59 g.) of ketone (VIII) characterised as before [total yield of (VIII), 5·37 g.].

The above aqueous alkaline layer was acidified and extracted with ether. The extract yielded a product which was distilled; the main fraction (2·44 g.), b. p. 108—116°/0·4 mm., partially solidified, and after being sublimed twice at 70°/12 mm. and crystallised from dilute acetic acid, formed needles, m. p. 76·5—78° (Found: C, 73·2; H, 7·6. Calc. for $C_{10}H_{12}O_2$: C, 73·2; H, 7·3%); the mixed m. p. with α-methyl-α-phenylpropionic acid (IX) (m. p. 77—78°) was 77—78°.

α-Methyl-α-phenylpropionic Acid (IX).—Powdered aluminium bromide (64 g.) was added to a vigorously stirred solution of α-bromo-α-methylpropionic acid (10 g.) in anhydrous benzene (64 ml.), and the stirred mixture heated in an oil-bath at 150° for 2 hr. The cooled mixture was poured into dilute hydrochloric acid, the benzene layer and extract were shaken with water and with 10% aqueous potassium carbonate; acidification of the alkaline solution precipitated α-methyl-α-phenylpropionic acid (8·24 g., 82%), m. p. 77—78°.

This acid was previously prepared by Wallach [6a] by condensation of ethyl α-bromo-α-methylpropionate with benzene in presence of aluminium bromide; the original paper is not readily available, and the only two abstracts [6b, c] erroneously state that the reaction was carried out with the *acid*, which, however, under the conditions described by Wallach for the ester, gives a negligible yield of α-methyl-α-phenylpropionic acid.

Oxidation of tert.-*Butylbenzene*.—To *tert.*-butylbenzene [7] (14·6 g.) in acetic acid (70 ml.) was added chromium trioxide (90 g.) in acetic acid (300 ml.) and water (150 ml.), and the mixture was kept at 80° for 8 hr., then poured into water; the acidic material other than acetic acid was isolated as in the case of the similar oxidation of the alcohol (VI). This product (1·2 g.) proved to be trimethylacetic acid; it was converted into the acid chloride by means of thionyl chloride and thence into the anilide which, after crystallisation from ethanol, had m. p., and mixed m. p. with an authentic specimen,[8] 133°.

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[5] Hoffman, *J. Amer. Chem. Soc.*, 1929, **51**, 2543.

[6] (a) Wallach, *Nachr. K. Ges. Wiss. Göttingen*, 1899, 126; (b) *Chem. Soc. Abstracts*, 1900, **78**, 229; (c) *Chem. Zentr.*, 1899, II, 1047.

[7] Norris and Sturgis, *J. Amer. Chem. Soc.*, 1939, **61**, 1413.

[8] Degnan and Shoemaker, *ibid.*, 1946, **68**, 104.