Synthesis of Compounds Related to Muscarufin

V. Ethyl 5-(5-methoxy-*p*-benzoquinonyl)-valerate *

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Alkyl radicals, obtained by thermal decomposition of diacyl peroxides, may react with quinones to give alkylated products [1,2]. However, no alkylation was observed when bis-(5-ethoxycarbonylvaleryl)-peroxide in acetic acid was thermally decomposed in the presence of dimethyl 2,2′-(*p*-benzoquinon-2,5-ylene)-dibenzoate[3]. Instead the quinone was reduced and converted into the dilactone of 2′,5′-dihydroxy-*p*-terphenyl-2,2″-dicarboxylic acid [3]. Also *p*-benzoquinone was found to be reduced under the same conditions.

However, a 32 % yield of ethyl 5-(5-methoxy-*p*-benzoquinonyl)-valerate was obtained by decomposition of the peroxide in toluene solution in the presence of 2-methoxy-*p*-benzoquinone. The structure of the alkylation product was established by reduction, methylation and oxidation to 2,4,5-trimethoxybenzoic acid. The intermediate 5-(2,4,5-trimethoxyphenyl)-valeric acid could also be obtained, in very good yield, by acylation of 1,2,4-trimethoxybenzene with glutaric anhydride using boron trifluoride as the catalyst, followed by catalytic hydrogenation.

During these studies on the synthesis of compounds related to muscarufin evidence has accumulated which casts some doubt on the correctness of the proposed structure. The work has therefore been discontinued.

Experimental. The melting points were determined on a Kofler block.

*Ethyl 5-(5-methoxy-*p*-benzoquinonyl)-valerate.* 2-Methoxy-*p*-benzoquinone [4] (0.025 mole) in toluene (100 ml, chosen as the solvent because of the sensitivity of the quinone to acids) was heated on a vigorously boiling water bath and a solution of bis(5-ethoxycarbonylvaleryl)-peroxide [2] (0.025 mole) in ether added slowly through a capillary extending to the bottom of the flask while the ether was distilled off. After addition of the peroxide the heating was continued until the evolution of carbon dioxide ceased. The solvent was removed under reduced pressure until the product started to sublime. The mixture was cooled and the crystalline mass collected and recrystallised from methanol, m.p. 100–101° and 112–113° (dimorphism) (yield 32 %). On sublimation the high-melting form was obtained. (Found: C 62.7; H 7.1. Calc. for $C_{14}H_{18}O_5$: C 63.1; H 6.8).

5-(2,4-5-Trimethoxyphenyl)-valeric acid. The quinone (0.27 g) was boiled with acetic anhydride, sodium acetate and zinc dust until the solution was colourless. The mixture was filtered and water was added to precipitate the ethyl 5-(2,5-diacetoxy-4-methoxyphenyl)-valerate, which was recrystallised from methanol, m.p. 41–42.5°. (Found: C 61.1; H 7.0. Calc. for $C_{18}H_{24}O_7$: C 61.4; H 6.9.) The acetate was dissolved in methanol and excess dimethyl sulphate and a concentrated solution of potassium hydroxide added under coal gas. The mixture was then heated to ensure complete saponification of the ester. The reaction product was precipitated and recrystallised from acetic acid-water. The trimethoxyphenylvaleric acid, m.p. 46–47° (0.1 g) was distilled at *ca.* 0.5 mm and then solidified as a higher melting form, m.p. 59–61°. (Found: C 62.7; H 7.4. Calc. for $C_{14}H_{20}O_5$: C 62.7; H 7.5.)

The acid was also prepared by another procedure: A solution of 1,2,4-trimethoxybenzene (0.01 mole) and glutaric anhydride (0.011 mole) in ether was saturated with boron trifluoride and left in the refrigerator for 3 days. The mixture was poured onto ice and the ether evaporated. The 4-(2,4,5-trimethoxybenzoyl-) butyric acid was collected and recrystallised from methanol, m.p. 164–165° (95 %). (Found: C 59.2; H 6.4. Calc. for $C_{14}H_{18}O_6$: C 59.6; H 6.4.)

The synthesis of this acid under somewhat different conditions has been reported but the yield then was lower [5]. A portion (1.03 g) was dissolved in ethanol and hydrogenated over palladised charcoal (0.33 g, 10 %) to absorb 2 mole of hydrogen in 15 h. The 5-(2,4,5-trimethoxyphenyl)-valeric acid was recrystallised from methanol, m.p. 46–48° alone or in admixture with the product obtained from the quinone (95 %). On distillation the same dimorphism was encountered.

Oxidation of 5-(2,4,5-trimethoxyphenyl)-valeric acid with potassium permanganate gave 2,4,5-trimethoxybenzoic acid in 30 % yield,

* Part IV. *Acta Chem. Scand.* **12** (1958) 1830. In the present communication the nomenclature has been changed from that previously used in this series to conform with current usage.

m.p. 144° alone or in admixture with an authentic specimen.

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The Crystal Structure of Hf_2Al_3

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In the course of phase analyses and crystal structure determinations in the binary metal systems hafnium-aluminium [1-3] and zirconium-aluminium [1], a phase with the composition Hf_2Al_3 has been studied.

The structure has been determined from complete single crystal data using Patterson and electron density maps. The alloy was prepared by arc-melting and single crystals could be obtained from the crushed melt. The single crystal and Guinier powder data showed the structure to be orthorhombic with the following unit cell dimensions:

$a = 9.52_3$ Å $b = 13.76_3$ Å $c = 5.52_2$ Å

The following structure was derived:

Unit cell content: 8 Hf_2Al_3 (observed density 8.00, calculated density 8.04).

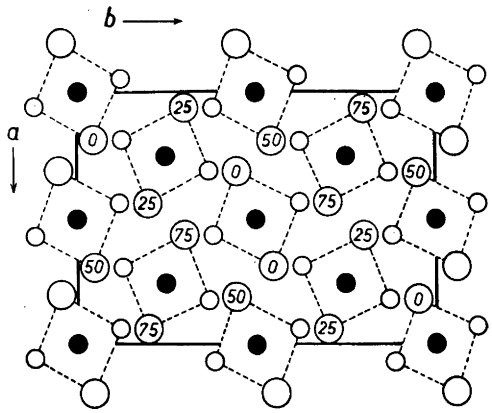

Fig. 1. The structure of Hf_2Al_3 seen along the *c*-axis. The figures in the large circles indicate the height of the Hf-atoms in percent of *c*. Small open circles: Al at *c*/4 above the Hf atoms in the pyramid. Small black circles: Al at 0.39 *c* below the Hf atoms in the pyramid.

Space-group: *Fdd*2 (No. 43).

16 Hf in 16(*b*): $x = 0.185$ $y = 0.052$ $z = 0.000$
16 Al in 16(*b*): $x = 0.185$ $y = 0.133$ $z = 0.500$
8 Al in 8(*a*): $x = 0$ $y = 0$ $z = 0.61$

The structure may be described as built up by triangular-bipyramids, Hf_2Al_3, with the hafnium-atoms forming the apices of the pyramids (*cf.* Fig. 1).

An examination of the zirconium-aluminium system shows the existence of an isotypic structure Zr_2Al_3.

Full details on these investigations and a discussion of the structures in the hafnium-aluminium system will be given elsewhere.

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