H—C(3). MS.: *m/e* 172 (M^+, 53), 155 (63), 123 (36), 105 (25), 95 (38), 81 (100), 79 (49), 67 (41), 55 (38). $C_8H_{12}SO_2$ Ber. C 55,80 H 7,03% Gef. C 55,60 H 6,94%

Die Elementaranalysen wurden im mikroanalytischen Laboratorium der ETH Zürich (Leitung: *W. Manser*) ausgeführt. Die NMR.-Spektren wurden in unserer Instrumentalabteilung (Leitung für NMR.-Service: Prof. *J. F. M. Oth*) aufgenommen. Die massenspektroskopischen Analysen verdanken wir Herrn PD Dr. *J. Seibl*.

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281. Pinacol-Pinacolone Rearrangement of 1,2-Di-(*p*-methoxyphenyl)-ethane-1,2-diol and Bis-(4-methoxyphenyl)-acetaldehyde in Acid Media

by **Wadie Tadros, Alfy Badie Sakla, Sami Bassili Awad** and **Abdul-Aziz Amine Helmy**

Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt

(15. II. 72)

Summary. 1,2-Di-(*p*-methoxyphenyl)-ethane-1,2-diol gave in acid media bis-(4-methoxyphenyl)-acetaldehyde, 4,4'-dimethoxy-deoxybenzoin, and 1,2-di-(*p*-methoxyphenyl)-ethylene oxide; their respective yields being influenced by at least 3 factors: (i) the acid, (ii) its concentration, and (iii) the reaction period.

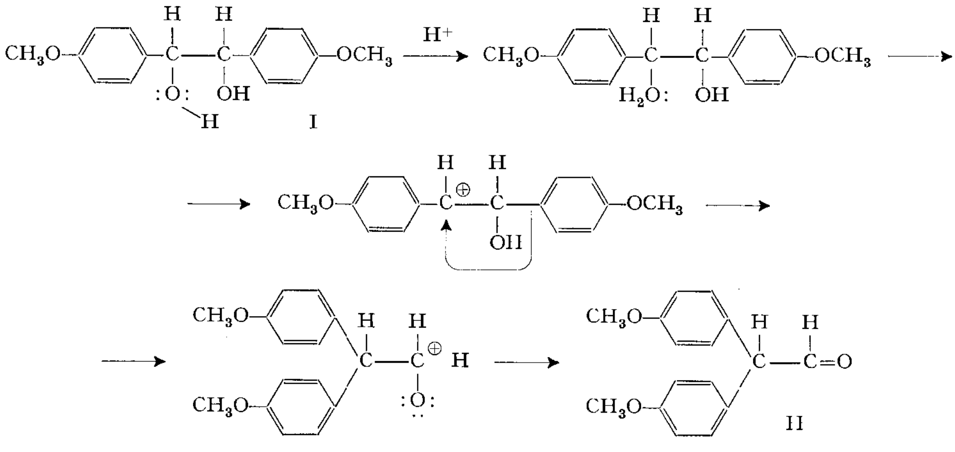
Bis-(4-methoxyphenyl)-acetaldehyde rearranged to the deoxybenzoin in boiling sulfuric (50%) or phosphoric (75%) acids (*w/w*), and to two isomeric 1,2-diacetoxy-1,2-di-(*p*-methoxyphenyl)-ethanes when it was heated with acetic anhydride.

The mechanisms of these reactions are discussed.

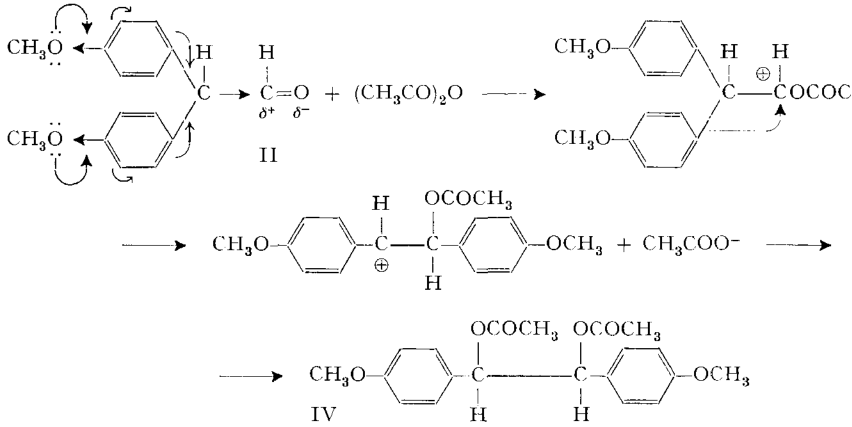
Rossel [1] reported that the reaction of 1,2-di-(*p*-methoxyphenyl)-ethane-1,2-diol (I) with sulfuric and chromic acids afforded a compound with m.p. 95°, which was described as 4,4-dimethoxy-deoxybenzoin. Later *Tiffeneau* & *Orékhoff* [2] noted that they obtained bis-(4-methoxyphenyl)-acetaldehyde (II) with m.p. 100–102° on heating to boiling for 1 h a mixture of the diol I and 50% sulfuric acid. They stated [2] that *Rossel*'s compound was bis-(4-methoxyphenyl)-acetaldehyde (II), m.p. 100–102°, and not 4,4'-dimethoxy-deoxybenzoin.

It is shown here that the reactions of the diol I in acid media are influenced by at least 3 factors: (i) the acid, (ii) acid concentration, and (iii) the reaction period. When repeating the experiment of *Tiffeneau* & *Orékhoff* [2] using sulfuric acid (50%, *w/w*), the aldehyde II was obtained together with a small quantity of the deoxybenzoin. When the reaction was stopped after 1 min, the aldehyde II together with a small quantity of a compound $C_{16}H_{16}O_3$ with m.p. 112–113° were isolated. The latter compound was formulated as 1,2-di-(*p*-methoxyphenyl)-ethylene oxide (III) by: (i) oxidation with potassium permanganate in acetone, and (ii) its IR. spectrum, that showed an absorption band at 1250 cm^{-1} characterising [3] [4] the oxirane ring. When the concentration of sulfuric acid was lowered (25%, *w/w*) and the reaction period was 1 h, the diol I gave the aldehyde II together with a minute quantity of the ethylene oxide III, but practically no 4,4'-dimethoxy-deoxybenzoin could be isolated. In boiling phosphoric acid (50%, *w/w*) and by heating for a short time (1 min), the diol I was recovered mainly unchanged. When the reaction period was extended for 1 h, the aldehyde II was mainly obtained; the deoxybenzoin and the ethylene oxide III could not be isolated. With 97% acetic acid, the diol I gave the aldehyde II and a small quantity of 1,2-diacetoxy-1,2-di-(*p*-methoxyphenyl)-ethane (IV).

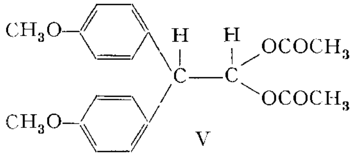
By analogy with the mechanism proposed [5] [6] for rearrangement of other substituted vicinal diols, the following mechanism may be advanced to explain the conversion of the diol I to the aldehyde II:

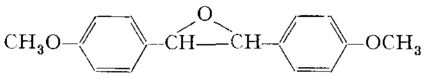


The reversibility of the above reaction, *i.e.* reversal of pinacol-pinacolone rearrangement, was achieved by heating the aldehyde II with acetic anhydride on the water-bath. Two isomeric 1,2-diacetoxy-1,2-di-(*p*-methoxyphenyl)-ethanes (IV), probably the racemic and the *meso* forms, were obtained. In boiling acetic anhydride a minute quantity of 2,2-diacetoxy-1,1-di-(*p*-methoxyphenyl)-ethane (V) could also be isolated, which on hydrolysis with sulfuric acid (25%, *w/w*) gave back the aldehyde II. Compound V was recovered unchanged when heated with boiling acetic anhydride, indicating that it was not an intermediate in the formation of the two diacetoxy compounds IV. The formation of these two compounds IV offers for the first time an experimental proof of the reversibility of pinacol-pinacolone rearrangement. The mechanism may be as presented in the following scheme:



It was interesting to note that the aldehyde II was recovered mainly unchanged when its mixture with sulfuric acid (25%, *w/w*), phosphoric acid (50%, *w/w*) or acetic acid (97%) was heated to boiling for 3 h. However, when using higher concentrations of sulfuric acid (50%, *w/w*) or phosphoric acid (75%, *w/w*), the aldehyde II rearranged to the deoxybenzoin. The formation of the deoxybenzoin could apparently be due to an aldehyde-ketone rearrangement [5] [6].


V


III

Experimental Part

Preparation of 1,2-di-(p-*methoxyphenyl)-ethane-1,2-diol and* iso-*1,2-di-*(p-*methoxyphenyl)-ethane-1,2-diol.* To a mixture of anisoin (5.44 g, 0.02 mole) and dry ether (200 ml) powdered lithium aluminium hydride (2.28 g; 0.06 mole) was gradually added. The mixture was heated to boiling for 3 h and then left overnight at room temperature. The mixture was decomposed with cold water and the inorganic residue, after separation, was digested with acetone. Ether and acetone were distilled and the residue crystallised from 95% ethanol to give 1,2-di-*p*-methoxyphenyl)-ethane-1,2-diol (4.8 g) with m.p. and mixed (cf. [7]) m.p. 168–169°.

The ethanolic mother-liquor was concentrated, diluted with water and extracted with ether. Ether was distilled off and the residue was recrystallised from petrol (b.p. 60–80°), from which *iso*-1,2-di-(*p*-methoxyphenyl)-ethane-1,2-diol (0.2 g) separated as colourless crystals with m.p. and mixed (cf. [1]) m.p. 115°.

Preparation of 1,2-diacetoxy-1,2-di-(p-*methoxyphenyl)-ethane.* A solution of 1,2-di-(*p*-methoxyphenyl)-ethane-1,2-diol (2.0 g) in acetic anhydride (20 ml) was heated to boiling for 1 h. The solution was cooled and diluted with water. The precipitate was filtered off and recrystallised from 95% ethanol, from which 1,2-diacetoxy-1,2-di-(*p*-methoxyphenyl)-ethane (2.2 g) separated as almost colourless crystals with m.p. 149–150°.

$C_{20}H_{22}O_6$ Calc. C 67.0 H 6.1% Found C 67.3 H 6.2%

Preparation of iso-*1,2-diacetoxy-1,2-di-*(p-*methoxyphenyl*)*-ethane.* A solution of *iso*-1,2-di-(*p*-methoxyphenyl)-ethane-1,2-diol (0.5 g) in acetic anhydride (10 ml) was heated to boiling for 1 h. It was diluted with water and extracted with ether. The ethereal layer was washed with sodium carbonate solution (5%), water, and dried (Na_2SO_4). The solvent was distilled off, and the residue crystallised from petrol (60–80°) from which *iso*-1,2-diacetoxy-1,2-di-(*p*-methoxyphenyl)-ethane (0.5 g) separeated as colourless crystals with m.p. 87°.

$C_{20}H_{22}O_6$ Calc. C 67.0 H 6.1% Found C 66.8 H 6.3%

Hydrolysis of the two 1,2-diacetoxyethanes. 1,2-Diacetoxy-1,2-di-(*p*-methoxyphenyl)-ethane, m.p. 149–150° (0.5 g), and m.p. 87° (0.5 g), gave the corresponding diols with m.p. 168–169° and 115° (see above), respectively, when heated to boiling for 1 h with ethanolic potassium hydroxide (1 g in 15 ml 95% ethanol).

Reactions of 1,2-di-(*p*-methoxyphenyl)-ethane-1,2-diol. – a) *With sulfuric acid* (*50%* w/w). – (i) A mixture of the diol and sulfuric acid (50%, *w/w*, 100 ml) was heated to boiling for 1 h. The mixture was cooled, diluted with ice/water and the residue was extracted with ether. The ethereal solution was washed with 5% sodium carbonate solution, water, and dried (Na_2SO_4). Ether was recovered and the residue fractionally crystallised from benzene/petrol (60–80°) to give *bis-(4-methoxyphenyl)-acetaldehyde* (1.3 g), m.p. and mixed (cf. [7]) m.p. 100–102°, and *4,4'-dimethoxy-deoxybenzoin* (0.2 g), m.p. and mixed (cf. [8]) m.p. 110–111°.

(ii) The repetition of experiment (i), heating the diol (2.0 g) for 1 min, gave *bis-(4-methoxyphenyl)-acetaldehyde* (1.4 g), m.p. and mixed (c.f [7]) m.p. 100–102°, and *1,2-di-*(p-*methoxyphenyl*)*-ethylene oxide* (0.05 g), m.p. 112–113°, depressed when admixed with either 4,4'-dimethoxybenzoin (m.p. 112–113°) or 4,4'-dimethoxy-deoxybenzoin (m.p. 111–112°).

$C_{16}H_{16}O_3$ Calc. C 75.0 H 6.3% Found C 75.1 H 6.3%

b) *With sulfuric acid* (*25%*, w/w). Repetition of experiment (a, ii) above, using sulfuric acid (25%, *w/w*) and heating to boiling for 5 min, gave bis-(4-methoxyphenyl)-acetaldehyde (1.5 g) and 1,2-di-(*p*-methoxyphenyl)-ethylene oxide (0.05 g). – Almost, the same products were obtained when heating was extended to 60 min.

The *ethylene oxide* was recovered unchanged when its mixture with sulfuric acid (25%, *w/w*) was heated to boiling for 1 h.

c) *With phosphoric acid* (*50%*, w/w). – (i) When experiment (a, ii) was carried out using phosphoric acid (50%, *w/w*, 20 ml) and heating to boiling for 1 min, unchanged diol (1.8 g) and *bis-(4-methoxyphenyl)-acetaldehyde* (0.1 g) were isolated. – (ii) Repetition of experiment (i), heating for 10 min, gave the diol (1.1 g), and bis-(4-methoxyphenyl)-acetaldehyde (0.7 g). – (iii) By heating longer (1 h), only bis-(4-methoxyphenyl)-acetaldehyde (1.6 g) was obtained.

d) *With acetic acid.* – (i) When experiment (a, i) was carried out, using a mixture of the diol (2 g) and acetic acid (80%, 20 ml) and heating for 1 h, *bis-(4-methoxyphenyl)-acetaldehyde* (1.7 g) was obtained. – (ii) The repetition of experiment (d, i) above, using acetic acid (97%), gave *1,2-diacetoxy-1,2-di-*(p-*methoxyphenyl*)*-ethane* (0.1 g) and *bis-(4-methoxyphenyl)-acetaldehyde* (1.1 g).

Oxidation of 1,2-di-(p-*methoxyphenyl*)*-ethylene oxide.* A mixture of the ethylene oxide (0.3 g) and potassium permanganate (0.3 g) in acetone (30 ml) was heated on the water-bath for 30 min. The mixture was filtered while hot, acetone was recovered and the residue treated with a little hot water. The solution was filtered, the filtrate cooled and acidified with a few drops of hydrochloric acid. A precipitate was formed and recrystallised from water: *anisic acid* separated as colourless crystals, m.p. and mixed m.p. with an authentic sample [8] 178–180°.

Reactions of bis-(4-methoxyphenyl)-acetaldehyde. – a) *With sulfuric acid.* – (i) A mixture of bis-(4-methoxyphenyl)-acetaldehyde (2.0 g) and sulfuric acid (50%, *w/w*, 20 ml) was heated to boiling for 3 h. The mixture was cooled, diluted with water and the residue extracted with ether. The ethereal solution was treated with 5% sodium carbonate solution, water, and dried (Na_2SO_4).

Ether was recovered and the residue crystallised from benzene/petrol (60–80°) to give unchanged bis-(4-methoxyphenyl)-acetaldehyde (0.9 g) and *4,4'-dimethoxy-deoxybenzoin* (0.5 g). – (ii). When the aldehyde (2.0 g) was treated with boiling sulfuric acid (25%, *w/w*) for 3 h, it was mainly recovered unchanged (1.8 g).

b) *With phosphoric acid.* – (i) When experiment (a, i) was repeated using phosphoric acid (50%, *w/w*, 20 ml), only unchanged bis-(4-methoxyphenyl)-acetaldehyde (1.8 g) was obtained. – (ii) The repetition of experiment (i) using phosphoric acid (75%, *w/w*, 20 ml) gave unchanged aldehyde (0.6 g) and *4,4'-dimethoxy-deoxybenzoin* (1.0).

c) *With acetic acid.* When experiment (a, i) was repeated using acetic acid (97%, 20 ml), bis-(4-methoxyphenyl)-acetaldehyde (1.8 g) was recovered unchanged.

d) *With acetic anhydride.* – (i) A solution of bis-(4-methoxyphenyl)-acetaldehyde (2.9 g) in acetic anhydride (20 ml) was heated on the water-bath for 10 min. The solution was cooled, diluted with water, and the residue formed was extracted with ether. The ethereal layer was washed with cold sodium carbonate solution (5%), water, then dried (Na_2SO_4). The solvent was recovered, and the residue crystallised from 95% ethanol, from which *1,2-diacetoxy-1,2-di-*(p-*methoxyphenyl*)-*ethane* (0.6 g) separated as colourless crystals, m.p. 149–150°, not depressed when admixed with the corresponding compound prepared above (p. 2811).

The ethanolic mother-liquor was concentrated and the residue crystallised from petrol (60–80°) to give iso-*1,2-diacetoxy-1,2-di-*(p-*methoxyphenyl*)-*ethane* (1.5 g) m.p. 87°, not depressed when admixed with the corresponding *iso* compound prepared above (p. 2811).

(ii) The repetition of experiment (i), but boiling for 10 min, gave 1,2-diacetoxy-1,2-di-(*p*-methoxyphenyl)-ethane (0.5 g), *iso*-1,2-diacetoxy-1,2-di-(*p*-methoxyphenyl)-ethane (1.2 g), and *2,2-diacetoxy-1,1-bis-(4-methoxyphenyl)-ethane* (0.15 g), m.p. 110°.

$C_{20}H_{22}O_6$ Calc. C 67.0 H 6.1% Found C 67.0 H 6.2%

Hydrolysis of the latter compound (0.3 g), using sulfuric acid (25%, *w/w*, 20 ml) and heating to boiling for 1 h, gave *bis-(4-methoxyphenyl)-acetaldehyde* (0.2 g) with m.p. and mixed (cf. [7]) m.p. 100–102°.

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