198. Reactions with Stilbenes and Related Derivatives. Part I. Reactions of 1,2-Dihalogeno-1,2-*bis*-(4-methoxyphenyl)ethanes with Alcohols

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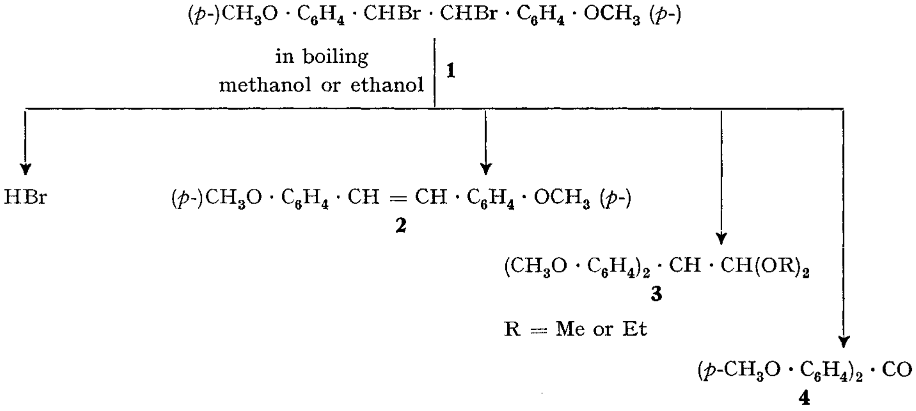
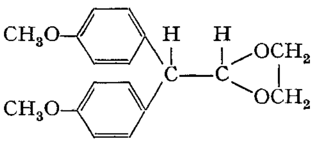
Summary. The reaction of 1,2-dibromo-1,2-bis(4-methoxyphenyl)ethane with alcohols was associated with rearrangement to give the corresponding bis(4-methoxyphenyl)acetals. In boiling ethylene glycol 4,4'-dimethoxy-deoxybenzoin was also obtained due to an aldehyde-ketone rearrangement. 4,4'-Dimethoxybenzophenone was also formed being apparently derived from the acetals. The mechanism of formation of the acetals has been discussed.

When 1,2-dibromo-1,2-bis(4-methoxyphenyl)ethane (**1**) in solution in methanol or ethanol was heated to boiling, hydrogen bromide was liberated and a number of products were isolated.



When the reaction was carried out in boiling ethylene glycol, hydrogen bromide was liberated, and in addition to compounds **2** and **4**, 1,1–bis(4-methoxyphenyl)–2,2–ethylene dioxyethane (**5**), 4,4'–dimethoxydeoxybenzoin (**6**) together with a trace of an oil were obtained.



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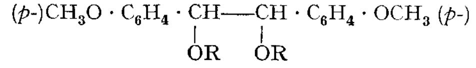
$(p\text{-})CH_3O \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot C_6H_4 \cdot OCH_3\ (p\text{-})$ **6**

When the reaction was carried out with methanolic sodium methoxide two isomers of 1,2-dimethoxy-1,2-bis(4-methoxyphenyl)-ethane with melting points 110° and 136° were obtained. Both had the same analytical data, molecular weight and almost the same electronic spectra (see experimental part). They were oxidized with difficulty to give anisic acid. It was notable, that when the isomer with m.p. 110° in solution in acetic anhydride (b.p. 139.9°) was heated to boiling for one hour, it was converted to the other isomer with m.p. 136°.



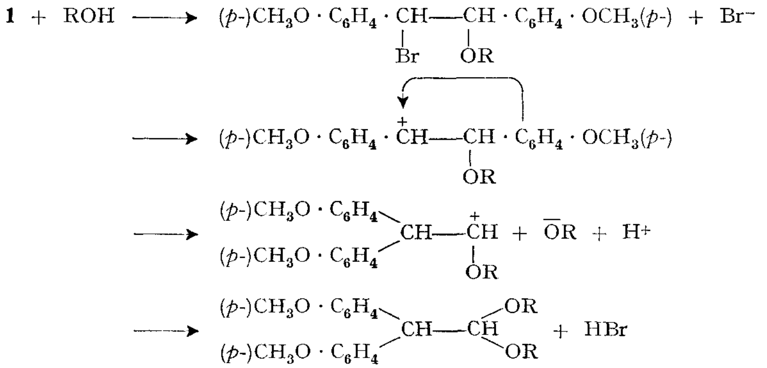
$$(p\text{-})CH_3O \cdot C_6H_4 \cdot \underset{OR}{CH}-\underset{OR}{CH} \cdot C_6H_4 \cdot OCH_3\ (p\text{-})$$

7

a) R = Me with two isomers with m.p. 110 and 136°.
b) R = Et
c) R = $CH_2 \cdot CH_2OH$

The reaction with ethanolic sodium ethoxide gave 1,2-bis(4-methoxyphenyl)-1,2-diethoxyethane (**7b**) with m.p. 90–91° together with a product with m.p. 76° and a minute quantity of an oil. Both products were recovered unchanged after heating their solutions in acetic anhydride. The oxidation of the product with m.p. 76° gave anisic acid only and its analytical data ($C_{16}H_{15}BrO_2$ Calc. Br 25.1% Found Br 25.6%) corresponds to monobromostilbene; the nature of this product is being further investigated. The ethers **7a** and **7b** did not show deviation in polarized light and possess either the DL- or the meso-form.

The formation of 4,4'-dimethoxystilbene is accompanied by the removal of the two atoms of bromine which contribute to the liberation of hydrogen bromide. A concurrent reaction to give the acetals **3** and **5** may describe a pinacol-pinacolone rearrangement of the type previously suggested by *Tadros* et al. [1] which would lead to the formation of bis(4-methoxyphenyl)acetaldehyde. The latter in the presence of hydrogen bromide in solution in alcohol will give the acetals **3** (R = Me or Et). Pending further confirmation, the above mechanism may be also suggested with regard to the formation of the acetals.



In the above scheme the anisyl group migrates with the two electrons.

The structures of these acetals were confirmed synthetically (see experimental part).

When a mixture of compound **1** and asymmetric bis(4-methoxyphenyl)ethylene in solution in glacial acetic acid was heated to boiling, both 4,4'-dimethoxystilbene and 1,1,4,4-tetrakis(4-methoxyphenyl)buta-1,3-diene were obtained. The formation of the former compound was apparently related to the liberation of bromine as indicated above. The butadiene was formed from the asymmetric ethylene as previously reported [2].

The reaction of 1,2-bis(4-methoxyphenyl)-1,2-dichloroethane with alcoholic sodium ethoxide gave 4,4′-dimethoxystilbene and the diethoxyethane ether **7b**.

The formation of 4,4′-dimethoxydeoxybenzoin in the reaction of the 1,2-dibromoethane **1** in boiling ethylene glycol was apparently associated with an aldehyde-ketone rearrangement [1] of bis(4-methoxyphenyl)acetaldehyde (see above). The formation of 4,4′-dimethoxybenzophenone was apparently derived from the aldehyde or acetals.

Experimental Part

The electronic spectra were measured on *Beckman* DK-1 Spectrophotometer. Molecular weights were determined by the thermoelectric method using thermistors (*Knauer* apparatus) [3].

1. Preparation of Educts. – 1.1. *1,1-bis(4-methoxyphenyl)acetaldehyde.* This was prepared according to the method of *Tiffeneau et al.* [4] (see also *Tadros et al.* [1]).

1.2. *Bis(4-methoxyphenyl)acetaldehyde dimethyl acetal.* 1.2.1. A solution of the aldehyde (0.5 g) in methanol containing 5% hydrogen chloride (25 ml) was left at room temp. (20°) for 7 days during which the aldehyde went into solution. Neutralisation with methanolic sodium methoxide followed by dilution, gave an oily product which was extracted with ether. Evaporation of ether gave an oil which crystallized from methanol to give bis(4-methoxyphenyl)acetaldehyde dimethyl acetal (0.4 g) which had m.p. 73–74°.

$C_{18}H_{22}O_4$ (312.15) Calc. C 71.5 H 7.3% Found C 71.6 H 7.3%

1.2.2. A solution of the aldehyde (0.14 g) in methanol (25 ml) to which was added 4 drops of 48% hydrobromic acid was heated on the steam-bath for two min. The solution was worked out as in 1.2.1. to give bis(4-methoxyphenyl)acetaldehyde dimethyl acetal (0.1 g), m.p. and mixed m.p. 73–74°, and 4,4′-dimethoxybenzophenone (0.01 g), m.p. and mixed m.p. with an authentic sample 142° [5].

1.3. *Bis(4-methoxyphenyl)acetaldehyde diethyl acetal.* A mixture of bis(4-methoxyphenyl)-acetaldehyde (0.15 g) and ethanol (10 ml) was elaborated as under 1.2.2. to give an oil (0.1 g) which could not be induced to crystallise.

$C_{20}H_{26}O_4$ (330.18) Calc. C 72.7 H 7.9% Found C 72.8 H 8.1%

Attempts to crystallize this oil from ethanol were accompanied by partial conversion into 4,4′-dimethoxybenzophenone with m.p. and admixed m.p. 142°.

1.4. *1,2-Dibromo-1,2-bis(4-methoxyphenyl)ethane.* a) Preparation by treatment of 1,2-bis(4-methoxyphenyl)ethane-1,2-diol (hydroanisoin) with phosphorus tribromide, see [6]. b) Preparation by addition of equimolecular quantity of bromine in solution in chloroform to 1,2-bis(4-methoxyphenyl)ethylene (4,4′-dimethoxystilbene) [7] [8] in solution in the same solvent. Recrystallized from benzene or carbon disulfide, it separated as colourless crystals, m.p. 178°.

1.5. *1,2-Dichloro-1,2-bis(4-methoxyphenyl)ethane (4,4′-dimethoxystilbene dichloride)*, was prepared according to the method of *Henne et al.* [6]. It crystallized from petroleum ether (80–100°) to give colourless crystals, m.p. 183–184°.

2. Reactions of 1,2-dibromo-1,2-bis-(4-methoxyphenyl)ethane with Alcohols. – 2.1. *With methanol.* A solution of 1,2-dibromo-1,2-bis(4-methoxyphenyl)ethane (2.0 g) in methanol (25 ml) was heated on the steam-bath for 30 min. On cooling a precipitate was formed and was filtered off. When crystallized from benzene, it separated as colourless crystals (0.02 g), m.p. 210–212° not depressed on admixture with an authentic sample of 4,4′-dimethoxystilbene. The methanolic mother-liquor which contained the liberated hydrogen bromide was neutralized with methanolic sodium methoxide, diluted with water, and the oily product thus formed was extracted with ether. Evaporation of ether gave an oil which solidified on standing. When fractionally crystallized from methanol or ethanol, the first fraction (0.65 g) separated as colourless crystals, m.p. 73–74°. It recrystallized from methanol to give 1,1-bis(4-methoxyphenyl)acetaldehyde dimethyl acetal, m.p. 73–74° ($\lambda_{\max}$ 283 nm, log ε 3.51; 276 nm, log ε 3.59; 230 nm, log ε 4.35; 196 nm, log ε 4.81; solvent *n*-hexane). The alcoholic mother-liquor gave on standing 4,4'-dimethoxybenzophenone (0.28 g), m.p. 142° not depressed on admixture with an authentic sample [5].

2.1.1. *Oxidation of bis(4-methoxyphenyl)acetaldehyde dimethyl acetal.* A mixture of the acetal (0.2 g) and potassium permanganate (0.05 g) in acetone (20 ml) was heated on the steam-bath for 30 min. The solution was filtered and acetone was distilled. The residue crystallized from ethanol to give 4,4'dimethoxybenzophenone (0.11 g), m.p. and mixed m.p. 142°.

2.1.2. *Conversion of bis(4-methoxyphenyl)acetaldehyde dimethyl acetal into 4,4'-dimethoxybenzophenone.* When the acetal (0.2 g) was left in methanol (25 ml) containing one drop of 48% hydrobromic acid for 10–15 days, it was gradually converted into 4,4'-dimethoxybenzophenone (0.11 g), m.p. and mixed m.p. 142°.

2.2. *With 95% ethanol.* A solution of 1,2-dibromo-1,2-bis(4-methoxyphenyl)ethane (2.0 g) in 95% ethanol (25 ml) was heated on the steam bath for 15 min. On cooling, a precipitate was formed, and was filtered off. When crystallized from benzene, a product separated as colourless crystals (0.07 g), m.p. 210–212° not depressed on admixture with an authentic sample of 4,4'-dimethoxystilbene. The ethanolic mother-liquor which contained liberated hydrogen bromide was neutralized with ethanolic sodium ethoxide, diluted with water, and the oily product thus formed was extracted with ether. Evaporation of ether gave an oil (0.4 g) which could not be induced to crystallize from different organic solvents. Analysis and oxidation of the oil showed that it was 1,1 bis(4-methoxyphenyl)acetaldehyde diethyl acetal.

$C_{20}H_{26}O_4$ (330.18) Calc. C 72.7 H 7.9% Found C 72.8 H 8.1%

1,1-Bis(4-methoxyphenyl)acetaldehyde diethyl acetal and 4,4'-dimethoxybenzophenone were obtained when the above experiment was repeated, but heating longer (30 min. instead of 15 min.).

2.2.1. *Oxidation of bis(4-methoxyphenyl)acetaldehyde diethyl acetal.* Oxidation was carried out with potassium permanganate as described above (diethyl acetal, 0.2 g; potassium permanganate, 0.1 g; acetone, 20 ml). The residue crystallized from ethanol gave 4,4'-dimethoxybenzophenone (0.14 g), m.p. and mixed [5] m.p. 142°.

2.3. *With ethylene glycol.* A solution of 4,4'-dimethoxystilbene dibromide (2.0 g) in ethylene glycol (20 ml) was heated to boiling for 5 min. The solution became yellowish brown and acidic due to the liberation of hydrogen bromide. On cooling 4,4'-dimethoxystilbene (0.24 g) separated, and was crystallized from benzene, m.p. and mixed m.p. with an authentic sample 212°. The ethylene glycol mother-liquor was neutralized with aqueous sodium hydroxide and extracted with ether. Ether was evaporated and the residue was fractionally crystallized from ethanol, from which the first fraction (0.21 g) separated as colourless crystals, m.p. 102–103° not depressed when mixed with an authentic sample [9] of the cyclic acetal 1,1-bis(4-methoxyphenyl)-2,2-ethylenedioxyethane, but depressed with bis(4-methoxyphenyl)acetaldehyde. The second fraction (0.04 g) had m.p 110° and showed no depression on admixture with an authentic sample of 4,4'dimethoxydeoxybenzoin. Evaporation of the solvent of the mother-liquor gave an oily product (0.44 g). Trituration of this oil with cold ethanol gave 4,4'-dimethoxybenzophenone (0.01 g), m.p. and mixed m.p. 142°.

3. Reactions in alkaline media. – 3.1. *Reaction with methanolic sodium methoxide.* A solution of 1,2-dibromo-1,2-bis(4-methoxyphenyl)ethane (2.0 g) in methanolic sodium methoxide (sodium, 0.23 g; methanol, 25 ml) was heated on the steam-bath for 30 min. The precipitate which separated on cooling was filtered off. The first fraction was recrystallized from ethanol as colourless crystals of 1,2-dimethoxy-1,2-bis(4-methoxyphenyl)ethane (0.86 g), m.p. 136°. – UV.: ($\lambda_{\max}$ 281 nm, log ε 3.56; 275 nm, log ε 3.58; 229 nm, log ε 4.45; 197 nm, log ε 4.88; solvent *n*-hexane).

$C_{18}H_{22}O_4$ (302.15) Calc. C 71.5 H 7.3% Found C 71.7 H 7.5% Mol.-Wt. 308

When the methanolic mother-liquor obtained after filtering off the first crop was cooled, a second fraction separated. It crystallized from 95% ethanol as colourless crystals (0.21 g), m.p. 110°. – UV.: ($\lambda_{\max}$ 281 nm, log ε 3.46; 275 nm, log ε 3.49; 227 nm, log ε 4.33; 196 nm, log ε 4.81; solvent *n*-hexane).

$C_{18}H_{22}O_4$ (302.15) Clac. C 71.5 H 7.3% Found C 71.2 H 7.2% Mol.-Wt. 303

It proved to be isomeric with the first fraction (m.p. 136°), and as shown above, both isomers showed the same electronic spectra.

3.1.1. *Conversion of the isomer with m.p. 110° into the second isomer with m.p. 136°.* A solution of 1,2-Dimethoxy-1,2-bis(4-methoxyphenyl)ethane with m.p. 110° (0.1 g) in acetic anhydride (10 ml) was heated to boiling for 1 h, diluted with ice water and extracted with ether. Ether was evaporated and the residue was crystallized from 95% ethanol to give colourless crystals (0.08 g), m.p. 136° showing no depression on admixture with the sample with m.p. 136°.

3.1.2. *Oxidation of the two isomers 1.2-dimethoxy-1,2-bis(4-methoxyphenyl)ethanes.* Oxidation was effected as described above (the isomer 0.14 g; potassium permanganate, 0.2 g; acetone, 20 ml; heating on the steam-bath for 2 h). The acetone solution was filtered and the manganese dioxide precipitate was treated with hot water (3 ml). The alkaline aqueous solution was evaporated on the steam-bath almost to dryness and then acidified with two drops of concentrated hydrochloric acid. The precipitate thus formed was extracted with acetone (5 ml). Evaporation of acetone left anisic acid which separated from dilute ethanol as colourless crystals, m.p. and mixed m.p. with an authentic sample 179–180°. Extraction of the manganese dioxide residue with acetone and evaporation of the latter gave back a partly unchanged isomer (0.1 g).

3.2. *Reactions with ethanolic sodium ethoxide.* 3.2.1. *Reactions of 1,2-Dibromo-1,2-bis(4-methoxyphenyl)ethane.* A solution of the dibromoethane (2.0 g) in ethanolic sodium ethoxide (sodium, 0.23 g; in 95% ethanol, 25 ml) was heated on the steam-bath for 30 min. The precipitate which separated on cooling was filtered off and crystallized from benzene to give 4,4′-dimethoxystilbene (0.04 g) m.p. and mixed m.p. 210–212°. The alkaline mother-liquor was diluted with water and the oily product thus obtained was extracted with ether. Evaporation of ether gave an oily product. It crystallized from 95% ethanol to give first 1,2-diethoxy-1,2-bis(4-methoxyphenyl)ethane (0.5 g) m.p. 90–91°.

$C_{20}H_{26}O_4$ (330.18) Calc. C 72.72 H 7.9% Found C 72.55 H 7.88%

Concentration of the mother-liqour gave an oily product which could not be induced to crystallise.

3.2.1.1. *Oxidation of 1,2-diethoxy-1,2-bis(4-methoxyphenyl)ethane.* This was carried out as described above (the ethane, 0.17 g; potassium permanganate, 0.2 g; acetone, 20 ml), and gave anisic acid.

3.2.2. *Reaction of 1,2-dichloro-1,2-bis(4-methoxyphenyl)ethane.* This reaction was carried out analogously to 3.2.1. (the dichloroethane, 1.56 g; sodium, 0.23 g; 95% ethanol, 20 ml) gave 4,4′-dimethoxystilbene (0.1 g) m.p., and mixed m.p 210–212°, and 1,2-diethoxy-1,2-bis(4-methoxyphenyl)ethane (0.3 g), m.p. and mixed m.p. 90–91°.

4. Reaction with sodium 2-hydroxyethoxide in ethylene glycol. – A mixture of 1,2-dibromo-1,2-bis(4-methoxyphenyl)ethane (2.0 g) and sodium 2-hydroxyethoxide in ethylene glycol (sodium, 0.575 g; dissolved in ethylene glycol, 15 ml) was refluxed for 3 h, cooled, diluted with water and extracted with ether. Ether was distilled and the residue was crystallized from ethanol to give colourless crystals of 4,4′-dimethoxystilbene (0.16 g), m.p. 212° showing no depression on admixture with an authentic sample. Cooling the alcoholic mother-liquor gave 1,2-di-β-hydroxyethoxy-1,2-bis(4-methoxyphenyl)ethane as colourless crystals (0.06 g), m.p. 104–105°.

$C_{20}H_{26}O_6$ (362.17) Calc. C 72.07 H 6.87% Found C 72.48 H 6,78%

The alkaline filtrate was acidified, and the precipitate was filtered off. The residue was recrystallized from petroleum ether (40–60°) to give a product (0.3 g) which was methylated (sodium, 0.2 g; ethanol, 15 ml; methyl iodide, 2.5 ml; heating on the steam-bath for 30 min). Recrystallization of the product obtained from ethanol gave colourless crystals, m.p. 211–212° showing no depression on admixture with 4,4′-dimethoxystilbene.

5. Reaction of 1,2-dibromo-1,2-bis(4-methoxyphenyl)ethane and 1,1-bis (4-methoxyphenyl)ethylene in glacial acetic acid. – A mixture of the dibromoethane (1.66 g) and the ethylene (1.0 g) in glacial acetic acid (15 ml) was heated to boiling for 2 min, cooled and the product was filtered off. Fractionation of the precipitate from boiling ethanol gave first an insoluble fraction which crystallized from acetic acid to give 1,1,4,4-tetrakis(4-methoxyphenyl)buta-1,3-diene as colourless crystals, m.p. 204–205° not depressed when admixed with an authentic sample [2]. The alcoholic mother-liquor gave on standing 4,4′-dimethoxystilbene (0.1 g), m.p. and mixed m.p. with an authentic sample 210°.

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199. Physico-Chemical Properties of Deuteriated Compounds

2nd Communication[1])

The Isotope Partition Coefficient in Methylcyclohexane-Hydrogen

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Summary. The deuterium isotope partition coefficient α has been determined as a function of total pressure, temperature and degree of deuteriation for methylcyclohexane/hydrogen over Ni/Al_2O_3. Good agreement with theory has been obtained for the dependence on temperature but not for that on total pressure or on the degree of deuteriation.

1. Introduction. – In a recent short communication we described the deuteriation of saturated hydrocarbons by exchange, catalysed by nickel on alumina [2]. A convenient procedure for the production of deuteriated hydrocarbons has been developed on a laboratory scale [3]. In order to optimize this process we need to know the values of the isotope partition coefficient between hydrogen and hydrocarbons, which is defined as

$$\alpha \equiv (x_1/(1 - x_1))/(x_2/(1 - x_2)) \tag{1}$$

where x_1 and x_2 are the mole fraction of deuterium in the hydrocarbon and hydrogen, respectively. Work in this field has been reviewed by *Roginsky* [4]. Several authors have used statistical thermodynamics to estimate this coefficient in terms of the partition function ratios (β-factors) of the isotopic species [5] [6]

$$\alpha = \beta_1/\beta_2. \tag{2}$$

According to *Vaisberg & Varshavsky* [6] β_1 and β_2 are approximate to the partition function ratios of totally deuteriated and protiated hydrocarbon and hydrogen respectively.

The temperature dependence of the β-factor is given by the following expression

$$\beta_i = a_i \cdot \exp (b_i/T) \tag{3}$$

where a_i and b_i are calculated from the vibration frequencies of the totally deuteriated and the protiated compounds. This procedure has the advantage that only one value of β (*e.g.* for hydrogen) is needed to obtain β-values for other compounds from experimental partition coefficients. The present work was undertaken to test the validity of this assumption.

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[1]) 1st communication see [1].