

**274.** *Bromination of Dimethoxystilbenes.*

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2 : 2'- and 3 : 3'-Dimethoxystilbene can be converted in a two-step process into symmetrical dibromodimethoxystilbenes. The 2 : 2'-compound is substituted in positions 5 and 5'.

IN a recent publication (Bergmann and Schapiro, *J. Org. Chem.*, 1947, **12**, 57) it was reported that 2-methoxystilbene undergoes nuclear bromination with such ease that in place of the expected dibromide there was obtained 5-bromo-2-methoxystilbene dibromide. We have now extended this observation to symmetrical dimethoxystilbenes.

Auwers (*Ber.*, 1903, **36**, 1888), using excess of bromine, converted 4 : 4'-dimethoxystilbene into 3 : 5 : 3' : 5'-tetrabromo-4 : 4'-dimethoxystilbene dibromide. In this case, both positions

ortho to the methoxyl group are equivalent, whereas the para position is substituted by an olefinic chain. However, no disturbing effect is to be expected from this chain, as in all known cases the speed of addition of bromine to the central double bond of a stilbene is greater than that of nuclear substitution. The CHBr group is unlikely to exert any influence on this latter reaction, because Bance, Barber, and Woolman (*J.*, 1943, 1) observed the complete inertness of stilbene dibromide towards bromination in the ring. Therefore we assumed that in 2:2'-dimethoxystilbene dibromide the methoxy-groups would direct the attack of bromine exclusively. This was borne out by experiment.

After saturation of the double bond of 2:2'-dimethoxystilbene by bromine, substitution proceeded slowly, and although exactly 3 mols. of bromine were added, the reaction product was a mixture which could not be separated. It was, therefore, treated directly with potassium iodide. The mixture of bromostilbenes, so obtained, could be separated by fractional crystallisation into two substances of m. p. 214° and 130°, severally, which upon addition of 1 mol. of bromine yielded "dibromides" of m. p. 256° and 225° respectively. The compound of m. p. 214° is a dibromo-2:2'-dimethoxystilbene and was identified as the 5:5'-dibromo-derivative by direct comparison with an authentic specimen (Ashley and Harris, *J.*, 1946, 567).

The substance of m. p. 130° contains only one bromine atom. That it was 5-bromo-2:2'-dimethoxystilbene was proved by its conversion *via* its dibromide into 5:5'-dibromo-2:2'-dimethoxystilbene dibromide. The reason for the incomplete conversion of 2:2'-dimethoxystilbene into the latter is to be found in the low reaction velocity. The monobromo-dibromide is sparingly soluble in chloroform, and if the bromine solution is added slowly, this compound has time to crystallise out, thus avoiding further bromination in the second ring. The preparation of the dibrominated bromide in nearly quantitative yield is, however, achieved easily, if excess bromine is added *at once* to a very dilute chloroform solution of 2:2'-dimethoxystilbene. This method thus presents a much easier route to 5:5'-dibromo-2:2'-dimethoxystilbene than the procedure of Ashley and Harris (*loc. cit.*).

3:3'-Dimethoxystilbene is converted smoothly into a dibromo-3:3'-dimethoxystilbene dibromide and hence into the corresponding stilbene; by analogy, these are deemed to be the 2:2'-dibromo-5:5'-dimethoxy-compounds, although we were unable to oxidise the stilbene to the expected 2-bromo-5-methoxybenzoic acid.

#### EXPERIMENTAL.

**2:2'-Dimethoxystilbene.**—By the procedure of Baumann and Fromm (*Ber.*, 1891, **24**, 1441), the required *o*-methoxythiobenzaldehyde is obtained mainly as a tough syrup and crystallizes only partly. However, the syrupy mass gave as good a yield (*ca.* 30%) upon thermal decomposition as did the crystalline portion. The crude stilbene was purified by distillation, b. p. 180–190°/0.5 mm., and then crystallized quickly upon trituration with methanol. It formed clusters of needles from butanol and prisms from toluene; m. p. 140°.

**Bromination.** (1) The stilbene (0.7 g.) was dissolved in chloroform (5 c.c.), and bromine (1.4 g.; 3 mols.) in the same solvent (5 c.c.) was added dropwise during 5 mins. The first third was decolorised instantaneously, then the speed of reaction slackened, and after addition of the second third of bromine a precipitate appeared. Decolorisation of the last third of bromine was very slow and was completed by warming on a water-bath. After the evolution of hydrogen bromide had ceased, the solvent was evaporated and the residue treated with methanol; yield 1.3 g., m. p. 218–220°. The product was not homogeneous, and crystallisation from xylene did not give a pure compound. It was, therefore, suspended in acetone (25 c.c.) and heated under reflux with sodium iodide (1 g.) for 3 hours. After evaporation of the solvent and addition of thiosulphate, a white substance was obtained. Upon recrystallisation from toluene, appeared first needles, then plates. They were separated by fractional crystallisation. The needles finally had m. p. 214° (Found: C, 48.4; H, 3.6. Calc. for C<sub>16</sub>H<sub>14</sub>O<sub>2</sub>Br<sub>2</sub>: C, 48.2; H, 3.5%) and were identified (mixed m. p.) as 5:5'-dibromo-2:2'-dimethoxystilbene described by Ashley and Harris (*loc. cit.*). The plates, recrystallised from *isopropanol* and then from light petroleum (b. p. 80°), formed glistening, elongated plates, m. p. 130° (Found: C, 60.0; H, 4.7. C<sub>16</sub>H<sub>14</sub>O<sub>2</sub>Br requires C, 60.2; H, 4.7%), of the *monobromostilbene*.

(2) 2:2'-Dimethoxystilbene (0.8 g.) was treated with bromine (2 mols.) in chloroform solution, and the product trituated with light petroleum. The 5-bromo-dibromide (1.6 g.; 100%) crystallised from toluene in colourless parallelepipeds with cut-off ends, m. p. 225° (Found: C, 39.8; H, 3.2. C<sub>16</sub>H<sub>14</sub>O<sub>2</sub>Br<sub>3</sub> requires C, 40.1; H, 3.1%). It was identical with the compound formed by addition of bromine to the above monobromostilbene, into which it was converted by debromination with sodium iodide in acetone.

When the monobromostilbene was dissolved in chloroform and treated *at once* with excess of bromine, the dibromo-dibromide, m. p. 244° (see below), resulted.

(3) To 2:2'-dimethoxystilbene (6 g.; 1/40 mol.) in chloroform (50 c.c.) was added *at once* a solution of excess of bromine (20 g.; 5/40 mol.) in chloroform (50 c.c.), and the solution left overnight. The crude product (13.5 g.; 97%) had m. p. 244° and was difficult to recrystallise in greater amounts, because of decomposition. Small samples could be recrystallised from acetic anhydride, large volumes of xylene, or nitrobenzene. The products then showed different m. p.s; *e.g.*, from xylene prisms of m. p. 245°, and from nitrobenzene of m. p. 256°. All these samples of 5:5'-dibromo-2:2'-dimethoxystilbene dibromide

showed identical analyses (Found : C, 34.2; H, 2.6.  $C_{16}H_{14}O_2Br_4$  requires C, 34.4; H, 2.5%) and were quantitatively converted into the corresponding stilbene by debromination with sodium iodide or by the cuprous chloride-pyridine procedure of Bance *et al.* (*loc. cit.*).

**3 : 3'-Dimethoxystilbene.**—The desulphuration of *m*-methoxythiobenzaldehyde started at 200° and was completed by heating to 230° for 35 mins. The crude reaction product was mixed with an equal weight of copper-bronze and distilled in a vacuum; b. p. 180—182°/0.1 mm. The distillate crystallised spontaneously. From *isopropanol* it formed prismatic plates, m. p. 101°; yield 10%.

**Bromination.** To the stilbene (1.3 g.) in chloroform (10 c.c.) was added dropwise a solution of bromine (2.6 g.) in chloroform (8.3 c.c.). When addition was complete, 2 : 2'-dibromo-5 : 5'-dimethoxystilbene dibromide crystallised out. The solvent was evaporated, and the residue treated with ethanol; yield 2.7 g. (90%). From acetic anhydride the substance crystallises in hexagonal plates, m. p. 236° (Found : C, 34.6; H, 2.5.  $C_{16}H_{14}O_2Br_4$  requires C, 34.4; H, 2.5%). Debromination with potassium iodide in acetone, as above, gave a 90% yield of 2 : 2'-dibromo-5 : 5'-dimethoxystilbene, which crystallised from toluene as prismatic rods, m. p. 154—155° (Found : C, 48.3; H, 3.7.  $C_{16}H_{14}O_2Br_2$  requires C, 48.2; H, 3.5%).

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