

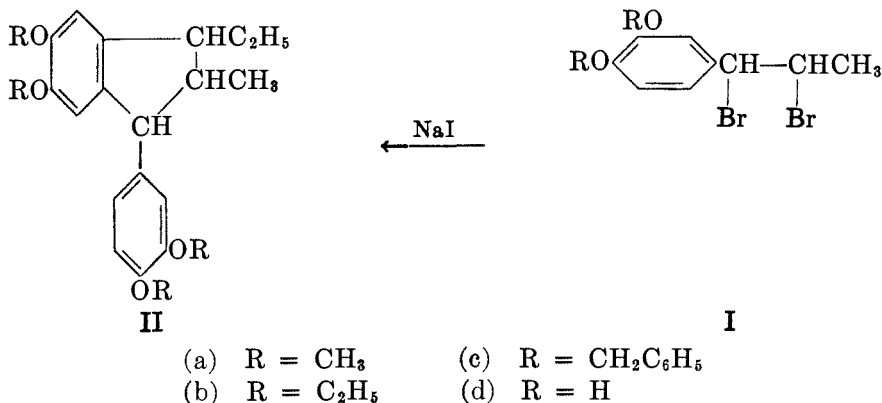
THE REACTION OF PROPENYLPHENOL ETHER DIBROMIDES
WITH SODIUM IODIDE

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Sodium iodide has been used in the past to some extent as an agent for removal of halogen from certain dibromo and dichloro compounds. For example, the geminal dihalogen compound, benzophenone dichloride, was converted into tetraphenylethylene in acetone solution with sodium iodide, with separation of iodine (1). From ethylene dibromide under similar conditions ethylene is formed. Other vicinal dibromides and dichlorides react in the same manner to form a double bond (2).

This communication deals with the reaction of one of the vicinal dibromide groups, namely the reaction of propenylphenol ether dibromides with sodium iodide. The reaction proceeds in anhydrous acetone and can be well controlled by titration of the iodine formed.¹ The experimental results show that some of the propenylphenol ether dibromides, the dibromides of anethole, isosafrole, isoeugenol benzyl ether, and 3-benzyloxy-4-ethoxypropenylbenzene react with sodium iodide to regenerate the double bond. The dibromides of isoeugenol methyl ether, 3,4-diethoxypropenylbenzene, and 3,4-dibenzyloxypropenylbenzene, on the other hand, react under similar conditions unexpectedly with formation of dimeric compounds. Besides the dimeric compound, usually, more or less propenylphenol ether is also formed. The dimerization proceeds most readily with 3,4-diethoxypropenylbenzene.



The dimeric compound of m.p. 99–100°, formed from isoeugenol methyl ether dibromide (Ia) in mixture with the dimer of isoeugenol methyl ether (IIa) m.p.

¹ Davis and Heggie (3) examined the reactions of α,β -dibromides, *e.g.*, benzalacetophenone dibromide with sodium iodide, from the point of view of the reaction rate, but did not examine the structure of the compound formed.

100–101° [from isoeugenol methyl ether by the action of hydrogen chloride (4, 5)], showed no melting point depression. Müller and co-workers (5) suggested the IIa hydrindene structure for diisoeugenol dimethyl ether on the basis of oxidative degradation. Cartwright and Haworth are also of Müller's opinion (6). Both groups synthesized diisoeugenol methyl ether. Although its melting point is identical with the melting point of the dimer prepared from isoeugenol methyl ether by the action of hydrogen chloride, nevertheless the melting point of a mixture of these two specimens was depressed. In their opinion, however, this does not signify that the hydrindene structure is incorrect, as four racemic modifications are possible.

Based on analogy, the dimeric 3,4-diethoxypropenylbenzene (IIb) arising from 1-(3,4-diethoxyphenyl)-1,2-dibromopropane (Ib) (7) may also be considered to have a hydrindene structure, as it showed no depression with the dimeric compound obtained from 3,4-diethoxypropenylbenzene by the action of hydrogen chloride. To decide whether the iodine formed is a dimerizing agent, the 3,4-diethoxypropenylbenzene was treated under these conditions for forty-eight hours in acetone solution with iodine (8). No dimerization took place, as only the unchanged starting compound was isolated.

The dimeric compound of m.p. 116° (IIc), formed from 1-(3,4-dibenzyloxyphenyl)-1,2-dibromopropane (9, 10) (Ic), was converted into 1-(3,4-dihydroxyphenyl)-2-methyl-3-ethyl-5,6-dihydroxyindane (IIId) by catalytic debenzoylation. As was to be expected, the compound is very readily oxidized. It was converted by the action of diazomethane into IIa. The resulting compound of m.p. 106° (though it crystallized from alcohol like diisoeugenol dimethyl ether) showed a melting point depression with an authentic specimen of diisoeugenol dimethyl ether. It can nevertheless be assumed that the difference between the two compounds is also stereochemical, as we suggest for Müller's and Haworth's compounds.

All these dimeric compounds react with bromine, forming a monobromo derivative, like diisoeugenol dimethyl ether.

Concerning the reaction mechanism, it is most probable that dibromide is first converted into diiodide, and the unstable diiodide gives off iodine. The remaining radicals, or the intermediate containing the activated ethylenic double bond, stabilize through dimerization.

Experiments are in progress to decide how the different radicals influence the reaction resulting in the formation of a double bond or dimeric compound.

EXPERIMENTAL

Diisoeugenol dimethyl ether (IIa). A solution of 3.4 g. of 1-(3,4-dimethoxyphenyl)-1,2-dibromopropane (Ia) in 15 ml. of anhydrous acetone was treated with a solution of 3 g. of sodium iodide in 30 ml. of acetone. Free iodine formed immediately. After twenty-four hours at room temperature, the mixture was treated with a solution of sodium bisulfite, or sodium thiosulfate, to remove iodine. Dilution with water gave an oily product, which was brought into ether. The ether layer was washed with water, dried, and evaporated. The resulting pale yellow oil crystallized from methanol, yielding 0.4 g. of colorless needles, m.p. 99–100°. Mixed melting point with an authentic sample of diisoeugenol dimethyl ether m.p. 101° [prepared according to the method of Széki (4b) with hydrogen chloride from iso-

eugenol methyl ether] showed no depression. In some cases the oily product did not crystallize. It was treated with bromine in ether solution. The crystals melted at 100° and showed no depression with the starting dibromide.

1-(3,4-Diethoxyphenyl)-1,2-dibromopropane (Ib). A solution of 8 g. of 3,4-diethoxypropenylbenzene (7) in 20 ml. of dry chloroform was cooled to -5°. On adding a mixture of 6.2 g. of bromine and 10 ml. of dry chloroform dropwise, colorless crystals deposited. These were recrystallized from ligroin (with charcoal), plates, m.p. 116°, yield 10 g.

Anal. Calc'd for $C_{13}H_{18}Br_2O_2$: C, 42.6; H, 5.1.

Found: C, 42.6; H, 5.0.

Dimeric 3,4-diethoxypropenylbenzene (IIb) [*1-(3,4-diethoxyphenyl)-2-methyl-3-ethyl-5,6-diethoxyindane*]. (a) One gram of 1-(3,4-diethoxyphenyl)-1,2-dibromopropane (Ib) was treated with sodium iodide as described above. The method was simplified by pouring off the solvent from the oily product after diluting the acetone solution with water. The oil was covered with water; it solidified in twenty-four hours. This product was crystallized from ethanol, m.p. 99°, yield 0.3 g. (53.3%). Molecular weight (acetone), 379.

Anal. Calc'd for $C_{26}H_{36}O_4$: C, 75.7; H, 8.8.

Found: C, 75.3; H, 8.6.

(b) *From diethoxypropenylbenzene.* A solution of 1 g. of 3,4-diethoxypropenylbenzene in 5 ml. of ether was saturated with hydrogen chloride. After standing overnight, the ether was removed in a vacuum. The residue was crystallized from methanol; colorless needles, m.p. 99°, undepressed by mixture with a specimen of dimeric diethoxypropenylbenzene prepared according to method (a).

Bromo derivative of the dimeric 3,4-diethoxypropenylbenzene. A solution of dimeric 3,4-diethoxypropenylbenzene (method a) in abs. ether was allowed to stand overnight with an excess of bromine. On removing the solvent, a crystalline residue was obtained, which recrystallized from alcohol in long needles, m.p. 114°. Molecular weight (acetone), 471, 507. In the dimeric compound one hydrogen atom was replaced by bromine.

Anal. Calc'd for $C_{26}H_{35}BrO_4$: C, 63.5; H, 7.2.

Found: C, 63.3, 63.2; H, 7.0, 7.2.

Dimeric 3,4-dibenzyloxypropenylbenzene (IIc) [*1-(3,4-dibenzyloxyphenyl)-2-methyl-3-ethyl-5,6-dibenzyloxyindane*]. A solution of 4.5 g. of Ic (9, 10) and 3 g. of sodium iodide in 30 ml. of acetone was allowed to stand two days. The iodine was removed with sodium thiosulfate, 150 ml. of 0.1 N. The oily product solidified on standing overnight, 1.5 g. After two recrystallizations (charcoal) from alcohol, it had m.p. 114-116°, colorless needles, yield 0.5 g. It can also be crystallized from ether.

Anal. Calc'd for $C_{46}H_{44}O_4$: C, 83.6; H, 6.7.

Found: C, 83.5; H, 6.4.

In some cases, nevertheless, from the semisolid oily product only 3,4-dibenzyloxypropenylbenzene was isolated. Three recrystallizations from ether-alcohol gave colorless needles, m.p. 70-71°. Bruckner's 3,4-dibenzyloxypropenylbenzene (9) melts at 64°, but a mixture showed no depression (65-66°). The compound of m.p. 70-71° was converted into its dibromide in ether solution (10). The crystalline product was recrystallized from ligroin, m.p. 120°, undepressed by mixture with a specimen of Ic (10) of m.p. 116°.

Dimeric 3,4-dibenzyloxypropenylbenzene, 0.08 g., in 50 ml. of alcohol was hydrogenated in the presence of previously hydrogenated Pd-charcoal. The calculated four moles of hydrogen was taken up in 15 minutes. The catalyst-free solution was treated with excess diazomethane, and removal of solvent left a brown oil which crystallized from alcohol. Two recrystallizations gave colorless needles, m.p. 106°, depressed to 85-95° by mixture with a specimen of IIa prepared from isoeugenol methyl ether according to the hydrogen chloride method. The debenzylated dimeric compound is very easily oxidized; removal of methanol gave a dark oil, which did not solidify.

Bromo derivative of dimeric 3,4-dibenzyloxypropenylbenzene. IIc was treated with bromine as described above, m.p. 141°.

Anal. Calc'd for $C_{46}H_{43}BrO_4$: C, 75.1; H, 6.0.

Found: C, 75.0; H, 6.2.

3-Benzoyloxy-4-ethoxypropenylbenzene. To a solution of 0.6 g. of sodium in 25 ml. of abs. alcohol, 4.5 g. of 3-hydroxy-4-ethoxypropenylbenzene and 3.3 ml. of benzyl chloride were added. The mixture was refluxed for three hours. On standing at room temperature, long flat needles deposited. The crystals were washed with water and dil. sodium hydroxide; recrystallized from alcohol, yield 5 g., m.p. 75°.

Anal. Calc'd for $C_{18}H_{20}O_2$: C, 80.5; H, 7.5.

Found: C, 80.3; H, 7.5.

1-(3-Benzoyloxy-4-ethoxyphenyl)-1,2-dibromopropane. A solution of 2.7 g. of 3-benzoyloxy-4-ethoxypropenylbenzene was treated with bromine as described above; yield of dibromide compound 3.5 g., m.p. 114°, from ligroin.

Anal. Calc'd for $C_{18}H_{20}Br_2O_2$: C, 50.5; H, 4.7.

Found: C, 50.4; H, 4.6.

The reaction of 1-(3-benzoyloxy-4-ethoxyphenyl)-1,2-dibromopropane with sodium iodide was carried out as above. The crystals melted at 75°, not depressed by mixture with a specimen of 3-benzoyloxy-4-ethoxypropenylbenzene.

Isoeugenol benzyl ether. The reaction of 1-(3-methoxy-4-benzoyloxyphenyl)-1,2-dibromopropane (11) with sodium iodide gave isoeugenol benzyl ether, m.p. 58°. It was converted into its dibromide, which showed no depression with the starting dibromide, m.p. 122°.

Isosafrole. The reaction of 1-(3,4-methylenedioxyphenyl)-1,2-dibromopropane with sodium iodide was carried out as described above. The oil was purified by distillation in steam. Its dibromide showed no depression with the starting dibromide.

Anethole. Anethole was prepared from 1-(4-methoxyphenyl)-1,2-dibromopropane as described for isosafrole, m.p. 21°.

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