REACTIONS OF DIHYDROAROMATIC COMPOUNDS--III

IODINE CATALYSED HYDROGEN TRANSFER FROM 1,4-DIHYDROBENZENE TO STYRENE¹

M. K. EBERHARDT

Radiation Research Laboratories, Mellon Institute, Pittsburgh, Pa.

and

Institut für Radiochemie Technische Hochschule Munich, Germany

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Abstract—Styrene in 1,4-dihydrobenzene was quantitatively reduced to ethylbenzene by small amounts of iodine. This hydrogenation is also applicable to other α -phenyl substituted olefins, like 1,1-diphenylethylene and 1-phenylcyclohexene. No hydrogenation takes place with phenylacetylene, 2-phenylcyclohexene, and stilbene. The mechanism of this reaction is discussed.

IN previous publications⁴ we have reported the iodine catalysed disproportionation of 1,4 and 1,2-dihydrobenzene to give cyclohexene and benzene. This formal hydrogen transfer from one dihydrobenzene to another is also possible between 1,4-dihydrobenzene and a foreign acceptor like styrene and 1-phenylcyclohexene.

RESULTS AND DISCUSSION

Styrene (1:3 mmoles) in 1,4-dihydrobenzene (7.4 mmoles) is reduced in quantitative yield to ethylbenzene by small amounts of iodine (0.315 mmoles) after about 5-24 hr in daylight (depending on the light conditions). The iodine colour disappears very quickly (2 min), and the analysis immediately after the iodine has disappeared shows, that two moles of styrene are consumed for each mole of iodine, and one mole of benzene is formed. The styrene has reacted to give 1-phenyl-1-iodoethane. which was detected by NMR (Experimental). No 1-phenyl-2-iodoethane was present in the reaction mixture. An authentic sample of 1-phenyl-1-iodoethane (1.3 mmoles) in 1,4-dihydrobenzene (7.4 mmoles) was found to react in daylight in about 5 hr to give in quantitative yield ethylbenzene. The intermediate formation of 1-phenyl-1iodoethane could possibly be explained by a reaction of iodine with 1,4-dihydrobenzene to give HI and benzene, followed by HI addition to styrene. However, the rate of HI formation in the reaction of 1,4-dihydrobenzene with jodine is much slower than the rate of 1-phenyl-1-iodoethane formation. The iodine (0.315 mmoles) disappears in 1,4-dihydrobenzene (7.4 mmoles) in about 30 min, after which time only a small amount of iodine has reacted to give HI, the main reaction being addition to the double bond.^{*} In presence of styrene (1.3 mmoles) the iodine disappears in 2 min. On the basis of our experimental evidence we conclude, that the formation of 1-phenyl-1-iodoethane involves in the first step a direct reaction between styrene and iodine, unless there is some mechanism by which styrene can accelerate the HI formation from 1,4-dihydrobenzene and iodine.

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^a M. K. Eberhardt, Tetrahedron 21, 1383 (1965); Ibid. 21, 1391 (1965).

In the reaction of iodine with styrene,^{3,4} the formation of diiodostyrene and 1,4-diiodo-2,3-diphenylbutane was observed:

$$I_{s} \phi -CH -CH_{s} -I$$

$$2\phi CH -CH_{s} + I_{s} \rightarrow 2\phi CH -CH_{s}I$$

$$f = I$$

$$\phi -CH -CH_{s}I$$

$$f = -CH -CH_{s}I$$

The radical ϕ -CH-CH₂I cannot explain the formation of 1-phenyl-1-iodoethane, but would be expected to lead to 1-phenyl-2-iodoethane by hydrogen abstraction from 1,4-dihydrobenzene. No 1-phenyl-2-iodoethane was found in the reaction mixture. We therefore propose the intermediate formation of a bridged iodoalkyl radical:

$$2 \phi - CH = CH_s + I_s \longrightarrow 2 \phi - CH = CH_s$$

This radical can react in different ways, depending on the reaction conditions. In pure styrene the bridge opens at the α -position to form 1,4-diiodo-2,3-diphenylbutane, but in 1,4-dihydrobenzene the radical reacts by hydrogen abstraction to form the stronger carbon-hydrogen bond:



Simultaneously the reactions between iodine and 1,4-dihydrobenzene, which lead to cyclohexene and benzene, are taking place. These reactions have been discussed in detail in previous papers.³

* D. J. Trifan and P. D. Bartlett, J. Am. Chem. Soc. 81, 5573 (1959).

⁴ G. Fraenkel and P. D. Bartlett, J. Am. Chem. Soc. 81, 5582 (1959).

Bridged halogen radicals have recently received considerable attention. A bridged iodoalkyl radical has been proposed⁵ in the photochemical addition of iodine to 2-butene, and $\phi - CH - CH$ was postulated as intermediate in the $\vdots \circ$

dehalogenation of (1-chloro-2-bromoethyl) benzene by chromous sulfate.⁶

The described hydrogenation reaction is a convenient way to selectively hydrogenate α -phenyl substituted olefins under extremely mild conditions. A useful application of this hydrogenation was found in the preparation of completely phenyldeuterated 5-phenylnonane. The synthesis of this compound proceeds via 5-phenyl-d₅-nonene (4,5), which has to be hydrogenated in such a way that the deuterium in the ring does not exchange. An isotopic exchange usually occurs with conventional hydrogenation procedures (like Pd–C). The hydrogenation with 1,4dihydrobenzene-iodine however leads in quantitative yield to the desired 5-phenyld₅-nonane. The NMR spectrum of the product did not reveal any hydrogen atoms in the phenyl group.

EXPERIMENTAL

Reagents. 1,4-dihydrobenzene and styrene were commercially obtained (Aldrich Chemical Company, Columbia Chemical Company and Eastman Kodak). The styrene was distilled prior to use. The iodine was Fisher certified reagent. The 1-phenyl-1-iodoethane was prepared according to the method of Landauer and Rydon.⁷

Analytical technique. The products were identified by VPC using two columns and two detectors in series combined with a dual channel recorder. The first column was a 3 ft GESF (silicone) column at 100° and the second column was a 6 ft DEGS (diethyleneglycolsuccinate) column at 50° and a flowrate of 25 mlHe/min. The first column separates styrene and ethylbenzene from the low boiling components, which are separated on the DEGS column. The products have further been identified by their mass spectra. The 1-phenyl-1-iodoethane cannot be detected by VPC, because of its thermal instability. This product was therefore identified using the following procedure: 3.5 ml 1,4-dihydrobenzene, 0.75 ml styrene and 400 mg iodine were mixed. After 2 min (the iodine color has disappeared) the excess 1,4-dihydrobenzene and styrene was taken off with a flask evaporator. The residue was dissolved in CCl₄ and analysed by NMR. The spectrum showed the same peaks as an authentic sample of 1-phenyl-1-iodoethane, and the peaks corresponding to 1-phenyl-2-iodoethane were absent.

Preparation of 5-phenyl-d₅-nonane. From 12 g Mg (0.5 mole) and 81 g bromobenzene-d₅ (0.5 mole) in 300-400 ml ether a Grignard soln was prepared. To this soln, 71 g (0.5 mole) di-n-butylketone was added slowly under stirring. The resulting soln was boiled at reflux for 12 hr, then decomposed with dil HCl, the ether layer separated, washed with water and dried. After removal of the ether, the carbinol remained as a yellow oil, to which ca. 10% dehydration catalyst (KSF, Südchemie, München) was added and heated to 120° in an oilbath. The dehydration was finished in ca. 5-10 min. The olefin was fractionated: b.p. 240-260°. The crude olefin was then dissolved in pure pentane and chromatographed on silicagel, yield ca. 20 g, b.p. 126-127° at 7 mm Hg.

26 g Olefin as dissolved in 60 g 1,4-dihydrobenzene and cooled down to ca. 5°. Then 8 g iodine was added in small portions. The soln became hot, and the iodine was consumed in about 5 min. The mixture was left in direct sunlight (daylight will suffice) for 48 hr yielding a dark brown soln. The excess 1,4-dihydrobenzene, iodine, benzene and cyclohexene was distilled off *in vacuo*. The crude compound was then distilled over a little Zn dust, to remove the last traces of iodine, B.p. 126-127° (7 mm Hg). The final purification was carried out by preparative VPC, yield: 10 g.

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⁵ P. S. Skell and R. R. Pavlis, J. Am. Chem. Soc. 86, 2956 (1964).

⁶ W. C. Kray, Jr. and C. E. Castro, J. Am. Chem. Soc. 86, 4603 (1964).

⁷ S. R. Landauer and H. N. Rydon, J. Chem. Soc. 2228 (1953).