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REACTIONS OF DIHYDROAROMATIC COMPOUNDS—II

THE REACTION OF 1,2-DIHYDROBENZENE WITH IODINE[1]

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Abstract—1,2-Dihydrobenzene disproportionates in presence of small amounts of iodine (0·5 M) to cyclohexene and benzene. The mechanism of this reaction is discussed in reference to previous work on the iodine catalyzed disproportionation of 1,4-dihydrobenzene.

IN THE first paper of this series,[2] the disproportionation of 1,4-dihydrobenzene in presence of iodine (0·5 M) was reported. This reaction proceeds in 3 days in daylight to give in quantitative yield benzene, cyclohexene, and some 1,2-dihydrobenzene and 4-iodocyclohexene. In 0·5 M solution of iodine in 1,4-dihydrobenzene the yield of 1,2-dihydrobenzene was found to increase at the beginning of the reaction and then decrease again. The reaction of iodine with 1,2-dihydrobenzene has, therefore, been studied.

RESULTS

1,2-Dihydrobenzene disproportionates at room temperature in presence of iodine (0·5 M) to give after one day an almost quantitative yield of cyclohexene and benzene (Table 1). This result is analogous to the disproportionation of 1,4-dihydrobenzene. The reaction is catalyzed by light. The rate of disproportionation is strongly influenced by the iodine concentration (Table 1). In addition to the disproportionation reaction, polymerization becomes the exclusive reaction at higher iodine concentrations (1·5 M). If iodine (240 mg) is added to 1,2-dihydrobenzene (0·7 ml) all at once a violent reaction takes place with spattering and the formation of a dark green viscous solution. After one week the viscous solution on dilution with benzene and addition of methanol precipitated a light green polymer (average mol. wt. 1586). At low iodine concentration (0·5 M) disproportionation predominates and only an insignificant amount of polymeric material (average mol. wt. after 2 hr reaction time 1240; after 10 days reaction time 1446) could be isolated. The experiments (results are listed in Tables 1 and 2) were all carried out in a pyrex vessel under nitrogen, but they can also be carried out in an open test tube without any significant effect on the final results. In addition to iodine, hydrogen iodide (1·0 M) was found to catalyze the disproportionation of 1,2-dihydrobenzene to cyclohexene and benzene. The reaction is complete after about one day in diffuse laboratory daylight. Iodine atoms produced by photolysis of alkyl iodides also cause disproportionation of 1,2-dihydrobenzene. The results of the photolysis of 1,2-diiodoethane in 1,2-dihydrobenzene are summarized in Table 2.

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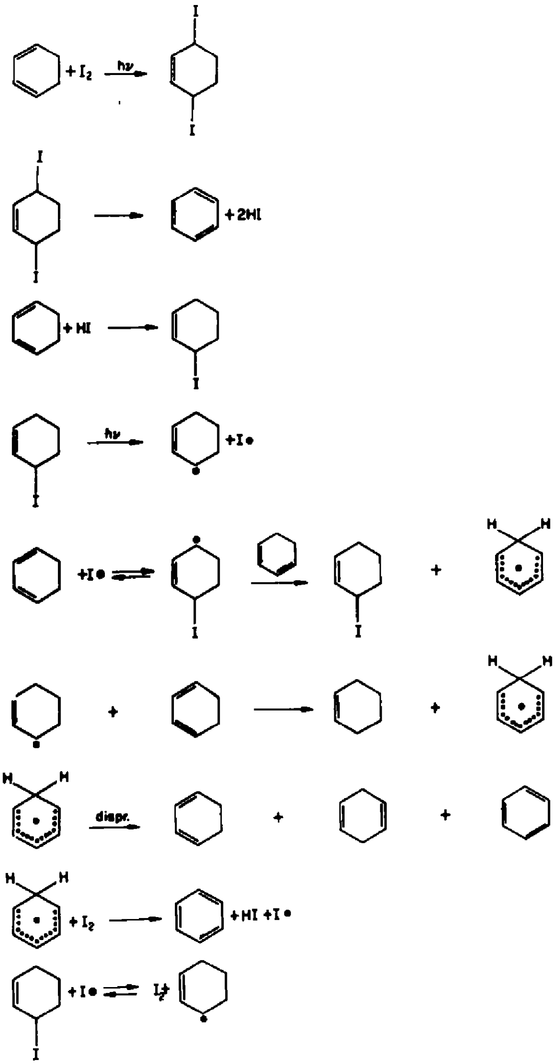
[1] Supported, in part, by the U.S. Atomic Energy Commission.

[2] Manfred K. Eberhardt, *Tetrahedron* **21**, 1383 (1965).

DISCUSSION

There is strong evidence[2] that in the reaction of iodine with 1,4-dihydrobenzene addition rather than hydrogen abstraction takes place in the first step of the reaction. In the case of 1,2-dihydrobenzene direct abstraction appears to be even less likely because of the greater strength of the methylene carbon–hydrogen bonds. The following mechanism is proposed:



Hydrogen iodide does not disproportionate 1,4-dihydrobenzene,[2] but only leads to the formation of 4-iodocyclohexene. Hydrogen iodine, however, does catalyze the disproportionation of 1,2-dihydrobenzene. Addition of HI to 1,2-dihydrobenzene leads to an allylic iodide which has a more labile carbon–iodine bond than 4-iodocyclohexene and decomposes photochemically in daylight to give a cyclohexenyl radical. The rate of disproportionation of 1,2-dihydrobenzene is by a factor of 3 faster than the reaction of the 1,4-compound. This result is easily understood on the basis of the proposed mechanism. The 1,2-dihydrobenzene is known to be considerably more reactive towards radical addition than the 1,4-dihydrobenzene.[3] This accelerates the formation of 3-iodocyclohexene which in turn is more photolabile than the corresponding 4-iodocyclohexane.

TABLE 1. EFFECT OF IODINE CONCENTRATION

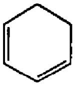
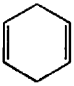
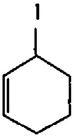
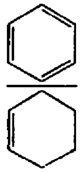
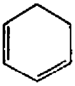
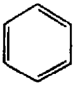
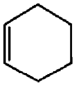
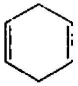
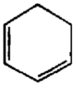
Reactants (in mmoles)		Time (in hr)	Products (in mmoles)					
	I_2							
7·4	0·157	1	6·68	0·46	0·27	trace	trace	1·7
		2	6·05	0·77	0·55	trace	0·05	1·4
		4	5·05	1·2	0·95	0·12	0·09	1·26
		24	2·15	2·25	2·17	0·13	0·26	1·03
7·4	0·315	1	6·68	0·46	0·19	—	trace	2·43
		2	5·42	0·99	0·69	trace	0·05	1·44
		4	4·1	1·62	1·29	0·06	0·09	1·26
		24	0·34	3·23	2·93	—	0·26	1·1
7·4	0·63	1	6·0	0·17	0·05	—	—	3·4
		2	5·55	0·39	0·1	—	—	3·9
		4	5·25	0·55	0·15	—	—	3·67
		24	4·08	1·20	0·75	—	0·03	1·6

TABLE 2. PHOTOLYSIS OF 1,2-DIIODOETHANE IN 1,2-DIHYDROBENZENE

Reactants (in mmoles)		Irradiation[a] time (in hr)	Composition of low boiling fraction[b] in mole%			
	ICH_2CH_2I					
7·4	0·32	10	12·5	9·75	4·2	73·55
		24	36·0	30·7	5·2	29·5
7·4	0·64	10	24·1	17·6	2·3	56·0
		24	43·0	35·6	2·0	19·3
7·4	0·96	10	20·0	14·6	1·55	63·85
		24	44·9	34·4	2·4	18·3

[a] A Hanovia medium pressure mercury lamp was used at a distance of 6 inches from the sample.
[b] The low boiling fraction amounts to 90% or more of the total reaction mixture.

EXPERIMENTAL

1,2-Dihydrobenzene was commerically obtained (Columbia Chemical Co.). The I_2 was resublimed (Fisher certified reagent). All experiments were carried out in a small pyrex vessel (1 cm ϕ and ca. 7 cc volume), which had a sidearm with a silicone stopper through which samples could be withdrawn for analysis. In the experiments listed in Table 2 the samples were irradiated with a Hanovia medium press. Hg lamp.

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[3] A. Rajbenbach and M. Szwarc, *Proc. Chem. Soc.* 347 (1958).

All products were identified by vapour phase chromatography (retention time on two different columns) and by mass spectrometry. The column set-up was as previously described.[2] The 3-iodocyclohexene was collected with the detector bypassed and analysed by mass spectrometry. The cracking pattern was almost identical with the pattern obtained from 4-iodocyclohexene.[2] The compound was found to decompose partly on the chromatographic column (DEGS 3 ft, 155°) and the values given in Table 1 are therefore too small.

Reaction of 1,2-*dihydrobenzene with hydrogen iodide.* 1,2-Dihydrobenzene (7·4 mmoles) was degassed and 0·63 mmoles HI condensed into the sample under vacuum. After 1 day in daylight almost complete disproportionation to cyclohexene and benzene had taken place.