Tetrahedron, 1965, Vol. 21, pp. 1383 to 1390. Pergamon Press Ltd. Printed in Northern Ireland

REACTIONS OF DIHYDROAROMATIC COMPOUNDS—I

THE REACTION OF 1,4-DIHYDROBENZENE WITH IODINE[1]

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(*Received* 11 *November* 1964)

Abstract—1,4-Dihydrobenzene disproportionates in presence of small amounts of iodine (0·5 molar) to cyclohexene and benzene. The mechanism of this reaction is discussed.

Dehydrogenation and disproportionation of hydroaromatic compounds have been reported to proceed catalytically at room temperature with palladium black,[2,3] by an ionic mechanism at elevated temperatures with quinones[4] and via a free radical reaction with diphenylpicrylhydrazyl.[5] Non-catalytic dehydrogenations yielded the aromatic compound as the only reaction product.

RESULTS

We have found that 1,4-dihydrobenzene reacts at room temperature in daylight with small amounts of iodine (0·25–0·5 molar) to give in quantitative yield (on the basis of dihydrobenzene consumed) benzene, cyclohexane, 1,2-dihydrobenzene and 4-iodocyclohexene. The rate of disproportionation was found to be subject to the following variables: light (Tables 1, 3), iodine concentration (Table 3), cyclohexane concentration (Table 4), oxygen (Table 5), and concentration of RI. The first stage of the reaction is the disappearance of iodine. A solution of iodine in 1,4-dihydrobenzene shows a brown-red colour (compared with a violet colour in cyclohexane), which indicates that some complex formation is taking place. All the above mentioned variables affect the rate of iodine disappearance. A 0·25 and 0·5 molar solution of iodine in 1,4-dihydrobenzene is discoloured in daylight under nitrogen in 0·2 and 0·5 hr respectively. A more concentrated solution always retains an iodine colour. In the dark a 0·5 M solution retains a weak iodine colour even after 3 days. The rate of iodine disappearance is retarded if cyclohexane, 4-iodocyclohexene or CH_3I is added at the start of the reaction. The disappearance of the iodine can be reversed. If ether is added to a colourless solution the iodine reappears. The reaction was usually carried out under nitrogen. If the reaction is carried out in an open test tube a colour gradation can be observed along the length of the tube from a dark brown-red colour on the bottom to an almost colourless zone on the top. The accelerated disappearance of iodine in the top layer is due to the effect of oxygen (Table 5). 1,4-Dihydrobenzene is oxidized to benzene only very slowly in an oxygen atmosphere, but 4-iodocyclohexene considerably accelerates this oxidation (Experimental). If hydrogen iodide (0·63 mmoles) is added to 1,4-dihydrobenzene (7·4 mmoles) under nitrogen only

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

[2] H. Wieland, *Ber. Dtsch. Chem. Ges.* 45, 484 (1912).

[3] J. Boeseken, *Rec. Trav. Chim.* 37, 255 (1918); N. D. Zelinsky and G. S. Pawlow, *Ber. Dtsch. Chem. Ges.* 66, 1420 (1933).

[4] E. A. Braude, L. M. Jackman and R. P. Linstead, *J. Chem. Soc.* 3564 (1954).

[5] E. A. Braude, A. G. Brook and R. P. Linstead, *J. Chem. Soc.* 3574 (1954).

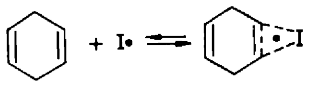
4-iodocyclohexene is formed. Even after 2 days only a very insignificant amount of disproportionation occurs. The small amount of disproportionation being due to iodine present as an impurity in the hydrogen iodide. If tritium labeled 4-iodocyclohexene (5T) is added to the reaction mixture all the activity shows up in the cyclohexane (Table 2). This shows that 4-iodocyclohexene is the precursor of cyclohexene and therefore plays an important role in the mechanism of this disproportionation reaction. With increasing iodine concentration the amount of 4-iodocyclohexane increases, but the rate of cyclohexene and benzene goes through a maximum at 0·5 M concentration (Table 3). In order to obtain material balance between oxidized and reduced products one would expect that benzene and cyclohexane are formed in an approximate 1:1 mole ratio. This is experimentally born out (Table 3). As the reaction approaches completion cyclohexyliodide is formed (Table 3). It was found that cyclohexene competes quite favourably with 1,4-dihydrobenzene in the reaction with iodine and hydrogen iodide (Experimental).

DISCUSSION

Iodine atoms can react with 1,4-dihydrobenzene *a priori* either by hydrogen abstraction or addition to the double bond. At ordinary temperatures no hydrogen abstraction by iodine has been reported, the process possessing high activation energy,[6] but the photochemical addition of iodine to double bonds is well known,[7] and has been described as a free radical chain process. Recently it has been shown that the addition involves a bridged iodoalkyl radical intermediate.[8] The resulting vicinal diiodides are known to be very unstable, decomposing thermally and photochemically to give back the starting olefin and iodine. The analogous addition of bromine to 1,4-dihydrobenzene is known to yield 4,5-dibromocyclohexene.[9] This compound has been reported to decompose readily in daylight to give hydrogen bromide and benzene. Because of the expected thermal and photochemical instability of 4,5-diiodocyclohexene no effort was made to isolate this compound from the reaction mixture. Evidence against direct abstraction can be deduced from the results summarized in Table 3. After 1 hr reaction time of 0·25 and 0·5 M solutions (the iodine colour has disappeared) the 4-iodocyclohexene accounts only partly for the iodine consumed. Therefore, there must be another iodine containing compound in the reaction mixture. This compound cannot be hydrogen iodide, because hydrogen iodide was found to add rapidly to 1,4-dihydrobenzene to give 4-iodocyclohexene. If all the iodine atoms react by direct abstraction, a solution of 4-iodocyclohexene in 1,4-dihydrobenzene would result and this has been found not to disproportionate (Experimental). The following mechanism is consistent with the experimental results:

a $I_2 \overset{h\nu}{\rightleftarrows} 2I\cdot$

b



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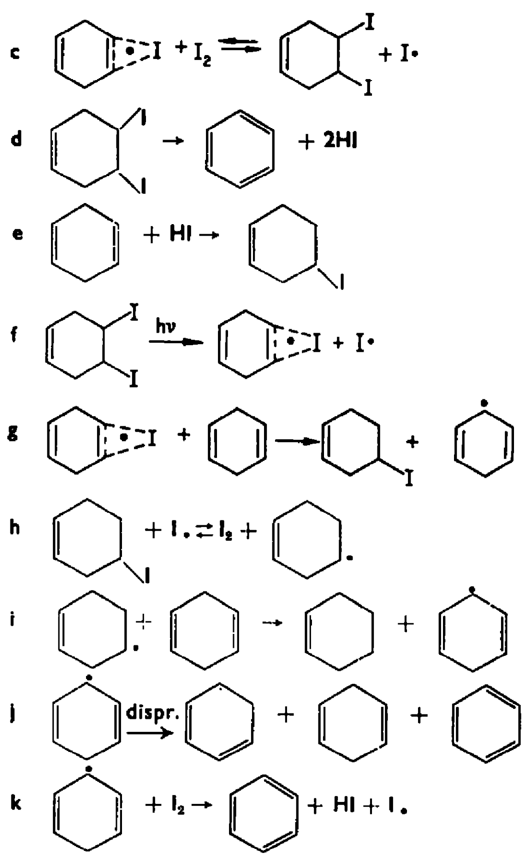
[6] J. H. Raley, R. D. Mullineaux and C. W. Bittner, *J. Amer. Chem. Soc.* **85**, 3174 (1963), and Ref therein.

[7] G. S. Forbes and A. F. Nelson, *J. Amer. Chem. Soc.* **59**, 693 (1937).

[8] P. S. Skell and R. R. Pavlis, *J. Amer. Chem. Soc.* **86**, 2956 (1964).

[9] J. P. Wibaut and F. A. Haak, *Rec. Trav. Chim.* **67**, 85 (1948).



Iodine abstraction reactions: $RI + I\cdot \rightleftarrows R\cdot + I_2$ are well known. They have been reported in the photolysis of 1,2-diiodoethane in CCl_4[10] and in the photochemical iodine exchange of alkyliodides.[11] The 4-iodocyclohexene appears to hold a central position in the mechanism of this disproportionation. The cyclohexenyl radical reacts to give cyclohexene and via the cyclohexadienyl radical 1,2-dihydrobenzene and benzene. Every factor that influences the formation of the cyclohexenyl radical will therefore affect the rate of cyclohexene and benzene formation. The increase in 4-iodocyclohexene with increasing iodine concentration accelerates the formation of cyclohexenyl radicals (according to step *h*), but at a certain concentration (>0·5 M) this acceleration is offset by complex formation between unreacted iodine and 4-iodocyclohexene, which decreases the rate of cyclohexene formation due to the reversibility of the iodine abstraction reaction (step h). Molecular complexes between alkyl iodides and iodine are described in the literature.[12,13] The retarding effect of cyclohexene on the rate of iodine disappearance as well as on the rate of disproportionation is also due to complex formation between cyclohexene and iodine, which is known to occur.[14] A significant amount of 1,2-dihydrobenzene is only formed at low iodine

[10] R. E. DeRight and E. O. Wiig, *J. Amer. Chem. Soc.* 57, 2411 (1935).

[11] R. M. Noyes and D. F. Sibbett, *J. Amer. Chem. Soc.* 75, 767 (1953).

[12] R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.* 74, 1891 (1952).

[13] D. E. Schuler and R. H. Schuler, *J. Amer. Chem. Soc.* 76, 3092 (1954).

[14] L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.* 74, 458 (1952).

concentration, where reaction step *j* can effectively compete with step *k*. The ratio of 1,2-dihydrobenzene to benzene decreases during the course of the reaction. As the 1,2-dihydrobenzene builds up it competes with the 1,4-dihydrobenzene for iodine atoms.[15] Since the experiments in presence of oxygen were only of a qualitative nature the elucidation of the mechanism of the oxygen effect requires further investigation.

The disproportionation of 1,4-dihydrobenzene to benzene and cyclohexene can also be accomplished by photolyzing a series of alkyliodides in 1,4-dihydrobenzene. Preliminary results are summarized in Table 6.

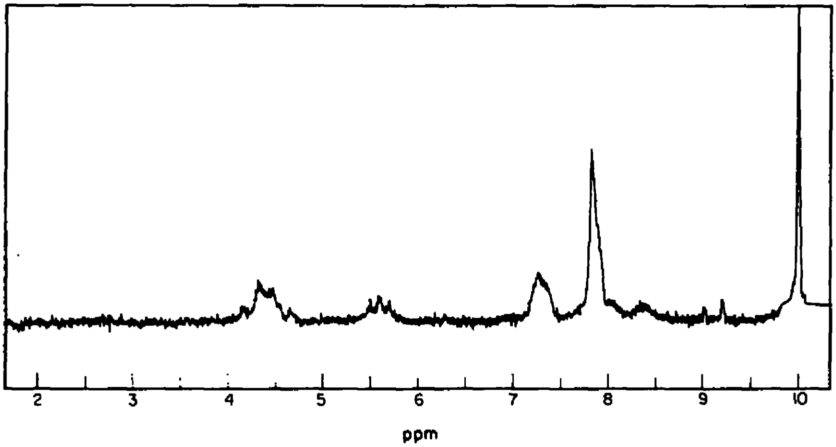


FIG. 1. NMR spectrum of 4-iodocyclohexene.

EXPERIMENTAL

Materials and technique. 1,4-Dihydrobenzene was commercially obtained (Columbia Chemical Co.). The iodine 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 6, the samples were irradiated with a Hanovia medium press. Hg lamp. In the experiments in air the samples were not saturated with air, but the reaction was carried out in an open test tube. In the reactions with O_2 the samples were saturated with O_2 several times during the course of the reaction. The experiments in Table 3 were all carried out simultaneously under identical light conditions. The times listed in column 3 of Table 3 were not all times of exposure to light. The results at 24 hr were obtained after the samples had been kept on the laboratory shelf for one day and one night. Therefore, the light energy, $h\nu$, absorbed by the samples is not proportional to the times given in the Table. The experiments in Table 5, however, were not carried out simultaneously and since the reaction rate is very sensitive to light the reproducibility of the results (last two experiments in Table 5) is not good.

Identification of products. All products were identified by vapour phase chromatography (retention time on two different columns) and by mass spectrometry. The products were separated on a temp programmed (80°–200°) silicone column (6 ft 30 ml He/min). On this column the products appeared in the following sequence: benzene, 1,2-dihydrobenzene, cyclohexene, 1,4-dihydrobenzene, and 4-iodocyclohexene. Another technique was the use of 2 columns and 2 detectors in series combined with a 2 pen recorder. The first was a DEGS column (3 ft, 155°) and the second a DEGS column (6 ft, 45°, 25 ml He/min). The first column separated the low boiling compounds in the following order: cyclohexene, 1,2-dihydrobenzene, 1,4-dihydrobenzene, and benzene. The results in Table 5 were obtained with a setup in which the first column was a GESF 96 column. This column did not separate cyclohexyliodide and 4-iodocyclohexene and therefore the data given in Table 5 for 4-iodocyclohexene actually are the sum of the two iodides. The products were collected and analyzed

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[15] M. K. Eberhardt, to be published.

TABLE 1. THE DARK REACTION OF 1,4-DIHYDROBENZENE WITH IODINE

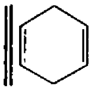
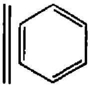
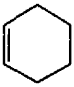
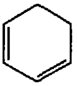
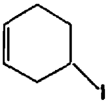
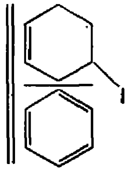
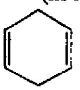
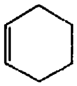
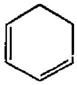
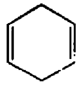
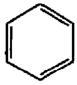
Reactants (in mmoles)		Conditions	Time in dark (in days)	Product (in mmoles)				ratio
	I_2							
7·4	0·315	oxygen	3	2·34	0·93	0·44	0·43	
7·4	0·315	nitrogen	3	0·34	trace	trace	0·53	1·56
7·4	0·315	vacuum	3	0·243	trace	trace	0·45	1·85

TABLE 2. THE REACTION OF TRITIATED 4-IODOCYCLOHEXENE WITH IODINE IN 1,4-DIHYDROBENZENE

Reactants (in mmoles)			Time in daylight (in hrs.)	Products[b] (in mmoles)			
	TI[a]	I_2					
7·4	0·157	0·157	5	0·28 (16500)	0·028 (1000)	6·28 (2000)	0·41 (0)
			24	0·57 (21500)	0·028 (0)	5·66 (2300)	0·74 (0)
			48	1·11 (22700)	0·042 (0)	4·47 (1300)	1·39 (0)
			72	1·46 (23600)	0·042 (0)	3·77 (1400)	1·73 (0)

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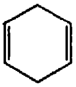
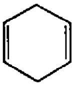
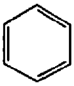
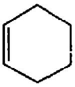
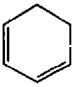
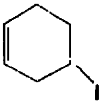
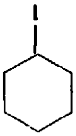
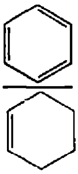
[a] The TI reacted immediately with 1,4-dihydrobenzene to give 4-iodocyclohexene. The total activity of the reaction mixture was 31500 cts in 6 μl.

[b] The numbers in brackets refer to counts in 6 μl of the reaction mixture.

TABLE 3. EFFECT OF IODINE CONCENTRATION

Reactants (in mmoles)		Time in daylight under N_2 (in hr)[a]	Products (in mmoles)						
	I_2								
7·4	0·157	1	6·45	0·26	0·16	0·32	0·09	0	1·63
		4	5·58	0·39	0·34	0·83	0·153	0	1·15
		8	5·10	0·54	0·51	1·10	0·24	0	1·06
		24	4·97	0·57	0·59	1·36	0·21	0	0·97
		74	3·55	0·975	0·925	1·57	0·285	0	1·05
7·4	0·315	1	6·83	0·29	0·03	0·04	0·135	0	9·7
		4	5·30	0·95	0·73	0·12	0·255	0	1·3
		8	3·57	1·78	1·53	0·15	0·28	0·056	1·16
		24	2·62	2·15	2·15	trace	0·35	0·10	1·0
		74	1·24	2·88	2·65	—	0·43	0·20	1·08
7·4	0·63	1	6·50	0·53	0·02	0·05	0·235	0	26·5
		4	6·05	0·71	0·02	0·05	0·57	0	35·5
		8	5·95	0·65	0·08	0·06	0·615	0·035	8·1
		24	5·68	0·72	0·11	0·08	0·79	0·04	6·5
		74	5·00	0·92	0·25	0·09	1·06	0·09	3·7

[a] See experimental.

TABLE 4. EFFECT OF CYCLOHEXENE CONCENTRATION

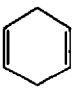
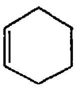
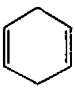
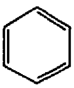
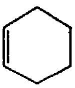
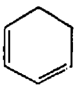
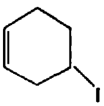
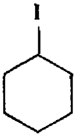
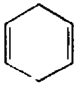
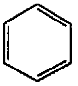
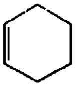
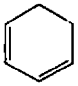
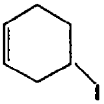
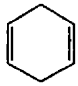
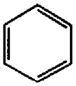
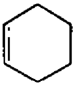
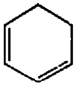
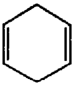
Reactants (in mmoles)			Time in daylight under N_2 (in hr)	Products (in mmoles)					
		I_2							
7·4	0	0·315	4	5·55	0·84	0·47	0·15	0·12	0
			24	4·40	1·36	0·89	—	0·21	0·05
7·4	1·0	0·315	4	6·9	0·39	0·83	—	0·11	0·10
			24	6·9	0·46	0·69	—	0·21	0·18
7·4	2·0	0·315	4	7·3	0·44	1·80	—	0·09	0·18
			24	7·3	0·5	1·60	—	0·13	0·295

TABLE 5. EFFECT OF OXYGEN

Reactants (in mmoles)		Conditions[a]	Time (in hr)	Products (in mmoles)				
	I_2							
7·4	0·315	dl N_2	1	0·25	0·026	trace	0·12	7·0
		dl O_2	1	2·07	1·05	0·35	0·17	3·76
		dl O_2	3	2·85	1·85	0·57	0·23	1·90
		dl N_2	74	2·57	2·38	0·59	0·64	1·21
		dl vacuum	74	3·12	2·75	—	0·65	0·86
		dl air	74	2·52	2·07	0·75	0·65	1·24
		dl air	74	3·77	2·9	—	0·64	0

[a] dl = daylight.
O_2 = solution saturated with oxygen.

TABLE 6. PHOTOLYSIS[a] OF ALKYLIODIDES IN 1,4-DIHYDROBENZENE

Alkyliodide (in 1 molar concentration)	Composition of low boiling fraction[b] in mole %			
				
Methyliodide	2·16	0·99	17·9	79·66
Ethyliodide	3·72	2·23	19·3	71·89
3-Iodopentane	5·83	4·97	23·17	66·03
Methyleneiodide	17·55	13·57	12·86	56·01
Iodoform	35·65	26·51	0	37·84
Allyliodide	50·21	40·64	2·02	7·13
1,2-Diiodoethane	42·51	37·22	5·78	15·49

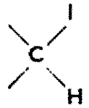
[a] All samples were photolysed under nitrogen in a pyrex vessel with a medium pressure mercury lamp for 25 hr at a distance of 7 inches.

[b] The low boiling fraction amounts to 90% or more of the total reaction mixture.

TABLE 7. MASS SPECTRUM OF 4-IODOCYCLOHEXENE

m/e	Relative intensities at 70 volts	m/e	Relative intensities at 70 volts
26	7·20	63	2·04
27	22·9	65	4·60
28	6·90	66	3·49
29	4·18	67	5·50
37	2·91	77	19·6
38	5·25	78	23·2
39	25·1	79	37·0
40	3·15	80	15·9
41	21·6	81	100·0
50	10·8	82	8·35
51	14·5	127	7·05
52	10·4	208	3·46
53	22·8		
54	6·95		
55	5·27		

on a Consolidated 21-103C mass spectrometer. The 4-iodocyclohexene had to be collected with the detector bypassed, because the compound decomposes on the hot detector wire. The unknown 4-iodocyclohexene was isolated from a preparative run (7 ml 1,4-dihydrobenzene and 0·8 g iodine) by vacuum distillation (bp. 2 m/m = 31°). It is a slightly iodine coloured liquid (sp. gr. at 25°: 1·645). The cracking pattern is characteristic of an alkyl iodide, with small parent and small iodine (127) peaks. The NMR spectrum (Fig. 1) shows 4 groups of peaks at around 4·4τ, 5·6τ, 7·25τ and 7·83τ (area ratio 2:1:2:4). The peaks at 4·4τ are typical of vinyl hydrogens, the peaks at 5·6τ are due to a



group in a cyclohexane ring. The high field absorptions are due to $\text{—CH}_2\text{—}$ groups.[16] The mass and NMR spectra, and the formation of the compound from 1,4-dihydrobenzene and hydrogen iodide clearly establish the structure as 4-iodocyclohexene.

Reaction of 1,4-*dihydrobenzene with hydrogen iodide.* 1,4-Dihydrobenzene (7·4 mmoles) was degassed and 0·63 mmoles HI condensed into the sample under vacuum. The HI reacted immediately to give 4-iodocyclohexene. After 1 day in daylight only an insignificant amount of disproportionation took place. This amount being due to traces of I_2 present in the HI.

Autoxidation of 1,4-*dihydrobenzene.* 1,4-Dihydrobenzene is oxidized only very slowly in an O_2 atm. If, however, 0·63 mmoles of 4-iodocyclohexene are added to 7·4 mmoles 1,4-dihydrobenzene a very rapid O_2 consumption is observed and benzene and water (solution turns turbid and water drops collect on the bottom of the vessel) are formed.

Competitive reaction of hydrogen iodide with cyclohexene and 1,4-*dihydrobenzene.* 1,4-Dihydrobenzene (3·7 mmoles) and cyclohexene (3·7 mmoles) were degassed and 0·63 mmoles HI condensed into the sample under vacuum. The HI reacted immediately to give 4-iodocyclohexene and cyclohexyliodide in a 1:7·4 mole ratio.

Competitive reaction of iodine with 1,4-*dihydrobenzene and cyclohexene.* Iodine (0·63 mmoles) was added to an equimolar mixture of 1,4-dihydrobenzene (3·7 mmoles) and cyclohexene (3·7 mmoles). After 2 hr (still dark brown colour) the mixture was analysed for 4-iodocyclohexene and cyclohexyliodide. These two products were formed in a 1:6·3 mole ratio.

Experiment with tritiated 4-iodocyclohexene. The analysis was performed by using a vapour phase chromatograph and a counter (Baird Atomic Precision Dual Ratemeter No. 412) in series. The total activity of the sample was measured with a liquid scintillation counter.

Acknowledgment—The author wishes to thank Mr. Tom G. Krivak for technical assistance and Dr. D. Perner for a supply of TI.

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[16] L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon Press (1959).