797. *Effects of γ-Radiation. Part V.* Irradiation of Cyclohexene and Cyclohexanol.*

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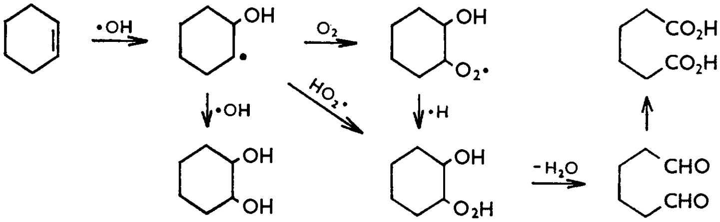
Irradiation of aqueous suspensions of cyclohexene containing oxygen gave mainly cyclohexane-*trans*-1,2-diol, adipdialdehyde and adipic acid. The rates of production of *vic*-glycols and carbonyl compounds during irradiation of aqueous solutions of cyclohexanol *in vacuo* have been determined.

Irradiation of cyclohexene was carried out principally to study, first, the stereospecificity, if any, of the hydroxylation of the double bond and, secondly, the extent to which scission of the carbon–carbon double bond occurred. The products obtained from cyclohexanol *in vacuo* were examined to evaluate the relative amounts of dimerisation and oxidation at a secondary alcohol site in a six-membered ring. Both studies were required as models for related derivatives containing the pyranose ring.

The cyclohexane-1,2-diol fraction isolated after irradiation of cyclohexene in the presence of oxygen was shown to consist principally of the more stable *trans*-isomer by three methods. The *cis*-diol formed a weak complex with borate and had M_G 0·09 in a borate buffer of pH 10.[1] The isolated diol fraction, like that of the authentic *trans*-diol, was largely immobile in this buffer but a small amount of the *cis*-diol could be detected. The isolated diol was converted into the dibenzoate (m. p. 177°) and *p*-phenylazobenzoate (m. p. 182—184°). The melting point [2] of the *p*-phenylazobenzoate of the *cis*- is rather lower (162°) than that of the *trans*-isomer (184—185°); our values confirm the preponderance of the latter in our product. Criegee [3] showed that oxidation by lead tetra-acetate was faster for the *cis*- than the *trans*-isomer. By comparison (Table 1) with the rates of oxidation of synthetic mixtures and the diols themselves the concentration of *cis*-isomer in our product was estimated to be $\not>10\%$.



Other components of the irradiation mixture have been tentatively identified as *cis*- and *trans*-2-hydroxycyclohexyl hydroperoxide. The two compounds were oxidised by periodate and liberated iodine from potassium iodide.[4] A general method [5] for the preparation of hydroxy hydroperoxides is the reaction between the epoxide and a peroxide; cyclohexene oxide was therefore prepared by the oxidation of cyclohexene with perbenzoic acid and treated with hydrogen peroxide in the presence of sulphuric acid. Chromatography of the product revealed the presence of two spots, presumably the *cis*- and the *trans*-form, both reacting with potassium iodide [4] and of R_F values identical with those of the components of the irradiation mixture. Scholes and Weiss [4] reported the formation of stable *cis*- and *trans*-hydroxy-hydroperoxides on irradiation of thymine in aqueous solution

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* Part IV, *J.*, 1959, 2871.

[1] Foster, *Chem. and Ind.*, 1953, 1050; *J.*, 1953, 982.

[2] Brimacombe, Foster, Hancock, Overend, and Stacey, *J.*, 1960, 201.

[3] Criegee, *Ber.*, 1931, **64**, 260; 1932, **65**, 1770.

[4] Scholes and Weiss, *Nature*, 1960, **185**, 305.

[5] Barusch and Payne, *J. Amer. Chem. Soc.*, 1953, **75**, 1987.

in the presence of oxygen. Both isomers were synthesised by Ekert and Monier [6] and they were separated by chromatography.

The annexed scheme shows the postulated breakdown of cyclohexene which accounts also for the fission products, adipdialdehyde and adipic acid.

The ratio of fission to hydroxylation has been estimated to be 1·8 to 1. Oxidation by periodate sufficed to determine total *vic*-glycol and its related oxidation products (3·35%); fission at the ethylenic bond was estimated by the total acid content (as adipic acid, 1·85%) and aldehyde content (as adipdialdehyde, 4·1%). Paper chromatography of the products from irradiation of aqueous cyclohexene *in vacuo* again revealed hydroxylation, but adipdialdehyde and adipic acid could not be detected: instead, extensive polymerisation of cyclohexene occurred.

Irradiation of aqueous cyclohexanol *in vacuo* would be expected to result in the formation of the radical $C_5H_{10}{>}\dot{C}{\cdot}OH$ by hydrogen abstraction; competing reactions of this radical should then yield the dimeric *vic*-glycol or cyclohexanone. The *G* value for *vic*-glycol formation was 0·34 after 17·5 hours' irradiation at $1{\cdot}28 \times 10^{17}$ ev ml.$^{-1}$ min.$^{-1}$ which is of the order [7] found for secondary alcohols irradiated as pure liquids. The *G* value for the formation of carbonyl compounds (calculated as cyclohexanone) after the same time was 0·89.

EXPERIMENTAL

Irradiation of Cyclohexene.—Deionized distilled water (1·7 l.) was degassed by vigorous boiling at *ca.* 0·3 mm. and then saturated with oxygen. Cyclohexene (1·6204 g.; b. p. 83°; n_D^{20} 1·4455) was added, oxygen added (to 5 lb./sq. in.), and the vigorously stirred suspension irradiated with a ^{60}Co source (200 c) [8] for 24 hr. (dose $12{\cdot}2 \times 10^{19}$ ev/ml.). A brown viscous liquid (0·267 g., 16·5%) was obtained on freeze-drying of the irradiated solution.

A solution of the products showed no significant ultraviolet absorption peaks and contained acids corresponding to 0·44 milliequiv. per g. of cyclohexene irradiated. Paper chromatography in butan-1-ol–ethanol–water (4 : 1 : 5 v/v) and isopentyl alcohol–5N-formic acid (1 : 1), with sprays of alkaline silver nitrate,[9] periodate–benzidine,[10] 2,4-dinitrophenylhydrazine–potassium hydroxide,[11] and Chlorophenol Red,[12] suggested that the major products were the cyclohexane-1,2-diols and adipic acid, with adipdialdehyde and probably 2-hydroxycyclohexyl hydroperoxides.

The irradiation mixture was stirred with Deacidite FF (CO_3 form), and the neutral components were eluted from the resin with water. Acid components were eluted with N-ammonium carbonate, and the ammonium ions removed from the eluate with Amberlite IR-120 (H^+ form). The aqueous solutions were freeze-dried (neutral components, 60%; acid components, 8%).

The neutral components were separated on a cellulose column irrigated with the butanol solvent mentioned above. Fractions (R_F 0·84) containing mainly the diols were treated with 2,4-dinitrophenylhydrazine to remove a carbonyl impurity. The excess of reagent was removed by passage down Amberlite IR-120 (H^+ form). Ionophoresis [1] in borate buffer of pH 10·0 showed that the mixture was mainly cyclohexane-*trans*-1,2-diol (M_G 0), with a small amount of the *cis*-1,2-diol (M_G 0·09). The diol (50 mg.), on treatment [2] with *p*-phenylazobenzoyl chloride in pyridine, gave the ester (125 mg.), m. p. 182—184°.

Relative concentration of cis- *and* trans-*diol.* The rates of oxidation of cyclohexane-*cis*- and *trans*-1,2-diol (25 mg. portions) by 0·1315N-lead tetra-acetate (25 ml.) were determined at ambient temperature by Hockett and McClenahan's procedure.[13] The rates of oxidation of synthetic mixtures of the *cis*- and *trans*-isomers were also determined. Results are in Table 1.

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[6] Ekert and Monier, *Nature*, 1959, **184**, BA 58.

[7] McDonell and Newton, *J. Amer. Chem. Soc.*, 1954, **76**, 4651.

[8] Gibson and Pearce, *Chem. and Ind.*, 1957, 613.

[9] Trevelyan, Procter, and Harrison, *Nature*, 1950, **166**, 444.

[10] Cifonelli and Smith, *Analyt. Chem.*, 1952, **26**, 1132.

[11] Block, Durrum, and Zweig, " A Manual of Paper Chromatography," Academic Press, New York, 1955, p. 344.

[12] Brown, *Nature*, 1951, **167**, 441.

[13] Hockett and McClenahan, *J. Amer. Chem. Soc.*, 1932, **61**, 1667.

TABLE 1.

Oxidation of cyclohexane-*cis*- and *trans*-1,2 diol.

	Lead tetra-acetate consumed (mol.)				
Time (hr.	100% *cis*	50% *cis* +50% *trans*	25% *cis* +75% *trans*	100% *trans*	Diols from cyclohexene
0·1	0·64				
0·5	1·00	0·68			
1·0		0·71	0·55	0·42	0·50
2·0		0·78	0·63		0·61
3·0		0·83	0·71	0·62	
4·0					0·74
5·0			0·82		
5·5				0·77	
6·0		0·91			0·83
8·0		0·95	0·93		0·90
10·0				0·95	

Identification of adipdialdehyde. This product was eluted in the first fraction (R_F 0·9) from the cellulose column. Its ultraviolet spectrum was identical with that of the authentic compound. This fraction yielded a bis-2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 167—169°.

Tentative identification of 2-hydroxycyclohexyl hydroperoxides. The fraction from the cellulose column with R_F 0·57 reacted [4] with ethanolic potassium iodide containing the starch derivative, " Thyodene," alkaline silver nitrate, benzidine–periodate,[10] and 2,4-dinitrophenylhydrazine,[11] but not with an alkaline hydroxylamine–nickel sulphate spray.[14] It had M_G 0·15 in borate buffer pH 10. It showed no absorption at 262 mμ. The diol fraction (R_F 0·84) also contained a component reacting with ethanolic potassium iodide containing " Thyodene." Two components (R_F 0·57 and 0·84) exhibiting the same reaction were present in 2-hydroxycyclohexyl hydroperoxides prepared by treatment of cyclohexene oxide (2 ml.) with 30% hydrogen peroxide (2 ml.) and concentrated sulphuric acid (1 drop) for 2 hr. at room temperature and ether-extraction of the mixture from which the excess of hydrogen peroxide had been removed by addition of titanium sulphate.

Identification of adipic acid. The free-acid fraction obtained after separation of the neutral components consisted mainly of a component having R_F 0·72 in pentyl alcohol–formic acid, identical with that of adipic acid. Three other acidic components (R_F 0·3, 0·47, 0·57) were present in small amounts. After paper chromatography the adipic acid was characterised as its *S*-benzylthiouronium salt, m. p. and mixed m. p. 122—124° (Found: C, 55·6; H, 6·4; N, 11·8. Calc. for $C_{22}H_{30}N_4O_4S_2$: C, 55·2; H, 6·2; N, 11·8%).

Irradiation of Cyclohexanol.—Solutions of carbonyl-free cyclohexanol (0·1% in distilled deionised water) in 20-ml. irradiation vessels were degassed for 1 hr. at *ca.* 0·3 mm. and were then irradiated for various times at a dose rate of $1·28 \times 10^{17}$ ev ml.$^{-1}$ min.$^{-1}$.

The amounts of *vic*-glycols formed were determined by Dixon and Lipkin's procedure.[15] Solutions were diluted 10 times, to give concentrations suitable for spectrometry. Results are in Table 2.

TABLE 2.

Formation of *vic*-glycols.

Irradiation time (hr.)	17·5	47	51·5	73·5 *
Glycol (10^{-3} mole/ l.)	7·6	5·3	2·0	4·1
G (glycol)	0·34	0·09	0·03	0·05

* Deposited polymer removed before analysis.

The total carbonyl-containing products were determined (see Table 3) by reaction with 2,4-dinitrophenylhydrazine.[16] Yields were calculated from the molar extinction coefficient determined for cyclohexanone 2,4-dinitrophenylhydrazone (ε_{430} $1·33 \times 10^4$).

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[14] Ferguson and Banks, *Analyt. Chem.*, 1951, **23**, 448.

[15] Dixon and Lipkin, *Analyt. Chem.*, 1954, **26**, 1092.

[16] Lappin and Clark, *Analyt. Chem.*, 1951, **23**, 541.

TABLE 3.

Formation of carbonyl compounds.

Irradiation time (hr.)	17·5	47	73·5	95·5	125
CO compounds (10^{-3} mole/l.)	2	5·9	2·3	1·02	0·35
G (carbonyl)	0·89	0·98	0·25	0·084	0·023

Circular paper chromatography of the 2,4-dinitrophenylhydrazones showed, *inter alia*, a component having R_F 0·99 in light petroleum (b. p. 60—80°)–benzene (3 : 2 v/v), identical with that of cyclohexanone 2,4-dinitrophenylhydrazone. After removal of the hydrazone, the excess of 2,4-dinitrophenylhydrazine was absorbed on Amberlite IR-120 (H^+ form), and the acids were removed on Amberlite IR-4B (OH^- form). The colourless neutral eluate was concentrated to a syrup. Paper chromatography in the above-mentioned butan-1-ol solvent revealed a component giving a positive reaction with periodate–benzidine.[10]

Periodate oxidation of the eluate followed by treatment with 2,4-dinitrophenylhydrazine in 2N-hydrochloric acid gave, *inter al.*, a component with the mobility of cyclohexanone 2,4-dinitrophenylhydrazone in two solvent systems.

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