370. *Decomposition Reactions of the Aromatic Diazo-compounds. Part IX. A Note on Oxidation Mechanisms.*

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Benzenediazoacetate reacts with *cyclo*hexene to give a little Δ^2-*cyclo*hexenyl acetate, and benzenediazonium chloride, in presence of acetone, reacts similarly to give some Δ^2-*cyclo*hexenyl chloride. Analogous to these reactions are the oxidations of *cyclo*hexene by lead tetra-acetate and by oxygen in presence of osmium. It is suggested that all these reactions have a common mechanism in which neutral radicals are involved.

SINCE the occurrence of an addition reaction between an olefin and the radicals left by the fission of nitrogen from an aromatic diazo-compound would be evidence in favour of the production of free radicals from the latter, a study of decomposition reactions in unsaturated solvents was projected.

Instances of addition to the nitrile group of acetonitrile are described in Part VII (this vol., p. 1792), and, quite recently, Meerwein, Büchner, and van Emster (*J. pr. Chem.*, 1939, **152**, 260) have shown that the radicals Ar• and •Cl, derived from diazonium chlorides on decomposition in aqueous acetone or pyridine, can add on to such unsaturated compounds as methyl cinnamate, methyl fumarate, and phenylpropiolic acid. Hence, radicals derived from decomposing aromatic diazo-compounds show some additive properties towards unsaturated organic molecules as well as towards metals. The experimental results now obtained in a preliminary study of the reaction between *cyclo*hexene and aromatic diazo-compounds afford an interesting contrast.

Benzenediazoacetate is insoluble in *cyclo*hexene, but when stirred under this liquid it gradually decomposes, giving chiefly tar. The *cyclo*hexene layer however then yields, on fractionation, a small quantity of Δ^2-*cyclo*hexenyl acetate, together with traces of other unsaturated substances of high boiling point. Δ^2-*cyclo*Hexenyl acetate can also be obtained by the procedure of Meerwein and his collaborators, *viz.*, by the decomposition of aqueous benzenediazonium chloride, in a mixture of *cyclo*hexene and acetone containing also an excess of sodium acetate, whereas decomposition of the solid in the same two solvents in presence of chalk affords Δ^2-*cyclo*hexenyl chloride.

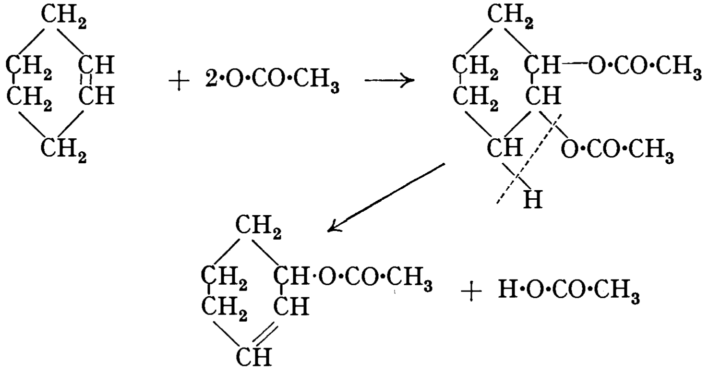
These reactions are evidently substitutions of the reactive CH_2 group of *cyclo*hexene by the acetoxy- and chloro-radicals derived from the decomposing diazo-compounds,

$$C_6H_{10} + \cdot O\cdot CO\cdot CH_3 \longrightarrow C_6H_9\cdot O\cdot CO\cdot CH_3 \qquad (A)$$

and are closely related reactions to the substitution (B) which occurs with acetone alone :

$$CH_3\cdot CO\cdot CH_3 + \cdot Cl \longrightarrow Cl\cdot CH_2\cdot CO\cdot CH_3 \qquad (B)$$

though it is possible to depict reaction (A) as involving a primary addition process (C), just as one can depict substitutions of acetone by schemes including additions to its enolic form.

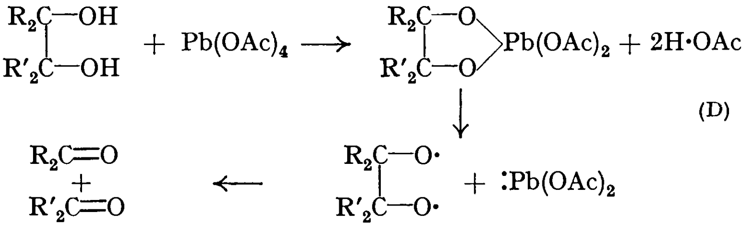


(C)

Exactly analogous substitutions of the CH_2 group of *cyclo*hexene occur when it is treated with certain oxidising agents. For instance, Willstätter and Sonnenfeld (*Ber.*, 1913, **46**, 2952) found that Δ^2-*cyclo*hexenol is a major reaction product when *cyclo*hexene is oxidised by atmospheric oxygen in presence of osmium, and Guillemonat (*Compt. rend.*, 1937, **205**, 67) obtained the same product by using selenium dioxide in glacial acetic acid solution. Again, Criegee (*Annalen*, 1930, **481**, 263) obtained Δ^2-*cyclo*hexenyl acetate as the chief product on treatment of *cyclo*hexene with lead tetra-acetate in glacial acetic acid solution.

One may therefore suggest that all the above oxidation processes have in common a reaction mechanism which involves attack on the *cyclo*hexene by neutral radicals formed from the oxidising agent.

Criegee, Kraft, and Rank (*Annalen*, 1933, **507**, 159) have already suggested that a free-radical fission of quadricovalent lead compounds may occur when glycols are oxidised by lead tetra-acetate :



(D)

and a similar decomposition $Pb(O\cdot CO\cdot CH_3)_4 \longrightarrow :Pb(O\cdot CO\cdot CH_3)_2 + 2\cdot O\cdot CO\cdot CH_3$ may occur with lead tetra-acetate itself, which, it may be noted, can effect substitution in the side chain of toluene (Dimroth and Schweizer, *Ber.*, 1923, **56**, 1375) just as do free atoms of bromine at room temperature (Kharasch, White, and Mayo, *J. Org. Chem.*, 1938, **3**, 33).

Attention has already been directed to the rôle played by free radicals in the reactions of oxygen (Waters, " Physical Aspects of Organic Chemistry," 1935, pp. 150—153), and, in this connection, Ziegler and Ewald's observation (*Annalen*, 1933, **504**, 162), that triphenylmethyl is an exceedingly efficient catalyst for the oxidation of olefins, makes it probable that many catalysed oxidation processes involve univalent free radicals of the general type $R\cdot O\cdot O\cdot$ (*e.g.*, $Ph_3C\cdot O\cdot O\cdot$).

The oxidation of *cyclo*hexene is by no means an isolated example of oxidation by aromatic diazo-compounds, and, in addition to the reactions discussed in Part III (J., 1937, 2014), attention may be directed to the work of Quilico and Freri (*Gazzetta*, 1928, **58**, 380; 1932, **62**, 253) and of Quilico (*Atti R. Accad. Lincei*, 1930, **12**, 341), who have given examples of oxidation of olefins such as anethole.

A still wider generalisation with regard to the mechanism of oxidation processes, though supported by the fact that the vast majority of them are chain reactions, would however be premature.

EXPERIMENTAL.

(i) 100 G. of benzenediazoacetate and 30 g. of chalk were stirred mechanically with 600 g. of *cyclo*hexene (distilled over sodium). After a week, the solvent was evaporated and the residue distilled in steam. The steam-distillate gave 6 g. of a liquid (*a*), b. p. 160—190°, and 3 g. of a liquid, b. p. 105—108°/15 mm. On repeated fractionation, (*a*) gave a colourless oil, b. p. 170—171°, with an ester-like smell (Found : C, 70·2; H, 8·5. Calc. for *cyclo*hexenyl acetate, $C_8H_{12}O_2$: C, 68·6; H, 8·6%); and (*b*) gave a little liquid hydrocarbon (Found : C, 89·6; H, 10·3%). Both (*a*) and (*b*) were unsaturated. After treatment with alkali and redistillation, (*a*) gave an oil, b. p. 160—170°, which, when warmed with phenyl *iso*cyanate, gave the phenylurethane of Δ^2-*cyclo*hexenol, m. p. 107° (Found : C, 71·8; H, 7·0. Calc. : C, 71·85; H, 7·0%); Willstätter and Sonnenfeld (*loc. cit.*) give Δ^2-*cyclo*hexenol, b. p. 167°; phenylurethane, m. p. 107°.

Oxidation of fraction (*b*) was attempted : it did not yield benzoic acid.

(ii) 23 G. of aniline were diazotised in 150 c.c. of dilute hydrochloric acid, and then treated with 100 c.c. of *cyclo*hexene, 200 c.c. of acetone, 80 g. of sodium acetate, and 10 g. of cupric chloride. The mixture was decomposed by warming, and volatile products were separated by steam-distillation. These yielded 2 g. of an unsaturated oil, b. p. 80—86°/15 mm., and a little product, b. p. 100—120°/15 mm., which in part solidified on cooling and eventually yielded 0·3 g. of diphenyl, m. p. and mixed m. p. 70°. The fraction of lower b. p. was refluxed with alcoholic potash and yielded potassium acetate and 1·2 g. of Δ^2-*cyclo*hexenol, b. p. 168—170°, identified by preparation both of its phenylurethane, m. p. and mixed m. p. 107°, and of its α-naphthylurethane, m. p. 156° (for the latter, Willstätter and Sonnenfeld, *loc. cit.*, give m. p. 156°).

(iii) 40 G. of benzenediazonium chloride, 30 g. of chalk, 300 c.c. of *cyclo*hexene, and 150 c.c. of acetone were mixed and warmed to 60°; decomposition then set in, and was completed by refluxing for some hours. After removal of the solvents from the cooled and filtered mixture, the residue was distilled in steam and gave 2·7 g. of a very readily hydrolysed unsaturated aliphatic chloride, b. p. 130—150°, and about 2 g. of a heavier unsaturated oil, b. p. 117—120°/20 mm., which was practically free from chlorine. Chloroacetone could not be detected. The aliphatic chloride (redistilled, b. p. 134°) was Δ^2-*cyclo*hexenyl chloride, since, after standing with cold sodium bicarbonate solution, it gave an oil which reacted with phenyl *iso*cyanate to give the phenylurethane of Δ^2-*cyclo*hexenol, m. p. and mixed m. p. 107°. The fraction of higher b. p. (Found : C, 86·8; H, 10·5%) gave no detectable quantity of benzoic acid on oxidation either with chromic acid or with potassium permanganate in dilute acetone, nor did it yield diphenyl on heating with selenium. The quantities of these products of higher b. p. resulting from reactions (i)—(iii) were too small for any further investigation.

The analyses for carbon and hydrogen are by Dr. Weiler, Oxford.

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