[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

ON THE AROMATIC CHARACTER OF DIOXADIENE

GERALD R. LAPPIN[1] AND R. K. SUMMERBELL

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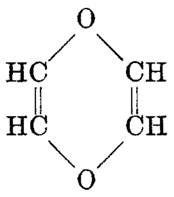
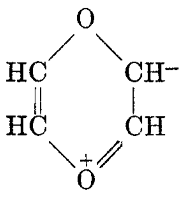
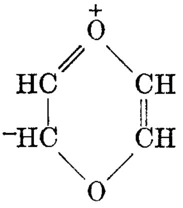
The structural similarity of dioxadiene (I) to furan (II) has led to speculation concerning the possibility of this compound possessing aromatic character similar to that of furan. Aromatic character, usually attributed to resonance among several structures (as IIa and IIb) manifests itself physically in furan by alteration of the bond distances in normal structure II (1) and by contributing a resonance stability of 17.2 kcal. per mole to the molecule (2). Chemically this results in resistance of furan to addition reactions and increased ease of substitution in the furan nucleus. For example, the furan nucleus reacts with chlorine (3), bromine (3), nitric acid (4), and in the Friedel-Crafts acylation (5) to give substitution products. With metallic potassium furan gives 2-furyl potassium (6). All of these reactions have been used to define and evaluate aromatic character in heterocyclic compounds.



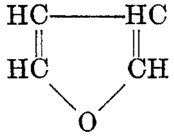
I



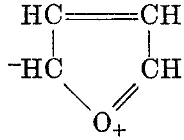
Ia



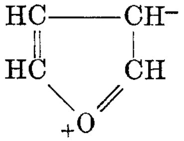
Ib



II



IIa



IIb

Dioxadiene could exhibit resonance similar to furan among such structures as Ia and Ib. This would be expected to result in physical and chemical manifestations similar to those in furan. Determination of the bond lengths in I has established that the deviations from the normal bond lengths are of the same magnitude as in the furan molecule (1). The ultraviolet absorption spectrum of I also indicates that structures such as Ia contribute to the state of the molecule (7). However, the only known chemical reactions of dioxadiene are those of an aliphatic unsaturated compound, for it reacts with hydrogen chloride, chlorine, and bromine to give addition products (8) and, on standing, polymerizes to an infusible substance (8). This investigation was undertaken in an attempt to discover whether dioxadiene exhibited any chemical manifestation

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[1] Present address, Chemistry Department, Antioch College, Yellow Springs, Ohio.

of the aromaticity which physical measurements seem to indicate may be present in the molecule.

It has been found that dioxadiene does not react with any of the reagents commonly causing substitution in an aromatic compound. Nitric acid caused some oxidation of I to tarry material but no nitrodioxadiene could be isolated. When dioxadiene was heated with acid anhydrides or acid chlorides in the presence of such acylation catalysts as zinc chloride, ferric chloride, stannic chloride, and iodine no ketonic material could be detected and most of the dioxadiene could be recovered, the rest being accounted for as dioxadiene polymer. No reaction occurred between refluxing I and metallic potassium.

The conclusion must be drawn, therefore, that dioxadiene does not exhibit any aromatic character in its chemical reactions but behaves as a typical aliphatic unsaturated ether. Thus it should be compared to vinyl ether (III) which, though resonance is possible among forms such as IIIa and IIIb, has almost no resonance energy (2).

$$\begin{array}{ccc} H_2C{=}CH{-}O{-}CH{=}CH_2 & H_2C{=}CH{-}\overset{+}{O}{=}CH{-}\overset{-}{C}H_2 & H_2\overset{-}{C}{-}CH{=}\overset{+}{O}{-}CH{=}CH_2 \\ \text{III} & \text{IIIa} & \text{IIIb} \end{array}$$

It undergoes no substitution reactions but readily adds bromine (9). When the possible resonance structures of furan, dioxadiene, and vinyl ether are compared it will be seen that the charge separation in some of the furan structures (as IIa) is only one bond length, while for the other two compounds all of the structures except the normal bond structure must have the much more unstable charge separation of two bond lengths. Thus the inherent instability of all but one of the possible resonance structures of dioxadiene would lead to an insignificant amount of resonance in this compound, resulting in turn in the manifestation of little or no aromatic character from the standpoint of chemical reactivity.

EXPERIMENTAL

Attempted nitration of I. A solution of 2.5 g. (0.03 mole) of dioxadiene in 15 ml. of acetic anhydride was cooled to 0° and to it was slowly added a solution of 2.0 g. of fuming nitric acid in 15 ml. of glacial acetic acid. The mixture, which became dark brown, was allowed to stand at room temperature for one hour and then poured over ice. The precipitated material was collected and found to consist of 2.2 g. (88%) of dioxadiene polymer identified by comparison with an authentic sample. No other material could be isolated except a small amount of tar.

Attempted acylation of I. A solution of 2.5 g. (0.03 mole) of I, 1.5 ml. of benzoyl chloride, and about 0.1 g. of anhydrous zinc chloride in 20 ml. of carbon disulfide was heated on the steam-bath for twenty-four hours. No hydrogen chloride was evolved. The solution was filtered, yielding 2.1 g. (84%) of dioxadiene polymer. The filtrate was treated with sodium carbonate solution to destroy the benzoyl chloride and the solvent was removed *in vacuo.* No precipitate was formed when the residue was treated with 2,4-dinitrophenylhydrazine.

This experiment was varied using acetic anhydride and acetyl chloride as acylating agents and using ferric chloride, stannic chloride, and iodine as catalysts. The use of other inert solvents and of excess of one reagent as solvent were also investigated. In every case only dioxadiene polymer could be isolated and no evidence of formation of ketonic products was found.

Attempted metallation of I. About 2 ml. of dioxadiene which had been freshly distilled from sodium was dissolved in 10 ml. of dry ether and 0.2 g. of clean potassium metal was added. The solution was refluxed for two days but no evidence of reaction was observed. Filtration of the solution gave 0.8 g. of dioxadiene polymer and distillation of the filtrate through a 10-cm. Vigreux column gave about 1 ml. of dioxadiene, representing a nearly quantitative recovery.

SUMMARY

The behavior of dioxadiene under conditions which yield various substitution products with furan was investigated. It was found that dioxadiene was not nitrated, acylated, or metallated under conditions for such reactions with furan. It was concluded, therefore, that chemically dioxadiene does not exhibit aromatic character but rather behaves as an unsaturated aliphatic ether comparable to vinyl ether.

EVANSTON, ILL.

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