[Contribution from the Converse Memorial Laboratory of Harvard University]

The Diels–Alder Reaction in the Fulvene Series

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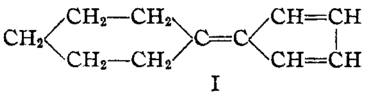
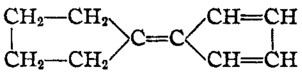
For reasons which need not be considered here we have condensed cyclopentadiene with cyclohexanone and with cyclopentanone and have isolated the corresponding fulvenes



I

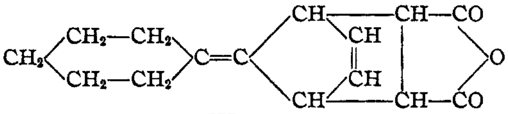


II

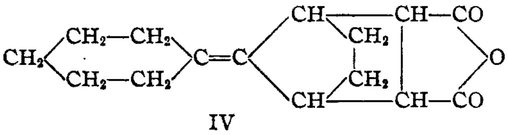
These very reactive hydrocarbons are highly colored oils. In order to transform them into solids suitable for identification we tried the reaction between the cyclohexane derivative (I) and maleic anhydride. Like the three fulvenes examined by Diels and Alder[1] this substance reacted vigorously at the ordinary temperature, forming a colorless crystalline addition product. In the solid state the addition product was stable but its solutions in indifferent solvents like ethyl acetate and benzene gradually assumed the color of the fulvene—suggesting dissociation into its components. That the development of color was actually due to dissociation was established both by proving the presence of maleic anhydride in the solution and by freezing point determinations which showed that in dilute solutions the addition product is dissociated almost completely.

This dissociation of the maleic anhydride addition product was somewhat surprising because while it has been known that the Diels–Alder reaction can be reversed, its reversal has, heretofore, been observed only when the addition products have been heated at or above their melting points.[2] In order to ascertain whether the ease with which our addition products are dissociated in solution is a peculiarity of dicyclic fulvenes we also examined the fulvene addition products described by Diels and Alder. In solution these also developed color at the ordinary temperature. Molecular weight determinations showed that the addition product from diphenyl fulvene is dissociated much more slowly but there is little difference in the ease with which the addition products from cyclohexylidene, dimethyl and styryl fulvene are dissociated in benzene.

Owing to the rapidity with which our addition products were dissociated in solution, their structure could not be established by ozonization. An attempt to stabilize them by converting them into the corresponding acids failed because they are dissociated more rapidly than they are hydrolyzed. We found, however, that all the products formed by adding maleic anhydride to fulvenes can be hydrogenated in steps. By the addition of two atoms of hydrogen they are converted into stable substances which can then be degraded with ozone. The degradation products show that the semi-cyclic double linkage of the fulvenes is not affected by the addition of maleic anhydride and also that it is the last to be hydrogenated



III



IV

Experimental Part

Cyclohexylidene Cyclopentadiene, I.—A mixture of 26.4 g. of freshly distilled cyclopentadiene and 39.2 g. of cyclohexanone was added slowly with constant shaking and, when necessary, with cooling to a solution of 9.2 g. of sodium in 110 cc. of dry methyl alcohol. The resulting mixture was immediately diluted with water and the condensation product was extracted with chloroform. The chloroform solution was dried and fractioned under diminished pressure. The product boiled at 78–80° (25 mm.) and the yield was 26.1 g. or 45%.

Anal. Calcd. for $C_{11}H_{14}$: C, 90.3; H, 9.7. Found: C, 90.1; H, 9.8.

The fulvene is a bright yellow colored oil of pleasant odor. It readily absorbs oxygen from the air, and when oxygen is passed into its solution in carbon tetrachloride it forms an amorphous peroxide. It is also readily hydrogenated in the presence of Adams catalyst, becoming colorless when one mole of hydrogen has been taken up but requiring three moles for complete saturation.

Polymerization.—When the fulvene is left to itself it slowly loses color and ultimately becomes completely colorless. An analysis showed that the loss of color is not due to oxidation and a molecular weight determination in ben-

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[1] Diels and Alder, *Ber.*, **62**, 2081 (1929).

[2] Albrecht, *Ann.*, **348**, 31 (1906); Diels and Alder, *Ber.*, **62**, 554 (1929); *Ann.*, **490**, 246 (1931).

zene showed that the colorless oil is a dimer. It is completely depolymerized to the yellow monomer when it is distilled under diminished pressure.

Anal. Calcd. for $C_{22}H_{28}$: C, 90.3; H, 9.7; mol. wt., 292. Found: C, 90.1; H, 9.7; mol. wt., 278.

Addition of Maleic Anhydride, III.—A suspension of 9.8 g. of maleic anhydride in benzene was treated with 14.6 g. of the fulvene, the vigorous reaction being moderated by cooling when necessary. The anhydride dissolved and the addition product gradually separated in beautiful colorless crystals melting at 132°.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.7; H, 6.6. Found: C, 73.5; H, 6.7.

Dissociation.—Solutions of the addition product become colored slowly at the ordinary temperature, rapidly when warmed on a steam-bath. A solution of 2.6 g. in benzene was warmed on a steam-bath for thirty minutes, then cooled rapidly and extracted with small quantities of water. The water solutions on heating and evaporating left 0.4 g. of maleic acid. Solutions in glacial acetic acid and in benzene which had been kept at the ordinary temperature for several days gave almost exactly the same value for the molecular weight by the freezing point method —140 instead of 244 calculated for the addition product.

Hydrogenation of the Addition Product, IV.—A suspension of 0.08 g. of platinum oxide in 20 cc. of ethyl acetate was reduced in the usual manner. Then 2.7 g. of the addition product was added and the mixture was shaken with hydrogen until 248 cc., the quantity required for saturating one double bond, had disappeared. The reduction was then interrupted and the product was isolated in the usual manner. It separated in colorless crystals melting at 148°.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.1; H, 7.4; mol. wt., 246. Found: C, 73.0; H, 7.4; mol. wt., 251.

Ozonization of the Dihydro Product.—When ozonized oxygen was passed through a solution of the reduction product in chloroform it slowly precipitated an amorphous ozonide. This was separated from the solvent and hydrolyzed with water. The product was separated into acid and neutral fractions in the usual manner and the neutral fraction was treated with semicarbazide. It deposited a solid which melted at 163° and which was identified as the semicarbazone of cyclohexanone by comparison with a sample on hand.

Cyclopentylidene Cyclopentadiene, II.—The fulvene from cyclopentanone was obtained in a yield of 48%. It is an orange colored liquid which has a pleasant odor and which boils at 55–57° (2 mm.). Its chemical properties are similar to those of the cyclohexanone derivative.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.8; H, 9.2. Found: C, 90.7; H, 9.2.

Diphenyl Fulvene.—In order to compare the properties of our dicyclic fulvenes with those of the open chained analogs, we added maleic anhydride to diphenyl fulvene. Our product, like that obtained by Diels and Alder, melted at 168°. Its solutions in ethyl acetate, in glacial acetic acid and in benzene slowly became colored at the ordinary temperature. In freezing glacial acetic acid we found a molecular weight of 180 instead of 328 calculated for the undissociated compound. In benzene the molecular weight was, at the outset, almost normal—305 instead of 328—but it fell off with time and after ten days was found to be 183.

Partial Hydrogenation.—The dihydro derivative was obtained, quantitatively, by the method described under the corresponding cyclic compound, the most satisfactory solvent being dioxane. The reduction product melted at 213°.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 80.0; H, 5.5; mol. wt., 330. Found: C, 79.9; H, 5.6; mol. wt., 326.

When the dihydro compound was degraded with ozone, benzophenone was the neutral product; in this case, therefore, the double linkage in the ring is likewise the first to be reduced.

Dimethyl Fulvene.—The maleic anhydride addition product dissociated as rapidly as that of the dicyclic fulvenes. Its molecular weight in benzene was 126 instead of 204 calculated for the undissociated compound. It was converted into a stable dihydro derivative which melted at 128°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.9; H, 6.9; mol. wt., 206. Found: C, 69.7; H, 6.9; mol. wt., 202.

The maleic anhydride addition product of styryl fulvene also dissociated at the ordinary temperature, its molecular weight in benzene being 170 instead of 278 calculated.

Summary

The maleic anhydride addition products of all types of fulvenes dissociate in solution at all temperatures. They cannot be stabilized by conversion into the corresponding acid because they are dissociated faster than they are hydrolyzed. They are, however, rapidly hydrogenated to dihydro compounds which are stable, the double linkage in the cyclopentene ring being saturated while the semi-cyclic double linkage remains intact.

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