

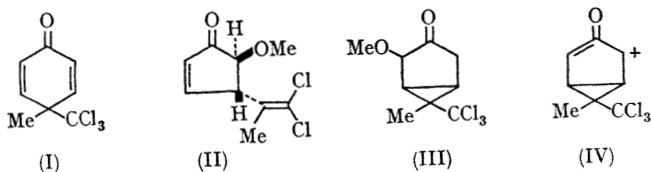
Isolation of a Bicyclo[3,1,0]hexan-3-one on Photolysis of a Cyclohexa-2,5-dienone: Direct Evidence for a Zwitterion Intermediate

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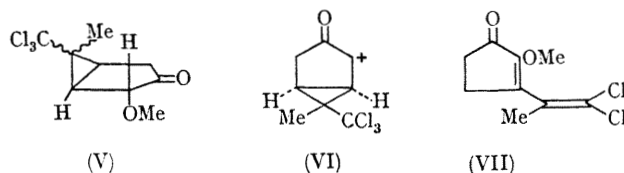
Summary A bicyclo[3,1,0]hexan-3-one derivative, formed on photolysis of 4-methyl-4-trichloromethyl cyclohexa-2,5-dienone, is the first dienone photo-product in which the carbon skeleton of the previously postulated zwitterion intermediate has been trapped intact.

It was reported previously that photolysis of the dienone (I) in neutral or basic methanol gave the cyclopentenone derivative (II).^{1,2} A second product, noted on photolysis of (I) in acidified methanol, was not isolated, although structure (III) was tentatively assigned on the basis of spectral properties of the substance in solution.¹ This compound has now been isolated, and its structure unambiguously confirmed as (III). Its isolation is important in dienone photochemistry¹⁻⁴ since (III) results from trapping of the zwitterion (IV), a species long suspected but previously only indirectly implicated as an intermediate in this type of reaction.^{3,4} This is the first reported case in which the carbon skeleton of the postulated zwitterion intermediate remains intact in an isolated photoproduct of a cyclohexa-2,5-dienone.



The competition between formation of (II) and (III) could be studied by analysis of photolysates by g.l.c. on 10% SE-30 on Chromosorb, as long as column, injector, and detector temperatures were kept at or below 125°. In neutral or basic methanolic solution, (II) was the major and often the

exclusive product. In methanol acidified with gaseous HCl, yields of (III) were increased at the expense of (II), and only (III) was formed in a ten-fold molar excess of HCl to (I), under conditions where (I) underwent no reaction in the dark. The new product (III) is thermally unstable, but can be isolated as a colourless oil by preparative g.l.c. under the conditions given above. The composition $C_9H_{11}Cl_3O_2$ was established by elemental and mass-spectral analysis. The mass spectrum and the n.m.r. and i.r. spectra are consistent with the structure given and the stereochemistry indicated by structure (V). The *exo-endo*-orientations of the methyl and CCl_3 groups in (V) are not as yet determined. The stereochemistry in (V) is consistent with attack of methanol on cation (VI) from the less hindered side of the molecule.



If compound (III) is allowed to stand for some time in CCl_4 solution at 0°, or chromatographed on a column of neutral alumina, it is transformed into the enol ether (VII), whose spectral properties were previously reported.¹ Compound (II) is also transformed into (VII) on long exposure to acid, or slow chromatography on alumina.

These results support our previous suggestion² regarding the sequence of intermediates involved in the photochemistry of cyclohexa-2,5-dienones, and specifically to the role of zwitterions in these reactions.

It is well-established that protonation of 4-dichloromethylcyclohexa-2,5-dienones in very strong acid is

accompanied by a marked bathochromic shift in the u.v. absorption spectra.⁵ Solutions of (I) in MeOH-HCl even more strongly acidic than those used in the photolysis studies above do not show any such shift in their u.v. spectra compared with spectra in the absence of HCl. Thus it seems highly unlikely that the reactions reported above are due to 3,5-bond formation following excitation

of the protonated dienone (I), reactions that would not involve zwitterions at any stage. This type of reaction has been recently reported in the photolysis of several benzenonium cations to give bicyclo[3,1,0]hexenyl cations.⁶

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