Cyclohexadienone Photochemistry: Chemical Trapping and Stereochemistry of the Type A Zwitterion

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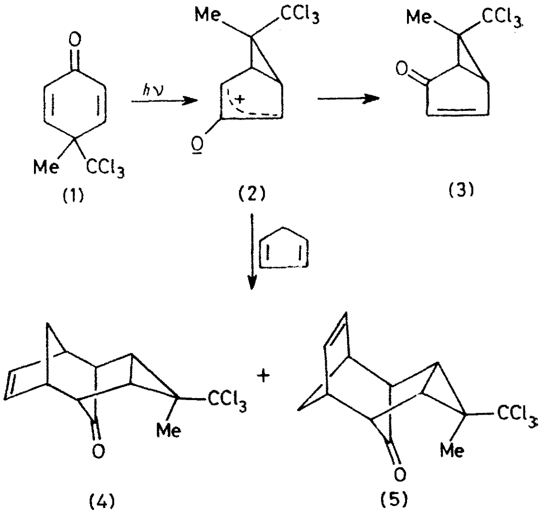
Summary Irradiation of 4-methyl-4-trichloromethylcyclohexa-2,5-dienone in the presence of cyclopentadiene gives two 1:1 adducts whose structures demonstrate the intermediacy of the type A zwitterion and whose stereochemistry shows that the walk rearrangement to the lumiketone proceeds with inversion of configuration.



(1) (2) (3)

(4) (5)

Most of the photochemistry of the cross-conjugated cyclohexadienones[1] has been interpreted in terms of initial 3,5-bonding to form a zwitterionic intermediate such as (**2**), first proposed by Zimmerman.[2] This can then undergo a walk rearrangement to give the lumiketone or form other products. Alternative mechanisms have been discussed,[3] and, while Zimmerman[4] has reinforced his original suggestion by finding that a 2-bromobicyclo[3.1.0]hexan-3-one undergoes an anomalous Favorskii rearrangement involving such a walk, the only photoproduct yet described which retains the three-membered ring present in the zwitterion is a methanol adduct of (**1**),[5] for formation of which alternative mechanisms are possible. Direct evidence for the intermediacy of species such as (**2**) has not been obtained.

In order to rationalise the stereochemistry of the lumiketones, Rodgers and Hart[6] assumed that the walk step [*e.g.* (**2**) $\rightarrow$ (**3**)] proceeds with inversion at the migrating carbon atom. While Zimmerman[4] has shown that this does occur in an anomalous Favorskii rearrangement, this stereochemical result has never been demonstrated in an unconstrained photochemical system.

Irradiation of the dienone (**1**) in benzene containing 10% freshly prepared cyclopentadiene gave, in addition to the bicycloheptenone reported by Schuster[7] and hydrocarbons assumed to be cyclopentadiene dimers, two new products. The major new product† was shown by elemental and mass spectrometric analysis to be a 1 : 1 adduct of the dienone and cyclopentadiene. The presence of only nine signals in the ^{13}C n.m.r. spectrum and the simplicity of the ^{1}H n.m.r. spectrum imply an element of symmetry in the molecule. The u.v. and i.r. spectra imply a strained unconjugated carbonyl group, and the details of the n.m.r. spectrum establish the gross structure as 8-methyl-8-trichloromethyltetracyclo[$4.3.1.1^{2,5}.0^{7,9}$]undec-3-en-10-one.

Similar considerations showed that the minor new product had the same gross structure. The stereochemistry of the two adducts was established on the basis of the n.m.r spectra with and without the addition of a lanthanide shift reagent. In particular, addition of Eu(fod)$_3$‡ to the major adduct resulted in the ^{13}C resonance due to the methyl group shifting downfield *ca.* 4 times as much as that due to the trichloromethyl group. The structures of the major and minor adducts are thus assigned as (**4**) and (**5**) respectively, in which the methyl group is *endo.*

These are the products that would be expected from cycloaddition[8] of cyclopentadiene to the less hindered face of the zwitterion (**2**) in which the methyl group is *endo*. Orientation of the addends in *exo* and *endo* fashion gives rise to the two adducts.

This result provides direct evidence for the intermediacy of the zwitterion (**2**) in the type A rearrangement. Furthermore, since it is known that the lumiketone (**3**) has the methyl group *endo*,[7] the stereochemical assignment of the adducts shows that the walk rearrangement does occur with inversion *in a photochemical system.*

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† ^{1}H N.m.r. data: δ(CDCl$_3$) 6·17 (2H, br s), 2·97 (2H, br s), 2·74 (1H, d, *J* 11·2 Hz), 2·51 (2H, d, *J* 5·6 Hz), 2·20 (2H, s), 1·59 (1H, dt, *J* 11·2 and 3·2 Hz), and 1·49 (3H, s); ^{13}C n.m.r. data: δ(CDCl$_3$) 212·5 (s), 137·5 (d), 106·2 (s), 51·9 (d), 47·6 (d), 44·6 (s), 39·5 (d), 32·0 (q), and 13·5 p.p.m. (t); i.r. (CHCl$_3$) ν_{max} 1753s cm^{-1}; u.v. (MeOH) λ_{max} 280 nm (sh, ϵ23) and end absorption; *m/e* 290 (0·1%) and 255 (100%).

‡ fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato.

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