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STRUCTURAL EFFECTS ON 2,4-CYCLOHEXADIENONE PHOTOCHEMISTRY; IRRADIATION OF A BICYCLO[4.2.0]OCTA-1,5-DIEN-3-ONE

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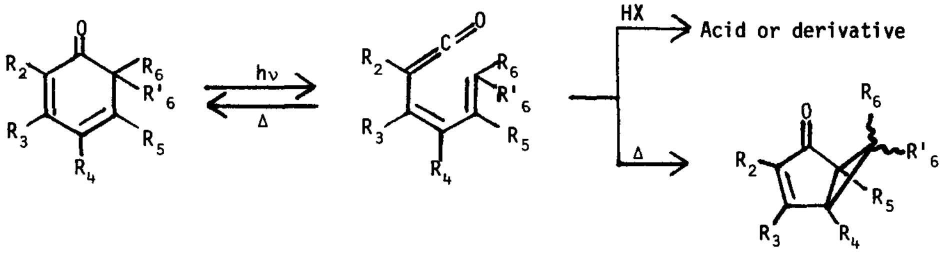
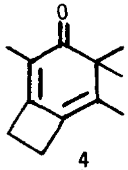
Irradiation of 2,4-cyclohexadienones (1) usually produces ketenes. Most commonly, these ketenes either thermally recyclize to dienone or, in the presence of nucleophiles, react to form open-chain unsaturated acids or their derivatives.[1-4] In special cases, however, the ketene may thermally cyclize to a bicyclo[3.1.0]hexenone (3).[3,5,6] Cyclization to 3 is favored by polar solvents[3] and even occurs in methanol, though in the presence of stronger nucleophiles, such as amines, open-chain products are formed.



1 2 3

The structural features which determine whether a particular ketene will cyclize to dienone or bicyclic ketone, or will react with a nucleophile, are still not well delineated, so that predictions are difficult, especially for highly substituted ketenes. Those ketenes which do give bicyclic products are usually highly substituted.[5-7]

In the present paper, we describe the synthesis and irradiation of dienone 4, and compare the results with those previously obtained[5a] for the closely related 1a.



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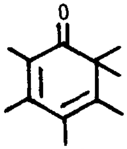
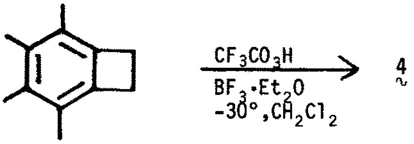


1a

Dienone 4 was prepared in 34% yield by the oxidation of tetramethylbenzocyclobutene 5[8,9] with peroxytrifluoracetic acid-boron trifluoride at -30°.[10] No other low molecular weight



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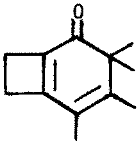
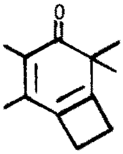
oxidation products were isolated. Dienone 4 had a λ_{max}^{MeOH} 320 nm (ε 4,800) and an nmr spectrum (CCl_4) with bands at τ 8.90 (6H, s, gem-Me_2), τ 8.31, 8.36 (6H, br s, C-2 and C-5 methyls) and τ 7.14 (4H, br s, cyclobutyl protons).

The structure of 4 was distinguished from its isomers 4a and 4b in the following way. Deuterium exchange (1M NaOMe in MeOD) at room temperature for one hour resulted in the uptake of two deuterium atoms (mass spec). Since alkyl groups on C-3 exchange much faster than those

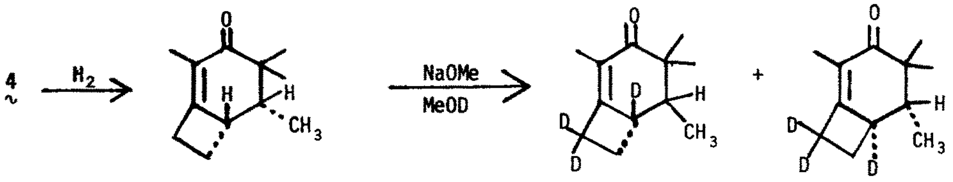


4a



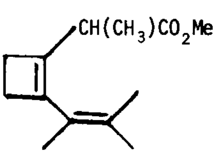
4b

on C-5[5a] this result eliminates structure 4b. Partial hydrogenation of the dienone (1 atm H_2, Pt, EtOH, rt, 13 min) gave a single α,β-unsaturated ketone which still had one allylic methyl group (τ 8.45). On exchange with NaOMe-MeOD as above, this ketone gave two labeled products. Each was an α,β-unsaturated ketone which contained three deuterium atoms. These results are explained as shown in the equation. All spectra of 6, 7c and 7t are consistent with this interpretation. In particular, the allylic methyl in 6, which was coupled homoallylically (J=0.9 Hz) became a singlet in 7.



6 7c 7t

Irradiation of a 1% solution of 4 in methylene chloride (Pyrex, Hanovia 450 watt lamp) gave no net reaction in 8 hours. In contrast, when irradiated in methanol under identical conditions, 4 was consumed in less than 2 hours. Five photoproducts were obtained, one (8) in 50-55% yield and the other four all in significant amounts.[11] The products were isomeric methyl esters and are assigned structures 8 and 9.[12]



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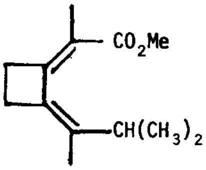
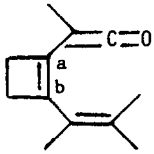


9 (4 geometric isomers)

These experiments show that ketenes 10 and 11, though different only in that the asterisked carbons in 11 are drawn together to form a cyclobutene ring in 10, behave differently in thermal reactions and toward nucleophiles. In methylene chloride 10 simply recyclizes to dienone, whereas 11 in addition cyclizes to bicyclic ketone 12.[3] The strain in the corresponding product 13 prohibits this path for 10. In methanol, 11 only cyclizes to 12 (none recyclizes to dienone or reacts with methanol 3). On the other hand 10 reacts rapidly with methanol to produce esters. It may be that the greater reactivity of 10 toward methanol is due to a widening of angles a and b (compared with a' and b'), thus making the carbonyl in 10 less hindered.



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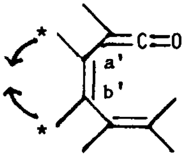

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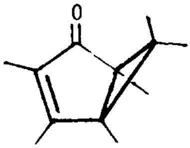

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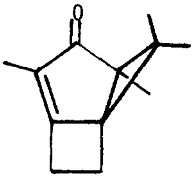

13

Dienones which should give ketenes analogous to 10, but with larger rings, are being studied.[13]

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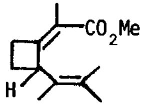
3. J. Griffiths and H. Hart, J. Am. Chem. Soc., 90, 3297 (1968).
4. For a review, see P. J. Kropp in "Organic Photochemistry-Volume 1" edited by O. L. Chapman, Marcel Dekker, Inc., New York, 1967.
5. (a) H. Hart, P. M. Collins and A. J. Waring, J. Am. Chem. Soc., 88, 1005 (1966); (b) P. M. Collins and H. Hart, J. Chem. Soc., C, 895 (1967); (c) H. Hart and D. C. Lankin, J. Org. Chem., 33, 4398 (1968); (d) M. R. Morris and A. J. Waring. Chem. Commun., 526 (1969); (e) H. Perst and K. Dimroth, Tetrahedron, 24, 5385 (1968).
6. Examples include R_2-R_6' = Me[5a]; R_2-R_6' = Et[5a]; R_3 or R_5 = H, all others = Me[5b]; R_2-R_6 = Me, R'$_6$ = OAc[5d]; R_2, R_4, R_6 = Me, R_3, R_5 = CH_2Cl, R'$_6$ = OAc[5d]; R_2-R_3, R_4-R_5 and R_6-R'$_6$ = -$(CH_2)_4$-;[5c] R_2, R_4, R_6 = ϕ, R_3, R_5 = H, R'$_6$ = OAc.[5e]
7. Some less substituted 2,4-cyclohexadienones can be converted to bicyclo[3.1.0]hexenones, but without the intermediacy of a ketene; see J. Griffiths and H. Hart, J. Am. Chem. Soc., 90, 5296 (1968).
8. H. Hart. J. A. Hartlage, R. W. Fish and R. R. Rafos, J. Org. Chem., 31, 2244 (1966).
9. A synthetic procedure for 5 which is superior to that given in ref. 8 will be given in a separate publication (D. J. H. and H. H.).
10. For a typical oxidation procedure, see H. Hart and R. K. Murray, Jr., J. Org. Chem., 32, 2448 (1967).
11. The ratios varied if different light sources were used. The possible interconversion of isomers of 9 under photolysis conditions is being studied.
12. The structures of 8 and the four isomers of 9 are based on their spectra. All the evidence will be presented in a full paper, but a few salient facts are given here. The uv spectrum of 8 (λ_{max}^{MeOH} 239 nm, ε 8,100) differed from those of all four isomers of 9 (λ_{max}^{MeOH} 288-290 nm, ε 6,700-17,000). Also, the nmr spectrum of 8 showed three allylic methyls (all at τ 8.30), whereas all isomers of 9 had only two allylic methyl signals, whose positions varied with geometry. The nmr data also exclude the two geometric isomers of i, which would have four allylic methyls. Careful examination of the uv and nmr spectra of all four isomers of 9 allowed each structure to be uniquely assigned.



i

13. All new compounds gave elemental analyses in accord with the assigned structures.