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PHOTODECARBONYLATION - A GENTLE ROUTE TO ANNELATED CYCLOHEXADIENES

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Cheletropic elimination of carbon monoxide from cyclic β,γ-unsaturated ketones has been observed to occur under thermal and photochemical conditions (1). Recently we reported (2) an example of this type of reaction in which the irradiation was carried out in solution and at low temperatures. This reaction has now emerged as a powerful synthetic route to annelated cyclohexadienes, illustrated in the present letter by the synthesis of the thermally labile tricyclo[6.2.1.0^{2,7}]undeca-3,5,9-triene (IV). Thus irradiation of the ketone (III)* in chloroform or acetone solution (-40°, vycor filter, 254nm Hg lamp, N_2 atmosphere) formed 3,6-dimethyl-4,5-diphenyl-tricyclo[6.2.1.0^{2,7}]undeca-3,5,9-triene (IV)†. The triene was identified by its pmr spectrum run at -40° ($CDCl_3$, δ ppm: 7.20 - 6.90 (m, 10H, phenyl); 6.26 (m, 2H, vinylic); 3.24 (m, 2H, bridgehead adjacent to vinylic); 2.20 (s, 2H, allylic methine); 1.61 (s, 6H, allylic methyl); bridge-methylene protons are obscured), and characterised by reaction at -40° with *N*-methyl tria-

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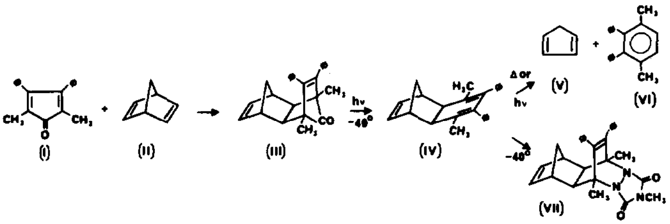
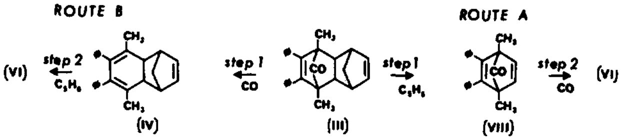
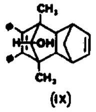
* The synthesis of this ketone has been reported previously (3) (cf. Scheme 1). The *exo, endo* stereochemistry of this adduct followed from a consideration of its pmr spectrum ($CDCl_3$: δ ppm): lack of coupling of bridgehead protons, $H_{2,7}$, (δ 2.01 s) with the adjacent allylic bridgehead protons $H_{3,6}$ (δ 3.05, m, due to coupling with $H_{4,5}$ and H_{12}) supported *exo*-bonding to the norbornadiene; Steric compression (4) (Δν ca. 66Hz) of the methylene bridge protons H_{12} (AB quartet δ 2.50, 1.40), essentially unchanged in the related alcohol (XV), supported *endo*-addition to the dienone.

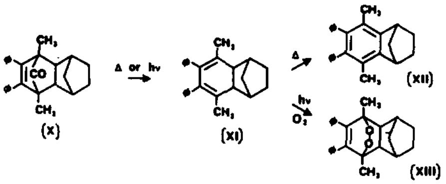
† The yield is limited in this case due to secondary photochemical fragmentation (*vide infra*). The yield is higher when the generated cyclohexadiene is photostable [e.g. irradiation of (X) formed (XI), >60% isolated yield].



zoline-3,5-dione to form the adduct (VII), m.p. 218° [pmr spectrum ($CDCl_3$), δ ppm: 7.40 - 6.80 (m, 10H, phenyl); 6.37 (dd, 2H, vinylic); 3.07 (s, 3H, *N*-CH_3); 2.95 (m, 2H, allylic methine); 2.18 (s, 2H, methine); 1.81 (s, 6H, *C*-CH_3); 2.50 1.35 (AB quartet, J = 9.5 Hz, 2H methylene bridge)]. Here again the pmr supported *exo, endo* stereochemistry (see footnote, previous page), resulting from attack by the triazoline-3,5-dione onto the least hindered side of the diene system. Variable temperature pmr studies indicated that the triene was stable at -10°, but decomposed thermally above ca. +20° to yield hydrocarbons (V) and (VI) [unimolecular reaction: t½ 33° = 19 min.].





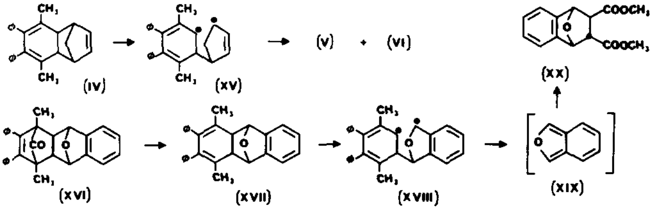


While speculation about the intermediacy of triene (IV) has been forthcoming (5,6) for the thermal decomposition of ketone (III), one cannot discount the alternative intermediate, norbornadiene-7-one (VIII). Evidence bearing on this point was obtained as follows:

1. Ketone (III) was reduced with sodium borohydride to form the alcohol (IX) single isomer, m.p. 190-192°. This alcohol was stable in solution to temperatures in excess of 200°, which thus reflected the reluctance of this molecule to participate in the retro (4+2)π cycloaddition reaction. A similarly high $\Delta G^{\ddagger}$ would be predicted for the initial step, proposed in *route A*.

2. Catalytic reduction of (III) formed the dihydro derivative (X), m.p. 164-5°. This compound exhibited a stability similar to that of ketone (III) (t½ 132° = ca. 30 min.) and eliminated carbon monoxide on heating (t½ 132° = 70 min.) to form the diene (XI), m.p. 94-5° (*N*-methyl maleimide adduct, m.p. 255°); more vigorous thermal conditions yield the aromatic product (XII). These results taken in conjunction with the observed thermal lability of triene (IV) fully support the reaction sequence outlined in *route B*.

A more interesting result from a theoretical point of view concerns the photochemical breakdown of triene (IV). Continued irradiation of triene (IV) [or of ketone (III)] at -40°, well below the temperature at which thermal fragmentation occurred (*vide supra*), still produced the aromatic hydrocarbon (V) and cyclopentadiene (isolated as its *N*-methyl triazoline-3,5-dione adduct). One route for the photochemical fragmentation of (IV), which does not breach the orbital symmetry requirements (7), involves a non-concerted (4+2)π cycloreversion pathway. In the case of triene (IV) this is initiated by breakage of the $C_{1,2}$ σ bond to generate the bis allylic diradical (XV), followed by fragmentation to yield (V) and (VI). The stability of diene (XI)* towards further irradiation is then explained in similar terms, since cleavage of the $C_{1,2}$ σ bond would not be as favoured, leading only to a mono allylic diradical. The fragmentation of the diene (XVII) further supported this proposal. Thus while the thermal stability (t½ = ca. 2-3 days at 33°) of (XVII) was greater than (IV), the photofragmentation was more rapid due to production of the favourable diradical (XVIII). The



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* Rapid conversion to the cyclic peroxide (XIII), m.p. 171° occurred on irradiation in the presence of air at 254 nm, or by eosin sensitised addition of oxygen (tungsten light source).

spectrum obtained after irradiation of (XVI) (8) at -45° (Fig. 1) clearly indicated the presence of the diene intermediate (XVII) as well as the aromatic fragmentation product (VI). [The spectrum of the other photoproduct, isobenzofuran was obscured. It was characterised (in poor yield) in a separate experiment run in the presence of added dimethyl fumarate, as the adduct (XX)].

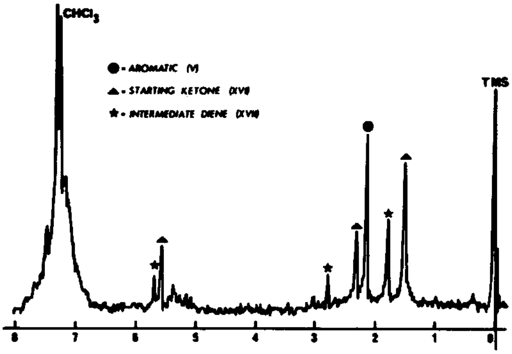

FIG. 1. P.m.r. spectrum (CAT, 45 runs) after irradiation of ketone (XVI) for 1 hr. (vycor, 254 nm) in $CDCl_3$ solution (130 mg/4 ml) at -45°.

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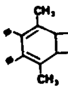
7. An alternative explanation involves the initial [1,3]sigmatropic shift to form (XXI), followed by (2+2)π cycloreversion. These are both photochemically allowed processes, but are rejected in the present case since no evidence for an unsymmetrical intermediate was observed in the pmr spectrum during the course of irradiation of (III) or (IV).



(XXI)

8. Formed in high yield by the reaction of 1,4-epoxynaphthalene and dienone (I) in refluxing benzene solution, m.p. 211° p.m.r. $CDCl_3$ δ ppm: 7.4 - 7.1 [singlet at 7.17 superimposed on multiplet, 14H, aromatic protons] 5.48 (s, 2H methine adjacent to oxygen) 2.24 (s, 2H, methine) 1.45 (s, 6H, C-CH_3). The lack of coupling of methine protons supports attack of dienone onto the *exo* side of the dienophile.