Ketene *vs.* Oxacarbene Formation in the Photolysis of Tricyclic Ketones Incorporating the 2-Norbornanone System

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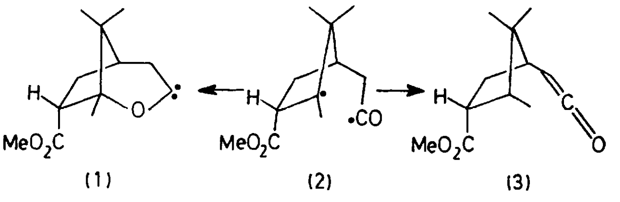
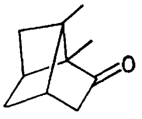
Summary Evidence is presented that the unusual formation of ketene-derived products in the photolysis of certain tricyclic ketones incorporating the 2-norbornanone system results from conformational constraints in the biradical formed by α-cleavage that facilitate the hydrogen abstraction process leading to ketene formation.

In the preceding Communication[1] we have reported that irradiation of 6-*endo*-methoxycarbonyl camphor in MeOH gives, as the major product, a mixture of epimeric acetals formed from the oxacarbene (**1**) *via* the biradical (**2**), together with a diester (6%) derived from the ketene (**3**), which is also formed *via* (**2**). This is in contrast to the earlier observation of Meinwald *et al.*[2] that irradiation of the tricyclic ketone, carvonecamphor (**4**), where structural features prohibit enal formation, gives the ketene-derived compound (**5**) (70%) unaccompanied by any oxacarbene-derived product.† This anomaly could be accounted for in terms of the nature of the biradical (**6**) formed by α-cleavage of (**4**). Because of the conformational constraints imposed by the four-membered ring, the hydrogen abstraction process leading to ketene formation should be greatly favoured in comparison with a simple 2-norbornanone, because the conformational mobility is reduced, and in the conformation leading to the ketene (**6**) the hydrogen atom undergoing abstraction approaches the alkyl radical more closely [*cf.* (**6**) *vs.* (**7**)].‡



(1) (2) (3)



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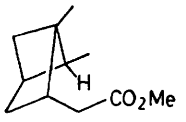

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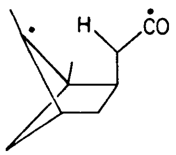

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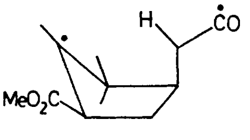
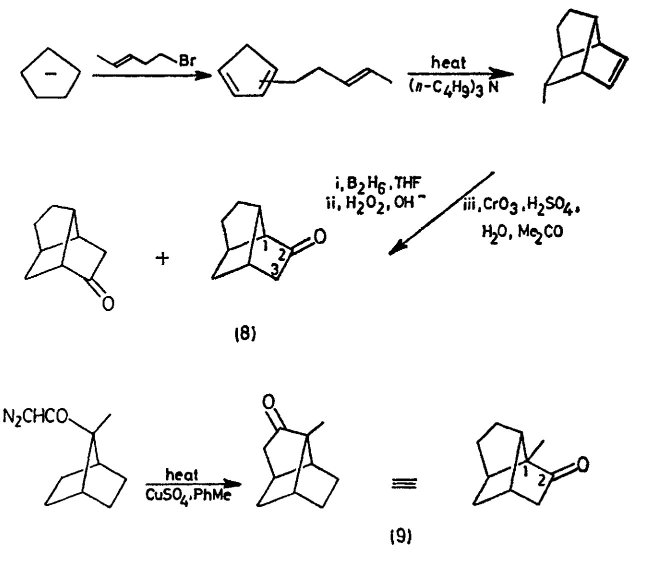
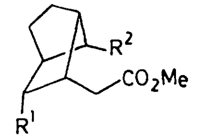


(7)

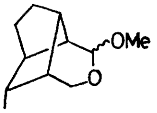
To test this hypothesis and to exclude the possibility that the effect is caused by some special feature of the bonding in the cyclobutane ring, we synthesized the tricyclic ketones (**8**)[3] and (**9**)[4] (Scheme) and examined their photochemistry.§



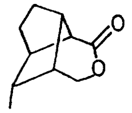
Scheme



(10) R^1 = Me, R^2=H
(13) R^1 = H, R^2=Me



(11)



(12)

Irradiation of (**8**) in MeOH in the presence of NaHCO$_3$ gave the ketene-derived product (**10**) which was analogous to (**5**), and was the only product formed by cleavage of the C(1)–C(2) bond. The product (**10**) was however formed in a small amount only, the major product being the oxacarbene-derived acetals (**11**) formed by cleavage of the C(2)–C(3) bond; oxidation of this mixture with chromic acid gave the lactone (**12**), which was also obtained by Baeyer–Villiger oxidation of (**8**). We attribute this unusual regioselectivity to the circumstance that cleavage at the more highly substituted α-position, which would normally be expected,[5] is inhibited since the resulting alkyl radical is situated at the C(7) position of a norbornyl system.[6] A similar interpretation can account for the Baeyer–Villiger oxidation of (**8**). Although the only product from C(2)–C(3) cleavage was oxacarbene derived as anticipated,[1] and the only product from C(1)–C(2) cleavage was ketene derived in accord with our present interpretation, the latter was obtained only in a small amount. We therefore examined the ketone (**9**), where the tertiary nature of the alkyl radical formed by cleavage of the C(1)–C(2) bond would be expected to override the destabilization referred to above, as in the case of (**4**). Irradiation of (**9**) in MeOH resulted in exclusive cleavage of the C(1)–C(2) bond and gave only the ketene-derived product (**13**). We conclude that the unusual formation of such products from the ketones (**4**), (**8**), and (**9**), is attributable to favourable conformational factors for hydrogen abstraction by the alkyl radical of the type proposed above.

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† A deliberate search for oxacarbene-derived products in the reaction mixture failed to reveal their presence.

‡ Oxacarbene formation is subject to similar conformational factors; however, it is anticipated that these factors will be considerably more important in the case of the five-membered cyclic transition state involved in ketene formation.

§ New compounds were characterized by elemental analysis and i.r., ^{1}H n.m.r., and mass spectroscopy.

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[6] *Cf.* C. Rüchardt, *Angew. Chem. Internat. Edn.*, 1970, **9**, 830.