

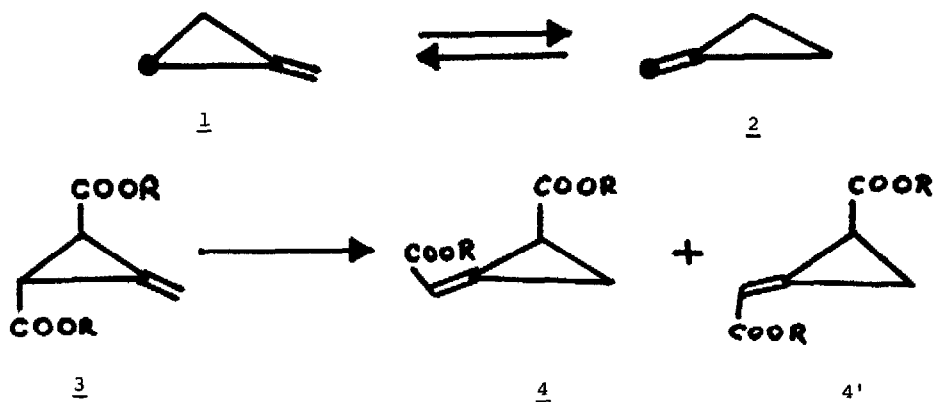
THE PHOTOCHEMICAL AND THERMAL REARRANGEMENTS
OF 2-ACETYL-METHYLENECYCLOPROPANE

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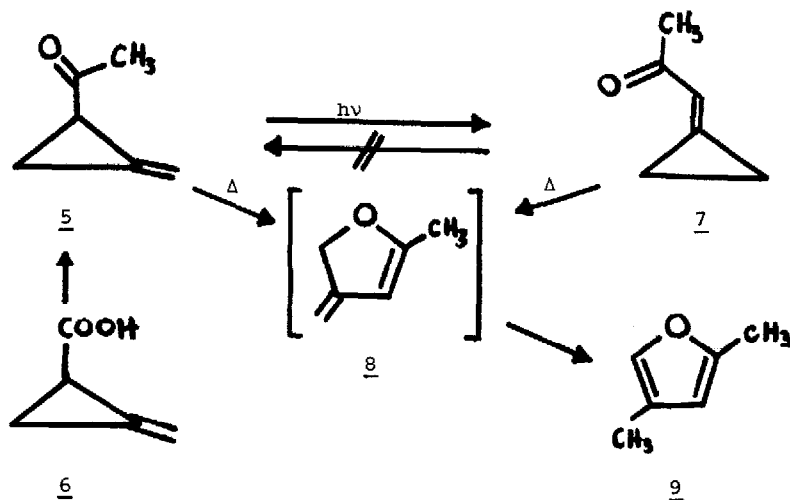
Although the mechanistic details of the degenerate methylenecyclopropane rearrangement (1 \rightleftharpoons 2) have been under active investigation for a long time, the precise nature of the intermediates has only recently been evaluated by the prominent studies of Doering *et al.*, on the thermal rearrangement of Feist's ester (3 + 4 + 4')¹ and related derivatives,² which point toward a non-concerted "pivot" mechanism.¹ This mechanism is supported by recent calculations on the geometry of the ground and excited states of trimethylenemethane.³ Much less explicit is the photochemical picture of this rearrangement. While it is generally accepted that the methylenecyclopropane photorearrangements start with an electronic excitation to the singlet manifold,⁴⁻⁷ it is not clear whether it is this excited state or a "hot" vibrational state^{4,6} which is actually responsible for the rearrangement, and whether a planar⁵ or a chirality-retaining, configuration-inverting diradical intermediate should be invoked.⁶



In order to gain more insight into the mechanistic details of this rearrangement, we have studied the photochemical and thermal transformations of 2-acetylmethylenecyclopropane (5). Having a carbonyl group conjugated to the cyclopropane ring, ketone 5 has the advantage of possessing a definite "bisected" conformation as well as a restricted site for the initial excitation both of which are characteristic to cyclopropyl ketones.⁸ In addition, being the first and simplest member of the methylenecyclopropyl ketones, 5 is free from steric effects caused by substituents. It should also be noted that 5

represents an unusually strained member of the β,γ -unsaturated ketones, a group which recently received considerable attention in the area of mechanistic organic photochemistry.⁹

Scheme I.



The synthesis of 2-acetyl-methylenecyclopropane (5) was accomplished via reaction of methylenecyclopropane-2-carboxylic acid (6)¹⁰ with MeLi¹¹ (Scheme I). The structure of ketone 5 (bp. 50°/15mm) was confirmed by elemental analysis and from spectroscopic data: m/e (70 eV) 96; ν_{\max} 1670 cm^{-1} ; λ_{\max} (cyclohexane) 218 ($\epsilon=270$), 283 (28) nm; nmr (CDCl_3) δ 1.5-1.79 (2H,m), 1.98 (3H,s), 2.39 (1H,m), 5.4 (2H,m).

Irradiation of a 1% ethereal solution of 5 (300nm Rayonet lamps, pyrex) resulted in a fast initial disappearance of starting material ($\Phi = 0.2$) with the concomitant formation of a single volatile product which was separated by vpc and identified as the conjugated photoisomeric ketone 7 [λ_{\max} (cyclohexane) 215 (14,000), 337 (27) nm; ν_{\max} 1670 cm^{-1} ; nmr (CDCl_3) δ 1.36 (4H,m), 2.2 (3H,s), 6.3 (1H,s)]. It was noticed that after a short build-up time of the product (ca. 10%), the rate of product formation is slowed down. Prolonged irradiation led to a considerable loss of both starting material and product. the ratio between the isomers 5 and 7 does not represent a photoequilibrium since irradiation of pure 7 under the same conditions did not result in a detectable amount of 5 or any other volatile material.

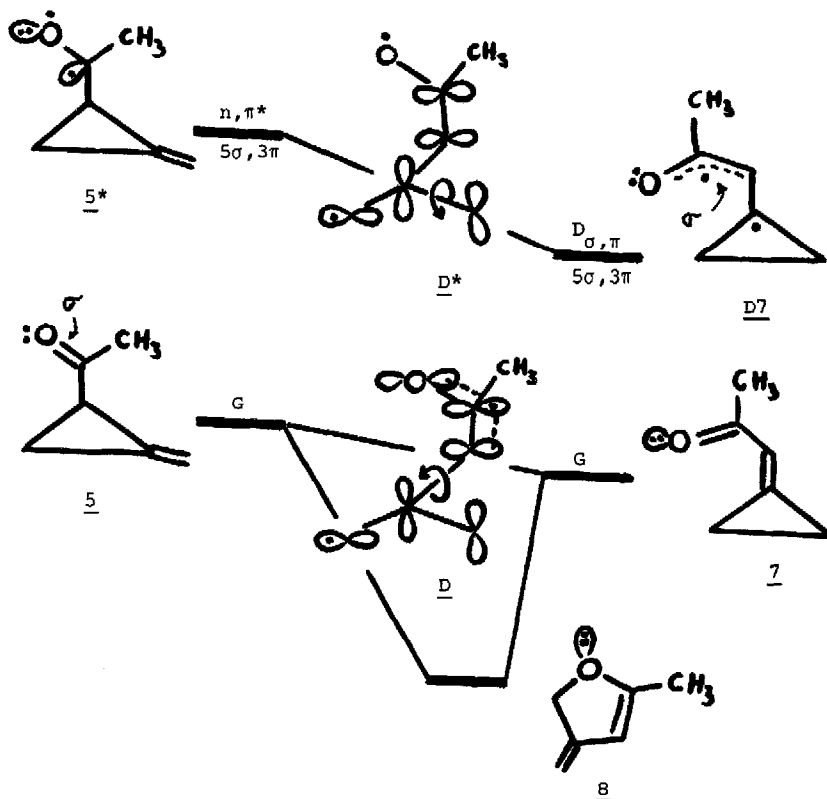
Attempts to bring about rearrangement by acetone or acetophenone sensitization failed, and the addition of piperilene did not quench the reaction. It is thus clear that the rearrangement takes place from the n,π^* singlet excited state.

The thermolysis of 5 took place via a completely different route. Heating ketone 5 in a sealed tube either neat or in solution (e.g. decaline) at 170° for 40 hr. gave a single product in low yield (<10%) which was separated by vpc and identified as the 2,4-dimethylfuran (9)¹² [nmr (CDCl_3) δ 1.94 (3H,s), 2.2 (3H,s), 5.7 (1H,bs), 6.9 (1H,bs)]. Similarly, thermolysis of the isomeric ketone 7 under milder conditions (120°, sealed tube) gave only 9.

Further experiments on the thermal rearrangements were conducted in the gas phase.¹³ When 5 was pyrolysed at 500°C, the furane 9 was isolated in 55% yield as the sole constituent of the gaseous mixture. Similarly, heating ketone 7 at 350°C afforded only furane 9 in 82% yield. At temperatures higher than 200° a mixture of starting material and furane was obtained and at 200° the starting material was recovered unchanged. Under no conditions were the two isomeric methylenecyclopropanes present in the reaction mixture.

These results clearly demonstrate the existence of two different pathways for the excited versus the ground state rearrangement. Following orbital symmetry conservation rules¹⁴ we observe here a photochemically allowed supra-[1,3]-sigmatropic shift to give 7 and a thermally allowed supra-[3,3]-sigmatropic shift to give 8. The latter subsequently rearranges by a prototropic shift to 9. However, recent evidence for a "diradical" mechanism in methylenecyclopropane transformations calls for an alternative mechanistic rationalization. Scheme II combines two possible approaches. The first adopted by Salem¹⁵ shows that the n, π^* singlet state 5* correlates¹⁶ with twisted ground state singlet diradical D7, e.g. with a vibrationally hot ground state of 7, which then relaxes to 7 but not to furane. On the other hand, ground state 5 correlates either directly with ground state 8 or alternatively through the ground state of isomer 7, both leading finally to the observed furane.

Scheme II.



The second approach which leads to essentially the same results utilizes the "conducted tour"¹⁷ or the dynamically continuous diradical mechanism.¹⁸ According to this mechanism one starts with a β -cleavage of the bisected conformation in both the photochemical and thermal rearrangement. However, while the initially formed excited diradical D^* continues its series of bending-stretching modes by twisting around the methylene double bond, ground state diradical D begins its sequence by turning the oxallyl moiety into the molecular plane for maximum conjugation, ending up as 8 .

Finally it should be noted that none of the characteristic rearrangements of β,γ -unsaturated ketones⁹ plays a role in the observed photochemistry, probably because of the more efficient β rather than α cleavage. Further elaboration of these reactions are under examination.

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