

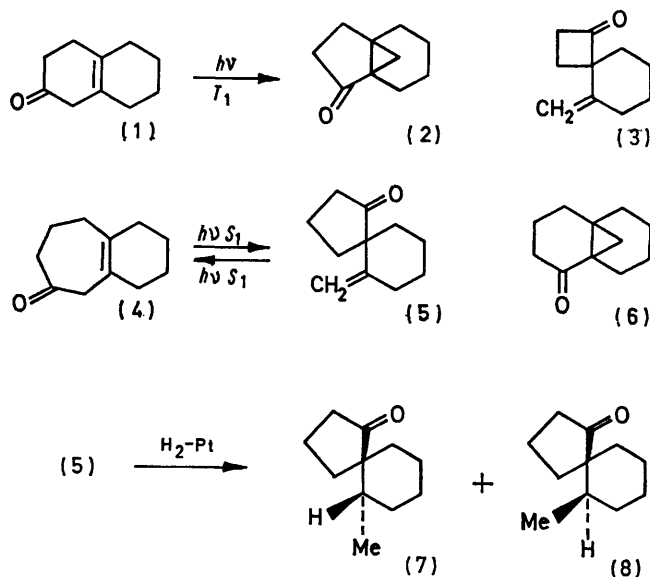
[1,3]- vs. [1,2]-Sigmatropic Photorearrangements in Cyclic $\beta\gamma$ -Unsaturated Ketones. Conversion of Bicyclo[5,4,0]undec-1(7)-en-3-one into 6-Methylene-spiro[4,5]decan-1-one

By JOHN R. WILLIAMS* and GEORGE M. SARKISIAN

(Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122)

Summary Bicyclo[5,4,0]undec-1(7)-en-3-one is photoisomerised to 6-methylenespiro[4,5]decan-1-one *via* a singlet state whereas bicyclo[4,4,0]dec-1(6)-en-3-one yields tricyclo[4,3,1,0^{1,6}]decan-7-one *via* a triplet state.

ULTRAVIOLET irradiation causes cyclic $\beta\gamma$ -unsaturated ketones to react *via* a number of routes.¹⁻⁵ Photoisomerization to a new $\beta\gamma$ -unsaturated ketone by a [1,3]-¹ and [1,2]-sigmatropic shift to a conjugated cyclopropyl ketone² are the most frequently encountered pathways. Recently we reported^{2b,d} the photoisomerization of the $\beta\gamma$ -unsaturated ketone (1) to the cyclopropyl ketone (2) but found no corresponding $\beta\gamma$ -unsaturated ketone (3). To elucidate these two modes of reaction, we have examined the photochemistry of bicyclo[5,4,0]undec-1(7)-en-3-one (4) and report its photoisomerization to 6-methylenespiro[4,5]decan-1-one (5).



Irradiation of (4)[†] in benzene with a medium-pressure mercury arc (Hanovia 450 W) through a Pyrex filter gave the $\beta\gamma$ -unsaturated ketone[‡] (5) (40%), ν_{\max} (CCl₄) 3080, 1735 (five-membered ring ketone), 1630, 895 cm⁻¹ (exocyclic methylene), λ_{\max} (EtOH) 303 nm (ϵ 68), δ (CDCl₃) 4.42 (1H, s) and 4.74 p.p.m. (1H, s, exocyclic methylene).

Catalytic reduction of the exocyclic methylene group in (5) with Adam's catalyst consumed 1.05 equiv. of hydrogen and yielded the two isomeric methyl ketones (7) and (8).

[†] The synthesis of (4) will be reported later.

[‡] Satisfactory analyses were obtained for all new compounds reported.

The structure of (7) was confirmed by comparison (i.e., n.m.r., and mass spectroscopy) with material synthesised independently.⁶

The formation of (5) from the seven-membered ring ketone (4) is in sharp contrast to the results observed for the six-membered ring homologue (1) where the conjugated cyclopropyl ketone (2) is the observed photoproduct.^{2b,d} Furthermore, the photoisomerization of (4) to (5) proceeds *via* a singlet or short-lived triplet state, since the reaction could not be quenched with 2,5-dimethylhexa-2,4-diene or cyclohexa-1,3-diene, and photosensitization experiments with acetophenone and benzophenone led to the disappearance of starting material without the formation of (5) or the conjugated cyclopropyl ketone (6). This photoisomerization is reversible and a photochemical equilibrium between (4) and (5) (2:3) was reached after irradiation for 5 h. Re-examination of the photoisomerisation of (1) to (2) indicates that the process proceeds *via* a triplet state since the reaction can be quenched with 2,5-dimethylhexa-2,4-diene.⁷ These results are in agreement with other photochemically induced [1,3]-sigmatropic shifts of $\beta\gamma$ -unsaturated ketones which have also been shown to proceed *via* a singlet or very short-lived triplet state, whereas [1,2]-sigmatropic shifts leading to conjugated cyclopropyl ketones proceed *via* a triplet state.^{1h,1} Recently an explanation for this divergent behaviour has been proposed based on spin distribution.⁸

This difference in reactivity between (1) and (4) depends on the relative rates of reaction from their singlet states. If the rate constant for α -cleavage from the singlet state is faster than the rate constant for intersystem crossing, then α -cleavage will occur and the singlet product formed by a [1,3]-shift will be observed. This is the case for (4). However, with (1) intersystem crossing occurs at a faster rate and the triplet product (2), formed by a [1,2]-shift, is observed.

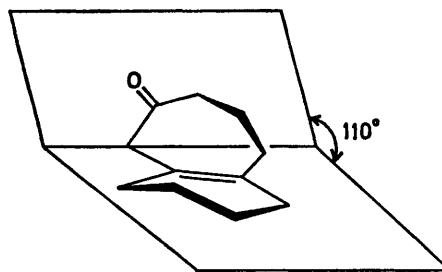


FIGURE. Stereochemistry of bicyclo[5,4,0]undec-1(7)-en-3-one (4)

TABLE

Correlation of photorearrangement with carbonyl band^a of some cyclic $\beta\gamma$ -unsaturated ketones

Ketone	Acyl shift		Ref.
	[1,3]-	[1,2]-	
1,4,4-Trimethylbicyclo[3,2,0]hept-6-en-2-one	303(174) ^b		1a
4,4,6-Trimethylbicyclo[3,2,0]hept-6-en-2-one	303(230) ^b		1a
Bicyclo[2,2,1]hept-5-en-2-one	307(251) ^c		1b
10,11-Dimethyltricyclo[4,3,2,0 ^{1,6}]undec-10-en-7-one	307(340) ^b		1c
2,3-Dimethyltricyclo[5,4,0,0 ^{3,7}]undec-1-en-4-one	310(460)		1c
Bicyclo[5,1,1]non-2-en-8-one	299(45) ^b		1d
<i>cis</i> - and <i>trans</i> -Cyclodec-3-enone	287(67) ^b		1e
Cyclo-oct-3-enone	290(60) ^d		1f
17 β -Acetoxy-A-homoandrost-4a-en-3-one	286(251) ^d		1g
2,2-Dimethylcyclohept-3-enone	282(41) ^d		1h
(1)		281(38) ^d	
17 β -Hydroxyoestr-5(10)-en-3-one ^{2c}		284(34) ^d	2c
3-Acetyl-1,2,3-trimethylcyclopent-1-ene	300(151) ^e		1i

^a λ_{\max} /nm (extinction coefficient). ^b In EtOH. ^c In cyclohexane. ^d In MeOH. ^e In iso-octane.

Since both (1) and (4) have $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot$ groups and the strain in the rings is approximately the same, it is difficult to rationalize the difference in reactivity.

A possible explanation may lie in the stereochemistry of the cyclic $\beta\gamma$ -unsaturated ketone. It is well known that geometrical and electronic requirements exist for the intensification of the $n\text{-}\pi^*$ absorption of $\beta\gamma$ -unsaturated ketones.⁹ When the angle between the two planes formed by the carbonyl group and the double bond is decreased from 180°, the carbonyl $n\text{-}\pi^*$ transition is enhanced,⁹ and α -cleavage is more likely to occur, since the orbital formed by α -cleavage overlaps to a much greater extent with the olefinic double bond, *i.e.* α -cleavage should be assisted.

Therefore, α -cleavage now occurs at a much faster rate [*cf.* $k(\text{cyclohexanone}) = 3 \times 10^7 \text{ s}^{-1}$]¹⁰ in (4), *i.e.* α -cleavage occurs from the singlet state. Drieding models indicate that (4) is much more rigid and that the angle between the two planes is approximately 110° (see Figure)

whereas (1) is very flexible and the angle between the two planes oscillates about 180° \pm 40°.

The u.v. spectra of (1) [λ_{\max} (EtOH) 281 nm (ϵ 38)]^{2b} and (4) [λ_{\max} (EtOH) 292 nm (ϵ 252)] agree with the values anticipated from the molecular models (see the Table).

Usually direct irradiation leads to a single product being produced. However, recently, products from both [1,3]- and [1,2]-shifts have been observed:¹¹ it appears that inter-system crossing is competing successfully with α -cleavage from the singlet state.

The photorearrangement described here should be operative for larger bicyclic $\beta\gamma$ -unsaturated ketones where the olefin is at the ring junction and should provide an alternative synthesis for spiro-molecules.

We acknowledge partial support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(Received, August 16th, 1971; Com. 1430.)

¹ (a) G. Buchi and E. M. Burgess, *J. Amer. Chem. Soc.*, 1960, **82**, 4333; (b) G. O. Schenck and R. Steinmetz, *Chem. Ber.*, 1963, **96**, 520; (c) R. L. Cargill, M. E. Beckham, A. E. Siebert, and J. Dorn, *J. Org. Chem.*, 1965, **30**, 3647; (d) W. F. Erman and H. C. Kretschmar, *J. Amer. Chem. Soc.*, 1967, **89**, 3842; (e) R. G. Carlson and J. H. Bateman, *Tetrahedron Letters*, 1967, 4151; (f) J. K. Crandall, J. P. Arrington, and J. Hen, *J. Amer. Chem. Soc.*, 1967, **89**, 6208; (g) M. Fischer and B. Zeeh, *Chem. Ber.*, 1968, **101**, 2360; (h) L. A. Paquette, R. F. Eizember, and O. Cox, *J. Amer. Chem. Soc.*, 1968, **90**, 5153; (i) E. Baggiolini, K. Schaffner, and O. Jeger, *Chem. Comm.*, 1969, 1103.

² (a) L. P. Tenny, D. W. Boykin, jun., and R. E. Lutz, *J. Amer. Chem. Soc.*, 1966, **88**, 1835; (b) J. R. Williams and H. Ziffer, *Chem. Comm.*, 1967, 194; (c) J. R. Williams and H. Ziffer, *ibid.*, 469; (d) J. R. Williams and H. Ziffer, *Tetrahedron*, 1968, **24**, 6725.

³ K. Kojima, K. Sakai, and K. Tanabe, *Tetrahedron Letters*, 1969, 3399.

⁴ (a) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, 1966, **31**, 1393; (b) P. S. Engel and H. Ziffer, *Tetrahedron Letters*, 1969, 5181.

⁵ R. K. Cargill, J. R. Damewood, and M. M. Cooper, *J. Amer. Chem. Soc.*, 1966, **88**, 1330.

⁶ K. Grimm, P. S. Venkataramani, and W. Reusch, *J. Amer. Chem. Soc.*, 1971, **93**, 270.

⁷ J. R. Williams, unpublished results. The same observation has also been made by Drs. R. S. Engel and H. Ziffer of the National Institutes of Health, Bethesda.

⁸ D. I. Schuster, G. R. Underwood, and T. P. Knudson, *J. Amer. Chem. Soc.*, 1971, **93**, 4304.

⁹ D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc. (B)*, 1967, 215, and references therein.

¹⁰ P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, 1969, **91**, 4437.

¹¹ D. I. Schuster and D. Sussman, *Tetrahedron Letters*, 1970, 1661; J. Ipaktschi, *ibid.*, 3179.