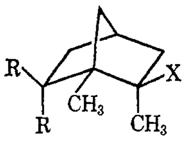
γ-isotope effect would be insignificant (as for the *endo* isomer) if ionization were unassisted and involved a classical transition state.

We wish to report that we have put this assumption to the test by examining the γ-isotope effect in an *exo*-norbornyl system which is known to involve unassisted ionization. In this work we have compared the rates of solvolysis of 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate (Ia-OPNB)[4] and the 6,6-dideuterio ester (Ib-OPNB) in 90% aqueous acetone. It has been shown[5] that under these conditions I undergoes unassisted ionization, at least in part, to give the asymmetric classical carbonium ion.



Ia, R = H
b, R = D

The 6,6-dideuterated tertiary system Ib was prepared by the π route[6] as follows. Reduction of methyl 3,4-dimethyl-Δ^3-cyclopentenylacetate with $LiAlD_4$ gave 2-(3,4-dimethyl-Δ^3-cyclopentenyl)ethanol-1,1-d_2 which was converted[6] to 1,2-dimethyl-*exo*-2-norbornanol-6,6-d_2 (Ib-OH). The *p*-nitrobenzoate derivative,[4] Ib-OPNB, contained 1.98 atoms of deuterium per molecule. Hydride shifts that result in scrambling of the deuterium atoms in the synthesis[7] and solvolysis[2,3] of the parent norbornyl system are not involved in this tertiary system.

Three independent comparisons of the rates of solvolysis of the undeuterated (Ia-OPNB) and dideuterated (Ib-OPNB) esters are presented in Table I. In each case the esters were solvolyzed simultaneously. The initial concentrations were the same and solvent was taken from the same batch. Reactions were followed from 20 to 70% completion by titration, and in each comparison points for the two experiments were taken at the same times.

Table I. First-Order Rate Constants and Isotope Effects (k_H/k_D) for Solvolysis of Undeuterated and 6,6-Dideuterated 1,2-Dimethyl-*exo*-norbornyl *p*-Nitrobenzoate in 90% Aqueous Acetone at 78.47°

Ester (I-OPNB)[a]	$k \times 10^4$ [b] min^{-1}	k_H/k_D[c]
6,6-Dideuterated[d]	7.34 ± 0.05	1.02 ± 0.01
Undeuterated	7.47 ± 0.02	
6,6-Dideuterated[d]	7.31 ± 0.03	1.02 ± 0.01
Undeuterated	7.47 ± 0.02	
6,6-Dideuterated[d]	7.33 ± 0.04	1.02 ± 0.01
Undeuterated	7.47 ± 0.03	

[a] Initial concentration 0.030 *M* for each experiment. [b] Each value is the average, and average deviation, of eight point-by-point determinations of the rate constant between 20 and 70% reaction. [c] Uncertainties determined from limiting values of the rate constants. [d] Substrate contained 1.98 atoms of deuterium per molecule.

These results show that the γ-isotope effect for two C-6 deuterium atoms in the tertiary *exo*-norbornyl system is barely detectable; this is in sharp contrast to the remarkable isotope effect for one deuterium atom in the parent *exo*-norbornyl system (k_H/k_D = 1.02 *vs.* 1.10).[8] This striking difference cannot be attributed simply to the change from a secondary brosylate to a tertiary *p*-nitrobenzoate or to the change in solvent and temperature because the β-deuterium isotope effect for acetolysis of 3,3-d_2-*endo*-norbornyl brosylate (k_H/k_D = 1.26)[9a] is very similar to that for solvolysis of *exo*- or *endo*-3,3-d_2-2-methyl-2-norbornyl *p*-nitrobenzoate in 70% acetone (k_H/k_D = 1.30).[9b] Also, typical β-deuterium isotope effects have been observed for solvolysis of *exo*- and *endo*-2-phenyl-2-norbornyl *p*-nitrobenzoate in aqueous dioxane.[10]

The present results show that the γ-isotope effect for unassisted ionization in an *exo*-norbornyl system is small, as previously assumed,[2,3] and support the view that the large γ-isotope effect for solvolysis of the parent *exo*-norbornyl system[8] is a manifestation of assisted ionization.

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[8] In the parent *exo*-norbornyl system the γ-isotope effect is the same for *exo* and *endo* deuterium at C-6[2,3] and there is evidence[7] that these effects are additive, in which case the γ-isotope effect for the 6,6-d_2-*exo*-norbornyl system is $k_H/k_D \sim (1.10)^2 \sim 1.21$.

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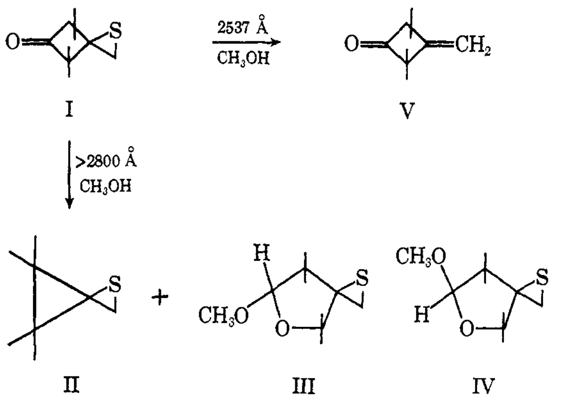
Received May 15, 1969

Wavelength Effect in Photolysis of 4,4,6,6-Tetramethyl-1-thiaspiro[2.3]hexan-5-one

Sir:

We have found that the photochemistry of 4,4,6,6-tetramethyl-1-thiaspiro[2.3]hexan-5-one (I)[1] displays a remarkable dependence on the wavelength of the exciting light (Scheme I).

Scheme I



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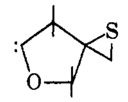
[1] I was prepared by treatment of 2,2,4,4-tetramethyl-3-thio-1,3-cyclobutanedione with diazomethane at 0° in ether; white, crystalline solid, mp 84.5–85.5°; ir (CCl_4) 1708 cm^{-1} (s); nmr ($CDCl_3$) δ (ppm) 2.55 (s, 2 H), 1.12 (s, 6 H), and 1.18 (s, 6 H). A more detailed account of the preparation and reactions of I will appear in a forthcoming paper.

Photolysis[2] of a 5% (w/v) solution of I[3] in methanol for 18 hr with light of wavelength >2800 Å gave[4] a 22.5% yield of 4,4,5,5-tetramethyl-1-thiaspiro[2.2]-pentane (II) [ir(CCl$_4$) 1445 (s), 1350 (s), 1210 cm^{-1} (s); nmr (CDCl$_3$) δ 2.59 (s, 2 H), 1.14 (s, 6 H), 1.08 ppm (s, 6 H); mass spectrum (70 eV) *m/e*(parent ion)142], a 27.6% yield of the *trans* cyclic acetal III [ir (CCl$_4$) 1190 (s), 1065 cm^{-1} (s); nmr (CDCl$_3$) δ 4.59 (s, 1 H), 3.31 (s, 3 H), 1.32 (s, 6 H), 1.16, 0.73 (s, 3 H) each), 2.41 (d, 1 H, J = 1.8 Hz), 2.47 ppm (d, 1 H, J = 1.8 Hz); mass spectrum (70 eV) *m/e*(parent ion) 202] and an 8.9% yield of the *cis* cyclic acetal IV [ir (CCl$_4$) 1198 (s), 1065 cm^{-1} (s); nmr (CDCl$_3$) 4.58 (s, 1 H), 3.35 (s, 3 H), 1.26 (s, 6 H), 1.11, 0.83 (s, 3 H each), 2.23 (d, 1 H, J = 1.8 Hz), 2.36 ppm (d, 1 H, J = 1.8 Hz); mass spectrum (70 eV) *m/e*(parent ion) 202].

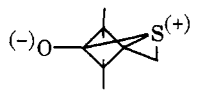
Photolysis with 2537-Å light[5] in methanol gave a 56.1% yield of the methylenecyclobutanone V as the major volatile product,[6] plus 7.3, 8.9, and 2.8% yields of II, III, and IV, respectively; in addition, a nonvolatile residue was formed.

Products formed by photolysis with >2800-Å light are consistent with the formation of an alkylacyl biradical resulting from a Norrish type I cleavage of the n,π^* state of the carbonyl group. The intermediate biradical can eliminate carbon monoxide to form II or undergo ring closure on the oxygen atom to form the intermediate oxacarbene VI. The formation of oxacarbenes as intermediates in the photolysis of substituted cyclobutanones has been demonstrated.[8–11]



VI

Unlike the electronic spectra of other keto sulfides,[12–15] the electronic spectrum of I gave no evidence for charge-transfer states resulting from transannular interaction of a lone pair of electrons on sulfur with the carbonyl group. Such interactions would give rise to structures such as VII and result in both perturbation of the n–π^* carbonyl frequency and the appearance of an intense absorption band in the 240- to 270-nm region. Since the geometry of the molecule is such that significant orbital overlap will not occur, this observation is not surprising. The high-energy 265-nm band, interpreted as an n,σ^* state associated with sulfur, has been observed in the electronic spectrum of other substituted episulfides.[16,17] Loss of sulfur was the major process which occurred upon excitation with 2537-Å light. The products resulting from the n,π^* state of the carbonyl are assumed to be a result of stray 3100-Å light associated with the 2537-Å fluorescent lamps used. The fact that loss of sulfur is the major process indicates that intermolecular and intramolecular energy transfers from the n,σ^* state to the n,π^* state of the carbonyl group are inefficient and that scission of the carbon–sulfur bond is a rapid process.



VII

The absence of V in the products from the long-wavelength photolysis showed that no interaction occurred between the carbonyl group and sulfur. The photochemistry of γ-keto sulfides has been found to be strongly influenced by the presence of a perturbed carbonyl group.[15]

A recent example of a photochemical reaction in which wavelength is a controlling factor is the photolysis of 3-benzoyl-2-phenyl-1-azirine.[18] With light of wavelength >3340 Å, 3,5-diphenylisoxazole was formed as the major product, whereas with light of wavelength <3130 Å, 2,5-diphenyloxazole was formed. Sensitization experiments suggested that the isoxazole is formed *via* the ^{3}(n,π^*) state of the carbonyl chromophore and that the oxazole is formed *via* the ^{1}(n,π^*) state of the ketimine chromophore. Although the multiplicities of the excited states arising from the two chromophores in I have not been determined, a ^{3}(n,π^*) state of the carbonyl group and a ^{1}(n,σ^*) state of the sulfur atom probably account for the observed results.

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(2) Photolyses were performed in Pyrex vials (degassed and sealed prior to photolysis) with a Hanovia 550-W medium-pressure mercury arc.

(3) $\lambda_{\max}^{\text{hexane}}$ 300 (log ϵ 1.27), 314 (1.28), 265 nm (1.80).

(4) Yields reported are not those of products isolated; the mixture was analyzed by gas chromatography on a 6-ft column of 20% silicone rubber UC W98 on Diatoport S; the column was operated isothermally at 100°; analytical samples were collected at 85°.

(5) An air-cooled Rayonet Photochemical reactor (Southern New England Ultraviolet Co., Middletown, Conn.) and Vycor reaction vessels were used. The light source consisted of 16 2537-Å fluorescent lamps.

(6) The melting point (42–43°), ir (CCl$_4$) [1800 (s), 1675 cm^{-1} (s)], and nmr (CCl$_4$) [δ 5.03 (s, 2 H), 1.22 (s, 12 H)] agreed with the values reported by Hamon.[7]

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Received March 20, 1969

α-Lactams. VII.[1] An Insertion-Type Alkylation on α-Lactams by Action of Alkylmagnesium Halides

Sir:

Reactions of α-lactams have been reported recently[1–5] which establish these compounds as useful intermediates in organic synthesis. The present communication is concerned with the action of alkylmagnesium halides

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