Photochemical Transformations in the 9-Heterobicyclo[3.3.1]nonenone System[1]

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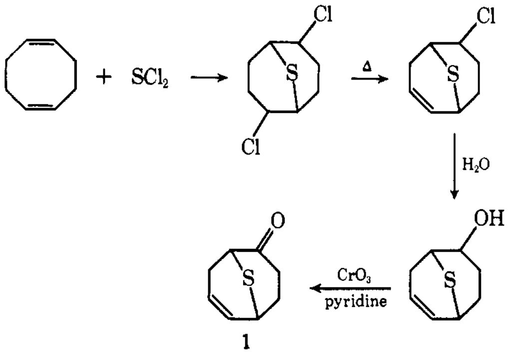
Abstract: 9-Thiabicyclo[3.3.1]non-6-en-2-one (**1**) and its 9-oxa analog have been found to rearrange principally to methyl 5,6-dihydro-2*H*-pyran-2-propionate derivatives upon irradiation in methanol. When the irradiation of the thia system was carried out in deuteriomethanol, the product formed was found to have incorporated the deuterium atom in the thiapyran portion of the molecule. Irradiation of the oxa analog in deuteriomethanol, however, gave ester which had the deuterium atom located adjacent to the carbonyl group. This result indicates that the thia system is significantly different from its oxa analog in its photobehavior and that carbonyl-sulfur interactions in the excited state play an important role in the photochemistry of cyclic β-keto sulfides. Wavelength and solvent effects were also observed in the photochemistry of **1**. Possible mechanistic pathways to the observed photoproducts are discussed.

Light-induced transformations of keto sulfides have been the subject of intensive study during the past several years.[3-14] The recent interest to be accorded such molecules is due in part to the unusual ultraviolet characteristics of these compounds. Past investigations of cyclic keto sulfides have shown that their uv spectra are substantially different from those of other saturated ketones.[15-19] This difference has been attributed to transannular interaction of a lone pair of electrons on sulfur with the carbonyl group, the coupling being strongly dependent on the orientation of the two groups.[20] Such interactions result both in the perturbation of the $n-\pi^*$ carbonyl frequency and in the appearance of a charge-transfer absorption band in the 240–270-mμ region. Of the various effects which can be ascribed to the $S-C_{CO}$ interaction, that which involves structural reorganization of the molecule in the excited state continues to attract widespread interest. As part of a general study on the photochemical transformations of heterocyclic ketones, it became our intent to investigate systems in which charge-transfer interactions lead to novel photochemical changes.[21,22] For reasons of synthetic accessibility and for its spectroscopic characteristics, 9-thiabicyclo[3.3.1]non-6-en-2-one (**1**) was chosen as a model substrate.[23] The present investigation began with three goals: first, a search for unusual photochemistry as a result of charge-transfer interaction of the two chromophores present in **1**; secondly, determination of the importance of wavelength and solvent effects in this system; and thirdly, exploration of the photochemical behavior of the related oxa system which is devoid of excited-state interaction of the two chromophores.

9-Thiabicyclo[3.3.1]non-6-en-2-one (**1**) was conveniently prepared by transannular addition of sulfur dichloride to 1,5-cyclooctadiene[24,25] followed by thermal dehydrochlorination, aqueous solvolysis, and Sarett oxidation. The uv spectrum of **1**, with λ_{max} at 253 and 305 mμ (290 and 275), indicates charge-transfer interaction and perturbation of the $n-\pi^*$ state of the carbonyl group. The location of a band at 253 mμ is typical of a $S-C_{CO}$ charge-transfer transition[16,20] and suggests effective electron transfer from divalent sulfur to the proximate carbonyl group in **1**. Such inter-



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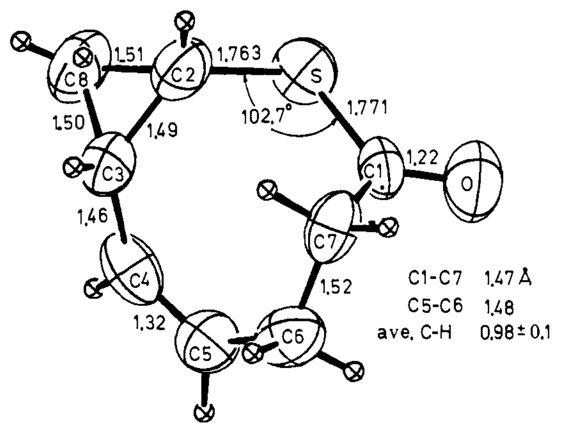
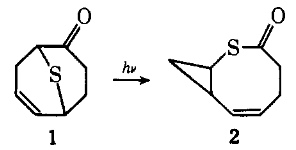


Figure 1. A view of 2-thiabicyclo[6.1.0]non-6-en-3-one showing pertinent intramolecular bonding parameters.

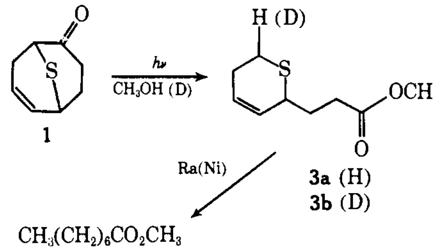
action is completely absent in the related 9-oxabicyclo[3.3.1]non-6-en-2-one (**16**) system. The inability of the related oxygen system to manifest transannular interaction is not surprising since the lone pair of electrons on oxygen is less polarized than those on sulfur and is not capable of being transferred transannularly to the carbonyl group. β-Keto sulfides are also known to exhibit abnormal n–π* absorption[15,19] ($\lambda_{\max} \sim 300$ mμ ($\epsilon \sim 200$)) relative to simple ketones. Interaction of the empty d orbitals on sulfur with the electron density localized on the carbonyl carbon in the n–π* singlet apparently lowers the transition energy. The forbiddenness of the transition is decreased somewhat due to a favorable inducement by the d orbitals on the transition probability. The ultraviolet absorption maxima of **1** did not show any dependence on solvent polarity (cyclohexane *vs.* 10% aqueous methanol). We cannot offer a simple explanation for this result, but can note similar invariance in the literature.[20]

Irradiation of **1** in dilute pentane solution using a Hanovia 450-W mercury arc with a Pyrex filter was followed by withdrawal of small aliquots at various time intervals and examination of these by vapor-phase chromatography. Careful monitoring of the course of the reaction indicated the formation of a lone photoproduct **2**. Chromatographic separation of the reaction residue gave pure **2** (35%) which was assigned as 2-thiabicyclo[6.1.0]non-6-en-3-one on the basis of its elemental analysis (isomeric with starting material) and spectral data. The infrared spectrum of **2** was characterized by bands at 3.32, 5.96, 8.81, and 10.40 μ. The presence of a cyclopropyl moiety was demonstrated by the absorption at 1.633 μ (ε 0.271) in the near-infrared.[26] The uv spectrum (95% ethanol) with maxima at 229 and 283 mμ (ε 8900 and 2100) is characteristic of a thiol ester.[27] The 100-MHz nmr spectrum (CDCl$_3$) showed three distinct cyclopropyl hydrogens at τ 9.25 (doublet of triplets, J = 7.0, 5.0 Hz), 8.48 (triplet of doublets, J = 8.5, 7.0 Hz), and 8.02 (multiplet). The fourth cyclopropyl hydrogen was part of a four-proton multiplet centered at τ 7.50 (two allylic hydrogens and one methylenic hydrogen). The remainder of the nmr spectrum consisted of a multiplet at τ 6.05 (1 H) and an AB quartet (with complex fine structure of the low-field proton) at 4.37 (2-vinyl H). These assignments for the spin–spin coupling interactions were tested through double-resonance experiments. When the broad envelope at τ 7.50 was saturated with an external field, the multiplet at 6.05 collapsed to a singlet and the vinyl region sharpened into a clean AB quartet. Saturation of the signal at τ 9.25 resulted in a simplification of the patterns at 8.48 and 8.02.

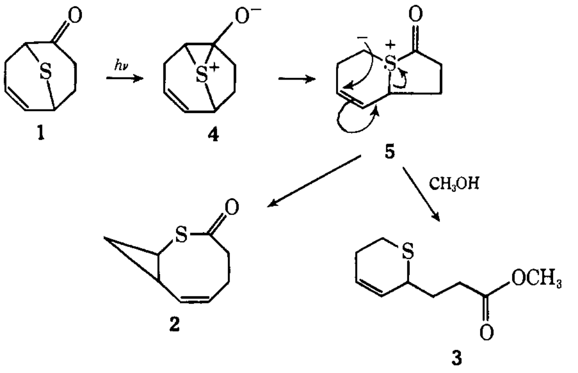


The structure of the photoproduct was unequivocably proved by a X-ray single-crystal structure analysis. The three-dimensional intensity data were measured by the stationary-counter–stationary-crystal method, using Cu Kα radiation and balanced filters (Ni *vs.* Co). A GE XRD-6 diffractometer equipped with a single-crystal orientator was utilized for the measurements. In the range of intensity measurements (0–110° in 2θ) 492 reflections of the 524 unique ones examined for the space group $P2_12_12_1$ had peak counts significantly greater than their respective background. The structure was derived from Patterson and Fourier syntheses and refined by least squares to an R value of 0.058 for all the data. The overall geometry of the molecule is shown in Figure 1.

Irradiation of **1** in methanol instead of pentane gave methyl 5,6-dihydro-2*H*-thiopyran-2-propionate (**3a**) as the major product (40%) together with small amounts of **2** (5%). Identification of ester **3a** is based on its hydrogenation (Raney Ni) to methyl octanoate coupled with its spectral data. Compound **3a** has infrared absorption for an ester (5.73, 8.25, 8.60) function and shows vinyl (τ 4.25, 2 H), methyl ester (τ 6.35, 3 H), allylic (τ 6.68, 1 H), and methylenic hydrogens (τ 7.70, 8 H) in the nmr. The mass spectrum of **3a** shows the



Mechanism A



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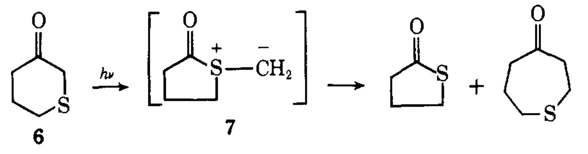
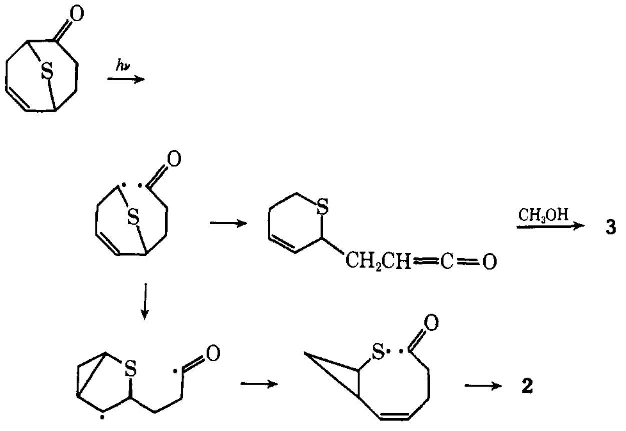
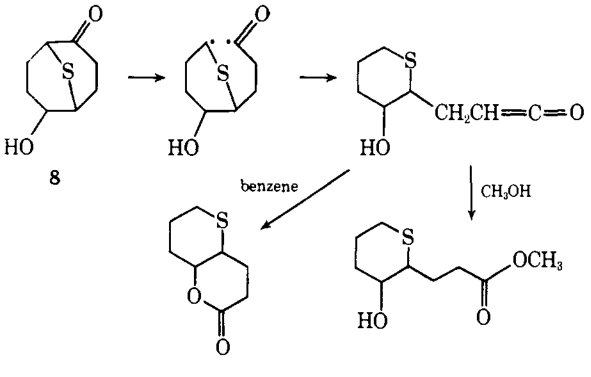
parent ion at *m/e* 186 and fragment ions at *m/e* 112 and 99 (base) in accord with expectation for the proposed structure.

Two structurally distinct mechanistic paths may be considered for the formation of products **2** and **3**. One mechanism (A) involves the formation of a charge-transfer structure such as **4** which can then undergo bond reorganization to the observed products *via* a ylide intermediate **5**. This mechanism is formally analogous to that observed by Berchtold and Maheshwari in the ring expansion–contraction reaction of thiacyclohexan-3-one (**6**).[13] These authors suggest ylide **7** as an intermediate in this methylene transfer reaction. An alternate route (B) that would rationalize the observed products would involve Norrish type I homolysis followed by diradical reorganization. Ganter and Moser [10] have in fact suggested that the products obtained from the irradiation of 9-thiabicyclo[3.3.1]-nonan-6-ol-2-one (**8**) proceed *via* Norrish type I cleavage (mechanism B) followed by internal hydrogen abstraction and subsequent ketene trapping. The formation of thiol ester **2** *via* mechanism B is also related to the α-cleavage–reclosure reaction of hexahydronaphthalen-2(1*H*)-one reported by Williams and Ziffer.[28]

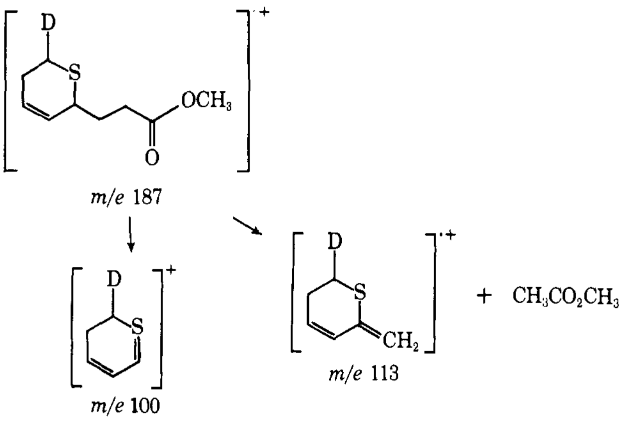


Mechanism B

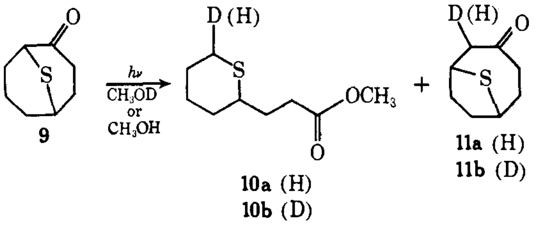




In order to distinguish between these two possible mechanisms, the irradiation of **1** was performed in deuteriomethanol. Under these conditions ester **3b**, containing >98% of one deuterium at C-6, as evidenced by mass spectroscopy (*i.e.*, *m/e* 187 (parent), 113 (P − $CH_3CO_2CH_3$), and 100 (base)) was isolated.[29] The fragmentation pattern excludes the structure where the deuterium atom is located adjacent to the carbonyl group. This observation *cannot* be interpreted in terms of the intermediacy of a ketene formed *via* Norrish type I cleavage (mechanism B), since the deuterium atom should appear α to the carbonyl group if this path was followed. This result, however, may be readily accommodated by mechanism A which involves formation of charge-transfer structure **5**.[30]



Efforts to firmly establish the generality of this path led us to examine the photochemistry of the reduced 9-thiabicyclo[3.3.1]nonan-2-one (**9**) system. β-Keto sulfide **9** (mp 155–156°) prepared by the catalytic reduction of **1** was irradiated in deuteriomethanol and gave ester **10** and ketone **11** as the major products.[30] The structure of **10** was established by its independent synthesis (catalytic reduction) from **3**. The mass spectrum of **10** clearly indicates that the deuterium atom is located on the thiapyran portion of the molecule. This product has prominent peaks at *m/e* 115 (corresponding to loss of methyl acetate) and 102 (base). The structure of **11a** (mp 148–149°) was elucidated on the basis of the physical and chemical data cited. The infrared spectrum of **11a** was characterized by bands at 3.41, 5.85, 7.41, and 8.96 μ. The nmr spectrum ($CDCl_3$) shows a two-proton multiplet at τ 6.30 and a ten-proton multiplet between 7.15 and 8.35. The mass spectrum of **11b** included peaks with *m/e* 157 (parent), 129, and 101. The deuterium adjacent to the carbonyl group could be readily washed out with potassium



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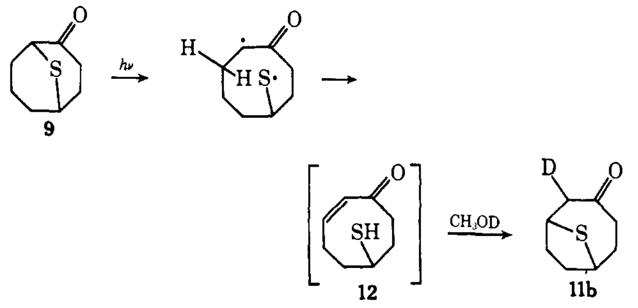
(28) J. R. Williams and H. Ziffer, *Chem. Commun.*, 194, 469 (1967).

(29) The location of the deuterium atom at C-6 of the thiapyran ring is not unambiguously established, although this location is most probable on mechanistic grounds.

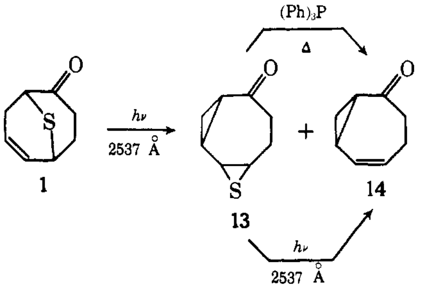
(30) Recovered starting material (**1** and/or **9**) was examined by nmr and mass spectroscopy; the spectra obtained gave no evidence for any incorporation of deuterium under both irradiative and nonirradiative conditions. Similarly, thiapyrans **3a** and/or **10a** did not incorporate deuterium under the reaction conditions.

carbonate in methanol. Chemical confirmation of structure **11** was obtained by reaction with Raney nickel. The product obtained was identical with an authentic sample of cyclooctanol.

The formation of compound **10** may be rationalized by a path analogous to the one outlined above (mechanism A) for ester **3**. The formation of **11** from **9** may be visualized as occurring by scission of the C–S bond followed by internal hydrogen abstraction and subsequent intramolecular cyclization of the transient intermediate **12**. This latter step may be either a ground-state or photoinduced process. This rationalization readily accommodates the incorporation of deuterium at the α position and is mechanistically similar to previous results encountered in the photochemistry of 2-oxo-6-hydroxy-9-thiabicyclo[3.3.1]nonane.[10]

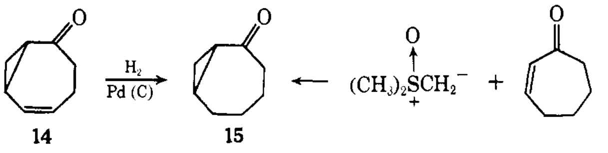


In order to check the wavelength dependence of these photoreactions, **1** was irradiated in pentane at 2537 Å with a low-pressure mercury arc to effect excitation *via* the charge-transfer band. Irradiation under these conditions gave only trace amounts of thiol ester **2** (2%). Preparative thick-layer chromatography of photolysis mixtures obtained from runs in pentane solution permitted the purification and isolation of two major components; in addition, a nonvolatile residue was formed. The products were identified as 3-thiatricyclo[6.6.0.0^{2,4}]nonan-7-one (**13**) (28%) and bicyclo[5.1.0]octan-2-one (**14**) (15%).



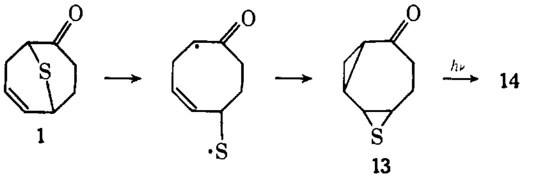
The major product was assigned structure **13** on the basis of its elemental analysis, molecular weight (*m/e* 154), spectral data, and subsequent desulfurization with triphenylphosphine to **14**. The infrared spectrum (neat) shows a strong carbonyl band at 5.95 μ. The presence of a cyclopropyl moiety was demonstrated by the absorption at 1.624 μ (ϵ 0.20) in the near infrared. The 100-MHz nmr spectrum ($CDCl_3$) showed three distinct cyclopropyl hydrogens at τ 9.10 (doublet of triplets, J = 6.5, 5.0 Hz, 1 H) 8.75 (triplet of doublets, J = 10, 8.5, 5.0 Hz, 1 H), and 8.20 (multiplet, 2 H). The remainder of the nmr spectrum consisted of multiplets at τ 7.60 (four methylenic protons), 6.70 (1 H), and a triplet at 6.38 (J = 7.0, 4.0 Hz). When the multiplet at τ 8.20 was saturated with an external field the triplet at 6.38 collapsed to a doublet. Saturation of the signal at τ 7.60 collapsed the multiplet at 6.70 into a sharp doublet. Irradiation of the triplet at τ 6.38 resulted in a simplification of the pattern at 8.20.

The minor product was shown to be bicyclic ketone **14**. In agreement with this formulation, this substance exhibited a mass spectral molecular ion peak at *m/e* 122, an intense infrared (neat) carbonyl stretching band at 5.95 μ, and a compatible nmr spectrum (see Experimental Section). Conclusive evidence for this structure was derived by catalytic hydrogenation. The product obtained was identical with an authentic sample of bicyclo[5.1.0]octan-2-one (**15**) prepared from cycloheptenone and dimethylsulfoxonium methylide.



During several irradiation runs an increase in the amount of **14** at the expense of **13** was encountered and we therefore undertook an investigation of the photochemistry of **13**. On irradiation at 2537 Å, **13** was transformed to **14** in high yield. Therefore, it appears that **14** is not a primary photoproduct of **1**, but results preponderantly, if not exclusively, by desulfurization of **13**.

The products formed by photolysis with 2537-Å light are consistent with homolytic cleavage of the C–S bond followed by diradical addition to the adjacent double bond to form product **13** which on further irradiation produces **14**. The formation of **14** from **13** is analogous to the photochemical behavior of other substituted episulfides.[31]



A number of reports have appeared in the literature where substantial structural changes occur in the photochemistry of certain compounds by varying the wavelength of exciting light.[14,32–35] 9-Thiabicyclo[3.3.1]non-6-en-2-one (**1**) appears to be another example of a system which displays a remarkable dependence on the wavelength of exciting light. The energy band of **1** at 253 mμ, previously interpreted as a charge-transfer band, may also have a significant amount of n–σ^* character associated with the sulfur atom. The fact that C–S bond scission is the major process at 2537 Å indicates that intermolecular and/or intramolecular energy transfer from the n,σ^* state (or charge-transfer state) to the n,π^* state of the carbonyl group is inefficient and that scission of the C–S bond is a rapid

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[31] A. Padwa, D. Crumrine, and A. Shubber, *J. Amer. Chem. Soc.*, **88**, 3064 (1966).

[32] E. F. Ullman and B. Singh, *ibid.*, **88**, 1844 (1966); **89**, 6911 (1967); E. F. Ullman, *Accounts Chem. Res.*, **1**, 353 (1968).

[33] R. W. Hoffmann and K. R. Eicken, *Tetrahedron Lett.*, 1759 (1968).

[34] H. Wehrli, C. Lehmann, P. Keller, J. J. Bonet, K. Schaffner, and O. Jeyer, *Helv. Chim. Acta*, **49**, 2218 (1966).

[35] J. Streith and J. M. Cassal, *C. R. Acad. Sci. Paris, Ser. C*, **264**, 1307 (1967).

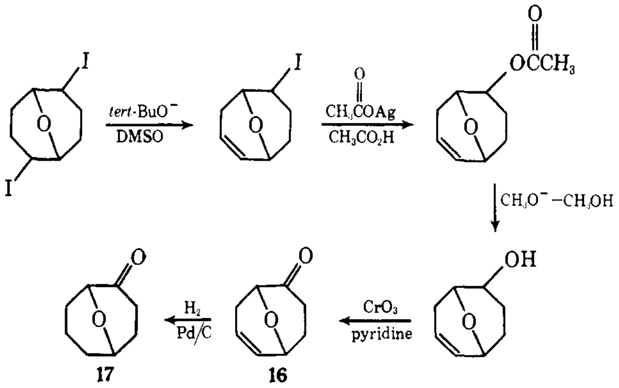
process. Alternatively, it could be argued that the short-wavelength irradiation is a dissociative process which occurs instantaneously upon excitation. The small amount of thiol ester **2** (2%) produced on irradiation at 2537 Å may be the result of stray 3100-Å light associated with the 2537-Å fluorescent lamps used.

In order to determine whether wavelength variation can have an effect on the distribution of deuterium in ester **3**, 9-thiabicyclo[3.3.1]non-6-en-2-one (**1**) was irradiated in deuteriomethanol at 2537 Å. Under these conditions, ester **3b** was isolated in low yield (6%). The mass spectrum of pure **3b**, isolated by preparative glpc, clearly established the location of deuterium at C-6, in agreement with results previously encountered at 3100 Å. This observation indicates that wavelength variation fails to alter the mode of formation of ester **3**.

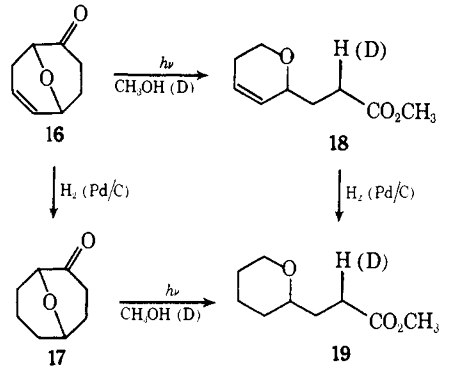
The quantum yields for appearance of products **2** (Φ = 0.16 at 3100 Å in pentane) and **3** (Φ = 0.05 at 3100 Å in methanol) were determined using benzophenone–benzhydrol actinometry.[36] Degassed and sealed Pyrex tubes containing solutions of **1** were irradiated along with actinometer tubes in the rotating photochemical assembly. The light from a 450-W Hanovia lamp was filtered through a nickel–cobaltous sulfate solution. Reactions were carried to low conversions to prevent appreciable light absorption by products and yields of product were determined by glpc using internal standards. The photolysis of **1** in pentane or methanol does not appear to be sensitized by acetone nor was it quenched by naphthalene or piperylene. At the concentrations used piperylene is known to be a good triplet quencher[37] but only a poor singlet quencher.[38] These results suggest the photorearrangement of **1** to **2** or **3** proceeds *via* the excited singlet state of **1**.

At this point we recognized that the influence of the heteroatom on the photochemistry of 9-heterobicyclo[3.3.1]non-2-ones needed to be assessed. We therefore turned our attention to the related oxa system in order to make a comparison with the photochemistry of the above β-keto sulfides. In the present instance, the photochemical behavior of 9-oxabicyclo[3.3.1]non-6-en-2-one (**16**) and 9-oxabicyclo[3.3.1]nonan-2-one (**17**) was examined. 9-Oxabicyclo[3.3.1]non-6-en-2-one (**16**) was synthesized from 2,5-diiodo-9-oxabicyclo[3.3.1]nonane[39] by dehydrohalogenation followed by reaction with silver acetate, hydrolysis, and oxidation. Catalytic reduction of **16** afforded ketone **17** in good yield. These operations are summarized in Chart I.

Chart I



A critical difference between the two systems under consideration is that the oxa system is devoid of an excited state interaction of the two chromophores (uv (95% ethanol) of **16**, 290 mμ (ϵ 35); **17**, 300 mμ (ϵ 20)). Irradiation of **16** in methanol afforded ester **18** in high yield. Similarly, irradiation of **17** gave ester **19** as the sole photoproduct. The structure of **19** was established by its analytical and spectral data as well as by an independent synthesis which involved treatment of tetrahydropyran 2-methyl bromide with sodium ethyl malonate followed by hydrolysis and esterification. Of specific interest was the observation that irradiation of **16** (or **17**) in deuteriomethanol gave ester **18** (or **19**) in which the deuterium atom was located adjacent to the carbonyl group as evidenced by mass spectroscopy (*i.e.*, fragment peaks for **18** appear at *m*/*e* 96 (P − $CH_2DCO_2CH_3$) and 83 (base)). This result may be rationalized by initial formation of a ketene *via* Norrish type I cleavage and internal disproportionation (see mechanism B above). The behavior of the oxa system is substantially different from the thia system and suggests that carbonyl–sulfur interactions in the excited state play an important role in the photochemistry of cyclic β-keto sulfides.



Experimental Section[40]

9-Thiabicyclo[3.3.1]non-6-en-2-one (1). To a solution of 31 g of chromium trioxide in 450 ml of pyridine at 0° was added a solution of 15.6 g of 9-thiabicyclo[3.3.1]non-6-en-2-ol[25] in 50 ml of pyridine. The mixture was stirred for 1 hr and was then allowed to stand at room temperature for an additional 20 hr. At the end of this time 1000 ml of ether was added to the mixture and the insoluble salts were removed by filtration. The filtrate was washed five times with 500 ml of a 5% hydrochloric acid solution and the ethereal layer was dried over magnesium sulfate. The solvent was removed under reduced pressure to give 4.4 g (28%) of a viscous yellow oil. The oil was crystallized from pentane to give 3.5 g (23%) of a colorless solid, mp 79–81°. The infrared spectrum (potassium bromide

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(36) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961).

(37) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).

(38) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *ibid.*, **88**, 3665 (1966).

(39) A. C. Cope, M. A. McKervey, and N. M. Weinshenker, *J. Org. Chem.*, **34**, 2229 (1969).

(40) All melting points are corrected and boiling points uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 MHz with the Varian Associates high-resolution spectrometer. Tetramethylsilane was used as an internal standard.

Table I. Final Least-Squares Parameters for Nonhydrogen Atoms of 2-Thiabicyclo[6.1.0]non-6-en-3-one with Respective Standard Deviations in Parentheses × 10^4

Name	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	1846 (1)	519 (3)	2500 (1)	81 (1)	328 (5)	123 (2)	−41 (4)	44 (4)	41 (7)
O	657 (5)	3759 (9)	2067 (6)	151 (7)	335 (16)	156 (8)	8 (17)	−27 (12)	136 (18)
C-1	636 (6)	2148 (10)	2678 (7)	90 (6)	222 (16)	80 (8)	−27 (15)	−13 (11)	−79 (20)
C-2	1481 (7)	−1665 (12)	3433 (9)	89 (6)	265 (21)	136 (10)	71 (20)	13 (13)	15 (24)
C-3	1386 (6)	−1519 (11)	4848 (8)	94 (7)	276 (20)	118 (9)	74 (20)	−7 (13)	42 (24)
C-4	1527 (7)	409 (13)	5575 (8)	85 (6)	417 (26)	86 (7)	−102 (21)	−29 (12)	50 (25)
C-5	880 (7)	2100 (11)	5575 (8)	100 (6)	269 (21)	116 (9)	−55 (19)	1 (13)	−12 (23)
C-6	−171 (6)	2519 (13)	4831 (9)	98 (7)	318 (21)	142 (10)	16 (22)	58 (15)	−35 (28)
C-7	−307 (6)	1535 (12)	3525 (8)	58 (5)	268 (19)	152 (10)	22 (17)	−24 (13)	83 (24)
C-8	2409 (8)	−2571 (14)	4275 (10)	122 (8)	355 (25)	181 (12)	183 (25)	23 (17)	80 (36)

pellet) showed major bands at 2.94, 3.45, 5.82, 7.00, 8.87, 11.13, and 12.95 μ. The nmr spectrum ($CDCl_3$) displayed peaks at τ 3.86 (2 H, m), 6.65 (2 H, m), and 7.54 (6 H, m). The ultraviolet spectrum exhibited peaks at 305 and 250 nm (ε 275, 290). The mass spectrum showed the molecular ion at *m/e* 154 and had major bands at *m/e* 112, 110, 99, 98, 97 (base), and 79.

Anal. Calcd for $C_8H_{10}SO$: C, 62.39; H, 6.54; S, 20.82. Found: C, 62.13; H, 6.50; S, 20.51.

Irradiation of 9-Thiabicyclo[3.3.1]non-6-en-2-one (1) in Pentane. A sample of 0.77 g of **1** in 1 l. of pentane was irradiated with a 450-W Hanovia mercury lamp using a Pyrex filter for 20 hr. The solution was filtered to remove an amorphous polymer and the solvent was removed under reduced pressure. The yellow oil obtained was chromatographed on a Florisil column (12 × $^1/_2$ in.). The column was eluted with benzene and the clear oil obtained solidified on cooling. The solid isolated was recrystallized twice from pentane to give 0.16 g (20%) of 2-thiabicyclo[6.1.0]non-6-en-3-one (**2**) as colorless needles, mp 44–45°. The infrared spectrum (potassium bromide pellet) showed major bands at 3.32 and 3.44 (doublet), 5.96, 6.92, 8.81, 9.20, 9.50, 9.81, 10.00, and 10.40 μ. The 100-MHz nmr spectrum ($CDCl_3$) showed three distinct cyclopropyl hydrogens at τ 9.25 (doublet of triplets, *J* = 7.0, 5.0 Hz), 8.48 (triplet of doublets, *J* = 8.5, 7.0 Hz), and 8.02 (multiplet). The fourth cyclopropyl hydrogen was part of a four-proton multiplet centered at τ 7.50 (two allylic hydrogens and one methylenic hydrogen). The remainder of the nmr spectrum consisted of a multiplet at τ 6.05 (1 α H) and an AB quartet (with complex fine structure of the low-field proton) at 4.37 (2-vinyl H). The peak areas are in the ratio of 1:1:1:4:1:2. The ultraviolet spectrum (95% ethanol) displayed bands at 229 (ε 8950) and 283 nm (ε 2100). The mass spectrum exhibited the molecular ion at *m/e* 154 and had major peaks at 112, 110, 97, 85, 79 (base), 77, and 67. The near-infrared spectrum ($CHCl_3$) showed a peak at 1.633 μ (ε 0.271). The structure of the product was unequivocally established as 2-thiabicyclo[6.1.0]non-6-en-3-one on the basis of an X-ray single-crystal structure analysis.

Anal. Calcd for $C_8H_{10}SO$: C, 62.39; H, 6.54; S, 20.82. Found: C, 62.28; H, 6.58; S, 20.65.

X-Ray Single-Crystal Structure Analysis of 2-Thiabicyclo[6.1.0]non-6-en-3-one (2). 2-Thiabicyclo[6.1.0]non-6-en-3-one crystallized from pentane as needles. The crystal data obtained are: $a = 11.693 \pm 0.002$, $b = 10.462 \pm 0.002$, and $c = 6.4303 \pm 0.001$ Å, space group $P2_12_12_1$, $d_m = 1.30 \pm 0.01$ g/cm^3 (by flotation $ZnCl_2$), $d_c = 1.29$ g/cm^3, and $Z = 4$ molecules. The cell dimensions and intensity data were measured on a General Electric Model XRD-6 spectrogoniometer and goniostat using a scintillation counter and Cu Kα radiation. The intensities were collected by the stationary counter–stationary crystal method[41] using balanced filters for the copper radiation (Ni *vs.* Co). A crystal fragment (approximate size 0.03 mm × 0.15 mm × 0.15 mm) was mounted in a capillary about the *c* axis. In the range of the intensity measurements (0–110° in 2θ) 492 reflections of the 524 unique ones examined for the space group $P2_12_12_1$ had peak counts significantly greater than their respective backgrounds. Lorentz and polarization factors were applied to these data as well as a correction for the $\alpha_1 - \alpha_2$ splitting (analogous to that applied by Tulinsky, *et al.*[42]). The data were also adjusted for the anisotropy of transmission about the φ axis as a way of correcting absorption. This factor was determined by measuring the intensity of the 0.0.3 reflection at $\chi = 90°$ as a function of the angle φ. The structure factors were put on an absolute scale by use of Wilson statistics.[43]

The position of the sulfur atom was readily derived from a three-dimensional Patterson synthesis.[44] Subsequent electron density maps, calculated first with the phases of the structure factors based on the sulfur position, enabled the positions of all the nonhydrogen atoms to be found. The positional and thermal parameters of these atoms were refined by least squares using a block diagonal approximation to the normal least-squares equations. A three-dimensional difference electron density synthesis, calculated after anisotropic temperature factors had been introduced and after *R* (usual discrepancy index) was 0.076, showed positive regions where hydrogens were expected. These positions were then refined in the final cycles of least squares with isotropic temperature factors. The weighting scheme used in the latter stages of the refinement was $\text{wt}^{-1} = ((|F_o| - 2.5)/20)^2 + 1$, such that $\langle \text{wt}\Delta^2 \rangle$ was relatively constant over the whole range of the $|F_o|$'s. The unobserved data were given zero weight. The final *R* value was 0.050 for the observed data, and the "goodness of fit" ($\text{wt}\,\Delta^2/m - n$), 1.03.

In all of the above calculations the atomic form factors utilized were those of Cromer and Waber,[45] except for those of hydrogen. The sulfur atom was corrected for the real part of the anomalous scattering curve. Tables I and II showed the final least-squares parameters for the various atoms. The estimated standard deviations (esd's) were calculated from the inverse of the full normal equation blocks. The esd's for the bond lengths and angles between the nonhydrogen atoms are on the average 0.011 Å and 0.5°, respectively. The hydrogen atoms were found to have standard deviations about ten times greater than the other atoms, which precludes any detailed discussion of them.

Table II. Positional Parameters and Estimated Standard Deviations in Parentheses for Hydrogen Atoms × 10^3

Name	x/a	y/b	z/c	B_{iso}, Å^2
H-1	114 (7)	−253 (13)	297 (7)	6.6 (2.0)
H-2	333 (10)	−197 (23)	422 (16)	16.5 (4.8)
H-3	228 (8)	−393 (16)	450 (11)	9.5 (2.5)
H-4	78 (5)	−246 (10)	512 (7)	4.5 (1.5)
H-5	222 (5)	63 (8)	609 (6)	2.7 (1.2)
H-6	114 (6)	323 (11)	624 (9)	6.3 (1.9)
H-7	−89 (7)	163 (16)	523 (11)	9.3 (2.5)
H-8	−26 (7)	382 (14)	462 (9)	7.5 (2.2)
H-9	−84 (5)	199 (9)	306 (6)	3.6 (1.4)
H-10	−35 (6)	−3 (12)	372 (7)	5.6 (1.7)

Irradiation of 9-Thiabicyclo[3.3.1]non-2-en-6-one (1) in Methanol. A solution of 250 mg of **1** in 500 ml of absolute methanol was irradiated with an internal water-cooled mercury arc lamp (Hanovia Type L, 450 W) with a Pyrex filter to eliminate wavelengths below 280 mμ. At the end of 24 hr the solvent was removed under reduced pressure and the oil obtained was subjected to preparative gas chromatography using a 10% FS-1265 column (12 ft × $^3/_8$ in.) on Diataport S at 160°. The structure of the major product

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(41) T. F. Furnas and D. Harker, *Rev. Sci. Instrum.*, 26, 449 (1955).

(42) A. Tulinsky, C. R. Wrothington, and E. Pignataro, *Acta Crystallogr.*, 12, 623 (1959).

(43) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination, A Practical Guide," Macmillan, New York, N. Y., 1968, p 205.

(44) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

(45) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

eluted from the vpc column was assigned as methyl 5,6-dihydro-2*H*-thiopyran-2-propionate (**3**) (30%). The infrared spectrum (neat) was characterized by bands at 3.42, 5.73, 6.91, 7.25, 7.89, 8.25, 8.60, and 13.88 μ. The mass spectrum showed the parent ion at 186 and had major peaks at 126, 112, and 99. The nmr spectrum ($CDCl_3$) showed a two-proton multiplet at τ 4.25, a three-proton singlet at 6.35, a one-proton multiplet at 6.68, and an eight-proton multiplet centered at 7.70.

Anal. Calcd for $C_9H_{14}SO_2$: C, 58.05; H, 7.58. Found: C, 58.05; H, 8.00.

Chemical confirmation of this structure was obtained by hydrogenation with Raney nickel to methyl octanoate. A mixture of 20 mg of methyl 5,6-dihydro-2*H*-thiopyran-2-propionate, 10 mg of W-2 grade Raney Ni, and 2.5 ml of absolute ethanol was heated at reflux for 12 hr. The catalyst was removed by filtration and the solvent removed under reduced pressure. The resultant oil was subjected to preparative gas chromatography using a 12 ft × $^3/_8$ in. FS-1265 column on Diataport S at 150°. The infrared and mass spectra of the major component (90%) were identical with an authentic sample of methyl octanoate.

Irradiation of 9-Thiabicyclo[3.3.1]non-6-en-2-one in Pentane at 2537 Å. A solution of 2.0 g of **1** in 2 l. of freshly distilled pentane was irradiated for 5 hr using a large quartz tube (2 in. × 16 in.) with ten 15-W low-pressure mercury arc lamps. A significant quantity (*ca.* 500 mg) of a polymeric solid formed during the irradiation and it was necessary to filter the solution several times as the solvent was being removed. The yellow oil obtained on removal of the solvent was subjected to preparative thick-layer chromatography. Elution with a 1:1 mixture of pentane–ether afforded two bands, which were taken up in acetone. Removal of the solvent from the upper band gave recovered starting material. The lower band contained 0.5 g (25%) of a pale yellow oil which was identified as 3-thiatricyclo[6.1.0.0^{2,4}]nonan-7-one (**13**) on the basis of the following physical and chemical data. The infrared spectrum (neat) was characterized by bands at 5.95, 7.35, 7.45, 8.81, and 14.72 μ. The presence of a cyclopropyl moiety was demonstrated by the absorption at 1.624 μ (ϵ 0.20) in the near-infrared. The mass spectrum showed the parent ion at *m/e* 154 and had major bands at *m/e* 85, 80, 77, 65, 55, and 43. The 100-MHz nmr spectrum ($CDCl_3$) showed a one-proton doublet of doublets at τ 6.38, a one-proton quartet at 6.70, a four-proton multiplet centered at 7.60, a two-proton multiplet at 8.20, a one-proton multiplet at 8.75, and a one-proton multiplet centered at 9.10.

Anal. Calcd for $C_8H_{10}OS$: C, 62.39; H, 6.54. Found: C, 62.04; H, 6.78.

Chemical confirmation of this structure was obtained by ring desulfurization of **13** to bicyclo[5.1.0]oct-5-en-2-one (**14**) by reaction with triphenylphosphine. A mixture of 50 mg of **13** and 50 mg of triphenylphosphine in benzene was refluxed for 12 hr. Removal of the solvent under reduced pressure left a crude oil which was subjected to preparative gas chromatography using a $^3/_8$ in. × 12 ft FS-1265 (8%) on Diataport S at 170°. The colorless liquid obtained on collection was identified as bicyclo[5.1.0]oct-5-en-2-one. The 2,4-dinitrophenylhydrazone derivative had mp 177–178°. The infrared spectrum (neat) of **14** showed bands at 5.95, 7.32, and 8.20 μ. The mass spectrum showed the molecular ion at *m/e* 122 and had major peaks at 80 (base), 79, and 77. The nmr spectrum ($CDCl_3$) showed a doublet of doublets at τ 4.12 (1 H), a doublet of triplets at 4.40 (1 H), and multiplets centered at 7.65 (5 H), 8.29 (1 H), 8.55 (1 H), and 8.85 (1 H).

Anal. Calcd for $C_{14}H_{14}N_4O_4$: C, 55.62; H, 4.67. Found: C, 55.86; H, 4.64.

The structure of this product was further confirmed by catalytic hydrogenation. A mixture of 25 mg of **14**, 10 ml of ethyl acetate, and 25 mg of Adams catalyst was subjected to hydrogenation at atmospheric pressure in a Paar shaker. The catalyst was removed by filtration and the solvent was evaporated under reduced pressure. The oil obtained was purified by preparative gas chromatography and was identical in all respects with an authentic sample of bicyclo[5.1.0]octan-2-one (**15**) prepared from cycloheptenone and dimethylsulfoxonium methylide as described below.

Bicyclo[5.1.0]octan-2-one. To a solution of dimethylsulfoxonium methylide[46] in dimethyl sulfoxide was added 2.0 g of cycloheptenone[47] in 10 ml of dimethyl sulfoxide. The mixture was allowed to stir at room temperature for 4 hr and then at 50° for an additional hour. At the end of this time the reaction mixture was poured into 80 ml of water and extracted three times with 100-ml portions of ether. The combined ether extracts were washed with water and dried over magnesium sulfate. The solvent was removed to give 1.6 g of a crude oil which was distilled through a short column to give 1.2 g (49%) of bicyclo[5.1.0]octan-2-one, bp 40–41° (0.2 mm). The 2,4-dinitrophenylhydrazone derivative had mp 188–189°. The infrared spectrum (CCl_4) of **15** showed bands at 3.42, 5.92, 6.88, 7.32, 8.35, and 11.48 μ. The mass spectrum showed the parent ion at *m/e* 124 and had major bands at 81, 80, 55 (base), and 54. The nmr spectrum ($CDCl_3$) showed a two-proton triplet at τ 7.60 and a ten-proton multiplet at 8.50.

Anal. Calcd for $C_{14}H_{16}N_4O_4$: C, 55.25; H, 5.30; N, 18.41. Found: C, 55.08; H, 5.24; N, 18.27.

9-Thiabicyclo[3.3.1]nonan-2-one (9). To a solution of 500 mg of **1** in 200 ml of absolute methanol was added 1.0 g of 5% palladium on charcoal. The mixture was hydrogenated using a Paar shaker at 50 psi for 24 hr. The catalyst was removed by filtration and the solvent evaporated under reduced pressure. The white solid obtained was recrystallized from hexane to give 372 mg of 9-thiabicyclo[3.3.1]nonan-2-one (**9**) as colorless crystals, mp 154–156°. The infrared spectrum (KBr) had bands at 3.45 and 5.89 μ. The ultraviolet spectrum (methanol) had maxima at 251 and 304 nm (ϵ 300, 250). The mass spectrum showed the parent ion at *m/e* 156 and had prominent peaks at 128, 100, 94, 85, and 67 (base). The nmr spectrum ($CDCl_3$) showed multiplets centered at τ 6.90 (2 H) and 7.50–8.50 (10 H).

Anal. Calcd for $C_8H_{12}OS$: C, 61.52; H, 7.75; S, 20.18. Found: C, 61.43; H, 7.78; S, 20.28.

Irradiation of 9-Thiabicyclo[3.3.1]nonan-2-one in Methanol. A solution of 300 mg of **9** in 500 ml of methanol was irradiated using a 550-W Hanovia lamp with a Pyrex filter for 15 hr. At the end of this time the solvent was evaporated under reduced pressure and the oil obtained was placed on a preparative thick layer plate. The plate was developed using 1:1 pentane–ether mixture and the two new bands (R_f = 0.6 and 0.4) formed were extracted with acetone. The first band amounted to 45 mg and was assigned as methyl tetrahydro-2-thiopyran-2-propionate (**10**) on the basis of the following data. The infrared spectrum (neat) showed major bands at 3.42, 5.77, and 6.94 μ. The nmr spectrum ($CDCl_3$) displayed a three-proton singlet at τ 6.38, a five-proton multiplet centered at 7.50, and an eight-proton multiplet centered at 8.30. The mass spectrum showed the molecular ion at *m/e* 188 and had major bands at 157, 114 (base), 101, 87, 67, 59, and 55.

Anal. Calcd for $C_9H_{16}O_2S$: C, 57.43; H, 8.57; S, 16.00. Found: C, 57.07; H, 8.67; S, 16.30.

Chemical confirmation of this structure was obtained by Raney–Ni hydrogenation to methyl octanoate by a procedure analogous to that described for methyl 5,6-dihydro-2*H*-thiopyran-2-propionate (**3**).

Methyl tetrahydro-2-thiopyran-2-propionate (**10**) could also be prepared by catalytic reduction of methyl 5,6-dihydro-2*H*-thiopyran-2-propionate (**3**). A mixture of 50 mg of **3** and 20 mg of 5% palladium-on-carbon was hydrogenated at 50 psi using a Parr shaker. The catalyst was removed by filtration and the solvent was evaporated under reduced pressure to give a pale yellow oil. The infrared and mass spectra of this compound were identical in all respects with that of methyl tetrahydro-2-thiopyran-2-propionate (**10**) obtained from the irradiation of 9-thiabicyclo[3.3.1]nonan-2-one.

9-Thiabicyclo[4.2.1]nonan-3-one (11). The second band isolated from the above thick layer plate (40 mg) was recrystallized from hexane to give colorless needles, mp 148–149°. This material was identified as 9-thiabicyclo[4.2.1]nonan-3-one (**11**) on the basis of the following data. The infrared spectrum ($CHCl_3$) showed major bands at 3.42 and 5.90 μ. The mass spectrum showed the molecular ion at *m/e* 156 (base) and had major bands at 128, 113, 100, 85, and 55. The ultraviolet spectrum (95% ethanol) exhibited bands at 320 and 231 nm (ϵ 90, 570). The nmr spectrum ($CDCl_3$) showed multiplets at τ 6.30 (2 H) and 7.15–8.40 (10 H).

Anal. Calcd for $C_8H_{12}OS$: C, 61.52; H, 7.75; S, 20.18. Found: C, 61.39; H, 7.68; S, 20.16.

Chemical confirmation of this structure was obtained by hydrogenation with Raney–Ni to cyclooctanol. A mixture of 20 mg of **11**, 250 mg of Raney nickel (W-2), and 25 ml of absolute ethanol was refluxed with stirring for 12 hr, and then filtered, and the filtrate was evaporated to dryness. The infrared and mass spectra of the residue were identical in every detail with those of cyclooctanol.

9-Oxabicyclo[3.3.1]non-6-en-2-one (16). To 9.45 g of 2,6-diiodo-9-oxabicyclo[3.3.1]nonane[37] in 350 ml of dimethyl sulfoxide was added 3.0 g of potassium *tert*-butoxide. The resulting mixture

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[46] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).

[47] E. W. Garbish, Jr., *J. Org. Chem.*, 30, 2109 (1965).

was heated at 90–100° for 12 hr. The resulting orange solution was cooled, poured onto 500 ml of water, and extracted three times with 300-ml portions of water and then dried over magnesium sulfate. Evaporation of the solvent under reduced pressure gave 6.25 g of crude 2-iodo-9-oxabicyclo[3.3.1]non-6-ene which was distilled under reduced pressure to give 4.5 g (72%) of a pale yellow oil, bp 95–97° (1.4 mm).

Anal. Calcd for $C_8H_{11}OI$: C, 38.42; H, 4.43; I, 50.75. Found: C, 38.58; H, 4.40; I, 50.57.

To 3.75 g of the above 2-iodo-9-oxabicyclo[3.3.1]non-6-ene in 175 ml of glacial acetic acid was added 2.5 g of silver acetate. The mixture was stirred at room temperature for 20 hr. At the end of this time the precipitated silver iodide was removed by filtration and the filtrate was concentrated under reduced pressure to 10–15 ml. The resulting residue was dissolved in 200 ml of ether and washed two times with 150-ml portions of saturated sodium bicarbonate solution. The ethereal layer was dried over magnesium sulfate and evaporated *in vacuo* to give 1.96 g (73%) of a crude oil. Distillation of the oil gave 1.74 g (65%) of 2-acetoxy-9-oxabicyclo[3.3.1]non-6-ene as a clear liquid, bp 95–97° (1.4 mm). The infrared spectrum (neat) showed major bands at 5.73, 7.31, 8.05 (strongest), 9.40, and 9.66 μ.

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 66.29; H, 7.65.

To 250 ml of a 0.1% sodium methoxide–methanol solution was added 9.1 g of the above acetate. The resulting solution was stirred at room temperature for 3 hr. The solvent was removed under reduced pressure and the product formed was distilled to give 5.0 g (72%) of 9-oxabicyclo[3.3.1]non-6-en-2-ol as a clear oil, bp 105–106° (1.4 mm). The infrared spectrum (neat) showed major bands at 3.0, 3.48, 9.28, 9.45, 9.70, 10.30, 11.15, 11.38, 12.28, and 14.05 μ. The nmr spectrum ($CDCl_3$) displayed a two-proton multiplet at τ 4.40, a three-proton broad envelope centered at 6.15, a one-proton singlet at 6.95, a two-proton multiplet at 7.75, and a four-proton multiplet at 8.32. The mass spectrum showed the molecular ion at *m*/*e* 140 and had major bands at 81, 68, and 67 (base).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.22; H, 8.71.

To 6.47 g of the above alcohol in 400 ml of acetone at 0° was added, with vigorous stirring, 12 ml of Jones reagent (2.65 *M* CrO_3 solution) over a 1-hr period. The mixture was poured into 500 ml of water and extracted three times with 300-ml portions of ether. The combined ethereal extracts were dried over magnesium sulfate and evaporated under reduced pressure to give 4.9 g (75%) of a pale yellow oil. Distillation of the oil, bp 73–75° (1.4 mm), gave 4.3 g (65%) of 9-oxabicyclo[3.3.1]non-6-en-2-one as a clear liquid. A 2,4-dinitrophenylhydrazone derivative was prepared and recrystallized from 95% ethanol, mp 150.5–152°. The infrared spectrum (neat) showed major bands at 2.46, 5.81, 9.34, and 11.11 μ. The nmr spectrum ($CDCl_3$) showed multiplets at τ 4.0 (2 H), 5.55 (2 H), and 7.70 (6 H). The ultraviolet spectrum (absolute ethanol) showed λ_{max} at 261 nm (ϵ 79). The mass spectrum showed the molecular ion at *m*/*e* 138 and had major bands at 94, 81 (base), 79, 68, and 67.

Anal. Calcd for $C_{14}H_{11}N_4O_5$: C, 52.83; H, 4.43; N, 17.60. Found: C, 52.55; H, 4.63; N, 17.52.

Irradiation of 9-Oxabicyclo[3.3.1]non-6-en-2-one (16) in Methanol. A solution of 500 mg of **16** in 1 l. of methanol was irradiated at room temperature with a Hanovia 550-W mercury arc lamp using a Pyrex filter to eliminate wavelengths below 280 mμ. At the end of 70 hr the solution was evaporated under reduced pressure to give 400 mg of a clear oil. This material was distilled to give 150 mg (30%) of methyl 5,6-dihydro-2*H*-pyran-2-propionate (**18**) as a colorless oil, bp 60–61° (1.0 mm). The infrared spectrum (neat) showed major bands at 3.45, 5.75, 6.96, 7.96, 8.58, and 9.19 μ. The mass spectrum showed the molecular ion at *m*/*e* 170 and had peaks at 139, 138, 110, 96, and 83 (base). The nmr spectrum ($CDCl_3$) had multiplets centered at τ 4.30 (2 H), 6.20 (3 H), and 7.50–8.40 (6 H), and a singlet at 6.37 (3 H).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.81; H, 8.08.

The structure of the photoproduct was confirmed by catalytic reduction to methyl tetrahydro-2-pyran-2-propionate (**19**). A mixture of 150 mg of methyl 5,6-dihydro-2*H*-pyran-2-propionate, 80 mg of 5% palladium-on-barium sulfate and 10 ml of methanol was hydrogenated at 50 psi in a Paar shaker at 30° for 20 hr. After filtration to remove the catalyst, the solution was evaporated to dryness to afford 140 mg of methyl tetrahydro-2-pyran-2-propionate (**19**). The identity of this material was established by its unequivocal synthesis described below.

Methyl Tetrahydro-2-pyran-2-propionate (19). To a suspension of 97 g of phosphorous tribromide in 100 ml of benzene, maintained at 0°, was added dropwise 116 g of tetrahydropyran-2-methanol followed by 12 g of pyridine. The mixture was allowed to stir overnight at room temperature. At the end of this time the solvent was removed under reduced pressure and the product was distilled to give 63.5 g of tetrahydropyran-2-methyl bromide as a clear oil, bp 75–78° (18 mm).

To 100 ml of absolute ethanol was added 5.6 g of sodium metal and 32 g of ethyl malonate. To this solution was added, over 20 min, 33.8 g of tetrahydropyran-2-methyl bromide and the resulting solution was refluxed with stirring for 12 hr. The solvent was removed under reduced pressure and the resulting oil was distilled at 13 mm, bp 163–166°, to give 11.8 g of tetrahydropyran-2-methyl diethyl malonate.

To a solution of 10 g of potassium hydroxide in 100 ml of 95% ethanol was added 10 g of the above ester. The mixture was allowed to reflux for 12 hr. At the end of this time the solvent was evaporated under reduced pressure and the residue was taken up in water and extracted three times with 150-ml portions of ether. The aqueous layer was acidified with 10% hydrochloric acid and then extracted with ether. The ethereal layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue obtained was distilled at 1 mm, bp 125–130°, to give 4.0 g of tetrahydro-2-pyran-2-propionic acid.

An ethereal solution of diazomethane was slowly added to a stirred solution of 2.4 g of the above acid in 100 ml of ether. The mixture was allowed to stir for 1 hr and the solvent and excess diazomethane were removed by heating on a steam bath. The solution was filtered and evaporated to dryness giving 1.6 g of a clear oil. This material was distilled at 1 mm, bp 58–61°, giving 1.3 g (51%) of methyl tetrahydro-2-pyran-2-propionate (**19**). The infrared spectrum (neat) showed major bands at 3.42, 3.52, 5.72, 8.33, 8.52, 9.17, and 9.52 μ. The mass spectrum showed the parent ion at *m*/*e* 172 and had other strong peaks at 141, 99, 98, and 85 (base). The nmr spectrum ($CDCl_3$) showed multiplets at τ 5.9–7.1 (4 H), 7.70 (2 H), 8.10–9.10 (7 H), and a singlet at 6.51 (3 H).

Anal. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.42; H, 9.49.

The infrared and nmr spectra of this material were identical with the product obtained from the catalytic reduction of methyl 5,6-dihydro-2*H*-pyran-2-propionate.

9-Oxabicyclo[3.3.1]nonan-2-one (17). A solution of 1.2 g of 9-oxabicyclo[3.3.1]non-6-en-2-one (**16**) in 400 ml of ethyl acetate was hydrogenated in a Paar shaker over 0.1 g of 5% palladium-on-barium sulfate. The catalyst was removed by filtration and the filtrate was concentrated to give a clear oil. The oil was purified by distillation at 0.1 mm, bp 68–70°. A 2,4-dinitrophenylhydrazone derivative was prepared, mp 157–158°. The infrared spectrum showed major bands at 3.42, 5.78, 9.28, 9.60, and 11.48 μ.[48] The mass spectrum showed the parent ion at *m*/*e* 140 and had major peaks at 112, 84, 68 (base), 57, and 55. The nmr spectrum ($CDCl_3$) showed multiplets centered at τ 5.55 (1 H), 5.85 (1 H), and 6.80–8.80 (10 H).

Anal. Calcd for $C_{14}H_{16}N_4O_5$: C, 52.49; H, 5.04. Found: C, 52.31; H, 5.01.

Irradiation of 9-Oxabicyclo[3.3.1]nonan-2-one (17) in Methanol. A solution of 0.25 g of **17** in 500 ml of methanol was irradiated for 21 hr under a nitrogen atmosphere with a 550-W medium-pressure Hanovia lamp in an immersion well apparatus fitted with a Pyrex filter. The solvent was removed under reduced pressure at 40° to yield 0.24 g of slightly crude methyl tetrahydro-2-pyran-2-propionate. The residue was purified by preparative gas chromatography using a $^3/_8$ in. × 10 ft 5% FS1265 column on Diataport S at 150°. The pure oil obtained was identical in all respects with an authentic sample of methyl tetrahydro-2-pyran-2-propionate (**19**).

Quantum Yield Determinations. All quantitative measurements were made on a rotating assembly with a central light source (internal water-cooled mercury arc lamp, Hanovia Type L, 450-W). Samples in 13-mm Pyrex ampoules were placed in holders on the assembly approximately 6 cm from the immersion well. The light was filtered by circulation of a solution containing 46 g of

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[48] The infrared and nmr spectra were identical in all respects with a sample of **17** supplied by Professor L. Paquette. We thank Professor Paquette for providing us with a comparison sample.

nickel sulfate hexahydrate and 14 g of cobaltous sulfate heptahydrate per 100 ml of water through the inner jacket. This solution permitted the following wavelength distribution to pass through: 6% 2967 Å, 20% 3025 Å, 62% 3130 Å, 10% 3340 Å. All studies were made at room temperature. Samples in 13-mm Pyrex test tubes were degassed to 5×10^{-3} mm in three freeze–thaw cycles and then sealed. Benzophenone–benzhydrol actinometry[34] was used for quantum yield determinations with the thiabicyclic ketones. Reliably reproducible output rates of 4.86×10^{16} quanta sec^{-1} were recorded. For the oxabicyclic ketones, a 2-hexanone solution was used as the chemical actinometer. An actinometer quantum yield of 0.33 was used[49] which gave a reproducible lamp output of 2.01×10^{16} quanta sec^{-1}. After the irradiation the degree of reaction was determined by quantitative vapor phase chromatography. The conversions were run to 15% or less. The mass balance in these runs was generally better than 90%.

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Cycloaddition of Azides to Hexamethyl(Dewar benzene)[1]

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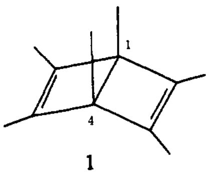
Abstract: The cycloaddition of various aryl azides and methyl azidoformate to hexamethyl(Dewar benzene) (**1**) results in exclusive exo bonding of the dipolar species. The stereochemistry of triazoline formation was adumbrated by nmr considerations and confirmed by X-ray crystal structure analysis of the *p*-bromophenyl derivative (**14**). Adduct **14** was noted to possess a very long internal cyclobutene σ bond (1.61 Å) and other interesting spatial features. No skeletal rearrangement of the diene occurred and attack from the exo direction was evidently not deterred by the presence of the 1- and 4-methyl groups at the corner positions of **1**, nor by the large steric demands of the concerted addition. Comparison is made with the behavior of 7,7-dimethylnorbornene. Hydrolysis of phenyltriazoline adduct **7** and the derived (photochemically) exo aziridine **11** in dilute aqueous acid affords unrearranged diol of unknown stereochemistry. Heating of this diol at its melting point (155°) results in dehydration and rearrangement to 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene.

Hexamethyl(Dewar benzene) (**1**), readily available from the bicyclotrimerization of 2-butyne in the presence of aluminum chloride,[4] is indeed a remarkable molecule. Despite the fact that its central bond is the longest on record (1.63 Å)[5] and its stability is 60 kcal/mol less than that of hexamethylbenzene,[6] the conversion of **1** to its aromatic counterpart occurs with a sizable activation energy (31–37 kcal/mol).[6,7] Woodward and Hoffmann have attributed the reluctance of central bond cleavage in **1** to orbital symmetry imposed barriers.[8] Additionally, protonation studies of **1** in "super acidic" media have indicated that several interesting carbonium ions of rearranged structure are generated therein.[9] Of considerable synthetic and mechanistic import have been the recent findings that a number of these cations can actually be trapped in addition reactions to **1**.[10]



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Presently, the most vexatious problem in hexamethyl(Dewar benzene) chemistry is full understanding of the causative factors behind the *seemingly* divergent directions of attack on the hydrocarbon by various reagents. To illustrate, electrophilic addition of chlorosulfonyl isocyanate to **1** appears to proceed by preferential endo attack to give ion **2**, which subsequently rearranges to **3** by migration of the central bond and ultimate C–N bond formation.[10a,b] In antithetical fashion, ethyl *N*-sulfonylcarbamate is believed to bond to **1** from the

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