

$\epsilon$  3.08), 325 (3.15), 312 (3.17), 297 (3.18), 283 (3.16), 241 (5.10), and 234  $m\mu$  (4.98). Addition of HCl shifts the long-wavelength bands about 500  $cm^{-1}$  to the blue with almost no change in band contour. The peak at 241  $m\mu$  is shifted about 200  $cm^{-1}$  to the red and the shoulder at 234  $m\mu$  disappears. The nmr (in  $CDCl_3$ ) shows three groups of protons in the ratio of 1:1:1. The peaks are situated at (relative to TMS)  $\delta$  8.3 (doublet, possibly quartet), 8.0 (doublet, possibly quartet), and 6.8 (sextet, possibly octet). The protons are assigned  $H_1 = \delta$  8.0,  $H_3 = \delta$  8.3, and  $H_4 = \delta$  6.8.

A strong case can be made that II is a pure compound; a weaker case can be made that II is the 2,6 isomer. II was separated first on an SE-30 column and then on a Carbowax column. The melting point range is 0.5°. The nitrogen atom in I acts like an electron-attracting substituent on benzyne.<sup>7</sup> If the dehydro bond is polarized significantly, a 2,6 isomer would be expected.<sup>8</sup> Four examples of substituted benzynes dimerizing to 2,6 isomers are known.<sup>9</sup> If the 2,6 isomer is indeed formed, no claim is made that the 2,7 isomer is not also formed.

**Acknowledgment.** This research was supported by the National Science Foundation under Grant No. NSF GP-5505.

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(10) National Science Foundation Trainee, 1965-1969.

Jerry M. Kramer,<sup>10</sup> R. Stephen Berry\*

Department of Chemistry, University of Chicago  
Chicago, Illinois 60637

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### Charge-Transfer Interactions in the Photochemistry of 9-Thiabicyclo[3.3.1]non-6-en-2-one

Sir:

There have been a number of recent reports dealing with the photochemical behavior of cyclic  $\beta$ -keto sulfides.<sup>1-5</sup> Much of the interest in these systems stems from the excited state interaction of the two groupings<sup>6-8</sup> and the unusual photochemistry exhibited by these systems as a result of this interaction. The photo-rearrangement of 9-thiabicyclo[3.3.1]non-6-en-2-one (**1**) to 2-thiabicyclo[6.1.0]non-6-en-3-one (**2**), recently reported from these laboratories,<sup>9</sup> was considered to proceed either by the formation of a charge-transfer structure such as **3** (Scheme I), or by a Norrish type I

(1) P. Y. Johnson and G. A. Berchtold, *J. Amer. Chem. Soc.*, **89**, 2761 (1967).

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(3) W. C. Lumma and G. A. Berchtold, *J. Amer. Chem. Soc.*, **89**, 2761 (1967); *J. Org. Chem.*, **34**, 1566 (1969).

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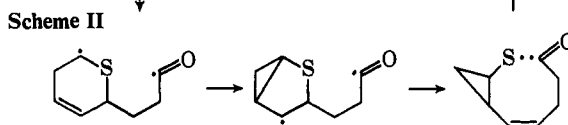
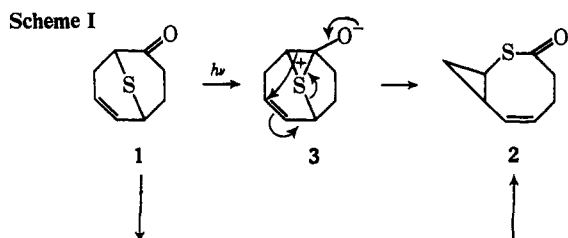
(5) J. G. Pacifici and C. Diebert, *J. Amer. Chem. Soc.*, **91**, 4595 (1969).

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(8) L. A. Paquette and L. D. Wisé, *J. Amer. Chem. Soc.*, **89**, 6659 (1967).

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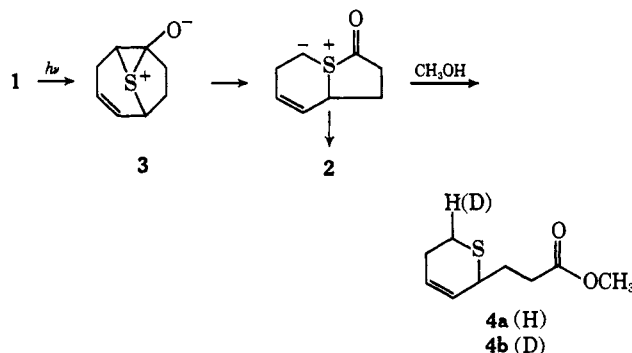


homolysis followed by diradical reorganization (Scheme II). The present work was initiated in the hope of distinguishing between these two possibilities. In this communication, we report evidence which indicates the intermediacy of a charge-transfer structure in this transformation.

Irradiation of **1** in methanol<sup>10</sup> ( $\lambda_{\max}$  253 and 305  $m\mu$  ( $\epsilon$  290 and 275)) instead of benzene gave methyl 5,6-dihydro-2H-thiopyran-2-propionate (**4a**) as the major product (40%) together with small amounts of **2** (5%). Identification of ester **4a**<sup>11</sup> is based on its hydrogenation (Raney Ni) to methyl octanoate coupled with its nmr spectrum, which shows the presence of two vinyl hydrogens. The mass spectrum of **4a** shows the parent ion at  $m/e$  186 and fragment ions at  $m/e$  112 and 99 (base) in accord with expectation for the proposed structure.

Irradiation of **1** in deuteriomethanol gave **4b** (nmr ( $CDCl_3$ ): singlet at  $\tau$  6.35 (3 H); multiplets at  $\tau$  4.25 (2 H), 6.68 (1 H), and 7.70 (7 H)) 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)). This observation *cannot* be interpreted in terms of the intermediacy of a ketene formed *via* Norrish type I cleavage followed by internal disproportionation, since the deuterium atom should appear  $\alpha$  to the carbonyl group if this path was followed. This result, however, may be readily accommodated by Scheme III which involves formation of charge-

Scheme III

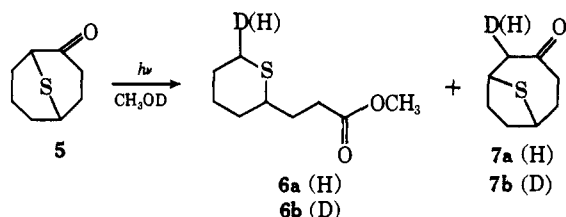


transfer structure **3**.

Efforts to firmly establish the generality of this path led us to examine the photochemistry of the related 9-thiabicyclo[3.3.1]non-2-one (**5**) system.  $\beta$ -Keto sulfide **5** (mp 155-156°) prepared by the catalytic reduction of **1** was irradiated in deuteriomethanol<sup>10</sup> and gave

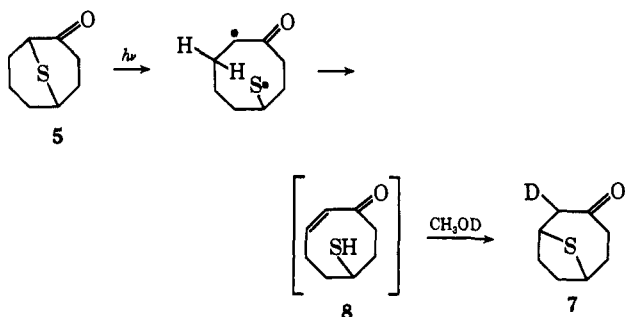
(10) All irradiations were done using a 450-W Hanovia lamp fitted with a Pyrex filter.

(11) All compounds analyzed satisfactorily. Complete spectroscopic and degradative details will be given in our full publication.



ester **6** (30%) and ketone **7** (32%) as major products.<sup>11</sup> The structure of **6** was established by its independent synthesis (catalytic reduction) from **4**. The mass spectrum of **6** 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 **7a** (mp 148–149°) was elucidated on the basis of the physical and chemical data cited. The infrared spectrum of **7a** was characterized by bands at 3.41, 5.85, 7.41, and 8.96  $\mu$ . The ultraviolet spectrum (95% ethanol) has maxima at 320 and 231  $m\mu$  ( $\epsilon$  90 and 570). The nmr spectrum ( $CDCl_3$ ) shows a two-proton multiplet at  $\tau$  6.30 and a ten-proton multiplet between  $\tau$  7.15 and 8.35. The mass spectrum of **7b** included peaks with  $m/e$  157 (parent), 129, and 101. The deuterium atom adjacent to the carbonyl group could be readily washed out with potassium carbonate in methanol. Chemical confirmation of structure **7** was obtained by reaction with Raney nickel. The product obtained was identical with an authentic sample of cyclooctanol.

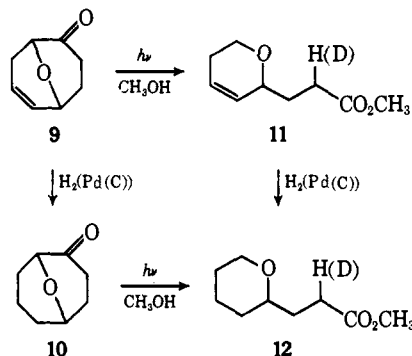
Compound **6** may be rationalized by a path analogous to the one outlined above (Scheme III). The formation of **7** from **5** may be visualized as occurring by scission of the C–S bond followed by internal hydrogen abstraction and subsequent intramolecular cyclization of the transient intermediate (**8**). This latter step may be either a ground state or photoinduced process. This rationalization readily accommodates the incorporation of deuterium at the  $\alpha$  position and is mechanistically similar to previous results encountered in the photochemistry of 2-oxo-6-hydroxy-9-thiabicyclo[3.3.1]nonane.<sup>4</sup>



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  $\beta$ -keto sulfides. Our initial experiments were involved with the photochemistry of 9-oxabicyclo[3.3.1]non-6-en-2-one (**9**) and 9-oxabicyclo[3.3.1]non-2-one (**10**).<sup>12</sup> A critical difference between

(12) The syntheses of **9** and **10** and their physical properties will be described in our full paper. All new compounds were analyzed by

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 **9**, 290  $m\mu$  ( $\epsilon$  35); **5**, 251 and 304  $m\mu$  ( $\epsilon$  300 and 250)). Irradiation of **9** in methanol afforded ester **11** in high yield. Similarly, irradiation of **10** gave ester **12** as the sole photoproduct. The structure of **12** was established by its



independent synthesis by treatment of tetrahydropyran-2-methyl bromide with sodium ethyl malonate followed by hydrolysis and esterification.

Most importantly, when the irradiation of **9** (or **10**) was carried out in deuteriomethanol the product formed incorporated the deuterium atom adjacent to the carbonyl group as evidenced by mass spectroscopy (*i.e.*, fragment peaks for **11** appear at  $m/e$  96 (P –  $CH_2DCO_2CH_3$ ) and 83 (base)). This may be rationalized by initial formation of a ketene *via* Norrish type I cleavage and internal disproportionation. 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  $\beta$ -keto sulfides.

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ir, nmr, and mass spectroscopy and gave satisfactory carbon and hydrogen analyses.

(13) Alfred P. Sloan Fellow, 1968–1970.

Albert Padwa,\*<sup>13</sup> Angelo Battisti  
Department of Chemistry  
State University of New York at Buffalo  
Buffalo, New York 14214  
Received December 10, 1970

### A Convenient Procedure for the Conversion of 1-Alkynes into Alkylcyclopropanes and *trans*-1-Halo-2-alkylcyclopropanes *via* the Hydroalumination Reaction<sup>1</sup>

Sir:

We wish to report a novel technique for the conversion of 1-alkynes into cyclopropyl derivatives which, in view of its experimental simplicity, should have broad synthetic utility. Thus, 1-alkenylalanes, which are readily prepared *via* the *cis* addition of dialkylaluminum hydrides to 1-alkynes,<sup>2</sup> react with methylene bromide in the presence of a zinc–copper couple<sup>3</sup> to

(1) This research was supported by the National Science Foundation through Grant No. GP-9398.

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