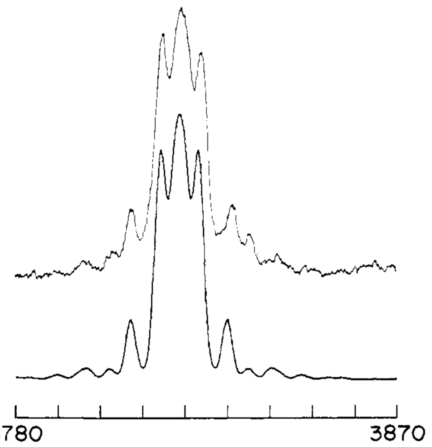

Figure 1. (a) Upper trace: fluorine nmr spectrum of **2e** at 56.4 MHz. (b) Lower trace: computed spectrum; the scale is in Hz upfield from internal $CFCl_3$.

BB′B′′ patterns of the ring-methylene protons in **2** unambiguously prove the desired propeller stereochemistry of the chiral sulfoxide groups.

Table I. Nmr Data for Compounds **2**

.Compd	$\delta_A{}^{a,b}$	$\delta_B{}^{a,b}$	J_{AB},^{b} Hz	$J_{AB'}$,^{b} Hz	Solvent
2a	3.77	2.81^c	15.1	2.4	SO_2
2c	3.92	2.74	14.3	2.2	$CDCl_3$
2d	4.51	2.98	14.5	2.1	Pyridine
2e	4.44	3.24	14.1	1.7	CF_3COOH

[a] Ppm downfield from internal TMS. [b] AA′A′′BB′B′′ patterns; the computed spectra are independent of the relative signs of the coupling constants. [c] These protons show long-range coupling (J = 1.2 Hz) to the methine proton.

The detection of a small chemical shift difference of the intrinsically diastereotopic benzyl protons in **2c** was hampered by the low solubility of this compound in most solvents. No splitting of the signal at δ 4.40 ppm ($CDCl_3$) could be resolved in $CDCl_3$ or DMSO. The intrinsically diastereotopic methyl groups in **2d** show up as a doublet centered at 2.30 ppm (pyridine) with a solvent-dependent chemical shift difference; $\Delta\nu$ in Hz at 60 MHz: pyridine, 2.3;[14] DMSO, 1.2; D_2O, 0.4; $CDCl_3$, <0.2. At 56.4 MHz one observes a tightly coupled A_3B_3 pattern (Figure 1a) for **2e** in DMSO whose analysis (Figure 1b) yielded $\Delta\nu$ = 15.9 Hz and J_{AB} = 12.3 Hz.

The structure, solvent, and temperature dependence of the intrinsic anisochronism in an extended series of bicyclic and open-chain propeller molecules is presently being investigated.

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(14) 3.56 Hz at 90 MHz. We are indebted to Professor J. B. Lambert and Mr. G. F. Jackson (Northwestern University) for the 90-MHz spectrum.

(15) Alfred P. Sloan Research Fellow.

(16) The Radiation Laboratory is operated by the University of Notre Dame under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-653.

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The Photoisomerization of 9-Thiabicyclo[3.3.1]non-6-en-2-one

Sir:

Past investigations of thioketones have shown that the ultraviolet characteristics of these compounds are substantially different from those of other saturated ketones.[1–5] 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.[6] Such interactions result both in the perturbation of the n–π* 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.[7] It was our intent to investigate systems in which these interactions lead to novel photochemical changes. In this communication we wish to report on a representative example involving the photochemistry of an unsaturated β-keto sulfide.

For reasons of synthetic accessibility and for its spectroscopic characteristics, 9-thiabicyclo[3.3.1]non-6-en-2-one (II) was chosen as the model substrate. 9-Thiabicyclo[3.3.1]-6-nonen-2-ol (I) was prepared by the transannular addition of sulfur dichloride to 1,5-cyclooctadiene[8,9] followed by thermal dehydrochlorination and aqueous solvolysis.[10] Sarett oxidation of I afforded 9-thiabicyclo[3.3.1]non-6-en-2-one (II) in good yield; mp 80–81°; λ_{max} (KBr) 5.82 μ; $\lambda\lambda_{max}$ (95% ethanol) 240 and 295 mμ (ε 290 and 275); nmr τ 7.54, 6.65, 3.86, ratio 6:2:2. *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.

The initial experiments were carried out in a nitrogen atmosphere using an internal water-cooled mercury

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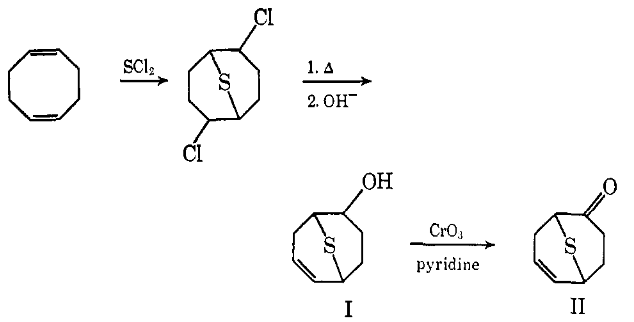
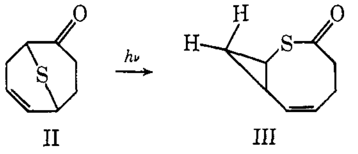
(10) All new compounds were properly characterized and acceptable chemical analyses were obtained.



arc lamp (Hanovia Type L, 450 W). In a typical case a solution of 0.75 g of II in 1 l. of pentane was irradiated for 20 hr. Conventional isolation procedures afforded 0.26 g of a solid (35%), mp 44–45°, whose structure is assigned as 2-thiabicyclo[6.1.0]non-6-en-3-one (III) on the basis of the physical data cited.[11] The elemental analysis of this component (*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) indicates that it is an isomer of II. The infrared spectrum of III 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.[12] The ultraviolet spectrum (95% ethanol) with maxima at 229 and 283 mμ (ϵ 8900 and 2100) is characteristic of a thiolester.[13] The 100-MHz nmr spectrum ($CDCl_3$) showed three distinct cyclopropyl hydrogens at τ 9.25 (doublet of triplets, J = 7.0, 5.0 cps), 8.48 (triplet of doublets, J = 8.5, 7.0 cps), and 8.02 (multiplet). The fourth cyclopropyl hydrogen was part of a 4-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 (1α H) and an AB quartet (with complex fine structure of the low-field proton) at τ 4.37 (2-vinyl H). The peak areas are in the ratio of 1:1:1:4:1:2. 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 τ 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 τ 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 to 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 over-all geometry of the molecule is shown in Figure 1.

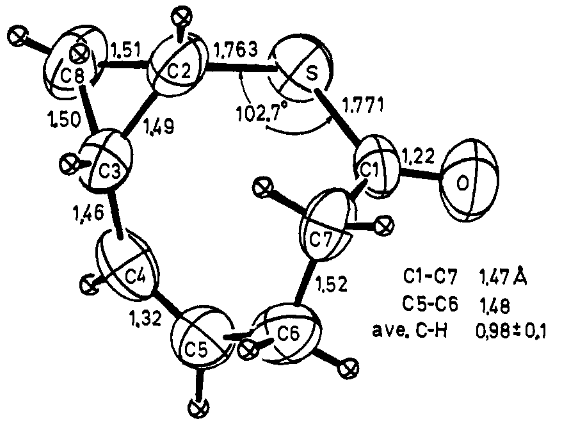
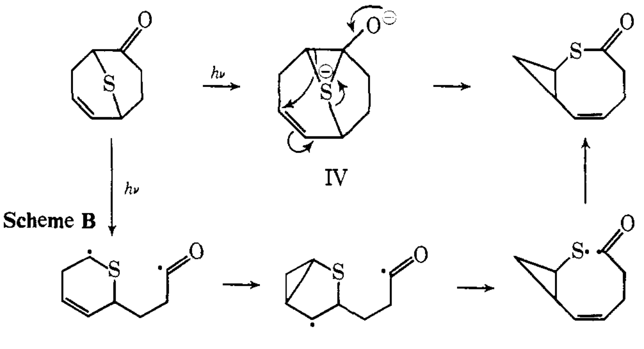


Figure 1. A view of 2-thiabicyclo[6.1.0]non-6-en-3-one showing pertinent intramolecular bonding parameters.

The quantum yield for formation of III in pentane is 0.16 at 3660 Å.[14] The reaction proceeded with nearly the same efficiency at 257 as at 366 mμ. The formation of III could not be quenched by piperylene or naphthalene. At the concentrations used piperylene is known to be a good triplet quencher[15] but only a poor singlet quencher.[16] In a separate experiment, irradiation of a solution of II and acetone, under conditions where acetone absorbs >95% of the light, resulted in the disappearance of II with the concurrent formation of only polymeric material. These results suggest the photorearrangement of II to III proceeds *via* the excited singlet state of II.

A possible mechanistic rationalization of the rearrangement would involve the formation of a charge-transfer structure such as IV which then undergoes bond reorganization to III (Scheme A). Alternatively, it may be argued that the reaction proceeds by a Norrish type I homolysis followed by diradical reorganization (Scheme B). At this time our data do not enable us to conclude whether the charge transfer or the n–π* state is responsible for the observed photoreaction.

Scheme A



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[11] A large amount of a high molecular weight polymer was also produced.

[12] P. G. Gassman and F. V. Zalar, *J. Org. Chem.*, 31, 166 (1966).

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It should be pointed out that these results contrast with previous results on the photochemistry of the 6-substituted 9-thiabicyclo[3.3.1]non-2-one system. For that case, ring fission followed by internal disproportionation between the radical centers was the preferred route.[17] The presence of a double bond in the 6 position of the thiabicyclic system seems to play an important role in the photochemistry of this ring system. In view of the novelty of the rearrangement and especially because the limited available data suggest that saturated β-keto sulfides react in a different manner, the photochemistry of a variety of unsaturated β-keto sulfides and related compounds is presently under investigation in this laboratory.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant GP-9385).

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Brønsted Coefficients Larger Than 1 and Less than 0 for Proton Removal from Carbon Acids

Sir:

The Brønsted equation is widely applicable to reactions involving general-acid and general-base catalysis.[1] Brønsted correlations also often hold for nucleophilic catalysis[2] and for proton abstractions from carbon acids, including nitroalkanes,[3] ketones,[1,4] sulfones,[5] and hydrocarbons.[6] For reactions involving proton transfers Brønsted coefficients have been generally assumed to be limited to the range of 0 to +1.[7] It is the purpose of this communication to point out that in the nitroalkane series Brønsted relationships with coefficients less than zero and greater than one exist, and to discuss the reasons for these "deviations."

It has been known for some time that an inverse relationship between rates of proton abstraction and acidities exists in the series CH_3NO_2, $MeCH_2NO_2$, Me_2CHNO_2. Here there is a progressive and substantial decrease in the rates of proton abstraction by hydroxide ion (relative rates 113:18:1.0), whereas the acidities change in the opposite manner (relative pK_a's: 10.2, 8.5, and 7.7).[8] Similarly, we have found that the rate of proton abstraction by base from nitrocyclobutane is 3.9 times that from nitrocyclopentane in 50% v/v $MeOH-H_2O$, despite the fact that the pK_a of nitrocyclobutane is 1.9 units *higher* than that of nitrocyclopentane in this medium.[9] In such instances a Brønsted plot would give a negative slope. It might be argued, however, that these deviations are caused because the structural variation occurs directly at the acidic site. This objection has now been removed by an investigation of the systems $ArCHMeNO_2$ and $ArCH_2CHMeNO_2$. A plot of $\log k_1$ for the rates of base-initiated proton abstraction *vs.* $\log K_a$, both in 50% v/v $MeOH-H_2O$, revealed for each system *a Brønsted coefficient larger than 1.* For the $ArCHMeNO_2$ system (12 substituents) a Brønsted plot (correlation coefficient = 0.992) gave a slope of 1.31. For the $ArCH_2CHMeNO_2$ system (13 substituents) a Brønsted plot (correlation coefficient = 0.977) gave a slope of 1.61. Since the Brønsted coefficients for the forward and reverse reactions must sum to 1, this means that the Brønsted coefficients for protonation of the $ArCMeNO_2^-$ and $ArCH_2CMeNO_2^-$ ions by the solvent (plot of $\log k_{-1}$ *vs.* $\log K_a$) must be −0.31 and −0.61, respectively.

$$\log k = \alpha \log K_a + C$$

$$HA + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A^- + H_3O^+$$

$$K_a = k_1/k_{-1}$$

The apparent restriction of the values of Brønsted coefficients to the range of 0 to +1 arises from the fact that application of the Brønsted relationship has been limited, hitherto, largely to oxygen acids and bases (RCO_2H and RCO_2^-) or nitrogen acids and bases ($ArNH_3^+$ and $ArNH_2$ or pyridinium ions and pyridines) where the positions of the equilibria (K_a) are more sensitive to structural changes than are the rates (k_1 and k_{-1}). This is a consequence of the fact that structural changes in these acids (and their conjugate bases) affect k_1 and k_{-1} in an *opposite manner*. For example, substitution of an electron-withdrawing substituent (*e.g.*, *m*-NO_2) for a hydrogen atom of $PhCO_2H$ will increase k_1 and decrease k_{-1}. For carbon acids, however, the extensive structural reorganization accompanying the formation of the anion can lead to situations in which substituent changes affect k_1 and k_{-1} in the *same manner*. For example, substitution of an electron-withdrawing group (*e.g.*, *m*-NO_2) for a hydrogen atom of $PhCHMeNO_2$ increases k_1 *but also increases* k_{-1}. As a result, the rate of proton removal (k_1) by a base, such as hydroxide, is more sensitive to structural changes than is the equilibrium constant (Brønsted coefficient larger than 1). For the reverse reaction (k_{-1}) the rate of proton abstraction by $ArCMe{=}NO_2^-$ from the solvent will be affected in an inverse manner by substituent effects relative to k_1 or K_a (negative Brønsted coefficient). For $ArCMe{=}NO_2^-$ and $ArCH_2CMe{=}NO_2^-$ this leads to the amusing situation where substitution of a *m*-NO_2 group for hydrogen in the parent nitronate ion causes an *increase* in the basicity of the nitronate ion.

In the series CH_3NO_2, $MeCH_2NO_2$, Me_2CHNO_2 proton abstraction by hydroxide ion is retarded by

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[1] R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1963, Chapter X.
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[9] H. Shechter and coworkers obtained similar results in other media some time ago (H. Shechter, unpublished results privately communicated).