

absorption between 220 and 360  $m\mu$  and the presence of two vinyl protons at  $\tau$  4.34 in its nmr spectrum.

Treatment of III with methylene iodide and excess zinc-copper couple<sup>6</sup> gave IV<sup>4</sup> in 60% yield after recrystallization from hexane, mp 69–70°. Analyses of the crude reaction product by vpc indicated there was less than 5% of other compounds produced in the reaction. The same reaction conducted on the acetate of III when subjected to vpc analyses showed at least four major products. This dramatic directing effect by hydroxyl in the placement of the cyclopropane ring has precedent<sup>7</sup> and suggests that in IV the cyclopropane ring and hydroxyl are in a *cis* relationship.<sup>7,8</sup> The structure of IV was confirmed by its nmr spectrum which displayed the following protons at  $\tau$  values relative to TMS: vinyl, 4.57 (multiplet), 2H;  $\alpha$  to hydroxyl, 5.69 (pentuplet), 1H; allylic methylene, 7.80 (multiplet), 4H; aliphatic methylene, 8.13 (doublet), 4H; cyclopropane, 9.14, 1H and 9.50, 1H (doublets,  $J = 4.5$  cps).

The epimeric chloride V was obtained stereospecifically by treatment with thionyl chloride in ether in the presence of tri-*n*-butylamine.<sup>9</sup> The chloride V,<sup>4</sup> bp 63–64° (1 mm), was homogenous to vpc on several columns and displayed an appropriate nmr spectrum with the two cyclopropane protons at  $\tau$  9.50 and 9.68 (doublets,  $J = 5.0$  cps).

Treatment of V with 1 mole of bromine in dichloromethane at  $-78^\circ$  and bisdehydrobromination of the resulting crude dibromide with excess potassium *t*-butoxide in *t*-butyl alcohol gave VI<sup>4</sup> in over-all 56% yield, bp 70–71° (1 mm). That VI was indeed a norcaradienyl derivative was clear from its ultraviolet absorption spectrum:  $\lambda_{\max}$  (cyclohexane) 245  $m\mu$  ( $\epsilon$  2100), 255 (2100), and 273 (2300), which is characteristic of this type chromophore.<sup>10</sup> The nmr spectrum of VI had the following protons at the  $\tau$  values indicated: vinyl, 4.04 (multiplet), 4H;  $\alpha$  to chlorine, 6.17 (multiplet), 1H; aliphatic methylene, 7.1–8.1 (multiplet), 4H; cyclopropane, 8.75, 1H and 10.16, 1H (doublets,  $J = 5.0$  cps).

The dehydrochlorination of VI required a less hindered base, 15% methanolic potassium hydroxide, and gave the triene VII<sup>4</sup> in 50% yield, bp 64–65° (10 mm),  $\lambda_{\max}$  (cyclohexane) 270  $m\mu$  ( $\epsilon$  2100) and 258  $m\mu$  ( $\epsilon$  2000), with the following nmr spectrum: vinyl,  $\tau$  3.92 (multiplet), 5H; vinyl, 4.68 (doublet triplet), 1H; allylic methylene, 7.35 (multiplet), 2H; cyclopropane, 8.53, 1H and 9.90, 1H (doublets,  $J = 3.5$  cps).

The anion I was produced immediately by treatment of VII with a solution of sodium methylsulfinyl anion<sup>11</sup> in dimethyl sulfoxide under nitrogen at room temperature.<sup>12</sup> An nmr spectrum of I in dimethyl sulfoxide- $d_6$  displayed protons at  $\tau$  2.94 (doublet,  $J = 2.0$  and 5.5 cps), 2H; 3.98 (multiplet), 5H; 10.45 (doublet,

$J = 7.5$  cps), 1H; and 10.95 (doublet,  $J = 7.5$  cps), 1H.<sup>13</sup> Quenching of I with water regenerated VII in excellent yield and demonstrated the reversible nature of the transformation of I to VII.

The low-field resonance of the ring protons<sup>14</sup> combined with the strong shielding of the methylene protons<sup>16</sup> located above the ring indicates the presence of a ring current and suggests that I is a  $10\pi$  electron aromatic system. Further studies are in progress.

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(13) The  $\tau$  values were measured using the peak attributed to protonated dimethyl sulfoxide as an internal standard.

(14) The nmr spectrum of indenyl anion<sup>15</sup> in dimethyl sulfoxide- $d_6$  taken in this laboratory shows protons at  $\tau$  2.72 (doublet,  $J = 3.0$  and 5.5 cps, 2H), 3.52 (multiplet, 3H), and 4.1 (doublet,  $J = 3.0$  cps, 2H).

(15) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

(16) The increase in the *gem*-coupling constant from 3.0 to 7.5 cps in VII and I, respectively, is consistent with the change from cyclopropane to methylene bridge type protons.<sup>17</sup>

(17) L. H. Knox, E. Verlarde, and A. D. Cross, *J. Am. Chem. Soc.*, **87**, 3727 (1965).

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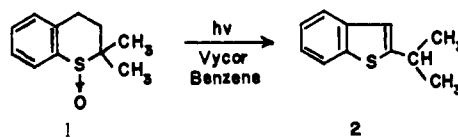
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## The Photochemical Rearrangement of a Sulfoxide

Sir:

Although the photoracemization of optically active aryl alkyl and aryl aryl sulfoxides, together with the photodecomposition of these sulfoxides and alkyl alkyl sulfoxides, has been reported,<sup>1</sup> there have been to the best of our knowledge no reported instances of rearrangements of sulfoxides upon irradiation. We now wish to report the photoinduced rearrangement of a sulfoxide.

A  $10^{-2}$  *M* benzene solution of 2,2-dimethylthiachroman 1-oxide (1) on irradiation under a dry nitrogen atmosphere using a 200-w Hanovia medium pressure mercury arc lamp with a Vycor filter gave as the major product 2-isopropylbenzothiophene (2),<sup>2</sup> which was isolated by alumina chromatography of the reaction mixture after removal of the benzene solvent.



The structure of 2 was suggested by the physical data: mol wt 176 and empirical formula  $C_{11}H_{12}S$ , confirmed by high-resolution mass spectrometry; nmr peaks ( $CDCl_3$ ) at  $\delta$  1.33 (6H doublet,  $J = 6.5$  cps,  $(CH_3)_2-CH-$ ), 3.25 (1H multiplet,  $(CH_3)_2-CH$ ), 6.98 (1H singlet,  $(-S-C=CH-)$ ), and 7.10–7.82 (4H multiplet, aromatic protons). An authentic sample of 2-isopropylbenzothiophene was prepared from benzothiophene by the unequivocal procedure described by

(1) K. Mislow, *et al.*, *J. Am. Chem. Soc.*, **87**, 4958 (1965).

(2) S. F. Bedell, E. C. Spaeth, and J. M. Bobbitt, *J. Org. Chem.*, **27**, 2026 (1962).

(6) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

(7) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235, 3244 (1961).

(8) A rigorous proof of this conclusion is currently under investigation.

(9) W. G. Young, F. Caserio, Jr., and D. Brandon, Jr., *J. Am. Chem. Soc.*, **82**, 6163 (1960).

(10) E. Vogel, W. Weidmann, H. Kiefer, and W. F. Harrison, *Tetrahedron Letters*, **11**, 673 (1963).

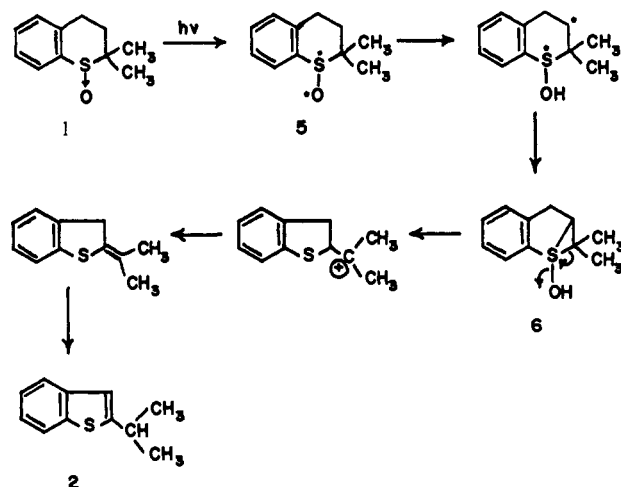
(11) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1345 (1965).

(12) Under identical conditions the hydrocarbon VIII, prepared by dehydrochlorination of V, was unreactive.

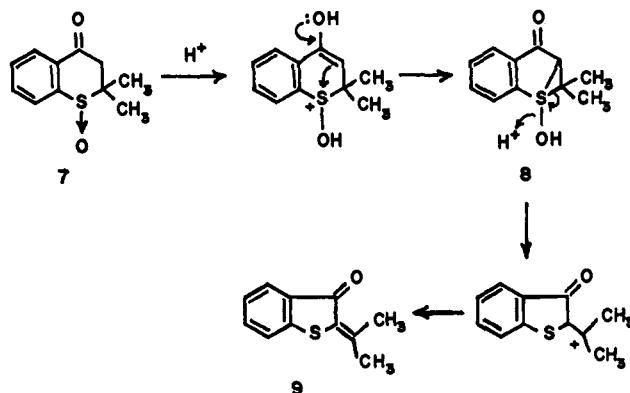
Bedell, Spaeth, and Bobbitt.<sup>2</sup> The mass spectrum of the synthetic compound and that obtained from photolysis were superimposable, as were their infrared and ultraviolet spectra.

The course of the photolysis was followed by gas chromatography, which also enabled detection of a small amount of disproportionation of the sulfoxide (1) to the corresponding sulfide (3) and sulfone (4). Such disproportionation of sulfoxides has also been induced thermally.<sup>3</sup>

A possible mechanism for the photoinduced rearrangement of 1 to 2 involves initial excitation of the sulfoxide to the excited-state species represented by 5, followed by intramolecular abstraction of a hydrogen atom to give, after recombination of radicals, the intermediate 6. This intermediate undergoes decomposition to 2 by way of the scheme depicted below.



The rearrangement of 2,2-dimethylthiachroman-4-one 1-oxide (7) in acetic anhydride has been found<sup>4</sup> to give 9. The following suggested mechanism for this acid rearrangement proceeding through the intermediate 8 is analogous to the suggested mechanism for the photorearrangement proceeding through the intermediate 6.



Initial attempts to sensitize the photorearrangement using naphthalene or acetophenone with a Pyrex filter have led to an entirely different array of products as observed on vapor phase chromatography. Thus, there is an indication that the unsensitized rearrange-

(3) F. Ostermeyer and D. S. Tarbell, *J. Am. Chem. Soc.*, **82**, 3572 (1960).

(4) R. B. Morin, presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug 31, 1964.

ment to give 2-isopropylbenzothiophene occurs by way of an excited state that differs from the excited state which leads to the products of the sensitized experiments.

Studies to establish the mechanism of this rearrangement along with other sulfoxide photolyses are currently under investigation in these laboratories.

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## A Photochemical Cyclopropylcarbinyl Rearrangement<sup>1</sup>

Sir:

In a previous publication<sup>2</sup> we reported that cyclopropylacrylic esters undergo photochemically two types of characteristic reactions: (1) a fragmentation to cyclopropenecarboxylic esters and/or to alkoxyfurans, and (2) a rearrangement to cyclopentenecarboxylic esters. In addition, whenever the structure permits, an isomerization to the  $\beta,\gamma$  isomer, a well-documented reaction of  $\alpha,\beta$ -unsaturated carbonyl compounds,<sup>3</sup> is also observed. The photochemical behavior of ethyl 3-cyclopropyl-2-butenate<sup>2</sup> exemplifies all of these processes. In this paper we wish to report on yet another observable pathway, one which appears to be the least general but promises to be the most interesting one mechanistically.

Of five cyclopropylacrylic esters investigated to date, all of which follow the behavioral pattern above, the photochemistry of ethyl 2-methyl-3-cyclopropyl-2-butenate (I) is the most complex. We have previously reported<sup>2</sup> as a preliminary result that the characteristic photoproducts, the cyclopentene ester III and ethyl 1,2-dimethyl-2-cyclopropene-1-carboxylate, form in 6 and 13% yield, respectively (Chart I). The  $\beta,\gamma$  isomer, ethyl 2-methyl-3-cyclopropyl-3-butenate, is also formed (in 5% yield). The remaining constituents of the product mixture are two new compounds, isomeric with I and formed photochemically in a ratio of 45:55, representing a 9.5 and 11.5% yield.<sup>4</sup> The two photoproducts could be separated by careful vapor phase chromatography at low-temperature settings. (Above 200° the two compounds are equilibrated in a very fast reaction.) The spectral data support an isomeric relationship between the two compounds:  $\lambda_{\text{max}}^{\text{CCl}_4}$  both isomers 5.80  $\mu$ ;  $\tau^{\text{CCl}_4}$  (in addition to the ethyl ester signals) predominant isomer: complex absorption in the 7.90–8.50 region (five protons) and methyl singlets at 8.70 and 8.80; less abundant isomer: complex absorption in the 7.90–8.50 region (five protons) and methyl singlets at 8.73 and 8.86. The absence of olefinic unsaturation was corroborated by the inertness of either isomer to hydrogenation in the presence of palladium.

The thermal interconvertibility, in the absence of olefinic unsaturation, was indicative of the presence of a

(1) Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

(2) M. J. Jorgenson and C. H. Heathcock, *J. Am. Chem. Soc.*, **87**, 5264 (1965).

(3) (a) M. J. Jorgenson, *Chem. Commun.*, 137 (1965); (b) N. C. Yang and M. J. Jorgenson, *Tetrahedron Letters*, **19**, 1203 (1964).

(4) These yields refer to irradiation in ether solution under conditions previously reported.<sup>2</sup> All of these photoproducts are also obtained when irradiations are carried out in methanol or pentane.