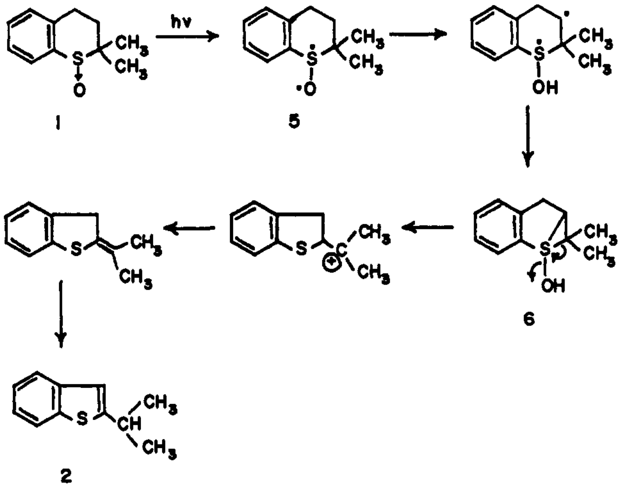
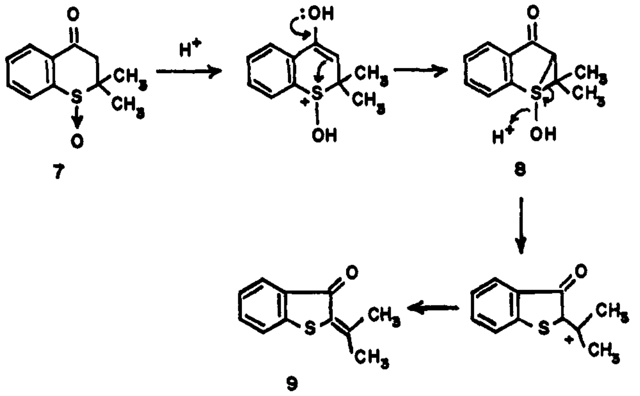
Bedell, Spaeth, and Bobbitt.[2] The mass spectrum of the synthetic compound and that obtained from photolysis were superimposable, as were their infrared and ultraviolet spectra.

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.[3]

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[4] 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 rearrangement 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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Received April 11, 1966

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(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.

A Photochemical Cyclopropylcarbinyl Rearrangement[1]

Sir:

In a previous publication[2] 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 β,γ isomer, a well-documented reaction of α,β-unsaturated carbonyl compounds,[3] is also observed. The photochemical behavior of ethyl 3-cyclopropyl-2-butenoate[2] 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-butenoate (I) is the most complex. We have previously reported[2] 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 β,γ isomer, ethyl 2-methyl-3-cyclopropyl-3-butenoate, 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.[4] 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: $\lambda_{\max}^{\mathrm{CCl_4}}$ both isomers 5.80 μ; $\tau^{\mathrm{CCl_4}}$ (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

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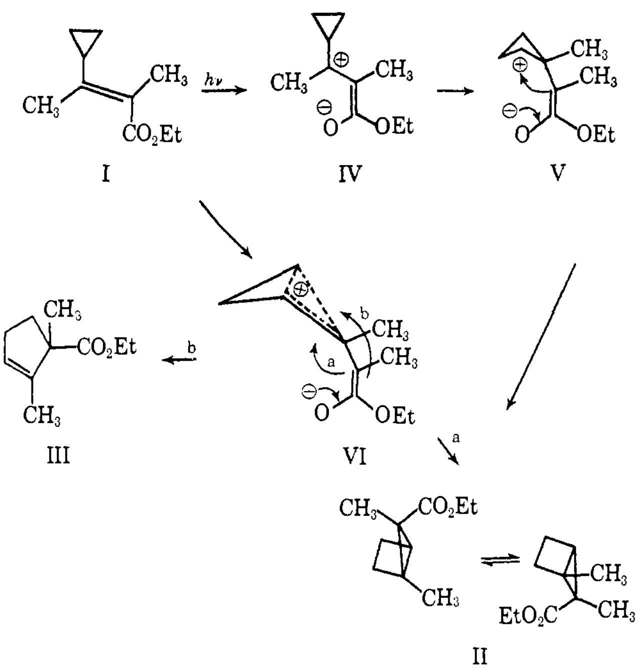
(1) Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

(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.[2] All of these photoproducts are also obtained when irradiations are carried out in methanol or pentane.

Chart I



labile σ bond. Two ring systems, the bicyclo[1.1.0]butane and the bicyclo[2.1.0]pentane, fit these specifications.[5] Although the former skeleton is readily derivable by a cyclopropane δ-hydrogen abstraction,[3a] the expected structure based on such a reaction mode is not reconcilable with the observed nmr spectrum. On the other hand, all the observed properties are consonant with a bicyclo[2.1.0]pentane structure. The very presence of this structural feature in the photoproduct was confirmed by hydrogenation experiments. In the presence of platinum both isomers reacted slowly with hydrogen, yielding ethyl 1,2-dimethyl-1-cyclopentanecarboxylate.[7] The structural assignment rests on spectral comparison of the hydrogenated product with ethyl 1,2-dimethyl-1-cyclopentanecarboxylate prepared by an independent synthetic route.[8]

Two structures, both mechanistically relatable to starting material, fit these data: these are ethyl 1,5-dimethylbicyclo[2.1.0]pentane-5-carboxylate (II) and ethyl 1,2-dimethylbicyclo[2.1.0]pentane-2-carboxylate. The absence of the characteristic cyclopropyl methylene absorption in the nmr and infrared spectra eliminates the second possibility, and II is presented, accordingly, as the structure of the new photoproduct. "Ring flip" isomerism accounts for the existence of two isomers of II.[9]

An attractive mechanism for the origin of II from I can be formalized by way of the cationic intermediates IV and V. This formulation is prompted by the striking resemblance of the photochemical ring expansion reaction to that commonly taking place among the reactions observed of simple cyclopropylcarbinyl cations in the ground state.[10] It is particularly interesting to note that such ring expansion reactions take place only in the cyclopropylcarbinyl cation and are not observed in the radical or anion in the ground state.[11] The latter two can undergo ring-opening reactions to give allylcarbinyl systems.[12] Alternatively, it is tempting to view the pathway as proceeding concertedly *via* the delocalized bicyclobutonium ion VI, as the common precursor to both II and III.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of these studies.

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[5] Isomerization about the central bond in bicyclo[1.1.0]butane derivatives is expected but has not been observed: A. Cairncross and E. P. Blanchard, *J. Am. Chem. Soc.*, **88**, 496 (1966). Isomerization about the internal bond in bicyclo[2.1.0]pentane has been reported in the 2-methyl derivative.[6]

[6] J. P. Chesick, *ibid.*, **84**, 3250 (1962).

[7] The hydrogenation is stereospecific. Each isomer yielded predominantly a different one of the two possible stereoisomers of 1,2-dimethyl-1-cyclopentanecarboxylate.

[8] R. Granger and H. Techer, *Compt. Rend.*, **250**, 1282 (1960).

[9] Exploratory rate studies indicate that thermal equilibrium, to a ratio of 28:72, is established within 30 min at 175°. The isomerization is, hence, considerably more facile than that reported for the simpler 2-methylbicyclo[2.1.0]pentane.[6]

[10] For a review of the cyclopropylcarbinyl rearrangement, see R. Breslow in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963. Under solvolytic conditions tertiary cyclopropylcarbinyl cations are known not to rearrange; under acid-catalyzed conditions rearrangements have been reported. See, for example, H. Hart and J. M. Sandri, *J. Am. Chem. Soc.*, **81**, 320 (1959); N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *ibid.*, **87**, 4533 (1965); H. M. Walborsky and L. Plonsker, *ibid.*, **83**, 2138 (1961); T. A. Favorskaya, *et al.*, *Zh. Obshch. Khim.*, **29**, 2894 (1959), and previous papers. It is evident that under these equilibration conditions the ultimate products which form are those derived from ring opening to give the more stable allylcarbinyl systems. The photochemical conditions of the irradiation of I resemble those of equilibrium control. If no other pathway for reaction other than return to I is open to IV, slow rearrangement to the less stable ions V and its corresponding allylcarbinyl ion is to be expected. While I is continuously reexcited to give IV, products II and III which correspond to the rearranged ions are stable under the photochemical conditions and should accumulate during the reaction course.

[11] M. E. H. Howden and J. D. Roberts, *Tetrahedron Suppl.*, **2**, 403 (1963); J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951); P. T. Lansbury, V. A. Pattison, W. A. Clement, and J. D. Sidler, *ibid.*, **86**, 2247 (1964).

[12] The rearrangements of I to III corresponds to a cyclopropylcarbinyl ⟶ allylcarbinyl interconversion. Employing ground-state analogy, this rearrangement can be formulated as well *via* an anionic or radical state.

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Book Reviews

Polyesters. By V. V. Korshak and S. V. Vinogradova. Translated from the Russian by B. J. Hazzard. Translation edited by J. Burdon. The Macmillan Co., 60 Fifth Ave., New York, N. Y. 1965. xv + 548 pp. 16.5 × 23.5 cm. $30.00.

This scholarly work will be particularly appealing to the industrial polymer researcher as a text book and reference book of polyester science. The book fulfills a real need for a compendium of polyester chemistry, mechanisms, analytical methods, structure, and properties of this important segment of polymeric materials.

It is well organized. The content of the individual chapters is complete which leads to some repetition, but this is not a fault. To aid the reader, extensive use has been made of page references and cross indexing when necessary, for the tables and the topical content of the text. Diagrams of laboratory equipment used for the prepa-