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THE USE OF SULFOLENES AS A VEHICLE FOR THE FORMATION OF DIVINYL CARBAMATES AND DIVINYL ETHERS

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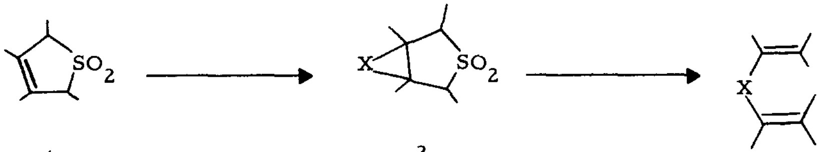
In the course of a program aimed at evaluating the synthetic utility of various heterocyclic compounds, we turned to the sulfolene system (1) in an effort to prepare suitable precursors (2) which would lead to hetero-substituted divinyl derivatives 3.



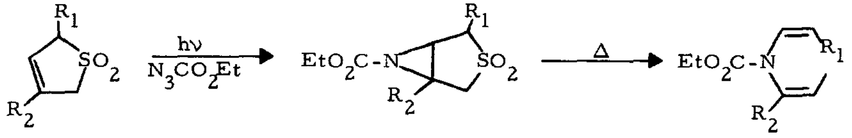
1 2 3

(X = O, NCO$_2$Et, CH$_2$)

The elegant study by Mock[1] has already provided a useful synthesis of 1, 4-dienes 3 (X = CH$_2$) by introduction of a methylene moiety into sulfolene via diazomethane. A similar transformation has also been reported by Berson[2] utilizing tetrahydropyradizine derivatives. While our study was in progress Mock reported that divinyl ethers 3 (X = O) are formed by thermal decomposition of epoxysulfolenes 2 in a stereospecific manner. We now report that not only are epoxysulfolenes useful precursors to divinyl ethers, but N-carbethoxyaziridino sulfolenes 2 (X = NCO$_2$Et) are likewise useful in the preparation of divinyl carbamates.

Formation and Fragmentation of N-Carbethoxy-6-aza-3-thiabicyclo 3, 1, 0 hexane-3,3-dioxide (2)

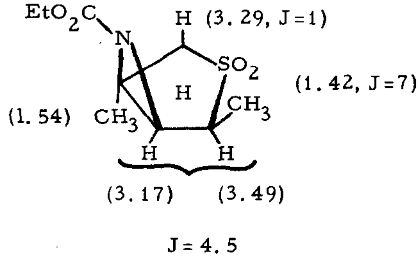
Irradiation[3] of a homogeneous (equimolar) mixture of ethyl azidoformate[4] and sulfolene 1a produced, after work-up, the photoadduct[5] 2a [41%, mp 88-89°, 1727 cm^{-1}, 3.41 ppm (m, 6H)]. In a similar fashion sulfolene 1b was converted to the aziridine derivative 2b [35%, mp 71-72°, 1724 cm^{-1}, 1.59 ppm (s, 3H)][6]. When these crystalline materials, contained in a flask fitted with a simple air condenser and receiver (nitrogen stream), were lowered into a Woods Metal bath preheated to 250°, decomposition followed in a few minutes and excellent yields of the divinyl carbamates 3a (93%, bp 159-160°, 1721, 1654, 1636 cm^{-1}, m/e 141)[6] and 3b (88%, bp 90-94/25 torr, 1724, 1667, 1633 cm^{-1}, m/e 155)[6] were obtained in a very pure state (vpc). In order to determine the stereospecificity of the thermal decomposition, we prepared the dimethylaziridinosulfolene 2c by addition of azidoformate to 2, 4-dimethylsulfolene, 1c. A



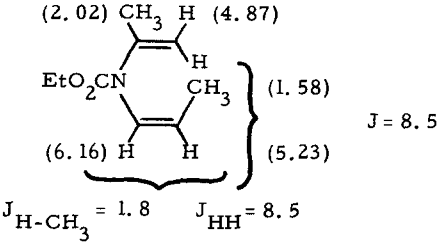
1 (a-c) 2 (a-c) 3 (a-c)

a) $R_1 = R_2 = H$; b) $R_1 = H$, $R_2 = CH_3$; c) $R_1 = R_2 = CH_3$

mixture of geometric isomers was obtained from which the endo-2, 4-dimethylaziridinosulfolene could be isolated by silica gel chromotography (mp 110°, 1730 cm^{-1}, 30% yield). Nmr assignments are given below.



2c

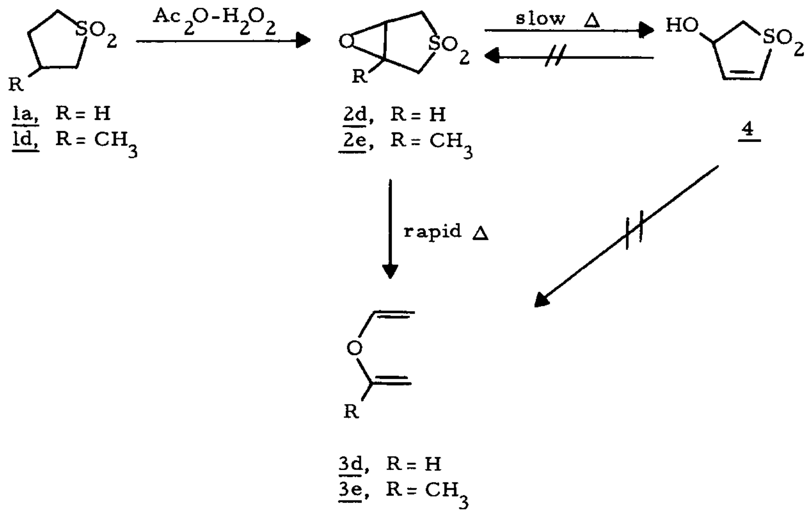


3c

Pyrolysis in the usual fashion gave a 94% yield of the divinyl carbamate 3c (bp 105-110/30 torr, 1717, 1616 cm^{-1}, m/e 169). The product obtained directly from the thermal decomposition was analytically pure (vpc) and distillation showed no change in the material. The product was assigned the cis-configuration based upon its nmr spectrum (given above). The cis-divinyl carbamate thus formed in a concerted ring opening which proceeded by a disrotatory process, similar to the cyclopropane and epoxide-fused sulfolenes reported earlier.[1]

Formation and Fragmentation of 6-Oxabicyclo[3, 1, 0]hexane-3, 3-dioxides, 2 (X = O)

The epoxysulfolenes 2d and 2e were prepared[7] by addition of sulfolenes to a solution of 30% hydrogen peroxide in acetic anhydride (1: 3 v/v) at 35° for 70-80 hr. In this manner, 2d (70%, mp 159-160)[1, 7] and 2e (84%, mp 85°)[8] were obtained. When epoxysulfolene, 2d, was gradually heated from ambient to 250° only traces ov volatile decomposition products were noted and this was also observed by Mock.[1] However, examination of the residue revealed the presence of



3-hydroxy-2, 3-dihydrothiophene-1, 1-dioxide, 4, in 50% yield [bp 240°/ 1 torr, 3365, 3020 cm^{-1}, δ (ppm) deuterioacetone, 3. 09 (s, -CH= CH-), 4. 85 (oct. HO-CH-),4. 93 (s, OH), 6. 33 (dd), 6. 97 (dd)]. Structure proof was further supported by conversion of 4 into its acetate (mp 110°) previously reported.[9] When the neat epoxysulfolene 2d was pyrolyzed as mentioned earlier (except that a Dry Ice-acetone trap was fitted in for the volatile components), there was obtained after 20 min an 88% yield of divinyl ether 3d and sulfur dioxide. The divinyl ether was characterized *via* nmr and conversion to the 2, 4-dinitrophenylhydrazone of acetaldehye. In order to determine whether or not the hydroxy-sulfolene 4 was an intermediate leading to divinyl ether or in equilibrium with the epoxysulfolene, it was heated similarly (rapidly) but was found to be completely stable, giving neither 2d nor 3d . The epoxysulfolene 2e was also subjected to flash heating and gave the vinylisopropenyl ether 3e in 80% yield. Structural proof was based upon nmr and hydrolysis to the 2, 4-dinitrophenylhydrazones of acetaldehyde and acetone which were separated on preparative tlc and had melting points identical to authentic samples.[10]

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2. J. A. Berson and S. S. Olin, ibid, **91**, 777 (1969); ibid, **92**, 1087 (1970).
3. Reaction performed using a quartz vessel mounted in a Rayonet Reactor containing sixteen medium pressure lamps. Irradiation proceeded at 25° for 40-72 hr, after which unreacted azidoformate was evaporated *in vacuo* and unreacted sulfolene decomposed by reflux in toluene solution. Residual material was purified by elution through silica gel (hexane-ether, 1 : 1).
4. M. O. Fiorster and H. E. Fierz, J. Chem. Soc., **93**, 72 (1908).
5. W. Lwowski and T. W. Mattingly, Tetrahedron Letters, 277 (1962).
6. Complete nmr assignments were made on all protons and will be reported in detail at a later date.
7. Epoxysulfolenes have been prepared in lower and erratic yields utilizing formic acid and hydrogen peroxide which also led to various quantities of glycols. [W. R. Sorenson, J. Org. Chem., **24**, 1796 (1959)].
8. This compound has been reported an "oil" from the reaction of the bromohydrin and alkali [E. Zuydewijn, Rec. Trav. Chim., **57**, 445 (1938)].
9. M. Prochazka and V. Horak, Coll, Czech. Chem. Comm., **24**, 1509 (1959).
10. All new compounds gave satisfactory elemental analyses.