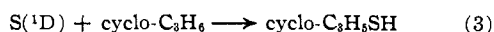
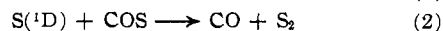
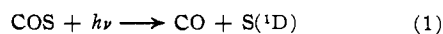


latter compound, and if a similar assignment is made here, peak A could be ascribed to the mercapto proton.

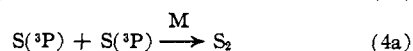
All of the C_3H_5SH isomers were considered as possible reaction products, and to this end the various spectra and other properties were determined directly or obtained from published reports. Comparison of the data permitted elimination of all isomers except cyclopropyl mercaptan. The ultraviolet spectrum of the mercaptan vapor showed absorption beginning at *ca.* 2600 Å., with a maximum at 2300 Å., followed by the onset of strong absorption at *ca.* 2200 Å. The compound eluted in 10.5 min. on both the silicone 550 column described above and on an 8-ft. 20% tricresyl phosphate on Kromat column operating at 25°, with H_2 carrier at 60 ml./min. The boiling point (extrapolated) was $60.0 \pm 1.3^\circ$ and the vapor pressure was 175 mm. at 25°. The compound is a colorless liquid with characteristic mercaptan odor. We have been unable to find previously published data on the synthesis or properties of cyclopropyl mercaptan.

A simple mechanism, similar to that already proposed for the reaction of S-atoms with olefins,¹ and which accounts qualitatively for the observed results here, is



The insertion reaction (3) is dictated by the fact that cyclo- C_3H_5SH is the only significant product arising from S-atom attack on cyclopropane. The S-atom involved in (3) is likely in the initially-formed (¹D) metastable state¹; otherwise the ground-state cyclopropane singlet would have to be converted to a triplet level of the mercaptan, for the spin to be conserved in reaction with S(³P) atoms. By analogy with alcohols and other mercaptans, a low-lying triplet state of the mercaptan product is unlikely.

The above mechanism predicts that in the pressure region where $R(CO)$ and $R(\text{cyclo-}C_3H_5SH)$ are constant ($P(\text{total}) > 300$ mm.) the ratio $R(CO)/R(\text{cyclo-}C_3H_5SH)$ should be unity; in fact, this ratio = 2.7 at $P(\text{total}) = 560$ mm. Collisional deactivation of S(¹D) atoms to S(³P) is therefore indicated, as previously observed in the olefin system.¹ Triplet sulfur may then disappear *via* the reactions



Thus any singlet \rightarrow triplet conversion occurring will have the dual effect of decreasing the mercaptan yield and increasing that of carbon monoxide. The importance of electronic relaxation is also substantiated by recent investigations in this Laboratory on the reaction of S-atoms with *cis*- and *trans*-butene-2.⁴ Here it was shown that the cyclic sulfide product arose from the addition of triplet sulfur to the olefin despite the fact that S(¹D) atoms are initially formed in (1), and, as a result, the sulfide yield was essentially quantitative.

The insertion of sulfur atoms into the C-H bond in paraffinic hydrocarbons, as exemplified in this communication by the formation of cyclopropyl mercaptan from cyclopropane substrate, would appear to be an excellent model for the detailed investigation of atomic insertion reactions because of the simplicity of the technique, the absence of complicating side reactions, and

(4) E. M. Beatty, J. A. Poole, O. P. Strausz and H. E. Gunning, to be published.

the remarkable stability of the products formed in the reaction.

The authors express their deep appreciation to Mr. Gene Fried for valuable assistance in the experimental work and to Drs. R. J. Crawford and W. G. Paterson for assistance in the infrared and n.m.r. analyses. This research was partially supported by a grant from Imperial Oil Limited, which assistance is gratefully acknowledged.

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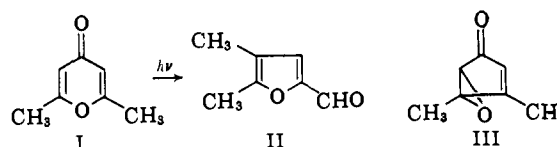
RECEIVED FEBRUARY 2, 1963

PHOTOREARRANGEMENT OF A 4-PYRONE TO A FURAN DERIVATIVE

Sir:

Ultraviolet irradiation of 2,6-dimethyl-4-pyrone (I) in either the solid state or in solution has been found to result in dimerization.¹ Investigation of the products formed on irradiation of I in aqueous solution at high dilution, *i.e.*, under conditions chosen to retard dimerization, has now led to the observation of a novel rearrangement of the 4-pyrone to a furan derivative.

An aqueous 0.2% solution of I was irradiated in a quartz apparatus in the absence of air with a Hanovia high-pressure mercury-vapor 450-w. lamp for 36 hr. Fractionation of the crude product by extraction and chromatography gave, in addition to photodimer, an oil (*ca.* 1%), $\lambda_{\text{max}}^{CCl_4}$ 3.52, 3.62 (shoulder), 5.93, 6.20, 6.60 μ , τ 0.54, 3.07, 7.68, 7.99 p.p.m. (intensities *ca.* 1:1:3:3). This was characterized by means of the following derivatives: **oxime**, m.p. 79.5–81°, $\lambda_{\text{max}}^{CHCl_3}$ 2.78, 3.05 (broad), 6.10 (shoulder), 6.18, 6.6 μ , $\lambda_{\text{max}}^{CH_3OH}$ 218 $m\mu$ ($\log \epsilon$ 3.62), 284 $m\mu$ ($\log \epsilon$ 4.24) (*Anal.* Calcd. for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.81; H, 6.65; N, 9.90); **2,4-dinitrophenylhydrazone**, red needles, m.p. 224–225°, $\lambda_{\text{max}}^{CHCl_3}$ 393 $m\mu$ (*Anal.* Calcd. for $C_{13}H_{12}N_4O_5$: C, 51.31; H, 3.98. Found: C, 51.50; H, 4.16); **semicarbazone**, m.p. 217° dec., $\lambda_{\text{max}}^{CH_3OH}$ 306 $m\mu$ ($\log \epsilon$ 4.34). On the basis of these data and its origin, the product was considered to be **4,5-dimethyl-2-furaldehyde** (II).



An authentic sample of II was synthesized by a modification of the method of Mndzhoyan, *et al.*² The bands in the infrared and nuclear magnetic resonance of this compound were identical in position with those in the spectra of the photochemical product, although some differences in relative intensities in the infrared spectra indicated that the latter product was impure. Comparison of derivatives fully established the formation of II in the photochemical reaction. The derivatives obtained from the authentic sample of II were: **oxime**, m.p. 79–81°, mixture m.p. 79–81°, infrared spectrum identical with that of the oxime of the photochemical product (*Anal.* Calcd. for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.62; H, 6.68; N, 9.94); **2,4-dinitrophenylhydrazone**, red needles, m.p. 226–227° (*Anal.* Calcd. for $C_{13}H_{12}N_4O_5$: C, 51.31; H, 3.98; N, 18.42. Found: C, 51.30; H, 4.06; N, 18.40); **semi-**

(1) E. Paternò, *Gazz. chim. ital.*, **44**, 151 (1914); P. Yates and M. J. Jorgenson, *J. Am. Chem. Soc.*, **80**, 6150 (1958).

(2) A. L. Mndzhoyan, V. G. Afrikyan, M. T. Grigoryan, and E. A. Markaryan, *Dokl. Akad. Nauk Arm. SSR*, **20**, 277 (1957); **27**, 301 (1958) [*Chem. Abstr.*, **52**, 12835 (1958); **54**, 481 (1960)].

carbazone, m.p. 220–222° dec., mixture m.p. 219–220° dec. (lit.,^{2,3} m.p. 220–221° dec., 220.5–221.5°) (Anal. Calcd. for C₈H₁₁N₃O₂: C, 53.03; H, 6.12. Found: C, 52.86; H, 6.17).

The juxtaposition of the methyl groups in the rearrangement product suggests that the photochemical reaction may proceed initially by a route analogous to that followed in the case of compounds possessing the corresponding carbocyclic system, *i.e.*, the 2,5-cyclohexadienones,⁴ with the "lumisantonin" rearrangement product III as an intermediate.

(3) T. Reichstein, and A. Grüssner, *Helv. Chim. Acta*, **16**, 28 (1933).

(4) D. H. R. Barton, *ibid.*, **42**, 2604 (1959); H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).

(5) This work was supported by a grant from the National Research Council of Canada, which is gratefully acknowledged.

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RECEIVED JANUARY 24, 1963

MECHANISM FOR THE FORMATION OF *cis*-ALKENES FROM α -CHLORO SULFONES

Sir:

In a previous paper¹ the rate of release of chloride ion during the formation of alkenes from α -chloro sulfones on treatment with alkali was shown to be consistent with the formation of an episulfone intermediate. One puzzling feature of the reaction was the formation of *cis*-2-butene, rather than *trans*-2-butene, in the reaction of α -chloroethyl ethyl sulfone.² This result cast a shadow on the postulate of an episulfone intermediate, and suggested that another mechanism might pertain. One such possibility is initial cleavage of a carbon-sulfur bond, rather than a carbon-chlorine bond, giving an intermediate MeCH(SO₂⁻)CH(Cl)Me, which then loses SO₂ and Cl⁻. (By making the proper assumptions, one can rationalize the stereochemistry using this mechanism.) We now wish to report further evidence for the formation of an episulfone intermediate.

Reaction of diazoethane in ether with sulfur dioxide³ gave a mixture from which the postulated intermediate episulfone (*cis*-2,3-dimethylthiirane 1,1-dioxide) was isolated in pure form. The corresponding *trans* isomer was obtained admixed with a smaller amount of the *cis* form. (Microanalyses, n.m.r. spectra, and infrared spectra are consistent with these structure assignments.) The *cis* episulfone underwent rapid decomposition when warmed neat, or in solution, to give 100% *cis*-2-butene. The episulfone mixture decomposed to a mixture of 78% *trans*- and 22% *cis*-2-butenes, which composition is identical with the episulfone isomer distribution in the mixture, as determined by n.m.r.

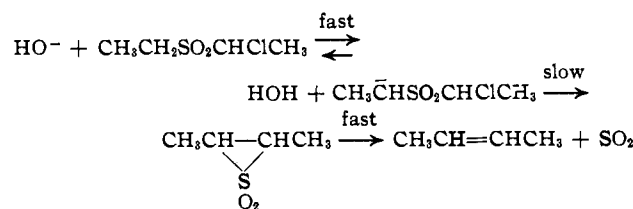
Starting from α -chloroethyl ethyl sulfone the percentages of *cis* isomer in the 2-butene mixture (g.l.c. analysis) using various alkaline media were: 78.8% (2 *N* NaOH), 78.2% (2 *N* KOH), 74.6% (1 *M* BuONa in BuOH), 77.9% (BuLi in heptane-hexane), and 78.1% (C₆H₅Li in C₆H₆). However, when 1 *M* *t*-BuOK in *t*-BuOH was used, the ratio was almost reversed, being now 18.6% *cis* and 81.4% *trans*. Significantly, the *cis* episulfone behaved similarly, giving only *cis*-2-

(1) F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **73**, 5187 (1951).
(2) L. Ramberg and B. Bäcklund, *Arkiv. Kemi Mineral. Geol.*, **1314**, No. 27 (1940), concluded from physical constant measurements made on the 2-butene dibromides that *cis*-2-butene predominated. An infrared analysis of the 2-butene mixture (N. P. Neureiter, Ph.D. Dissertation, Northwestern University, 1957) gave the composition as about 80% *cis*, and this result has been confirmed by gas-liquid chromatographic (g.l.c.) analysis (both by the present authors and, independently, by T. A. Whitney).

(3) The procedure was adapted from that for ethylene sulfone: G. Hesse, E. Reichold and S. Majmudar, *Chem. Ber.*, **90**, 2106 (1957).

butene with NaOH and predominantly *trans*-2-butene with *t*-BuOK. Furthermore, with *t*-BuOK in *t*-BuOH the 2-butene produced from the *cis* episulfone was over 90% CH₃CD=CDCH₃ (19% *cis*) whereas with 2 *N* NaOD in D₂O, the *cis* episulfone gave CH₃CH=CHCH₃ (100% *cis*), with less than 5% deuterium exchange. Finally, the 2-butene produced from α -chloroethyl ethyl sulfone with 2 *N* NaOD in D₂O was 98% CH₃CD=CDCH₃ (78% *cis*).

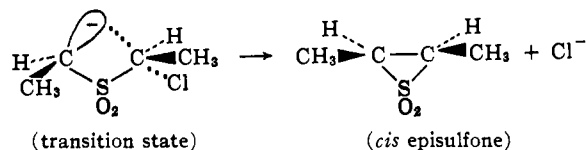
These results are consistent with the mechanism originally proposed,¹ the final step being a thermal elimination of sulfur dioxide.⁴



The deuterium exchange experiments show that with hydroxide ion all the α -hydrogen atoms in the α -chloro sulfone are rapidly exchanged, but that those in the episulfone are not exchanged prior to its decomposition. With the stronger base, *t*-butoxide ion, hydrogen exchange and epimerization precede decomposition of the episulfone. The latter experiment also shows that, as expected, the *trans* episulfone is favored over the *cis* episulfone at equilibrium.

When the reaction was carried out using 2 *N* KOH and α -chloropropyl ethyl sulfone 72.3 \pm 0.3% of *cis*-2-pentene was produced, as compared to 65.7 \pm 0.2% of *cis*-2-pentene from α -chloroethyl propyl sulfone. In contrast, the same per cent of *cis*-2-pentene (15.8%) was obtained from either chloro sulfone when *t*-BuOK in *t*-BuOH was used. These results are consistent with and support the interpretation given above. In 2 *N* KOH the *cis* episulfone is formed preferentially, a slightly different *cis/trans* ratio being obtained from the two chloro sulfones. When formed in the presence of the stronger base, *t*-BuOK, the episulfones are epimerized to the same *cis/trans* mixture with the *trans* isomer now predominating.

Although the present evidence does not completely rule out other mechanisms for the first stage in the reaction (carbene or dipolar ion rather than strictly carbanion), it does appear to provide conclusive evidence for the formation of an episulfone intermediate. A likely transition state for the formation of the preferred episulfone is then



Assuming this representation, the question immediately arises as to why this transition state is preferred to the alternative one in which the methyl groups are on opposite sides. One intriguing possibility is that the methyl groups may actually attract one another. In the transition state shown, the methyl groups have a relationship similar to that for the methyl groups in the skew conformation of butane, except that the central C-C bond distance is somewhat greater. In skew butane Pitzer and Catalano⁵ estimate that steric repulsive forces amounting to about 2.5 kcal. per mole

(4) Thermal decomposition of the episulfone is very rapid, but we have not excluded the possibility that the rate of cleavage may be accelerated by hydroxide ion.

(5) K. S. Pitzer and E. Catalano, *J. Am. Chem. Soc.*, **78**, 4844 (1956).