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suggestion regarding the influence of bromine atom bridging in alkyl bromide brominations.

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC., WILMINGTON 98, DEL.]

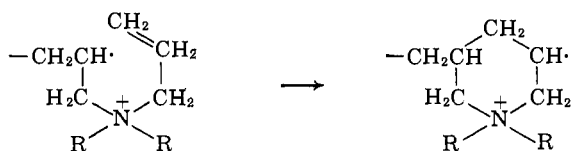
Bicyclo-copolymerization of Sulfur Dioxide and *cis,cis*-1,5-Cyclooctadiene¹

BY A. H. FRAZER AND W. P. O'NEILL

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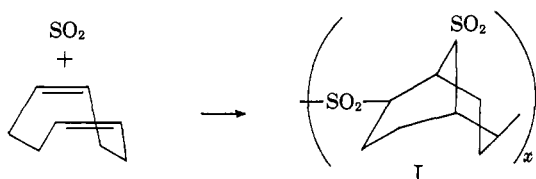
The copolymerization of sulfur dioxide with *cis,cis*-1,5-cyclooctadiene has been effected using radical initiation in dilute solutions. The soluble copolymer which was obtained in film- and fiber-forming molecular weights has no unsaturation and contains two moles of sulfur dioxide per mole of cyclooctadiene. A cyclization polymerization mechanism is proposed. The properties of the copolymer were determined and the thermal and hydrolytic stability studied.

In order to explain the solubility of polymers obtained from diallyl quaternary ammonium salts, Butler and Angelo² proposed an intermolecular-intramolecular propagation mechanism in this radical polymerization, the intramolecular step producing piperidinium units



A number of examples of inter-intramolecular polymerization have since appeared. These include, in addition to the free-radical type of initiation of Butler and Angelo, Ziegler-type,³ anionic,^{4a} and cationic.^{4b} Recently, the inter-intramolecular polymerization of triallyl- and tetrallylammonium bromide has been reported to yield polymers containing methylene-linked bicyclic and tricyclic rings.⁵ Similarly the transannular polymerization of bicyclic dienes has been reported to yield nortricyclic repeating units.⁶

Recently, the cyclo-copolymerization of 1,5-hexadiene and sulfur dioxide has been reported.⁷ This paper reports the bicyclo-copolymerization of sulfur dioxide with *cis,cis*-1,5-cyclooctadiene *via* inter-intramolecular propagation. To our knowledge, this is the first example of such a bicyclo-copolymerization.



Discussion and Results

Polymerization.—The copolymerization of sulfur dioxide with *cis,cis*-1,5-cyclooctadiene has been effected by using free radical initiators in solvents or diluents. Solvents and diluents such as tetramethylene sulfone, dimethyl sulfoxide, diethyl ether, and excess sulfur dioxide were found to be operable. Radical initiators such as ascaridole-hydrochloric acid, ascaridole-

hydrogen chloride, and methyl ethyl ketone peroxide were found to be effective. Unlike other radical polymerizations, this polymerization could be initiated with oxygen alone, and oxygen acted as a "promoter" for other radical initiators. Although initiation of polysulfone preparation with "combined oxygen" has been reported,⁸ polymerization in this case was initiated by merely bubbling oxygen through the reaction mixture. This "oxygen effect" will be discussed in greater detail in a later paper.

The preferred procedure for the preparation of high molecular weight polymer in high conversion consisted of using tetramethylene sulfone as reaction medium with methyl ethyl ketone peroxide as initiator and oxygen as a "promoter." In this manner, quantitative yields of soluble high molecular weight polymer were obtained. Representative copolymerizations of sulfur dioxide and 1,5-cyclooctadiene are summarized in Table I.

TABLE I^a

Reaction medium	Initiators ^d	Temp., °C.	Time, hr.	Atmos. phere	Yield, ^g %	η_{inh}^h	S, %
Diethyl ether	A	15	2	N ₂	37	0.62	26.42
...	B	-5	10	N ₂	23	.90	26.93
DMSO ^b	A	22	8	N ₂	84	.21	26.51
TMS ^c	A	25	16	N ₂	83	1.55	26.94
TMS ^c	A	25	16	Air ^e	89	1.95	26.85
TMS ^c	A	25	16	Air ^f	93	2.10	26.93
TMS ^c	..	25	16	Air ^f	50	1.20	26.84
DMSO ^b	C	22	16	N ₂	88	0.21	26.43
TMS ^c	C	25	16	N ₂	80	1.4	26.86
TMS ^c	C	25	16	Air ^e	98	2.2	26.76
TMS ^c	C	-4	2	N ₂	15	1.13	26.87

^a All reactions carried out with 10% wt. concn. of monomers; $M_{SO_2}/M_{C_8H_{12}} = 0.25/0.10$. ^b DMSO, dimethyl sulfoxide. ^c TMS, tetramethylene sulfone. ^d A initiator, 5 drops of ascaridole and 5 drops of concd. HCl; B initiator, 1 drop of ascaridole and 400 cc. of HCl (gas); C initiator, 5 drops of methyl ethyl ketone peroxide. ^e Reaction mixture opened to air. ^f Air bubbled through reaction mixture. ^g Yield, per cent based on 1,5-cyclooctadiene. ^h η_{inh} , inherent viscosity ($\ln \eta_{rel}/C$) for 0.5 g. of polymer/100 ml. of dimethyl sulfoxide solution.

Radical initiators usually effective in the copolymerization of sulfur dioxide with olefins or dienes such as cumene hydroperoxide, α,α' -azobis-(α,γ -dimethylvaleronitrile), benzoyl peroxide, ammonium nitrate, and hydrogen peroxide were ineffective in this system. As might be expected, cationic initiators such as boron trifluoride and boron trifluoride etherate gave low molecular weight hydrocarbon oligomers of 1,5-cyclooctadiene, but no polysulfone. Similarly, lithium naphthalene and a Ziegler-type catalyst from aluminum triisobutyl

(1) Presented at the 144th National Meeting of the American Chemical Society, March 31–April 5, 1963, Los Angeles, Calif.

(2) G. B. Butler and R. J. Angelo, *J. Am. Chem. Soc.*, **79**, 3128 (1957).

(3) C. S. Marvel and J. K. Stille, *ibid.*, **80**, 1740 (1958).

(4) (a) J. F. Jones, *J. Polymer Sci.*, **33**, 7 (1958); (b) J. F. Jones, *ibid.*, **33**, 513 (1958).

(5) D. S. Trifan and J. J. Hoglen, *J. Am. Chem. Soc.*, **83**, 2021 (1961).

(6) P. J. Graham, E. L. Buhle, and N. Pappas, *J. Org. Chem.*, **26**, 4658 (1961).

(7) J. K. Stille and D. W. Thomson, *J. Polymer Sci.*, **62**, 5118 (1962).

(8) T. Norther and F. Irany, U. S. Patent 2,505,833 (1950).

and titanium tetrachloride yielded only oily hydrocarbon products.

Structure.—When sulfur dioxide and *cis,cis*-cyclooctadiene were copolymerized in the absence of solvents or in large excesses of sulfur dioxide, insoluble polymer, analyzing for less than 2 moles of sulfur dioxide per mole of 1,5-cyclooctadiene, was obtained. These insoluble copolymers must therefore contain a three-dimensional cross-linked network structure formed by radical addition of each of the two internal double bonds with the growing radical chains.

When sulfur dioxide and *cis,cis*-1,5-cyclooctadiene were copolymerized in the presence of a nonsolvent such as diethyl ether such that the total concentration of the monomers in the reaction mixture was 10% or less, the product was a soluble copolymer. Similarly, when the copolymerization was carried out in the presence of a solvent for the product polysulfone such as dimethyl sulfoxide or tetramethylene sulfone, and such that the concentration of the monomer in the reaction mixture was 25% or less, a soluble copolymer was obtained. These soluble copolymers analyzed for 26.4 to 27.0% sulfur, which corresponds to two moles of sulfur dioxide per mole of cyclooctadiene per polymer repeat unit. Analysis of the soluble copolymer for residual double bond by infrared absorption in the 6.0 to 6.2 μ region and catalytic hydrogenation in tetramethylene sulfone solution was negative. Representative polymerizations to determine this concentration effect are given in Table II.

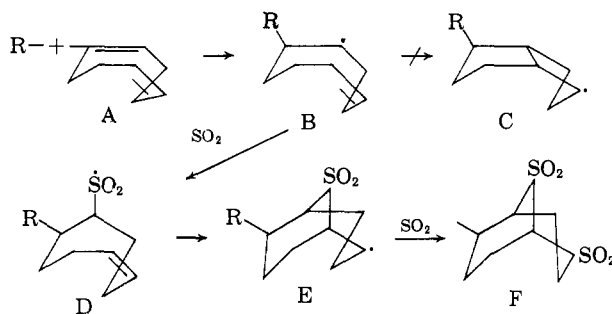
TABLE II^a

Reaction medium	Monomer ^d concn., %	Yield, ^e %	η_{inh} ^f	S, %	% 2/1 ^g
Diethyl ether	5	30	0.62	26.4	92
Diethyl ether	10	37	0.68	26.9	98
Diethyl ether	15	40	Insoluble polymer		
TMS ^b	10	80	1.95	26.8	97
TMS	25	98	2.2	26.7	96
TMS	30	98	Insoluble polymer		
DMSO ^c	10	83	0.21	26.8	97
DMSO	25	93	0.23	26.9	98
DMSO	30	90	Insoluble polymer		

^a $M_{SO_2}/M_{C_8H_{12}} = 0.25/0.1$. ^b TMS, tetramethylene sulfone. ^c DMSO, dimethyl sulfoxide. ^d Concentration in wt. %. ^e Yield based on 1,5-cyclooctadiene. ^f η_{inh} , inherent viscosity. ^g % 2/1 = $\frac{\% S - 18.6}{27.1 - 18.6} \times 100$ where 18.6% is theory for 1:1 copolymer and 27.1% S is theory for 2:1 copolymer.

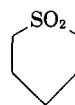
The polymer repeat unit containing two moles of sulfur dioxide per mole of cyclooctadiene, the absence of unsaturation, plus the solubility of high molecular weight film-forming copolymers strongly support the view of an intramolecular cyclization propagation step with the formation of a (3.3.1)bicyclosulfone ring. The reaction pathway can be considered as involving the attack of the growing radical chain on the diene A which may be presumed to be complexed with sulfur dioxide.^{9,10} The hydrocarbon radical B does not homopolymerize or bridge transannularly to C but reacts with sulfur dioxide to yield D. This radical (D) reacts with the closest double bond. The closest π -cloud is at the bond across the ring and so transannular intramolecular cyclization results (E). This radical reacts with sulfur dioxide and the chain is propagated.

The type of transannular bridging suggested for the D \rightarrow E step has been observed by others^{11,12} in the chemistry of 1,5-cyclooctadiene and would be expected

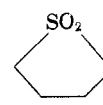


on the basis of the ease of formation of bicyclic ring systems in other similar intra-intermolecular polymerizations.^{5,13}

In addition, the (3.3.1)bicyclosulfone structure is supported by (1) the cyclization of a N-chloro-N-methylcyclooctylamine to a similar bicyclo structure¹⁴ and (2) a comparison of the infrared spectra of the copolymer I with those of pentamethylene sulfone (II) and tetramethylene sulfone (III).^{15,16}

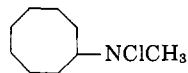


II



III

The cyclization of N-chloro-N-methylcyclooctylamine could give rise to 9-methyl-9-azabicyclo(3.3.1)nonane (N-methylgranatamine) (IV) or 9-methyl-9-azabicyclo(4.2.1)nonane (V).



IV

V

Although the formation of IV involves closure to a bridged piperidine structure, this is the only product isolated and, in yields as high as 23%, after only a 30-min. reaction period.

The spectra of the copolymer samples are quite similar to that of compound II, showing absorption at 1120 and 1300 cm^{-1} ($-\text{SO}_2-$) while the spectrum of compound III shows absorption at 1100 and 1270 cm^{-1} , a significant shift.

Polymer.—The copolymer I of sulfur dioxide and *cis,cis*-1,5-cyclooctadiene is a white solid which contains 26–27% sulfur, has no unsaturation, and does not melt but decomposes visibly (gas evolution) at temperatures over 250°. Compound I, which has a density of 1.5211 at 30° and water absorption (based on film) of 5.3%, has been prepared in film- and fiber-forming molecular weights with inherent viscosities as high as 2.2. Light scattering¹⁷ studies in dimethyl sulfoxide solution of this copolymer gave a molecular weight of 113,000 for copolymer with an inherent viscosity of 0.93. Unlike most copolymers from sulfur dioxide and olefins or dienes, I is amorphous or shows only trace crystallinity in bulk, film, or fiber form. All attempts to obtain this polymer in a highly crystalline state have been unsuccessful.

This copolymer of sulfur dioxide and *cis,cis*-1,5-cyclooctadiene is soluble in dimethyl sulfoxide, tetramethylene sulfone, sulfuric acid, N-methylpyrrolidone, and either N,N-dimethylformamide containing 5%

(9) F. S. Dainton and K. J. Irvin, *Proc. Roy. Soc. (London)*, **A212**, 96 (1952).

(10) W. G. Barb, *ibid.*, **A212**, 66, 177 (1952).

(11) R. Köster and G. Griaznov, *Angew. Chem.*, **73**, 171 (1961).

(12) A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1643 (1959).

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(14) S. Wawzonek and P. J. Thelan, *ibid.*, **72**, 2118 (1950).

(15) H. Bacher and C. Bolt, *Rev. trav. chim.*, **54**, 509 (1935).

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(17) The authors wish to thank Dr. J. B. Nichols and Mrs. Naomi Septon for the light scattering data.

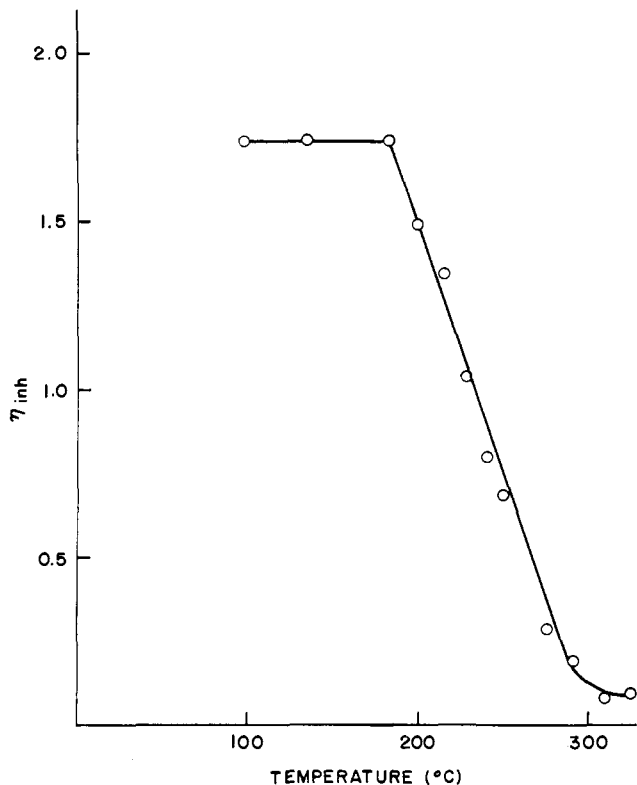


Fig. 1.—Thermal degradation of copolymer 1 hr. at indicated temperature under N₂.

TABLE III

Solvent	Inherent viscosity
Dimethyl sulfoxide	1.88
Tetramethylene sulfone	1.59
N-Methylpyrrolidone	1.36
Sulfuric acid	1.19

The level of stability of this polymer in aqueous bases is indicated in Table IV.

TABLE IV

Base	Temp., °C.	Time, hr.	Orig. η _{inh} ^b	Final η _{inh}
Distilled H ₂ O	25	18	1.83	1.88 ^c
Distilled H ₂ O	100	18	1.83	1.53 ^c
0.5% Dash ^a	25	18	1.83	0.46 ^e
0.5% Dash ^a	100	18	1.83	.26 ^e
1% NaOH	25	18	1.83	.26 ^d
1% NaOH	57	30	1.50	.72 ^f
1% NaOH	57	3	1.50	.20 ^g
10% NaOH	25	13	1.93	.38 ^e
10% NaOH	100	3	1.93	.10 ^e

^a Trademark for Proctor and Gamble's laundry detergent
^b η_{inh}, inherent viscosity. ^c Polymer remained insol. ^d Polymer dissolved in 2 hr. ^e Polymer dissolved in 30 min. ^f Neutral equivalent of product, 352. ^g Neutral equivalent of product, 286.

Similarly, I, like most polysulfones, is thermally unstable (see Fig. 1). However, unlike most polysulfones, this copolymer does not readily yield both monomers as degradation products. In one experiment, compound I was heated from 175 to 325° in

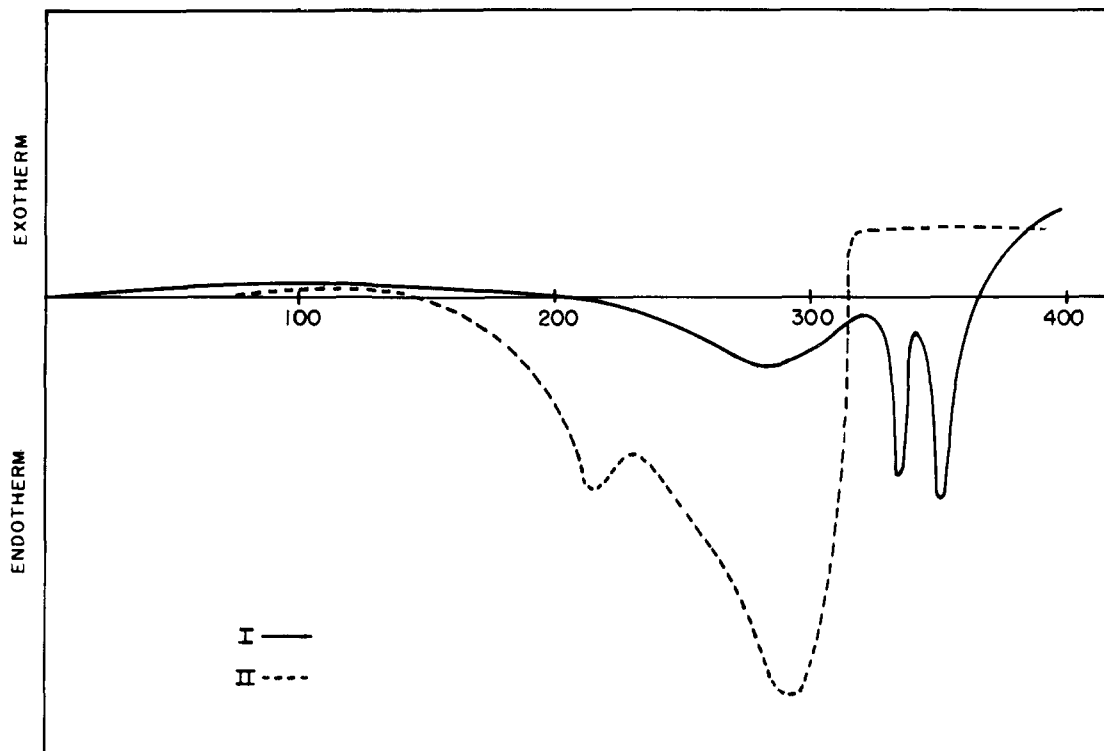


Fig. 2.—Differential thermograms of copolymer, I, and poly-(propylene sulfone), II. Numbers are degrees centigrade.

lithium chloride or N,N-dimethylacetamide containing 5% lithium chloride. None of the common low boiling polymer solvents were found to be solvents for I. A comparison (Table III) of inherent viscosities of a given sample of polymer in different solvents indicates the solvent power of the solvents in question.

Hot sulfuric acid and bases, in general, degrade I. This degradative effect of bases is a general property of copolymers of sulfur dioxide with olefins or dienes.

50° increments for half-hour intervals at each temperature. Only at this latter temperature were any products other than sulfur dioxide collected in a liquid nitrogen trap. Analysis of these degradation products by v.p.c. and infrared indicates that there is no sulfone, some 1,5-cyclooctadiene, and other hydrocarbon products which have not as yet been identified. Differential thermal analysis (Fig. 2) under nitrogen at 5°/min. heating rate showed a broad endotherm at 209 to 320°

with sharp peaks being observed at 335 and 350°. A more complete discussion of the thermal stability of I will be presented in a later paper.

Solutions of this copolymer of sulfur dioxide with *cis,cis*-1,5-cyclooctadiene in dimethyl sulfoxide yield clear, flexible, amorphous films. The properties of films from I, especially creasability, are markedly superior to those of other copolymers of sulfur dioxide with olefins or dienes. Films from these sulfones usually are so brittle that on attempted creasing, the film shatters. Similarly, the fibers from I spun from dimethyl sulfoxide solution are superior to those obtained from other polysulfones.

Experimental

1. Copolymerization of SO₂ with 1,5-Cyclooctadiene. General Method.—All polymerizations were carried out in round-bottom flasks fitted with a Dry Ice condenser, thermometer, and magnetic stirrer. Provisions were made so that the polymerization could be carried out under an inert atmosphere, open to the air, or with a gas bubbling through the reaction mixture.

After *cis,cis*-1,5-cyclooctadiene, b.p. 67–68° (46 mm.) (+99.8% pure by v.p.c.), and the distilled solvents were added, the flask was chilled to –70° and anhydrous sulfur dioxide, as a liquid, was transferred under nitrogen to the flask. With the flask still at –70°, the catalyst was added and the reaction mixture allowed to rise to the reflux temperature of the given mixture. The time of reaction noted in Table I refers to elapsed time from the addition of the catalyst to the precipitation of the reaction mixture. For those mixtures in which such polymer solvents as dimethyl sulfoxide and tetramethylene sulfone were used, the polymer remained in solution and was precipitated by the addition of methanol. For nonsolvent, polymer precipitated during the polymerization. In all cases, the isolated products were repeatedly washed with methanol to remove all traces of monomers and solvents.

The dried polymer was analyzed for sulfur, the inherent viscosities determined in dimethyl sulfoxide, and unsaturation determined by catalytic hydrogenation in tetramethylene sulfone and examination of the infrared absorption in the 6.0 and 6.2 μ range.

2. Viscosity Determinations.—Inherent viscosity, η_{inh} (in η_{rel}/C) for 0.5 g. of polymer/100 ml. of dimethyl sulfoxide solution was determined at 30° using an Ostwald-Fenske viscometer.

3. Determination of Residual Unsaturation. (a) **Catalytic hydrogenation of copolymers** was performed in a volumetric microhydrogenation apparatus. Tetramethylene sulfone was used as solvent and 10% palladium-on-charcoal as catalyst. In each case the reaction was allowed to run for 18 hr. to ensure complete reaction.

(b) **The infrared spectrum of I** showed the pertinent peaks as listed in Table V. For comparison, significant peaks of *cis,cis*-1,5-cyclooctadiene are listed in Table V.

TABLE V

INFRARED ABSORPTION BANDS OF *cis,cis*-1,5-CYCLOOCTADIENE AND I

Wave length, μ	Intensity	Wave length, μ	Intensity
(A) <i>cis,cis</i> -1,5-Cyclooctadiene			
3.30	Strong	7.90	Weak
3.45	Strong	8.10	Weak
6.00	Strong	8.27	Medium
6.15	Weak	9.22	Medium
6.70	Strong	9.95	Medium
6.98	Strong	11.05	Weak
7.36	Weak	12.53	Strong
(B) Copolymer of sulfur dioxide and <i>cis,cis</i> -1,5-cyclooctadiene (I)			
3.30	Medium	7.80	Strong
3.45	Medium	8.40	Strong
6.70	Medium	8.85	Strong
6.98	Medium	9.22	Weak
7.45	Strong	11.05	Weak
7.60	Strong	12.53	Strong

Unsaturation in the copolymer was determined using thin films (less than 1 mil) cast from dimethyl sulfoxide solutions by examination of the infrared absorption in the 6.0 and 6.2 μ region.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY 4, CALIF., AND IOWA STATE UNIVERSITY OF SCIENCE AND TECHNOLOGY, AMES, IOWA]

Photoisomerizations in the α -Tropolone Series: The Mechanistic Path of the α -Tropolone Methyl Ether to Methyl 4-Oxo-2-cyclopentenylacetate Conversion¹

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The photochemical rearrangement of α -tropolone methyl ether to methyl 4-oxo-2-cyclopentenylacetate has been resolved into a sequence of three discrete photochemical rearrangements. The first step is light-induced valence tautomerization of the tropolone ring. The mechanistically important second step is an unprecedented photochemical rearrangement in which the valence tautomer is literally turned inside out. The final step involves hydration of an enol ether followed by a reverse aldol process giving the ketoester product. The nature of this complex photochemical rearrangement is defined clearly by the photochemical rearrangements of 4-methyltropolone methyl ether, 6-methyltropolone methyl ether, and γ -thujaplicin methyl ether.

The rapidly expanding literature of photochemical rearrangements must be fitted into the framework of chemical theory. This task is complicated by an uncertainty in many photochemical rearrangements as to the number and nature of discrete intermediates (other than excited states) involved between starting material and product. It is not possible to interpret complex

(1) A brief report of this work has been published; W. G. Dauben, K. Koch, O. L. Chapman, and S. L. Smith, *J. Am. Chem. Soc.*, **83**, 1768 (1961). This constitutes paper XV in the Photochemical Transformations series (see W. G. Dauben and D. A. Cox, *ibid.*, **85**, 2130 (1963) for part XIV) and part VI of the Photochemical Transformation series (see O. L. Chapman, H. G. Smith, and R. W. King, *ibid.*, **85**, 806 (1963) for part V). Portions of this manuscript were abstracted from the thesis of K. Koch submitted to the Faculty of the University of California and the thesis of S. L. Smith submitted to the Faculty of Iowa State University of Science and Technology.

(2) National Science Foundation Cooperative Predoctoral Fellow, 1959–1961.

(3) National Institutes of Health Predoctoral Fellow, 1959–1961.

photochemical rearrangements without at least a knowledge of the number and nature of discrete photochemical excitations involved and the sequence of these excitations. Very few photochemical rearrangements have been examined in sufficient detail to permit resolution of a complex photochemical rearrangement into a sequence of separate photochemical rearrangements. Notable examples of such photochemical rearrangement sequences are the ergosterol series,⁴ the santonin series,⁵ and the 4,4-diphenyl-2,5-cyclohexadienone series.⁶ We wish to report a new sequence of photochemical rear-

(4) For recent reviews see: H. H. Inhoffen and K. Irmscher, *Fortsch. Chem. Org. Natur.*, **17**, 70 (1959); L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, Chapter IV; H. H. Inhoffen, *Angew. Chem.*, **72**, 875 (1960); B. Lythgoe, *Proc. Chem. Soc.*, 141 (1959).

(5) For a review see D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959).

(6) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961); **84**, 4527 (1962).