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 SO_2 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) *cis,cis*-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 *cis,cis*-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.

Photoisomerizations in the α-Tropolone Series: The Mechanistic Path of the α-Tropolone Methyl Ether to Methyl 4-Oxo-2-cyclopentenylacetate Conversion[1]

By W. G. DAUBEN, K. KOCH,[2] S. L. SMITH,[3] AND O. L. CHAPMAN

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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 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-

(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.

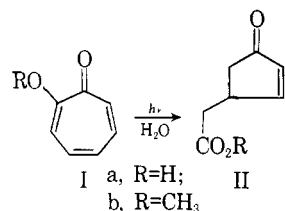(3) National Institutes of Health Predoctoral Fellow, 1959–1961.

(4) For recent reviews see: H. H. Inhoffen and K. Irmscher, *Fortsch. Chem. Org. Naturs.*, **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).
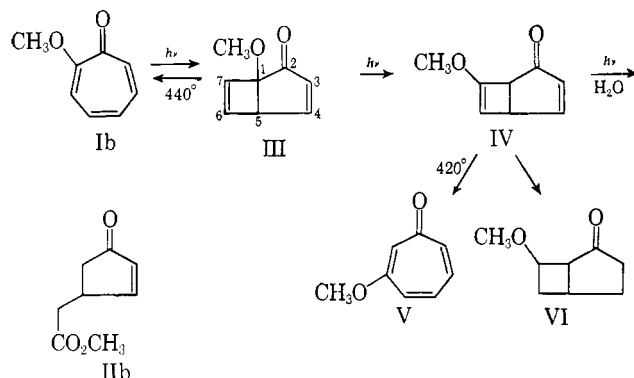
rangements which permits a detailed analysis of the α-tropolone to 4-oxo-2-cyclopentenylacetic acid transformation.

It has been reported that irradiation of an aqueous solution of α-tropolone (Ia) gives 4-oxo-2-cyclopentenylacetic acid (IIa)[7] and that similar irradiation of α-tro-

polone methyl ether (Ib) gives the methyl ester IIb[8] even in aqueous solution precluding a ketene intermediate. In sharp contrast to the dramatic photochemical rearrangement of I stands the relatively simple photochemical valence tautomerization of γ-tropolone methyl ether[9] and colchicine.[10] This sharp difference in photochemical transformation of closely related tropolones suggests that one or more discrete intermediates might be involved between I and II. This has proved to be the case.

Irradiation of α-tropolone methyl ether (Ib) in methanol gives two photoisomers, III (224 mμ, 5.82 μ) and IV (225 mμ, 5.84 μ), separated by vapor phase chromatography. The sequence Ib, III, IV, IIb is estab-


lished by vapor phase chromatographic analysis of aliquots removed during irradiation of Ib in methanol. As Ib decreases, III appears and, more slowly, IV is formed. Continued irradiation leaves only IV which after addition of water decays to IIb. The structures of III and IV are based on the following observations. Pyrolysis (440°) of III gives α-tropolone methyl ether (Ib), suggesting that only valence tautomerization has occurred. Pyrolysis (420°) of IV gives 3-methoxytropone (V), indicating a more complex rearrangement. Hydrogenation of IV over palladium–charcoal gives the tetrahydro derivative VI (5.75 μ). The nuclear magnetic resonance spectra of III and IV (see Table I) firmly establish the assigned structures. Treatment of IV with dilute aqueous acid gives the ester IIb.

The nature of the shift of the methoxyl group is defined clearly by study of the photochemical rearrangements of the methyl-substituted tropolone methyl ethers. Pure 4-methyltropolone methyl ether and 6-meth-

(7) W. G. Dauben, K. Koch, and W. E. Thiessen, J. Am. Chem. Soc., 81, 6087 (1959).

(8) E. J. Forbes and R. A. Ripley, Chem. Ind. (London), 589 (1960); W. G. Dauben and K. Koch, Abstracts of International Symposium on Chemistry of Natural Products, Sydney, Australia, 1960, p. 51.

(9) O. L. Chapman and D. J. Pasto, J. Am. Chem. Soc., 82, 3642 (1960).

(10) E. J. Forbes, J. Chem. Soc., 3864 (1955); P. D. Gardner, R. L. Brandon, and G. R. Haynes, J. Am. Chem. Soc., 79, 6334 (1957); O. L. Chapman and H. G. Smith, ibid., 83, 3914 (1961); O. L. Chapman, H. G. Smith, and R. W. King, ibid., 85, 803, 806 (1963).

yltropolone methyl ether were prepared by previously described procedures[11] and studied separately. Irradiation of 4-methyltropolone methyl ether (VII) in aqueous
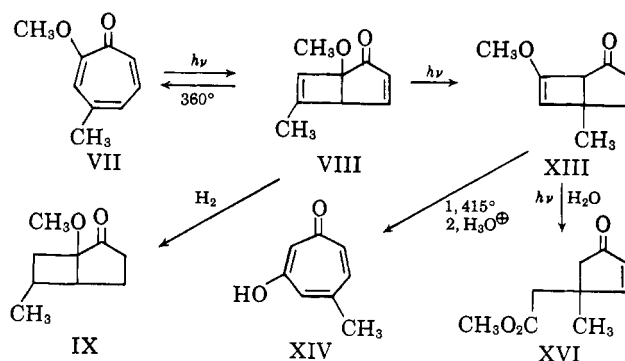
solution in a Pyrex vessel using an external mercury arc lamp gives the valence tautomer VIII.[12] Pyrolysis (360°) of VIII gives 4-methyltropolone methyl ether (VII) excluding gross rearrangement. Catalytic reduction of VIII gives the tetrahydro derivative IX (5.76 μ) characterized as the crystalline semicarbazone. The nuclear magnetic resonance spectrum of VIII (Table I) shows all the expected features, thus confirming the structural assignment. Similar irradiation of 6-methyltropolone methyl ether (X) gives the valence tautomer (229 mμ, 5.85 μ) which on pyrolysis (395°) gives X.
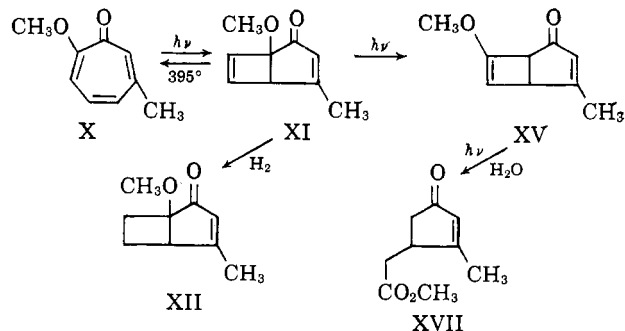
Catalytic reduction of XI gives only the dihydro derivative XII (5.88 μ) characterized as the 2,4-dinitrophenylhydrazone. Structure XI is confirmed by the nuclear magnetic resonance spectrum (Table I). Workable quantities of the valence tautomers VIII and XI are most easily obtained by irradiation of the mixture of 4- and 6-methyltropolone methyl ethers resulting from diazomethane methylation of 4-methyltropolone followed by separation of the valence tautomers by preparative scale vapor phase chromatography. This method circumvents the tedious separation of 4- and 6-methyltropolone methyl ethers by fractional crystallization of the picrates.

Irradiation of the valence tautomer VIII in anhydrous ether in a quartz vessel gives the rearranged bicyclic photoisomer XIII (226 mμ, 5.93 μ) as a sensitive, hygroscopic oil.[13] The structure XIII follows from the nuclear magnetic resonance spectrum (Table I) and the conversion of XIII by pyrolysis and acid hydrolysis to 3-hydroxy-5-methyltropone (XIV). The structure of the degradation product XIV is confirmed by direct comparison with authentic 3-hydroxy-5-methyltropone synthesized from 1,4-dihydro-3,5-dimethoxy-1-methyl-

(11) R. D. Haworth and J. D. Hobson, J. Chem. Soc., 561 (1951).

(12) In Pyrex only the 345 mμ absorption of the tropolone is excited.

(13) This process involves excitation of the n → π* transition of the ketone since the reaction can be carried out in Pyrex vessels with more intense sources. The absorption characteristics of the ketone and the emission characteristics of the mercury arc lamp employed (General Electric UA-3) are such that the reaction is exceedingly slow in Pyrex. The quartz vessel is used only to permit reasonably rapid reaction.

TABLE I
NUCLEAR MAGNETIC RESONANCE SPECTRA[a]

Compound	1	2	3	4	5	6	7
III	Methoxyl protons 6.74		4.33 doublet J_{34} 6.0	2.75 quartet J_{34} 6.0 J_{46} 2.0	6.40 J_{45} 2	3.68 J_{67} 4.0 J_{56} <0.2	3.90 J_{67} 4.0
IV	6.45–6.55 complex band with C$_5$		4.15 quartet J_{34} 7.0 J_{13} 2.0	2.42 quartet J_{34} 7.0 J_{45} 1.0	6.45–6.55 complex band with C$_1$	5.07	Methoxyl protons 6.40
VIII	Methoxyl protons 6.58		3.85 doublet J_{34} 6.3	2.28 quartet J_{34} 6.3 J_{45} 3.2	6.32	Allylic methyl protons 8.12	4.07
XIII	6.95		4.34 doublet J_{34} 6.0	2.55 doublet J_{34} 6.0	Saturated methyl protons singlet 8.60	5.07	Methoxyl protons 6.45
XVI	Saturated methyl protons singlet 8.70	2.43 doublet J_{23} 6.1	4.00 doublet J_{23} 6.1		a 7.65 doublet b 7.84 doublet J_{ab} 18.5	7.50 two proton singlet	Ester methoxyl protons 6.32
XI	Methoxyl protons 6.57		4.15 multiplet	Allylic methyl protons 7.88	6.32	3.21 quartet J_{56} ∼ 1 J_{67} 3.0	3.62 doublet J_{67} 3.0
XV	6.68		4.16 multiplet	Allylic methyl protons 7.99	6.42	4.91 doublet J_{56} 0.8	Methoxyl protons 6.33
XVII	[b]	Allylic methyl protons 7.90	4.07 multiplet		[b]	[b]	Ester methoxy protons 6.32

[a] All spectra were run in deuteriochloroform containing tetramethylsilane as internal standard. Resonance positions are given as τ-values relative to internal tetramethylsilane; J-values are given in c.p.s. [b] These protons give rise to complex absorption between 6.30 and 7.70 τ.

benzoic acid.[14] Similar irradiation of either 6-methyltropolone methyl ether (X) or the valence tautomer XI gives an analogous rearranged photoisomer (XV, 233 mμ, 5.89 μ). The observation that the methoxyl shift between VIII and XIII is accompanied by a shift in the position of the methyl group while the methoxyl shift between XI and XV is accomplished without a methyl shift is of great mechanistic significance. The sequence X, XI, XV is confirmed by analysis of aliquots removed periodically from an irradiation of X in anhydrous ether in quartz. As the concentration of X decreases, the concentration of XI rises to a maximum and then decreases. The concentration of XV increases slowly throughout the irradiation until it is the sole component.

Irradiation of the valence tautomer VIII or the rearranged photoisomer XIII in aqueous solution in a quartz vessel gives the ketoester XVI (218 mμ; 5.77 (sh), 5.86 μ).[13] The structure of the ketoester XVI is established by the nuclear magnetic resonance spectrum (Table I). The necessity of light in the conversion of the rearranged photoisomer XIII to the ketoester XVI was established by a control experiment. Treatment of either XIII or XV with dilute aqueous acid gives the corresponding ketoester XVI or XVII. Irradiation of 6-methyltropolone methyl ether (X), the valence tautomer XI, or the rearranged bicyclic photoisomer XV in aqueous solution in a quartz vessel gives the ketoester XVII.
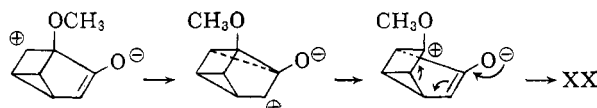
The photoisomerization of tropolones XVIII to bicyclic valence tautomers XIX is analogous to the photoisomerization of γ-tropolone methyl ether[9] and colchicine.[10] The hydration of the enol ether double bond and the reverse aldol reaction which generate the final ester are unexceptional. The transformation of vital mechanistic interest is the photochemical rearrangement of the valence tautomer XIX to the bicyclic photoisomer XX. Mechanistic expression of this deepseated change must account not only for the problematic methoxyl shift but also for the observation that a methyl group in the 6-position of the bicyclic system (XIXb) shifts simultaneously while a methyl group in the 4-position (XIXc) is unaffected. The net result of these requirements is the exchange of position between the two cyclobutene olefinic carbons and the two ring juncture

(14) O. L. Chapman and P. Fitton, J. Am. Chem. Soc., **85**, 41 (1963).

XVIIIa, R = R′ = H
b, R = CH$_3$; R′ = H
c, R = H; R′ = CH$_3$

carbons—completely turning the molecule inside out. This unprecedented rearrangement may be accounted for in the following manner. The valence tautomer XIX is a bent bicyclic system in which the geometry is such that the π-orbital of the nonconjugated double bond can interact with the π-orbital of the conjugated double bond during quantum absorption.[9] This interaction is manifest in the abnormally high wave length absorption of III, IV, VIII, and XIII.[15] The excited state which is directly responsible for rearrangement is schematically represented as a dipolar state (XXI) because the ensuing

(15) The anomaly is not apparent in XI and XV, presumably because of the 4-methyl substituent.

(16) The negative charge is shown on carbon rather than oxygen in the text to simplify the graphic representation of the acyl group migration. The rearrangement may be written in terms of structures with the negative charge on oxygen.

rearrangement is a characteristically polar process. Migration of the acyl group[16] leads to a new excited state (XXII) which collapses to a new ground state— the rearranged bicyclic photoisomer. The driving force for the acyl migration is presumed to be stabilization of the positive charge by the methoxyl in the rearranged excited state. The sequence of events leading to a dipolar state such as XXI can be expressed in reasonable terms by the Zimmerman theory.[6] Addition of water to the enol ether double bond (light-induced or acid-catalyzed) and a reverse aldol process gives the final ester XXIII.

The mechanistic sequence described for the photochemical rearrangements of the α-tropolone methyl ethers and their transformation products requires very specific changes for a 5-substituted tropolone methyl ether. This can be illustrated by γ-thujaplicin methyl ether (XXIV) which should give XXV and XXVI. Irradiation of γ-thujaplicin methyl ether (XXIV) in quartz in fact does give the rearranged bicyclic photoisomer XXVI, further confirming the mechanistic sequence shown.
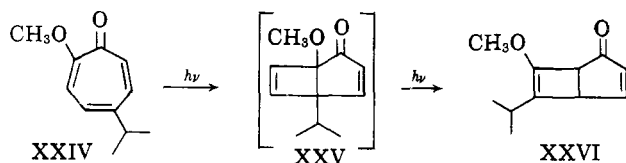
The mechanistic path of the α-tropolone methyl ether to methyl 4-oxo-2-cyclopentenyl acetate conversion, now firmly established, represents one of the most complex photochemical rearrangement sequences yet delineated. The complexity of this sequence emphasizes the danger of interpretations based on an inadequate knowledge of the number of excitation steps involved in a photochemical rearrangement and points the way to further work in the analysis of complex photochemical rearrangements.

Experimental

Irradiation of Tropolone (Ia) in Water.—A solution of 5.0 g. (41 mmoles) of tropolone (Ia) in 500 ml. of distilled water was irradiated with a G.E. A-H6 mercury arc for 2 hr. The aqueous solution was continuously extracted with ether for 24 hr. and the ether extract was washed with 5% sodium bicarbonate. The bicarbonate wash was back-extracted with ether and then acidified. The acidic aqueous layer was continuously extracted with ether. The semisolid (2.7 g.) isolated from the ether extract was crystallized from chloroform; yield of 4-oxo-2-cyclopentene-1-acetic acid (IIa), 0.91 g. (16%), m.p. 102–103°, λ_{max}^{EtOH} 218 mμ (ϵ 12,000); $\nu_{max}^{CHCl_3}$ 1710 cm.$^{-1}$ (5.85 μ), 1680 cm.$^{-1}$ sh (5.95 μ), and 1590 cm.$^{-1}$ (6.3 μ).

Anal. Calcd. for $C_7H_8O_3$ (140.13): C, 59.99; H, 5.75. Found: C, 60.04; H, 5.68.

3-Oxocyclopentane-1-acetic Acid.—A solution of 911 mg. (6.5 mmoles) of 4-oxo-2-cyclopentene-1-acetic acid (IIa) in 95% ethanol was hydrogenated over 11 mg. of prehydrogenated palladium-on-charcoal (157 ml., 1.05 mole % of hydrogen absorbed). The catalyst was removed by filtration through a layer of Super-Cel, the filtrate evaporated under reduced pressure, and the residual oil molecularly distilled; yield 812 mg. (88%), $n^{24}D$ 1.4766, $\nu_{max}^{CHCl_3}$ 1740 cm.$^{-1}$ (5.75 μ). The semicarbazone was formed by treatment of the acid with an aqueous solution of semicarbazide hydrochloride and sodium acetate and recrystallized from 20% ethanol; m.p. 202–203° (lit.[17] m.p. 199°).

Anal. Calcd. for $C_7H_{10}O_3$ (142.15): C, 59.14; H, 7.09. Found: C, 58.93; H, 6.88.

Irradiation of Tropolone (Ia) in 95% Ethanol.—A solution of 5.45 g. (44 mmoles) of tropolone in 50 ml. of 95% ethanol was irradiated for 20 hr. with an internal Hanau quartz probe. After evaporation of the solvent under reduced pressure, the residual oil (5.85 g.) was molecularly distilled; yield 3.92 g. (52%) of ethyl 4-oxo-2-cyclopentene-1-acetate, $n^{24}D$ 1.4728, λ_{max}^{EtOH} 216 mμ (ϵ 11,000); ν_{max}^{liq} 1740 (5.75 μ), 1710 (5.85 μ), and 1590 cm.$^{-1}$ (6.30 μ).

Anal. Calcd. for $C_9H_{12}O_3$ (168.19): C, 64.27; H, 7.19. Found: C, 64.26; H, 7.21.

Hydrolysis of Ethyl 4-Oxo-2-cyclopentene-1-acetate.—A solution of 966 mg. (5.7 mmoles) of ethyl 4-oxo-2-cyclopentene-1-acetate in 20 ml. of 5% hydrochloric acid was heated under reflux for 1 hr. The reaction mixture was neutralized with solid sodium bicarbonate and extracted with chloroform. Upon evaporation of the solvent under reduced pressure, 60 mg. of neutral material was isolated. The aqueous solution was acidified and continuously extracted with ether. The ether extract was dried over magnesium sulfate and evaporated under reduced pressure. The crude 4-oxo-2-cyclopentene-1-acetic acid (IIa) (514 mg., 64%) was recrystallized from chloroform–carbon tetrachloride; yield 140 mg. (18%), m.p. 99–101°, infrared spectrum identical with irradiation product IIa.

Irradiation of Tropolone Methyl Ether. (a) In Water.—A solution of 912 mg. (7.2 mmoles) of tropolone methyl ether (Ib) in 500 ml. of distilled water was irradiated with a G.E. A-H6 mercury arc for 30 min. The aqueous solution was continuously extracted with ether, the ether extract was dried over magnesium sulfate, and the ether was removed by evaporation under reduced pressure. The residual yellow oil (670 mg., 60%) was molecularly distilled; yield of methyl 4-oxo-2-cyclopentene-1-acetate (IIb), 419 mg. (38%), $n^{24}D$ 1.4830, λ_{max}^{EtOH} 215 mμ (ϵ 10,000); $\nu_{max}^{CCl_4}$ 1740 (5.75 μ), 1715 (5.84 μ), and 1580 cm.$^{-1}$ (6.32 μ). An authentic sample of the ester was prepared by allowing an ethereal solution of 4-oxo-2-cyclopentene-1-acetic acid to react with an ethereal solution of diazomethane.

Anal. Calcd. for $C_8H_{10}O_3$ (154.18): C, 62.32; H, 6.54. Found: C, 62.05; H, 6.45.

(b) In Methanol.—A solution of 2.0 g. (15 mmoles) of tropolone methyl ether in 600 ml. of absolute methanol was irradiated under anhydrous conditions with a G.E. A-H6 mercury arc for 45 min. The methanol was evaporated under reduced pressure and the crude oil was molecularly distilled; yield of 7-methoxy-3,6-bicyclo[3.2.0]heptadiene-2-one (IV), 1.1 g. (55%); λ_{max}^{EtOH} 225 mμ (ϵ 6,000), 5.84 μ.

Anal. Calcd. for $C_8H_8O_2$ (136.14): C, 70.57; H, 5.92. Found: C, 70.28; H, 6.17.

Hydrogenation of 7-Methoxy-3,6-bicyclo[3.2.0]heptadiene-2-one(IV).—A solution of 267 mg. (2 mmoles) of 7-methoxy-3,6-bicyclo[3.2.0]heptadiene-2-one in 25 ml. of 95% ethanol was hydrogenated over 10 mg. of prehydrogenated 10% palladium-on-charcoal (78 ml., 1.6 mole % of hydrogen absorbed). The catalyst was removed by filtration through a layer of Super-Cel and the ethanol was evaporated from the filtrate under reduced pressure. The crude product (181 mg.) was molecularly distilled, yield of 7-methoxybicyclo[3.2.0]heptane-2-one, 101 mg. (37%), ν_{max}^{liq} 1730 cm.$^{-1}$ (5.78 μ).

Anal. Calcd. for $C_8H_{12}O_2$ (140.18): C, 68.54; H, 8.63. Found: C, 68.24; H, 8.83.

Acid Rearrangement of 7-Methoxy-3,6-bicyclo[3.2.0]heptadiene-2-one (IV).—A solution of 95 mg. (0.71 mmole) of 7-methoxy-3,6-bicyclo[3.2.0]heptadiene-2-one (IV) in 15 ml. of 1 N sulfuric acid was saturated with ammonium sulfate and extracted with ether. The ether extract was dried over magnesium sulfate and the ether was evaporated under reduced pressure; yield of methyl 4-oxo-2-cyclopentene-1-acetate (IIb), 89 mg. (82%), λ_{max}^{EtOH} 218 mμ (ϵ 10,000); infrared spectrum identical with that of an authentic sample.

Anal. Calcd. for $C_8H_{10}O_3$ (154.16): C, 62.32; H, 6.54. Found: C, 62.62; H, 6.25.

Pyrolysis of 7-Methoxy-3,6-bicyclo[3.2.0]heptadiene-2-one-(IV).—7-Methoxy-3,6-bicyclo[3.2.0]heptadiene-2-one (IV) (287 mg., 2.1 mmoles) was pyrolyzed at 420°. The cooled tube was washed with chloroform and the solvent was evaporated under reduced pressure. The crude product (270 mg.) was treated with a solution of 329 mg. of picric acid in 4 ml. of ethanol and the picrate of 3-methoxytropone (V, 344 mg., 48%) which formed instantaneously was collected by filtration; m.p. 145–146° (lit.[18] m.p. 128° or 146°). The picrate was dissolved in chloroform, filtered through a short column of activity III alumina, and the solvent was evaporated under reduced pressure; yield of 3-methoxytropone, 126 mg. (75%, based on the picrate). Gaseous hydrogen bromide was bubbled into a solution of 116 mg. (0.86 mmole) of 3-methoxytropone in ether and the hydrobromide, 162 mg. (88%), m.p. 118° (lit.[18] m.p. 119°), was removed by filtration. 3-Methoxytropone hydrobromide (133 mg., 0.64 mmole) was dissolved in 1 ml. of 48% aqueous hydrogen bromide and 1 ml. of water and heated under reflux for 1 hr. at 110°. The solvent was partially removed by evaporation under reduced pressure and the final volume was adjusted to 1 ml. with water. A precipitate formed and was dissolved by heating the solution. The heated solution was neutralized with 2 N sodium hydroxide and then acidified slightly with 2 N hydrochloric acid. After

(17) E. H. Farmer, *J. Chem. Soc.*, 3324 (1933).

(18) R. B. Johns, A. W. Johnson, and M. Tisler, *ibid.*, 4605 (1954).

standing overnight at 0°, 3-hydroxytropone (24 mg., 28%), m. p. 158–161°, was removed by filtration and recrystallized from water; yield 9 mg., (11%), m.p. 161–162° (lit.[18] m.p. 179–180°). The filtrate was treated with picric acid and 14 mg. of the picrate, m.p. 165–167°, was isolated (lit.[18] m.p. 165°). The ultraviolet spectrum of this picrate was compared to that of an authentic sample of the picrate of 3-hydroxytropone, m.p. 161–166°, which was prepared from a sample of 3-hydroxytropone supplied by Johnson.[18] The ultraviolet spectra were taken using an equimolar solution of picric acid as the reference.

Anal. Calcd. for $C_{14}H_{11}O_9N_3$ (365.25): C, 46.03; H, 3.04; N, 11.51. Found: C, 46.21; H, 3.12; N, 11.66.

Irradiation of Tropolone Methyl Ether with External Sources. —A solution of 1.0 g. (7.4 mmoles) of tropolone methyl ether in 250 ml. of absolute methanol was irradiated for 11 hr. with a G.E. sun-lamp placed 10 cm. below the flask. The solvent was evaporated under reduced pressure and the crude oil (1.05 g.) was molecularly distilled; yield 0.63 g. (63%) of a mixture of isomeric products. The isomers could be separated by g.l.c. on a diethylene glycol succinate (DEGS). The ratio of isomers was two parts of 7-methoxy-3,6-bicyclo[3.2.0]-heptadiene-2-one (IV) to one part of 1-methoxy-3,6-bicyclo[3.2.0]heptadiene-2-one (III); properties of III, λ_{max}^{EtOH} 224 mμ (ε 6,600), 5.83 μ.

Anal. Calcd. for $C_8H_8O_2$ (136.14): C, 70.57; H, 5.92. Found: C, 70.22; H, 6.13.

Irradiation using a Hanau lamp, a G.E. A-H4 lamp, or a G.E. H85-C3 lamp as the external source gave the same products.

Pyrolysis of 1-Methoxy-3,6-bicyclo[3.2.0]heptadiene-2-one (III).—A 58-mg. (0.43 mmole) sample of 1-methoxy-3,6-bicyclo-[3.2.0]heptadiene-2-one (III) was pyrolyzed at 440°. The cooled column was washed with chloroform and the chloroform was evaporated under reduced pressure. The crude tropolone methyl ether (42 mg., 73%) was purified as its picrate; yield of picrate, 17 mg., m.p. 115–119° (lit.[19] m.p. 119–120°). The picrate was decomposed with activity III alumina and the product possessed λ_{max}^{EtOH} 234, 317, 333, 344, and 361 mμ (ε 22,000, 7,100, 6,200, 6,000, and 3,800).

Photoisomerization of 1-Methoxy-3,6-bicyclo[3.2.0]heptadiene-2-one (III).—A solution of 100 mg. of IV in 150 ml. of absolute methanol was irradiated with a G.E. sun-lamp. Aliquots were removed and analyzed by g.l.c. After 30 min. all of the starting material III had disappeared and only the 7-methoxy isomer IV and the ester IIb were present.

Photoisomerization of Tropolone Methyl Ether as a Function of Time.—A solution of 500 mg. of tropolone methyl ether (Ib) in 200 ml. of absolute methanol was irradiated with a G.E. sun-lamp. Aliquots were removed and analyzed by g.l.c. After 2.5 hr., 60% of the starting material had disappeared and the ratio of III/IV was 3. After 5.5 hr., 95% of the starting material had disappeared and the ratio of III/IV was 1/4, also 25% of ester IIb had formed.

Photoisomerization of the Mixture of 4-Methyltropolone Methyl Ether and 6-Methyltropolone Methyl Ether.—A solution of the mixture (7.30 g.) of 4-methyltropolone methyl ether and 6-methyltropolone methyl ether obtained by diazomethane methylation of 4-methyltropolone[11] in distilled water (2 l.) was irradiated in two 1-l. Pyrex vessels with an external mercury arc lamp (General Electric UA-3). The irradiation was stopped when the ultraviolet absorption at 345 mμ was reduced to 9% of the original value (16 hr.). Extraction of the reaction mixture with methylene chloride, drying over anhydrous sodium sulfate, and concentration under aspirator vacuum gave a red oil (5.90 g.) which was molecularly distilled (100°, 0.5 mm.). Vapor phase chromatographic analysis of the product showed two major components (VIII and XI) and two minor components which constituted approximately 5% of the total product. These minor components were identified as the esters XVI and XVII. The products were separated by preparative scale vapor phase chromatography on a column containing UCON-lb550x (20%) on 40–60 mesh Celite giving two fractions. Two molecular distillations of fraction I gave VIII (1.18 g.) as a pale yellow liquid; $\lambda_{max}^{H_2O}$ 230 mμ (6,310), 5.85 μ (C=O).

Anal. Calcd. for $C_9H_{10}O_2$: C, 71.31; H, 6.71. Found: C, 71.30; H, 6.71.

Two molecular distillations of fraction II gave XI (1.0 g.) as a pale yellow oil which slowly crystallized, m.p. 42.1–44.1°; $\lambda_{max}^{H_2O}$ 229 mμ (6,190), 5.85 μ (C=O).

Anal. Calcd. for $C_9H_{10}O_2$: C, 71.31; H, 6.71. Found: C, 71.54; H, 6.74.

Irradiation of 4-Methyltropolone Methyl Ether.—A solution of pure 4-methyltropolone methyl ether (2.85 g.) in water (1 l.) was irradiated in a Pyrex flask using an external mercury arc lamp (General Electric UA-3). The irradiation was stopped when the extinction at 345 mμ was reduced to 10% of the original value (26 hr.). The solution was extracted with methylene

chloride, and the extract dried over anhydrous sodium sulfate. Evaporation of the solvent gave a reddish oil which on molecular distillation (85° (0.08 mm.)) gave 2.0 g. (71%) of VIII identical in infrared and ultraviolet absorption with VIII obtained above.

Irradiation of 6-Methyltropolone Methyl Ether.—A solution of pure 6-methyltropolone methyl ether (2.5 g.) in water (1 l.) was irradiated in a Pyrex vessel using a General Electric UA-3 mercury arc lamp. The reaction was followed by vapor phase chromatography on a 4 ft. by 0.25 in. column packed with 20% silicone gum rubber on Chromosorb-P, programmed at 15°/min. between 50 and 225°. Extraction of the aqueous solution with methylene chloride (5 × 25 ml.) gave, after drying over sodium sulfate and evaporation of the solvent, the crude photoproduct. This material was dissolved in ether and passed through an alumina column. Evaporation of the ether gave a mixture of crystals and yellow oil. Several recrystallizations from ether gave XI (866 mg.), m.p. 43.5–45.5°, identical in infrared, ultraviolet, and nuclear magnetic resonance absorption with XI described above.

Pyrolysis of VIII.—The valence tautomer VIII (25 mg.) was dropped into a vertical, 6 × 0.75 in. column[20] packed with Pyrex helices at 360°. The column was swept with oxygen-free nitrogen, and the pyrolysate was collected in a tube immersed in a Dry Ice-acetone bath. The pyrolysate was identified by infrared comparison as 4-methyltropolone methyl ether. The pyrolysate was warmed (60–70°) for 6 min. with 10 N sodium hydroxide (10 ml.) to hydrolyze it to 4-methyltropolone. An aliquot (1 ml.) diluted 1:100 with distilled water showed the characteristic ultraviolet spectrum of 4-methyltropolone anion.

Pyrolysis of XI.—A solution of XI (50 mg.) in pentane (12 ml.) was dropped through the pyrolysis column (described above) at 395°. The pyrolysate was dissolved in chloroform, and the chloroform and pentane were removed, leaving a white solid. One recrystallization from hexane gave 6-methyltropolone methyl ether, m.p. 95–96° (authentic 6-methyltropolone methyl ether, m.p. 96–97°) identical in infrared absorption with authentic 6-methyltropolone methyl ether.

Hydrogenation of VIII.—A solution of VIII (106 mg.) in methanol (65 ml.) was permitted to absorb two equivalents of hydrogen over Adams catalyst. Evaporation of the solvent after filtration gave a brown oil. Molecular distillation of this oil gave IX (99 mg.) as a colorless oil which showed no high intensity ultraviolet absorption and infrared carbonyl absorption at 5.76 μ. A semicarbazone was prepared in the usual manner. Five recrystallizations of the semicarbazone from water gave fine, white crystals, m.p. 183–185°.

Anal. Calcd. for $C_{10}H_{18}N_3O_2$: C, 56.85; H, 8.11; N, 19.89. Found: C, 57.16; H, 8.07; N, 19.67.

Hydrogenation of XI.—A solution of XI (80 mg.) in methanol (30 ml.) absorbed one equivalent of hydrogen over Adams catalyst. Removal of the solvent after filtration gave a colorless liquid. Two molecular distillations of this liquid gave XII (57 mg.) as a colorless oil, $\lambda_{max}^{95\% EtOH}$ 232 mμ (12,450), λ_{max} 5.88 μ. A 2,4-dinitrophenylhydrazone of XII was prepared in the usual manner and separated from excess reagent by passing it through a Bentonite-Celite (1:3) column in benzene. The 2,4-dinitrophenylhydrazone was then crystallized rapidly from aqueous ethanol, giving red-orange crystals, m.p. 117.2–119.5°.

Anal. Calcd. for $C_{15}H_{16}N_4O_5$: C, 54.21; H, 4.85; N, 16.86. Found: C, 54.31; H, 4.87; N, 16.64.

Photoisomerization of VIII to XIII.—A solution of VIII (1.0 g.) in anhydrous ether (180 ml.) was placed in a brush flamed quartz tube, flushed with nitrogen, and irradiated with an external General Electric UA-3 mercury arc lamp. The progress of the reaction was followed by periodic vapor phase chromatographic analysis of aliquots on a 2 ft. by 0.25 in. silicone gum rubber column at 150°. Conversion was complete in 3 hr. Removal of the solvent left an oil which was molecularly distilled and then passed through an alumina column in ether. Removal of the ether followed by careful molecular distillation (35°, 0.08 mm.) gave XIII (0.4 g.) as a colorless, hygroscopic liquid, $\lambda_{max}^{95\% EtOH}$ 226 mμ (6,420), λ_{max} 5.93 μ (C=O).

Anal. Calcd. for $C_9H_{10}O_2$: C, 71.31; H, 6.71. Found: C, 71.67; H, 6.71.

Conversion of XIII to XIV.—A solution of XIII (35 mg.) in cyclohexane (10 ml.) was dropped through the pyrolysis column described above at 415°. The pyrolysate showed $\lambda_{max}^{cyclohexane}$ 217, 238, and 290 mμ. The pyrolysate was heated (105–115°) in 20% hydrobromic acid for 3.5 hr. Neutralization of this solution followed by acidification and cooling gave crystalline 3-hydroxy-5-methyltropone which after one recrystallization from water showed m.p. 134.5–136° and mixture melting point 135–139.5° with authentic 3-hydroxy-5-methyltropone. The infrared spectrum of the product was superimposable on the infrared spectrum of authentic 3-hydroxy-5-methyltropone.

(19) J. W. Cook, A. R. M. Gibb, R. A. Raphael, and A. R. Somerville, *J. Chem. Soc.*, 503 (1951).

(20) This is the same column used for acetate pyrolysis (D. H. Froemsdorf, C. H. Collins, G. S. Hammond, and C. H. DePuy, *J. Am. Chem. Soc.*, **81**, 643 (1959)).

Photoisomerization of XI to XV.—A solution of XI (855 mg.) in anhydrous ether (225 ml.) was flushed with nitrogen and irradiated in a quartz tube with an external mercury arc lamp (General Electric UA-3). Vapor phase chromatographic analysis of aliquots on a 4 ft. by 0.25 in. silicone gum rubber column at 185° showed the reaction to be complete after 11 hr. The reaction was retarded by a film of decomposition products which formed on the wall of the vessel. Evaporation of the solvent gave a red oil. After molecular distillation the product was dissolved in ether and passed through an alumina column. Removal of the ether followed by molecular distillation (50° (0.1 mm.)) of the residue gave XV (417 mg.) as a colorless, hygroscopic semisolid, m.p. *ca.* 33–35°, $\lambda_{max}^{H_2O}$ 233 mμ (9,730), λ_{max} 5.89 μ.

Anal. Calcd. for $C_9H_{10}O_2$: C, 71.31; H, 6.71. Found: C, 71.48; H, 6.68.

Photoisomerization of 6-Methyltropolone Methyl Ether (X) to XV *via* XI.—A solution of 6-methyltropolone methyl ether (470 mg.) in anhydrous ether (100 ml.) was flushed with nitrogen and irradiated (General Electric UA-3 mercury arc lamp) in a quartz vessel. Aliquots were withdrawn periodically, and the relative composition was determined by vapor phase chromatographic analysis on a 2-ft. silicone gum rubber column programmed at 15°/min. between 50 and 310°. It was necessary to change quartz vessels after 40 hr. because of a film of decomposition products deposited on the walls of the vessel.

Time, hr.	Relative composition (per cent)		
	X	XI	XV
0	100	0	0
4	88	10	2
8	76	17	7
12	66	24	10
28.5	31	42	27
32.5	18	40	42
35	11	41	48
40.5	5	43	52
44	0	28	72
46	0	20	80
48	0	14	86
50	0	8	92

The irradiation was stopped after 50 hr. Concentration of the reaction solution under a stream of dry nitrogen gave a dark oil (417 mg.). Two molecular distillations of this oil gave XV identical in infrared, ultraviolet, and nuclear magnetic resonance absorption to authentic XV.

Photoisomerization of VIII to XVI.—A solution of VIII (710 mg.) in 95% ethanol (10 ml.) was diluted to 560 ml. with distilled water. This solution was divided equally in three quartz tubes and irradiated with an external mercury arc lamp (General Electric UA-3). After 5 hr. irradiation vapor phase chromatographic analysis (4 ft. by 0.25 in. silicone gum rubber column at 150°) indicated complete conversion to a new product. Extraction with methylene chloride, drying, and removal of the solvent gave the crude product which was molecularly distilled. The distilled product was dissolved in ether, passed through an alumina column, and then molecularly distilled, giving XVI (103 mg.) as a colorless liquid; $\lambda_{max}^{95\% EtOH}$ 218 mμ (7,680), 5.77 (sh., ester C=O), 5.86 μ (ketone, C=O).

Anal. Calcd. for $C_9H_{12}O_3$: C, 64.21; H, 7.19. Found: C, 64.55; H, 7.14.

Photoisomerization of XI to XVII.—A solution of XI (500 mg.) in distilled water (200 ml.) was irradiated in a quartz tube with an external mercury arc lamp (General Electric UA-3) for 6.5 hr. Extraction with methylene chloride, drying, and evaporation gave a yellow oil. The crude product in ether solution was passed through an alumina column and then molecularly distilled, giving XVII (86 mg.) as a colorless liquid which crystallized on standing, m.p. *ca.* 29–30°; $\lambda_{max}^{H_2O}$ 228 mμ (14,100), 5.76 (ester, C=O), 5.85 μ (ketone, C=O).

Anal. Calcd. for $C_9H_{12}O_3$: C, 64.21; H, 7.19. Found: C, 64.35; H, 7.40.

Photochemical Conversion of XIII to XVI.—A solution of XIII (141 mg.) in 25% (by volume) ethanol–water (200 ml.) was divided into two equal portions in identical quartz vessels. One solution was irradiated with an external General Electric UA-3 mercury arc lamp. The other solution was maintained at 45° (the temperature of the solution being irradiated) in the dark. Aliquots were withdrawn periodically from each solution, extracted with methylene chloride, dried over anhydrous sodium sulfate, evaporated to dryness, and analyzed by vapor phase chromatography on a 4 ft. × 0.25 in. silicone gum rubber column at 135°. The dark (control) solution showed no change after 5 hr., after which time the irradiated solution contained only XVI. The product XVI was identical in vapor phase chromatographic retention time and ultraviolet absorption to authentic XVI.

Acid-Catalyzed Conversion of XIII to XVI.—A solution of XIII in 95% ethanol (8.8×10^{-5} M) was placed in a quartz cell Two drops of 1 N hydrochloric acid was added to this solution and to a matched reference cell filled with 95% ethanol. The ultraviolet absorption of the solution was determined periodically. The ultraviolet absorption maximum shifted from 226 (6,400) to 218 mμ (9,000), characteristic of XVI, in 350 min. Two isosbestic points were observed in the spectra, 206 and 230 mμ.

Acid-Catalyzed Conversion of XV to XVII.—A solution of XV in distilled water (6.95×10^{-4} M) was prepared. A 1-ml. aliquot of this solution was diluted 1:10 with 0.0211 N hydrochloric acid, giving a solution 6.93×10^{-5} M in XV and 0.0190 N in hydrochloric acid. An ultraviolet spectrum taken less than 2 min. after the dilution with hydrochloric acid showed only the characteristic ultraviolet absorption of the ester XVII (228 mμ, 14,000) which did not change with time.

Irradiation of γ-Thujaplicin Methyl Ether (XXIV).—A solution of 150 mg. (0.8 mmole) of γ-thujaplicin methyl ether in 200 ml. of absolute methanol was irradiated with a G.E. sun-lamp for 4 hr. The solvent was evaporated under reduced pressure. The products could be separated on a 0.25-in. DEGS column, $T = 150°$. Properties of the major product were λ_{max}^{EtOH} 218 mμ (ϵ 7,300), $\lambda_{max}^{EtOH-H^+}$ 218 mμ (ϵ 8,100), ν_{max}^{liq} 1710 (5.85 μ) and 1585 cm.$^{-1}$ (6.30 μ); n.m.r.: 2.40 τ, J_{34} = 4 c.p.s.; 3.98 τ, J_{34} = 4 c.p.s.; 6.30 τ (singlet, 3 H), 6.56 τ (multiplet, 206 c.p.s.), 7.67 and 8.10 τ (broad bands), and 8.95 τ, doublet of isopropyl methyl groups, J = 8 c.p.s.