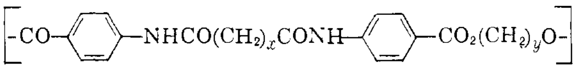
properties as measured on drawn monofils are: Young's modulus 7.47 × 10^4kg./cm.^{2}, yield stress 1100 kg./cm.^{2}, tensile strength 2700 kg./cm.^{2}, elongation 32%.

Polymers prepared by condensing bis-(*p*-carbethoxyphenyl)-amides with glycols and having the basic structure



are relatively high melting. The best products were obtained from the C_5–C_{10}-aliphatic dibasic acids. The lower molecular weight acids gave products with melting points so high that crystallization occurred before high molecular weights could be obtained. The physical properties are shown in Table IV. It would appear feasible on the basis of the melting points to extend the series to adipic acid, but preparative difficulties were encountered in all such efforts. The best fiber properties are found in the suberic acid derivatives.

ROCHESTER 4, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY]

Photochemical Transformations of Simple Troponoid Systems. I. Photo-γ-tropolone Methyl Ether[1]

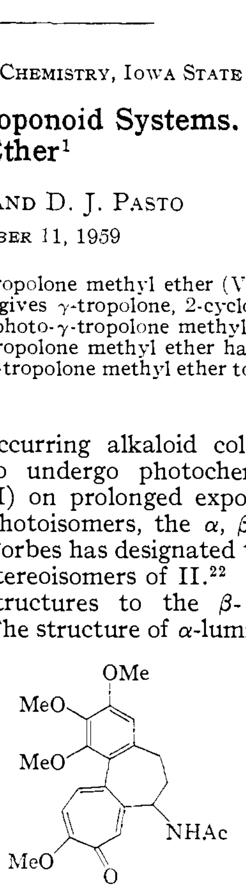
BY O. L. CHAPMAN AND D. J. PASTO

RECEIVED NOVEMBER 11, 1959

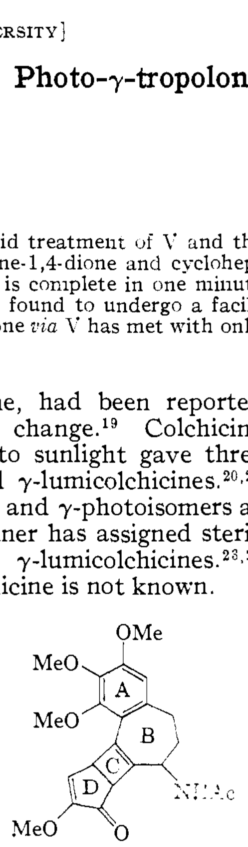
Irradiation of γ-tropolone methyl ether (IV) gives photo-γ-tropolone methyl ether (V). Acid treatment of V and the corresponding dihydro (VII) and tetrahydro derivative (VIII) gives γ-tropolone, 2-cycloheptene-1,4-dione and cycloheptane-1,4-dione. The acid-catalyzed ring opening of tetrahydrophoto-γ-tropolone methyl ether is complete in one minute under conditions in which V and VII do not react. Photo-γ-tropolone methyl ether has been found to undergo a facile pyrolysis to γ-tropolone methyl ether. An attempt to convert γ-tropolone methyl ether to tropone *via* V has met with only minor success.

Photochemical isomerization of unsaturated molecules has become a topic of rapidly increasing interest and significance. Recent examples of photoisomerization include conjugated dienones,[2,3] cross conjugated dienones,[4-7] conjugated dienes[8-11] and trienes,[12,13] α,β-unsaturated ketones,[14] unconjugated dienes[15,16] and even simple cyclic ketones[17] and ethers.[18]

Prior to the completion of our investigation of the photoisomerization of γ-tropolone methyl ether[1] only one troponoid compound, the naturally occurring alkaloid colchicine, had been reported to undergo photochemical change.[19] Colchicine (I) on prolonged exposure to sunlight gave three photoisomers, the α, β- and γ-lumicolchicines.[20,21] Forbes has designated the β- and γ-photoisomers as stereoisomers of II.[22] Gardner has assigned steric structures to the β- and γ-lumicolchicines.[23,24] The structure of α-lumicolchicine is not known.



I



II

Contemplation of the variety of valence tautomerization type photoisomerization reactions potentially available to simple troponoid systems leads to consideration of several quite novel chemical transformations. A simple tropolone or substituted tropone might, in principle, undergo three types of light-induced valence tautomerization. These reaction types are illustrated below for a 2-substi-

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[1] This report was presented in part before the Division of Organic Chemistry, April 8, 1959. A preliminary communication of a portion of the results now reported has been published (O. L. Chapman and D. J. Pasto, THIS JOURNAL, **80**, 6685 (1958)).

[2] G. Büchi and N. C. Yang, *Chemistry & Industry*, 357 (1957).

[3] D. H. R. Barton and G. Quinkert, *Proc. Chem. Soc.*, 197 (1958).

[4] D. H. R. Barton, *ibid.*, 61 (1958); D. H. R. Barton, P. de Mayo and M. Shafiq, *J. Chem. Soc.*, 3314 (1958); D. H. R. Barton and W. C. Taylor, *ibid.*, 2500 (1958).

[5] D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger and L. J. Krebaum, *Helv. Chim. Acta*, **40**, 1732 (1957).

[6] W. Cocker, K. Crowley, J. T. Edward, T. B. H. McMurray and E. R. Stuart, *J. Chem. Soc.*, 3416 (1957).

[7] E. E. van Tamelen, S. H. Levine, G. Brenner, J. Wolinsky and P. E. Aldrich, THIS JOURNAL, **81**, 1666 (1959).

[8] W. G. Dauben and G. J. Fonken, *ibid.*, **81**, 4060 (1959).

[9] R. L. Autrey, D. H. R. Barton and W. H. Reusch, *Proc. Chem. Soc.*, 55 (1959).

[10] L. Velluz, B. Goffinet and G. Amiard, *Tetrahedron*, **4**, 241 (1958).

[11] H. H. Inhoffen and H. Schaeffer, *Ber.*, **92**, 1126 (1957).

[12] W. G. Dauben, I. Bell, T. W. Hutton, G. F. Laws, A. Rheiner, Jr., and H. Urscheler, THIS JOURNAL, **80**, 4117 (1958).

[13] D. H. R. Barton and A. S. Kende, *J. Chem. Soc.*, 688 (1958).

[14] G. Büchi and I. M. Goldman, THIS JOURNAL, **79**, 4741 (1957); J. W. Wheeler and R. H. Eastman, *ibid.*, **81**, 237 (1959); J. J. Hurst and G. H. Whitham, *Proc. Chem. Soc.*, 160 (1959).

[15] S. J. Cristol and R. L. Snell, THIS JOURNAL, **80**, 1950 (1958).

[16] R. C. Cookson, E. Crundwell and J. Hudec, *Chemistry & Industry*, 1003 (1958); R. C. Cookson and E. Crundwell, *ibid.*, 1004 (1958).

[17] R. Srinivasan, THIS JOURNAL, **81**, 1546 2601, 2604 (1959).

[18] J. D. Margerum, J. N. Pitts, Jr., J. G. Rutgers and S. Searles, *ibid.*, **81**, 1549 (1959).

[19] We have since been informed by Professor W. G. Dauben that irradiation of α-tropolone in aqueous solution gives 4-oxo-2-cyclopentene-1-acetic acid (W. G. Dauben, K. Koch and W. E. Thiessen, *ibid.*, **81**, 6087 (1959).

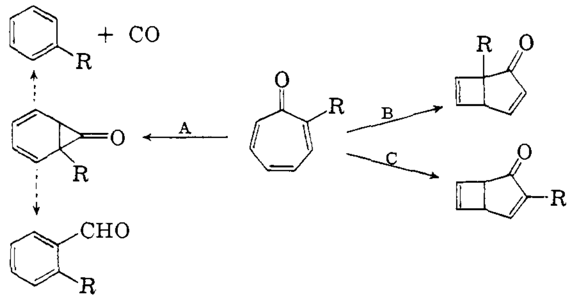
[20] R. Grewe and W. Wolf, *Ber.*, **84**, 621 (1951).

[21] F. Šantavý, *Biol. Listy*, **31**, 246 (1950).

[22] E. J. Forbes, *J. Chem. Soc.*, 3864 (1955).

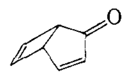
[23] P. D. Gardner, R. L. Brandon and G. R. Haynes, THIS JOURNAL, **79**, 6334 (1957).

[24] The unprecedented epimerization of β- to γ-lumicolchicine in base[23] has posed a major objection to acceptance of the structure II. This objection is now obviated by mechanistic considerations based on observations pertinent to photo-γ-tropolone methyl ether (*vide infra*).



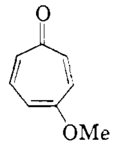
tuted tropone. This scheme easily can be generalized to include 3- and 4-substituted tropones. Reaction type A represents a form of valence tautomerization not yet encountered in the troponoid series but one which is well-known in cycloheptatriene chemistry.[25,26] Presumably the cyclopropanone intermediate would undergo further reaction (two possibilities are shown in the scheme above). Valence tautomerization of the type B also had not been recognized prior to our investigation of the photochemistry of γ-tropolone methyl ether. Reaction *via* process C is known only in the formation of β- and γ-lumicolchicine.

If type B or C reactions could be realized in simple, monocyclic troponoid systems, a direct synthetic route would be available to a variety of interesting and unique derivatives of the bicyclo[3.2.0.]hepta-3,6-diene-2-one system (III). This system, of unusual interest because of its geometry and electronic arrangement, would be difficultly available by classic synthetic methods. Derivatives of III might also be useful as intermediates in the preparation of new troponoid systems. Photoisomerization of troponoid systems *via* processes A, B or C should provide new methods for the characterization of troponoid systems of unknown constitution. Such methods of characterization would be of prime importance in the study of β- and γ-tropolone derivatives in which the classic mode of characterization of α-tropolones—base-catalyzed rearrangement to benzoic acids—is an exceedingly difficult reaction.[27] Delineation of the photoisomerization reactions of a variety of troponoid systems under various reaction conditions should also provide useful information concerning the nature and chemistry of excited states in troponoid compounds.



III

We have begun our study of the photoisomerization reactions of simple troponoid compounds with an investigation of the light-catalyzed transformations of γ-tropolone methyl ether (IV). Tropone which would appear to offer the least complex system for study poses experimental problems and will be the subject of a subsequent report. Selection of IV as the starting point for our investigation was based on our wish to determine the feasibility of photoisomerization in the γ-tropolone series, the availability of γ-tropolone methyl ether[28] and our more general interest in γ-tropolone chemistry.[29]



IV

Irradiation of γ-tropolone methyl ether (IV) under a variety of conditions gave varying amounts of a single photoisomer and a red, amorphous polymer. The source of ultraviolet light—sunlight or a mercury arc lamp—had relatively little effect on product composition. The duration of irradiation had, however, a profound effect on product composition. Separate experiments showed that the photoisomer was converted to the red polymer under the conditions of the irradiation.[30] Irradiation of IV in non-polar solvents gave minor amounts of the photoisomer and large amounts of polymer. Irradiation of aqueous solutions of IV gave the highest ratio of photoisomer to polymer. The most satisfactory set of conditions for the formation of the photoisomer, photo-γ-tropolone methyl ether, was irradiation of IV in aqueous solution with a mercury arc lamp for 18–24 hours.

Photo-γ-tropolone methyl ether showed infrared carbonyl absorption at 5.86 μ and ultraviolet maxima at 243 and 328 mμ. Hydrogenation of the photoisomer over platinum required two moles of hydrogen. A plot of the volume of hydrogen absorbed against time revealed a pronounced reduction in the rate of hydrogen uptake after one mole had been absorbed. Taking advantage of the difference in rates of hydrogenation of the two sites of unsaturation, it was possible to prepare dihydrophoto-γ-tropolone methyl ether (215 mμ, 5.85 μ) and tetrahydrophoto-γ-tropolone methyl ether (no high intensity maxima in the ultraviolet; 5.76 μ). The infrared carbonyl absorption of photo-γ-tropolone methyl ether and its dihydro and tetrahydro derivatives strongly suggested the presence of a cyclopentenone carbonyl in the photoisomer and the dihydro derivative and a cyclopentanone carbonyl in the tetrahydro derivative. The ultraviolet absorption maximum (215 mμ) of the dihydro derivative and the absence of a high intensity maximum in the ultraviolet spectrum of the tetrahydro derivative are in accord with this suggestion. The ultraviolet spectrum of photo-γ-tropolone methyl ether is, however, not that expected for a simple cyclopentenone. If reaction occurred in a manner analogous to process B or C as suggested by the spectra and hydrogenation data, two structures (V and VI) are possible for photo-γ-tropolone methyl ether. Mild acid treat-

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(25) See for example K. Alder and G. Jacobs, *Ber.*, **86**, 1528 (1953).

(26) It may be that α-lumicolchicine is a substituted benzaldehyde formed *via* process A. This would be in good accord with the observation[20] that α-lumicolchicine does not absorb hydrogen (platinum catalyst) under conditions in which β- and γ-lumicolchicine absorb two molar equivalents of hydrogen.

(27) R. B. Johns, A. W. Johnson and M. Tišler, *J. Chem. Soc.*, 4605 (1954).

(28) J. Meinwald and O. L. Chapman, THIS JOURNAL, **80**, 633 (1958).

(29) O. L. Chapman and D. J. Pasto, *ibid.*, **81**, 3696 (1959).

(30) It is not known whether the photoisomer goes directly to the polymer or is in equilibrium with γ-tropolone methyl ether which goes irreversibly to polymer.

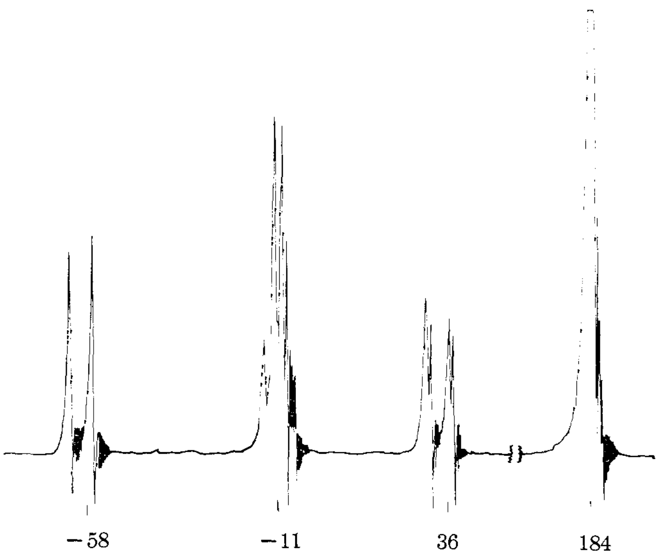
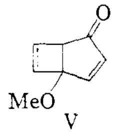


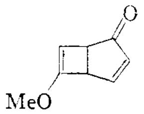
Fig. 1 (left).—Nuclear magnetic resonance spectrum of photo-γ-tropolone methyl ether. The shifts are given as c.p.s. relative to benzene in an annular cell.

Fig. 2 (right).—Expanded view of the multiplet due to the cyclobutene hydrogens of photo-γ-tropolone methyl ether.

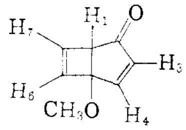
ment which should have produced a diketone from VI was ineffective. More vigorous acid treatment of the photoisomer gave γ-tropolone.[31] The acid-catalyzed opening of photo-γ-tropolone methyl ether to γ-tropolone is in dramatic contrast to the properties of β- and γ-lumicolchicine. Forbes[22] has noted the stability in acid of the C–D ring juncture in these compounds and Gardner[23] has substantiated the observation. In fact the C–D ring juncture of β- and γ-lumicolchine has not yet been opened by any means.[32] On this basis structure V is favored over VI because of the strategic location of the methoxyl group for electronic assistance in the rupture of the C_1–C_5 bond. The presence of a peak at 6.42 μ (cyclobutene double bond)[34] in the infrared spectrum of photo-γ-tropolone methyl ether which was absent in the dihydro derivative and the tetrahydro derivative also favored V as the correct structure. The n.m.r. spectrum of photo-γ-tropolone methyl ether rigorously established V as the correct structure.[35] The hydrogens of the double bond conjugated with the carbonyl (H_3 and H_4) appear as doublets at 36 and −58 c.p.s., respectively.[36] The doublet structure arises from spin–spin coupling of H_3 and H_4.[37] The additional splitting of the 36 c.p.s. doublet is due to coupling of the bridgehead hydrogen (H_1) and H_3.



V



VI



The multiplet centered at −11 c.p.s. is produced by the hydrogens of the cyclobutene double bond (H_6 and H_7) which are coupled to each other and to a lesser degree to H_1. This multiplet is of the ABX type[38] and requires two adjacent, quite similar hydrogens (A and B) such that the chemical shift difference is of the same order of magnitude as the coupling constant coupled to a third hydrogen (X) of widely separated chemical shift.[38] The structure of this multiplet (shown in expanded form in Fig. 2) thus explicitly requires two hydrogens on the cyclobutene double bond rigorously excluding VI from consideration. The resonance signal due to H_1 is obscured by the intense signal at 184 c.p.s. produced by the hydrogens of the methoxyl group but can be observed in a slow scan of this region. The formation of V from γ-tropolone methyl ether thus represents the first instance of a type B photoisomerization leaving only the type A photoisomerization without experimental realization.

On the basis of structure V for photo-γ-tropolone methyl ether and the spectral properties cited above, it is possible to assign structures VII and

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[31] The hydrolysis of γ-tropolone methyl ether is quite rapid under the conditions of the experiment.

[32] Gardner[23] has unsuccessfully attempted to open the bicyclic system by the solvolytic method used by Dryden[33] in the preparation of cyclobeptatriene from a bicyclic precursor.

[33] H. L. Dryden, Jr., and B. E. Burgert, This Journal, **77**, 5633 (1955); H. L. Dryden, Jr., *ibid.*, **76**, 2841 (1954).

[34] R. C. Lord and R. W. Walker, *ibid.*, **76**, 2518 (1954).

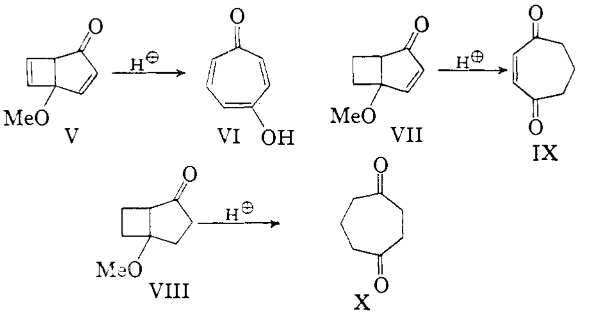
[35] The n.m.r. spectrum was obtained by the Applications Laboratory of Varian Associates, Palo Alto, Calif. We are indebted to this laboratory for assistance in the interpretation of the spectrum.

[36] For chemical shift measurements see L. H. Meyer, A. Saika and H. S. Gutowsky, This Journal, **75**, 4567 (1953), and N. F. Chamberlain, *Anal. Chem.*, **31**, 56 (1959).

[37] For a brief discussion of spin–spin coupling see J. D. Roberts, "Nuclear Magnetic Resonance Applications to Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 42–60.

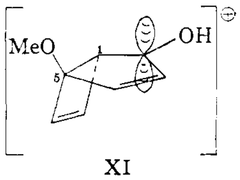
[38] H. J. Bernstein, J. A. Pople and W. G. Schneider, *Can. J. Chem.*, **35**, 65 (1957).

VIII, respectively, to dihydrophoto-γ-tropolone methyl ether and tetrahydrophoto-γ-tropolone methyl ether. These structural assignments are

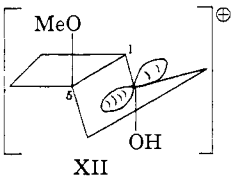


supported by acid-catalyzed ring opening of VII to 2-cycloheptene-1,4-dione (IX) and of VIII to cycloheptane-1,4-dione (X). An authentic sample of 2-cycloheptene-1,4-dione (characterized as the bis-2,4-dinitrophenylhydrazone) was prepared by oxidation[39] of 2-cycloheptene-1,4-diol obtained by reductive hydrolysis of the corresponding diacetate.[40]

The opening of tetrahydrophoto-γ-tropolone methyl ether to X is exceedingly rapid. The conversion of VIII to X in 0.1 *N* acid at room temperature is complete in one minute while the acid-catalyzed opening of photo-γ-tropolone methyl ether is only 55% complete after 18 hours at 80° in 0.1 *N* acid. The rate of ring opening of dihydrophoto-γ-tropolone methyl ether (VII) is slightly lower than that of V under the same conditions. It is instructive to consider the cause of the phenomenally rapid acid-catalyzed ring opening of tetrahydrophoto-γ-tropolone methyl ether relative to that of photo-γ-tropolone methyl ether. *A priori* one might have expected V to open more rapidly because of the greater strain inherent in V and because the product, γ-tropolone, must be considerably more stable than cycloheptane-1,4-dione (X). Consideration of the carbonium ions formed by protonation of the carbonyl oxygen of V and VIII leads to a reasonable explanation of the relative rates of opening. The carbonium ion XI derived from V is contained in a rigid, planar, five-membered ring. The C_1–C_5 bond which must interact with the vacant p-orbitals of the carbonium ion is rigidly confined in the nodal plane of the carbonium ion and thus is in the worst possible steric orientation for such interaction. The carbonium ion XII derived from VIII is in a flexible, five-membered ring which can comfortably achieve a conformation such as XII in which the C_1–C_5 bond is in excellent steric position for interaction with the vacant p-orbital. In the ring opening reactions of V, VII and VIII the unshared electron pairs of the methoxyl group must assist substantially in the rupture of the C_1–C_5 bond. On the basis of the reasoning developed above, the observation that dihydrophoto-γ-tropolone methyl ether undergoes acid-catalyzed ring opening at a rate comparable to V rather than VIII is anticipated.[41]

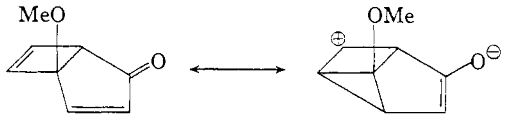


XI



XII

The problem of the structure of photo-γ-tropolone methyl ether having been resolved in favor of V, it is necessary to comment on the anomalous ultraviolet absorption of V. A cyclopentenone derivative which shows ultraviolet absorption at unexpectedly long wave lengths is not without precedent.[42–46] The source of the unusually long wave length ultraviolet absorption of V might be attributed to an electronic interaction of the non-conjugated double bond and the cyclopentenone system, an effect of the methoxyl group or steric destabilization of the ground state relative to the excited state. Because dihydrophoto-γ-tropolone methyl ether (VII) shows normal cyclopentenone absorption (215 mμ) and the degree of strain and the situation of the methoxyl are similar in VII and in V we prefer to ascribe the anomalous absorption of V to an electronic interaction between the cyclobutene double bond and the cyclopentenone system (see below). Electronic interaction between non-conjugated double bonds and α,β-unsaturated carbonyl systems has been recognized previously.[47] Two features of the anomalous absorption of V are noteworthy: (1) this is the first instance of an anomalous cyclopentenone spectrum due to electronic interaction with a non-conjugated double bond and (2) the shift produced by interaction with the cyclobutene double bond, 28 mμ (relative to VII), is the largest such shift yet observed.[48] It is somewhat surprising



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[39] This oxidation was more difficult than anticipated. Manganese dioxide gave quite low yields of ketonic products. More vigorous oxidizing agents gave relatively large amounts of carboxylic acids together with small amounts of the desired 2-cycloheptene-1,4-dione. Somewhat similar difficulties have been encountered in the oxidation of 2-cyclopentene-1,4-diol (private communication from Professor C. H. DePuy).

[40] A. C. Cope, T. A. Liss and G. W. Wood, THIS JOURNAL, **79**, 6287 (1957).

[41] The authors are indebted to Professor E. Wenkert for stimulating discussion of the problems involved in the acid-catalyzed ring openings of V, VII and VIII (see E. Wenkert's forthcoming paper on cleavage reactions of small ring ketones).

[42] H. Conroy, THIS JOURNAL, **74**, 491 (1952).

[43] J. Fajkos, *Coll. Czech. Chem. Comm.*, **23**, 1559 (1958).

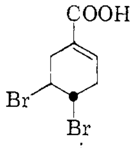
[44] K. Wiesner, F. Bickelhaupt and D. R. Babin, *Experientia*, **15**, 93 (1959).

[45] K. Wiesner, F. Bickelhaupt and Z. Valenta, *Tetrahedron*, **4**, 418 (1959).

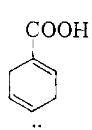
[46] K. Wiesner, M. Götz, D. L. Simmons, L. R. Fowler, F. W. Bachelor, R. F. C. Brown and G. Büchi, *Tetrahedron Letters*, No. 2, 15 (1959).

[47] See for example S. L. Emerman and J. Meinwald, *J. Org. Chem.*, **21**, 375 (1956), and references therein cited.

[48] Emerman and Meinwald[47] have reported a shift of 23 mμ in going from i to ii

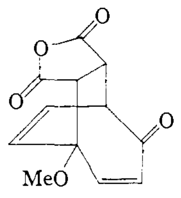


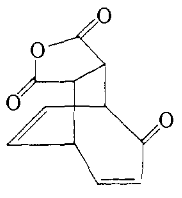
i



ii

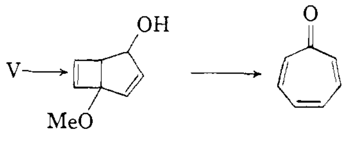
in view of the anomalous absorption of V that XIII[29] and XIV[49], which are geometrically similar to V, show normal ultraviolet spectra. Chemical evidence for the interaction of the cyclobutene double bond and the cyclopentenone system has been obtained recently in the facile base-catalyzed transformation of photo-γ-tropolone methyl ether to γ-tropolone methyl ether.[50] It is possible to interpret the problematic base-catalyzed epimerization of β-lumicolchicine to γ-lumicolchicine[23] in similar fashion.[51]


XIII


XIV

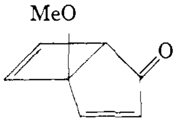
The distinct difference in properties between photo-γ-tropolone methyl ether and β- and γ-lumicolchicine, especially in regard to opening of the bicyclic system to a troponoid system, is further illustrated by the discovery that V undergoes a facile pyrolytic opening to γ-tropolone methyl ether. Photo-γ-tropolone methyl ether when dropped through a helices-packed pyrolysis column[52] preheated to 360° (contact time approximately 10 seconds) was converted completely to γ-tropolone methyl ether. This pyrolysis of V to IV represents, to the best of our knowledge, the first instance of the pyrolytic generation of a troponoid system from a bicyclic precursor.[53] The facile pyrolysis of V is in sharp contrast to the stability of VIII under the same conditions.

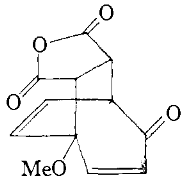
An attempt to utilize photo-γ-tropolone methyl ether as a precursor for tropone met with only minor success. Reduction of V gave an alcohol (XVI) which after 11 hours in refluxing 1 *N* hydrochloric acid was only 28% converted to tropone (ultraviolet analysis). Prolonged refluxing did not increase the conversion. The difficulty encountered in the conversion of XVI to tropone is probably related mechanistically to the difficulty encountered in the acid-catalyzed ring opening of V and VII.



XVI

It is interesting to note the similar selectivity manifest in the Diels–Alder reaction[29] and the photoisomerization of γ-tropolone methyl ether. In each reaction a single product is observed and in each case the same atoms are bridged (V and XIII). It may well be that the excited state of the tropolone system is the same for each of these reactions, the excited state being produced thermally in one reaction and photochemically in the other. If this is the case, light-catalyzed Diels–Alder reactions of IV may be anticipated.


V


XIII

Acknowledgment.—The authors express their appreciation for financial support of this investigation to Research Corporation for a Frederick Gardner Cottrell grant and to the Cancer Division of the National Institutes of Health, Public Health Service, for a research grant (CY-4253).

Experimental

Irradiation of γ-Tropolone Methyl Ether (IV). A.—A solution of 5.00 g. of γ-tropolone methyl ether[28] in 2.5 l. of distilled water was flushed with nitrogen, sealed in a Pyrex flask under reduced pressure, and placed on the roof of the laboratory for 14 days (8 days actual sunshine). The solution became turbid, and a red amorphous powder precipitated. Centrifugation of the solution gave 1.45 g. of a dark red amorphous powder, m.p. 50–200° dec., which showed infrared maxima at 5.72, 5.84 and 5.98 μ; the ultraviolet absorption spectrum showed end absorption and a low intensity maximum at 325 mμ.[54]

The solution, after centrifugation, was extracted with three portions of methylene chloride. The extract was dried over sodium sulfate and concentrated under reduced pressure. Distillation of the extract residue gave 1.19 g. of a colorless liquid, 5-methoxybicyclo[3.2.0]hepta-3,6-diene-2-one (V), b.p. 34° at 0.1 mm., n^{25}_{D} 1.4952, and 1.22 g. of a pale yellow liquid, b.p. 97° at 0.07 mm., identified as IV by its characteristic infrared and ultraviolet spectra.

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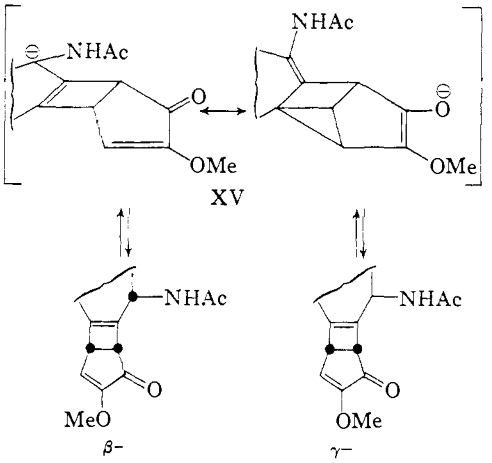
[49] The adduct of tropone and maleic anhydride (XIV) shows (95% EtOH) λ_{max} 228 mμ (6300).

[50] O. L. Chapman and D. J. Pasto, THIS JOURNAL, **81**, 5510 (1959).

[51] Abstraction of the hydrogen on the carbon atom bearing the acetamido group leads to the resonance stabilized ion XV which on



protonation can lead to either β- or γ-lumicolchicine. The γ-lumicolchicine thus formed should be enantiomeric to the γ-lumicolchicine formed by irradiation of colchicine.

[52] This is the same column used by Professor C. H. DePuy for acetate pyrolysis (D. H. Froemsdorf, C. H. Collins, G. S. Hammond and C. H. DePuy, THIS JOURNAL, **81**, 643 (1959)). The authors are indebted to Dr. R. King for assistance in the pyrolysis.

[53] A recently published synthesis of α-tropolone makes use of the pyrolysis of a bicyclo[3.2.0]heptene at an intermediate stage (J. J. Drysdale, W. W. Gilbert, H. K. Sinclair and W. H. Sharkey, THIS JOURNAL, **80**, 245, 3672 (1958)).

[54] Repeated attempts to purify this amorphous solid by chromatography gave only continuous bands of varying molecular weight.

B.—A solution of 5.0 g. of IV in one liter of distilled water in a Pyrex vessel with internal cooling (temperature maintained at 15–20°) was irradiated with a General Electric UA-3 mercury arc lamp for 24 hours at a distance of 15 cm. The solution became turbid and a red solid precipitated. The solution was extracted with three portions of methylene chloride. The extract was dried over sodium sulfate and concentrated under reduced pressure. Fractional distillation of the residue gave 1.2 g. of photo-γ-tropolone methyl ether (V) and 3.0 g. of IV. The infrared absorption spectrum of V showed maxima at 3.26, 3.38, 3.41, 3.53, 5.86, 6.31, 6.42, 6.52 and 6.85 μ in the 2–7 μ region. The ultraviolet absorption spectrum showed maxima at 243 and 328 mμ.[55]

Anal. Calcd. for $C_8H_8O_2$: C, 70.57; H, 5.92. Found: C, 70.34; H, 6.05.

The 2,4-dinitrophenylhydrazone of V was prepared in the usual manner and recrystallization from ethanol gave orange-red needles. m.p. 171–172°, and ultraviolet absorption spectrum $\lambda_{\max}^{\mathrm{CHCl_3}}$ 262 (11,600) and 375 mμ (25,400).

Anal. Calcd. for $C_{14}H_{12}N_4O_5$: C, 53.17; H, 3.83. Found: C, 53.29; H, 4.09.

Irradiation of V.—A solution of 121 mg. of V in 50 ml. of distilled water was flushed with nitrogen and irradiated in a Pyrex vessel with internal cooling coils as in method B above. After 10 hours the solution which had become turbid was extracted with methylene chloride, the extract dried over sodium sulfate, and the solution concentrated under reduced pressure. The infrared absorption spectrum of the residue was identical in the carbonyl region to that of the red powder obtained above.[56]

5-Methoxybicyclo[3.2.0]-3-heptene-2-one (VII).—The hydrogenation curve of V (volume of hydrogen absorbed *versus* time) showed a distinct change in the rate of hydrogen uptake after one mole had been absorbed. A solution of 0.797 g. (0.00586 mole) of V in 30 ml. of methanol was hydrogenated with one molar equivalent of hydrogen over Adams catalyst. The catalyst was removed by filtration, and the methanol was removed under reduced pressure. Distillation of the residue gave a colorless, sweet-smelling liquid, b.p. 65° at 1.0 mm., $n^{25}\mathrm{D}$ 1.4833. The infrared absorption spectrum showed a single carbonyl maximum at 5.85 μ. The ultraviolet absorption spectrum showed $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 215 (6,470) and 331 mμ (195).

Treatment of VII with a cold solution of 2,4-dinitrophenylhydrazine in ethanolic acid gave the 2,4-dinitrophenyl hydrazone. Recrystallization of the 2,4-dinitrophenylhydrazone from ethanol gave dark orange-red needles, m.p. 174.5–175.5°, and ultraviolet absorption spectrum $\lambda_{\max}^{\mathrm{CHCl_3}}$ 258 (15,500) and 377 mμ (29,800).

Anal. Calcd. for $C_{14}H_{14}N_4O_5$: C, 52.82; H, 4.44. Found: C, 52.99; H, 4.51.

5-Methoxybicyclo[3.2.0]heptane-2-one (VIII).—A solution of 0.420 g. of dihydrophoto-γ-tropolone methyl ether (VII) in 20 ml. of methanol was permitted to absorb 1 molar equivalent of hydrogen over Adams catalyst. The catalyst was removed by filtration, and the methanol was removed under reduced pressure. Distillation of the residue gave a colorless, sweet-smelling liquid, b.p. 61° at 0.9 mm., $n^{25}\mathrm{D}$ 1.4677. The infrared absorption spectrum showed a single maximum at 5.76 μ in the carbonyl region. The ultraviolet absorption spectrum showed no high intensity absorption.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.53; H, 8.65. Found: C, 68.32; H, 8.82.

Treatment of VIII with 2,4-dinitrophenylhydrazine in ethanolic acid gave the bis-2,4-dinitrophenylhydrazone of cycloheptane-1,4-dione.[1] Recrystallization from nitrobenzene–ethanol mixtures gave orange needles, m.p. 246–247° (reported[40] 242.0–242.4°) with maxima in the ultraviolet absorption spectrum at 256 (19,800) and 363 mμ (40,200).

Anal. Calcd. for $C_{19}H_{18}N_8O_8$: C, 46.92; H, 3.73. Found: C, 47.26; H, 3.76.

All attempts to prepare a mono-2,4-dinitrophenylhydrazone failed.

Mild Acid Treatment of V.—A solution of V in 0.1 *N* sulfuric acid showed no change in ultraviolet spectrum after one hour at 22°. Extraction of the solution with methylene chloride gave back V (identical in infrared spectrum to the starting material).

Acid-catalyzed Opening of V to γ-Tropolone.—A solution of 19.6 mg. of V in 25.0 ml. of 0.095 *N* sulfuric acid was heated at 80°. One-ml. aliquots were removed periodically and diluted to 2.88 × 10^{-5} molar with 0.1 *N* sodium hydroxide for ultraviolet analysis (based on the 360 mμ peak of γ-tropolone anion). The product of the reaction was identified as γ-tropolone by its characteristic ultraviolet spectra (maxima at 227 and 360 mμ in 0.1 *N* base and 228 and 337 mμ in neutral solution).[57]

ACID-CATALYZED OPENING OF V TO γ-TROPOLONE

Time, hr.	(360 mμ)	Reaction,[58] %
1	1,150	5
2	2,530	12
3	3,640	17
4	4,790	22
5	5,680	27
7.25	7,500	35
18.25	11,800	55

Acid-catalyzed Opening of VIII to Cycloheptane-1,4-dione (X).—A solution of 40 mg. of VIII in 25.0 ml. of methanolic 0.1 *N* hydrochloric acid was allowed to stand at room temperature. After one minute a 1-ml. aliquot was removed and immediately evaporated to dryness under reduced pressure. The residue was dissolved in chloroform and dried over sodium sulfate. The infrared absorption spectrum of this solution showed a single intense carbonyl maximum at 5.87 μ (starting material shows a single carbonyl maximum at 5.76 μ).

The remainder of the methanol solution then was evaporated under reduced pressure giving a colorless liquid (infrared carbonyl absorption 5.87 μ) which on treatment with 2,4-dinitrophenylhydrazine in ethanolic acid gave the bis-2,4-dinitrophenylhydrazone of cycloheptane-1,4-dione, identical in melting point and mixed melting point and ultraviolet absorption spectrum with authentic cycloheptane-1,4-dione bis-2,4-dinitrophenylhydrazone.[40]

Acid-catalyzed Opening of VII to 2-Cycloheptene-1,4-dione (IX).—A solution of 92 mg. of VII in 10 ml. of methanol and 5 ml. of 1.0 *N* hydrochloric acid was refluxed for 10 hr. giving rise to a 229 mμ maximum in the ultraviolet (ε 9,300). The solvent was removed under reduced pressure leaving a pale yellow, pasty residue. The infrared absorption spectrum in chloroform showed maxima at 5.98 (carbonyl) and 6.22 μ (double bond) which was identical in every respect to that of authentic 2-cycloheptene-1,4-dione prepared as described below. The bis-2,4-dinitrophenylhydrazone prepared in the usual manner showed ultraviolet absorption maxima at 271 and 397 mμ superimposable on the ultraviolet absorption spectrum of the authentic derivative described below.

Preparation of 2-Cycloheptene-1,4-dione Bis-2,4-dinitrophenylhydrazone.—A solution of 4.2 g. (0.0198 mole) of 2-cycloheptene-1,4-diol diacetate[40] in 25 ml. of anhydrous ether was added dropwise to 0.95 g. (0.025 mole, 0.1 equivalent) of lithium aluminum hydride in 50 ml. of ether. The mixture was allowed to stir overnight at room temperature. The excess hydride was decomposed with saturated ammonium chloride solution. The ether layer was decanted, and the aqueous layer was continuously extracted with ether for 60 hr. The ethereal solutions were combined, dried over sodium sulfate and evaporated to dryness under reduced pressure leaving 2.55 g. of a colorless viscous liquid. The infrared absorption spectrum showed significant maxima at 2.98 (broad) and 6.10 μ (double bond).

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(55) Characteristic extinction coefficients for these maxima are difficult to obtain. The value of the 243 mμ maximum particularly diminishes on standing in ethanol and disappears completely on heating in this solvent.[50] The ε value previously reported[1] is in any event too high.

(56) The remainder of the spectrum is so poorly resolved that comparison is virtually useless.

(57) The ultraviolet absorption spectrum of authentic γ-tropolone shows $\lambda_{\max}^{\mathrm{MeOH}}$ 228 (18,700) and 337 mμ (12,900); $\lambda_{\max}^{0.1\ N\ \mathrm{NaOH}}$ 227 (20,500) and 360 mμ (21,500) (T. Nozoe, T. Mukai, Y. Ikegami and T. Toda, *Chemistry & Industry*, 66 (1955); R. S. Coffey, R. B. Johns and A. W. Johnson, *ibid.*, 658 (1955); R. S. Coffey and A. W. Johnson, *J. Chem. Soc.*, 1741 (1958).

(58) Calculations based on $\lambda_{\max}^{0.1\ N\ \mathrm{NaOH}}$ 360 mμ (21,400) for authentic γ-tropolone.

A solution of 1.3 g. (0.010 mole) of crude 2-cycloheptene-1,4-diol in 30 ml. of acetone was cooled to −10° in an ice-salt-bath. A solution of 1.40 g. (0.0140 mole) of chromic anhydride in 6 ml. of distilled water and 2.5 ml. of concentrated sulfuric acid was added dropwise during the course of 0.5 hour with vigorous stirring. The reaction mixture was allowed to stir at room temperature for 3 hr., diluted with 100 ml. of distilled water and extracted with three portions of ether. The yellow ether extract was washed with 5% sodium bicarbonate solution and with water and dried over sodium sulfate. The ether was removed under reduced pressure giving 0.44 g. (35% of the theoretical) of a pale-yellow paste. The infrared absorption spectrum of the crude material showed maxima at 5.98 and 6.22 μ in chloroform. The ultraviolet absorption spectrum showed $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 229 mμ (10,900).

The bis-2,4-dinitrophenylhydrazone was prepared in the usual manner and was recrystallized twice from nitrobenzene–ethanol giving scarlet cubes, m.p. 294–295°. The ultraviolet absorption spectrum showed maxima at $\lambda_{\max}^{\mathrm{CHCl_3}}$ 271 (51,900) and 397 mμ (72,400).

Anal. Calcd. for $C_{19}H_{16}N_8O_8$: C, 47.11; H, 3.33. Found: C, 47.40; H, 3.52.

Pyrolysis of V.—Photo-γ-tropolone methyl ether (V, 50 mg.) was dropped into a neutral Pyrex-helices packed, vertical column[52] 6 inches in length preheated to 360°. A stream of nitrogen was passed through the column to sweep the product through (contact time approximately 10 sec.). The column was cooled to room temperature and washed with chloroform. This chloroform wash was combined with a chloroform solution of the collected product. The infrared absorption spectrum of this chloroform solution was identical in every respect with that of authentic γ-tropolone methyl ether. The residue obtained by removal of the chloroform *in vacuo* showed $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 223 and 325 mμ (authentic γ-tropolone methyl ether 223 and 325 mμ). There was no visible charring or decomposition during the pyrolysis.

Pyrolysis of VIII.—Pyrolysis of 20 mg. of VIII under conditions identical with those described above gave, after washing the column with chloroform, a product which had infrared absorption identical to pure tetrahydrophoto-γ-tropolone methyl ether.

Conversion of V to Tropone.—An excess of sodium borohydride was added to a solution of 100 mg. of V in 10 ml. of methanol. The solution was then heated at reflux for 0.5 hr., and the excess hydride was decomposed with 1.0 *N* hydrochloric acid. The resulting solution was extracted with ether, and the ether extract was dried over sodium sulfate. The ether was removed under reduced pressure. The residue was then triturated with ethyl acetate, filtered and the ethyl acetate removed under reduced pressure giving 65 mg. of a colorless liquid. The infrared absorption spectrum of this liquid showed hydroxyl absorption (2.96 μ) but no carbonyl absorption. The ultraviolet absorption spectrum showed only low intensity end absorption.

A solution of 24.7 mg. of the crude alcohol in 5.0 ml. of 1.0 *N* hydrochloric acid was heated at reflux. Aliquots were removed periodically for determination of the ultraviolet spectrum. The typical tropone ultraviolet absorption spectrum[59] with maxima at 225, 228, 231.5, 239, 304 and 312 mμ developed to maximum intensity (28% conversion to tropone) in 11 hr.

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[59] H. J. Dauben, Jr., and H. J. Ringold, THIS JOURNAL, **73**, 876 (1951), and W. von E. Doering and F. L. Detert, *ibid.*, **73**, 877 (1951).

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Terpenoids. XLIII.[1] On the Absolute Configuration on Guaiol. Correlation with Nepetalinic Acid[2]

BY E. J. EISENBRAUN, THOMAS GEORGE,[3] B. RINIKER[4] AND CARL DJERASSI

RECEIVED DECEMBER 21, 1959

The sesquiterpene guaiol (I) has been related *via* (+)-dihydroguaiol (IIa) with bis-homonepetalinic acid (IVa), which has been prepared from a nepetalinic acid (VI) of known stereochemistry. This interconversion establishes the absolute configuration of C-4, while a tentative assignment of the absolute configuration of C-10 has been made by optical rotatory dispersion studies on a relevant transformation product (Va) of guaiol (I).

Information on the absolute configuration of sesquiterpenes of the perhydroazulene type is rather meager and is largely based on optical rotatory dispersion studies among guaianolides[5a] and related sesquiterpenes.[5b] Guaiol (I) does not lend itself directly to such an approach and it was of interest to gain some stereochemical insight into this molecule by classical chemical interconversions. For this purpose, we selected as reference compounds the nepetalinic acids[6] (*e.g.*, VI) since several isomers with known absolute configuration[7] are available. It should be noted that a successful interrelation would settle the absolute configuration of guaiol (I) at C-4 and possibly at C-10 (*vide infra*), but that no conclusions could be reached with respect to the third center of asymmetry (C-7).

The initial steps involved a repetition and extension of transformations, which were first performed by Plattner and collaborators[8] in the guaiol (I) series. The catalytic hydrogenation of the double bond of guaiol is difficult[8] and if too drastic conditions are used, hydrogenolytic removal of the tertiary hydroxyl group is also encountered, leading to products which are of no utility for our purpose. According to Plattner,[8a] high pressure hydrogenation of I with Raney nickel catalyst led to a mixture from which a pure, *crystalline, levorotatory* dihydroguaiol could be separated. For reasons outlined below, we are assigning structure IIb to Plattner's

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[1] Paper XLII, E. J. Eisenbraun, F. Burian, J. Osiecki and C. Djerassi, THIS JOURNAL, **82**, 3476 (1960).

[2] The major portion of the experimental work was carried out in the Department of Chemistry of Wayne State University. We are indebted to the National Institutes of Health of the U. S. Public Health Service for financial support (grants No. RG-3863 and CY-2919 at Wayne State University and grants No. RG-6840 and CY-4818 at Stanford University).

[3] Predoctorate fellow (1959–1960) of the Danforth Foundation.

[4] Postdoctorate research fellow (1955–1956).

[5] (a) C. Djerassi, J. Osiecki and W. Herz, *J. Org. Chem.*, **22**, 1361 (1957); L. Dolejs, M. Soucek, M. Horak, V. Herout and F. Sorm, *Coll. Czech. Chem. Commun.*, **23**, 2195 (1958); D. H. R. Barton and J. E. D. Levisalles, *J. Chem. Soc.*, 4518 (1958); D. H. R. Barton and P. T. Gilham, *Proc. Chem. Soc.*, 391 (1959). (b) G. Büchi, S. W. Chow, T. Matsuura, T. L. Popper, H. H. Rennhard and M. S. Wittenau, *Tetrahedron Letters, No. 6*, 14 (1959).

[6] S. M. McElvain and E. J. Eisenbraun, THIS JOURNAL, **77**, 1599 (1955).

[7] R. B. Bates, E. J. Eisenbraun and S. M. McElvain, *ibid.*, **80**, 3420 (1958).

[8] (a) P. A. Plattner and L. Lemay, *Helv. Chim. Acta*, **23**, 897 (1940); (b) P. A. Plattner and G. Magyar, *ibid.*, **25**, 581 (1942).