molecules, silica gel was added in small increments to a solution of known concentration in the cell. The cells were then agitated and stirred with a fine wire until all air bubbles were absent and reproducible ϵ's were obtained. The net increase in volume subsequent to silica gel addition was never more than 10–15%.

Irradiation. For the stilbene photoisomerization, a 450-W Pyrex Hanovia immersion reactor was used. Between the water jacket and the sample tubes was placed a filter solution which allowed transmission only of a narrow wavelength band about 3130 Å. (The filter solution consisted of 72.5 g of $NiSO_4 \cdot 6H_2O$ and 20.75 g of $CoSO_4 \cdot 7H_2O$ in 250 ml of distilled water.) To ensure uniform irradiation of many samples, a merry-go-round apparatus continuously carried the sample tubes around the lamp for the entire reaction time. All samples were contained in evacuated quartz tubes.

The studies involving photoisomerization and photochromic transformations employed an apparatus consisting of an optical bench with light source (a 500-W high-pressure mercury arc made by PEK Manufacturing Co.), collimating lens, filter, and sample holder to permit simultaneous irradiation of a number of samples. The reactants were contained in 0.1-cm quartz Beckman cells. Depending upon the desired irradiating wavelength, the following Corning filters were used (transmitted light, in Ångstrom units, is given in parentheses: 7-60 ($5000 > \lambda > 3000$), 7-50 ($4000 > \lambda > 2000$), 7-39 ($4000 > \lambda > 3000$), 0-52 ($\lambda > 3500$). The mercury arc lamp was run at a current of 8 A.

The silica gel surface area was determined with methanol according to the method of Hoffmann, McConnell, *et al.*[14] **Silica gel surface capacities** for individual molecules were determined by adsorbing a decreasing series of concentrated solutions on a known quantity of silica gel and spectrophotometrically monitoring the disappearance of a characteristic absorbance in the supernatant liquid. By plotting ϵ *vs.* moles of adsorbate per gram of silica gel, a curve results which extrapolates to the monomolecular surface concentration. **Spectra utilizing silicic acid solvent matrices** were taken in the same manner as described above for silica gel. **Excimer fluorescence quenching** was observed by taking the emission spectra of an adsorbate determined to be completely adsorbed on silica gel in a solvent–silica matrix.

Stilbene photostationary states were determined by vapor phase chromatographic analysis. Solutions of both *cis*- and *trans*-stilbene, either in solution or determined to be completely adsorbed on silica gel, were irradiated *in vacuo* for varying time intervals. Then the stilbene sample was eluted from the matrix surface (using a mixture of 90% chloroform and 10% methanol) and injected into the vpc. An Aerograph dual column gas chromatograph was used with a 7-ft silicone SF-96 column. Separation of the *cis* and *trans* isomers was obtained with retention times of about 15 and 20 min, respectively. The relative amounts of each isomer were determined by cutting out the recorder peaks and weighing them.

Photochromic transformations for a number of spiropyrans were investigated both by nuclear magnetic resonance spectrometry and absorbance spectroscopy. Quite well-resolved nmr spectra of the closed spiropyran isomer were obtained using a Varian A-60A analytical spectrometer and either dimethyl sulfoxide or chloroform as a solvent. However, the insolubility of the precipitated open form necessitated using a different spectrometer at Eastman Kodak Research Laboratories with a computer averaged transient (C.A.T.) attachment. Studies of photochromic behavior of adsorbed species again utilized the ultraviolet and visible spectrophotometric techniques already described above.

Acknowledgments. The authors are indebted to A. F. Toth and D. R. Van Alstine for technical assistance; to Dr. Philip Rose of Eastman Kodak for the C.A.T. nmr spectra of the spiropyrans: to Dr. A. A. Lamola for reading the section on stilbenes prior to publication: and to the National Institutes of Health (Grant GM 13592) and the American Chemical Society Petroleum Research Fund for financial support.

Stereochemical Selectivities in the Electrocyclic Valence Isomerizations of Cyclobutenones and 2,4-Cyclohexadienones[1]

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Contribution from the Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois 61801. *Received May 3, 1968*

Abstract: Three 4-monosubstituted 3-phenylcyclobutenones are converted in the presence of methanol by way of the valence isomeric α-styryl ketenes to methyl 3-phenylbut-3-enoates. The reactions are highly stereoselective, giving one of the two possible geometric isomers photochemically, the other thermally. Photolysis of three 6-acetoxy-6-methyl-2,4-cyclohexadienones in the presence of methanol gives methyl 6-acetoxy-3,5-heptadienoates stereoselectively. The factors which may be controlling influences on the stereochemistry of such valence isomerizations, which fall beyond the compass of applicability of the Hoffmann-Woodward approach to related electrocyclic reactions, are discussed.

Valence isomerizations[4] of many cyclobutenes and cyclohexadienes are now known to be highly stereoselective. The experimental results have been impressively correlated and persuasively rationalized through the proposals of Hoffmann and Woodward based on the principle of the conservation of orbital symmetry.[5]

Thermally, *cis*-3,4-substituted cyclobutenes (**1**) and *cis,trans*-1,4-substituted butadienes (**2**) are interconverted in a concerted fashion; *trans*-3,4-substituted cyclobutenes (**5**) and *trans,trans*- or *cis,cis*-1,4-substituted butadienes (**3** or **4**) may equilibrate. Photolytically, the stereochemical modes of these reactions are reversed.[6–12]

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[2] Alfred P. Sloan Foundation Fellow. Address inquiries to the Department of Chemistry, University of Oregon, Eugene, Ore. 97403.

[3] National Institute of General Medical Sciences Predoctoral Fellow, 1966–1967.

[4] S. J. Rhoads in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 696.

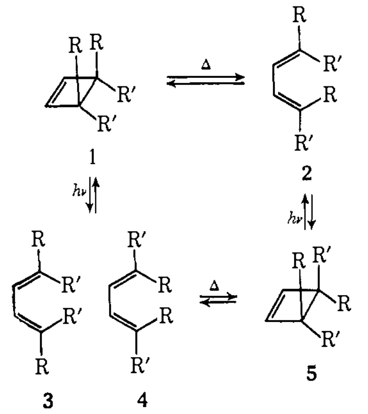
[5] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968).

[6] E. Vogel, *Angew. Chem.*, **66**, 640 (1954); *Ann.*, **615**, 14 (1958).

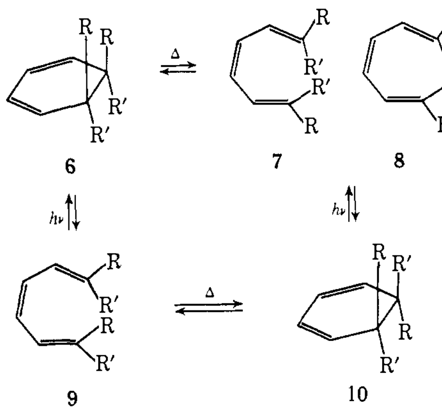
[7] R. Criegee and K. Noll, *ibid.*, **627**, 1 (1959).

[8] R. E. K. Winter, *Tetrahedron Letters*, 1207 (1965).

[9] R. Criegee, D. Seebach, R. E. Winter, B. Börretzen, and H. A. Brune, *Chem. Ber.*, **98**, 2339 (1965).



Thermally, *cis*-5,6-substituted 1,3-cyclohexadienes (**6**) are in equilibrium with *trans,cis,trans*- or *cis,cis,*-*cis*-trienes (**7** or **8**); a *trans*-cyclohexadiene (**10**) gives a *cis,cis,trans*-triene (**9**). Photolytically, the opposite stereochemical relationships are observed.[13–18]

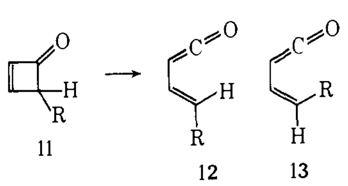


The concerted thermal reactions interconverting a cyclobutene and a butadiene, and photochemical isomerizations between a cyclohexadiene and a hexatriene are *conrotatory* processes; the concerted photochemical equilibrations of cyclobutenes with butadienes and thermal electrocyclic transformations between cyclohexadienes and hexatrienes are *disrotatory*. Only through strict adherence to these stereochemical patterns can there be effective overlap in the highest occupied molecular orbital across the single bond made or broken in the transformation.[5,19–21]

There are situations in which the Hoffmann-Woodward generalizations do not uniquely specify the stereochemical course of a concerted electrocyclic reaction. When there are two allowed products, for example in the thermal reactions **5** → **3** or **4** and **6** → **7** or **8**, or the thermal cleavages of 3-methyl-, 1,3-dimethyl-, and 1,4-dimethylcyclobutene,[22–25] the principle of conservation of orbital symmetry offers no insight as to which of two allowed processes will predominate.

Knowledge of the configuration of starting material and product in these examples remains a sufficient basis for characterizing a reaction as "conrotatory" or "disrotatory." This sufficiency holds in principle for cases such as the isomerizations of 3-methyl-, 1,3-dimethyl-, and 1,4-dimethylcyclobutene, even though one terminus of the k π-electron system has no stereochemical options available; the conrotatory or disrotatory stereochemistry of the isomerizations may be readily demonstrated through experiments with appropriately isotopically labeled analogs.

In another class of electrocyclic transformations, exemplified by the valence isomerizations of cyclobutenones (**11** → **12** or **13**), knowledge of the stereochemistry of the ring-opened isomer would offer no insight regarding the conrotatory or disrotatory nature of the reaction; and no isotopic labeling experiment could circumvent this limitation.



Indeed, it is not clear whether the categories "conrotatory" and "disrotatory" are defined or may be assigned meaning for such transformations. If definition of the concepts is based on the stereochemistry of the starting material and product,[26] then, for the cyclobutenone-vinyl ketene and similar valence isomerizations, the conrotatory/disrotatory dichotomy is inapplicable and meaningless. But through focusing attention instead on the relative spatial positions during the reaction of the two orbitals centered on the termini of the k π-electron system,[5] the reaction may be imagined to be conrotatory or disrotatory. It might conform with the pattern and principles established for systems where the terms may be unambiguously defined if, during the isomerization, the oxygen atom moves out of the plane defined by the two termini and oxygen in the starting material and product. Although no experiment will ever establish a conrotatory or disrotatory stereochemistry for a cyclobutenone-vinyl ketene or analogous interconversion, the physical basis for the extremely powerful and significant principle of conservation of orbital symmetry may still exert a decisive influence controlling the configuration of the ring-opened isomer preferentially formed.

Earlier studies have indicated that cyclobutenones and vinyl ketenes do equilibrate thermally[27] and that 2,4-cyclohexadienones may be photochemically converted in the presence of nucleophiles to products most easily rationalized as being derived from an intermediate

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(10) K. M. Shumate and G. J. Fonken, *J. Am. Chem. Soc.*, **88**, 1073 (1966).

(11) K. M. Shumate, P. N. Neuman, and G. J. Fonken, *ibid.*, **87**, 3996 (1965).

(12) R. S. H. Lui, *ibid.*, **89**, 112 (1967).

(13) R. L. Autry, D. H. R. Barton, and W. H. Reusch, *Proc. Chem. Soc.*, 55 (1959).

(14) E. Havinga, R. J. de Kock, and M. P. Rappoldt, *Tetrahedron*, 11, 276 (1960).

(15) G. Fonken, *Tetrahedron Letters*, 549 (1962).

(16) D. S. Glass, J. W. H. Watthey, and S. Winstein, *ibid.*, 377 (1965).

(17) E. N. Marvell, G. Caple, and B. Schatz, *ibid.*, 385 (1965).

(18) E. Vogel, W. Grimme, and E. Dinnè, *ibid.*, 391 (1965).

(19) E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, 16, 146 (1961).

(20) Compare W. G. Dauben and F. G. Willey, *Tetrahedron Letters*, 893 (1962).

(21) Papers summarized in ref 2 of the review[5] by Hoffmann and Woodward.

(22) E. Gil-Av and J. Shabtai, *J. Org. Chem.*, **29**, 257 (1964).

(23) H. M. Frey, *Trans. Faraday Soc.*, **60**, 83 (1964).

(24) H. M. Frey, D. C. Marshall, and R. F. Skinner, *ibid.*, **61**, 861 (1965).

(25) H. M. Frey and D. C. Marshall, *ibid.*, **61**, 1715 (1965).

(26) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

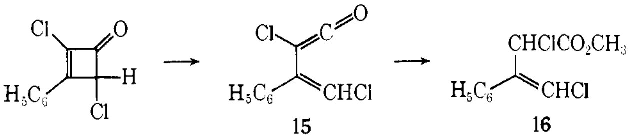
(27) E. F. Jenny and J. D. Roberts, *ibid.*, **78**, 2005 (1956).

dienyl ketene.[28] Recently, Chapman and Lassila have obtained infrared spectroscopic evidence for the photochemical transformation of both cyclobutenones and 2,4-cyclohexadienones into substituted ketenes.[29] No information on the stereochemical aspects of these valence isomerizations has been available.

The present work sought to discover whether the ring-opening isomerizations of cyclobutenones and 2,4-cyclohexadienones are stereoselective, to determine the stereochemistry of the favored product, and to consider critically possible interpretations of the experimental results in light of precedent and theory.

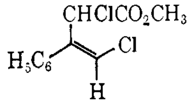
Results

Cyclobutenones.[30] The photolysis of a solution of 2,4-dichloro-3-phenylcyclobutenone (**14**) in methanol and the thermolysis of this solution at 100° in a sealed tube gave different methyl 2,4-dichloro-3-phenylbut-3-enoates (**16**).

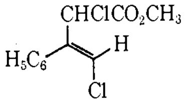


14 15 16

The thermal product isomerized on long heating to the photo ester; after 175 hr at 130°, the ratio of thermal to photo ester was 1:17. The thermal ester had a phenyl out-of-plane bending absorption at 701 cm^{-1}; the corresponding band in the photoproduct fell at 700 cm^{-1}.[31] The isomer with chlorine *trans* to phenyl (**17**), presumably the thermodynamically more stable of the two and the one expected[31] to have the lower energy out-of-plane bending absorption at 700 cm^{-1}, could thus be assigned as the product derived photochemically, and the isomer produced through thermal generation of the ketene intermediate in the presence of methanol was **18**.

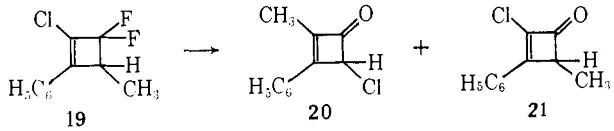


17



18

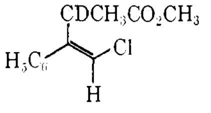
Both 2-methyl-3-phenyl-4-chlorocyclobutenone (**20**) and 2-chloro-3-phenyl-4-methylcyclobutenone (**21**) were obtained when the difluorocyclobutene **19**, obtained through dehydrochlorination of the thermal cycloadduct from β-methylstyrene and 1,1-difluoro-2,2-dichloroethylene, was treated with concentrated sulfuric acid. The isomerization is simply rationalized through a protonation–deprotonation sequence.



19 20 21

The isomer having a quartet at τ 4.3 (1, J = 1.5 Hz) and a doublet at 7.8 (3, J = 1.5 Hz) was identified as **20**. The other product, **21**, showed a one-proton quartet at τ 6.15 (J = 7 Hz) and the corresponding three-proton doublet at 8.6.[32]

These two cyclobutenones, **20** and **21**, were thermally and photochemically converted in the presence of CH_3OD into methyl 3-phenylbut-3-enoates and, as with the 2,4-dichloro-3-phenylcyclobutenone (**14**), one isomer was obtained from each starting material thermally and the other photochemically. The thermal ester from 2-methyl-3-phenyl-4-chlorocyclobutenone (**20**) had the higher energy out-of-plane bending absorption; the absorptions were at 699 and 698.5 cm^{-1} for the two geometric isomers. On this basis, a tentative assignment of structure **22** for the photo ester from **21**, and **23** for the thermal ester, could be made.



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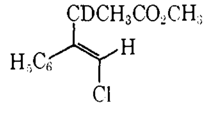
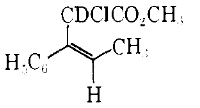


23

Attempts to isolate pure samples of thermal and photo esters derived from 2-chloro-3-phenyl-4-methylcyclobutenone (**21**) by glpc were unsuccessful; the compounds rearranged under all glpc conditions tried.

The nmr spectra of the six esters derived from 3-phenylcyclobutenones both confirmed the stereochemical assignments tentatively made on the basis of infrared data for the pairs of esters derived from **14** and **20** and indicated the same stereochemical pattern for the two esters derived from 2-chloro-3-phenyl-4-methylcyclobutenone (**21**). The photoproduct was assigned structure **24** and the thermal ester **25**.



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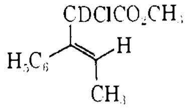

25

The nmr data for the thermal and photo 3-butenoates are summarized in Table I. The vinyl proton at C(4) was more deshielded in each of the three thermal esters than in the corresponding photoesters. The proton or the protons of the methyl group on C(2) were more deshielded in the photo isomer in each pair.

In the 1,3-dichloropropenes,[33] the absorptions for the methylene protons are 0.60 ppm apart; the lower field signals are found in the isomer having methylene protons *cis* to the vinyl chlorine. As a consequence of greater deviation from a planar disposition of phenyl and vinyl units in **18** than in **17**,[34] the observed difference in chemical shifts, 0.88 ppm, may be larger than the simple model predicts.

In structure **24**, the methyl protons may be much closer to the strongly deshielding carbomethoxy and chloro substituents than the vinyl proton in **25**; the experimentally observed differences in chemical shifts

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[28] For reviews see: A. J. Waring, *Advan. Alicyclic Chem.*, 1, 129 (1966); P. J. Kropp in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, pp 55–90.

[29] O. L. Chapman and J. D. Lassila, *J. Am. Chem. Soc.*, **90**, 2449 (1968).

[30] Preliminary account: J. E. Baldwin and M. C. McDaniel, *ibid.*, **89**, 1537 (1967).

[31] *Cf.* D. Y. Curtin and J. W. Hausser, *ibid.*, **83**, 3474 (1961).

[32] *Cf.* J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Ltd., Oxford, England, 1966, p 1137.

[33] F. S. Mortimer, *J. Mol. Spectry.*, **3**, 335 (1959).

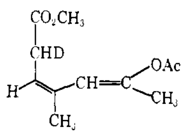
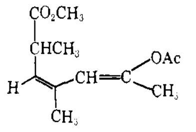
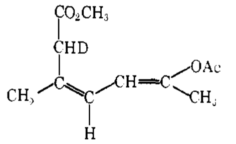
[34] R. R. Fraser, *Can. J. Chem.*, **38**, 549 (1960).

Table I. Nmr Spectral Data for Methyl 3-Phenylbutenoates[a]

		Position of proton or methyl group			
Compd	Source	C(2)H	C(4)H	$C(2)CH_3$	$C(4)CH_3$
17	**14** $\xrightarrow{h\nu}$	357[b]	384		
18	**14** $\xrightarrow{\Delta}$	304[b]	402		
22	**20** $\xrightarrow{h\nu}$		371	78	
23	**20** $\xrightarrow{\Delta}$		375	76	
24	**21** $\xrightarrow{h\nu}$		354		114
25	**21** $\xrightarrow{\Delta}$		363		96

[a] All spectra were determined with carbon tetrachloride solutions at 60 MHz. The tabulated data are chemical shifts in hertz downfield from internal tetramethylsilane. Absorptions for phenyl and methoxy protons came at τ 2.7 and 6.3 for all six esters. [b] This absorption was not observed in the product when the ketene intermediate was generated in the presence of CH_3OD.

Table II. Spectral Data for Acetoxydienoates from Photolyses of 6-Acetoxy-6-methylcyclohexa-2,4-dienones

			Nmr parameters[a]						
			Position of proton or methyl group						
Ester	Structure	$\lambda_{max}^{CH_3OH}$, mμ	C(1)	C(2)	C(3)	C(4)	C(5)	$C(6)CH_3$	C(6)OAc
29			6.4	6.8	4.55(m)	8.15 (m)	4.55 (m)	8.22	7.93
			0.2[b,c]	6[b,c]	~1[b,c]	~1[b,c]	1[b,c]		
		215			1.5[b,c]				
31			6.35	6.75 (q)	4.65	8.13	4.4	8.13	7.90
		220		8.8 (d)					
23		241	6.33	6.91	8.10[d]	4.02 (m)	4.02 (m)	8.04[d]	7.90

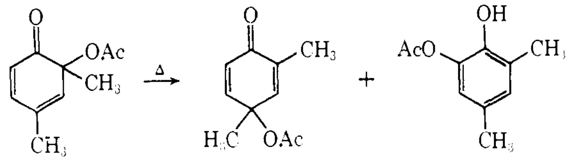
[a] Determined with carbon tetrachloride solutions and reported in τ units. [b] Determined through double irradiation techniques at 100 MHz. [c] J values, measured in hertz. [d] These two absorptions may be inverted in assignment.

for C(4)-methyl (18 Hz) and C(4)-hydrogen (9 Hz) absorptions are in the expected direction.

The criterion for stereoselectivity for the reaction of the cyclobutenones was nmr spectra taken at intervals during photolysis or thermolysis. The pure thermal ester could be obtained by heating the cyclobutenone. During photolysis, the thermal ester began to appear through photoisomerization of the initially formed isomer after the conversion of cyclobutenone to photo ester was about one-third complete.

Cyclohexadienones. Attempts to determine stereoselectivities for the electrocyclic ring-opening isomerizations of several cyclohexadienones were unsuccessful; when thermal products were obtained, they could be traced to other modes of reaction.

6-Benzyl-2,6-dimethylcyclohexadienone[35] gave no evidence of reaction after 2 hr at 130° in methanol. 6-Dichloromethyl-6-methylcyclohexa-2,4-diene[36] showed no apparent reaction after 25 hr at 205°. 4,6-Dimethyl-6-acetoxycyclohexadienone (**26**) at 130° in methanol or carbon tetrachloride gave a mixture of products. The major components were identified as 4,6-dimethyl-4-acetoxycyclohexadienone (**27**) (λ_{max} 238 mμ; nmr methyl singlets at τ 8.0, 8.15, and 8.45) and 2-acetoxy-4,6-dimethylphenol (**28**) (λ_{max} 278 mμ).[37,38] One trace component was observed when the reaction



26 **27** **28**

was run in methanol, but not in carbon tetrachloride.

Photolyses of cyclohexadienones, however, gave tractable results; in the presence of methanol, they were converted to methyl hexa-3,5-dienoates in a highly stereoselective fashion.

4,6-Dimethyl-6-acetoxycyclohexadienone, upon photolysis in CH_3OD, gave a single product as judged by glpc analysis. Mass spectral, infrared, ultraviolet, and nmr data were indicative of the formation of a single isomer of methyl 4-methyl-6-acetoxy-3,5-heptadienoate (**29**).

2,4,6-Trimethyl-6-acetoxycyclohexa-2,4-dienone (**30**) was photolyzed in methanol and gave a single methyl 2,4-dimethyl-6-acetoxy-3,5-heptadienoate (**31**). When the reaction was run in carbon tetrachloride, containing a slight molar excess of CH_3OD, the same ester and phenolic compounds were formed, but the over-all rate of conversion to photoproducts was greatly reduced. The observations are consistent with initial formation of an intermediate photoproduct, the ketene; the bimolecular trapping of this reactive species by methanol as nucleophile then competes with first-order processes available to the ketene, namely, electrocyclic ring closure to gave starting material or rearrangement to a phenol. Barton and Quinkert also noted formation of

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(35) D. Y. Curtin, R. J. Crawford, and M. Wilhelm, *J. Am. Chem. Soc.*, **80**, 1391 (1958).

(36) K. Auwers and G. Keil, *Chem. Ber.*, **35**, 4207 (1902).

(37) E. Zbiral, F. Wessely, and E. Lahrmann, *Monatsh. Chem.*, **91**, 331 (1960); E. Zbiral, F. Wessely, and J. Jorg, *ibid.*, **92**, 654 (1961).

(38) B. Miller, *J. Am. Chem. Soc.*, **89**, 1685, 1690 (1967).

phenols upon photolyses of cyclohexadienones in the absence of nucleophile.[39]

3,6-Dimethyl-6-acetoxycyclohexadienone (**32**) gave upon photolysis one isomer of methyl 3-methyl-6-acetoxy-3,5-heptadienoate (**23**).

The three acetoxy esters produced photolytically from 6-acetoxycyclohexa-2,4-dienones had the ultraviolet and nmr spectral characteristics summarized in Table II.

These esters are formulated as $\beta\gamma:\delta\epsilon$ dienoates, although the calculated[40] value, λ_{max} 237 mμ, is in poor agreement with the first two esters in the set. Indeed, Barton and Quinkert[39] assigned the $\alpha\beta:\delta\epsilon$ structures to such compounds to account for the ultraviolet spectra, but the assignments have been corrected by Collins and Hart.[41] Both compounds listed in Table II with high energy ultraviolet maxima are substituted with methyl at C(4), and the conjugated diene system is not planar.

High-resolution nmr spectroscopy at 100 MHz with frequency sweep spin–spin decoupling gave the data summarized in Table II. The results fully support the structural assignment as a $\beta\gamma:\delta\epsilon$ unsaturated ester.

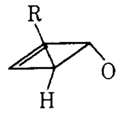
Although the gross structures of the photolytically produced hepta-3,5-dienoates and the great stereoselectivity of the ring-opening reactions of the cyclohexa-2,4-dienones were evident, the experimental data did not permit a positive determination of the stereochemical sense of the electrocyclic isomerization.

Discussion

The thermal and photolytic ring-opening reactions of three cyclobutenones have been demonstrated to be highly stereoselective and to give different isomers thermally and photolytically; the photoproduct is derived from a rotation of the larger substituent on C(4) (methyl or chloro) in toward C(1) while the smaller (hydrogen) moves out during the isomerization of a cyclobutenone to a vinyl ketene. The photolytic ring-opening reactions of three cyclohexa-2,4-dienones have been shown to be highly stereoselective. What principles determine this stereochemical selectivity?

The thermal reactions of the cyclobutenones may be easily (if not totally satisfactorily) dismissed by noting that they, like 3-methyl-, 1,3-dimethyl-, and 1,4-dimethylcyclobutene, give the stereochemical mode of reaction consistent with minimizing nonbonded steric interactions in the transition-state region; the larger substituent on one terminus of the bond being cleaved moves away from the other bond terminus.

The photochemical behavior of the cyclobutenones and cyclohexadienones is harder to rationalize. Three conceptual models are now being used in these laboratories to guide further experimental work. First, the stereochemical outcome of these valence isomerizations may be controlled by the ground-state geometry of the reactants. The isomerizations may be so fast that the products are initially formed without significant changes in nuclear configuration in the substrate, then relax to the most accessible ground-state product geometry.[42] Second, following the excitation of the α,β-unsaturated ketone, the oxygen atom may move away from its original location prior to the ring-opening phase of the reaction; the propensity of the reactant to be converted initially to **34** or **35** and the stereochemistry of the electrocyclic isomerizations of these intermediates would be decisive.[43] Third, some inherent difference in the C–R and C–H bonds in **36**, an initially formed species in which the ketene moiety is made before the substituents on C(4) rotate to give product, is responsible for the observed stereoselectivity. This model would feature the controlling influence of electronic rather than steric factors.



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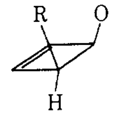

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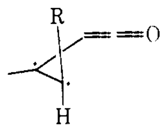
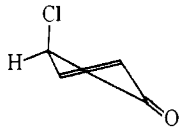


36

The first suggestion implies that the cyclobutenones investigated are nonplanar in the sense shown in structure **37**, and that the cyclohexa-2,4-dienones **38** are photochemically converted to product **39** through rotation of the bulkier C(6) substituent (methyl) in toward C(1).



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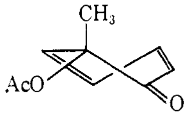

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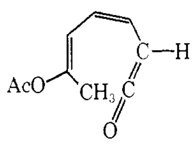

39

The structure of 2-methyl-3-phenyl-4-chlorocyclobutenone has been determined by X-ray crystallography[44] and, indeed, the cyclobutenone ring is *nonplanar*—but the sense of the distortion from planarity does not match the geometry postulated in **37**.

Experimental Section

All melting and boiling points are uncorrected. Except where noted otherwise, the nmr spectra were determined at 60 MHz using Varian A-60, A-60A, and A56/60 analytical spectrometers; infrared spectra were obtained on CCl_4 solutions with a Perkin-Elmer Model 521 grating infrared spectrophotometer; ultraviolet spectra were recorded with a Perkin-Elmer 202 spectrophotometer; and mass spectra were run by Mr. J. Wrona on an Atlas CH-4 spectrometer. Infrared bands near 700 cm^{-1} for the methyl 3-phenyl-3-butenoates given in Table I were measured accurately as CCl_4 solutions on a Beckman IR-4 with an expanded scale. Microanalyses were done by Mr. J. Nemath and associates, Urbana, Ill. Gas–liquid partition chromatographic (glpc) analyses and preparative separations were done with Aerograph instruments, Models A-90-P and A-90-P3 on 1 or 2 m × 6 mm Apiezon L columns (5% with 15% silicon rubber on Chromosorb W-HMDS) at 150–175°. An Hanovia 450-W, medium-pressure mercury lamp was used for all photolyses.

2,4-Dichloro-3-phenylcyclobutenone was prepared by way of 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene-3 and 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene-2 according to the procedure given by Roberts, Kline, and Simmons.[45] Recrystallization from aqueous ethanol gave analytically pure material of mp 75–76°; $\lambda_{max}^{CH_3OH}$ 295 mμ (ϵ 2.4 × 10^4); nmr, aryl proton absorptions centered at τ 2.0

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[39] D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960).

[40] J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 11.

[41] P. M. Collins and H. Hart, *J. Chem. Soc., C*, 1197 (1967).

[42] J. P. Malrieu, *Photochem. Photobiol.*, **5**, 291, 301 (1966); W. G. Dauben, Seminar at the University of Illinois, Urbana; Oct 11, 1967.

[43] Although the excited $^1A_2$ state of formaldehyde is pyramidal, the corresponding state reached through an n $\rightarrow$ π^* transition in acrolein is planar or nearly planar; S. I. Chan, J. Zinn, and W. D. Gwinn, *J. Chem. Phys.*, **34**, 1319 (1961).

[44] S. M. Krueger, J. E. Baldwin, and I. C. Paul, *J. Am. Chem. Soc.*, in press.

[45] J. D. Roberts, G. K. Kline, and H. E. Simmons, *ibid.*, **75**, 4765 (1953).

and 2.35 (5) and a singlet at 4.3 (1); infrared bands (KBr) at 1807 s, 1776 s, 1598 s, 1570 s, 1490 m, 1450 m, 1332 m, 1312 m, 1280 m, 1215 m, 1155 m, 1065 m, 820 s, 772 s, 688 s, 682 s, 669 m, 650 s, and 550 m cm^{-1}.

Methyl 2,4-Dichloro-3-phenyl-3-butenoates. Thermal Reaction. 2,4-Dichloro-3-phenylcyclobutenone (1.5 g) and 7 ml of methanol were heated and shaken in a sealed tube for 24 hr at 100°; the reaction mixture was cooled, concentrated, and distilled. The product showed a parent peak of *m/e* 244 with 244:246:248 in a 100:65:10 ratio, as calculated for $C_{11}H_{10}Cl_2O_2$;[46] the base peak was 209. The nmr absorptions were at τ 2.7 (5 H), 3.3 (s, 1), 4.9 (s, 1), and 6.35 (s, 3). The principal infrared absorptions (neat) were at 2850 m, 1755 s, 1735 sh, 1495 w, 1445 m, 1280 m (broad), 1190 sh, 1165 m, 1000 m, 910 w, 770 m, and 700 m cm^{-1}.

For nmr studies of this thermal reaction, the 2,4-dichloro-3-phenylcyclobutenone (0.051 g) and CH_3OD (0.7 ml) were sealed in an nmr tube and heated at 130.1° in a constant-temperature bath; spectra were taken at appropriate intervals.

Photoreaction. A solution of 0.48 g of 2,4-dichloro-3-phenylcyclobutenone in 10 ml of methanol was photolyzed through Vycor for 55 min as the reaction was followed by glpc. The product was collected by glpc; the colorless solid had mp 40–42°; $\lambda_{\max}^{\mathrm{CH_3OH}}$ 244 mμ; nmr ($CDCl_3$) τ 2.6 (s, 5), 3.55 (s, 1), 4.1 (s, 1), and 6.3 (s, 3); the infrared spectrum (Nujol mull) showed absorptions at 1775 s, 1745 s, 1295 s, 1260 w, 1225 w, 1195 w, 1170 s, 1010 s, 830 s, 780 w, 760 m, 745 m, 720 w, and 695 s cm^{-1}. The mass spectrum showed a parent peak at *m/e* 244 (calcd for $C_{11}H_{10}O_2Cl_2$: M, 244) and the expected ion intensities at 246 and 248 for the chlorine isotopes; base peak, 209.

1,1-Dichloro-2,2-difluoro-3-methyl-4-phenylcyclobutane. β-Methylstyrene (5.24 g) and an equal volume of dichlorodifluoroethylene were heated in a sealed tube at 180° for 109 hr. The yellow product was distilled to afford unreacted β-methylstyrene and the cycloadduct, bp 78–79° (0.65 mm), 4.97 g (45% yield).

The nmr spectrum (CCl_4) showed absorptions at τ 2.75 (5), 6.6 (m, 2), and 8.7 (d, 3, J = 12 Hz). The infrared spectrum (neat) showed absorptions at 3070 m, 3030 m, 2980 m, 2940 m, 2890 m, 1600 m, 1500 m, 1455 s, 1380 m, 1340 m, 1270 s, 1235 m, 1155 m, 1135 m, 1080 m, 1010 m, 1000 m, 935 m, 880 m, 840 s, 760 s, 700 s, 660 m, and 640 m cm^{-1}.

1-Chloro-2-phenyl-3-methyl-4,4-difluorocyclobutene. The adduct prepared immediately above was heated at reflux for 1 hr in a solution of 1.5 g of potassium hydroxide in 50 ml of absolute ethanol. The reaction mixture was filtered, concentrated, and filtered again; the filtrate was diluted with ether, washed with water, and dried over sodium sulfate. Filtration, concentration, and distillation gave a clear, colorless liquid, bp 88–90° (2.5 mm), 2.96 g (70% yield). *Anal.* Calcd for $C_{11}H_9F_2Cl$: C, 61.53; H, 4.19. Found: C, 61.90; H, 4.37.

The nmr spectrum had absorptions at τ 2.6 (m, 5), 6.4 (apparent quintet, 1, J = 12 Hz), and 8.65 (d with fine splitting, 3, J = 12 Hz). The infrared spectrum (neat) showed absorptions at 2980 w, 2940 w, 1645 w, 1495 m, 1450 m, 1340 s, 1280 s, 1200 m, 1130 m, 1080 m, 1000 m, 880 m, 870 m, and 695 m cm^{-1}.

2-Chloro-3-phenyl-4-methylcyclobutenone. 1-Chloro-2-phenyl-3-methyl-4,4-difluorocyclobutene (2.9 g) was added to hot concentrated sulfuric acid on a steam bath with stirring. The reaction mixture was poured into an ice slush 17 min after the addition. The organic material was extracted with ether; the ethereal solution was washed with dilute sodium bicarbonate, dried, and concentrated. Distillation gave a yellow oil, bp 113–115° (0.5 mm), 1.41 g (53%).

The nmr spectrum of this distillate indicated the presence of a mixture of two products. By both nmr spectroscopic and glpc estimates, the two components were present in a 5:2 ratio. The major component was isolated by preparative glpc. The nmr spectrum of the major component (CCl_4) had absorptions at τ 2.0–2.5 (5), 6.15 (q, 1, J = 7 Hz), and 8.6 (d, 3, J = 7 Hz) and was identified as 2-chloro-3-phenyl-4-methylcyclobutenone. The infrared spectrum showed absorptions at 2960 w, 1780 s, 1595 m, 1450 m, 1260 m, 1110 m, 870 m, and 685 m cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 298 mμ (ϵ 3 × 10^4). *Anal.* Calcd for $C_{11}H_9ClO$: C, 68.57; H, 4.67. Found: C, 68.46; H, 4.92.

2-Methyl-3-phenyl-4-chlorocyclobutenone. When the reaction of 1-chloro-2-phenyl-3-methyl-4,4-difluorocyclobutene with concentrated sulfuric acid was allowed to proceed for 1 hr, a crystalline compound was obtained when the dry ethereal extract was concentrated. Recrystallization from petroleum ether (bp 60–70°) gave colorless crystals, mp 75.5–76.5°. It was recognized from its nmr spectrum as the minor component noted in the preparation employing the short reaction time, 2-methyl-3-phenyl-4-chlorocyclobutenone.

The nmr (CCl_4) showed signals at τ 2.2–2.5 (5), 4.3 (q, 1, J = 1.5 Hz), and 7.8 (d, 3, J = 1.3 Hz); infrared bands (KBr) at 1755 s, 1605 s, 1560 w, 1440 m, 1368 m, 1338 s, 1200 w, 1005 w, 805 w, 755 w, 745 m, 680 m, 650 w, 565 w, and 550 w cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 287 mμ (ϵ 3 × 10^4). *Anal.* Calcd for $C_{11}H_9ClO$: C, 68.57; H, 4.67. Found: C, 68.44; H, 4.65.

Methyl 2-Chloro-3-phenyl-4-methyl-3-butenoates. 2-Chloro-3-phenyl-4-methylcyclobutenone (17 mg), 0.35 ml of CCl_4, and 15 μl of CH_3OD were sealed in an nmr tube, heated at 130°, and examined periodically by nmr spectroscopy. The photochemical reaction was done with a similarly prepared tube at −18°. The nmr spectral parameters for the two products are given in Table I.

Attempts to isolate the product esters by glpc were not successful; the nmr spectra of the compounds collected did not match the spectra of the compounds injected.

Methyl 2-Methyl-3-phenyl-4-chloro-3-butenoates. Thermal Reaction. 2-Methyl-3-phenyl-4-chlorocyclobutenone (19 mg), 0.3 ml of CH_3OD, and TMS were sealed in an nmr tube, heated at 130°, and examined periodically by nmr spectroscopy. After 1 hr, the two products were detected by glpc analysis, and the major product was collected. The mass spectrum showed a parent peak at 225; the 225:227 ratio, 100:35, was as calculated for $C_{12}H_{12}DClO_2$. The base peak was 190 (P − 35). The infrared spectrum showed absorptions at 3000 w, 2970 w, 1750 s, 1450 w, 1445 w, 1260 (broad) m, 1140 s, 890 w, and 700 m cm^{-1}.

Photoreaction. The cyclobutenone (17 mg), 0.3 ml of CH_3OD, and TMS were placed in an nmr tube and photolyzed; nmr spectra were taken at intervals. Analysis by glpc revealed the same two products as secured thermally, with the relative proportions reversed. The major components produced photolytically had a parent peak at *m/e* 225 and a 225:227 ratio of 100:38.

The infrared spectrum showed absorptions at 3000 w, 2960 w, 1740 s, 1440 w, 1430 w, 1200 (broad) m, 1125 s, and 690 m cm^{-1}.

4,6-Dimethyl-6-acetoxycyclohexa-2,4-dienone was prepared through the reaction of 2,4-dimethylphenol with lead tetraacetate in benzene.[47] Recrystallization from petroleum ether (bp 30–60°) gave analytically pure material of mp 70–70.5° (lit.[44] mp 70–71.5°). The nmr spectrum showed multiplets at τ 3.1, 3.3, 3.9, 4.1 (3), 8.0 (s, 3), 8.05 (d, 3, J = 2 Hz), and 8.7 (s, 3). The infrared spectrum (KBr) showed absorptions at 2980 w, 1735 s, 1675 s, 1645 m, 1560 w, 1440 m, 1405 m, 1365 m, 1240 s, 1185 m, 1100 m, 1050 s, and 810 s cm^{-1}; $\lambda_{\max}^{\mathrm{CH_3OH}}$ 305 mμ (ϵ 3 × 10^3) (lit.[47] 310 mμ).

Photolysis of 4,6-Dimethyl-6-acetoxycyclohexa-2,4-dienone. The cyclohexadienone (211 mg) dissolved in CH_3OD was placed in an nmr tube and photolyzed for 30 min. The reaction mixture was concentrated and analyzed by glpc; unreacted cyclohexadienone and one product were detected. The photoproduct was collected. The mass spectrum showed a parent peak at 213 (calcd for $C_{11}H_{15}DO_4$: 213) and a base peak at 171 (P − 42); infrared bands at 2960 w, 1755 s, 1680 w, 1440 m, 1565 m, 1220 s, 1140 s, and 1030 m cm^{-1}; $\lambda_{\max}^{\mathrm{CH_3OH}}$ 215 mμ (ϵ 4 × 10^3). The nmr data are given in Table II.

2,4,6-Trimethyl-6-acetoxycyclohexa-2,4-dienone was obtained through treating 2,4,6-trimethylphenol with lead tetraacetate in chloroform.[48, 49] Recrystallizations from petroleum ether (bp 60–75°) produced clumps of needles, mp 85–86° (lit.[48] mp 82–84°), analyzing correctly for $C_{11}H_{14}O_3$. The nmr spectrum showed bands at τ 3.45 (broad singlet, 1), 4.30 (s, 1), 8.0 (s, 3), a partially resolved triplet at 8.3 (6), and 8.7 (s, 3); infrared spectrum (KBr), 2980 w, 2920 w, 1730 s, 1665 s, 1650 s, 1445 m, 1385 sh, 1370 m, 1255 s, 1230 m, 1065 m, 1040 m, 1015 m, 985 w, 970 w, 940 w, 930 w, 915 w, 865 w, 840 w, 765 w, and 620 w cm^{-1}; $\lambda_{\max}^{\mathrm{CH_3OH}}$ 311 mμ (ϵ 4 × 10^3).

Photolysis of 2,4,6-Trimethyl-6-acetoxycyclohexa-2,4-dienone. The cyclohexadienone (164 mg) in 0.5 ml of methanol was photolyzed 1 hr at −8°. A single product was detected by glpc. It was collected by preparative glpc for analysis and spectral measurements. The infrared spectrum showed absorptions at 2950 m, 1740 s, 1680 w, 1430 m, 1370 m, 1210 s, 1160 m (sh), 1140 s, and 1050 m cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 220 mμ; the nmr data are included in Table

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(46) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 66.

(47) F. Wessely and F. Sinwel, *Monatsh. Chem.*, **81**, 1055 (1950).

(48) F. Wessely and E. Schinzel, *ibid.*, **84**, 425 (1953).

(49) F. Wessely, L. Holzer, F. Langer, E. Schinzel, and H. Vilcsek, *ibid.*, 86, 831 (1955).

II. *Anal.* Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.74; H,7.93.

When the photolysis was done in CCl_4 with a slight molar excess of CH_3OD, the ester was not obtained; other products formed very slowly.

3,6-Dimethyl-6-acetoxycyclohexa-2,4-dienone, from 2,5-dimethylphenol and lead tetraacetate,[50] was purified for elemental and spectral analyses by glpc. The nmr spectrum had a broad singlet at τ 3.9 (2), a broad multiplet at 4.1 (1), 7.95 (d, 3, J = 1 Hz), 8.0 (s, 3), and 8.73 (s, 3); infrared bands at 3020 w, 2980 w, 2920 w, 1745 s, 1670 s, 1575 w, 1440 m, 1400 m, 1365 m, 1315 w, 1245 s, 1215 m, 1165 m, 1115 w, 1070 s, 1015 m, and 865 w cm^{-1}; $\lambda_{\max}^{CH_3OH}$ 300 mμ (ϵ 4 × 10^3). *Anal.* Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.77; H, 6.90.

Photolysis of 3,6-Dimethyl-6-acetoxycyclohexa-2,4-dienone. A 50-mg sample of the cyclohexadienone, purified by glpc, was dissolved in 0.4 ml of CCl_4 and 15 μl of CH_3OD. At the end of 10 min of photolysis, approximately one-third of the starting material had been converted to a new compound as estimated by nmr and glpc analyses. The product had $\lambda_{\max}^{CH_3OH}$ 241 mμ (ϵ 6 × 10^3); infrared bands at 2950 m, 1750 sh, 1735 s, 1620 w, 1515 m, 1430 m, 1365 m, 1200 s, 1140 m, 980 (broad), 910 w, and 720 s (broad) cm^{-1}; parent peak at m/e 213 (calcd for $C_{11}H_{15}DO_4$: 213) (61%), 212 (38%), 171 (P − 42) (100%), and 170 (80%). The nmr data are in Table II.

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[50] W. Metlesics, E. Schinzel, H. Vilcsek, and F. Wessely, *Monatsh. Chem.*, **88**, 1069 (1957).

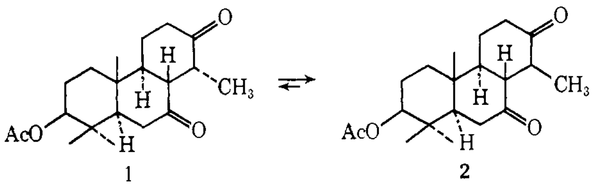
Stereochemical Investigations of Methyl Epimerization in Derivatives of 1-Methyl-*trans*-decalin[1]

Richard B. Turner, R. B. Miller, and Jeen-Lee Lin

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001. *Received May 11, 1968*

Abstract: It has been established that in both 1-methyl-*trans*-decalone-2 and 1-methyl-*trans*-decalin-2,8-dione the thermodynamically favored orientation of the methyl group is equatorial. The thermodynamically unstable axial epimers have been prepared, and equilibration studies have been carried out with various hydroxy and ketal derivatives. The literature statement that 4β-methylcholestan-3-one is not epimerized to 4α-methylcholestan-3-one is incorrect.

Some time ago, in connection with a study of the chemistry and synthesis of cassaic acid, we observed that the diketone **1**, obtained by ozonolysis of cassaic acid acetate methyl ester, is thermodynamically unstable with respect to the methyl epimer **2**.[2] It was noted further that hydroxy ketone **3** is stable under enolizing conditions and that ketal ketones **4** and **5** furnish an equilibrium mixture on treatment with p-toluenesulfonic acid in benzene, which consists of approximately equal amounts of the two epimers.



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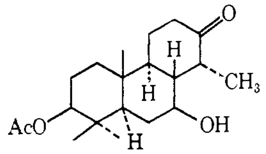

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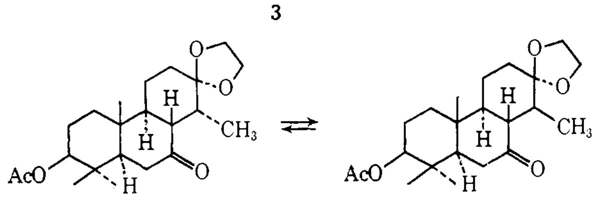

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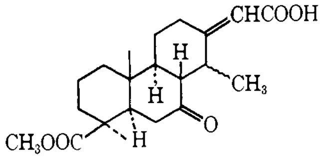
The stereochemistry assigned to the ring C methyl group in compounds of this series was based upon the thought that steric repulsions involving the ketal function in the pair **4** and **5** might serve to destabilize the methyl configuration favored in **2** if that group were equatorial, but not if it possessed an axial orientation. The stability of **3** was attributed to the fact that epimerization of the methyl group in this compound would result in an energetically unfavorable 1,3 methyl–hydroxyl interaction.

During the period in which this work was in progress, arguments in support of opposite assignments to the methyl group analogously situated in various derivatives of cassamic acid (**6**) were presented by Chapman, Jaques, Mathieson, and Arya.[3] In view of structural



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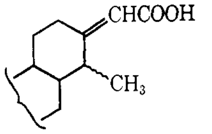

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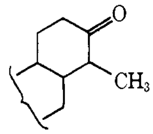

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(1) This work was supported by the Robert A. Welch Foundation and in part by the National Science Foundation.

(2) R. B. Turner, E. Herzog, R. B. Morin, and A. Riebel, *Tetrahedron Lett.*, No. 2, 7 (1959); R. B. Turner, O. Burchardt, E. Herzog, R. B. Morin, A. Riebel, and J. M. Sanders, *J. Amer. Chem. Soc.*, **88**, 1766 (1966).

(3) G. T. Chapman, B. Jaques, D. W. Mathieson, and V. P. Arya, *J. Chem. Soc.*, 4010 (1963).