Photochemical Reactions of 2-Pyrone and Thermal Reactions of the 2-Pyrone Photoproducts

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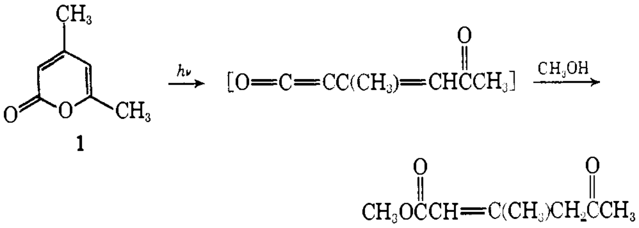
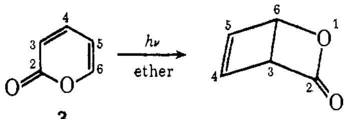
Abstract: Direct irradiation of ethereal 2-pyrone leads to bicyclo[2.2.0]pyran-2-one (**4**) or, in the presence of 10% added methanol, methyl *trans*-4-formyl-3-butenoate (**5**). Lactone **4** reacts thermally with methanol to yield 5-methoxy-2-*cis*-4-*trans*-pentadienoic acid (**7**), presumably *via* the intermediacy of cyclobutenyl cation **12** and *cis*-4-methoxycyclobut-2-ene carboxylic acid (**14**). Treatment of an ethereal solution of **4** with hydrogen chloride affords the *trans*- and *cis*-4-chlorocyclobut-2-ene carboxylic acids (**15** and **16**), which are readily opened to the *trans*–*trans* and *cis*–*trans* isomers of 5-chloro-2,4-pentadienoic acid (**20** and **21**). Deuterium-labeling experiments support the intervention of a symmetrical intermediate such as cyclobutenyl cation (**12**). Nmr spectral assignments of most of these compounds are discussed.

It has been reported by de Mayo that irradiation of methanolic solutions of 4,6-dimethyl-2-pyrone (**1**) leads to a methyl 4-acetonylcrotonate (**2**) of undetermined stereochemistry.[2] To rationalize the observed products, de Mayo has proposed a ketene intermediate using the photochemistry of cyclic dienones as an analogy. Corey and Streith, finding that irradiation of ethereal 2-pyrone (**3**) leads to bicyclo[2.2.0]pyran-2-one (**4**), have suggested that de Mayo's photochemical methanolysis of pyrone **1** may proceed *via* a similar bicyclic intermediate rather than by a ketene.[3] In the present study of bicyclo[2.2.0]pyran-2-one and tricyclo[$2^{3,6}$.1.1.0]pyran-2-one (**10**),[4] data have been obtained which are relevant to the question of possible intermediates in the photolytic alcoholysis of 2-pyrones.



$$\xrightarrow{h\nu} [O{=}C{=}CC(CH_3){=}CH\overset{O}{\overset{\|}{C}}CH_3] \xrightarrow{CH_3OH} CH_3O\overset{O}{\overset{\|}{C}}CH{=}C(CH_3)CH_2\overset{O}{\overset{\|}{C}}CH_3$$

1 **2**



3 **4**

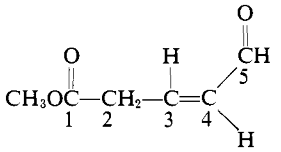
Results and Discussion

Irradiation of either methanolic solutions or methanol-containing ethereal solutions of 2-pyrone leads to methanolysis with methyl *trans*-4-formyl-3-butenoate (**5**) being the major reaction product and presumably arising *via* ketene **6** or lactone **4**. The structure of **5** is deduced from its infrared spectrum,

$$O{=}C{=}CHCH{=}CHCHO$$

6

ν_{CO} 5.77 and 5.93 μ, and from its particularly informative nmr spectrum. The observation of a 16.0-Hz coupling common to both vinyl protons is indicative of a *trans* double bond whose location is conclusively demonstrated by the doublet aldehydic proton resonance.[5] The rather unstable oily aldehyde has been further characterized as its crystalline 2,4-dinitrophenylhydrazone.



5

δ, ppm	J, Hz
H_1 3.71	2,3 6.8
H_2 3.38	3,4 16.0
H_3 6.96	4,5 7.5
H_4 6.13	2,4 1.3
H_5 9.53	

To obtain information on the possible intermediacy of ketene **6**, a 10% solution of 2-pyrone in a 2:1 tetrahydrofuran–methylene chloride glass was irradiated at −190° in a special low-temperature infrared cell using a Corex filter equipped 450-W Hanovia medium pressure mercury arc as a light source. On irradiation, this glass, which initially shows only 2-pyrone carbonyl absorption in the carbonyl region of the infrared spectrum, reproducibly gives rise to a new absorption band at 4.70 μ which grows in intensity until a photostationary state is reached after 2 hr. At photoequilibrium, the intensity of the new band is no more than 5% of the intensity of the pyrone carbonyl band. The band persists on extinguishing the arc but disappears if the glass is allowed to warm to its melting point (< −78°). Irradiation of the tetrahydrofuran–methylene chloride matrix alone does not give rise to this absorption band. From its absorption frequency, its thermal instability, and the establishment of a photostationary state, it is presumed that ketene **6** is being directly observed although it is present in but low concentration. Carbon monoxide is deemed a less likely source of the 4.70-μ absorption since one would

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(1) National Institutes of Health Predoctoral Fellow, 1965–1968.

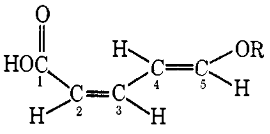
(2) P. de Mayo, *Advan. Org. Chem.*, **2**, 394 (1960).

(3) E. J. Corey and J. Streith, *J. Amer. Chem. Soc.*, **86**, 950 (1964). The direct observation of a ketene formed from a photochemical electrocyclic ring-opening has recently been reported [see O. L. Chapman and J. D. Lassila, *ibid.*, **90**, 2449 (1968)].

(4) E. J. Corey and W. H. Pirkle, *Tetrahedron Lett.*, 5255 (1967).

(5) To rationalize the formation of *trans* **5** from a ketene intermediate **6**,[2] which would presumably have a *cis* stereochemistry, one might suggest that the ketene **6** initially adds methanol to afford an enol which subsequently tautomerizes to *trans* **5**.

Table I. Nmr Parameters of the 5-Alkoxy-2-*cis*-4-*trans*-pentadienoic Acids



7–9

Compd	R	Chemical shifts (δ)[a] H$_2$	H$_3$	H$_4$	H$_5$	Coupling constants, Hz $J_{2,3}$	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$
7	CH_3	5.42[b]	6.5	6.9	6.92				
		5.35[c]	6.59	6.81	7.15	10.9	11.6	~0.8	11.2
8	$CH(CH_3)_2$	5.33[c]	6.58	6.82	7.07	10.7	11.2	~1.5	10.6
9	$C(CH_3)_3$	5.33[b]	6.46	6.81	7.0	11.3	12.2[e]	0.9[e]	11.7
		5.31[d]	6.59	6.95	7.15	10.6	11.8	0.6	11.0

[a] Tetramethylsilane as internal reference. [b] Carbon tetrachloride solution. [c] Dimethyl-d_6 sulfoxide solution. [d] Acetone-d_6 solution. [e] Calculated by ABX treatment.

not expect a photostationary state to obtain in a photochemical decarboxylation reaction. More compelling evidence for the intermediacy of ketene **6** was obtained in the subsequently described experiment. A solution of 1 g of purified 2-pyrone in 30 ml of 2:1 tetrahydrofuran–methylene chloride (both freshly dried), was placed in a cylindrical reaction vessel which surrounded a Hanovia quartz immersion well containing the previously mentioned arc and filter. The nitrogen swept outer vessel was chilled in liquid nitrogen while the partially filled vessel was turned so as to uniformly coat the vessel walls with the transparent glass. The glass was maintained at −190° and irradiated for 4 hr. The lamp was extinguished and 160 ml of anhydrous methanol was slowly added to the vessel, which was then removed from the liquid nitrogen bath and allowed to slowly warm to room temperature. Excess solvent was removed at reduced pressure and the residual material examined by 100-MHz nmr spectroscopy. At sensitivities sufficiently high to render the low-field ^{13}C satellites of 2-pyrone clearly visible, the doublet previously ascribed to the aldehyde proton resonance of adduct **5** is observed to be half as intense as the neighboring ^{13}C satellite of the C-6 proton of 2-pyrone which is the principal component of the mixture. When the experiment is repeated save for the methanol quench, no aldehyde resonances are observed although the 2-pyrone ^{13}C satellites are again readily visible. Aldehyde **5** is not afforded by the action of methanol on 2-pyrone. These reactions are reproducible and clearly require that some photochemically generated precursor of adduct **5** persists for several minutes after the light source is extinguished and then reacts thermally with methanol to afford aldehyde **5** (*ca.* 0.3% yield). In conjunction with the low-temperature infrared study, this precursor is most reasonably assigned ketene structure **6** since the frequency of the photochemically produced absorption band (4.70 μ) corresponds closely to those expected for ketenes (*ca.* 4.65 μ) but is rather different from that reported[3] for bicyclic lactone **4** (5.41 and 5.50 μ). Although little of ketene **6** is present at photoequilibrium, the reaction with methanol continuously consumes the ketene and affords adduct **5** in high yield.

Thermal reaction at 25° between bicyclo[2.2.0]pyran-2-one (**4**) and methanol leads to a crystalline acid **7** rather than aldehyde ester **5**. The elemental composition and molecular weight of **7** show it to be a 1:1 adduct of methanol and lactone **4**. Treatment of adduct **7** with acidified aqueous acetonitrile causes hydrolysis to *trans*-4-formyl-3-butenoic acid, characterized by its nmr spectrum, which is very similar to that of adduct **5**. Hydrogenation of adduct **7** over platinum leads to the comsumption of 2.4 molar equiv of hydrogen and yields a mixture of valeric acid and 5-methoxyvaleric acid.[6] The infrared spectrum of adduct **7** suggests the presence of hydroxyl, 3.38 μ, conjugated carboxyl, 5.9 μ, and vinyl ether groups, 6.14 and 8.28 μ. The ultraviolet absorption spectrum of **7** in ethanol (λ_{max} 277 mμ (ϵ 20,100)) indicates the presence of extended conjugation. Taken together, these data require that **7** be a 5-methoxy-2,4-pentadienoic acid. The nearly first-order, 100-MHz spectrum of acid **7** (Table I) substantiates this view and yields information concerning the adduct's stereochemistry.

In the 100-MHz nmr spectrum of **7**, the doublets at δ 5.35 and 7.15 show spin–spin splittings of 10.9 and 11.2 Hz, respectively. The doublet nature of these resonances indicates that they arise from the terminal vinyl protons (*i.e.*, H_2 and H_5) and the chemical shift of δ 5.35 is more reasonably assigned to H_2 than to H_5.[7] These chemical-shift assignments (see Table I) are verified by the nmr spectra of the deuterated pentadienoic acids which result from the action of methanol upon the deuterated bicyclic lactones[8] derived from 2-pyrone-3-$d^{4,9}$ and -5-d.[9] These two acids, deuterated in the 2 and 4 positions, respectively, have nmr spectra from which are missing the resonances at δ 5.42 and 6.9, respectively. Similarly, 2-pyrone-6-d^9 is converted to a deuterated methoxypentadienoic acid

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(6) The *p*-bromophenacyl esters prepared from the mixed acids have been separated by preparative thin layer chromatography and identified through comparison with authentic samples.

(7) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, New York, N. Y., 1966, pp 721, 735.

(8) After having examined the nmr spectra of all four of the monodeuterated bicyclo[2.2.0]pyran-2-ones, it would appear that the original nmr assignments of the two vinyl protons were reversed.[3] The correct chemical-shift assignments and absolute values of the observed spin–spin couplings are: H_3, δ 4.40; H_4, δ 6.73; H_5, δ 6.58; H_6, δ 5.26; $J_{3,4}$ = 0.8 Hz; $J_{3,5}$ = 1.4 Hz; $J_{3,6}$ = 1.9 Hz; $J_{4,5}$ = 2.5 Hz; $J_{4,6}$ = 4.4 Hz; $J_{5,6}$ = 0.0 Hz. These values were obtained in carbon tetrachloride solution.

(9) W. H. Pirkle and M. Dines, *J. Amer. Chem. Soc.*, **90**, 2318 (1968).

having an nmr spectrum in which the relative intensities of the resonances assigned to H_3 and H_5 have been reduced by one-half.[10] Additionally, the 15.4-MHz deuterium magnetic resonance spectrum of this last acid (in acetone-d_6) shows a broad singlet at δ 6.77 and a doublet at 7.19. The doublet nature of the latter resonance (1.6 ± 0.1 Hz) is most reasonably assigned to the spin–spin coupling of the 5-deuterium with H_4. After multiplication by the usual factor (*i.e.*, 6.5), one sees that the proton coupling, $J_{4,5}$, is 10.4 ± 0.7 Hz, a value in agreement with that obtained from the 100-MHz nmr spectrum of acid **7**. The 10.9-Hz coupling between H_2 and H_3 corresponds closely to the vicinal coupling constants (*i.e.*, 11–13 Hz) observed for a series of *cis*-α,β-unsaturated acids and esters[7,11] but is smaller than the values (*i.e.*, 15–17 Hz) obtained for the analogous *trans* isomers.[7,11] Thus, the 10.9-Hz coupling clearly reflects the *cis* configuration of the double bond in the 2 position. The 11.2-Hz coupling observed for $J_{4,5}$ suggests, since this is a methoxyl-substituted double bond, that the coupled vinyl protons, H_4 and H_5, are *trans* to one another.[12] Accordingly adduct **7** must be 5-methoxy-2-*cis*-4-*trans*-pentadienoic acid. Consistent with the structural assignment of **7** is the observation that its infrared spectrum shows, in addition to those absorptions previously mentioned, bands indicative of both *cis* (13.35 μ) and *trans* (10.25 and 10.7 μ) double bonds.

Treatment of β-lactone **4** with either ethyl, isopropyl, or *t*-butyl alcohol leads to the corresponding 5-alkoxy-2-*cis*-4-*trans*-pentadienoic acids, the infrared and 60-MHz nmr spectra of which are quite similar to those of **7**. As in the case of the methoxy acid **7**, the isopropoxy acid **8** gives, in dimethyl-d_6 sulfoxide a nearly first-order 100-MHz spectrum. The *t*-butoxy acid **9** gives a complex but interpretable 100-MHz spectrum in carbon tetrachloride and a virtually first-order spectrum in acetone-d_6 (*cf.* Table I).

Clearly, since thermal alcoholysis of bicyclo[2.2.0]-pyran-2-one (**4**) leads to adducts different from those obtained by irradiation of 2-pyrone in the presence of alcohols, bicyclic lactone **4** cannot be, in a ground-state reaction, an intermediate leading to aldehyde ester **5**. Bicyclic lactone **4** does undergo a photolytic conversion to aldehyde ester **5** when irradiated in methanol through Vycor, but is inert to irradiation through Corex. Since 2-pyrone yields aldehyde ester **5** under either set of conditions, lactone **4** is not, in the absence of an energy-transfer process, a necessary intermediate[14] in the photolytic methanolysis of 2-pyrone. To determine whether excited 2-pyrone might sensitize the conversion of bicyclic lactone **4** to aldehyde ester **5**, an ethereal solution containing 10% methanol and equimolar amounts of 2-pyrone and bicyclo[2.2.0]pyran-2-one-3-*d* was irradiated through Corex for 2 hr at −11°. Nmr analysis of the subsequently isolated aldehyde ester **5** demonstrated that no deuterium (within the limit of nmr detection) had been incorporated into the product. Thus it would appear that no energy-transfer process obtains and that bicyclo[2.2.0]pyran-2-one is not an intermediate in the production of the methanolysis product **5** on irradiation through Corex.

It is likely that both bicyclo[2.2.0]pyran-2-one (**4**) and methyl *trans*-4-formyl-3-buteneoate (**5**) arise *via* singlet excited states. The rate of formation of neither **5** nor **6** is depressed by the presence of 0.1 *M* piperylene. Additionally, photosensitization of 2-pyrone with acetophenone leads, in either the presence or absence of methanol, to photodimers[15] rather than to **5** or **6**.[15,16] Photosensitization of bicyclic lactone **4** affords no reaction.

The thermal alcoholysis of bicyclo[2.2.0]pyran-2-one (**4**) to produce 5-alkoxy-2-*cis*-4-*trans*-pentadienoic acids **7–9** is an interesting reaction, and the question of the mechanism of this reaction is an intriguing one. It is known that 2-pyrone reacts (thermally) with cyanide ion, leading to 5-cyano-2-*cis*-4-*trans*-pentadienoic acid.[17] Although the cyano acid is structurally analogous to the alkoxy acids **7**, **8**, and **9**, the mechanism for the formation of the alkoxy acids must be very different from that for the cyano acid. The trivial possibility that β-lactone **4** is simply a source of 2-pyrone which reacts further to give the observed products is excluded by the observation that 2-pyrone is stable toward methanol. Upon treatment with methanolic sodium methoxide, 2-pyrone yields methyl *trans*-4-formyl-3-butenoate (**5**) rather than acid **7**.

Of more mechanistic relevancy is the recent suggestion by Corey and Pirkle[4] that the isomerization of bicyclo-[2.2.0]pyran-2-one (**5**) to tricyclo[$2^{3,6}$.1.1.0]pyran-2-one (**10**) may proceed through a zwitterionic intermediate **11**. Extension of this idea leads to a hypothetical reaction sequence capable of explaining the observed 5-alkoxypentadienoic acids.

Protonation of either lactone **4** or zwitterion **11** could lead to cyclobutenyl cation **12** which might be trapped internally to afford tricyclic lactone **10**, be trapped externally, or regenerate bicyclic lactone **4**. This latter reaction must be rare; in the conversion of deuteriochloroform solutions of bicyclo[2.2.0]pyran-2-one-6-*d* to lactone **10**, no deuterium scrambling is detectable (by nmr) in the residual bicyclic lactone. Thus, while lactones **4** and **10** may each be good sources of cyclobutenyl cation **12**, this symmetrical ion does not often regenerate lactone **4**. If cyclobutenyl cation **12** were trapped by alcohol, it would afford a kinetically controlled mixture of *trans*- and *cis*-alkoxycyclobut-2-enoic acids (**13** and **14**). Although neither **13** nor **14**

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(10) The significance of this label scrambling will be discussed in the mechanistic section of the paper.

(11) C. Rappe, *Acta Chem. Scand.*, **18**, 818 (1964).

(12) Electron-withdrawing substituents generally reduce the coupling constants of the remaining vinyl protons. The β-methoxy styrenes, alkyl-1,3-enyne ethers[13] and a series of vinyl alkyl ethers[6] show *cis*-vinyl couplings of *ca.* 7 Hz and *trans*-vinyl coupling constants of *ca.* 13–14 Hz.

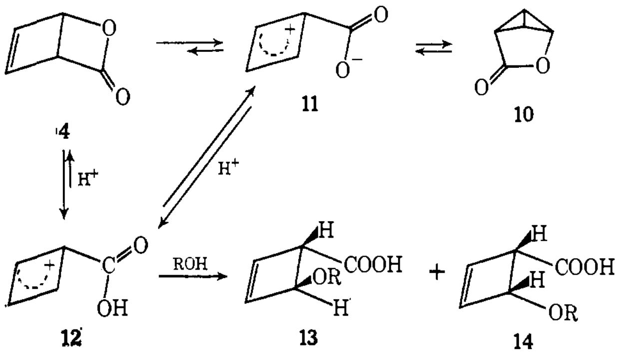
(13) P. P. Montyn, H. M. Schmidt, J. H. van Boom, J. H. T. Bos, L. Brandsma, and J. F. Arens, *Rec. Trav. Chim.*, 84, 271 (1965).

(14) Lactone **4** may, when irradiated through Vycor, simply be in photoequilibrium with 2-pyrone.

(15) W. H. Pirkle and L. H. McKendry, *Tetrahedron Lett.*, 5279 (1968).

(16) One cannot exclude the unlikely possibility that **4** and **5** arise not from a singlet state but rather from triplet states other than those attainable by photosensitization. In this eventuality, **4** and the ketene precursor of **5** must be formed faster than these triplets can either be quenched by piperylene or internally convert to the (presumably) lower lying triplet state(s) which affords the photodimers. For a recent report of a photochemical reaction proceeding *via* more than one triplet state, see O. L. Chapman, *et al.*, *J. Amer. Chem. Soc.*, **90**, 1657 (1968).

(17) G. Vogel, *J. Org. Chem.*, 30, 203 (1965).

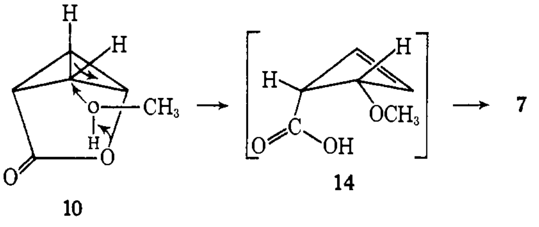


have yet been directly observed as products in the alcoholysis of lactone **4**, they are plausible precursors of the 5-alkoxy-2,4-pentadienoic acids, since it is well established that cyclobutenes may undergo thermal ring opening to butadienes. Assuming that cyclobutenes may indeed be formed during the course of the alcoholysis of lactone **4**, one concludes that the ring opening of cyclobutenes **13** and **14** must be rather facile to occur under the mild reaction conditions which suffice to afford the alkoxypentadienoic acids. Conceivably, the electron-donating alkoxyl group and the electron-withdrawing carboxyl group could stabilize a dipolar transition state for ring opening. Should there be extensive resonance stabilization of such a transition state, it would be of interest to know whether the rules for predicting the stereochemical outcome of the ring opening are valid.[18] Should they be, *cis*-**14** is implicated as the major cyclobutene intermediate inasmuch as its conrotatory ring opening would lead to the observed *cis–trans* acids **7**, **8**, and **9**. Minor amounts (*ca.* 20%) of an impurity, tentatively suggested to be 5-methoxy-2-*trans*-4-*trans*-pentadienoic acid, have been detected in unrecrystallized samples of acid **7** by nmr spectroscopy. Assuming that the relative amounts of the two stereoisomeric pentadienoic acids reflects the relative amounts of *cis*-**13** and *trans*-**14** formed, one estimates this ratio to be 4:1.

The reaction sequence advanced to account for the formation of the 5-alkoxy-2,4-pentadienoic acids leads to several additional postulates. (a) The reaction should be susceptible to acid catalysis. (b) The symmetry of a cyclobutenyl cation intermediate should lead to scrambling of C-4 or C-6 deuterium between the C-3 and C-5 positions of the pentadienoic acids. (c) Trapping of the cyclobutenyl cation by nucleophiles other than alcohols might lead to isolable cyclobutene carboxylic acids in which deuterium-label scrambling should be observable. (d) The stability of these 4-substituted carboxycyclobut-2-enes toward ring opening should be controlled by the electronic nature of the 4 substituent.

The validity of postulate a, that the alcoholysis of bicyclo[2.2.0]pyran-2-one should be acid catalyzed, is easily demonstrated. To one of two identical 50-ml portions of a 4:1 ether–methanol solution 2.8×10^{-2} *M* in bicyclo[2.2.0]pyran-2-one, was added three drops of 70% perchloric acid. The rate of formation of pentadienoic acid **7** at 27° was monitored by ultraviolet spectroscopy for both solutions, and it was found that the acid-catalyzed reaction was *ca.* 30 times faster than the uncatalyzed reaction.

Postulate b, that deuterium in either the 4 or 6 positions of 2-pyrone should be equally scrambled between the 3 and 5 positions of the pentadienoic acids, is also valid. The 100-MHz nmr spectrum of a purified sample of the *t*-butoxypentadienoic acid derived from 2-pyrone-6-*d* shows that the multiplets previously assigned to H_3 and H_5 are reduced to one-half their former intensity. The deuterium resonance spectrum (15.4 MHz) of this sample shows two equally intense[19] resonances whose chemical shifts, δ 6.7 and 7.3, correspond to those of H_3 and H_5. The nmr spectra of the methyl alcohol adducts derived from either 2-pyrone-4-*d* or 2-pyrone-6-*d* also show the deuterium label to have been equally scrambled between the 3 and 5 positions of the adducts. These results are consistent with the intervention of an intermediate having the symmetry of cyclobutenyl cation **12** or tricyclic lactone **10**. The tricyclic lactone does in fact react with methanol to afford pentadienoic acid **7**, possibly through the intervention of ion **12**, and has been observed (nmr) to form under the methanolysis conditions. The possibility that the alkoxydienoic acids arise directly from the tricyclic lactone **10** cannot be rigorously excluded, but it must be noted that the labeling experiments require that **10** be attacked at either the 4 or 5 positions to break the C_4–C_5 bond with concomitant (or subsequent) opening of the lactone bridge to afford either the methoxycyclobutenoic acid precursor of **7** or, possibly, **7** itself. Relevant to this question is the observation that the action of methanolic sodium methoxide on tricyclic lactone **10** affords aldehyde ester **6** rather than acid **7**, apparently as a consequence of attack of methoxide ion at the carbonyl rather than at C_4 or C_5.



Further indication of the intermediacy of cyclobutenyl cation **12** and of the validity of postulate c comes from the observation that treatment of a cold ethereal solution of bicyclic lactone **5** with anhydrous hydrogen chloride affords a 1.0:2.2 mixture of two isomeric 1:1 adducts, the *trans*- and *cis*-4-chlorocyclobut-2-ene carboxylic acids. The isomers, one liquid, **15**, and the other crystalline, **16**, are separable by fractional molecular distillation and/or sublimation and have elemental compositions and molecular weights in accord with the assigned structures. The infrared spectrum of the liquid isomers, **15**, shows bands at 3.35, 5.86, 7.83, 8.18, and 12.85 μ. Its nmr spectrum consists of four resonances

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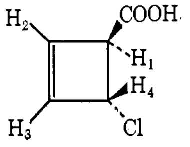
[18] (18) See R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968), and references therein.

[19] (19) Owing to experimental limitations imposed by the amount of sample available, the term equally intense should be taken qualitatively (*i.e.*, 1:1 ±10%) rather than quantitatively. Manifestation of secondary isotope effects on the rates of formation of the two isomers would be expected to render them present in slightly dissimilar amounts.

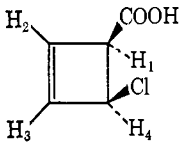
of 1:2:1:1 area ratios: a singlet at δ 9.59, complex multiplets at 6.24 and 3.77, and a quartet at 4.95.

The infrared spectrum of the crystalline adduct **16** shows absorption at 3.38, 5.83, and 11.30 μ. Its nmr spectrum consists of a singlet at δ 11.6, complex multiplets at 6.24 and 5.12, and a quartet at 4.13. The relative intensities of these four resonances are 1:2:1:1. The magnitude of the spin–spin couplings derived from analysis of the nmr spectra of **15** and **16** indicate these compounds have *trans* and *cis* stereochemistry, respectively. In particular, the observed values of $J_{1,4}$ for **15** (2.1 Hz) and for **16** (4.3 Hz) correspond closely to the values reported for cyclobutene[20] and for a series of substituted *trans* (*ca.* 1–2 Hz) and *cis* (*ca.* 4 Hz) cyclobutenes.[21] The chemical-shift assignments shown are in accord with the results of deuterium-labeling studies to be subsequently described.



15

	δ, ppm		J, Hz
H_1	3.79	1,2	1.0
H_2	6.27	1,3	0.4
H_3	6.27	1,4	2.1
H_4	4.99	2,4	~0.0
		3,4	1.1



16

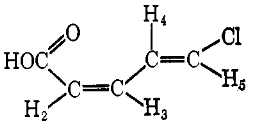
	δ, ppm		J, Hz
H_1	4.13	1,2	0.4
H_2	6.24	1,3	~0.0
H_3	6.24	1,4	4.3
H_4	5.12	2,4	0.85
		3,4	0.85

Confirmation of the stereochemistry assigned to **15** and **16** obtains from the formation of the known *cis*-2-chlorocyclobutane carboxylic acid,[22] upon hydrogenation of **16** over platinum.

Analysis of the nmr spectra of deuterated analogs of chloro acids **15** and **16** gives insight into possible mechanisms by which these acids arise as well as to substantiate the chemical-shift assignments. Treatment of bicyclo[2.2.0]pyran-2-one-6-*d* with ethereal hydrogen chloride results in the formation of a 1.0:1.1:1.1 mixture of *trans*-4-chlorocyclobut-2-ene carboxylic acid-4-*d* (**17**), *cis*-4-chlorocyclobut-2-ene carboxylic acid-2-*d* (**18**), and *cis*-4-chlorocyclobut-2-ene carboxylic acid-4-*d* (**19**). The absence (judging from nmr spectroscopy) of label scrambling in the formation of the *trans* adduct **17** precludes the intervention of a symmetrical intermediate and suggests that this compound arises *via* nucleophilic attack of chloride upon the bicyclic lactone **4**, presumably while the latter is protonated. The formation of equal amounts of the *cis* adducts, **18** and **19**, indicates these compounds do arise *via* a symmetrical intermediate such as cyclobutenyl cation **12**. Apparently, both chloride (or hydrogen chloride) and alcohols prefer to approach ion **12** from the endo side and give predominately *cis* products.

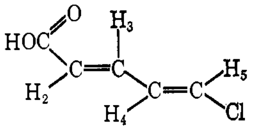
Under rather mild conditions, chlorocyclobutenoic acids **15** and **16** undergo ring opening to 5-chloropentadienoic acids. In refluxing carbon tetrachloride, *trans*-**15** leads exclusively to 5-chloro-2-*trans*-4-*trans*-pentadienoic acid (**20**) while the *cis* isomer **16** leads exclusively to 5-chloro-2-*cis*-4-*trans*-pentadienoic acid (**21**). The structures of these two acids follow from their elemental compositions, their infrared, ultraviolet, and, especially, their nmr spectral properties (see Figure 2). Decoupling experiments on the methyl ester of **20** support the spectral assignments. The observation of vinyl coupling constants (*i.e.*, $J_{2,3}$ and $J_{4,5}$) of 15.7 and 12.7 Hz, respectively, indicates the *trans–trans* stereochemistry for **20**. The latter value, 12.7 Hz, is in accord with values (J_{trans} = 13–14 Hz) noted for *trans*-β-chlorostyrene,[23] *trans,trans*-1,4-dichloro-1,3-butadiene,[24] and other *trans*-vinyl chlorides[25] but is larger than the usual coupling (*i.e.*, J_{cis} = 7–8 Hz) observed for the *cis* isomers.[23–25] Additionally, an absorption band at 10.7 μ which is observed in the infrared spectrum of **20** supports the presence of one or more *trans* double bonds. No bonds attributable to a *cis* double bond could be detected.

Chloro acid **21** has a first-order 100-MHz nmr spectrum which consists of doublets at δ 5.69 and 6.58 and quartets at 6.56 and 7.79. The multiplets centered at δ 6.58 and 6.56 are reduced to one-half of their normal intensities in the spectrum of an equimolar mixture of 5-chloro-2-*cis*-4-*trans*-pentadienoic acid-3-*d* and -5-*d* obtained by thermolysis of an equimolar mixture of the deuterated *cis*-4-chlorocyclobut-2-ene carboxylic acids **18** (2-*d*) and **19** (4-*d*). These intensity diminuations and attendant multiplicity changes are consistent with the spectral assignments shown for **21**. The *cis–trans* stereochemical assignment for acid **21** follows from the observation of values of 12.0 and 13.2 Hz, respectively, for the two vinyl coupling constants, $J_{2,3}$ and $J_{4,5}$. The latter value corresponds closely to the values (*i.e.*, 13–14 Hz) observed for *trans*-vicinal vinyl coupling constants of vinyl chlorides.[23–25] Moreover, acid **21** shows infrared absorption bands at 13.7 and 10.6 μ which are indicative of the presence of both *cis* and *trans* double bonds.



21

	δ, ppm		J, Hz
H_2	5.69	2,3	12.0
H_3	6.56	3,4	11.5
H_4	7.79	4,5	13.2
H_5	6.58		



20

	δ, ppm		J, Hz
H_2	5.98	2,3	15.7
H_3	7.28	3,4	11.0
H_4	6.70	3,5	0.5
H_5	6.95	4,5	12.7

It can be seen that both chlorocyclobutene carboxylic acids **15** and **16** undergo thermal conrotatory ring opening to the stereochemically predicted[18] chloropentadienoic acids. By analogy, it is presumed that,

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(20) E. A. Hill and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2047 (1967).

(21) H. Hart, J. A. Hartlage, R. W. Fish, and R. R. Rafos, *J. Org. Chem.*, **31**, 2244 (1966), and references therein.

(22) W. A. Nevill, D. S. Frank, and R. D. Frepka, *ibid.*, 27, 422 (1962).

(23) L. A. Singer and N. P. Kong, *J. Amer. Chem. Soc.*, **89**, 5251 (1967).

(24) A. A. Bothner-By and R. K. Harris, *ibid.*, **87**, 3445 (1965).

(25) See ref 7, pp 714, 722.

despite their facile ring opening, the 4-alkoxycyclobut-2-ene carboxylic acids **13** and **14** also undergo thermal conrotatory ring opening.

Experimental Section[26]

Methyl *trans*-4-Formyl-3-butenoate (5). Photolytic Methanolysis of 2-Pyrone. To a photolysis apparatus consisting of an inner Vycor immersion well and an outer Pyrex vessel, was added 250 ml of anhydrous ether, 20 ml of anhydrous methanol, and 1 ml (1.2 g) of 2-pyrone.[27] The system was flushed with dry nitrogen, cooled to −11°, and irradiated for 20 hr with a Hanovia 450-W medium pressure ultraviolet lamp. The ether and excess methanol were removed under reduced pressure, and the yellow oily residue molecularly distilled (25°, 0.005 torr) onto a Dry Ice cooled cold finger to afford colorless methyl *trans*-4-formyl-3-butenoate (70%): infrared (neat) 5.77 (C=O), 5.93 (conjugated C=O), 6.18 (conjugated C=C), and 10.30 μ (*trans* CH=CH); nmr (CCl_4) δ 9.53 (d, 1 H), 6.96 (m, 1 H), 6.13 (m, 1 H), 3.71 (s, 3 H), and 3.38 (q, 2 H).

Anal. Calcd for $C_6H_8O_3$: C, 56.25; H, 6.25. Found: C, 55.91; H, 6.36.

Using standard procedures, **5** was converted to its 2,4-dinitrophenylhydrazone which was purified by chromatography (alumina, chloroform) and recrystallized from hot aqueous methanol: mp 151–154°; infrared ($CHCl_3$) 5.85, 6.29, 6.44, 6.74, 7.10, 9.01, 10.28, 10.6, and 12.25 μ.

Anal. Calcd for $C_{12}H_{12}N_4O_6$: C, 46.75; H, 3.90; N, 18.18. Found: C, 46.77; H, 3.91; N, 17.97.

Thermal Stability of 2-Pyrone in Methanol. 2-Pyrone (*ca.* 1.2 g) in 10 ml of methanol was allowed to stand at room temperature for 7 days. Analysis by 100-MHz nmr spectroscopy at high sensitivity showed that no reaction had occurred.

Photolysis of 2-Pyrone in a Low-Temperature Infrared Cell. A few drops of 1:2 methylene chloride–tetrahydrofuran solution was added to the special infrared cell. The system was cooled until the solution became viscous, then evacuated to 0.025 torr and cooled to −190°. An initial infrared spectrum was taken, and the glass was irradiated by placing the sodium chloride cell windows in contact with a Quartz immersion well containing a Corex filter and a Hanovia 450-W medium pressure lamp. After 1.33 hr of irradiation, the infrared spectrum of the glass was identical with that prior to irradiation. In neither spectrum did absorption occur between 4.50 and 5.00 μ. The matrix was replaced with one containing 10% 2-pyrone and a spectrum was obtained which again contained no bands between 4.50 and 5.00 μ. However, the spectrum of this sample after 0.73 hr of irradiation (Corex filter, Hanovia 450-W medium pressure lamp) contained a sharp band at 4.70 μ which increased in size until photoequilibrium was attained after 1.7 hr. No diminution of the 2-pyrone carbonyl absorption could be noted and it was estimated that less than *ca.* 5% of the 2-pyrone had been consumed. After cessation of irradiation, the sample stood at −190° for 10 min while connected to a high vacuum system with no diminution in intensity of the 4.70-μ band. However, this infrared band disappears if the glass is warmed to its melting point (below −78°), recooled to −190°, and reexamined.

Preparative Low-Temperature Photolysis of 2-Pyrone. Nitrogen-swept, oven-dried apparatus consisting of a quartz immersion well inserted into a Pyrex vessel was partially filled by means of a syringe with a solution of 10 ml of methylene chloride, 20 ml of tetrahydrofuran, and 0.9 ml of 2-pyrone. The tetrahydrofuran had been freshly distilled from lithium aluminum hydride and the methylene chloride had been freshly dried over molecular sieves. The system was cooled to −190° and then rotated in order to form a glass on the sides of the outer Pyrex vessel. The bottom of this vessel was hand warmed several times to facilitate uniformity in forming the glassy matrix. The matrix was irradiated with a Hanovia 450-W medium pressure lamp (Corex filter), the heat from which was dissipated by running cold water through the Quartz well. After 4 hr, the irradiation was stopped and methanol (160 ml) was added to the system at −190° *via* a 20-ml syringe. The glass was allowed to warm to room temperature, the solvent was removed from the solution *in vacuo*, and the cloudy liquid residue (1.01 g) was filtered into an nmr tube. The 100-MHz nmr spectrum contains, besides the intense 2-pyrone multiplets at δ 7.66 and 6.40, a doublet at 9.69 (J = 7.8 Hz), a singlet at 3.79, and a doublet of doublets at 3.66 (J = 6.9, 1.3 Hz).

A second sample prepared and irradiated as above but warmed in the absence of methanol, has a 100-MHz nmr spectrum which shows the 2-pyrone multiplets but not the multiplets previously assigned to aldehyde ester **5**.

2-Pyrone-4-*d*. To 10.56 g (5.23×10^{-2} mol) of diethyl acetonedicarboxylate cooled to 0° was added dropwise (nitrogen atmosphere) a solution of 0.597 g (1.42×10^{-2} mol) of sodium borodeuteride in 30 ml of absolute ethanol. After 1 hr, 20 ml of 8 *M* hydrochloric acid was added, and the aqueous layer was extracted with 50 ml of ether. The ether layer was dried with brine and anhydrous sodium sulfate, then concentrated. The liquid residue was diluted with carbon tetrachloride and filtered to remove a small amount of suspended solid. Evaporation of the carbon tetrachloride left 11.67 g (100%) of slightly cloudy diethyl 3-hydroxyglutarate-3-*d*. The ester was divided into portions of 5.70 g (A) and 5.97 g (B), respectively, and each was dissolved in 25 ml of 60% sulfuric acid. Sample A, in a 100-ml, round-bottomed flask, was connected to a 30-torr vacuum source and gradually heated from 75 to 145° over a 1-hr period and then maintained at 145° for an additional 1.7 hr, the course of the dehydration being monitored by nmr spectroscopy. Prolonged heating appears to cause decarboxylation. Continuous ether extraction of the aqueous solution afforded 1.6 g of glutaconic acid-3-*d*. Sample B, treated similarly, afforded 1.58 g of crude acid. Both acid samples were washed with several portions of carbon tetrachloride to remove small amounts of residual ester and dried under reduced pressure to yield 1.00 g (A) and 1.39 g (B) (total yield 35%) of glutaconic acid-3-*d*.

The above samples of glutaconic acid-3-*d* were converted to 2-pyrone-4-*d* by a procedure analogous to that used by Pirkle and Dines[9] to convert glutaconic acid to 2-pyrone-6-*d*. In the present instance, acetic acid was used in place of deuterioacetic acid. By this procedure, distilled 2-pyrone-4-*d* (0.25 g from sample A and 0.19 g from sample B) was obtained and was shown to be of 94% isotopic purity by mass spectrometric analysis: nmr (CCl_4) δ 7.58 (m, 1 H) and 6.30 (m, 2 H).

Bicyclo[2.2.0]pyran-2-one (4). Following the procedure of Corey and Streith,[3] 2-pyrone in ether (4 g/l) was irradiated (Corex filter) at −11°. After 14 hr, the ether was evaporated (reduced pressure) and the reactive β-lactone molecularly distilled (0°, 0.005 torr) onto a Dry Ice cooled cold finger. The infrared spectrum is as reported:[3] nmr (CCl_4) δ 6.73 (H_4, m, $J_{3,4}$ = 0.8 Hz, $J_{4,5}$ = 2.5 Hz, $J_{4,6}$ = 4.4 Hz), 6.58 (H_5, m, $J_{3,5}$ = 1.4 Hz), 5.26 (H_6, m, $J_{3,6}$ = 1.9 Hz), and 4.40 (H_3, m).

Bicyclo[2.2.0]pyran-2-one-3-*d*. This lactone, prepared from 2-pyrone-3-*d*[9] following the procedure of Corey and Streith,[3] has an nmr spectrum showing a quartet at δ 6.73, doublets at 6.58 and at 5.26, and the absence of the multiplet normally at δ 4.40.

Bicyclo[2.2.0]pyran-2-one-4-*d*. 2-Pyrone-4-*d* (0.25 g) was dissolved in 35 ml of anhydrous ether and placed into two 20-ml Vycor tubes. Each tube was flushed with nitrogen, strapped to a Vycor immersion well (Corex filter, Hanovia 450-W medium pressure lamp), cooled to −11°, and irradiated for 10 hr. After the usual work-up and molecular distillation, 0.15 g (60%) of bicyclo[2.2.0]-pyran-2-one-4-*d* was obtained. The nmr spectrum of this material shows a doublet at δ 6.68 (1 H), a broad singlet at 5.26 (1 H), and a complex multiplet at 4.40 (1 H). The intensity of the band at δ 6.73 is greatly diminished, the isotopic purity of the sample being 92% as determined from integration of the spectrum.

Bicyclo[2.2.0]pyran-2-one-5-*d*. The distilled lactone, prepared from 2-pyrone-5-*d*[9] by the reported procedure,[3] has an nmr spectrum showing a doublet at δ 6.73 (1 H), a quartet at 5.30 (1 H), and a doublet at 4.40 (1 H). The intensity of the multiplet normally observed at δ 6.58 is greatly diminished and integration of the spectrum indicates an isotopic purity of 87%.

Bicyclo[2.2.0]pyran-2-one-6-*d*. After distillation, the bicyclic lactone prepared from 2-pyrone-6-*d*[9] (91% isotopic purity) has an nmr spectrum showing three equal area multiplets at δ 6.73, 6.58, and 4.40.

5-Methoxy-2-*cis*-4-*trans*-pentadienoic Acid (7). A 125-ml erlen-

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[26] Nmr spectra were measured with Varian A-60, A-60A, A56-60, and HA-100 spectrometers (using TMS as an internal standard). Infrared, ultraviolet, and mass spectra were measured with Perkin-Elmer Infracord or 521 spectrometers, Perkin-Elmer 202 or Cary 14 spectrometers and an Atlas CH-4 spectrometer. Microanalyses were performed by J. Nemeth and his associates. Deuterium resonance spectra (15.4 MHz) and 100-MHz proton spectra were obtained by Mr. R. Thrift. Mass spectra were obtained by Mr. J. Wrona.

[27] H. E. Zimmerman, G. S. Grunwald, and R. M. Paufler, *Org. Syn.*, **46**, 101 (1966).

meyer flask containing 0.553 g of bicyclo[2.2.0]pyran-2-one in 25 ml of methanol was sealed with a serum cap, flushed with nitrogen, and allowed to stand at room temperature for 22 hr. Sublimation (0.005 torr, 40°) of the white solid remaining after reduced pressure evaporation of the excess methanol afforded 0.625 g (85%) of acid **7**. The acid was further purified by recrystallization from cold acetone (−78°) to afford white crystalline product: mp 73–75°; infrared (KBr) 5.90 (conjugated C=O), 6.14 (C=CO), 6.29 (conjugated C=C), 10.7 (*trans*-CH=CH), and 13.35 μ (*cis*-CH=CH); nmr (see Table I).

Anal. Calcd for $C_6H_8O_3$: C, 56.25; H, 6.25; mol wt, 128. Found: C, 56.24; H, 6.33; mol wt, 128 (mass spectrometric).

5-Methoxy-2-*cis*-4-*trans*-pentadienoic Acid-2-*d*. By the above-described procedure, bicyclo[2.2.0]pyran-2-one-3-*d*[9] was converted to 5-methoxy-2-*cis*-4-*trans*-pentadienoic acid-2-*d*, the 60-MHz nmr spectrum of which shows the absence of the band originally at δ 5.42.

5-Methoxy-2-*cis*-4-*trans*-pentadienoic Acid-4-*d*. The acid obtained (as described earlier) from the reaction of bicyclo[2.2.0]pyran-2-one-5-*d* and methanol was purified by sublimation. Its nmr spectrum shows singlets at δ 12.3, 6.90, and 3.72 and doublets at 6.55 (J = 11.3 Hz) and at 5.41 (J = 11.2 Hz). After correcting for the presence of 13% undeuterated material, the relative intensities were 1.2:1.2:3.6:1.0:1.0. Bands possibly due to the presence of the *trans–trans* isomer (estimated 19% of total) occur at δ 7.30 (1.0 H, J = 15.4 Hz) and at 5.68 (1.0 H, J = 15.4 Hz). The remaining bands of the *trans–trans* isomer might be expected to be buried under those of the major *cis–trans* isomer at δ 12.3, 6.90, and 3.72 as the relative intensities seemingly indicate.

A 1:1 Isotopic Mixture of 5-Methoxy-2-*cis*-4-*trans*-pentadienoic Acids-3-*d* and -5-*d*. A. From Bicyclo[2.2.0]pyran-2-one-6-*d*. Bicyclo[2.2.0]pyran-2-one-6-*d* (isotopic purity 91%) was converted to the methoxypentadienoic acid in the aforementioned manner. The 60-MHz proton nmr spectrum (CCl_4) of the sublimed acid shows a singlet at δ 12.3 (1.1 H), a complex multiplet at 6.9 (1.4 H), a triplet at 6.54 (0.6 H), a doublet and a singlet at 5.42 (1.0 H), and a singlet at 3.72 (3.6 H). The relative amounts of the 3-*d* to the 5-*d* isomer were determined to be 1.0:1.2 by integration of the multiplet at δ 5.42 which occurs as a singlet for the 3-*d* isomer and as a doublet for the 5-*d* isomer. Owing to partial overlap of these bands, the integration values are believed to be within experimental accuracy in a 1:1 ratio.

B. From Bicyclo[2.2.0]pyran-2-one-4-*d*. Bicyclo[2.2.0]pyran-2-one-4-*d* was converted to the methoxy acid in the aforementioned manner and sublimed. The nmr spectrum of this material is identical with that described in part A. The same relative 3-*d* to 5-*d* isomer ratio of 1.0:1.2 was obtained by comparison of the intensities of the singlet and doublet at δ 5.32.

Hydrolysis of 5-Methoxy-2-*cis*-4-*trans*-pentadienoic Acid (7). To an nmr tube was added 0.19 g of acid **7** in 0.5 ml of acetonitrile. An initial nmr spectrum was taken and 0.1 ml of 5% hydrochloric acid was added. The hydrolysis, monitored by nmr, was complete within 4 hr. The 60-MHz spectrum contained multiplets at δ 9.47 (doublet, J = 7.7 Hz), 7.02 (doublet of triplets, J = 6.65, 15.6 Hz), 6.16 (multiplet, J = 1.25, 7.7, 15.6 Hz), and at 3.41 (doublet of doublets, J = 1.25, 6.65 Hz) attributed to the hydrolysis product, *trans*-4-formyl-3-butenoic acid.

Hydrogenation of 5-Methoxy-2-*cis*-4-*trans*-pentadienoic Acid (7). A 100-ml, three-necked flask containing 0.1 g of platinum oxide in 20 ml of methanol was evacuated and filled with hydrogen at atmospheric pressure and room temperature. After equilibration of the system, acid **7** (0.825 g) in 30 ml of anhydrous methanol was introduced. Hydrogen uptake ceased after 389 ml of hydrogen had been consumed. The solution was filtered, concentrated to 10 ml, and the *p*-bromophenacyl esters of the mixed acids were prepared by standard procedures. The crude mixed esters were separated by preparative tlc (silica gel G, methylene chloride) and recrystallized. The higher R_f component, *p*-bromophenacyl *n*-valerate, mp 73–74° (from ethanol) (lit.[28] mp 75°), has an infrared spectrum identical with that of an authentic sample. The lower R_f component, *p*-bromophenacyl 5-methoxyvalerate, mp 44–45° (from pentane), has an infrared spectrum (KBr disk) showing absorption at 5.75, 5.88, 6.30, 7.00, 8.55, 8.92, 9.3, 10.3, and 12.3 μ and an nmr spectrum ($CDCl_3$) showing a singlet at δ 5.36 (2 H), and complex multiplets at 7.8 (4 H), 3.4 (5 H), 2.55 (2 H), and 1.75 (4 H).

Preparation of *p*-Bromophenacyl 5-Methoxypentanoate. One gram of sodium in 10 ml of anhydrous methanol was added to 6.30 g of 4-chloro-*n*-butyl cyanide and the resulting solution was warmed on a steam bath. After 20 min, 2 g of sodium dissolved in 14 ml of anhydrous methanol was added and heating was continued for 3 hr. The solution was diluted with 200 ml of water and extracted with two 50-ml portions of ether, and the ether extracts were combined. The ether was removed under reduced pressure, and the residue was heated overnight on a steam bath with 30 ml of 10 *N* sulfuric acid. The solution was cooled and extracted twice with ether, and the ether extracts were concentrated. The crude acid mixture was titrated to the phenolphthalein end point with 0.1 *M* sodium hydroxide solution and the neutral solution extracted twice with methylene chloride to remove neutral impurities. A solution of *p*-bromophenacyl bromide (2.8 g) in 50 ml of 95% ethanol was added and the mixture was heated for 2 hr. The alcohol was removed under reduced pressure; the precipitated ester was collected and twice recrystallized from *n*-pentane to yield white flakes, mp 42–43°. The nmr and infrared spectra of this material are identical with those of the low R_f ester from the hydrogenation of acid **7**.

Anal. Calcd for $C_{14}H_{17}O_4Br$: C, 51.08; H, 5.17. Found: C, 51.18; H, 5.21.

5-Isopropoxy-2-*cis*-4-*trans*-pentadienoic Acid (8). In a manner similar to that described for the methoxy analog, the reaction of 0.354 g of bicyclo[2.2.0]pyran-2-one with excess isopropyl alcohol affords, after recrystallization from cold (−78°) *n*-pentane, 0.329 g (57% yield) of white crystalline 5-isopropoxy-2-*cis*-4-*trans*-pentadienoic acid. The acid was separated from minor impurities (detected by nmr spectroscopy) by recrystallization from cold (−78°) acetone: mp 75–76.5°; infrared (KBr disk) 5.92 (conjugated C=O), 6.15 (C=CO), 6.28 (conjugated C=C), 10.75 (*trans*-CH=CH), and 13.15 μ (*cis*-CH=CH). The 100-MHz nmr spectrum is summarized in Table I.

Anal. Calcd for $C_8H_{12}O_3$: C, 61.54; H, 7.69. Found: C, 61.69; H, 7.69.

5-*t*-Butoxy-2-*cis*-4-*trans*-pentadienoic Acid (9). The reaction of bicyclo[2.2.0]pyran-2-one and *t*-butyl alcohol gives the *t*-butoxy acid which is recrystallizable from cold (−78°) *n*-hexane and melts at 109.5°; infrared (KBr disk), 5.96 (conjugated C=O), 6.19 (C=CO), 6.30 (conjugated C=C), 10.75 (*trans* CH=CH), and 13.15 μ (*cis*-CH=CH). The 100-MHz nmr spectrum is summarized in Table I.

Anal. Calcd for $C_9H_{14}O_3$: C, 63.53; H, 8.24. Found: C, 63.15; H, 8.28.

A 1:1 Isotopic Mixture of 5-*t*-Butoxy-2-*cis*-4-*trans*-pentadienoic Acids-3-*d* and -5-*d*. The reaction of bicyclo[2.2.0]pyran-2-one-6-*d* (isotopic purity 91%) and *t*-butyl alcohol gives the isotopically labeled product. After recrystallization from acetone, the 100-MHz nmr spectrum (acetone-d_6) of the acid shows a doublet at δ 7.22, a broad doublet at 6.96, a quartet at 6.66, and a doublet and a broad singlet at 5.36 with relative intensities of 0.54:1.0:0.49:0.53:0.44 (corrected for the isotopic purity of the sample). Considering the intensity of the multiplets at δ 7.22 (H_5) and 6.66 (H_3), the relative ratio of 5-*t*-butoxy-2-*cis*-4-*trans*-pentadienoic acids-3-*d* and -5-*d* is 1.0:0.91. As in the previous cases with the methoxy acid the relative intensities of the doublet and singlet at δ 5.36 give a ratio of 1.0:1.2 for the 3-*d* and 5-*d* isomers, respectively.

Acid-Catalyzed Methanolysis of Bicyclo[2.2.0]pyran-2-one. Bicyclo[2.2.0]pyran-2-one (0.269 g, 2.8 × 10^{-3} mol) was added to 20 ml of anhydrous methanol in a 100-ml volumetric flask and the flask was filled to the mark with anhydrous ether. After vigorous mixing, the solution was decanted into two 50-ml volumetric flasks, A and B, and an initial ultraviolet spectrum was taken. Acetic acid (0.073 g) was added to A and the rate of methanolysis in each flask was monitored by periodically measuring the intensity of the ultraviolet absorption band at 277 mμ due to 5-methoxy-2-*cis*-4-*trans*-pentadienoic acid. After 9.91 hr the reactions in samples A and B were 43.2 and 42.9% complete, thus indicating that no appreciable rate enhancement had occurred in sample A. To A was added three drops of 70% perchloric acid. After vigorous mixing an ultraviolet spectrum showed the reaction to be 100% complete while that in B was only 44.9% complete. Thus, the reaction in A was at least 28 times faster than in B when perchloric acid was added.

5-Methoxy-2-*cis*-4-*trans*-pentadienoic acid can be isolated from an acid-catalyzed reaction. To a 50-ml volumetric flask was added 0.199 g of bicyclo[2.2.0]pyran-2-one and 40 ml of anhydrous ether. The flask was filled with methanol and three drops of 70% perchloric acid were added. After 0.5 hr the solution was washed with

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[28] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1964, p 311.

two 15-ml portions of water and dried with sodium sulfate, and the solution was filtered. Removal of solvent *in vacuo* gave 0.157 g of solid residue identified by 60-MHz nmr spectroscopy as 5-methoxy-2-*cis*-4-*trans*-pentadienoic acid (59% yield).

Photolytic Methanolysis of Bicyclo[2.2.0]pyran-2-one (4). A. Irradiation through Vycor. To a Pyrex vessel containing a Vycor immersion well was added 0.76 g of bicyclo[2.2.0]pyran-2-one, 250 ml of anhydrous ether (distilled from lithium aluminum hydride), and 25 ml of methanol. The system was flushed with nitrogen, cooled to −11°, and irradiated (Hanovia medium pressure lamp) for 27 hr. The yellow oily residue remaining upon removal of solvent *in vacuo* was molecularly distilled (25°, 0.005 torr). Analysis of the distillate by 60-MHz nmr spectroscopy showed it to consist of methyl *trans*-4-formyl-3-butenoate and 5-methoxy-2-*cis*-4-*trans*-pentadienoic acid in a 4:1 ratio.

B. Irradiation through Corex. To a Pyrex vessel surrounding a Vycor immersion well was added 1.033 g of bicyclo[2.2.0]pyran-2-one, 175 ml of anhydrous ether (distilled from lithium aluminum hydride), and 20 ml of methanol. The solution was cooled to −11° and irradiated (Corex filter, Hanovia 450-W medium pressure lamp). The photolysis was monitored by periodically withdrawing a 20-ml aliquot, removing the solvent *in vacuo*, and analyzing the residue in chloroform-*d* by 60-MHz nmr spectroscopy. After 2-hr irradiation the intensity of a doublet at δ 9.59 ($J = 7.4$ Hz), presumably owing to the presence of methyl *trans*-4-formyl-3-butenoate, indicated the ester had formed to an extent of *ca.* 0.3%. Nine additional hours of irradiation wrought little change.

Photolytic Methanolysis of a 1:1 Mixture of 2-Pyrone and Bicyclo[2.2.0]pyran-2-one-3-*d*. To a Pyrex vessel containing a Vycor immersion well was added 250 ml of anhydrous ether, 25 ml of methanol, 0.166 g of 2-pyrone, and 0.184 g of bicyclo[2.2.0]pyran-2-one-3-*d* (81% isotopic purity). The system was flushed with nitrogen, cooled to −11°, and irradiated (Corex filter, Hanovia 450-W medium pressure lamp) for 2 hr. The solvent was removed at reduced pressure, and the residue was shown by 60-MHz nmr spectroscopy to consist of methyl *trans*-4-formyl-3-butenoate (**5**), 5-methoxy-2-*cis*-4-*trans*-pentadienoic acid (**7**), and of bicyclo[2.2.0]-pyran-2-one-3-*d*. Analysis by 60-MHz nmr spectroscopy showed that no deuterium had been incorporated into aldehyde ester **5**.

Thermal Methanolysis of Tricyclo[$2^{3,6}$.1.1.0]pyran-2-one. Tricyclo[$2^{3,6}$.1.1.0]pyran-2-one (0.2 g) was dissolved in 5 ml of methylene chloride containing 0.5 ml of methanol. After 19.7 hr, the solvent was removed at reduced pressure and the residue sublimed to yield 5-methoxy-2-*cis*-4-*trans*-pentadienoic acid (**7**).

***cis*- and *trans*-4-Chlorocyclobut-2-ene-1-carboxylic Acids (16 and 15).** To a 100-ml flask containing 50 ml of 0.150 *N* ethereal hydrogen chloride solution cooled to 0° and blanketed with nitrogen, was added 0.534 g of bicyclo[2.2.0]pyran-2-one. After 14 hr, the solvent was removed (reduced pressure). Nmr analysis of the yellow oily residue showed that the *trans* and *cis* isomers of 4-chlorocyclobut-2-ene-1-carboxylic acid were present in a 1.0:2.1 ratio. Fractional molecular distillation afforded a liquid distillate and a solid residue.

The solid was sublimed (0.005 torr, *ca.* 25°) to give 0.221 g of white crystalline *cis*-4-chlorocyclobut-2-ene-1-carboxylic acid (**16**). In order to remove completely the minor quantity of *trans* isomer still present the solid was sublimed for 1–2 hr and the sublimate collected followed by continued sublimation of the residue. Three such fractional sublimations gave the relatively unstable crystalline *cis* isomer in analytically pure form: molecular weight (mass spectrometric) 132; infrared (CCl_4), 3.38 (OH) 5.83 (C=O), and 8.07, 8.20, and 11.0 μ (CCl). The nmr spectrum is discussed in the text.

Anal. Calcd for $C_5H_5O_2Cl$: C, 45.28; H, 3.77; Cl, 26.79. Found: C, 45.51; H, 3.80; Cl, 25.96.

The unstable liquid *trans* isomer **15** was molecularly distilled (5°, 0.005 torr) several times to give colorless product: molecular weight (mass spectrometric) 132; infrared (neat), 3.35 (OH), 5.86 (C=O), 7.83 and 8.18 (CCl), and 12.85 μ (*cis*-CH=CH). The nmr spectrum of **15** is discussed in the text.

Anal. Calcd for $C_5H_5O_2Cl$: C, 45.28; H, 3.77; Cl, 26.79. Found: C, 45.77; H, 4.09; Cl, 26.31.

***cis*-2-Chlorocyclobutane Carboxylic Acid.** Isomerically pure *cis*-4-chlorocyclobut-2-ene-1-carboxylic acid (0.074 g) was dissolved in 25 ml of ether and 20 mg of platinum oxide was added. The adduct was then reduced in a Parr hydrogenator (40 psi of hydrogen). After 1.75 hr, the solution was filtered, and the solvent was removed (reduced pressure) leaving a solid residue. Three recrystallizations from *n*-hexane at −78° gave white crystalline *cis*-2-chlorocyclobutane carboxylic acid, mp 96.5–97.5° (lit.[22] mp 97.0–98.5°).

A 1:1 Isotopic Mixture of *cis*-4-Chlorocyclobut-2-ene-1-carboxylic Acids-2-*d* and -4-*d*. Bicyclo[2.2.0]pyran-2-one-6-*d* (isotopic purity 94%) containing 27% of a 1:1 isotopic mixture of tricyclo-[$2^{3,6}$.1.1.0]pyran-2-ones-4-*d* and -6-*d* was caused to react with ethereal hydrogen chloride solution to give a 1.0:2.26 ratio of *trans* to *cis* product as determined by 60-MHz nmr spectroscopy. The *trans* isomer was molecularly distilled (25°, 0.005 torr) from the *cis* isomer and the latter adduct was further purified by sublimation (25°, 0.005 torr). Analysis of the sublimate by 60-MHz nmr spectroscopy (CCl_4) showed the presence of 11% *trans* adduct. Bands attributed to the *cis* isomer at δ 11.23 (s), 6.28 (m), 5.13 (d, J = 4.2 Hz), and 4.12 (doublet, J = 4.2 Hz, and singlet) had relative intensities (after correcting for the isotopic purity and *trans* adduct present) of 1.1:1.5:0.5:0.9, respectively. Thus, a 1.0:1.0 ratio of *cis*-4-chlorocyclobut-2-ene-1-carboxylic acids-2-*d* and -4-*d* is present.

***trans*-4-Chlorocyclobut-2-ene-1-carboxylic Acid-4-*d* (17).** Analysis of the 100-MHz nmr spectrum (CCl_4) of the distillate in the preceding reaction shows that it consisted of 20% *cis*- and 80% *trans*-4-chlorocyclobut-2-ene-1-carboxylic acids. For the *trans* isomer, bands occurred at δ 10.44 (s, 1.1 H), 6.28 (m, 2.0 H), and 3.75 (m, 1.0 H) after correcting for the isotopic purity and the 1:1 isotopic mixture of tricyclo[$2^{3,6}$.1.1.0]pyran-2-ones-4-*d* and -5-*d* present which will cause deuterium scrambling in the product.

5-Chloro-2-*cis*-4-*trans*-pentadienoic Acid (21). *cis*-4-Chlorocyclobut-2-ene-1-carboxylic acid (**16**) (0.112 g) containing 10% of the *trans* isomer (nmr spectroscopy) was dissolved in 5 ml of carbon tetrachloride and heated to reflux for 1 hr. The solvent was removed *in vacuo* and the solid residue twice sublimed (25°, 0.3 torr) to give 0.077 g (67.8% yield) of white powdery 5-chloro-2-*cis*-4-*trans*-pentadienoic acid: mp 78.5–79°; uv max (absolute C_2H_5OH) 255 mμ (ϵ 20,900); infrared (KBr disk) 5.94 (conjugated C=O), 6.18 (conjugated C=C), 10.65 (*trans*-CH=CH), 11.15 and 11.9 (C=CCl), and 13.7 μ (*cis*-CH=CH). The nmr spectrum is outlined in the text.

Anal. Calcd for $C_5H_5O_2Cl$: C, 45.28; H, 3.77; Cl, 26.79; mol wt, 132. Found: C, 45.28; H, 3.86; Cl, 26.30; mol wt, 132 (mass spectrometric).

5-Chloro-2-*trans*-4-*trans*-pentadienoic Acid (20). *trans*-4-Chlorocyclobut-2-ene-1-carboxylic acid (**15**) was dissolved in 5 ml of carbon tetrachloride, and the solution was heated to reflux for 1 hr. The solution was cooled, and the precipitate collected by filtration and purified by two sublimations (25°, 0.005 torr): mp 168.5°; uv max (absolute C_2H_5OH) 253 mμ (ϵ 19,100); infrared (KBr disk) 5.99 (conjugated C=O), 6.18 (conjugated C=C), 10.7 (*trans*-CH=CH), and 11.5 and 12.05 μ (C=CCl). The nmr spectrum is summarized in the text.

Anal. Calcd for $C_5H_5O_2Cl$: C, 45.28; H, 3.77; mol wt, 132. Found: C, 45.61; H, 3.96; mol wt, 132 (mass spectrometric).

A 1:1 Isotopic Mixture of 5-Chloro-2-*cis*-4-*trans*-pentadienoic Acids-3-*d* and -5-*d*. The acid was produced in the usual manner from the 1:1 isotopic mixture of *cis*-4-chlorocyclobut-2-ene-1-carboxylic acids-2-*d* and -4-*d* and was purified by two sublimations. A 100-MHz nmr spectrum (CCl_4) consisted of doublets at δ 7.79 and 6.58, a doublet of doublets at 6.56, and a singlet and a doublet at 5.69. The relative intensities for the multiplets at δ 7.79, 6.58, and 6.56 and 5.69 were 1.0:1.1:1.0. A 1.0:1.0 isomeric ratio of 5-chloro-2-*cis*-4-*trans*-pentadienoic acids-3-*d* and -5-*d* was determined by comparing the relative intensities of the doublet and singlet at δ 5.69 after correcting for 6% undeuterated product.

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