IIIC, 13283-36-8; IIID, 13283-35-7; IIIE, 13283-37-9; IV, 5010-79-7; 2-chlorohept-2-en-1-yl phenyl ether, 13283-39-1.

Acknowledgment—Nmr and infrared spectra were obtained and largely interpreted by Dr. F. J. Impastato; elemental analyses by W. J. Easley.

Photochemistry of Cycloalkenes. IV. Comparison with Crotonic Acid[1]

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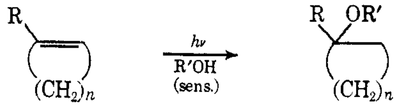
Recent studies have revealed that either direct or photosensitized irradiation of cycloalkenes (I, R = H or alkyl) in alcoholic or aqueous solvents results in addition of the alcohol or water in Markovnikov fashion to give the corresponding ether or alcohol (II).[2,3] The reaction was found to be limited to six- or seven-membered cyclic olefins; larger ring and acyclic systems, which are capable of easily undergoing instead the well-established *cis–trans* photoisomerization,[4] showed no evidence of adduct formation.[2,5,6]



I II

The similarity of this reaction of cycloalkenes to that of various examples of light-initiated, Michael-type addition of alcohols, water, or acetic acid to the β positions of cyclohexenones,[7] cyclooctenone,[8] and thymines and uracils[9] suggests the possibility of parallel mechanistic features in some, or perhaps even all, of these cases. However, in contradiction to this possibility is the long-standing report of Stoermer and Stockmann that irradiation of crotonic acid (**1a**) in methanol results in formation of the β-methoxy derivative **4a**.[10] Since, to the best of our knowledge, this is the only claim of a light-initiated, Michael-type addition to an *acyclic* α,β-unsaturated carbonyl system, it was deemed worthy of reinvestigation.

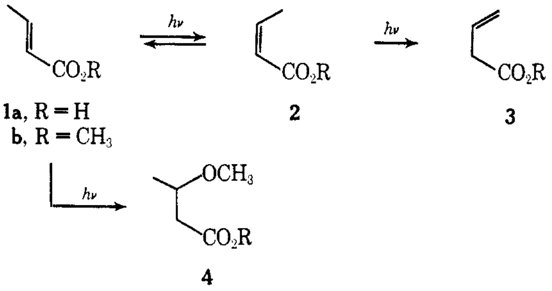
When methanolic solutions of crotonic acid (**1a**) were irradiated and aliquots were removed periodically, esterified with diazomethane, and analyzed by gas chromatography, there was observed a rapid establishment of the *cis–trans* equilibrium $1 \rightleftarrows 2$ followed by a slower formation of the deconjugated isomer **3** (Table I). On extended irradiation **3** became the principal component of the reaction mixture. Identical results were obtained by similar irradiation of methyl crotonate (**1b**) in methanol with or without the addition of xylene as a photosensitizer, although the reaction proceeded more slowly in the latter case. *In no instance was there any detectable formation of the adduct* **4**, despite the fact that a specimen of **4b** independently prepared by base-catalyzed addition of methanol to **1b** was found to be adequately stable under the irradiation conditions.

TABLE I

IRRADIATION OF CROTONIC ACID AND METHY CROTONATE[a]

Starting material	Time, hr	Yield, % 1	2	3	4
1a	4	24	17	59	...[b]
1b	4	20	19	39	...[b]
4b	4	...	...	...	56
1b[c]	1	79	17	3	...[b]
	4	50	28	8	...[b]
	8	35	29	16	...[b]
4b[c]	8	...	...	...	88

[a] See Experimental Section for details. [b] None detectable. [c] Contained 2% xylene.



The migration of the double bond to the β,γ position, which probably occurs in the *cis* isomer **2**,[11] is a familiar process which has been previously documented for a number of α,β-unsaturated esters, including **1b**.[12] Although it is not as well documented, similar behavior in the corresponding carboxylic acid series is not surprising.[13] Unfortunately, occurrence of the migration process competes with any potential addition of methanol across the double bond of the crotonic system. Nonetheless, there was still a considerable amount of the conjugated esters **1b** and **2b** remaining in the xylene-sensitized irradiation under conditions in which the cyclic analog **5**[14] incorporated a substantial amount of

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[1] Part III: P. J. Kropp and H. J. Krauss, *J. Am. Chem. Soc.*, **89**, 5199 (1967).

[2] (a) P. J. Kropp, *ibid.*, **88**, 4091 (1966); (b) P. J. Kropp and H. J. Krauss, unpublished data.

[3] J. A. Marshall and R. D. Carroll, *ibid.*, **88**, 4092 (1966).

[4] See, for example, the summary by R. B. Cundall, *Progr. Reaction Kinetics*, **2**, 165 (1964).

[5] Smaller ring systems undergo hydrogen abstraction rather than protonation; see P. J. Kropp, *J. Am. Chem. Soc.*, **89**, 3650 (1967).

[6] It is not yet clear whether the protonation of cyclohexenes and -heptenes involves the orthogonally oriented triplet species or a highly strained ground-state *trans*-cycloalkene intermediate.

[7] O. L. Chapman, J. B. Sieja, and W. J. Welstead, Jr., **88**, 161 *ibid.*, (1966); T. Matsuura and K. Ogura, *ibid.*, **88**, 2602 (1966).

[8] T. K. Hall, Ph.D. Dissertation, Iowa State University of Science and Technology, Ames, Iowa, 1965; *Dissertation Abstr.*, **26**, 5034 (1966).

[9] See S. Y. Wang, *Federation Proc.*, **24**, Suppl. 15, 71 (1965), and references cited therein.

[10] R. Stoermer and H. Stockmann, *Chem. Ber.*, **74**, 1786 (1914).

[11] See N. C. Yang and M. J. Jorgenson, *Tetrahedron Letters*, 1203 (1964).

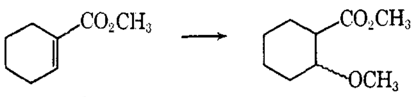
[12] M. J. Jorgenson, *Chem. Commun.*, 137 (1965).

[13] For one precedent, involving sorbic acid, see K. J. Crowley, *J. Am. Chem. Soc.*, **85**, 1210 (1963).

[14] Prepared as described by W. J. Bailey and R. A. Baylouny, *ibid.*, **81**, 2126 (1959).

methanol to afford a 1:4 mixture of the two epimeric methanol adducts **6**.[15,16,16a]

Thus, it is apparent that there is a fundamental difference in behavior between **1** and **5** which parallels the differences previously observed between analogous cyclic and acyclic alkenes.[2] To what extent this parallel behavior indicates similar mechanistic features between the addition reactions of cycloalkenes and cycloalkenones is under further investigation.



5 **6**

Experimental Section[17]

Irradiations. A. General.—Irradiations were conducted with 150-ml methanolic solutions containing 30 mmoles of acid or ester using a Hanovia 450-w, medium-pressure mercury arc and a water-cooled Vycor immersion well. Vigorous stirring of the reaction mixture was effected by the introduction of a stream of nitrogen through a jet opening in the bottom of the outer jacket. The progress of reactions was followed by gas chromatographic analysis of aliquots removed periodically from the reaction mixture. (In the case of crotonic acid aliquots were treated with diazomethane prior to analysis.) Yields were calculated relative to an internal hydrocarbon standard. For product identification the irradiation mixtures were concentrated on an 18-in. spinning-band column, and the individual components were isolated by preparative gas chromatography and characterized as described below. None of the photochemical reactions reported occurred under identical conditions in the absence of ultraviolet light.

B. Crotonic Acid (1a) and Methyl Crotonate (1b).—From irradiation of methyl crotonate (**1b**), or of crotonic acid (**1a**) followed by treatment with diazomethane, as outlined in Table I, the following products were isolated.

Methyl isocrotonate (**2b**) was obtained as a colorless liquid: λ_{max} 5.78 and 6.04 μ; nmr spectrum, τ ~3.75 (m, 1, CH-3),[18] 4.25 (d, 1, J = 11 Hz, CH-2), 6.34 (s, 3, CO_2CH_3), and 7.90 (2 d, 3, J = 7 and ~1 Hz, CH_3-4). An identical sample was obtained by esterification of a commercial sample of isocrotonic acid (**2a**).

Methyl 3-butenoate (**3b**) was obtained as a colorless liquid: λ_{max} (CH_2Cl_2) 5.74 and 6.08 μ; nmr spectrum, τ ~4.20 (m, 1, CH-3), ~4.90 (2 m, 2, CH_2-4), 6.39 (s, 3, CO_2CH_3), and 6.98 (2 m, 2, CH_2-2). Direct comparison with an authentic sample prepared as described below failed to reveal any detectable formation of methyl 3-methoxybutyrate (**4b**).

C. Methyl 1-Cyclohexene-1-carboxylate (**5**).—A 150-ml methanolic solution containing 2.97 g (21 mmoles) of ester **5**[14] and 3 ml of xylene was irradiated as described above for 8 hr. Gas chromatographic analysis at this point revealed the presence of recovered starting material (33%) accompanied by a poorly resolved mixture of **methyl *cis*- and *trans*-2-methoxycyclohexanecarboxylate** (**6**) (23%), which were formed in an approximately 1:4 ratio. Isolation of the mixture as described above afforded a colorless liquid: λ_{max} 5.75 and 9.15 μ; nmr spectrum, τ 6.22 (m, 1, CH-2), 6.34 (s, 3, CO_2CH_3), and 6.71 and 6.75 (2 s, 3, OCH_3).

Methyl 3-Methoxybutyrate (**4b**).—Treatment of 10.0 g of methyl crotonate (**1b**) with 10 ml of anhydrous methanol and several small pieces of sodium for 16 hr under reflux in an atmosphere of nitrogen followed by extraction with ether and distillation at 60–61° (1 mm) afforded 9.3 g (71% yield) of the methoxy adduct **4b**, a colorless liquid: λ_{max} 5.72 μ; nmr spectrum, τ 6.28 (m, 1, CH-3), 6.38 (s, 3, CO_2CH_3), 6.73 (s, 3, OCH_3), ~7.56 (m, 2, CH_2-2), and 8.83 (d, 3, J = 6 Hz, CH_3-4) (lit.[19] bp 149–150°).

Registry No.—**1a,** 107-93-7; **2b,** 4358-59-2; **3b,** 3724-55-8; **4b,** 3136-17-2; **6** (*cis*), 13640-65-8; **6** (*trans*), 13640-66-9.

Acknowledgment.—The authors are indebted to Dr. R. A. Damico for a generous supply of methyl 1-, 2-, and 3-cyclohexenecarboxylates.

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(15) These adducts are assumed on the basis of mechanistic reasoning to be the two 2-methoxycyclohexane carboxylates **6**, which were previously described by M. A. Febrer and J. Pascual, *Anales Real Soc. Espan. Fis. y Quim.*, **52B**, 541 (1956) (*Chem. Abstr.*, **51**, 5711 (1957)). That they are not the corresponding 1-methoxy isomers is evident by the presence of absorption equivalent to one proton at τ 6.22. The possibility that they are 3- or 4-methoxy isomers has not been rigorously precluded, but comparison with authentic specimens revealed no detectable evidence for the formation of the 2- or 3-cyclohexene isomers of **5** during the course of the irradiation. Treatment of **5** with methanolic sodium methoxide afforded a 1.5:1 mixture of two adducts exhibiting spectral behavior similar to that of the photoadducts. It is characteristic of the photochemical addition reactions of cycloalkenes to afford product ratios different from those obtained by thermodynamically controlled ground-state reactions.[2,3]

(16) It is not unlikely that the 6.5% conversion of crotonic acid (**1a**) into 3-methoxybutyric acid (**4a**) observed by Stoermer and Stockmann[10] after *3 weeks'* irradiation with a "Uviollampe" was the result of an acid-catalyzed dark reaction.

(16a) NOTE ADDED IN PROOF.—A similar photochemical addition of alcohols to 1-acetylcyclohexene has recently been reported by B. J. Ramey and P. D. Gardner, *J. Am. Chem. Soc.*, **89**, 3949 (1967).

(17) Infrared spectra were obtained on neat samples with a Perkin-Elmer Infracord spectrophotometer. Nuclear magnetic resonance (nmr) spectra were determined in chloroform-d_3 solution with a Varian HA-100 spectrometer, using tetramethylsilane as an internal standard. Gas chromatographic analyses were performed on an Aerograph 90-P instrument using 10 ft × 0.25 in. columns packed with 20% SE-30 or Carbowax 20 M on 60/80 mesh Chromosorb W.

(18) Indicates multiplicity (s = singlet, d = doublet, q = quartet, and m = unresolved multiplet), integration, and assignment.

(19) W. von E. Doering and R. W. Young, *ibid.*, **74**, 2997 (1952); T. Purdie and W. Marshall, *J. Chem. Soc.*, **59**, 477 (1891).

Hydrogenation Product of Tetraphenylmethane. The Cyclohexyl, Phenyl Tetrasubstituted Methanes

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It has been previously shown that the catalytic hydrogenation of tetraphenylmethane proceeds smoothly to tetracyclohexylmethane,[1] despite the failure of early attempts[2] and the suggestion that steric requirements would preclude the bonding of four cyclohexyl groups to a single carbon atom.[3] To verify this conclusion and to observe reaction intermediates, hydrogenation of tetraphenylmethane has now been performed under conditions conducive to partial reaction

Cyclohexyltriphenylmethane[4] (I) was isolated when the hydrogenation at 95° and 500 psig over rhodium was interrupted after 3 moles of hydrogen was absorbed, while dicyclohexyldiphenylmethane (II) was the major product (74%) at the point when hydrogenation slowed substantially after 6 moles was absorbed. The partial hydrogenation of II at 97.5° furnished tricyclohexylphenylmethane (II) in 19% yield.

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(1) G. R. Buell and L. Spialter, *J. Org. Chem.*, **30**, 1662 (1965).

(2) V. N. Ipatiev and B. N. Dolgov, *Compt. Rend.*, **185**, 210 (1927).

(3) M. Kanazashi and M. Takakusa, *Bull. Chem. Soc. Japan*, **27**, 441 (1954).

(4) H. Wieland and A. Meyer, *Ann.*, **551**, 249 (1942).