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The Photo-induced Addition of Acetic Acid to Cyclohexene Derivatives¹⁾

Ta-Yan LEONG, Takeshi IMAGAWA, Koichi KIMOTO, and Mituyosi KAWANISI

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606

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The irradiation of methyl 3-cyclohexene-1-carboxylate in acetic acid in the presence of benzene as a sensitizer yields methyl *trans*-4-acetoxycyclohexanecarboxylate predominantly, together with a small amount of methyl *trans*-3-acetoxycyclohexane-1-carboxylate; the corresponding *cis*-isomers are not detected. Under the same conditions, on the irradiation of dimethyl esters of *cis*- and *trans*-4-cyclohexene-1,2-dicarboxylic acids, the two possible isomers of acetic-acid adducts with respect to each starting substance are obtained. The irradiation of *trans*-8-oxabicyclo[4.3.0]non-3-ene gives the two possible acetic-acid adducts, whereas in the case of the irradiation of the *cis*-isomer, only two equatorially-substituted acetic-acid adducts are obtained. The structural elucidation and the mechanism of the formation of these compounds are discussed.

The incorporation of protic solvents in excited cycloalkenes by sensitization has proved a fertile field for

mechanistic as well as synthetic olefin photochemistry.²⁻⁸⁾ We have been engaged in studies aimed at

1) Partly presented at the 25th Annual Meeting of the Chemical Society of Japan, Tokyo, October, 1971.

2) a) P. J. Kropp and H. J. Krauss, *J. Amer. Chem. Soc.*, **91**, 7466 (1969) and references cited therein. b) P. J. Kropp, *Pure Appl. Chem.*, **24**, 585 (1970).

3) a) J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969). b) J. A. Marshall, *Science*, **170**, 137 (1970). c) For recent related paper, J. A. Marshall and J. P. Arrington, *J. Org. Chem.*, **36**, 214 (1971).

4) a) H. Compaignon de Marcheville and R. Beugelmans,

Tetrahedron Lett., **1968**, 6331. b) R. Beugelmans and H. Compaignon de Marcheville, *Chem. Commun.*, **1969**, 241. c) D. Guénard and R. Beugelmans, *Tetrahedron Lett.*, **1970**, 1705.

5) J. A. Waters and B. Witkop, *J. Org. Chem.*, **34**, 3774 (1969).

6) M. Tada and H. Shinozaki, *This Bulletin*, **43**, 1270 (1970).

7) S. Fujita, Y. Hayashi, T. Nōmi, and H. Nozaki, *Tetrahedron*, **27**, 1607 (1971).

8) H. Prinzbach and W. Eberbach, *Chem. Ber.*, **101**, 4083 (1968).

the application of this reaction;⁹⁾ we have found that cyclohexenes and cycloheptenes containing an acyloxy group at the allylic and homoallylic positions gave products resulting from the regiospecific addition of polar solvents,^{9b)} and have assumed the participation of the oxygen functions in the orientation of the reaction pathways.^{9d,e)} As an extension of this research, as well as a comparison with the results obtained previously, we have now studied the stereochemistry of the polar addition of acetic acid to methyl 3-cyclohexene-1-carboxylate (I) together with cyclohexenes with two substituents, VIII and XI, and bicyclic compounds, XIV and XVII.

Results and Discussion

When methyl 3-cyclohexene-1-carboxylate (I) was irradiated in acetic acid in the presence of benzene as a sensitizer, methyl *trans*-4-acetoxycyclohexane-1-carboxylate (II) was obtained predominantly, together with a small amount of methyl *trans*-3-acetoxycyclohexane-1-carboxylate (III) in a 60% yield (II: III = 97: 3). Authentic specimens of II and III were obtained by using the previously-reported method.¹⁰⁾ The identity of the photoproducts with the authentic specimens was satisfactory. We had already observed that, in the case of cyclohex-3-en-1-yl acetate under similar conditions, only a *cis-trans* mixture (*ca.* 1: 1) of 1,4-diacetoxycyclohexane was obtained regiospecifically; here the contribution of the oxygen functions to the transition state and/or to the intermediate at the

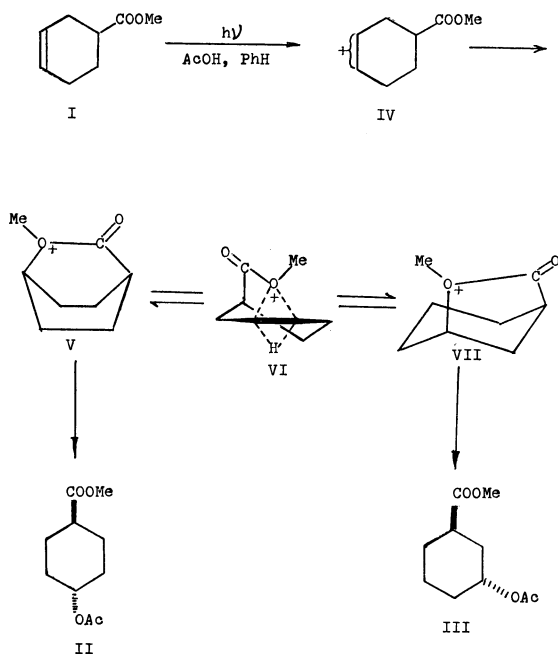
protonation stage had been assumed.^{9d)} In the present case, a possible mechanism for the formation of II and III is depicted in Scheme 1, which indicates that the formation of II and III is due to the intermediacy of oxonium ions. The protonation of photo-excited six-membered cyclic olefin in protic media giving carbonium-ion species appears to be established.^{2,3)} Therefore, the formation of a carbonium ion (IV) is not exceptional; this in turn collapses into oxonium ions (V) and (VII). The incorporation of the 1,4- or 1,3-bridged ions, such as (V) or (VII), was advanced by Noyce in speaking of the reaction of methoxycyclohexanecarboxylic acids with acetic anhydride.¹¹⁾ If we assume an equilibrium between these oxonium ions (V) and (VII), in which the doubly-bridged ion (VI) represents the transition state, the exclusive formation of *trans*-products (1,4- and 1,3-) can be understood. It should be noted that this mechanism can also explain the predominant formation of the thermodynamically more stable 1,4-isomer (II). Thus, in the present case, the participation of the oxygen function presumably plays an important role in directing the reaction pathways as well. We will return to the discussion of the mechanistic aspects of the protonation stage after more experimental facts are known.

When dimethyl 4-cyclohexene-*cis*-1,2-dicarboxylate (VIII) was irradiated in acetic acid under the same conditions, dimethyl *c*-4-acetoxycyclohexane-*r*-1,*c*-2-dicarboxylate (IX) and dimethyl *t*-4-acetoxycyclohexane-*r*-1,*c*-2-dicarboxylate (X)¹²⁾ were obtained in a 25% yield (IX: X = 71: 29).

The photoreaction of dimethyl 4-cyclohexene-*trans*-1,2-dicarboxylate (XI) was effected similarly; dimethyl *c*-4-acetoxycyclohexane-*r*-1,*t*-2-dicarboxylate (XII) and dimethyl *t*-4-acetoxycyclohexane-*r*-1,*t*-2-dicarboxylate (XIII) were obtained in a 25% yield (XII: XIII = 34: 66). The structures of IX, X, XII, and XIII were deduced from the respective IR and NMR spectra and were further elucidated by comparison with the authentic specimens prepared by the acetylation of the corresponding known alcohols.^{13,14)}

Judging from the products of these photoreactions, it can be deduced that, in the cases of VIII and XI, the role of the participation of the oxygen functions is unimportant.

The irradiation of *trans*-8-oxabicyclo[4.3.0]non-3-ene (XIV) yielded the two possible acetic-acid adducts, *t*-3-acetoxy-*r*-1-*trans*-8-oxabicyclo[4.3.0]nonane (XV) and *c*-3-acetoxy-*r*-1-*trans*-8-oxabicyclo[4.3.0]nonane (XVI), in a ratio of XV: XVI = 80: 20 (yield = 6%). The NMR spectra of XV and XVI showed half-band widths, W_H , of 14 and 8 Hz respectively for the $-\text{CH}-\text{OAc}$ protons; thus, the structures of XV and XVI were unambiguously proved to have the structures shown in Scheme 2, since the fused systems have a *trans*-configuration and an inversion of the structure



Scheme 1.

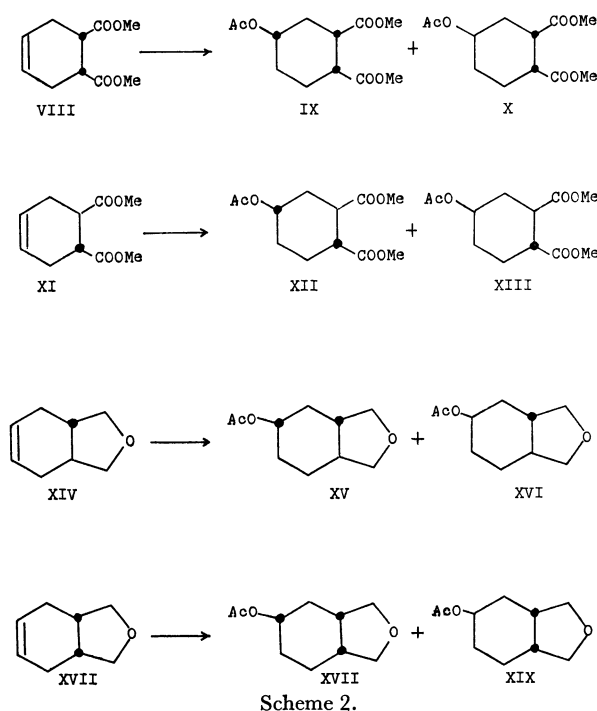
9) a) M. Kawanisi and H. Kato, *Tetrahedron Lett.*, **1970**, 721. b) T. Okada, K. Shibata, M. Kawanisi, and H. Nozaki, *Tetrahedron Lett.*, **1970**, 859. c) H. Kato and M. Kawanisi, *Tetrahedron Lett.*, **1970**, 865. d) M. Kawanisi, Symposium on Photochemistry 1970, Kyoto, p. 122. e) K. Shibata, T. Okada, and M. Kawanisi, *Nippon Kagaku Kaishi*, in press.

10) E. Hardegger, Pl. A. Plattner, and F. Blank, *Helv. Chim. Acta*, **27**, 793 (1944).

11) D. S. Noyce and H. I. Weingarten, *J. Amer. Chem. Soc.*, **79**, 3098 (1957).

12) To designate the relative configuration the IUPAC 1968 Tentative Rules, Section E, have been adopted throughout this work. See *J. Org. Chem.*, **35**, 2849 (1970).

13) J. Klein and E. Dunkelblum, *Tetrahedron*, **23**, 205 (1966).



is impossible. An independent synthesis of XV and XVI was possible by means of the hydroboration of XIV, followed by alkaline oxidation and acetylation.¹⁴

On the other hand, when the photochemical reaction of *cis*-8-oxabicyclo[4.3.0]non-3-ene (XVII) was effected under the same conditions, two isomeric adducts were obtained, *t*-3-acetoxy-*r*-1-*cis*-8-oxabicyclo[4.3.0]nonane (XVIII) and *c*-3-acetoxy-*r*-1-*cis*-8-oxabicyclo[4.3.0]nonane (XIX) in a ratio of 67:33 (yield=5%); both had broad signals of $W_H=14-17$ Hz for the methine protons of $-\text{CH}-\text{OAc}$ in their NMR spectra, indicating that the protons are situated axially. The adducts were assumed to have the structures indicated as XVIII and XIX, with equatorial acetoxy groups, which are thermodynamically more stable. A detailed description of the conformations of the alcoholic analogs of XVIII and XIX will appear in a separate paper.¹⁵

The small yield in the reaction of these bicyclic olefins can be ascribed to the inefficiency of the conversion into the distorted transoid olefins^{2,3} via their triplet state because of the rigidity of the ring system. Bicyclic olefins such as bicyclo[3.3.1]non-3-ene were found to be fairly reactive toward the photoreaction in protic media, presumably because their structure has some flexibility.^{9a}

Although Mundy succeeded in demonstrating the possibility of the long-range nonbonded electronic participation of the oxygen atom in XVII in ground-state chemistry,^{16,17} the small yield in the present case restrains us from further discussion of the possible

existence of such interaction in excited-state chemistry.

Experimental

All the temperature are uncorrected. Microanalyses were performed by Mrs. Kiyoko Fujimoto of our laboratory. The IR spectra were obtained in neat liquid film on a Shimadzu IR-27-G spectrophotometer. The NMR spectra were taken in 10% CCl_4 solutions on a JEOL C-60-H spectrometer, and the chemical shifts (δ) are reported relative to TMS as an internal standard. The glc analysis and separations were performed with a Shimadzu GC-4APT using a $3\text{ m} \times 3\text{ mm}$ column with 15% polyethylene glycol on 60/80 Chromosorb W operating at 180°C with a He flow rate of 40 ml/min. The MS spectra were taken using a Hitachi RMS-4 mass-spectrometer operated at 70 eV.

Starting Materials. Compounds I, VIII, and XI were prepared in the manner described in the literature.¹⁴ The method of preparing XIV followed the one proposed by Eliel and Pillar;¹⁸ XVII was obtained in asimilar manner and had properties identical with those reported by Christol *et al.*¹⁹

Photoreaction of Methyl 3-Cyclohexene-1-carboxylate (I) in Acetic Acid. A solution of I (3.27 g; 0.023 mol) and benzene (3 ml) in acetic acid (80 ml) was irradiated for 48 hr by means of a medium-pressure mercury arc in a quartz vessel. The photolysate was diluted with water (100 ml), neutralized (Na_2CO_3), extracted (ether), washed (water), and dried (Na_2SO_4). The adducts, II and III, were separated from the unreacted I by column chromatography (Al_2O_3) and isolated by preparative glc. II and III were obtained in a 60% yield in a ratio of 97:3. They were identical in all respects with the authentic samples synthesized by the reported methods.¹⁴

Photoreaction of Dimethyl 4-Cyclohexene-*cis*-1,2-dicarboxylate (VIII). A mixture of VIII (5 g; 0.025 mol), benzene (3 ml), and acetic acid (85 ml) was irradiated for 48 hr and then treated in the manner described above. The adducts were obtained as a mixture by column chromatography and were purified by distillation. The mixture of IX and X (IX:X=71:29) boiled at $114^\circ\text{C}/4\text{ mmHg}$ (Yield: 25%). Found: C, 55.70; H, 6.52%. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_6$: C, 55.80; H, 7.03%. IX and X were separated by glc. The structure of IX was characterized by the following spectral data: IR: 2943(s), 1765(s), 1755(s), 1255(s), 1210(s), 1135(m), 1115(w), 1091(m), 1055(s), 1032(m), 1015(m), 923(w), 902(w), 855(w), 830(w), and 774(w) cm^{-1} . NMR: δ 4.91–4.41(m, 1H), 3.67(s, 6H), 3.08–2.31(m, 2H), 1.95(s, 3H), 2.31–1.30(m, 6H). MS: m/e 258(M^+ small), 227($\text{M}^+ - 31$, 4%), 198($\text{M}^+ - 60$, 20%), 185(43%), 166(80%), 138(100%). The structure of X was characterized similarly: IR: 2950(s), 1755(s), 1740(s), 1250(s), 1202(s), 1120(m), 1072(m), 1041(m), 1035(m), 999(m), 958(w), 832(w), 776(w), cm^{-1} . NMR: δ 5.06–4.73(m, 1H), 3.65(s, 6H), 3.03–2.09(m, 2H), 1.98(s, 3H), 2.27–1.35(m, 6H). MS: m/e 258(M^+ small), 227($\text{M}^+ - 31$, 32%), 198($\text{M}^+ - 60$, 21%), 166(79%), 138(80%), 79(100%).

Dimethyl *c*-4-acetoxycyclohexane-*r*-1,*c*-2-dicarboxylate (IX) was synthesized by the acetylation of the dimethyl *c*-4-hydroxycyclohexane-*r*-1,*c*-2-dicarboxylate obtained by the reduction of dimethyl 4-oxocyclohexane-*cis*-1,2-dicarboxylate as has been described by Klein *et al.*¹⁴ Dimethyl *t*-4-acetoxycyclohexane-*r*-1,*c*-2-dicarboxylate (X) was obtained independently by the acetylation of the dimethyl *t*-4-hydroxycyclohexane-*r*-1,*c*-2-dicarboxylate prepared by the hydro-

14) J. Klein, E. Dunkelblum, and D. Avrahami, *J. Org. Chem.*, **32**, 935 (1967).

15) K. Kimoto, T.-Y. Leong, T. Imagawa, and M. Kawanisi, *Can. J. Chem.*, **50**, 3805 (1972).

16) B. P. Mundy, A. R. DeBernardis, and R. D. Otzenberger, *J. Org. Chem.*, **36**, 3830 (1971).

17) Cf. B. Rickborn and S.-Y. Low, *ibid.*, **30**, 2212 (1965).

18) E. L. Eliel and C. Pillar, *J. Amer. Chem. Soc.*, **77**, 3600 (1955).

19) H. Christol, A. Donche, and M. F. Plenar, *Bull. Soc. Chim. Fr.*, **1966**, 1315.

boration of dimethyl 4-cyclohexene-*cis*-1,2-dicarboxylate.¹³ The IR and NMR of IX and X synthesized in the above manner were identical in all respects with those of the photochemical products.

Photoreaction of Dimethyl 4-Cyclohexene-*trans*-1,2-dicarboxylate (XI). The irradiation of XI was similarly carried out using 6 g (0.03 mol) of XI in 100 ml of acetic acid, with 3.6 ml of benzene as a sensitizer. The isomeric mixture (bp 114°C/4 mmHg) of the photoproducts, XII and XIII in a ratio of 34:66, was obtained in a 25% yield. Found: C, 55.70; H, 7.07%. Calcd for C₁₂H₁₈O₆: C, 55.80; H, 7.03%. The adducts, XII and XIII, were isolated in the manner described before. The structure of XII was assigned according to the following data: IR: 2950(m), 1742(s), 1244(s), 1072(w), 1040(s), 1018(s), 978(w), 941(w), 901(w), 853(w), 754(w) cm⁻¹. NMR: δ 4.91–4.19(m, 1H), 3.66(s, 6H), 2.89–1.81(m, 8H), 1.98(s, 3H). MS: *m/e* 258(M⁺ small), 227(M⁺ –31, 4%), 198(M⁺ –60, 12%), 185(20%), 166(100%), 138(88%).

The structure of XIII was deduced similarly from the following spectral data: IR: 2970(m), 1741(s), 1240(s), 1039(s), 1019(s), 990(m), 958(w), 895(w), 857(w), 761(w) cm⁻¹. NMR: δ 5.15–4.96(m, 1H), 3.64(s, 6H), 2.85–1.30(m, 8H), 2.02(s, 3H). MS: *m/e* 258(M⁺ small), 227(M⁺ –31, 9%), 198(M⁺ –60, 16%), 185(36%), 167(45%), 166(96%), 138(100%).

XII and XIII were independently obtained by the acetylation of the mixture of dimethyl *c*-4- and *t*-4-hydroxycyclohexane-*r*-1,*t*-2-dicarboxylates prepared from the hydroboration of XI, as has been previously reported.¹⁴ The products synthesized in this manner were identical with the photochemical products.

Photoreaction of *trans*-8-Oxabicyclo[4.3.0]non-3-ene (XIV).

A mixture of XIV (1.245 g; 0.1 mol), benzene (2 ml), and acetic acid (50 ml) was irradiated in the way previously described. A mixture of the photoproducts, *t*-3-acetoxy-*r*-1-*trans*-8-oxabicyclo[4.3.0]nonane (XV) and *c*-3-acetoxy-*r*-1-*trans*-8-oxabicyclo[4.3.0]nonane (XVI), was obtained in a 6% yield (XV:XVI=80:20). The adducts were separated by glc. The structures of XV and XVI were supported by the following data. For XV: IR: 2932(s), 2890(s), 1736(s), 1242(s), 1090(w), 1060(w), 1018(s), 980(w), 955(w), 890(m) cm⁻¹. NMR: δ 5.11–4.40(m, 1H, W_H=14 Hz), 4.06–3.5(m, 2H), 3.51–2.81(m, 2H), 1.96(s, 3H), 2.31–1.01(m, 8H). MS: *m/e* 184(M⁺ small), 141(M⁺ –43, 13%), 124(M⁺ –60, 66%), 79(100%). For XVI: IR: 2960(s), 2890(s), 1748(s),

1218(m), 1121(w), 1018(s), 974(w), 895(m) cm⁻¹. NMR: δ 5.30–5.03(m, 1H, W_H=8 Hz), 4.11–3.65(m, 2H), 3.48–2.98(m, 2H), 1.99(s, 3H), 2.35–1.24(m, 8H). MS: *m/e* 184(M⁺ 3%), 141(M⁺ –43, 40%), 124(M⁺ –60, 14%), 43(100%).

Microanalyses were performed on the respective alcohols obtained by the LAH reduction of XV and XVI. For the alcohol from XV: Found: C, 67.57; H, 9.93%. For the alcohol from XVI: Found: C, 67.36; H, 10.19%. Calcd for C₈H₁₄O₂: C, 67.57; H, 9.93%.

Independent Synthesis of XV and XVI.

A solution of XIV (1 g) in 5 ml of tetrahydrofuran was subjected to hydroboration, followed by alkaline oxidation, as has been described by Klein *et al.*¹⁴ The alcohols thus obtained were converted into the corresponding acetates with a mixture of acetic anhydride and boron trifluoride etherate. The acetates obtained in this way were shown to have an isomeric ratio of XV:XVI=54:46. The mixture of the acetates was separated into XV and XVI by glc; they were shown to be identical in all respects with those obtained photochemically.

Photoreaction of *cis*-8-Oxabicyclo[4.3.0]non-3-ene (XVII).

The procedure was essentially the same as that for XIV; the adducts obtained in a 5% yield. Found: C, 65.01; H, 8.76%. Calcd for C₁₀H₁₆O₃: C, 65.19; H, 8.75%. This mixture was separated into *t*-3-acetoxy-*r*-1-*cis*-8-oxabicyclo[4.3.0]nonane (XVIII) and *c*-3-acetoxy-*r*-1-*cis*-8-oxabicyclo[4.3.0]nonane (XIX) by preparative glc (XVIII:XIX=67:33); the isomers had the following properties. For XVIII: IR: 2950(s), 2900(s), 1742(s), 1460(w), 1370(m), 1255(s), 1236(s), 1083(s), 1050(s), 1034(s), 1016(s), 995(w), 960(w), 900(m), 720(w) cm⁻¹. NMR: δ 5.01–4.52(m, 1H, W_H=17 Hz), 3.91–3.40(m, 4H), 2.51–1.09(m, 11H). MS: *m/e* 184(M⁺ 2%), 141(M⁺ –43, 24%), 124(M⁺ –60, 28%), 43(100%). For XIX: IR: 2950(s), 2900(s), 1741(s), 1370(m), 1240(s), 1060(w), 1020(s), 895 cm⁻¹. NMR: δ 5.12–4.66(m, 1H, W_H=14 Hz), 4.04–3.33(m, 4H), 2.64–1.14(m, 11H). MS: *m/e* 184(M⁺ 2%), 141(M⁺ –43, 30%), 124(M⁺ –60, 30%), 43(100%).

The elemental analysis of each isomer was performed upon the corresponding alcohol derived from the LAH reduction of XVIII and XIX. For the alcohol from XVIII; Found: C, 67.57; H, 10.17%. For the alcohol from XIX; Found: C, 67.35; H, 9.65%. Calcd for C₈H₁₅O₂: C, 67.57; H, 9.93%.

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