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ACETOXYTHALLATION AND ACETOXYMERCURATION OF *endo*- AND *exo*-DICYCLOPENTADIENES AND BICYCLO[3.2.1]OCTA-2,6-DIENE

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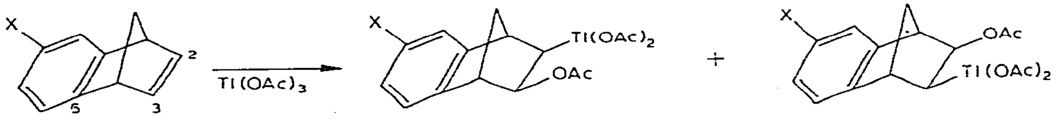
Summary

Treatment of *endo*- (I) and *exo*-dicyclopentadiene (II) with thallium(III) acetate in methanol, chloroform or dichloromethane affords a regioisomeric mixture of the *cis-exo*-acetoxythallation adducts. The isomer ratios in the adducts were determined directly by ^{13}C NMR spectra of the crude products. Acetoxymercuration of the same dienes also affords the corresponding regioisomeric *cis-exo* adducts, the selectivity being lower compared with that of acetoxythallation. Acetoxythallation and acetoxymercuration of bicyclo[3.2.1]octa-2,6-diene (XIII) in dichloromethane gives single *cis-exo* adducts, respectively.

Introduction

It has been reported recently that acetoxythallation of substituted benzonorbornadienes affords a regioisomeric mixture of the *cis-exo* adducts (eq. 1), the isomer ratio being reversed according to the electron-withdrawing or electron-releasing nature of substituent X [1], caused by polarization in the C(2)—C(3) double bond induced by the homoallylic interaction between C(5) and C(3).

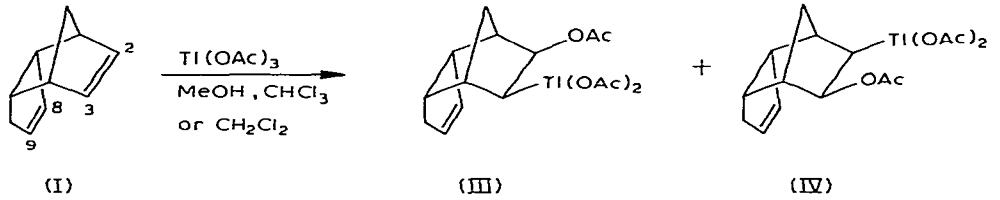


(1)

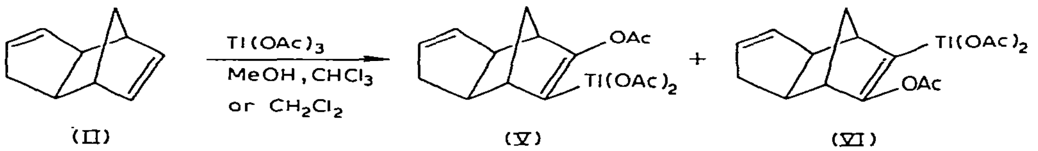
Since it seemed of interest to investigate whether other types of polarization effects might affect the isomer ratio of the products in similar reactions of some cyclic dienes, we carried out a study of the product ratios of acetoxythallation of *endo*- (I) and *exo*-dicyclopentadiene (II) and bicyclo[3.2.1]octa-2,6-diene (XIII). This paper describes the results, comparing them with those of oxymercuration.

Results and discussion

The reactions of I and II with thallium(III) acetate in methanol gave the acetoxythallation adducts in more than 80% yield, no methoxythallation products being formed as had been found in the cases of other norbornene derivatives [1]. The adducts were regioisomeric mixtures in each case; III and IV from I; and V and VI from II, respectively (eq. 2 and 3). Isomer ratios of III/IV and V/VI in the crude products were found to be about 3/1 and 4/5, respectively, by ^{13}C NMR spectroscopy by comparison of the peak heights of acetoxy group substituted carbon signals in each isomer *. The reaction proceeded in chloroform or dichloromethane as well to afford the same adducts in 80—90% yield, the isomer ratios of III/IV and V/VI being ca. 5/1 and 4/5, respectively, in this case. The results show that the reactivity difference in the attack of the thallium moiety on C(2) and C(3) is larger in the case of the *endo*-isomer than for the *exo*-isomer, and that a cationic thallium moiety attacks C(3) in preference to C(2) in I.



(2)



(3)

Oxymercuration of both dicyclopentadienes in dichloromethane at room temperature proceeded more smoothly than acetoxythallation and afforded the adducts VII and VIII from I, and IX and X from II, respectively (eq. 4 and 5).

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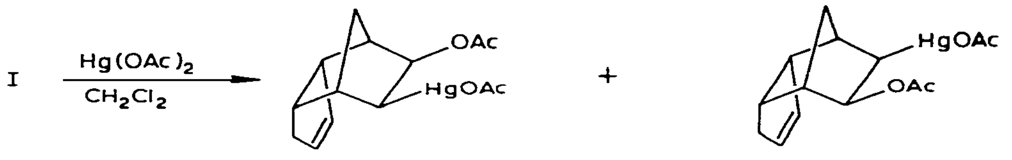
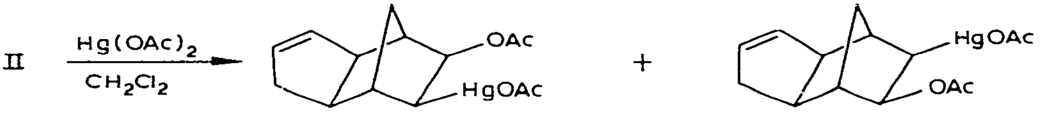
* The ^{13}C NMR spectrum of a mixture was quite complicated, but an assignment was possible by use of the di-t-butyl nitroxide radical as a nuclear spin decoupling reagent [2] and also by use of the information obtained by solvent effects. The results obtained in $CDCl_3$ are shown in Table 1. The assignments of III and IV were based on the presence or absence of $^{13}C—^{205}Tl$ couplings at the C(10) and C(8) signals, while that of V and VI was on that at C(8) signals. The numbering in the products is arbitrary as shown in Table 1 and is not always consistent with that in the starting dienes.



(VII) (VIII)

(4)

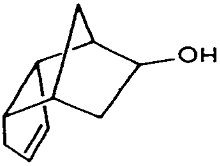


(IX) (X)

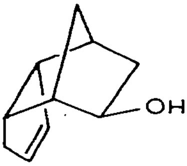
(5)

The isomer ratios of VII/VIII and IX/X in the crude products were determined to be about 2/1 and 2/3, respectively, by ^{13}C NMR spectroscopy by comparison of peak heights of the signals due to the acetoxy-substituted carbon atoms in the former case and to those of the acetoxymercuri-substituted carbon atoms in the latter case *.

Although methoxy- or hydroxy-mercuration of these dienes has been reported to give similar adducts [3,4], regioselectivity is clear in only one case [5] in which hydroxymercuration of I followed by alkaline sodium borohydride reduction afforded a regioisomeric mixture of alcohols, XI and XII (XI/XII ca. 7/3). Our results, together with the reported results [5] on oxymercuration of I, shows that an electrophilic mercury moiety also attacks preferentially at C(3) (rather than C(2) of I. The fact that the isomer ratio of III/IV is larger than that of VII/VIII shows that oxythallation is slightly more selective than oxymercuration [6]. The attempt to determine the isomer ratio of III and IV by reduction with sodium borohydride in alkaline medium was unsuccessful because of the low yield of XI and XII. The main product was I as has been observed in several other oxythallation adducts [1,7] (see Experimental).



(XI)



(XII)

The acetoxythallation and acetoxymercuration of bicyclo[3.2.1]octa-2,6-diene is a more clear-cut example of the regiospecific oxymetallation of bicyclic dienes. When XIII was treated with thallium(III) acetate in dichloromethane at room temperature for 0.5—1 h, the acetoxythallation adduct XIV

(Continued on p. 136)

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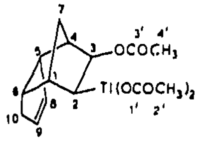
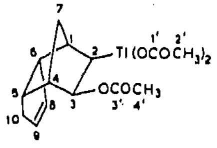
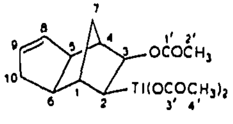
* The assignment of VII and VIII was based on comparison of the chemical shifts of each carbon, especially C(3) and C(10), with those of III and IV, while that of IX and X was based primarily on the presence or absence of ^{13}C—^{199}Hg couplings at C(8) signals (see Table 1).

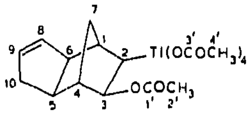
TABLE 1

^{13}C CHEMICAL SHIFTS [a] AND ^{13}C—$^{203,205}Tl$ AND ^{13}C—^{199}Hg COUPLING CONSTANTS [b] OF III ~ X [c]


(III)


(IV)


(V)

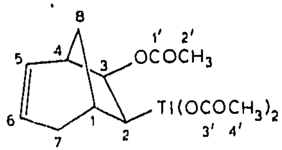

(VI)

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(1′)	C(2′)	C(3′)	C(4′)
III	45.0 (311)	70.6 (5812) [5759]	77.0 (681)	50.5 (83)	45.9 (25)	41.8 (1124)	37.8 (12)	131.6 (0)	131.0 (34)	32.2 (37)	169.0 (58)	22.0 (33)	179.1	22.6
IV	d	d	74.3 (681)	d	d	d	38.8 (12)	130.0 (37)	131.8 (43)	31.5 (0)	169.0 (58)	22.0 (33)	179.1	22.6
VII[III(Hg)]	44.6 (53)	49.1 (1732)	78.0 (141)	50.5 (15)	45.8 (0)	42.3 (212)	38.7	131.7 [e]	131.0 [e]	32.5	169.8 f	21.6 (19)	177.0	23.4
VIII[IV(Hg)]	43.2 f	53.2 (1720)	75.7 f	d	47.3 (0)	39.6 f	39.9	131.0 [e]	131.7 [e]	31.1	169.8 f	21.6 (19)	177.0	23.4
V	46.0 (304)	75.8 (5774)	78.3 (676)	50.0 (98)	47.0 (40)	44.1 (1275)	38.1 (30)	130.3 (<3)	132.8 (15)	29.2 (32)	169.3 (58)	20.6 (75)	179.1	22.5
VI	d	76.7 (5770)	78.0 (674)	d	d	d	d	130.6 (288)	133.4 (44)	29.9 (0)	169.3 (58)	20.6 (75)	179.1	22.5
IX[V(Hg)]	46.3 (48)	55.9 (1733)	80.0 (141)	50.3	38.7	44.7 (291)	38.9	130.5 (0)	132.5 (0)	29.9	170.0	21.2 (18)	177.0	23.4
X[VI(Hg)]	46.8 f	56.7 (1705)	79.4 (143)	49.2	38.9	44.0 d	38.2	131.2 (30)	132.8 (0)	29.9	170.0	21.2 (18)	177.0	23.4

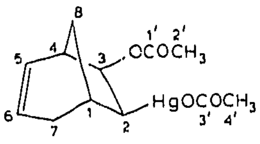
[a] Given in ppm downfield from internal Me_4Si. [b] $J(^{13}C$—$^{205}Tl)$ and $J(^{13}C$—$^{199}Hg)$ in parentheses (Hz); $J(^{13}C$—$^{203}Tl)$ in brackets (Hz). [c] Determined in $CDCl_3$ as solvent. [d] Not identified. [e] Maybe reversed. [f] Not observed.

TABLE 2

^{13}C CHEMICAL SHIFTS AND ^{13}C—$^{203,205}Tl$ AND ^{13}C—^{199}Hg COUPLING CONSTANTS OF XIV AND XV [a]



(XIV)



(XV)

Compound	Solvent	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(1′)	C(2′)	C(3′)	C(4′)
XIV	$CDCl_3$	38.9 (340)	76.1 (5846) [5790]	81.3 (657)	40.1 (185)	129.3 (27)	126.2 (66)	36.3 (1077)	31.2 (46)	169.3 (52)	21.2 (69)	179.0	22.6
XIV	DMSO-d_6	38.5 (356)	71.6 (6516) [6457]	80.3 (654)	38.8 (156)	129.0 (25)	126.5 (60)	36.0 (1027)	30.6 (51)	168.8 (47)	20.8 (59)	175.8	22.6
XIV	Py-d_5	40.0 (349)	70.7 (6467) [6406]	82.0 (635)	39.7 (161)	129.6 (25)	126.8 (59)	36.9 (979)	30.9 (58)	169.4 (46)	21.2 (56)	177.5	23.1
XV	$CDCl_3$	38.0 (41)	55.1 (1735)	83.2 (137)	41.0 (51)	129.4 (0)	126.1 (12)	36.8 (197)	31.8 (12)	169.9 (<3)	21.5 (16)	177.0	23.3

[a] See footnotes *a* and *b* in Table 1.

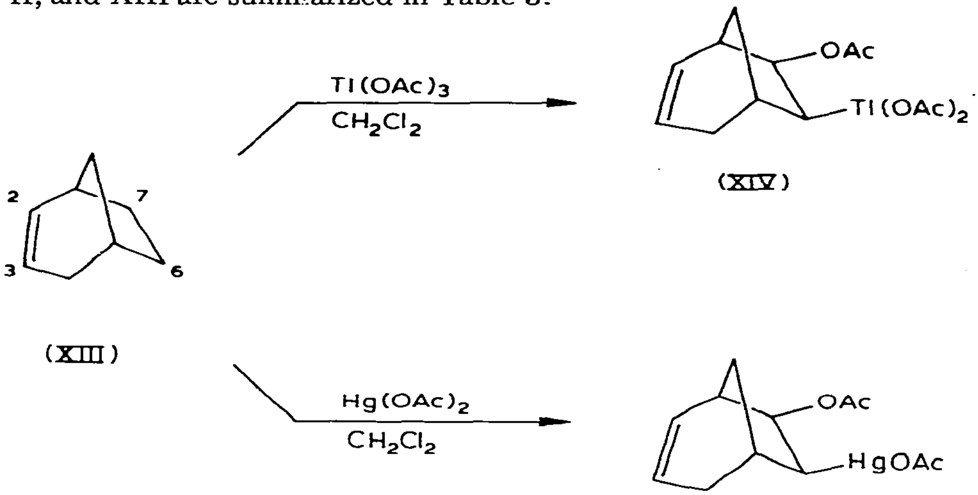
TABLE 3

ACETOXY-THALLATION AND -MERCURATION OF I, II, AND XIII

Olefin (mmol)	$M(OAc)_n$ (mmol)	Solvent (20 ml)	Reaction Temperature (°C)	Reaction time (h)	Products (isomer ratio [a])	Yield (%) [b]
I (20)	$Tl(OAc)_3$ (10)	MeOH	20	1	III + IV (III/IV 3/1)	94
II (10)	$Tl(OAc)_3$ (5)	MeOH	20	1	V + VI (V/VI 4/5)	80
I (20)	$Tl(OAc)_3$ (10)	$CHCl_3$	20	1	III + IV (III/IV 5/1)	88
II (10)	$Tl(OAc)_3$ (5)	CH_2Cl_2	20	1	V + VI (V/VI 4/5)	83
I (10)	$Hg(OAc)_2$ (5)	CH_2Cl_2	20	0.5	VII + VIII (VII/VIII 2/1)	72
II (10)	$Hg(OAc)_2$ (5)	CH_2Cl_2	20	0.2	IX + X (IX/X 2/3)	81
XIII (3)	$Tl(OAc)_3$ (3)	CH_2Cl_2	25	1	XIV	84
XIII (3)	$Hg(OAc)_2$ (3)	CH_2Cl_2	25	1	XV	83

[a] Determined approximately by ^{13}C NMR spectra of the crude products. [b] Isolated yield: based on metal acetate charged.

was obtained exclusively in over 80% yield. None of its regioisomers which might have been formed by attack of the thallium moiety on C(7) of XIII was detected in the crude product by ^1H and ^{13}C NMR spectroscopy (eq. 6). Similarly, acetoxymercuration of XIII in dichloromethane afforded XV in good yield (eq. 7). The formation of this product has already been reported by Sakai [8] in acetoxymercuration of XIII in acetic acid. The regioisomer of XV was also not detected in the crude product. Reaction conditions, yields and isomer ratios of the products of acetoxythallation and acetoxymercuration of I, II, and XIII are summarized in Table 3.



(XIV) (6)

(XIII)

(7)

(XV)

A preferential attack of an electrophile such as a thallium or mercury moiety on C(3) of I and C(6) of XIII means that the π-electron density at those carbons is higher than that at C(2) of I and C(7) of XIII, respectively. Such polarization of the double bond under the attack of an electrophile may be attributed to the through-space homoconjugation with the C(8)—C(9) double bond of I or the C(2)—C(3) double bond of XIII. The formation of nearly equal amounts of V and VI or IX and X from II may be attributed to the absence of such polarization, as expected from the structure of II.

Experimental

^{1}H NMR spectra ($CDCl_3$ solvent, TMS as internal standard) were recorded with a Varian EM-360 and a JEOL FX-100 spectrometer, and IR spectra (hexachlorobutadiene and paraffin mulls) with a Hitachi EPI-S2 spectrometer. ^{13}C NMR spectra (Table 1 and 2) were recorded in the pulsed Fourier transform mode on a JEOL PFT-100 and a JEOL FX-100 spectrometer operating at 25.15 MHz in $CDCl_3$, DMSO-d_6 or pyridine-d_5 [1,2]. GLC analyses were carried out on a Shimadzu 5APTF apparatus using EGSS-X (15%) on Chromosorb W (1 m) and PEG-6000 (25%) on Chromosorb W (3 m) columns (N_2 as carrier gas). II was prepared from commercial I by addition—elimination of hydrogen iodide [9]. XIII was prepared by the reaction of norbornadiene with dichlorocarbene [10] followed by reduction with lithium and t-butanol [11]. I and other organic and inorganic materials were commercial products and used without further purification.

Acetoxythallation of I

Treatment of I (2.68 g, 20 mmol) with thallium(III) acetate (3.82 g, 10 mmol) in methanol (20 ml) at 20°C for 1 h afforded a clear homogeneous solution. Evaporation of solvent left a white solid which was washed with n-hexane to leave 4.84 g (94% yield) of a white solid, a mixture of III and IV (m.p. 140—144°C). The ^{13}C NMR spectrum of the mixture showed that the isomer ratio of III/IV is about 3/1. Anal.: Found: C, 37.36; H, 3.98. $C_{16}H_{21}O_6Tl$ calcd.: C, 37.41; H, 4.12%. A similar reaction in chloroform gave a mixture of III and IV (4.55 g, 88% yield, III/IV 5~6/1) which was recrystallized from chloroform/n-hexane to afford almost pure III (2.7 g); m.p. 158—162°C. ^{1}H NMR of III; δ(ppm) 2.60 (J(Tl—H) 548 Hz, H(1)), 2.60 (J(Tl—H) 308 Hz, H(4)), 2.70 (J(Tl—H) 740 Hz, H(6)), 3.67 (J(Tl—H) 876 Hz, H(2)), 4.84 (J(Tl—H) 536 Hz, H(3)). IR 1740 (ν(C=O)), 1605 ($\nu_{as}(CO_2)$), 1525 ($\nu_{as}(CO_2)$), 1420 ($\nu_s(CO_2)$), 1370 ($\nu_s(CO_2)$) cm^{-1}.

Alkaline sodium borohydride (2 mmol) reduction of a mixture of III and IV (2 mmol) in methanol (20 ml, 1 *N* NaOH) at 20°C for 0.5 h gave I (72%) and alcohols (7%; XI + XII). GLC analyses on several different columns could not resolve the two alcohols. Their GLC retention time was the same as that of the same alcohols prepared almost quantitatively by alkaline sodium borohydride reduction of a mixture of VII and VIII in methanol.

Acetoxythallation of II

By a similar procedure as above, using thallium(III) acetate (1.91 g, 5 mmol), II (1.32 g, 10 mmol), and methanol (20 ml), a white solid, a mixture of V and VI, was obtained (2.05 g (80% yield); m.p. 139—142°C (dec.)). Anal.: Found: C, 37.32; H, 4.09%. From the ^{1}H NMR spectrum of the mixture, which did not distinguish between V and VI, the following four protons were assigned: δ(ppm) 2.37 (J(Tl—H) 240 Hz, H(4)), 2.67 (J(Tl—H) 644 Hz, H(1), 3.70 (J(Tl—H) 768 Hz, H(2)), 4.97 (J(Tl—H) 616 Hz, H(3)). The main absorptions in the IR spectrum were essentially the same as those of III. The ^{13}C NMR spectrum revealed that the ratio of V/VI is about 4/5. The reaction also proceeded in chloroform or dichloromethane, the isomer ratio of the products being almost the same as that obtained in methanol.

Acetoxymercuration of I and II

To a suspension of mercury(II) acetate (1.59 g, 5 mmol) in dichloromethane (20 ml) was added I (1.32 g, 10 mmol) at 20°C and the resulting suspension was stirred for 0.5 h to give a clear homogeneous solution. n-Hexane (500 ml) then was added and the solution was allowed to stand overnight at 0—10°C to give 1.61 g (3.60 mmol, 72% yield) of a white solid, a mixture of VII and VIII; m.p. 136—138°C. Anal.: Found: C, 37.06; H, 3.97. $C_{14}H_{18}O_4Hg$ calcd.: C, 37.24; H, 4.02%. The ^{13}C NMR spectrum revealed that the ratio of VII/VIII is about 2/1.

A similar reaction of II on the same scale at 20°C for 0.2 h afforded 1.82 g (4.04 mmol, 81% yield) of a white solid, a mixture of IX and X; m.p. 111—114°C. Anal.: Found: C, 37.04; H, 3.95%. The ratio of IX/X was about 2/3 by ^{13}C NMR analysis. The strong absorptions in the IR spectra of these acetoxymercuration adducts were essentially the same as those of the acetoxythallation adducts.

Acetoxythallation and acetoxymercuration of XIII in dichloromethane

A mixture of XIII (0.32 g, 3 mmol) and thallium(III) acetate (1.15 g, 3 mmol) in dichloromethane (20 ml) was stirred at 25°C for 1 h to give a white solid. To this reaction mixture dichloromethane (100 ml) was added to dissolve the solid. After filtration of a small amount of insoluble solid, dichloromethane was evaporated from the filtrate to leave an oil to which was added n-hexane to afford almost pure solid XIV; 1.23 g (2.52 mmol, 84%): m.p. 177—179°C (dec.). Anal.: Found: C, 34.31; H, 3.84. $C_{14}H_{19}O_6Tl$ calcd.: C, 34.48; H, 3.93%. No appreciable amounts of organic products, except a small amount of XIII, were detected in the n-hexane washings (by GLC). ^{1}H NMR of XIV; δ(ppm) 1.08—1.50 and 1.70—2.00 (H(8)), 2.01 (acetate), 2.04 (acetoxy), 2.38 (*endo*-H(7)), 2.43 (J(Tl—H) 424 Hz, H(1)), 2.66 (J(Tl—H) 284 Hz, H(4)), 3.01 (J(Tl—H) 1176 Hz, *exo*-H(7)), 3.78 (J(Tl—H) 948 Hz, H(2)), 5.28 (J(Tl—H) 464 Hz, H(3)), 5.53 (J(Tl—H) 56 Hz, H(6)), 5.76 (H(5)) (by JEOL FX-100, 100 MHz). IR 1740 (ν(C=O)), 1630 (ν(C=C)), 1610 ($\nu_{as}(CO_2)$), 1520 (ν_{as}-(CO_2)), 1420 ($\nu_s(CO_2)$), 1375 ($\nu_s(CO_2)$) cm^{-1}.

Similar treatment of XIII with mercury(II) acetate (3 mmol each) afforded XV, a white solid; 1.07 g (2.51 mmol, 83%): m.p. 123—124°C (lit. [8], m.p. 124—126°C). Anal.: Found: C, 33.95; H, 3.74. $C_{12}H_{16}O_4Hg$ calcd.: C, 33.93; H, 3.80%. ^{1}H NMR of XV; δ(ppm) 1.4—1.7 (m, H(8)), 2.0 and 2.1 (acetate and acetoxy), 2.1—2.4 (m, 1 H), 2.4—2.7 (m, 2 H), 2.7—2.9 (m, 1 H), 2.9—3.1 (m, 1 H), 4.7—6.0 (m, H(5) and H(6)), 5.15 (J(H—H) 7 Hz, H(3)). The IR spectrum of this compound was slightly different from that of XIV; 1740 (sh), 1710 (ν(C=O)), 1630 (ν(C=C)), 1600 (sh), 1575 ($\nu_{as}(CO_2)$), 1425 ($\nu_s(CO_2)$), 1370 ($\nu_s(CO_2)$) cm^{-1}. All spectra and the m.p. of authentic XV, which was prepared in acetic acid [8], were the same as those of XV obtained here.

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