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OXYTHALLATION OF NORBORNENE DERIVATIVES WITH THALLIUM(III) ACETATE IN METHANOL

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Summary

Treatment of norbornene, norbornadiene, benzonorbornadiene, and chloro- and methoxy-benzonorbornadiene with thallium(III) acetate in methanol affords only the corresponding *cis-exo*-acetoxythallation adducts in a sharp contrast to oxymercuration of such strained olefins where methoxymercuration prevails. In the cases of substituted benzonorbornadienes the products are obtained as the regioisomeric mixtures, the isomer ratio being determined by ^{13}C NMR. In the cases of 5-norbornene-2,3-dicarboxylic anhydride, 5-norbornene-2-methyl-2,3-dicarboxylic anhydride, and 5-norbornene-2-*endo*-carboxylic acid, lactonization occurs to give a *trans*-oxythallation adduct having a lactone ring, no introduction of either methoxy or acetoxy groups being observed. ^{1}H and/or ^{13}C NMR data for several new oxythallation adducts are provided. The alkaline sodium borohydride reduction of adducts in methanol affords mainly the parent olefin together with 10—16% yields of the corresponding *exo*-alcohol.

Introduction

Oxymercuration of norbornene and related olefins has been well studied [1]. Except for the cases of 5-*endo*-substituted norbornenes with which *trans*-oxymercuration occurs through neighboring group participation [2], the addition usually is completely *cis-exo* and its high selectivity has been explained by factors such as bond strain or steric hindrance [3]. On the other hand, oxythallation of similar olefins has been studied less [4—7] and there are no reports of this reaction in alcohol medium. In our studies of oxythallation of olefins in alcohols [8], we have carried out reactions of norbornene and related olefins with thallium(III) acetate in methanol. Unexpectedly, no methoxythallation occurred and

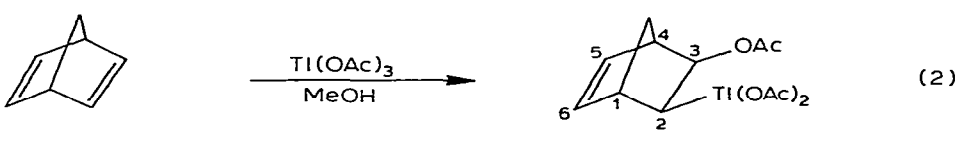
only *cis-exo*-acetoxythallation adducts were isolated in high yield. This result is in sharp contrast to the oxymercuration of norbornenes and some other strained olefins where alkoxymercuration prevails [1,3a,9]. On the other hand, from 5- and/or 6-*endo* substituted norbornenes, various *trans*-oxythallation adducts having a lactone ring [7] were isolated in high yield without introduction of acetoxy or alkoxy groups as in the case of oxymercuration [2]. This paper describes the details of these results together with the elucidation of the composition of regioisomeric mixtures of the adducts from substituted benzonorbornadienes by ^{13}C NMR spectroscopy.

Results and discussion

Treatment of 2-norbornene (I), 2,5-norbornadiene (III), and benzonorbornadiene (V) with thallium(III) acetate in methanol at room temperature (ca. 15—20°C) for 0.5—1 h afforded the corresponding acetoxythallation adducts (II, IV, and VI, respectively) in 55—80% yield (eq. 1—3). The methoxythallation adduct was not detected, even in the crude product, by the NMR analysis. The structure of each compound was confirmed by comparison of ^{1}H and ^{13}C

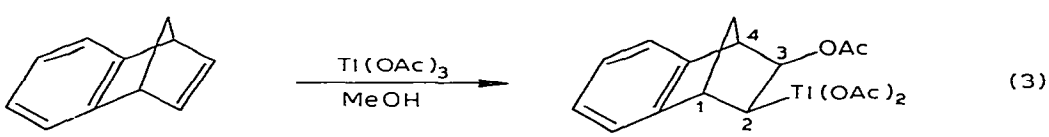
(1)

(I) (II)



(2)

(III) (IV)



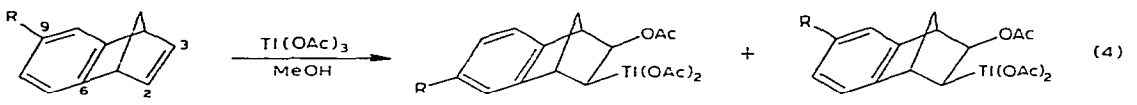
(3)

(V) (VI)

NMR and IR spectra and melting point with those of authentic samples prepared in chloroform or dichloromethane by reported methods [4,6]. Similar reaction of 9-methoxybenzonorbornadiene (VII) gave VIII almost exclusively *, while the 9-chloro analogue (IX) afforded a regioisomeric mixture of X and XI

* The ^{13}C NMR spectra of the crude products revealed the presence of a small amount of unidentified compound other than VIII. Even if this compound is a regioisomer of VIII, its yield is at most 10% that of VIII.

(X/XI 20/80) (eq. 4), no methoxythallation adducts being formed in both cases. The yields are rather poor, compared with that of VI, because of slow reaction of IX and a facile decomposition of VIII under the reaction conditions.



(4)

(VII, R = MeO)
(IX, R = Cl)

(VIII, R = MeO)
(X, R = Cl)

(XI, R = Cl)

VIII, X, and XI are new compounds and their structural elucidation and the determination of the isomer ratio were carried out by ^{13}C NMR using a di-t-butyl nitroxide (DTBN) radical as a nuclear spin decoupling reagent [10]. By this method location of the chemical shift of each carbon signal was made possible, and eventually each ^{13}C—Tl coupling constant was readily identified (Table 1). The assignments of benzene peripheral carbon signals for VI, VIII, X, and XI were performed in such a way that the ring ^{13}C chemical shifts predicted with the aid of well-established substituent effects of methoxy and chloro groups [11] become self-consistent with the observed shifts for these compounds: the C(6) signals can be readily assigned with recourse to its large ^{13}C—Tl coupling constants and the location of the methoxy and chloro group on the benzene ring was then determined by the use of the substituent effect on the *meta* and *para* carbon with respect to the C(6) carbon *. The isomer ratio between X and XI was determined by comparison of the peak heights of the C(2) signals. The fact that VIII and XI were formed from VII and IX almost exclusively or preferentially, respectively, demonstrates the preferred attack by positive thallium moiety on C(3) of VII and on C(2) of IX. This result is in accord with the known preferential electrophilic (H^+ and Al^+) attack at C(3) and C(2) in the cases of VII and 9-fluorobenzonorbornadiene, respectively [12,13]. The higher electron density on C(3) (than C(2)) in VI and on C(2) (than C(3)) in IX can be explained by considering the polarization in C(2)—C(3) double bond induced by the homoallylic interaction between C(6) and C(2) [14] **.

The reactions of 5-norbornene-2,3-dicarboxylic anhydride (XII), 2-methyl-5-norbornene-2,3-dicarboxylic anhydride (XIV), or 5-norbornene-2-*endo*-carboxylic acid (XVI) with thallium(III) acetate in methanol resulted in lactonization to afford the *trans*-oxythallation adduct having a lactone ring (XIII, XV, XVII) in 90—95% yield, no methoxythallation adducts being formed (eq. 5 and 6). In dichloromethane or chloroform XII or XIV did not react at all, while XVI gave the same product in either methanol, dichloromethane, or chloroform. The formation of XVII from XVI in acetic acid has already been clarified by McKillop et al. [7]. Similar treatment of 2-norbornene-5-carbomethoxy-6-carboxylic acid (XVIII) and its methyl analogue (XIX) afforded XIII and XV, respectively, in either methanol or dichloromethane (eq. 5), while the methyl

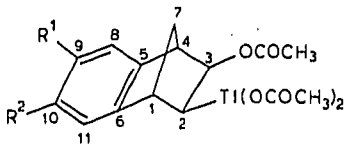
(continued on p. 14)

* The detailed study of the ^{13}C NMR spectral assignments of organothallium compounds examined here will appear in a separate paper.

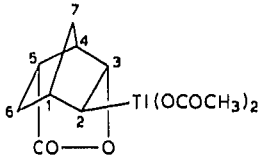
** In fact, calculation by the CNDO MO method (by Dr. H. Fujimoto) showed the difference of π-electron density on C(2) and C(3) to be consistent with the experimental results.

TABLE 1

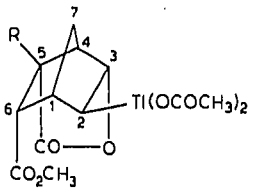
^{13}C CHEMICAL SHIFTS [a] AND ^{13}C—$^{203,205}Tl$ COUPLING CONSTANTS [b] OF OXYTHALLATION ADDUCTS



(VI, VIII, X, XI)



(XVII)



(XIII, XV)

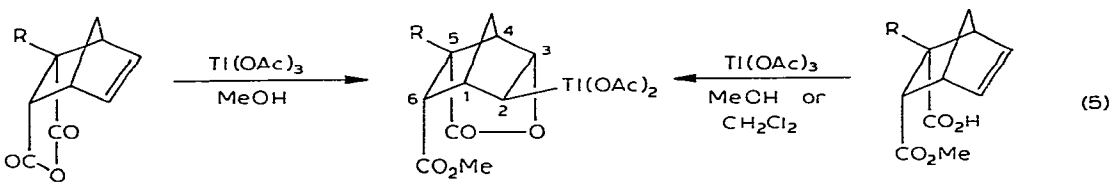
Compound	Solvent	1	2	3	4	5	6	7	8	9
VI (R^1 = H, R^2 = H)	$CDCl_3$	47.3 (244)	73.9 (5645) [5593]	76.3 (569)	50.0 (45)	142.9 (11)	147.2 (1149)	47.5 (7)	121.3 (86)	127.3 (18)
VIII (R^1 = H, R^2 = OMe)	$CDCl_3$	47.6 (232)	73.1 (5945) [5889]	76.7 (569)	49.2 (54)	135.0 (<3)	149.3 (1154)	47.2 (<3)	123.7 (61)	111.2 (81)
X (R^1 = H, R^2 = Cl)	$CDCl_3$	47.0 (242)	73.0 (5789)	76.0 (566)	50.0 (46)	n.i. [c]	n.i. [c]	47.5 (10)	122.4 (90)	127.2 (17)
XI (R^1 = Cl, R^2 = H)	$CDCl_3$	47.3 (230)	73.0 (5847) [5776]	76.0 (566)	49.5 (49)	141.4 (10)	149.3 (1157)	47.5 (10)	121.9 (85)	132.0 (0)
XVII	DMSO-d_6	43.7 (218)	67.6 (6631) [6567]	85.4 (64)	39.4 (78)	47.5 (71)	37.4 (1282)	39.0 (127)		
XIII	DMSO-d_6	45.5 [d] (153)	62.5 (6838) [6775]	85.5 (90)	45.9 [e] (108)	49.4 (73)	51.2 (1111)	38.8 (149)		
XV	DMSO-d_6	46.1 (161)	62.0 (6816) [6753]	83.5 (64)	54.3 (71)	47.4 (71)	58.7 (1111)	37.8 (169)		

TABLE 1 (continued)

Compound	Solvent	10	11	10-CH_3O	3-$\overset{\star}{C}H_3CO_2$	3-$CH_3\overset{\star}{C}O_2$	$Tl(O\overset{\star}{C}OCH_3)_2$	$Tl(OCO\overset{\star}{C}H_3)_2$
VI (R^1 = H, R^2 = H)	$CDCl_3$	127.0 (77)	123.2 (65)		21.4 (68)	169.7 (51)	179.1	22.8
VIII (R^1 = H, R^2 = OMe)	$CDCl_3$	159.0 (7)	108.2 (81)	55.5 (0)	21.3 (56)	169.7 (46)	178.7	23.8
X (R^1 = H, R^2 = Cl)	$CDCl_3$	n.i. [c]	123.8 (63)		21.2 (59)	169.6 (47)	179.1	22.7
XI (R^1 = Cl, R^2 = H)	$CDCl_3$	126.9 (73)	124.3 (56)		21.2 (59)	169.6 (47)	179.1	22.7
			5-CH_3	6-$\overset{\star}{C}O_2CH_3$	6-$CO_2\overset{\star}{C}H_3$	5-CO		
XVII	DMSO-d_6					180.7 (0)	177.5	23.0
XIII	DMSO-d_6			172.0 (68)	52.0 (0)	178.3 (0)	177.6	22.9
XV	DMSO-d_6		20.6 (22)	172.0 (71)	51.9 (0)	179.7 (0)	179.7	23.0

[a] Given in ppm downfield from internal Me_4Si. [b] $J(^{13}C-^{205}Tl)$ is shown in parentheses (Hz); $J(^{13}C-^{203}Tl)$ is shown in brackets (Hz). [c] Not identified. [d] Might be 45.2(142). [e] Might be 46.2(119).

ester of XVI did not react at all in either solvent. These results show that neighboring group participation did not occur with the carboxymethoxy group in this oxythallation reaction. This is consistent with the fact that only XIII (or XV) was formed from XVIII (or XIX) in either solvent. Since it was confirmed sepa-

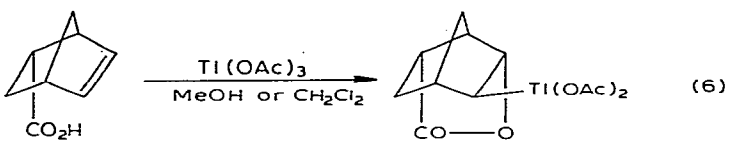


(5)

(XII, R = H)
(XIV, R = Me)

(XIII, R = H)
(XV, R = Me)

(XVIII, R = H)
(XIX, R = Me)



(6)

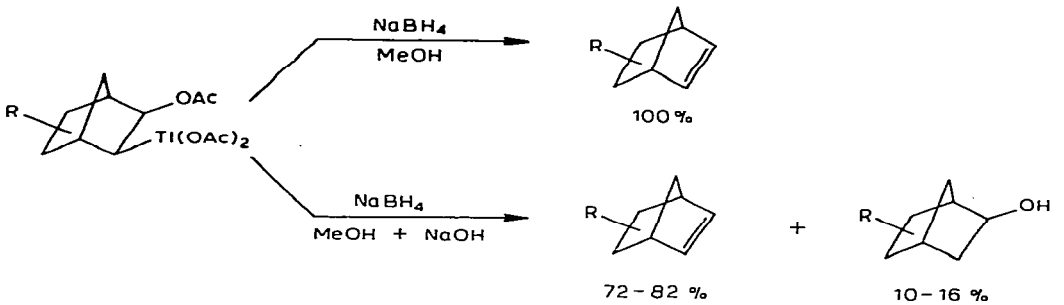
(XVI)

(XVII)

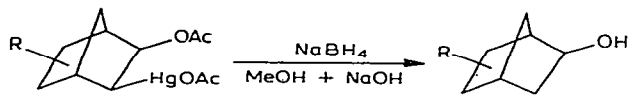
rately that the anhydride (XII, XIV or maleic anhydride) can be solvolyzed by methanol to the corresponding half methyl ester, slowly in the absence of thallium(III) acetate, or rapidly in its presence, it is reasonable to assume that the reaction of XII or XIV giving XIII or XV proceeds through XVIII or XIX, respectively.

Sodium borohydride reduction of II and IV has been reported to give only the parent olefins almost quantitatively. It has been known, however, that alkaline sodium borohydride reduction of the alkoxythallates of styrene and α-methylstyrene gave the corresponding alkyl ethers together with the parent olefins and dialkylthallium(III) compounds [15]. We have carried out sodium borohydride reductions of all oxythallation adducts obtained here in methanol under neutral and alkaline conditions. In neutral conditions all adducts afforded the parent olefins almost quantitatively, XVIII or XIX being formed in the case of XIII or XV. Under alkaline conditions, however, 10—16% yields of the corresponding alcohol were produced together with 72—82% yields of the parent olefin, except from XIII or XV, which afforded only XVIII or XIX even under alkaline conditions (eq. 7). The respective alcohol was prepared by alkaline sodium borohydride reduction of the corresponding acetoxymercuration adducts and used as authentic samples for GLC and NMR analysis (eq. 8). No appreciable formation of dialkylthallium(III) compounds was observed, in contrast to the case of alkoxythallates of styrene, probably because of the large steric hindrance in alkyl group. It should be noted here that the reduction of IV under alkaline conditions afforded two alcohols (XX and XXI) in 13% yield (eq. 9), the ratio of these being almost the same as that obtained from the corresponding oxymercuration adduct (XX/XXI 4/6) [16]. Since it has been shown that alkaline sodium borohydride reduction of oxymercuration adducts of olefins proceeds through an alkyl radical by a homolytic dissociation of the intermediate organo-

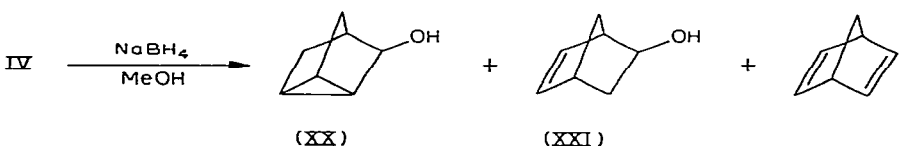
mercuric hydride [16], the results suggest that the same alkyl radical may be involved in the reduction of IV *.



(7)

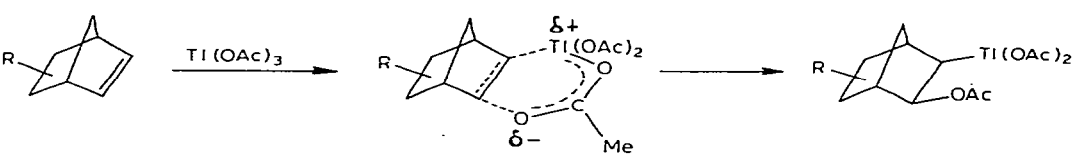


(8)



(9)

In order to explain the observed exclusive acetoxythallation of these olefins even in the presence of methanol, a concerted or near-concerted addition of thallium(III) acetate to norbornene through a cyclic intermediate as shown in eq. 10 may be most plausible. One explanation for the reactivity difference be-



(10)

tween mercury(II) acetate and thallium(III) acetate may be that the mercury(II) salt ionizes more readily than the thallium(III) species in methanol. Thus, oxymercuration is generally much faster than oxythallation of olefins in aqueous or alcoholic solvent [18]. Another explanation may be that if the reaction proceeds through a mercurinium ion intermediate and its thallium analogue, the attack of solvent alcohol from the frontside (giving *cis-exo* product) may be prevented in the thallium case by the presence of two large acetate groups on thallium.

Experimental

^{1}H NMR spectra were recorded with a Varian EM-360 and a JEOL MH-100 spectrometer, and IR spectra (hexachlorobutadiene and paraffin mulls) with a

* Involvement of alkyl radicals in the reduction of alkylthallium(III) compounds with several reducing agents has been observed recently [17].

Hitachi EPI-S2 spectrometer. ^{13}C NMR spectra were recorded in the pulse Fourier transform mode on a JEOL PFT-100 spectrometer operating at 25.15 MHz in $CDCl_3$ or DMSO-d_6 [10]. GLC analyses were carried out using 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). V was prepared from anthranilic acid, isoamyl nitrite, and 1,3-cyclopentadiene [19]. VII and IX were prepared from 3-bromo-4-iodoanisole and 3-bromo-4-fluorochlorobenzene, magnesium, and 1,3-cyclopentadiene, respectively [20]. XIV was prepared from methyl maleic anhydride and 1,3-cyclopentadiene [21]. XVIII and XIX were obtained by heating XII and XIV in methanol at refluxing temperature for 5 h, respectively [21]. XVI or its methyl ester was prepared from acrylic acid or methyl acrylate and 1,3-cyclopentadiene [22]. I, III, XII, and other organic and inorganic materials were commercial products and used without further purification.

Acetoxythallation of I in methanol

To a suspension of thallium(III) acetate (3.82 g, 10 mmol) and methanol (20 ml) was slowly added I (1.88 g, 20 mmol) at 20—25°C, and the resulting clear solution was stirred for 0.5 h. Evaporation of methanol left white solids. These were dissolved in chloroform and the insoluble part was filtered [unreacted $Tl(OAc)_3$, 0.54 g, 1.4 mmol]. Evaporation of chloroform from the filtrate left a white solid, II, which was purified by several washings with n-hexane and diethyl ether [3.62 g, 88% yield based on the reacted $Tl(OAc)_3$, m.p. 150—151°C (dec.) (lit. [4], m.p. 150—151°C (dec.)]. ^1H NMR ($CDCl_3$) and IR spectra were identical with those of an authentic sample prepared separately in chloroform [4,23] or dichloromethane. The ^{13}C NMR spectrum was also consistent with the structure [10].

No methoxy product was present even in the crude products of any oxythallation adducts described in this report (by ^1H NMR).

Acetoxythallation of III in methanol

By a similar procedure as above, using thallium(III) acetate (3.82 g, 10 mmol), III (1.84 g, 20 mmol), and methanol (20 ml) (reaction time, 0.5 h), 3.54 g (75% yield) of pure IV was obtained. Almost no unreacted $Tl(OAc)_3$ was left in this case. IV was apt to decompose slowly on several washings with diethyl ether and n-hexane. M.p. 119—121°C (dec.) (lit. [4], m.p. 116—119°C (dec.)). ^1H NMR ($CDCl_3$) and IR spectra were identical with those of an authentic sample prepared separately in chloroform [4,23] or dichloromethane; δ (ppm) 3.13 (J(Tl—H) 112 Hz, H(4)), 3.50 (J(Tl—H) 420 Hz, H(1)), 3.50 (J(Tl—H) 604 Hz, H(2)), 5,23 (J(Tl—H) 548 Hz, H(3)), 6.20 (J(Tl—H) 96 Hz, H(6)), 6.37 (J(Tl—H) 76 Hz, H(5)). The ^{13}C NMR spectrum was also consistent with the structure of IV [10].

Acetoxythallation of V in methanol

By a similar procedure as above using thallium(III) acetate (1.91 g, 5 mmol), V (1.42 g, 10 mmol), and methanol (20 ml) at 20°C for 1 h, 1.5 g [77% yield based on the reacted $Tl(OAc)_3$] of VI and 0.14 g of oxidation products of nearly two components were obtained, leaving 0.50 g (1.3 mmol) of $Tl(OAc)_3$

and 0.68 g (4.8 mmol) of V unreacted. M.p. of VI, 113—114°C (lit. [6], m.p. 130—133°C). ^{1}H NMR ($CDCl_3$) and IR spectra and melting point were identical with those of the compound prepared in dichloromethane [6], but melting point and the assignment of ^{1}H NMR spectra were not consistent with those reported [6]. Anal.: Found: C, 39.02; H, 3.63. $C_{17}H_{19}O_6Tl$ calcd.: C, 38.99; H, 3.66%. δ (ppm) 3.65 (J(Tl—H) 170 Hz, H(4)), 3.70 (J(Tl—H) 658 Hz, 658 Hz, H(2)), 3.98 (J(Tl—H) 486 Hz, H(1)), 5.17 (J(Tl—H) 580 Hz, H(3)), ^{13}C NMR spectral data which support the structure of VI are shown in Table 1 (see also ref. 10).

Acetoxythallation of VII and IX in methanol

After treating VII (0.67 g, 3.9 mmol) with thallium(III) acetate (0.58 g, 1.5 mmol) in methanol (20 ml) at 20°C for 1 h, methanol was evaporated and the residual white solid was washed with n-hexane to remove several oxidation products (alkyl acetates; by ^{1}H NMR) and unreacted VII. The insoluble part was then extracted with chloroform (ca. 20 ml) to leave a small amount of $Tl(OAc)_3$. Chloroform was evaporated from the extracts to afford 0.24 g [0.43 mmol, 28% yield based on $Tl(OAc)_3$ charged] of VIII; m.p. 123—124°C. The ^{13}C NMR spectrum revealed the presence of a small amount of unidentified compound in VIII (at the most 10% of VIII), probably the regioisomer of VIII; a signal at δ 72.4 ppm (J(^{13}C—^{205}Tl) 6001 Hz) may be assigned to C(2) of the minor component. Anal.: Found: C, 38.88; H, 3.80. $C_{18}H_{21}O_7Tl$ calcd.: C, 39.04; H, 3.82%. The ^{13}C NMR spectral data of VIII are shown in Table 1.

Similar treatment of IX (0.77 g, 4.4 mmol) with thallium(III) acetate (1.54 g, 4 mmol) in methanol (20 ml) afforded 0.91 g (1.63 mmol, 41%) of a mixture of X and XI; m.p. 118—120°C. No oxidation products were obtained in this case. Anal.: Found: C, 36.35; H, 3.27. $C_{17}H_{18}ClO_6Tl$ calcd.: C, 36.58; H, 3.25%. ^{13}C NMR spectrum of this mixture revealed that the isomer ratio of X/XI is about 1/4 (by comparison of the peak heights of C(2) signals). The data are shown in Table 1.

Oxythallation of XII and XIV in methanol

A mixture of thallium(III) acetate (3.82 g, 10 mmol) and XII (1.64 g, 10 mmol) in methanol (20 ml) was stirred at 20°C for 1 h. The precipitated white solid was filtered. It was found to be almost pure XIII [4.15 g, 80% yield, m.p. 155—160°C (dec.)]. ^{1}H NMR (DMSO-d_6), δ (ppm) 2.98 (J(Tl—H) 488 Hz, H(2)), 3.30 (J(Tl—H) 1000 Hz, *exo*-H(6)), 3.30 (J(Tl—H) 488 Hz, H(1), 5.32(J(Tl—H) 1176 Hz, H(3)), 3.60 (CO_2Me), 1.87[$Tl(OAc)_2$. IR 1780 (ν(C=O)), 1725 (ν(C=O)), 1600 ($\nu_{as}CO_2$), 1505 ($\nu_{as}(CO_2)$), 1410 ($\nu_s(CO_2)$), 1365 ($\nu_s(CO_2)$) cm^{-1}. Anal.: Found: C, 32.17; H, 3.55. $C_{14}H_{17}O_8Tl$ calcd.: C, 32.48; H, 3.31%.

A similar reaction of XIV afforded a 90% yield of XV; m.p. 154—156°C (dec.). Anal.: Found: C, 34.13; H, 3.30. $C_{15}H_{19}O_8Tl$ calcd.: C, 33.89; H, 3.60%. ^{1}H NMR (DMSO-d_6), δ (ppm) 2.88 (J(Tl—H) 4.72 Hz, H(2)), 2.92 (J(Tl—H) 480 Hz, H(1)), 3.21 (J(Tl—H) 46 Hz, H(4)), 3.34 (J(Tl—H) 980 Hz, *exo*-H(6)), 5.28 (J(Tl—H) 1152 Hz, H(3)), 1.17 (5-Me), 1.85 [$Tl(OAc)_2$], 3.60 (CO_2Me).

Both XIII and XV are soluble in pyridine and DMSO, and slightly soluble in alcohols, chloroform, and dichloromethane.

When both reactions were carried out in dichloromethane or chloroform, the reactants were recovered almost quantitatively.

^{13}C NMR spectra, the data of which are shown in Table 1, also supported each structure.

Oxythallation of XVI in dichloromethane

To a suspension of thallium(III) acetate (1.91 g, 5 mmol) in dichloromethane (20 ml) was added XVI (1.38 g, 10 mmol; contaminated by 35% of *exo*-isomer) at 20°C and the resulting mixture was stirred for 0.5 h. The precipitated XVII was collected by filtration and washed with n-hexane [1.48 g, 64% yield, m.p. 148—150°C (dec.); lit. [7], m.p. 144°C (dec.)]. The ^{13}C NMR spectrum of this compound was the same as that reported [24], while the ^{1}H NMR spectrum (DMSO-d_6) was assigned differently from that reported [7]: δ (ppm) 2.12 (J(Tl—H) 744 Hz, H(6)), 2.65 (J(Tl—H) 954 Hz, H(2)), 2.81 (J(Tl—H) 510 Hz, H(1)), 5.28 (J(Tl—H) 1148 Hz, H(3)). Similar reaction also occurred in methanol or chloroform as solvent. The methyl ester of XVI did not react at all in methanol or dichloromethane at 20—25°C for 2 h.

Reduction of acetoxythallation adducts

Two mmol each of II, IV, and VI was treated with 1 mmol of $NaBH_4$ in methanol (20 ml) at 0°C for 1 h. GLC analysis revealed the presence of almost quantitative yields of each parent olefin. When the reaction was carried out in methanol (20 ml) containing NaOH (0.8 g) (1 *N* solution), both the parent olefin and the corresponding alcohol, as shown in eq. 7 and 9, were obtained (by GLC analysis); I (75%) and *exo*-2-norborneol (16%) from II, III (74%) and two isomeric alcohols (XX and XXI, 13%, 4/6) from IV, V (82%) and *exo*-2-benzonorborneol (10%) from VI. Each alcohol was prepared separately by alkaline $NaBH_4$ reduction of the corresponding mercury compounds in methanol (eq. 8) [15,25]. Reduction of XIII afforded XVIII almost quantitatively under both neutral and alkaline conditions.

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