and acetone, 0.55 mol in 400 ml of ether, was added dropwise. The reaction was quenched using saturated aqueous NH_4Cl solution and filtered. After removal of the ether, distillation of the product mixture gave 4-hydroxy-3,3,4-trimethyl-1-pentene: 40% yield; bp 53-54° (10 mm); nmr (CCl_4) δ 0.92 [s, 6 H, $C(CH_3)_2$], 1.02 [s, 6 H, $C(CH_3)_2$], 4.9-6.1 (m, 3 H, $CH{=}CH_2$). The aldol condensation of acetone accounted for the major by-product, diacetone alcohol.

Synthesis of 4-Chloro-3,3,4-trimethyl-1-pentene. To 4-hydroxy-3,3,4-trimethyl-1-pentene (25 g) was added 200 ml of concentrated HCl at 0°. The mixture was stirred for 30 min and the organic layer was removed and neutratized with K_2CO_3. The product, 4-chloro-3,3,4-trimethyl-1-pentene, which previously has not been reported in the literature, was distilled: 100% yield; bp 55° (20 mm); mp 22-26°; nmr (CCl_4) δ 1.10 [s, 6 H, $C(CH_3)_2$], 1.48 [s, 6 H, $C(CH_3)_2$], 4.82-6.30 (m, 3 H, $CH{=}CH_2$).

Reaction of 4-Chloro-3,3,4-trimethyl-1-pentene with Trimethylaluminum. To a stirred solution of $AlMe_3$ (0.115 mol) in 200 mol of CH_2Cl_2 at 25° was added 4-chloro-3,3,4-trimethyl-1-pentene (0.10 mol) in 200 ml of CH_2Cl_2. After 30 min, the reaction was quenched by slowly adding 50 ml of methanol and extracted with saturated aqueous potassium sodium tartrate solution. Removal of the CH_2Cl_2 yielded an organic phase containing two products which were separated by distillation. The lower boiling component was identified[5] as 2,2,3-trimethyl-3-hexene: 69% yield; bp 56° (55 mm); mol wt 125.0 (calcd for C_9H_{18}, 126.2); nmr (CCl_4) δ 1.01 [s, 9 H, $C(CH_3)_3$], 0.98 (t, 3 H, CCH_3), 1.55 (m, 3 H, CCH_3), 1.98 (m, 2 H, CH_2-), 5.18 (t, 1 H, -$CH{=}$). The second component (31% yield) had bp 106° (3 mm), mol wt 238.0 (calcd for $C_{17}H_{32}$, 236.6). *Anal.* Calcd for $C_{17}H_{32}$: C, 86.5; H, 13.5. Found: C, 86.47; H, 13.50.

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Registry No.—Trimethylaluminum, 75-24-1; 4-hydroxy-3,3,4-trimethyl-1-pentene, 36934-19-7; γ,γ-dimethylallyl chloride, 503-60-6; acetone, 67-64-1; 4-chloro-3,3,4-trimethyl-1-pentene, 51751-72-5; 2,2,3-trimethyl-3-hexene, 51751-73-6.

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A Comment on the Acetoxythallation-Induced Lactonization of 2-*endo*-Norbornenecarboxylic Acids

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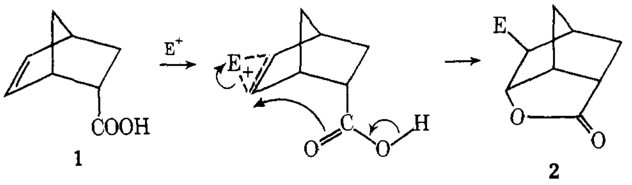
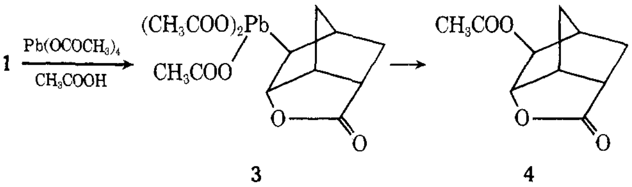
Electrophile-induced lactonization of 5-norbornene-2-*endo*-carboxylic acid (1) and related substrates is well known (Scheme I), and stable lactones 2 have been obtained when E is hydrogen,[1] halogen,[2] or acetoxymercury(II).[3] Neighboring-group participation has also been invoked to account for the formation of 4 when 1 is oxidized with lead(IV) acetate (Scheme II).[4,5] In this case, electrophile-induced lactonization presumably gives the oxymetalation adduct 3 as an unstable intermediate, and rapid conversion of 3 into 4 is fully consistent with the known lability of carbon-lead bonds in alkyllead(IV) triacetates.[6]

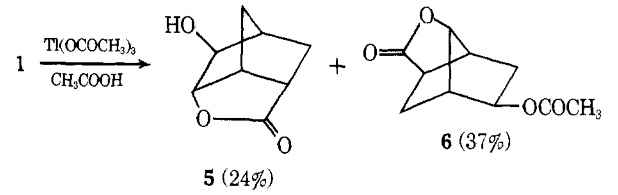
Scheme I



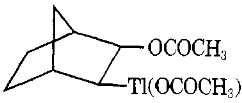
Scheme II



Scheme III



Oxidation of 1 with thallium(III) acetate has recently been reported by Moriarty and Gopal to give a mixture of 5 and 6 (Scheme III), formation of which was explained on the basis of the sequence (i) neighboring-group participation during acetoxythallation; (ii) generation of a norbornylthallium(III) diacetate; and (iii) facile heterolysis of this latter species to give the corresponding carbonium ion from which 5 and 6 are ultimately derived.[7] In principle this explanation is quite reasonable. Most oxythallation adducts are notoriously unstable, very few have ever been isolated, and their decomposition in solution is believed to involve heterolysis of the carbon-thallium bond and generation of carbonium ions.[8] Nevertheless, we were surprised by Moriarty and Gopal's comment *vis à vis* Scheme III that "Attempts were made, to no avail, to isolate the proposed organothallium intermediate in the present examples." Some 10 years ago Pande and Winstein showed that treatment of norbornene and norbornadiene with thallium(III) acetate gave the cis,exo-acetoxythallation adducts 7 and 8 as relatively stable, isolable solids,[9] and we have confirmed these results on a number of occasions in our own laboratories. As there appeared to us to be no obvious reason why the oxythallation adduct of 1 should be significantly less stable than compounds 7 or 8, we have reinvestigated the reaction of 1 and some related compounds with thallium(III) acetate.



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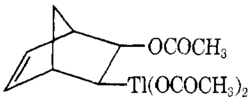

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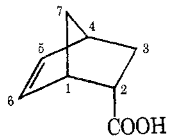
Oxidation of 1 with thallium(III) acetate in glacial acetic acid proceeded smoothly at room temperature to give the oxythallation adduct 9 in 88% yield as an easily handled, relatively stable, colorless, crystalline solid. The presence of the five-membered lactone ring was evident from the ir spectrum ($\nu_{C=O}$ 1780 cm^{-1}), while the nmr spectrum exhibited the expected large ^1H-$^{203/205}Tl$ coupling constants characteristic of organothallium compounds (Table I).[10,11] Similar treatment of the dicarboxylic acids 10 and 12 provided the analogous crystalline lactones 11 and 13 in virtually quantitative yield. As with compound 9, the ir spectra of 11 and 13 showed characteristic, strong lactone absorptions at 1780-1800 cm^{-1}; the presence of the covalent carbon-thallium bond was again confirmed by nmr spectroscopy (Table I).

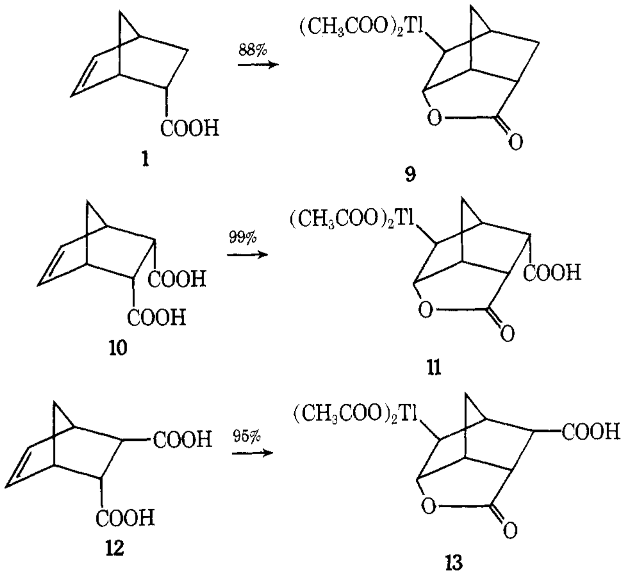
Table I
^{1}H–$^{203/205}$Tl Coupling Constants (Hertz) in Norbornylthallium Diacetates[a,b]

Compd	$J_{\text{Tl-H-3(exo)}}$	$J_{\text{Tl-H-4}}$	$J_{\text{Tl-H-5}}$	$J_{\text{Tl-H-6}}$
9	208	630	1200	909
11	223	515	1197	911
13		545	1204	898

[a] The numbering system used is that of the corresponding precursor norbornenecarboxylic acid, *viz.*



[b] Coupling constants are accurate to ±5 Hz.



The stability of the oxythallation adducts **9**, **11**, and **13** is comparable to that of **7** and **8**; all of these compounds can be handled easily in the atmosphere and do not decompose to any significant extent over a period of several days when stored in closed bottles. They do undergo slow decomposition during storage for several weeks, and are, predictably, completely destroyed when they are heated in acetic acid. Thus, heating of a solution of freshly made **9** in acetic acid at 60–65°[12] for 14 hr resulted in total destruction of the organothallium compound and gave the acetoxy lactone **4** in poor (19%) yield. A similar result was obtained when a mixture of **1** and thallium(III) acetate was heated in acetic acid at 60–65° for 16 hr; no **9** was obtained, and the acetoxy lactone **4** was again formed in very low (13%) yield.

The above results thus confirm and extend Pande and Winstein's earlier observations that certain norbornene derivatives react readily with thallium(III) acetate to give oxythallation adducts which, in comparison with those derived from almost all other types of olefinic substrate, show a remarkable degree of stability.

Experimental Section[13]

Acetoxythallation of 1. Thallium(III) acetate (4.1 g, 0.01 mol) was dissolved in a solution of 1.36 g (0.01 mol) of **1** in 30 ml of glacial acetic acid; the resulting mixture was stirred at room temperature for 4 hr, during which time a colorless solid precipitated. Addition of 25 ml of dry benzene, followed by 200 ml of petroleum ether (bp 40–60°), resulted in precipitation of more of this colorless solid, which was removed by filtration, washed with diethyl ether, and dried at room temperature to give 4.3 g (88%) of pure **9** as the dihydrate, mp 144° dec. *Anal.* Calcd for $C_{12}H_{15}O_6Tl \cdot 2H_2O$: C, 29.09; H, 3.84. Found: C, 28.91; H, 3.72. The infrared spectrum showed $\nu_{C=O\ \text{lactone}}$ 1780 cm^{-1}, $\nu_{C=O\ \text{acetate}}$ 1730 cm^{-1}, and a weak ν_{OH} at 3150 cm^{-1}. Details of the nmr spectrum are listed in Table I.

Acetoxythallation of 10. Thallium(III) acetate (4.1 g, 0.01 mol) was dissolved in a solution of 1.82 g (0.01 mol) of **10** in 35 ml of glacial acetic acid; the resulting mixture was stirred at room temperature for 24 hr, during which time a colorless solid precipitated. This was removed by filtration, washed with diethyl ether, and dried at room temperature to give 5.0 g (99%) of pure **11**, mp 200° dec. *Anal.* Calcd for $C_{13}H_{15}O_8Tl$: C, 30.83; H, 2.98. Found: C, 31.00; H, 3.26. The infrared spectrum showed $\nu_{C=O\ \text{lactone}}$ 1790 cm^{-1} and $\nu_{C=O\ \text{acetate}}$ 1730 cm^{-1}. Details of the nmr spectrum are listed in Table I.

Acetoxythallation of 12. Acetoxythallation of **12** (1.82 g, 0.01 mol) was carried out in the same manner as described for **10**, and gave 4.8 g (95%) of **13**, mp 138° dec. *Anal.* Calcd for $C_{13}H_{15}O_8Tl$: C, 30.83; H, 2.98. Found: C, 30.90; H, 3.14. The infrared spectrum showed $\nu_{C=O\ \text{lactone}}$ 1790 cm^{-1} and $\nu_{C=O\ \text{acetate}}$ 1725 cm^{-1}. Details of the nmr spectrum are listed in Table I.

Oxidation of 1 with Thallium(III) Acetate-Acetic Acid. A solution of 1.36 g (0.01 mol) of **1** and 4.1 g (0.01 mol) of thallium(III) acetate in 30 ml of glacial acetic acid was heated at 60–65° (bath temperature) with stirring for 16 hr. The reaction mixture was then cooled to room temperature and partitioned between ether and saturated aqueous sodium chloride solution; the ethereal extract was washed twice with distilled water, once with 10% aqueous sodium hydroxide solution, and twice more with distilled water. Subsequent drying ($MgSO_4$), filtration, and evaporation of the solvent gave 0.25 g (13%) of a colorless solid, **4**, mp (after washing with petroleum ether, bp 40–60°) 92–94° (lit.[14] mp 95–96°). The infrared spectrum of the product showed $\nu_{C=O\ \text{lactone}}$ 1800 cm^{-1} and $\nu_{C=O\ \text{acetate}}$ 1740 cm^{-1}.

Treatment of 9 with Hot Acetic Acid. A solution of 1.36 g (0.01 mol) of **1** and 4.1 g (0.01 mol) of thallium(III) acetate in 30 ml of glacial acetic acid was stirred at room temperature for 4 hr (during which time **9** precipitated from solution), and then heated at 60–65° (bath temperature) for 14 hr. Isolation of the product in the manner described immediately above gave 0.35 g (19%) of a white solid identical in melting point (after washing with petroleum ether, bp 40–60°) and infrared spectrum with the acetoxylactone **4** obtained above.

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Registry No.—**1**, 1195-12-6; **4**, 16479-66-6; **9**, 51510-07-7; **10**, 3853-88-1; **11**, 51510-08-8; **12**, 1200-88-0; **13**, 51606-65-6; thallium(III) acetate, 2570-63-0.

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(13) Melting points were determined on a Kofler hot-stage microscope melting point apparatus and are uncorrected. Microanalyses were performed by Mr. A. R. Saunders of the University of East Anglia. Infrared spectra were recorded on a Perkin-Elmer Model 257 grating infrared spectrophotometer using the normal Nujol mull technique. Nuclear magnetic resonance spectra were obtained with a Perkin-Elmer R12 60-MHz spectrometer using deuteriochloroform or DMSO-d_6 as solvents and TMS as internal standard.

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