(0.96 g, 0.18 mmol) in the manner described for **3a** followed by treatment of the product with 20% piperidine in DMF (2 mL) for 30 min, removal of DMF under high vacuum, and HPLC purification of the water-soluble extract of the residue gave **4**: yield 25 mg, 32%; mp 191-192 °C dec; $[\alpha]^{22.5}_D$ -10.9° (*c* 1, H_2O); ^{13}C NMR (400 MHz, D_2O) δ 25.62, 52.71 (d, J_{CP} = 5.9 Hz), 52.93, 110.25 (d, J_{CP} = 7.3 Hz), 113.89, 118.56, 121.36, 123.47, 129.18 (d, J_{CP} = 7.4 Hz), 129.43 (d, J_{CP} = 8.8 Hz), 137.38 (d, J_{CP} = 4.4 Hz), 171.86; ^{31}P NMR (D_2O) δ -3.60; ^1H NMR (400 MHz, D_2O) δ 3.36 (dd, *J* = 15.1 and 7.8 Hz, 1 H), 3.39 (d, *J* = 11.7 Hz, 3 H), 3.46 (dd, *J* = 15.4 and 5.1 Hz, 1 H), 4.33 (dd, *J* = 7.6 and 5.4 Hz, 1 H), 7.25 (ddd, *J* = 7.57 and 0.98 Hz, 1 H), 7.33 (ddd, *J* = 7.69 and 1.22 Hz, 1 H), 7.39 (d, *J* = 2.20 Hz, 1 H), 7.65 (d, *J* = 7.81 Hz, 1 H), 7.76 (d, *J* = 8.30 Hz, 1 H); FAB MS (Ar, positive mode) *m/z* (relative intensity) 299 (100, M^+), 262 (20), 224 (36), 186 (71), 130 (32).

Z-Trp-OBzl (1) by Fluoride Treatment of 2. Compound **2** (0.05 g, 0.14 mmol) was dissolved in THF (2 mL), and a solution of tetra-*n*-butylammonium fluoride trihydrate (0.44 g, 1.4 mmol) in THF (1 mL) was added. After 1 h, the solution was acidified to pH 3 with 1 M HCl, and the THF was removed under reduced pressure. The residue was dissolved in ethyl acetate (20 mL), washed with 1 M HCl (3 × 20 mL), brine (3 × 20 mL), and 5% $NaHCO_3$ (2 × 20 mL), dried over $MgSO_4$, and solvent was evaporated under reduced pressure to yield **1** as an oil: yield 0.037 g, 66%; R_f 0.47; ^{13}C NMR (90 MHz, $CDCl_3$) δ 28.0, 54.7, 66.9, 67.1, 109.6, 111.2, 118.6, 119.6, 122.1, 122.9, 127.5, 128.0, 128.4, 128.5, 135.2, 136.1, 155.7, 171.8; ^1H NMR (60 MHz, $CDCl_3$) δ 3.26 (d, *J* = 5 Hz, 2 H), 4.66 (m, 1 H), 5.07 (s, 4 H), 6.67-7.70 (m, 15 H), 8.17 (s, b, 1 H).

Boc-Trp(PO_3Me_2)-OH (8). Hydrogenolysis of **7** (3.46 g, 6 mmol) over 10% Pd/C (0.63 g, 100 mg/mmol) in methanol/acetic acid (95:5, 60 mL) at room temperature and atmospheric pressure for 3 h, filtration to remove the catalyst, extraction with 5% $NaHCO_3$ in several portions of an ethyl acetate solution of the residue followed by acidification with concentrated HCl of the aqueous extract, and reextraction of the free acid into $CHCl_3$, drying the organic phase over $MgSO_4$, and removal of solvent in vacuo yielded **8**: 2.12 g, 81%; $[\alpha]^{21.5}_D$ +49.15° (*c* 1, $CHCl_3$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 27.9, 53.9 (d, J_{CP} = 4.9 Hz), 79.4, 113.1, 115.9 (d, J_{CP} = 8.6 Hz), 119.1, 122.0, 123.6, 126.5 (d, J_{CP} = 8.2 Hz), 131.1 (d, J_{CP} = 9.8 Hz), 136.7 (d, J_{CP} = 3.7 Hz), 155.2, 173.6; ^{31}P NMR ($CHCl_3$) δ -0.12; ^1H NMR (60 MHz, $CDCl_3$) δ 1.43 (s, 9 H), 3.27 (d, *J* = 6 Hz, 2 H), 3.73 (d, *J* = 12 Hz, 6 H), 4.60 (m, 1 H), 6.80-7.80 (m, 5 H); FAB MS (Ar, positive mode) *m/z* (relative intensity) 413 (15, M^+), 357 (24), 313 (62), 267 (31), 236 (100), 130 (61).

Boc-Trp(PO_3Me_2)-Leu-NHMe (9). *N*-Methylmorpholine (NMM) (0.071 g, 0.7 mmol in 0.5 mL of THF) and isobutyl chloroformate (0.089 g, 0.65 mmol) in 0.5 mL of THF) were added to **8** (0.289 g, 0.7 mmol in 2 mL of THF) at -30 °C under a dry N_2 atmosphere, followed after 3 min by H-Leu-NHMe HCl (0.09 g, 0.5 mmol in 2 mL of THF) neutralized previously with NMM (0.051 g, 0.5 mmol). The reaction was quenched by addition of 5% $NaHCO_3$ (0.5 mL) after 2 h at -20 °C (dry ice/acetone), ethyl acetate (20 mL) was added, the product was washed with 5% $NaHCO_3$ (20 mL) and 1 M HCl (20 mL) and dried over $MgSO_4$, and solvent was removed under reduced pressure to yield **9** as an off-white foam: 0.24 g, 91%; $[\alpha]^{22.5}_D$ -25.25° (*c* 1, $CHCl_3$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 22.0, 22.7, 24.6, 26.1, 27.6, 28.1, 40.9, 51.7, 54.0 (d, J_{CP} = 4.9 Hz), 54.9, 80.3, 113.4, 115.8 (d, J_{CP} = 8.6 Hz), 119.4, 122.3, 124.0, 126.8 (d, J_{CP} = 6.1 Hz), 130.8 (d, J_{Cp} = 11.0 Hz), 137.0 (d, J_{CP} = 3.7 Hz), 155.7, 171.6, 172.2; ^{31}P NMR ($CHCl_3$) δ -0.12.

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Registry No. 1, 69876-37-5; **2**, 118869-29-7; **3a**, 118869-31-1; **3b**, 118890-31-6; **4**, 118869-33-3; **5**, 118869-35-5; **6**, 57229-69-3; **7**, 118869-36-6; **8**, 118869-37-7; **9**, 118869-38-8; H-Leu-NHMe·HCl, 99145-71-8; Z-Trp-OH, 7432-21-5; BOC-Trp-OH, 13139-14-5; $ClP(O)(OMe)_2$, 813-77-4.

Novel Rearrangement of Tricyclo[5.2.1.$0^{2,6}$]deca-3,8-dienes into 2-Oxatricyclo[6.3.0.$0^{3,7}$]undeca-4,10-dienes by Treatment with Periodic Acid

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Tricyclo[5.2.1.$0^{2,6}$]deca-3,8-dienes **1** on treatment with periodic acid (**6**) in aqueous *tert*-butyl alcohol undergo a novel rearrangement to give 2-oxatricyclo[6.3.0.$0^{3,7}$]undeca-4,10-dienes **7** in fair yields. Hypoiodic acid, IOH, was found to be generated in the course of the rearrangement of **1** into **7**. Independent reaction of **1** with hypoiodic acid derived from iodine and hydrogen peroxide gave the same rearranged product **7** in a yield comparable to that by **6**. The rearrangement of **1** to **7** seems to proceed via an iodonium ion intermediate.

endo-Tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**1a**), readily available from the dimerization of cyclopentadiene, is widely used as a starting material in organic synthesis.[1] The oxidation of **1a** afforded a wide range of compounds depending on the oxidants employed (e.g., allylic alcohol **2** by selenium dioxide,[2] glycol **3** or dialdehyde **4** by permanganate oxidation,[1a,3] and epoxide **5** by peracids[4] or aqueous hydrogen peroxide[5]). On the other hand, periodic acid (**6**), H_5IO_6, or periodates such as $NaIO_4$ and KIO_4 are often used not only as glycol fission reagents but also as the oxidant for a wide range of organic compounds,[6] i.e.,

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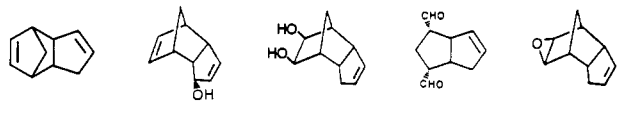
Table I. Reaction of 1a with 6 under Several Conditions[a]

run	solvent	temp, °C	time, h	convn, %	yield,[b] % 7a	yield,[b] % 8 + 9
1	*t*-BuOH	rt[d]	6	>98	46	16
2	CH_3CN	rt	3	>98	48	15
3	*t*-BuOH	50	0.5	>98	46	7
4		0	24	trace	–	–
5[c]		rt	24	trace	–	–

[a] **1a** (10 mmol) was allowed to react with **6** (10 mmol) in organic solvent–H_2O (3:2, 75 mL). [b] Determined by VPC analysis using an internal standard technique. [c] $NaIO_4$ was used in place of **6**. [d] rt = room temperature.

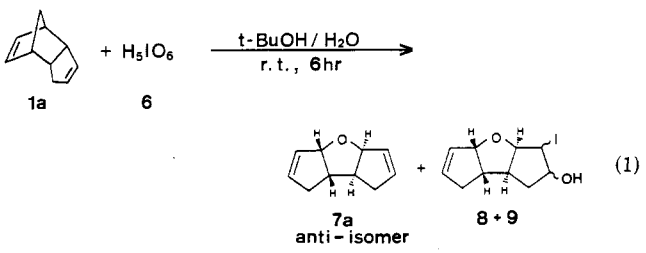
polycyclic aromatic hydrocarbons,[7] steroids,[8] amines,[7,9] and phenols,[6e,10] etc. Although, olefins fail to be oxidized by **6** or periodates alone, these reagents are utilized as co-oxidants with a wide variety of metal oxides (e.g., permanganate,[11] osmium tetraoxide,[12] and ruthenium tetraoxide[13]).



1 2 3 4 5

1a endo
1b exo

We now find that **1a** undergoes a novel rearrangement by treatment with **6** in aqueous organic solvents at room temperature to form *anti-cis*-2-oxatricyclo[6.3.0.$0^{3,7}$]-undeca-4,10-diene (**7a**) and iodohydrins **8** and **9** (eq 1).



1a 6 7a anti-isomer 8 + 9 (1)

Table I shows the rearrangement of **1a** by **6** under several reaction conditions.

The rearrangement of **1a** to **7a** was satisfactorily carried out in a mixed solvent of *tert*-butyl alcohol (*t*-BuOH) or acetonitrile containing about 40 vol % of water (runs 1 and 2), but no reaction took place in anhydrous organic solvents or water. For instance, the treatment of **1a** with stoichiometric amount of **6** in aqueous *t*-BuOH under ambient temperature for 6 h afforded **7a** (46%) together with a small amount of iodohydrins **8** + **9** (16%) and brownish oily substances,[14] which appear to be a complex mixture of iodides polymerized. When the same reaction was carried out at 50 °C, the rearrangement was effected within 0.5 h (run 3). However, no reaction took place at 0 °C in either aqueous *t*-BuOH or acetonitrile solutions (run 4). Sodium periodate, $NaIO_4$, was inadequate for the present rearrangement (run 5).

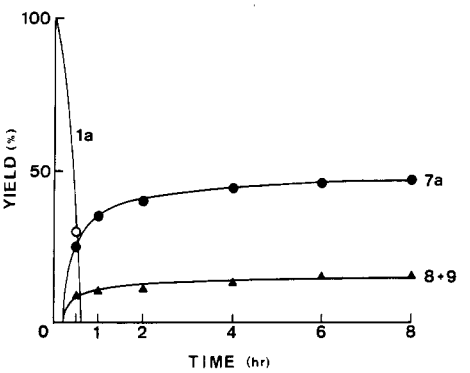
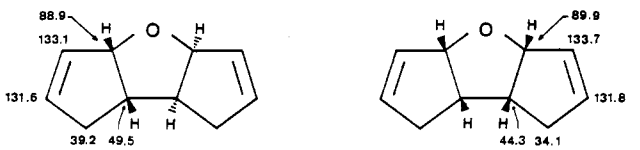


Figure 1. Time dependence curves for the reaction of **1a** with **6**: **1a** (10 mmol), **6** (10 mmol), *t*-BuOH (3:2, 75 mL) at room temperature.

In a similar manner as endo isomer **1a**, exo isomer **1b** reacted with **6** under the same conditions to give the corresponding rearranged product *syn-cis*-2-oxatricyclo-[6.3.0.$0^{3,7}$]undeca-4,10-diene (**7b**) in slightly lower yield (25%).



7a 7b

The stereochemical structure of **7a** and **7b** was established by measuring the NOE and 2D ^1H NMR chemical shift correlations. Upon irradiation of the H-1 protons of **7a** and **7b**, the intensity of the H-8 proton resonance increased by about 11.0%, respectively. These observations suggest that the H-1 and H-8 (or H-3 and H-7) protons on the furan ring in **7a** and **7b** lie in a cis relationship to one another. The location of the double bond was easily confirmed from 2D ^1H NMR chemical shift correlations in which the cross peaks appeared between H-4 and H-6 but not H-4 and H-7. From the comparison of ^{13}C NMR chemical shifts of **7a** and **7b**, it was found that ^{13}C signals of C-6 and C-7 of **7b** were shielded by about 3 and 5 ppm more than those of **7a**, respectively. The upfield shift of C-6 and C-7 signals in **7b** may depend on the steric compression effect of cyclopentene rings, which take sterically more crowded configurations than those of **7a**. Thus the stereochemistry of **7a** was assigned as *anti-cis*-2-oxatricyclo[6.3.0.$0^{3,7}$]undeca-4,10-diene in which two cyclopentene rings annelated to the furan ring assume the anti orientations, whereas **7b** was assigned as the corresponding syn compound. Although assignment of the configuration of iodohydrins **8** and **9** was difficult, these compounds were found to be stereoisomeric to each other.

The time dependence of the reaction of **1a** with **6** was monitored by VPC measurement (Figure 1). Despite a

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(14) The TLC of the oily residue, even by developing in a polar solvent such as ethyl acetate, provided only poorly characterized spots that are broadened close the bottom of the column. The residue easily turned to black resinous substances on standing.

Table II. Reactions of 1a and 10 with Hypohalo Acid Reagents[a]

run	substr	reagent	convn, %	product (yield,[b] %)
1	1a	6	>98	7a (48)
2		I_2	65	7a (14)
3		I_2–H_2O_2	>98	7a (40)
4		NBS	55	7a (5)
5	10	6	trace	–
6[c]		6 + 1a	35[d] + >98[e]	7a (58), 11 (23)
7		I_2–H_2O_2	90	11 (80)
8	7a	6	trace	–
9		I_2–H_2O_2	43	8 (23)

[a] Substrate (10 mmol) was allowed to react with reagent (10 mmol) in mixed solvent of CH_3CN–H_2O (3:2, 75 mL) at room temperature for 24 h. [b] Determined by VPC analysis. [c] 1a (10 mmol), 6 (10 mmol), and 10 (10 mmol) were used. [d] Conversion of 10. [e] Conversion of 1a.

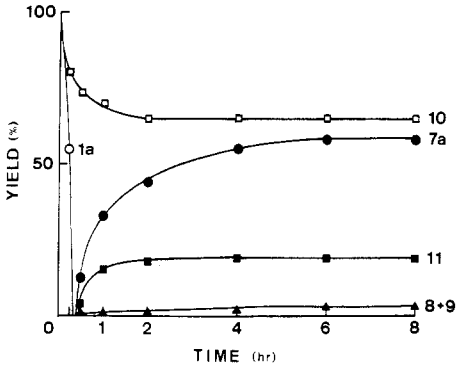


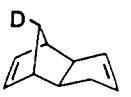
Figure 2. Time dependence curves for the reaction of 1a + 10 with 6: 1a (10 mmol), 6 (10 mmol), 10 (10 mmol), *t*-BuOH (3:2, 75 mL) at room temperature.

rapid decrease of the starting diene **1a**, **7a** and iodohydrins **8** and **9** increased very slowly with time. It is probable that the consumption of **1a** in early stages of the reaction is due to the formation of a complex of **1a** with **6**, which is gradually converted to reaction products. The formation of iodohydrins **8** and **9** suggests that hypoiodic acid, IOH, is generated in the course of the reaction of **1a** with **6**, since the independent reaction of **7a** with **6** did not produce any product. **1a** was allowed to react under several reaction conditions in which hypoiodic acid is expected to be generated in the medium (Table II) in order to reveal the role of hypoiodic acid in the present rearrangement.

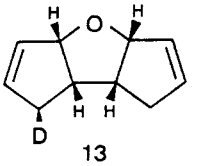
The reaction of **1a** with iodine in aqueous acetonitrile gave **7a** in a yield of 14%. However, treatment of **1a** by iodine–hydrogen peroxide, which produces IOH in the medium, afforded **7a** in comparable yield (40%) to that by periodic acid (**6**). The reaction with NBS, which generates hypobromic acid, BrOH, gave the rearranged product **7a** in poor yield (run 4). It is interesting to note that 1-octene (**10**) reacted with **6** in the presence of **1a** to form 2-iodo-1-octanol (**11**) (23%) along with **7a** (58%), although the treatment of **10** with **6** alone resulted in the recovery of the starting **10**. The time dependence curves of the reaction are shown in Figure 2.

Irrespective of the presence of the alternative olefin **10**, the concentration of **1a** again decreased very fast, and **7a** was gradually produced. The formation of iodohydrin **11** is attributed to the subsequent addition of hypoiodic acid, IOH, liberated during the reaction of **1a** with **6**. Indeed the treatment of olefin **10** in iodine–hydrogen peroxide gave iodohydrin **11** in good yield. An improved yield of **7a** and decrease of iodohydrins **8** and **9** are believed to be due to the addition of hypoiodic acid to 1-octene (**10**). The reaction of **7a** in iodine–hydrogen peroxide produced iodohydrin **8** (23%) but not **9**.[15]

To obtain mechanistic information for the present rearrangement *syn-exo*-10-deuteriotricyclo[5.2.1.$0^{2,8}$]deca-3,8-diene (**12**) prepared from **1a** by the action of D_2O and chlorotrimethylsilane/sodium iodide[16] was allowed to react with **6** giving the corresponding syn compound **13** in which the deuterium was incorporated into the C-6 position. This fact shows that the carbon–carbon bond of C-1 and C-2 of **12** is severed in the process of the rearrangement to **13**.



12



13

Although the detailed pathway concerning the rearrangement of **1a** to **7a** remains still unclear, the formation of hypoiodic acid appears to be important for the present rearrangement.[17]

Experimental Section

Unless otherwise noted, the materials were obtained from commercial suppliers and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on JEOL GSX-400 and Hitachi R-90H spectrometers in $CDCl_3$, using Me_4Si as internal standard. IR spectra were obtained on a JASCO Model A-202 spectrometer. GC-MS spectra were recorded with a JEOL JMS-D300 spectrometer. VPC analysis was performed with a Yanagimoto Model G-1800 chromatograph employing a thermal conductivity detector and a 3 mm × 3 m stainless column packed with PEG-20M 5% or Silicon OV-7 5% on Chromosorb W. The yields of products were estimated from the peak areas by using tetralin and *o*-xylene as internal standards.

Reaction of 1a with 6. To the stirred solution of **6** (10 mmol) in *t*-BuOH–H_2O (3:2, 75 mL) was added dropwise **1a** (10 mmol), and the mixture was allowed to react under the prescribed conditions. The reaction mixture was treated with a solution of sodium sulfate to decompose unreacted periodic acid and then treated with $NaHCO_3$ solution. Products **7a** and **8** + **9** were extracted with ether and isolated by distillation under reduced pressure or by chromatography on silica gel (hexane/ethyl acetate = 10:1 eluent). Reaction of **1b** or **12** with **6** was carried out in a similar manner as above.

Reaction of 1a or 10 with IOH Derived from I_2 and H_2O_2. To the stirred solution of I_2 (5 mmol) and 35% H_2O_2 (5 mmol) in *t*-BuOH–H_2O (3:2, 75 mL) was added dropwise **1a** (10 mmol).

(15) Simultaneous formation of **8** and **9** was expected from the reaction of **7a** with IOH, but **9** was not obtained. The formation path of **9** is not confirmed.

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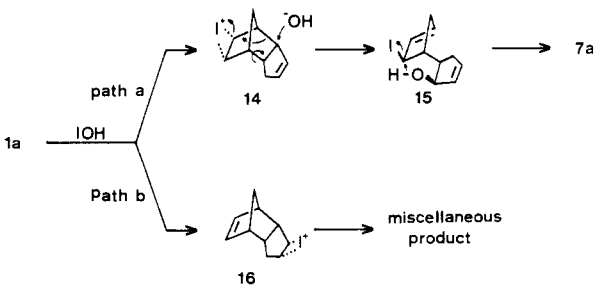
(17) For the rearrangement of **1a** to **7a**, it is possible to speculate the following reaction path, which involves hypoiodic acid, IOH. An attack



of IOH to the bicyclo[2.2.1]heptene double bond of **1a** gives an iodonium ion intermediate **14** (path a), which on subsequent cleavage of the C–C bond, followed by an addition of hydroxy anion, produces an iodohydrin intermediate, **15**. An intramolecular ring closure reaction of **15** provides the furan derivative **7a**. An alternative attack of IOH to the cyclopentene double bond (path b), which takes place in competition with the path a, seems to lead to miscellaneous products. The rearrangement of **1a** via the path b may involve the formation of iodohydrin **9**. The stereochemistry of the rearranged products **7a**, **7b**, and **13** can be satisfactorily explained by the above reaction sequences.

The mixture was then allowed to react at room temperature. The reaction mixture was treated with a solution of sodium thiosulfate. Treatment and isolation were carried out in a similar manner as above.

***anti-cis*-2-Oxatricyclo[6.3.0.0^{3,7}]undeca-4,10-diene (7a)**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.83–5.86 (m, 2 H), 5.74–5.77 (m, 2 H), 5.03–5.07 (m, 2 H), 2.62 (dm, J = 16.7 Hz, 2 H), 2.48–2.54 (m, 2 H), 2.33 (dm, J = 16.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 133.1 (d), 131.6 (d), 88.9 (d), 49.5 (d), 39.2 (t); IR (NaCl) 3070, 2950, 2920, 2860, 1450, 1360, 1110, 1070, 990, 890, 750, 700 cm^{-1}; GC-MS 148 (M^+). Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.32; H, 8.21.

***syn-cis*-2-Oxatricyclo[6.3.0.0^{3,7}]undeca-4,10-diene (7b)**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.81–5.84 (m, 2 H), 5.75–5.78 (m, 2 H), 5.08–5.10 (m, 2 H), 2.91–2.95 (m, 2 H), 2.36 (dm, J = 17.0 Hz, 2 H), 2.20 (dm, J = 17.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 133.8 (d), 131.8 (d), 89.9 (d), 44.3 (d), 34.1 (t); IR (NaCl) 3080, 2960, 2900, 2880, 1460, 1360, 1280, 1110, 1060, 1040, 1000, 970, 740, 720, 690 cm^{-1}; GC-MS 148 (M^+).

***anti*-10-Hydroxy-11-iodo-2-oxatricyclo[6.3.0.0^{3,7}]undec-4-ene (8)**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.91–5.94 (m, 1 H), 5.57–5.60 (m, 1 H), 5.38 (d, J = 6.6 Hz, 1 H), 4.55 (d, J = 4.0 Hz, 1 H), 4.35–4.39 (m, 1 H), 4.24 (s, 1 H), 3.53 (d, J = 9.3 Hz, 1 H), 2.83–2.88 (m, 1 H), 2.71–2.66 (m, 3 H), 2.30 (dm, J = 15.1 Hz, 1 H), 1.66 (dm, J = 9.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 134.8 (d), 129.5 (d), 90.7 (d), 90.6 (d), 82.4 (d), 50.5 (d), 47.5 (d), 40.0 (t), 39.8 (t), 34.0 (d); IR (KBr) 3450, 3070, 2950, 2870, 1630, 1440, 1360, 1050, 1000, 890 cm^{-1}; GC-MS 165 (M^+ - I). Anal. Calcd for $C_{10}H_{13}O_2I$: C, 41.12; H, 4.49. Found: C, 40.57; H, 4.55.

***anti*-10-Hydroxy-11-iodo-2-oxatricyclo[6.3.0.0^{3,7}]undec-4-ene (9)**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.88 (d, J = 5.6 Hz, 1 H), 5.64 (dd, J = 5.4, 2.2 Hz, 1 H), 5.25 (d, J = 5.4 Hz, 1 H), 4.66 (d, J = 6.1 Hz, 1 H), 4.48 (d, J = 4.2 Hz, 1 H), 3.73 (s, 1 H), 2.61–2.68 (m, 3 H), 2.30 (dm, J = 14.9 Hz, 1 H), 2.15 (s, 1 H), 2.03–2.13 (m, 1 H), 1.74–1.80 (m, 1 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 134.2 (d), 130.4 (d), 90.6 (d), 89.6 (d), 72.8 (d), 48.4 (d), 48.1 (d), 45.1 (d), 39.7 (t), 39.4 (t); IR (NaCl) 3420, 3060, 2940, 2860, 1440, 1360, 1040, 890, 680 cm^{-1}; GC-MS 165 (M^+ - I).

1-Iodo-2-octanol (11): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.49–3.54 (m, 1 H), 3.40 (dd, J = 10.0, 3.4 Hz, 1 H), 3.24 (dd, J = 10.0, 6.0 Hz, 1 H), 2.04 (d, J = 5.1 Hz, 1 H), 1.52–1.57 (m, 1 H), 1.37–1.26 (m, 9 H), 0.89 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 70.9 (d), 36.6 (t), 31.7 (t), 29.1 (t), 25.6 (t), 22.6 (t), 16.4 (t), 14.1 (q); IR (NaCl) 3370, 2970, 2940, 2860, 1470, 1420, 1380, 1180, 1120, 1020 cm^{-1}; GC-MS 129 (M^+ - I).

***syn*-6-Deuterio-2-oxatricyclo[6.3.0.0^{3,7}]undeca-4,10-diene (13)**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.81–5.84 (m, 2 H), 5.75–5.78 (m, 2 H), 5.08 (s, 2 H), 2.91–2.95 (m, 2 H), 2.36 (dm, J = 17.0 Hz, 1 H), 2.20 (dm, J = 17.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.7 (d), 133.6 (d), 131.8 (d), 89.9 (d), 44.3 (d), 44.2 (d), 34.1 (t), [34.0, 33.8, 33.6]; IR (NaCl) 3070, 2950, 2860, 2150, 1450, 1360, 1100, 1070, 1000, 880, 730 cm^{-1}; GC-MS 149 (M^+).

Registry No. **1a**, 1755-01-7; **1b**, 933-60-8; **6**, 10450-60-9; **7a**, 119297-94-8; **7b**, 119364-78-2; **8**, 119297-95-9; **10**, 111-66-0; **11**, 119297-96-0; **12**, 119297-97-1; **13**, 119297-98-2.

Carbanions. 24. Rearrangements of (*E*)- and (*Z*)-2,2-Diphenyl-3-pentenyl Alkali Metal Compounds[1]

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[(*E*)- and (*Z*)-2,2-diphenyl-3-pentenyl]lithium (**15** and **35**) were prepared by reaction of (*E*)- and (*Z*)-5-chloro-4,4-diphenyl-2-pentene, respectively, with lithium at −75 °C in diethyl ether or tetrahydrofuran (THF). These organolithium compounds when warmed in diethyl ether solution to 35 °C undergo [1,2]-sigmatropic rearrangement of the propenyl group with >95% retention of geometrical configuration of the *trans*-propenyl group and about 90% retention of configuration of the *cis*-propenyl group. The failure to incorporate an *n*-butyl group when **15** is warmed from −75 °C to 35 °C in the presence of an excess of *n*-butyllithium implies that these rearrangements are not likely to occur by elimination and then readdition of *cis*- or *trans*-propenyllithium. Instead an intramolecular syn-addition of the lithiomethyl group to the double bond of **15** or **35** followed by an anti-elimination in the intermediate cyclopropylcarbinyllithium (**33** or **36**) is proposed to account for the retention of configuration during propenyl migration (see Scheme V). A similar mechanism (Scheme VI) is suggested to account for retention of configuration during [1,2]-propenyl migration in the previously known Wittig rearrangements of benzyl propenyl ethers and methallyl propenyl ethers. In the solvent THF, rearrangement of **15** and **35** occurs on warming to 0 or 10 °C; however, here the *E* isomer **15** undergoes about a 50/50 ratio of [1,2]-phenyl to -propenyl migration. The *Z* isomer **35** similarly undergoes both phenyl and propenyl migration in THF but also undergoes evidently an intramolecular [1,5]-proton migration to give the allylic anion **42** (see Scheme VII). If **15** is treated with potassium *tert*-butoxide in THF at −75 °C, exclusive [1,2]-phenyl migration is observed. Possible interpretations of these cation and solvent effects are given.

While [1,2]-migrations of vinyl groups in organometallic compounds of magnesium and the alkali metals are well documented,[2-4] the stereochemistry of these rearrangements has been less well investigated. Rautenstrauch, Büchi, and Wüest[5] found that Wittig rearrangement of (*Z*)- and (*E*)-propenyl benzyl ethers brought about by *n*-butyllithium in an ethereal solution in the presence of tetramethylethylenediamine proceeded with retention of geometrical configuration of the migrating propenyl group. To account for the preservation of geometry of the migrating group, these workers proposed that the rear-

(1) A brief account of a portion of this work was presented at the Symposium on Carbanions, 190th National American Chemical Society Meeting, Chicago, Sept 10, 1985; *Prepr. Am. Chem. Soc., Div. Pet. Chem.* **1985**, *30*, 597–603. More complete details of this work may be found in the following M.S. Theses completed at the Georgia Institute of Technology: D. L. Streeter (June, 1980), J. H. Northrop (June, 1981), R. L. Hughes (June, 1982), and K. W. Black (March, 1987).

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