16: NMR ($CDCl_3$) δ 9.42 (s, 1), 5.67 (br s, 2), 3.67 (s, 3), 1.5–2.7 (m, 8), 1.23 (s, 3), 1.14 (d, 3, J = 7 Hz); MS (EI), m/e (relative intensity) ethyl ester corresponding to **16** 250 (M^+, 1.3), 222 (3), 221 (8), 205 (2), 192 (6), 177 (7), 175 (7.4), 165 (14), 164 (12), 163 (53), 150 (13), 149 (73), 148 (23), 147 (100), 135 (26), 133 (17), 131 (11), 129 (15), 123 (18), 121 (15), 119 (32), 109 (11), 108 (24), 107 (26), 105 (30).

Rearrangement of 13 and 14 with $LiClO_4$. A solution of a 5:1 mixture of **13** and **14** (0.057 g, 0.24 mmol) in 8 mL of benzene containing (0.212 g, 9.0 equiv) of solid $LiClO_4$ was heated at 78 °C for 1 h under nitrogen. The solution was cooled to 25 °C, diluted with ether, washed with water, dried ($MgSO_4$), and evaporated to give 0.047 g (83%) of a ~1:1 mixture of **15** and **16** as determined by NMR analysis. Chromatography of 0.041 g as described above gave 0.008 g (16%) of **16** and 0.010 g (20%) of **15**.

Rearrangement of 13 and 14 with $Eu(fod)_3$. A solution of 0.048 g (0.20 mmol) of a 5:1 mixture of **13** and **14** in 0.5 mL of $CDCl_3$ in an NMR tube was treated with 0.0241 g (0.20 mmol) of $Eu(fod)_3$. The solution was monitored for by NMR. After 6 days, the mixture was diluted with pentane and washed with water. The aqueous layer was extracted twice with pentane. The combined organic layers were dried ($MgSO_4$) and evaporated to give 0.053 g (110%) containing fod and a 4:1 mixture of **16** and **15** as determined by NMR analysis. Chromatography of 0.039 g as described above gave 0.006 g (16%) of **16** and 0.003 g (8%) of **15**.

Reduction of 15. Reduction of **15** (50 mg) with $BH_3{\cdot}NH_3$ in CH_3OH at 0 °C as reported by Roush and Hall[13] gave 38 mg (76%) of a 2:1 mixture of **17** and **18** which was separated by reverse-phase HPLC (Beckman Ultrasphere-ODS, 5 μm, 10 mm × 25 cm) with 60:40 H_2O–CH_3CN: **17**, t_R 33 min; **18**, t_R 44 min. The spectral data are identical with those previously reported.

Acknowledgment. We are grateful to the National Institutes of Health for financial support. The 270-MHz NMR spectrometer was purchased with funds provided by NIH Grant GM 20168.

Registry No. **4a**, 928-90-5; **4b**, 5390-04-5; **5a**, 87282-60-8; **5b**, 79532-18-6; **6a**, 87282-61-9; **6b**, 87282-62-0; **7a**, 87282-63-1; **7b**, 87282-64-2; **8a**, 87282-65-3; **9a**, 87282-66-4; **9a** ethyl ester, 87282-67-5; **10a**, 87282-68-6; **10b**, 87282-69-7; **11a**, 87282-70-0; **11a** ethyl ester, 87282-71-1; **12a**, 87282-72-2; **12b**, 87282-73-3; **13**, 87282-74-4; **14**, 87333-76-4; **15**, 78685-39-9; **16**, 87282-75-5; **17**, 78669-02-0; **18**, 78669-03-1; **19**, 41093-63-4; (*E*)-crotyl bromide, 29576-14-5; trimethyl phosphonoacetate, 5927-18-4; trimethyl 2-phosphonopropionate, 26530-60-9.

Diels–Alder Reaction of 6,6-Dimethylfulvene with 2-Acetoxyacrylonitrile. Preparation of 5-(2-Hydroxyethyl)-2-cyclopenten-1-one[1]

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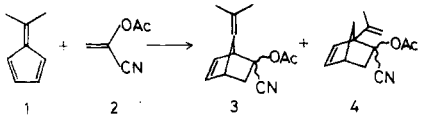
The Diels–Alder reaction of 6,6-dimethylfulvene with 1-acetoxyacrylonitrile gave two different adducts, 2-acetoxy-2-cyano-7,7-isopropylidenebicyclo[2.2.1]hept-5-ene (**3**, 70%) and 2-acetoxy-2-cyano-1-isopropenylbicyclo[2.2.1]hept-5-ene (**4**, 18%). The formation of **4**, which has not been reported before, can be suppressed by adding pyridine to the reaction mixture. Hydrolysis of **3** by sodium methoxide, followed by successive treatment with unsolvated hydroxide ion, peroxyformic acid, lithium aluminum hydride, and lead tetraacetate, gave 5-(2-hydroxyethyl)-2-cyclopenten-1-one (**15**, 35% from **3**).

The Diels–Alder reaction of 6,6-dimethylfulvene (**1**) with 1-acetoxyacrylonitrile (**2**) was reported by DePuy and coworkers,[2] where only a normal adduct, **3**, was obtained as a mixture of endo and exo isomers. Adduct **3** was then converted to (2-oxocyclopentyl)acetic acid through several-step transformations. We have found that this addition reaction often produces another adduct, **4**, as a byproduct which has not been reported before, and its yield sometimes exceeded 20%. The formation of **4**, however, can be suppressed by adding pyridine to the reaction mixture. Thus, this addition reaction, being endowed with a high chemoselectivity, can be adopted for the construction not only of bicyclo[2.2.1]heptenes but also of 5-(two-carbon chain)-substituted cyclopentenones.[3]

We have adopted adduct **3** as the starting material of a four-step synthesis of the title compound 5-(2-hydroxyethyl)-2-cyclopenten-1-one (**15**) which, as a family of 5-substituted cyclopentenones,[4] can be used in organic synthesis, but studies with regard to its preparation have been limited.[5]

Results and Discussion

The reaction of **1** with **2**, one of the ketene equivalents,[6] yielded a normal adduct **3** and an abnormal adduct **4**, each



1 2 3 4

as a mixture of endo and exo isomers, under usual reaction conditions. Results of some experiments which were carried out to optimize the reaction conditions and to suppress the formation of byproduct **4** are shown in Table I.

(1) Ketene Equivalents. 8. For part 7 see ref 6c.

(2) Depuy, C. H.; Story, P. R. *J. Am. Chem. Soc.* **1960**, *82*, 627.

(3) A preparative method of 4-(two-carbon)-substituted cyclopentenone was recently reported by: Drian, C. L.; Greene, A. E. *J. Am. Chem. Soc.* **1982**, *104*, 5473.

(4) For example: (a) Takahashi, T.; Hori, K.; Tsuji, J. *Chem. Lett.* **1981**, 1189. (b) Hayakawa, Y.; Yokoyama, K.; Noyori, R. *J. Am. Chem. Soc.* **1978**, *100*, 1799. (c) Rabiller, C.; Martin, G. J. *Tetrahedron* **1978**, *34*, 3281. (d) Tsuji, J.; Kasuga, K.; Takahashi, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 216.

(5) The preparation of **15** has not been reported. The corresponding acid **16** was reported by: Cassar, L.; Chiusoli, G. P.; Foa, M. *Chim. Ind. (Milan)* **1968**, *50*, 515; *Chem. Abstr.* **1969**, *70*, 114671; **1969**, *71*, P3047. A number of 5-(carbon chain)-substituted 2-cyclopenten-1-ones have been reported by, for example: (a) Paulsen, H.; Maass, U. *Chem. Ber.* **1981**, *114*, 346. (b) Brady, W. T.; Lloyd, R. M. *J. Org. Chem.* **1981**, *46*, 1322. (c) Toder, B. H.; Branca, S. J.; Dieter, R. K.; Smith, A. B., III. *Synth. Commun.* **1975**, *5*, 435.

(6) (a) Oku, A.; Arita, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3337. (b) Oku, A.; Nakaoji, S.; Kadono, T.; Imai, H. *Ibid.* **1979**, *52*, 2966. (c) Oku, A.; Hasegawa, H.; Shimadzu, H.; Nishimura, J.; Harada, T. *J. Org. Chem.* **1981**, *46*, 4152.

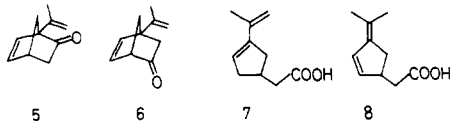
0022-3263/83/1948-4374$01.50/0

Table I. Diels-Alder Reaction of 6,6-Dimethylfulvene (1) with 1-Acetoxyacrylonitrile (2)[a]

entry	reactant molar ratio (1/2)	temp, °C	time, h	additive (molar ratio to 1)	product yield,[b] % 3	4
1	2.0	90	1		47	26
2	2.0	90	5		28	26
3	0.33	70	28		70	18
4	0.33	70	28	pyridine (0.02)	59	11
5	0.33	70	28	pyridine (0.1)	74	3
6	2.0	70	28	pyridine (0.08)	85	3
7	0.33	70	28	pyridine (0.51)	80	0
8[c]	0.33	70	28	AcOH (0.09)	24	12
9[c]	2.0	70	28	AcOH (0.01)	53	22
10	1.0	70	28	benzene[d]	37	22
11[c]	1.0	70	200	CH_3NO_2[d]	5	3

[a] Under a nitrogen atmosphere without solvent unless otherwise stated. [b] Yields are based upon ^1H NMR integrations of the isolated mixture of 3 and 4. [c] Polymeric products were mainly produced. [d] A 4-mmol sample of 1 was added to 4 mL of this solvent.

Abnormal Adduct 4. The structure of 4 was determined by the examination of ^1H NMR spectra of a bicyclic ketone 5 which was produced (84%) by the hydrolysis of 4. The presence of an isopropenyl group in 5 is indicated by the resonances appearing at δ 1.85 (3 H, t, J = 1 Hz) and 4.92 and 5.02 (1 H each, m, coupling with 1.85) and also by a characteristic IR absorption at 890 cm^{-1}. Olefinic protons at δ 6.10 and 6.57 couple with each other with J = 6 Hz and also couple with one methine proton at δ 3.15. These data together with other spectral data (see Experimental Section) inform us that the structure should be either 5 or 6.

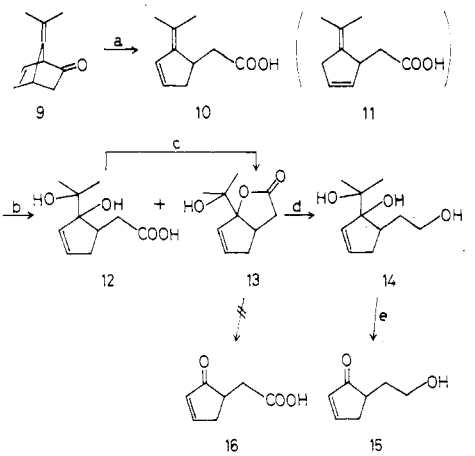


5 6 7 8

The evidence for structure 5 is available not only from the study of lanthanide-induced shift (LIS) with $Eu(fod)_3$ (see Experimental Section) but also from the following chemical transformation. Alkaline hydrolysis of the bicyclic ketone under relatively severe conditions (methanolic KOH) induced a hydrolytic ring opening to produce a mixture of two isomeric carboxylic acids. The ^1H NMR spectra of the mixture were analyzed. Three allylic methyl groups appear at δ 1.67, 1.75, and 1.90, and olefinic protons also appear at δ 4.83, 5.65, 5.85, and 6.35. The relative intensity of signals at δ 5.65, 4.83, and 1.90 is 1:2:3, while that of those at δ 6.35, 5.83, 1.67, and 1.75 is 1:1:3:3. When δ 3.13 was irradiated, the signals at δ 6.35 and 5.85 changed into doublets. These analyses inform us that the isomeric acid mixture consists of 7 and 8 (1:3 7/8). If the bicyclic ketone were 6, its hydrolytic ring opening would have produced a carbanion which is not conjugating with an isopropenyl double bond.

The formation of byproduct 4 is mechanistically interesting. First of all, the purity of 1 was analyzed by NMR and VPC to inspect if 1-isopropenylcyclopentadiene, an isomer of 1, was mixed in with the starting diene 1, but no evidence of this was obtained. It was reported that fulvene 1 undergoes a base-catalyzed isomerization to give an isomeric mixture of 1- and 2-isopropenylcyclopentadiene.[7] If this is the case, then the formation of 4 would be enhanced by adding a base such as pyridine or suppressed by adding an acid such as acetic acid.[8] However, the possibility of pyridine catalysis was experimentally ruled out (Table I, entries 4–7), and, surprisingly, the addition of pyridine suppressed the formation of 4, and the yield of 3 increased. On the other hand, the possibility of an acid-catalyzed isomerization of 1 seems likely because of the fact that pure 3 underwent retro-Diels–Alder conversion to 1 and 2 after being heated at 110 °C for 4 h, though to a small extent, but the formation of 4 was not observed.[9,10] Although some mechanistic details remain unclarified, the formation of byproducts in the Diels–Alder reactions of fulvene can be suppressed, and this seems to be important from a synthetic point of view.

Scheme I[a]



[a] (a) H_2O, t-BuOK, CH_3SOCH_3; (b) HCO_3H, HCO_2H; (c) CH_3OH–3% HCl; (d) $LiAlH_4$-ether; (e) $Pb(OAc)_4$-benzene.

5-(2-Hydroxyethyl)-2-cyclopenten-1-one (15). Treatment of a normal adduct, 3, with sodium methoxide gave the corresponding bicyclic ketone 9 (95%)[2] which is a formal adduct of ketene with 1, thus exemplifying the use of 2 as a ketene equivalent.[6] In general, bicyclic ketones such as 9 have been known to undergo a facile hydroxide ion-induced ring opening to give carboxylates.[11]

(7) Knight, D. B.; Hartless, R. L.; Jarvis, D. A. *J. Org. Chem.* **1972**, *37*, 688.

(8) Since dienophile 2 was synthesized from acetyl cyanide and acetyl chloride under the action of pyridine (see ref 6a), a trace amount of either or both acetic acid and pyridine may possibly be present in 2.

(9) The addition of acetic acid to the reaction mixture increased the formation of 4 relative to the lowered yield of 3, and a significant amount of polymer was formed (entries 8 and 9, Table I). The acid-catalyzed isomerization of 1, if it is the case, may predominantly form 1-isopropenylcyclopentadiene which undergoes polymerization competitively with the Diels–Alder reaction.

(10) The addition of 2,6-di-*tert*-butyl-*p*-cresol to the reaction mixture did not suppress the formation of 4; thus a free-radical pathway is also not likely.

(11) (a) Paasivirta, J. *Tetrahedron Lett.* **1968**, 2867. (b) Gassman, P. G.; Lumb, J. T.; Zalar, F. V. *J. Am. Chem. Soc.* **1967**, *89*, 946. (c) Erman, W. F.; Kretschmar, H. C. *Ibid.* **1967**, *89*, 3842. (d) Erman, W. F.; Wenkert, E.; Jeffi, P. W. *J. Org. Chem.* **1969**, *34*, 2196.

In fact, compound **9** produced **10** as the sole product (but not **11**) when it was treated with unsolvated hydroxide ion in Me_2SO. Such a high product selectivity in this sort of ring-opening reaction can be attained usually under aprotic conditions where intermolecular protonation, which normally favors the formation of **11**, can be suppressed whereas an intramolecular protonation path remains unchanged.[11c,d]

In the second step (Scheme I), some oxidative procedures were examined to remove the isopropenylidene group from the ring. Although the oxidation of **10** with *m*-chloroperoxybenzoic acid or peroxyacetic acid was unsatisfactory,[12] peroxyformic acid gave a mixture of diol–carboxylic acid **12** and its lactone **13** in relatively good yield.[13] The diol–acid **12** cyclized easily to **13** under treatment with methanolic HCl,[14] and the combined yield of **13** from **10** was 67%.

The attempt for preparing 1-oxo-2-cyclopentene-5-acetic acid (**16**) directly from **13** (or **12**) by oxidatively removing the hydroxypropyl group using lead tetraacetate was unsuccessful. Therefore, we adopted an indirect route as follows. The lithium aluminum hydride reduction of **13** gave triol **14** quantitatively.[13] In contrast to the unsuccessful result for **13** or **12**, the oxidation of **14** by lead tetraacetate in benzene worked successfully in removing the hydroxypropyl side chain from the ring, thus yielding 5-(2-hydroxyethyl)-2-cyclopenten-1-one (**15**, 73%). The overall yield of **15** from **3** was 35%.

Experimental Section

General Methods. ^1H NMR spectra were recorded on a Varian T-60A in $CDCl_3$, and chemical shifts are given in δ units. Infrared spectra were taken on a JASCO IRA-1 grating spectrometer, and mass spectra were taken on a Hitachi RMU-6L (relative intensities are given in parentheses). Combustion analyses were performed by the Microanalytical Laboratory of Kyoto University.

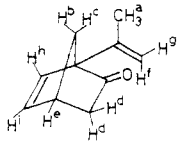
6,6-Dimethylfulvene and 2-acetoxyacrylonitrile were prepared according to the reported procedures.[15] Reagents unless otherwise specified were used without any special purification.

Diels–Alder Reaction of 6,6-Dimethylfulvene (1) with 2-Acetoxyacrylonitrile (2). Preparation of 2-Acetoxy-2-cyano-7,7-isopropylidenebicyclo[2.2.1]hept-5-ene (3). Dry pyridine (0.201 g, 2.5 mmol), **1** (0.529 g, 5.0 mmol), and **2** (1.653 g, 14.9 mmol) were mixed in a tube, which was then sealed under a nitrogen atmosphere. After the mixture was heated for 28 h at 90 °C, unreacted reagents were removed under reduced pressure, and the residue was fractionated by column chromatography (silica gel, benzene) to give **3** in 80% yield. **3a** (*endo*-CN): mp 123.5–124.5 °C; ^{13}C NMR ($CDCl_3$) δ 19.29, 19.50 (two allylic methyls), 20.47 (acetyl methyl), 41.96, 43.42 (two methines), 52.35 (CH_2), 73.38 (*C*OAc), 115.73 (CN), 119.63, 130.53 (CH=CH), 140.54, 142.77 (C=C), 169.01 (C=O); ^1H NMR δ 1.55 (1 H, d, J = 13 Hz, *endo*-H), 1.60 and 1.65 (3 H each, s, allylic methyls), 2.05 (3 H, s, acetyl), 2.55 (1 H, 2 d, J = 13, 4 Hz, coupled with 1.55 and 3.45, *exo*-H), 3.45 and 4.20 (1 H each, m, methines), 6.20 and 6.55 (1 H each, 2 d, J = 6, 3 Hz, olefinic); IR (KBr) 2730 (w), 2240 (w, CN), 1750 (s, C=O), 1380 (m), 1240 (s), 1170 (m), 1040 (m), 780 (m) cm^{-1}; mass spectrum, m/e 217 (M^+, 0.05), 174 (3.5), 119 (7.6), 107 (10), 106 (100), 105 (10), 91 (29), 43 (53), 39 (10). **3b** (*exo*-CN): mp 63.8–65.0 °C; ^{13}C NMR ($CDCl_3$) δ 19.49, 19.58 (two allylic methyls), 20.66 (acetyl methyl), 41.21, 43.52 (methines), 50.97 (CH_2), 74.30 (*C*OAc), 114.71 (CN), 131.07 131.79 (CH=CH), 142.39, 142.87 (C=C), 169.21 (C=O); ^1H NMR δ 1.55 and 1.65 (3 H each, s, allylic methyls) 2.00 and 2.10 (3 H each, *endo*- and *exo*-H, respectively), 2.10 (3 H, s, acetyl), 3.45 and 3.90 (1 H each, m, methines), 6.30 and 6.55 (1 H each, 2 d, J = 6, 3 Hz, olefinic); IR (KBr) 2225 (w, CN), 1755 (s, C=O), 1460 (m), 1390 (m) 1335 (m), 1240 (s), 1185 (m), 1040 (s), 780 (m), 730 (w) cm^{-1}.

Diels–Alder Reaction of 1 with 2 in the Absence of Pyridine. Compounds **1** (1.59 g, 15 mmol) and **2** (0.82 g, 7.4 mmol) were mixed, and the mixture was divided into three portions, each of which was sealed in a tube under a nitrogen atmosphere. After the tubes were heated at 90 °C for 1, 2, or 5 days, respectively, the reaction mixture was worked up analogously to that described above. Abnormal adduct **4** was formed besides normal adduct **3**. Product yields were as follows: after 1 day, **3** (47%), **4** (26%); after 2 days, **3** (54%), **4** (35%); after 5 days, **3** (28%), **4** (26%). 2-Acetoxy-2-cyano-1-isopropenylbicyclo[2.2.1]hept-5-ene (**4**): ^1H NMR δ 1.5 and 2.1 (2 H each, m, CH_2), 2.05 (3 H, s, allylic methyl), 2.1 (3 H, s, acetyl), 3.0 (1 H, m, methine), 5.0, 5.2 (2 H, a pair of d, CH_2=C<), 6.0–6.6 (2 H, m, olefinic); IR (neat) 2960 (m), 2200 (w, CN), 1740 (s, C=O), 1630 (m), 1430 (m), 1360 (m), 1220 (m), 1200 (m), 1180 (m), 1060 (m), 1040 (m), 970 (m), 890 (m), 720 (m) cm^{-1}. Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.86; H, 6.85; N, 6.38.

Hydrolysis of 3. Preparation of 7,7-Isopropylidenebicyclo[2.2.1]hept-5-en-2-one (9). To a methanolic solution (2 mL) of **3a** was added under stirring a methanolic solution (3 mL) of sodium methoxide (1.23 mmol) at ambient temperature under a nitrogen atmosphere. After 2 h, the solution was poured into 5 mL of water, extracted with methylene chloride, and dried (Na_2SO_4). Product **9**, smelling of a perfume-like odor, was obtained in 95% yield. **9**: ^1H NMR δ 1.60 and 1.65 (3 H each, s, allylic methyls), 2.0 (2 H, m, CH_2), 3.5 and 3.65 (1 H each, m, methine), 6.15 and 6.60 (1 H each, m, olefinic); IR (CCl_4) 2900 (m), 1740 (s, C=O), 1440 (m), 1115 (m), cm^{-1}; mass spectrum, m/e 148 (M^+, 1.4), 107 (10), 106 (100), 105 (31), 91 (68), 79 (11), 77 (12), 39 (15), 28 (12).

Hydrolysis of 4 and 5. To a methanolic solution (3 mL) of **4** (150 mg, 0.69 mmol) was added a methanolic solution of sodium methoxide (1.38 mmol) at −70 °C. After the mixture was stirred for 20 min, 2 mL of water and 2 mL of methylene chloride were added, and the mixture was warmed to room temperature. After the mixture was worked up with water and then with methylene chloride, a colorless liquid of 1-isopropylidenebicyclo[2.2.1]-hept-5-en-2-one (**5**) was obtained: 84%; ^1H NMR δ 1.85 (3 H,



5

t, J = 1 Hz, allylic), 2.05 and 2.18 (2 H each, m, CH_2), 3.15 (1 H, m, CH), 4.92 and 5.02 (1 H each, m, *exo*-methylene), 6.10 (1 H, 2 d, J = 6, 1 Hz, olefinic), 6.57 (1 H, 2 d, J = 6, 3 Hz, olefinic); IR (CCl_4) 3050 (m), 2960 (s), 2840 (m), 1740 (s, C=O), 1440 (m), 1380 (m), 1310 (w), 1120 (m), 895 (m) cm^{-1}; mass spectrum, m/e 148 (M^+, 2.6), 106 (92), 105 (30), 91 (100), 39 (17). Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.82; H, 8.21.

The structure shown was assigned to **5** in preference to **6** by using the ^1H NMR shift reagent Eu(fod)$_3$. The induced shift of the bridgehead proton (δ 3.15) was relatively smaller than that of the α-methylene protons to the carbonyl group. The LIS values for this product (in CCl_4) are listed as follows (δ, $\Delta\delta$/Eu(fod)$_3$ molar ratio to the substrate): H^a (1.82, 6.23), H^b (1.93, 5.38), H^c (1.93, 7.58), H^d (2.15 12.31), H^e (3.10, 4.12), H^f (4.83, 5.85), H^g (4.90, 3.85), H^h (6.08, 5.54), H^i (6.47, 3.46). The coupling constants (in hertz) are as follows: J(a,g) = 1, J(e,d) = 2, J(e,c) = J(e,b) = 2, J(b,c) = 9, J(h,i) = 5, J(i,e) = 3, J(h,e) = 1.

Hydrolysis of 4 to 7 and 8. To a methanolic solution (2 mL) of **4** (98 mg, 0.45 mmol) was added a 2.55 M methanolic KOH solution (1.0 mL, 2.5 mmol) at 20 °C, and the mixture was stirred at 20 °C for 0.5 h, at 50 °C for 0.5 h, and at 60 °C for 1.5 h. Water

(12) Applications of the reported procedure for permanganate or chromate oxidation were also unsuccessful: (a) Sharpless, K. B.; Williams, D. R. *Tetrahedron Lett.* **1975**, 3045. (b) Awasthy, A. K.; Rocek, J. *J. Am. Chem. Soc.* **1969**, *91*, 991.

(13) The NMR spectra as well as VPC analysis of products **12–14** demonstrated that each of these products consisted of a single stereoisomer. We assume the stereochemistry of these products is a cis configuration between the CH_2COOH and OH groups, based upon the stability of a cis-fused bicyclo[3.3.0]octene skeleton.

(14) Similar lactonization was reported: Danishefsky, S.; Hirama, M.; Gombatz, K.; Harayama, T.; Berman, E.; Schuda, P. F. *J. Am. Chem. Soc.* **1979**, *101*, 7020.

(15) Thiele, J.; Balhorn, H. *Justus Liebigs Ann. Chem.* **1908**, *348*, 5.

(2 mL) was added, the total mixture was extracted with CH_2Cl_2, and the extract (73 mg) was chromatographed (silica gel; benzene/ether, 9:1) to give a colorless mixture of **7** and **8** (ratio 1:3) in 71% yield. Mixture of **7** and **8**: ^1H NMR δ 1.67, 1.75, 1.90 (br s each), 2.0–3.5 (a broad spectrum of m), 4.83 (br s), 5.65, 5.85 (m each), 6.35 (2 d, J = 5, 2 Hz), 9.5 (br s); IR (CCl_4) 3300–2400 (m), 1700 (s), 1410 (m), 890 (w) cm^{-1}. The relative intensities of the NMR signals at δ 5.65, 4.83, and 1.90 were 1:2:3 and those of the signals at δ 6.35, 5.83, 1.67, and 1.75 were 1:1:3:3. Irradiation at δ 3.13 caused the change of the signals at δ 5.85 and 6.35 into a doublet for each.

Thermal Treatment of 3. When **3** was heated without additives at 110 °C for 4 h in a sealed tube under N_2, it melted and gradually formed a yellow liquid which consisted of **3**, **2**, and **1** in a ratio 7:1:1, but no evidence for the production of **4** was obtained by NMR analysis.

Ring Cleavage of 9. Preparation of 1-(Carboxymethyl)-2-isopropylidenecyclopent-3-ene (10). A mixed solution of *t*-BuOK (2.16 g, 97% grade, 18.7 mmol) and water (0.130 mL, 7.2 mmol) in 20 mL of dry dimethyl sulfoxide (Me_2SO) was added to a solution of **9** (0.515 g, 3.5 mmol) in 10 mL of dry Me_2SO under an N_2 atmosphere at room temperature. The solution changed from yellow-brown to dark green. After 1 h, the reaction mixture was worked up with cold water and methylene chloride. The aqueous layer was acidified with hydrochloric acid and extracted with ether which was then washed with saturated brine and dried (Na_2SO_4). A brown liquid of **10** was obtained; 0.56 g (97%). Because of the instability of **10**, it was treated with diazomethane to afford the corresponding methyl ester. Methyl ester of **10**: ^1H NMR 1.74 (6 H, s, CH_3), 1.85–3.40 (5 H, m, CH and CH_2), 3.65 (3 H, s, OCH_3), 5.80 (1 H, m, olefinic), 6.25 (1 H, 2 t, J = 5.5, 2 Hz, olefinic).

Oxidation of 10. Preparation of 1-(2-Hydroxy-2-propyl)-2-oxa-3-oxobicyclo[3.3.0]oct-7-ene (13). Peroxyformic acid was prepared according to a reported procedure. As soon as the carboxylic acid **10** (551 mg, purity <90%) was dissolved in cooled formic acid (10 mL), a solution of peroxyformic acid was added dropwise to it at 0 °C. After 1 h, the reaction was quenched with aqueous $NaHSO_3$ (357 mg, 3.4 mmol). Formic acid was removed under reduced pressure, and the residue was worked up with water and methylene chloride. The organic extract was washed with aqueous 1% NaOH and dried. A 177 mg of **13** was obtained. On the other hand, the combined aqueous layer was acidified with hydrochloric acid and extracted with methylene chloride to give **12** (305 mg). This was dissolved in methanol (4 mL), 2 mL of 3% HCl was added, and the mixture was stirred for 2 days at room temperature. The solution was made alkaline with 1% NaOH and extracted with methylene chloride to give 246 mg of **13**. The combined yield of **13** was 423 mg (67% from **9**). **13**: mp 66–68 °C; ^1H NMR δ 1.16 and 1.33 (3 H each, s, CH_3), 2.9–3.4 (6 H, m, CH, CH_2, and OH), 5.74 and 6.01 (1 H each, 2 t, J = 5.5, 2 Hz, CH=CH); IR (KBr) 3490 (s, OH), 3000 (m), 1750 (s, C=O, five-membered lactone ring), 1420 (m), 1270 (m), 1210 (m), 1120 (m), 1030 (m), 1000 (m), 970 (m), 850 (m), 780 (m), 740 (m) cm^{-1}; mass spectrum, m/e 164 ($M^+ - H_2O$, 3.3), 105 (100), 96 (71.9), 82 (60.9), 70 (40.2), 59 (72.7). Anal. Calcd for $C_{10}H_{14}O$: C, 65.92; H, 7.74. Found: C, 65.66; H, 7.87.

Reduction of 13. Preparation of 1-(1-Hydroxy-1-methylethyl)-2-(2-hydroxyethyl)-4-cyclopenten-1-ol (14). Lactone **13** (437 mg, 2.4 mmol) was dissolved in dry ether (5 mL) to which was added lithium aluminum hydride (169 mg, 3.3 mmol) at 0 °C. After 40 min, the mixture was warmed to 25 °C and stirred for 1.5 h. The reaction was quenched by a small amount of ethanol and subsequently by water, and the mixture was extracted with benzene and ether. A colorless solid of **14** (352 mg, 79%) was obtained. **14**: mp 89–91 °C; ^1H NMR δ 1.23 (6 H, s, CH_3), 1.5–2.8 (5 H, m, CH and CH_2), 2.95 (3 H, s, 3 OH), 3.70 (2 H, br t, J = 6 Hz, OCH_2), 5.66 and 5.96 (1 H each, m, olefinic); IR (KBr) 3470, 3360, and 3250 (s, OH for each), 3050 (m), 2980 (m), 1120 (m), 1070 (m), 1050 (m), 1030 (m), 1000 (m), 940 (m), 730 (m) cm^{-1}; mass spectrum, m/e 150 ($M^+ - 2H_2O$, 7.1), 135 (24.5), 110 (28.6), 109 (100), 82 (40.1), 81 (47.6).

Oxidation of 14. Preparation of 5-(2-Hydroxyethyl)-2-cyclopenten-1-one (15). Triol **14** (93 mg, 0.50 mmol) was dissolved in dry benzene (3 mL) to which was added, under stirring, powdered lead tetraacetate (251 mg, 0.57 mmol), which was recrystallized from acetic acid. After 2.5 h, the solution was filtered, and water was added to give a brown solution. Aqueous $NaHSO_3$ was added until the brown color disappeared. After addition of a small amount of $NaHCO_3$ and NaCl, the solution was extracted with ether. By removal of the solvents under a nitrogen stream a colorless liquid of **15** (46 mg, 73%) was obtained. **15**: ^1H NMR δ 1.5–3.4 (5 H, m, CH and CH_2), 3.80 (2 H, t, J = 6 Hz, OCH_2), 4.27 (1 H, s, OH), 6.20 (1 H, 2 t, J = 5.5, 2 Hz, olefinic), 7.73 (1 H, 2 t, J = 5.5, 2.5 Hz, olefinic); IR (neat) 3400 (br s, OH), 2940 (m), 1690 (s, C=O), 1595 (m), 1440 (m), 1360 (m), 1060 (m), 780 (m) cm^{-1}; mass spectrum, m/e 126 (M^+, 9), 108 (10), 97 (33.5), 95 (15), 82 (100), 81 (19), 79 (28.5), 67 (22); high-resolution mass spectrum, m/e 126.0655 (calcd for $C_7H_{10}O_2$ 126.0681).

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Registry No. 1, 2175-91-9; 2, 3061-65-2; 3a, 87371-52-6; 3b, 87371-53-7; 4 (isomer 1), 87371-54-8; 4 (isomer 2), 87371-55-9; 5, 87371-56-0; 7, 87371-57-1; 8, 87371-58-2; 9, 37939-82-5; 10, 87371-59-3; 12, 87371-60-6; 13, 87393-25-7; 14, 87371-61-7; 15, 87371-62-8.

Mercury in Organic Chemistry. 25.[1] Rhodium(I)-Catalyzed Alkenylation of Arylmercurials

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Arylmercurials and vinyl halides are catalytically cross-coupled to aryl olefins in fair to good yields by 10% $ClRh(PPh_3)_3$. This reaction appears to proceed through an arylvinylrhodium(III) intermediate.

Organomercurials are attractive synthetic intermediates due to their ready availability, stability, and ability to accommodate almost all important organic functional groups. A number of important synthetic applications of these compounds are now known.[2] Until recently, however, there have been few methods available for the direct alkylation of organomercurials. Lately, procedures based

(1) For part 24 see: Larock, R. C.; Liu, C. L. *J. Org. Chem.* **1983**, *48*, 2151.

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