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ENDO-TRICYCLO[6.2.1.$0^{2,7}$]UNDEC-9-ENE-3,6-DIONE:

A VERSATILE SYNTHETIC INTERMEDIATE

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Abstract: Low-temperature ozonolyses of acetone, methylene chloride, or methylene chloride-methanol solutions of the title compound (**1**) were studied. Five different reaction workup procedures were employed, each of which afforded a different major product. The structures of five of the reaction products (or solid derivatives prepared therefrom), i.e., compounds **3**, **5**, **6**, **8**, and **10**, were established unequivocally via single crystal X-ray structural analysis.

Introduction. Substituted norbornenes that result via Diels-Alder cycloadditions of cyclopentadienes to a variety of olefinic dienophiles have been employed extensively as intermediates in the synthesis of natural products.[1,2] In addition, the endo Diels-Alder adducts formed via [4 + 2] cycloaddition of substituted cyclopentadienes to substituted *p*-benzoquinones have served as intermediates for synthesizing pentacyclic cage compounds[3] and cis,cisoid,cis linear triquinanes.[4]

As part of a continuing program that is concerned with the synthesis and chemistry of novel polycyclic cage compounds,[3] we have investigated the ozonolysis of endo-tricyclo[6.2.1.$0^{2,7}$]undec-9-ene-3,6-dione (**1**). In particular, we find that the nature of the ozonolysis products obtained from **1** is influenced strongly by the reaction conditions and workup procedures employed. The results presented below suggest that **1** is an unusually versatile intermediate that can be used to synthesize a variety of oxygen-containing polycyclic systems.

Compound **1** has been synthesized previously from the readily available[5] endo-tricyclo[6.2.1.$0^{2,7}$]undeca-4,9-diene-3,6-dione (**2**, Scheme 1) via reduction of the enedione C=C double bond in **2** with Ti(III)[6] and also with NaI-HCl.[7] In the present study, we find that this reduction can be performed conveniently and in high yield (94%) by using Zn-HOAc.[8]

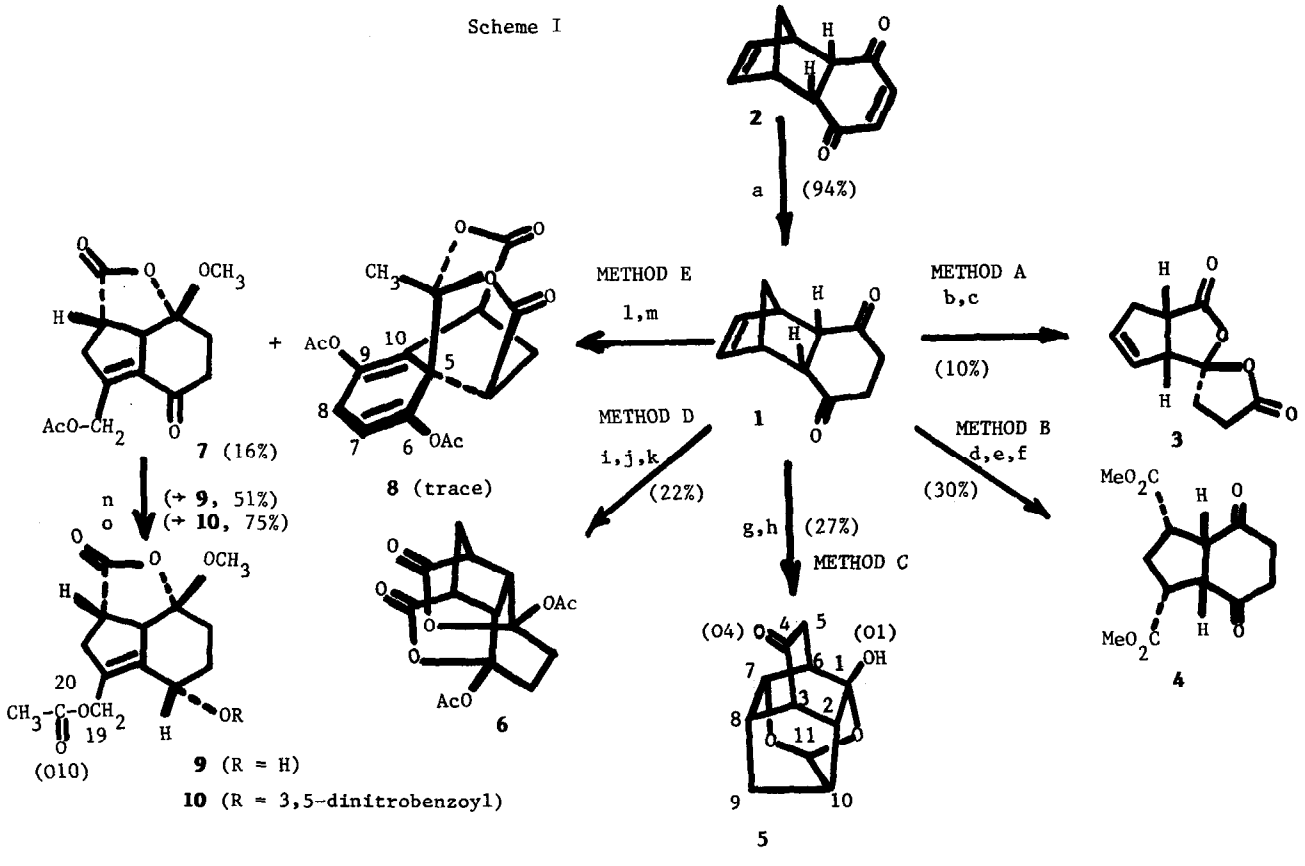
Results and Discussion. Acetone, methylene chloride, or methylene chloride-methanol solutions of **1** were ozonolyzed at -78 °C. Five different reaction workup procedures were employed (see the Experimental Section, Methods A-E), each of which afforded a different major product (see Scheme 1). In the first of these procedures, the product of low temperature ozonolysis (-78 °C) of an acetone solution of **1** was treated with Jones' reagent[9] at -78 °C → +25 °C. Column chromatographic purification of the material thereby obtained afforded a novel spiro bis(lactone), **3** (10% yield), whose structure was established via single crystal X-ray structural analysis (vide infra).

In Method B, the product of low temperature ozonolysis of a solution of **1** in acetone followed by sequential treatment of the reaction mixture with Jones' reagent[9] and with dimethyl sulfate in the presence of potassium carbonate afforded diester **4** in 30% yield. The structure of **4** was established readily via anlysis of its ^{13}C NMR spectrum. Thus, the proton noise-decoupled ^{13}C NMR spectrum of **4** contains only seven resonances, thereby indicating the presence of a twofold symmetry element in **4**. The presence of ester and ketone C=O moieties in **4** is suggested by the appearance of resonances at δ 173.47 and 206.10, respectively. Both peaks are singlets in the corresponding off-resonance decoupled ^{13}C NMR spectrum.

In the third procedure, low temperature ozonolysis of a methylene chloride solution of **1** followed by treatment of the reaction mixture with hydrogen chloride gas produced an unusual cage acetal, **5**, in 27% yield. The structure of **5** was established via X-ray crystallographic methods (vide infra).

In Method D, low temperature ozonolysis of a solution of **1** in acetone followed by sequential treatment of the reaction mixture with (i) Jones' reagent[9] at -78 °C → +25 °C and (ii) acetic anhydride-triethylamine afforded polycyclic bis(lactone) diacetate **6** in 22% yield. The structure of **6** was established via X-ray crystallographic techniques (vide infra).

Scheme I



(a) Zn, HOAc, 25 °C, 4 h; (b) O_3, acetone, -78 °C, 40 min; (c) Jones oxidation, -78 °C → +25 °C, 16 h; (d) O_3, acetone, -78 °C, 1 h; (e) Jones oxidation, -78 °C → +25 °C, 2 h; (f) $(MeO)_2SO_2$, K_2CO_3, 25 °C, 24 h; (g) O_3, CH_2Cl_2, -78 °C; (h) HCl (g), -78 °C → +25 °C, 20 h; (i) O_3, acetone, -78 °C, 1 h; (j) Jones oxidation, -78 °C → +25 °C, 1 h; (k) Ac_2O, Et_3N, 25 °C, 24 h; (l) O_3, 9:1 (v/v) CH_2Cl_2-CH_3OH, -78 °C, 40 min; (m) Ac_2O, Et_3N, 0 °C → +25 °C, 19 h; (n) $NaBH_4$, $CeCl_3 \cdot 7H_2O$, CH_3OH, 0 °C → +25 °C, 1 h; (o) 3,5-dinitrobenzoyl chloride, pyridine, 25 °C, 4.5 h.

Finally, low temperature ozonolysis of a solution of **1** in 9:1 dichlormethane-methanol followed by treatment of the reaction mixture with acetic anhydride-triethylamine gave two products: (i) tricyclic ketoester **7** (16%) and (ii) another novel polycyclic bis(lactone) diacetate, i.e., **8** (trace amount). Compound **7** was reduced stereospecifically by sodium borohydride-cerous chloride[10] to afford the corresponding alcohol, **9**, which was reacted subsequently with 3,5-dinitrobenzoyl chloride[11] to afford the corresponding 3,5-dinitrobenzoate ester, **10**. The structure of **10** was established via X-ray crystallographic methods (vide infra).

X-ray Structural Analyses of 3, 5, 6, 8, and 10. Pertinent X-ray data for these five reaction products appear in Table I. There are no unusual bond angles or bond lengths in **3**. The three five-membered rings in **3** occupy flattened envelope conformations. The calculated (MM2)[12] strain energy for this compound is 19.10 kcal/mol.

There are no unusual bond lengths in **5**. The C(2)C(3)C(8)C(9)(C10) five-membered ring in **5** (see Scheme 1 for numbering of atoms in **5**) occupies a sharply folded envelope conformation that results in three angles being less than 100°. Two of the six-membered rings in this compound are in twist- or skew-boat conformations, while the third, the C(1)O(11)C(11)O(7)C(7)C(6) heterocycle, would lie near the conformational energy maximum between boat and chair were the ring to instead be fully carbocyclic. Despite the small bond angles and unusual conformations noted above, the calculated[12] strain energy for **5** is only 27.67 kcal/mol. There is an intermolecular hydrogen bond between O(4) of one molecule and the hydroxyl O(1) of another, such that the bond distance O(4)...O(1) is 2.826 (2) A.

Compound **6** contains no unusual bond lengths or bond angles. The six-membered ring occupies a distorted 1,3-diplanar conformation. Two of the five-membered rings exist in flattened envelope conformtions, while the third occupies a flattened half-chair conformation. The calculated[12] strain energy of **6** is quite small, i.e., only 4.02 kcal/mol.

Compound **8** likewise contains no unusual bond lengths or bond angles. The C(5)C(6)C(7)C(8)C(9)C(10) six-membered ring in **8** exists in a very flattened boat conformation with a maximum internal torsion angle of 12.4 (4)°. The other six-membered ring occupies a twisted 1,2-diplanar conformation. The five-membered rings occupy twisted half-chair conformations. The calculated[12] strain energy of **8** is 19.10 kcal/mol.

Determination of the X-ray crystal structure of **10** was complicated by the fact that

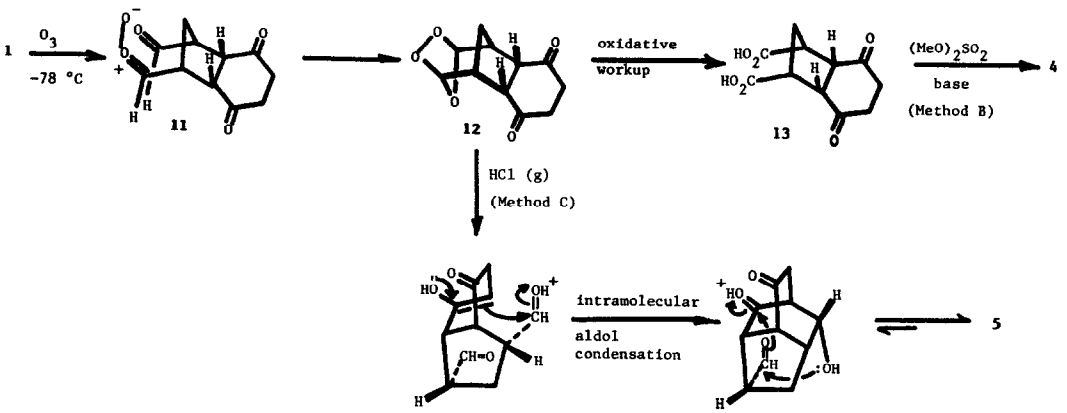
Table I. X-ray crystal structure data

	3	**5**	**6**	**8**	**10**
Formula	$C_{10}H_{10}O_4$	$C_{11}H_{12}O_4$	$C_{15}H_{16}O_8$	$C_{17}H_{16}O_8$	$C_{21}H_{20}O_{11}N_2$
Crystal Dimensions (mm)	.52 x .28 x .23	.42 x .27 x .25	.52 x .45 x .25	.45 x .30 x .06	.48 x .35 x .18
Space group	$P2_1/a$	Pccn	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	6.493 (1)	10.493 (3)	11.021 (3)	7.475 (1)	10.944 (4)
b (Å)	16.824 (5)	17.677 (4)	11.363 (2)	10.118 (3)	20.935 (9)
c (Å)	8.393 (2)	9.426 (2)	13.327 (2)	10.880 (3)	10.523 (4)
α (°)	-	-	-	91.69 (1)	-
β (°)	100.34 (2)	-	114.21 (1)	106.65 (1)	117.19 (3)
γ (°)	-	-	-	102.29 (2)	-
V (Å^3)	901.9 (4)	1748.4 (6)	1522.2 (4)	766.7 (5)	2145 (1)
Z	4	8	4	2	4
D_x (g-cm^{-3})	1.430	1.582	1.415	1.509	1.475
F(000)	408	880	680	364	992
μ(cm^{-1})	1.04	1.13	1.09	1.13	1.13
Transmission factors	.923-.961	.920-.938	.899-.962	.895-.967	.918-.963
2θ range (°)	3-55	3-55	3-55	3-55	3.50
Lattice parameters					
2θ range (°)	23.71-29.30	23.40-28.95	23.50-28.29	24,03-29.16	22.23-28.81
Check reflections	$(\bar{2}32)(\bar{2}44)$	$(1\bar{1}5)(\bar{3}70)$	$(02\bar{4})(03\bar{6})$	$(03\bar{2})(\bar{2}21)$	$(\bar{1}\bar{1}3)(250)$
hkℓ range	-8,8;0,21;0,10	-4,13;0,22;0,12	-14,14;-2,14;0,17	-9,9;-13,13;0,14	-13,13;0,24;-2,12
Total reflections	2329	3335	4603	3793	5027
R (merge)	.006	.006	.009	.006	.009
Independent reflections	2072	2018	3498	3524	3781
Number >3σ(I)	1601	1607	2684	2448	2413
Number parameters	167	184	272	290	389
R (R_{all})	.0440 (.0594)	.0455 (.0595)	.0476 (.0637)	.0536 (.0821)	.0731 (.1160)
wR (wR_{all})	.0438 (.0454)	.0417 (.0430)	.0511 (.0530)	.0473 (.0502)	.0339 (.0358)
$(\Delta/\sigma)_{max}$	.008	.066	.010	.029	.027
S	1.651	1.674	1.543	1.453	1.795
Residual peaks (eÅ^{-3})	-.16;.18	-.19;.30	-.19;.26	-.24,.35	-.30,.31
g (weighting)	.00017	.00014	.00036	.00021	.0000

its C(19) acetate group is disordered due to the existence of a 180° rotation about the C(20)-O(10) bond in crystalline **10**. Nevertheless, refinement of the X-ray structural data proceeded well (see X-ray data presented in the last column of Table I). There appear to be no unusual bond lengths in **10**.

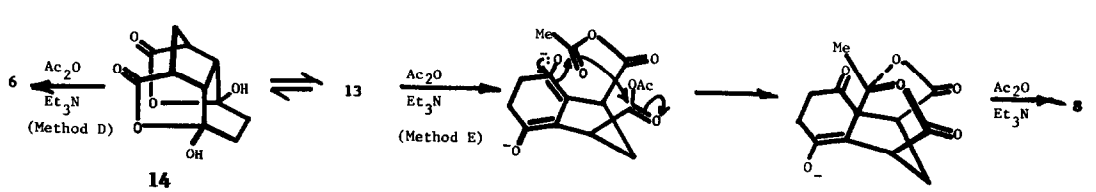
Mechanistic Considerations. Carbonyl ylide **11**[13] appears to play a pivotal role in the ozonolysis of **1**. Thus, recyclization of **11** can occur to afford the corresponding ozonide, **12**. Oxidative workup of **12** is expected[13] to afford the corresponding bicyclic diketo diacid, **13**, which is O-methylated by dimethyl sulfate in the presence of base, thereby affording **4** (Method B). Alternatively, acidic workup of **12** results in intramolecular aldol condensation, ultimately producing **5** (Method C; see Scheme 2).

Scheme 2



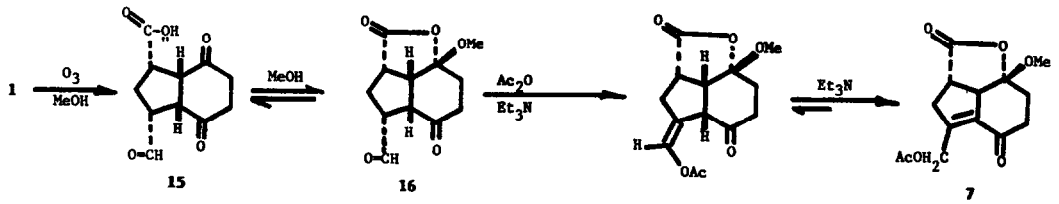
Compound **13** is in equilibrium with the corresponding bis(hemiketal), **14**. In Method D, **14** is trapped by acetic anhydride to afford **6** (Scheme 3). Alternatively, **13** can react with acetic anhydride-triethylamine in the manner shown in Scheme 3, thereby affording **8** (Method E).

Scheme 3



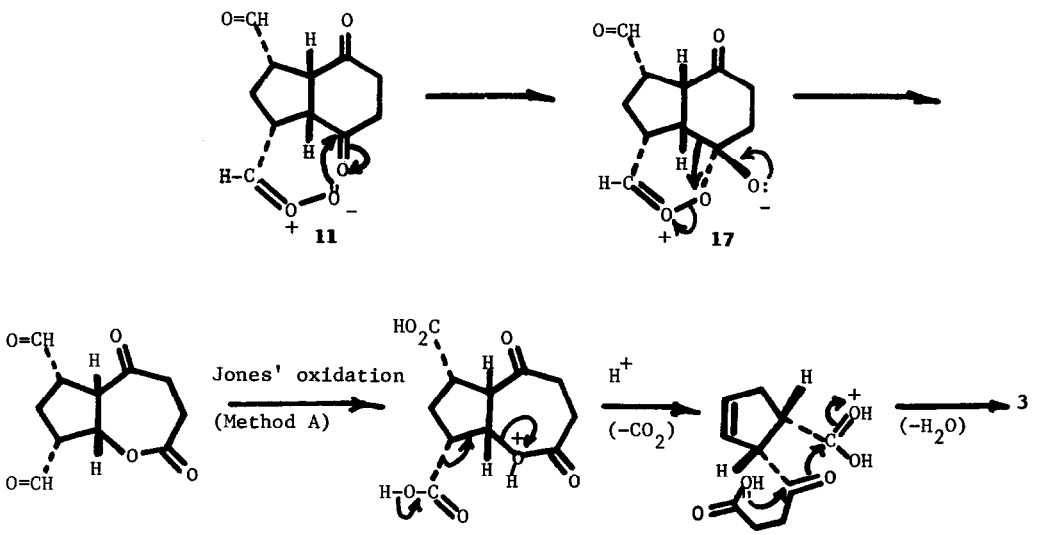
Formation of **7** via Method E can be accounted for in terms of the mechanism shown in Scheme 4. Schreiber and coworkers[14] have shown that ozonolytic cleavage of cycloalkenes when performed in the presence of methanol affords terminally differentiated products of the type $HO_2C-(CH_2)_n-CHO$. Thus, ozonolysis of methanolic **1** is expected to produce **15** which is then converted into the corresponding ketal, **16**. Workup of **16** with acetic anhydride in the presence of triethylamine results in O-acylation with subsequent base promoted isomerization of the C=C double bond in the resulting enol acetate, thereby affording **7**.

Scheme 4



Alternatively, carbonyl ylide **11** can cyclize to form **17**, which is related structurally to the indermediate produced in the Baeyer-Villiger reaction.[15] Further transformation of **17** then can occur in the manner shown in Scheme 5 to produce **3** (Method A).

Scheme 5



Summary and Conclusions. Low temperature ozonolysis of **1** has been employed as a method for synthesizing several unusual polycyclic compounds. The course of this reaction was found to be influenced strongly by the workup conditions employed. The results presented herein suggest that **1** is an astonishingly versatile intermediate that can be used to synthesize a wide variety of novel, oxygen-containing polycyclic compounds.

Experimental Section

Melting points are uncorrected. High-resolution mass spectra were obtained by personnel at the Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska, Lincoln, NE 68588-0362.

Reduction of 2 with Zinc-Acetic Acid. To a solution of **2**[5] (2.00 g, 11.5 mmol) in glacial acetic acid (20 mL) in a 50 mL round-bottom flask was added zinc dust (5.0 g, 0.076 g-atom, excess). The flask was fitted with a calcium chloride drying tube, and the resulting mixture was stirred at room temperature for 4 h. Methylene chloride (100 mL) was then added, and the resulting mixture was filtered. The filtrate was concentrated in vacuo. The residue, a pale brown oil, was purified via column chromatography on silica gel by using 30% ethyl acetate-hexane mixed solvent as eluent. Pure **3** (1.9 g, 94%) was thereby obtained as a colorless oil. The IR spectrum and ^{1}H and ^{13}C NMR spectra of this material were in agreement with corresponding literature values.[7]

Ozonolysis of 1. Method A. A solution of **1** (3.90 g, 22.1 mmol) in acetone (70 mL) was cooled externally to -78 °C. Ozone then was passed through this cold solution, and the progress of the reaction was monitored via thin layer chromatography. Passage of ozone was continued until all of the starting material had been consumed (ca. 40 min.). Meanwhile, Jones' reagent was prepared by adding concentrated sulfuric acid (11.5 mL, 210 mmol) dropwise with stirring to a cooled (external ice-water bath) solution of chromium(VI) oxide (13.35 g, 134 mmol) in water (20 mL) and then by diluting the resulting solution to a total volume of 50 mL.[9] The freshly prepared Jones' reagent (40 mL, excess) then was added dropwise with stirring to the ozonolyzed reaction mixture during ca. 30 min. The resulting mixture was stirred for 16 h, during which time the temperature of the reaction mixture rose gradually to room temperature. The reaction mixture was filtered via rapid passage through a short silica gel column, and the filtrate was concentrated in vacuo. The

residue thereby obtained was purified via column chromatography on silica gel by using 30% ethyl acetate-hexane mixed solvent as eluent. Pure **3** (450 mg, 10%) was thereby obtained as a colorless microcrystalline solid: mp 110-111 °C; IR (KBr) 1777 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 2.37 (m, 1 H), 2.55 (m, 2 H), 2.83 (m, 3 H), 3.42 (m, 1 H), 3.72 (m, 1 H), 5.66 (m, 1 H), 5.98 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.19 (t), 29.47 (t), 36.48 (t), 41.99 (d), 54.88 (d), 112.90 (s), 125.29 (d), 134.73 (d), 174.16 (s), 177.71 (s); mass spectrum (70 eV), m/e (relative intensity) (no molecular ion), 150 (8.2), 66 (100.0), 56 (9.2). Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.89; H, 5.14. The structure of **3** was established unequivocally via X-ray crystallographic methods (vide infra).

Method B. A solution of **1** (0.90 g, 5.1 mmol) in acetone (20 mL) was cooled externally to -78 °C. Ozone then was passed through this cold solution, and the progress of the reaction was monitored via thin layer chromatography. Passage of ozone was continued until all of the starting material had been consumed (ca. 60 min.), at which time Jones' reagent (prepared as described in Method A, above)[9] (10 mL, excess) was added. The reaction mixture was stirred for 2 h, during which time the temperature of the reaction mixture rose gradually to room temperature. Isopropanol (ca. 4-5 mL) was added gradually to the resulting red-brown reaction mixture to destroy excess Jones's reagent that might be present. Addition of isopropanol was stopped immediately after the red-brown color had been discharged. Diethyl ether (ca. 30-40 mL) then was added until all of the green Cr(III) salts had precipitated. The resulting mixture was filtered via rapid passage through a short silica gel column. The filtrate was concentrated in vacuo, and the residue, a viscous oil, was dissolved in dry acetone (30 mL). Dimethyl sulfate (1.70 g, 13.4 mmol) and anhydrous potassium carbonate (2.00 g, 14.4 mmol) were added, and the resulting mixture was stirred under argon at room temperature for 24 h. The reaction mixture then was filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography on silica gel by using a 30-50% EtOAc-hexane mixed solvent gradient elution scheme. The first chromatography fractions afforded pure **4** (409 mg, 30%) as a colorless microcrystalline solid: mp 104-105 °C; IR (KBr) 2966 (br, m), 1726 (vs), 1700 (vs) 1450 (s) 1187 cm^{-1} (vs); ^{1}H NMR ($CDCl_3$) δ 2.03 (ddt, J_1 = 13.2 Hz, J_2 = 1.0 Hz, J_3 = 9.3 Hz, 1 H), 2.31 (dt, J_1 = 13.2 Hz, J_2 = 7.8 Hz, 1 H), 2.61 (m, 2 H), 2.97

(m, 2 H), 3.17 (m, 2 H), 3.69 (s, 6 H), 3.74 (dd, J_1 = 4.6 Hz, J_2 = 2.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 32.73 (t), 37.15 (t), 44.93 (d), 52.39 (d), 54.43 (q), 173.47 (s), 206.10. Anal. Calcd for $C_{13}H_{16}O_6$: C, 58.20; H, 6.01. Found: C, 58.43; H, 5.99. The structure of **4** was established unequivocally via X-ray crystallographic methods (vide infra).

Continued elution of the chromatography column with 50% ethyl acetate-hexane gave another material (97 mg) that was not identified.

Method C. A solution of **1** (1.2 g, 6.8 mmol) in methylene chloride (25 mL) was cooled externally to -78 °C. Ozone then was passed through this cold solution, and the progress of the reaction was monitored via thin layer chromatography. Passage of ozone was continued until all of the starting material had been consumed and a blue color persisted, at which time argon gas was passed through the reaction mixture to purge excess ozone. Excess hydrogen chloride gas [prepared via reaction of sodium chloride (5.96 g, 102 mmol) with concentrated sulfuric acid (10.2 g, 102 mmol] was bubbled through the reaction mixture. The reaction mixture then was stirred for 20 h, during which time the temperature of the reaction mixture rose gradually to room temperature. The reaction mixture was concentrated in vacuo, and the residue, a black solid, was triturated with hot ethyl acetate (4 x 50 mL). The combined organic extracts were filtered, and the filtrate was concentrated in vacuo. The residue was purified via flash column chromatography on silica gel by eluting with pure ethyl acetate. Compound **5** (387 mg, 27%) was thereby obtained as a colorless microcrystalline solid. Recrystallization of this material from ethyl acetate-hexane mixed solvent afforded pure **5**: mp 235-240 °C (dec.); IR (KBr) 3346 (br, s), 1700 cm^{-1} (vs); ^1H NMR (DMSO-d_6) δ 1.19 (ddd, J_1 = 11.1 Hz, J_2 = 5.4 Hz, J_3 = 2.5 Hz, 1 H), 1.60 (d, J = 11.1 Hz, 1 H), 2.00 (dd, J_1 = 18.8 Hz, J_2 = 2.0 Hz, 1 H), 2.10-2.16 (m, 2 H), 2.31 (dd, J^1 = 18.8 Hz, J_2 = 4.1 Hz, 1 H), 2.47-2.60 (m, 2 H), 2.86-2.94 (m, 1 H), 3.48 (br s, 1 H), 4.30 (dd, J_1 = 8.1 Hz, J_2 = 4.1 Hz, 1 H), 5.34 (d, J = 5.2 Hz, 1 H); ^{13}C NMR (DMSO-d_6) δ 26.76 (t), 35.89 (t), 37.49 (d), 40.58 (d), 44.88 (d), 49.56 (d), 51.91 (d), 69.82 (d), 99.30 (d), 104.06 (s), 213.35 (s). Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.64; H, 5.89. The structure of **5** was established unequivocally via X-ray crystallographic methods (vide infra).

Method D. A solution of **1** (1.80 g, 10.2 mmol) in acetone (30 mL) was cooled externally to -78 °C. Ozone then was passed through this cold solution, and the progress of the reaction was monitored via thin layer chromatography. Passage of ozone was continued until all of the starting material had been consumed (ca. 60 min.). Argon gas was passed through the reaction mixture to purge excess ozone. Jones' reagent (prepared as described in Method A, above)[9] (10 mL, excess) was added to the reaction mixture at -78 °C. The cold bath was removed, and the reaction mixture was stirred for 1 h, during which time the temperature of the reaction mixture rose gradually to room temperature. Isopropanol (ca. 2-3 mL) was added gradually to the resulting red-brown reaction mixture to destroy excess Jones' reagent that might be present. Addition of isopropanol was stopped immediately after the red-brown color had been discharged. The supernatant liquid was decanted from the green precipitated Cr(III) salts. The remaining precipitate was washed with acetone (5 x 40 mL), and the washings were combined and added to the supernatant liquid. The resulting solution was filtered via rapid passage through a short silica gel column, and the filtrate was concentrated in vacuo. The residue, a viscous brown oil, was dried in vacuo (room temperature, 2 mm Hg) for 3 h. To this material was added triethylamine (5 mL, excess) and acetic anhydride (5 mL, excess), and the resulting mixture was stirred at room temperature for 24 h. The reaction mixture then was concentrated in vacuo, and the residual brown oil was purified by column chromatography on silica gel by using a 20-35% ethyl acetate-hexane gradient elution scheme. Pure **6** (743 mg, 22%) was thereby obtained as a colorless microcrystalline solid: mp 176-177 °C; IR (KBr) 1798 (vs), 1748 cm^{-1} (vs); ^{1}H NMR ($CDCl_3$) δ 2.07 (m, 10 H), 2.26 (m, 2 H), 2.64 (dt, J_1 = 14.0 Hz, J_2 = 9.0 Hz, 1 H), 3.60 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 21.72 (q), 29.92 (t), 32.55 (t), 48.72 (d), 49.29 (d), 105.94 (s), 169.46 (s), 175.25 (s). Anal. Calcd for $C_{15}H_{16}O_8$: C, 55.56; H, 4.97. Found: C, 55.90; H, 5.00. The structure of **6** was established unequivocally via X-ray crystallographic methods (vide infra).

Method E. A solution of **1** (850 mg, 4.7 mmol) in 9:1 (v/v) methylene chloride-methanol mixed solvent (10 mL) was cooled externally to -78 °C. Ozone then was passed through this cold solution for 40 min; argon gas then was passed through the reaction mixture to purge excess ozone. The resulting solution was concentrated in vacuo. Benzene (20 mL) was added,

and methanol was removed by azeotropic distillation. This process was repeated a total of four times to insure that all methanol had been removed. The residue, a viscous oil, was dried in vacuo (1 torr.); methylene chloride (10 mL) then was added, and the resulting solution was cooled externally by application of an ice-water bath. Triethylamine (4.8 g, 47 mmol) and acetic anhydride (4.8 g, 47 mmol) were added sequentially. The resulting mixture was stirred for 19 h, during which time the temperature of the reaction gradually increased to room temperature. The raction mixture was concentrated in vacuo, and the residual brown oil was purified via column chromatography on silica gel by using a 20-25% ethyl acetate-hexane gradient elution scheme. Pure **7** (211 mg, 16%) was thereby obtained as colorless needles: mp 106-107 °C: IR (KBr) 1765 (vs), 1717 (vs), 1681 (s), 1630 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.81 (dt, J_1 = 14.8 Hz, J_2 = 4.2 Hz, 1 H); 2.00 (s, 3 H), 2.39 (m, 2 H), 1.54 (m, 1 H), 2.95 (m, 2 H), 3.33-3.39 (complex m, which contains an OCH_3 singlet at δ 3.37, 4 H), 3.62 (dq, J_1 = 7.8 Hz, J_2 = 2.1 Hz, 1 H), 4.87 (AB, J_{AB} = 16.5 Hz, 1 H); 5.08 (AB, J_{AB} = 16.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.15 (q), 28.82 (t), 37.71 (t), 37.93 (t), 41.84 (d), 49.89 (d), 54.02 (q), 60.01 (t), 109.74 (s), 131.40 (s), 150.65 (s), 169.65 (s), 177.89 (s), 196.64 (s). Anal. Calcd for $C_{14}H_{16}O_6$: C, 60.00; H, 5.75. Found: C, 59.88; H, 5.77.

On one occasion, a minor product, **8**, was isolated when we attempted to purify the product of the above reaction via recrystallization from benzene-hexane mixed solvent. A very minute quantity of material (ca. 2 mg) was thereby obtained as tiny, colorless crystals: mp 191-192 °C; Anal. Calcd for $C_{17}H_{16}O_8$: (M_r + Li) 355.1006; Found (high-resolution fast atom bombardment mass spectrometry): (M_r + Li) 355.1010. The structure of **8** was established unequivocally via X-ray crystallographic methods (vide infra).

$NaBH_4$-$CeCl_3$ Reduction of 7.[10] A solution of **7** (320 mg, 1.14 mmol) and cerous chloride heptahydrate (426 mg, 1.14 mmol) in dry methanol (10 mL) was cooled externally (ice-water bath) to 0 °C. To this cooled solution was added with stirring sodium borohydride (48 mg, 1.26 mmol). After all of the reducing agent had been added, the cold bath was removed, and the reaction mixture was stirred for 1 h. Water (40 mL) and ethyl acetate (40 mL) then were added, and the layers were separated. The aqueous layer was extracted with ethyl

acetate (2 x 20 mL), and the combined organic extracts were dried (anhydrous sodium sulfate) and filtered. The filtrate was concentrated in vacuo, and the residue was purified via column chromatography on silica gel by using a 20–30% ethyl acetate–hexane gradient elution scheme. Compound **9** (164 mg, 51%) was thereby obtained as a colorless oil; IR (film) 3453 (br, s), 1771 (s), 1725 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.35 (dq, J_1 = 11.5 Hz, J_2 = 2.0 Hz, 1 H), 1.71 (dt, J_1 = 15.9 Hz, J_2 = 5.4 Hz, 1 H), 1.88–2.00 Hz (complex m which contains a methyl singlet at δ 1.94, 4 H), 2.42 (dt, J_1 = 14.4 Hz, J_2 = 4.0 Hz, 1 H), 2.62 (s, 2 H), 3.10 (s, 2 H), 3.26 (s, 3 H), 4.15–4.30 (complex m, 2 H), 4.70 (AB, J_{AB} = 12.5 Hz, 1 H), 4.99 (AB, J_{AB} = 12.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.72 (q), 28.38 (t), 31.69 (t), 37.00 (t), 42.51 (d), 49.94 (d), 56.32 (q), 60.31 (t), 70.63 (d), 107.60 (s), 129.93 (s), 139.97 (s), 172.09 (s), 180.03 (s). Compound **9** was further characterized via its corresponding 3,5-dinitrobenzoate derivative (i.e., **10**, vide infra).

Reaction of 9 with 3,5-Dinitrobenzoyl Chloride. Compound **9** (98 mg, 0.35 mmol) was converted into the corresponding 3,5-dinitrobenzoate derivative via reaction with 3,5-dinitrobenzoyl chloride (98 mg, 0.43 mmol) in the presence of dry pyridine (3 mL) at room temperature for 4.5 h.[11] The reaction was cooled externally to 0 °C and then was quenched via addition of 5% aqueous hydrochloric acid solution (30 mL). The resulting mixture was extracted with methylene chloride (3 x 30 mL). The combined organic extracts were washed with brine (30 mL), dried (anhydrous sodium sulfate), and filtered. The filtrate was concentrated in vacuo, and the residue was purified via column chromatography by using a 10–20% ethyl acetate–hexane gradient elution scheme. Pure **10** (123 mg, 75%) was thereby obtained as a colorless microcrystalline solid: mp 183–184 °C; IR (KBr) 3047 (m), 2948 (m), 1773 (s), 1733 (s), 1718 (s), 1548 (s), 1356 (s), 1286 (s), 1251 (s), 933 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.64–2.24 (complex m which contains a methyl singlet at δ 1.95, 7 H), 2.59 (dt, J_1 = 14.2 Hz, J_2 = 4.0 Hz, 1 H), 2.83 (br s, 2 H), 3.30 (m, 1 H), 3.38 (s, 3 H), 4.71 (s, 2 H), 5.86 (br d, J = 11.0 Hz, 1 H), 9.11–9.18 (m, 2 H), 9.21 (t, J = 2.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.51 (q), 28.33 (t), 26.68 (t), 37.92 (t), 42.53 (d), 50.28 (q), 56.80 (d), 59.44 (t), 73.69 (d), 107.08 (s), 122.76 (d), 129.41 (d), 132.86 (s), 133.17 (s), 148.73 (s), 161.72 (s), 170.50 (s), 179.38 (s), 179.43 (s). Anal. Calcd for $C_{21}H_{20}N_2O_{11}$: C, 52.95; H, 4.23. Found: C, 52.96. H, 4.19. The structure of **10** was

established unequivocally via single crystal X-ray structural analysis (vide infra).

X-ray Crystal Structure Determinations.[16] All X-ray data were collected on a Nicolet R3M/μ update of a $P2_1$ diffractometer. Intensity data were collected in the ω-scan mode by using a variable scan rate (4 to 29.3 deg min^{-1}) and graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Lattice parameters were obtained by a least-squares refinement of 25 reflections. Lorentz-polarization corrections and a ψ-scan based empirical absorption correction were applied. The structures were solved by direct methods, and the parameters were refined by using a block-cascade least-squares technique. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where the weighting factor is given by $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. All computer programs were supplied by Nicolet Instrument Company for Desktop 30 Microeclipse and Nova 4/C configuration. Atomic scattering factors and anomalous dispesion corrections were taken from the International Tables for X-ray Crystallography.[17]

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