Regiospecific Baeyer–Villiger Oxidation of Polycyclic Ketones with Ceric Ion

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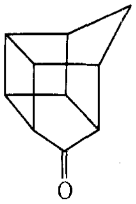
Received June 2, 1975

Efficient and preparatively useful Baeyer–Villiger (BV) oxidation of a few polycyclic ketones with ceric ion is reported. The BV oxidation of pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one (1,3-bishomocubanone, 1) and pentacyclo[6.2.1.0^{2,7}.0^{4,10}.0^{5,9}]undecane-3,6-dione (3) with ceric ion proceeds regiospecifically and the results differ from those of conventional peracid oxidation. A plausible mechanism is advanced to explain the regiospecificity of ceric ion oxidations.

A variety of organic functional groups can be conveniently oxidized with ceric ion and many of these reactions find some useful synthetic applications.[2,3] It has been shown that alicyclic ketones are rapidly consumed by ceric ion to furnish ω-nitratocarboxylic acids as the main products via a pathway involving α-cleavage.[4] A sole exception[4] is the ceric ion oxidation of adamantanone, which furnishes the corresponding Baeyer–Villiger lactone in good yield. In pursuit of certain synthetic objectives, we have investigated the ceric ion oxidation of three pentacyclic ketones, pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one (1,3-bishomocubanone, 1), pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one (1,4-bishomocubanone, 2), and pentacyclo[6.2.1.0^{2,7}.0^{4,10}.0^{5,9}]undecan-3,6-dione (3), and find that these compounds undergo efficient Baeyer–Villiger (BV) type oxidation. Furthermore, the oxidation of unsymmetrical 1,3-bishomocubanone (1) and pentacyclic diketone 3 proceeds in a highly regiospecific manner to yield a lactone different from that obtained by the conventional peracid oxidation. We believe that this observation may be of general synthetic utility in carrying out regiospecific BV oxidations[5] of geometrically constrained polycyclic ketones with ceric ion.



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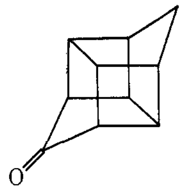

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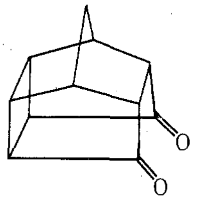

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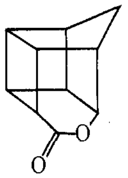
Reaction of 1,3-bishomocubanone (1) with a slurry of ceric ammonium sulfate (CAS) or ceric ammonium nitrate (CAN) in aqueous acetonitrile furnished a single product, mp 133–135 °C, in 78% yield. Mass spectral measurements (M^+ m/e 162) and strong infrared absorptions at 1760, 1180, and 1000 cm^{-1} suggested a δ-lactone (boat)[6] structure for the product. This contention was clearly supported by the ^{1}H NMR spectrum, which displayed a 1 H quartet at δ 5.05 (J_1 = 4 and J_2 = 3 Hz) due to the presence of a H–C–O–C=O type proton and mass spectral peaks at m/e 118 ($M^+ - CO_2$) and 117 ($M^+ - CO_2H$). These data are compatible with either structure 4 or 5 for the CAS oxidation product. At this stage, in order to confirm that the ceric ion oxidation product was indeed a BV product, peracid oxidation of 1 was investigated. When 1 was treated with *m*-chloroperbenzoic acid, a 5:1 mixture of two lactones was obtained. The major compound (M^+ m/e 162), mp 145–146 °C, showed typical δ-lactone (boat)[6] bands at 1755 and 1070 cm^{-1} and was distinctly different from the lactone obtained via CAS oxidation of 1. Its ^{1}H NMR spectrum, as expected, showed a triplet at δ 4.71 (J = 6 Hz) due to a H–C–O–C=O type proton. This data was suggestive of either structure 4 or 5 for the lactone. The minor product from the peracid oxidation, however, proved to be identical with the lactone obtained from CAS oxidation. The ^{1}H NMR data for the two lactones, particularly the multiplicity of the low-field signal, was strongly indicative of their being positional isomers 4 and 5 but was of little diagnostic value in distinguishing them. The possibility of any skeletal rearrangement was ruled out on the basis of the mass spectral fragmentation, which showed strong peaks at m/e 66 ($C_5H_6^+$) diagnostic[7] of this system and resulting from the cleavage of the carbon skeleton in half. A strong peak at m/e 91 ($C_7H_7^+$) attributed[7] to tropylium ion was also observed in all of these compounds. A straightforward degradative scheme[8] was therefore designed and is summarized in Scheme I.



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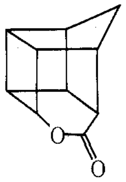

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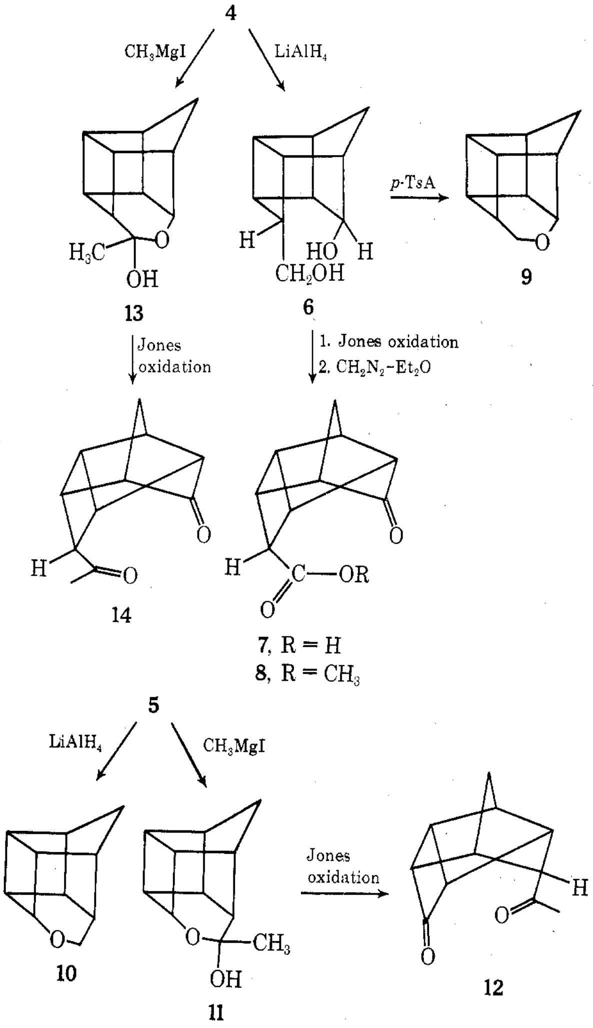
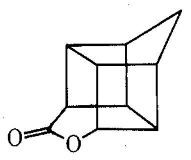
The CAS lactone was reduced by lithium aluminum hydride to the diol 6 and oxidized with Jones reagent to the keto acid 7. Diazomethane esterification of 7 gave the keto ester 8, which displayed ir absorptions at 1740 (cyclopentanone) and 1730 cm^{-1} (ester) along with expected ^{1}H NMR resonances and established the structure of this lactone as 4. Lithium aluminum hydride reduction of the peracid lactone did not furnish any diol and only a pentacyclic ether 10 was formed.[9] An isomeric ether 9 was also prepared from the dehydration of diol 6 but again a distinction between 9 and 10 could not be made on spectral grounds. Addition of methylmagnesium iodide to the peracid lactone yielded the lactol 11 [ir 3550, 1050, 1055 cm^{-1}; ^{1}H NMR δ 1.38 (3 H, singlet)] which was oxidized with Jones reagent to the diketone 12 exhibiting cyclobutanone absorption (1775 cm^{-1}) in the ir spectrum. Analogous degradation of CAS lactone via the lactol 13 [ir 3500, 1010, 1050 cm^{-1}; ^{1}H NMR δ 1.6 (3 H, singlet)] yielded the isomeric dilactone 14 displaying a cyclopentanone absorption (1740 cm^{-1}). The structures of Ce^{4+} and peracid lactones were thus established as 4 and 5, respectively.

The symmetrical 1,4-bishomocubanone (2) on CAS oxidation furnished a crystalline lactone 15, mp 130–132 °C, which showed ir bands at 1755 and 1260 cm^{-1} (δ-lactone)[6]

Scheme I





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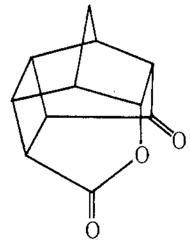

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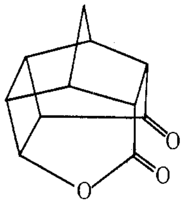

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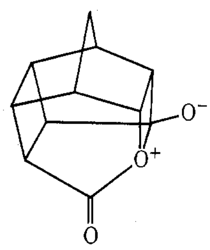

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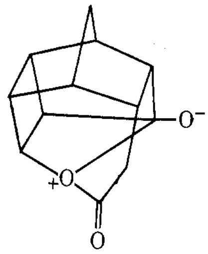

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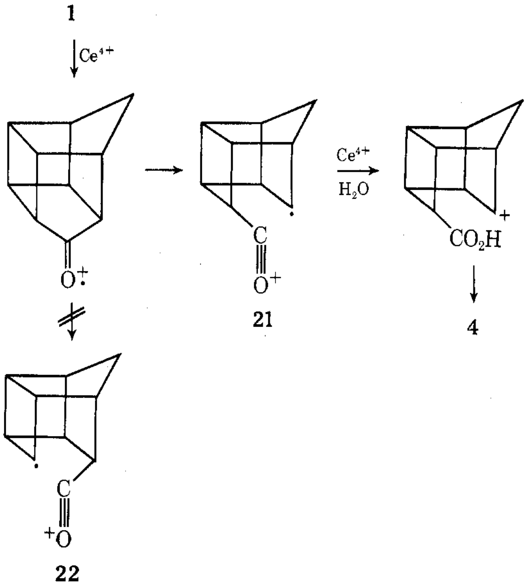
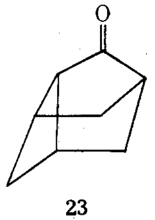
and a proton at δ 5.0 due to H–C–O–C═O type functionality. The same lactone was also obtained from the peracid oxidation of 2.

Oxidation of pentacyclic diketone 3 with CAN in aqueous acetonitrile yielded a single crystalline monolactone **16**, mp 280–282 °C, and its structure was derived from the following spectral characteristics. The δ-lactone 16 exhibited intense carbonyl bands at 1780 and 1725 cm^{-1} and displayed in its ^{1}H NMR spectrum a one-proton triplet at δ 5.17 (J = 7.5 Hz) due to H–C–O–C═O type grouping. The mass spectral (M$^+$ m/e 190) fragmentation with strong peaks at m/e 146 (M$^+$ − CO$_2$), 145 (M$^+$ − CO$_2$H), 118 (M$^+$ − CO$_2$ − CO), and 117 (M$^+$ − CO$_2$ − CO − H) was in complete harmony with a keto lactone structure. The hypsochromic shift of the δ-lactone carbonyl (1780 cm^{-1}) and the bathochromic shift of the cyclopentanone carbonyl (1725 cm^{-1}) in the ir spectrum of 16 can be attributed to the contribution of the form **18**. In the alternative structure **17** for this lactone such an spatial interaction **19** is precluded on account of unfavorable geometry. Reaction of **3** with m-chloroperbenzoic acid under a variety of conditions led to the isolation of only a dilactone **20**, mp >300 °C, ir 1760 cm^{-1} (δ-lactone), MS M$^+$ m/e 207?, and no monolactonic product could be detected. The presence of a second carbonyl group in **3** complicates its peracid oxidation and in this case the preparative utility of ceric ion in effecting BV oxidation is clearly demonstrated.

A plausible mechanism for the formation of lactone **4** in the CAS oxidation of **1** is outlined in Scheme II and is in harmony with the currently accepted mechanism[3] of ceric ion oxidations.[11] The regiospecificity of this reaction can be attributed to the greater stability[12] of cyclopentyl radical intermediate **21** over the cyclobutyl radical intermediate **22.** This selective α-cleavage to furnish the more stable radical intermediate should be useful in the regiospecific BV oxidation of polycyclic ketones and the efficient **3** → **16** oxidation with ceric ion further strengthens this contention. On the other hand, regioselective formation of lactone **5** in the peracid oxidation of **1** clearly indicated preferential migration of cyclobutyl ring vs. the cyclopentyl ring. Recently, Monti and Ward[13] observed in the BV oxidation of tricyclo[3.2.1.0^{3,6}]octan-7-one (**23**) that the cyclobutyl migration was overwhelmingly favored and lactone **24** was exclusively formed. Such preferential migration of cyclobutyl

Scheme II





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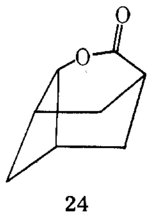

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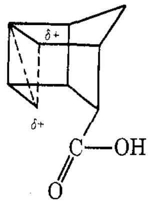
ring was not observed in simple model systems and therefore regiospecific formation of lactone **24** was attributed to the σ-assisted C–C bond cleavage and stabilization of the incipient positive charge through a cyclobutyl–cyclopropyl–carbinyl type resonance. The results obtained with **1** are likewise suggestive of σ participation by the strained C_3–C_4 cyclobutyl bond and stabilization of the developing positive charge via a cyclobutyl–cyclopropyl–carbinyl type resonance **25**. The rigid framework of **1** and the favorable geometrical disposition of the C_3–C_4 bond make this participation possible and it is fully borne out by an examination of molecular models.



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Experimental Section[14]

Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one (1,3-bishomocubanone, **1**),[15] pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one (1,4-bishomocubanone, **2**),[16] and pentacyclo[6.2.1.0^{2,7}.0^{4,10}.0^{5,9}]undecane-3,6-dione (**3**)[17] were prepared according to the literature procedures.

Oxidation of Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one (1) with Ceric Ammonium Sulfate. To a magnetically stirred slurry of ceric ammonium sulfate (18 g, 28 mmol) in water (35 ml) in a 100-ml round-bottom flask, a solution of bishomocubanone **1** (1 g, 6.9 mmol) in acetonitrile (18 ml) was added. The reaction mixture was heated at 60 °C for 1 h and cooled to room temperature. Dilution with water, extraction with methylene chloride (2 × 25 ml), washing, drying, and evaporation of solvent gave 1.05 g of a waxy solid. Elution of this material from a silica gel (30 g) column with benzene yielded 0.86 g (78%) of pure lactone **4**, which on sublimation (80 °C at 1 mm) gave white, glistening solid: mp 133–135 °C; ir (KBr) 1760, 1180, 1000 cm^{-1} (lactone): ^1H NMR (CCl_4) δ 5.05 (H-C-O-C=O, 1 H, q, $J_1 = 4$, $J_2 = 3$ Hz), 1.25–3.2 (CH ring, 9 H, envelope); MS *m/e* 162 (M^+), 118 ($M^+ - CO_2$), 117 ($M^+ - CO_2H$), 105, 103, 91 ($C_7H_7^+$), 84, 79, 66 ($C_5H_6^+$). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.3; H, 6.00.

Oxidation of 1,3-Bishomocubanone (1) with *m*-Chloroperbenzoic Acid. To a solution of **1** (0.1 g, 0.7 mmol) in dry benzene (10 ml), *m*-chloroperbenzoic acid (0.15 g, 0.87 mmol, Aldrich) and a catalytic amount of *p*-toluenesulfonic acid (50 mg) were added with gentle swirling of the flask. Reaction was completed in 2 h (TLC) and the mixture was poured into water (10 ml), extracted with ether (2 × 20 ml), and washed with aqueous sodium bicarbonate (3 × 10 ml). Removal of solvent yielded a waxy solid, 0.10 g (90%), which was found to be a mixture of lactones **5** and **4** in a ratio of 5:1 (^1H NMR integration). Separation of the two lactones was achieved by preparative TLC on silica gel plates (20 × 20 cm) using benzene–ethyl acetate (4:1) as the solvent system. The fast moving minor component was identical with the lactone **4** formed in the CAS oxidation of **1**. The major component was sublimed (80 °C, 1 mm) to yield 0.05 g of white crystals: mp 145–146 °C; ir (KBr) 1755, 1365, 1070 cm^{-1} (lactone); ^1H NMR (CCl_4) δ 4.7 (H-C-O-C=O, 1 H, t, $J = 6$ Hz), 1.6–3.4 (CH ring, 9 H, envelope); MS *m/e* 162 (M^+), 118 ($M - CO_2$), 117 ($M^+ - CO_2 - H$), 91 ($C_7H_7^+$), 66 ($C_5H_6^+$). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.36; H, 6.3.

LiAlH$_4$ Reduction of Lactone 4. Lactone **4** (0.7 g, 4.3 mmol) in dry ether (25 ml) was added slowly to a slurry of lithium aluminum hydride (0.3 g, 7.9 mmol) in dry ether (15 ml). The reaction mixture was stirred for 12 h at room temperature and then quenched by adding slowly 3 ml of water and 1 ml of 15% potassium hydroxide. Extraction with methylene chloride (2 × 20 ml) yielded 0.6 g of crude diol. Crystallization from ether gave glistening white needles, 0.5 g (68.7%), of **6**: mp 125 °C; ir (KBr) 3450 (hydroxyl), 1000, 1075 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.5 (**HCOH**, 1 H, m), 4.03 (**H$_2$COH**, 2 H, m), 1.2–2.65 (CH ring and -OH, 11 H, envelope); MS *m/e* 148 ($M^+ - H_2O$), 117, 120 ($C_9H_{12}^+$), 91 ($C_7H_7^+$), 79 ($C_5H_3O^+$ or $C_6H_7^+$), 66 ($C_5H_6^+$). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.21; H, 8.35.

Acid-Catalyzed Cyclization of Diol 6 to Pentacyclic Ether 9. The above diol **6** (0.1 g, 0.6 mmol) in dry benzene (10 ml) containing *p*-toluenesulfonic acid (10 mg) was refluxed for 2 h. The reaction mixture was poured into sodium carbonate solution (10 ml, 5%) and extracted with ether (2 × 20 ml); washing, drying, and removal of solvent gave a waxy residue showing a single spot on TLC. Sublimation (60 °C, 1 mm) of this material yielded 0.08 g (89.7%) of **9** as a white, crystalline solid: mp 140 °C; ir (KBr) 1025 cm^{-1} (ether); ^1H NMR (CCl_4) δ 4.8 (HCO–, 1 H, m), 4.0 (–CH$_2$O–, 2 H, m), 1.2–2.75 (CH ring, 9 H, envelope); MS *m/e* 148 (M^+), 120 ($M^+ - CO$), 117, 91 ($C_7H_7^+$), 79 ($C_5H_3O^+$ or $C_6H_7^+$), 69 ($C_4H_5O^+$). Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: 80.89; H, 8.09.

Jones Oxidation of Diol 6. An ice-cooled, stirred solution of the diol **6** (0.2 g, 1.2 mmol) in 5 ml of acetone was treated dropwise with Jones reagent (2 ml) until the brown color persisted. The mixture was stirred for 4 h, diluted with water, and extracted with ether (2 × 25 ml). The organic layer was successively washed with sodium carbonate and brine and dried. Removal of solvent gave 0.04 g of product, which was identified as lactone **4**. The water layer was acidified with 15% HCl and extracted with methylene chloride (3 × 25 ml) to give 0.13 g of keto acid **7**: ir (KBr) 3375, 1740, 1725, 1245 cm^{-1}.

Keto Ester 8. To a solution of the above keto acid **7** (0.1 g) in dry ether, an ethereal solution of diazomethane was added until a permanent yellow color persisted. The reaction mixture was left aside for 1 h and excess of diazomethane was neutralized by careful addition of acetic acid. Removal of solvent and direct distillation gave keto ester **8** as a colorless liquid: bp 110–115 °C (bath, 1 mm); ir (neat) 1740, 1730, 1180 cm^{-1}; ^1H NMR (CCl_4) δ 3.67 (CH$_3$OC=O, 3 H, s), 1.5–3.1 (CH ring, 9 H, envelope); MS *m/e* 192 (M^+), 164 ($M^+ - CO$), 161 ($M^+ - OCH_3$), 131 ($M^+ - CO_2Me$), 114, 79 ($C_5H_3O^+$ or $C_6H_7^+$). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.53; H, 6.14.

LiAlH$_4$ Reduction of Lactone 5. Lactone **5** (0.7 g, 4.3 mmol) in dry ether (25 ml) was added slowly to a slurry of lithium aluminum hydride (0.3 g, 7.9 mmol) in dry ether (15 ml). The reaction mixture was stirred for 8 h at room temperature. Work-up as described earlier and extraction with methylene chloride (2 × 25 ml), drying, and removal of solvent gave 0.65 g of waxy product. Elution of this material from a silica gel column with benzene yielded 0.3 g (44.4%) of ether **10**. On sublimation (140 °C, at 1 mm) it gave a white, crystalline solid: mp 192 °C; ir (KBr) 1025, 995 cm^{-1}; ^1H NMR (CCl_4) δ 5.52 (HCO–, 1 H, m), 4.13 (H$_2$CO–, 2 H, t, $J = 5$ Hz), 1.3–3.3 (CH ring, 9 H, envelope); MS *m/e* 148 (M^+), 117, 91 ($C_7H_7^+$), 81 ($C_5H_5O^+$), 79 ($C_5H_3O^+$ or $C_6H_7^+$). Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.94; H, 7.95.

Addition of Methylmagnesium Iodide to Lactone 5. Methylmagnesium iodide [from 0.1 g of magnesium turnings and methyl iodide (0.6 g) in 25 ml of dry ether] was prepared according to usual procedure and lactone **5** (0.25 g, 1.5 mmol) in 5 ml of dry ether was added dropwise with continuous stirring. The reaction mixture was quenched after 3 h with 10% ammonium chloride (5 ml) and extracted with ether (2 × 25 ml); washing, drying, and evaporation of solvent yielded 0.3 g of crude lactol **11**, which was crystallized from benzene–petroleum ether (1:4) to furnish white, stout crystals: 0.2 g (72%); mp 114–115 °C; ir (KBr) 3550 (hydroxyl), 1055, 920 cm^{-1} (ether); ^1H NMR (CCl_4) δ 4.05 (–CHO–, 1 H, t, $J = 5$ Hz), 1.38 (**H$_3$C**-COH, 3 H, s), 1.8–3.2 (CH ring and OH, 10 H, envelope). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.39; H, 8.17.

Jones Oxidation of Lactol 11. To an ice-cold solution of lactol **11** (0.1 g, 0.56 mmol) in acetone (5 ml) was added Jones reagent (0.5 ml) dropwise until the yellow color persisted. The reaction mixture was stirred overnight at room temperature and then poured into water (10 ml). Extraction with ether (2 × 20 ml), washing with 10% sodium carbonate solution (2 × 10 ml) and brine, and removal of solvent gave diketone **12**, 0.075 g (76%), ir (neat) 1775 (cyclobutanone), 1720 cm^{-1}.

Addition of Methylmagnesium Iodide to Lactone 4. Methylmagnesium iodide [from 0.15 g of magnesium turnings and methyl iodide (0.9 g) in 25 ml of dry ether] was prepared according to the usual procedure and lactone **4** (0.4 g, 2.25 mmol) in 10 ml of dry ether was added dropwise with continuous stirring. The reaction mixture was quenched after 2 h with 10% ammonium chloride (10 ml) and extracted with ether (2 × 25 ml); washing, drying, and removal of solvent yielded 0.48 g of crude lactol **13**. Filtration from a silica gel column using 1:4 ethyl acetate–benzene as a solvent and crystallization from petroleum ether–benzene mixture furnished white flakes: 0.31 g (70%); mp 89–90 °C; ir (KBr) 3500 (hydroxyl), 1010, 1050 cm^{-1} (ether); ^{1}H NMR (CCl$_4$) δ 4.8 (CHO–, 1 H, m), 1.6 (CH$_3$COH, 3 H, s), 1.3–3.95 (CH ring and OH, 10 H, envelope).

Anal. Calcd for C$_{11}$H$_{14}$O$_2$: C, 74.13; H, 7.92. Found: C, 74.41; H, 7.79.

Jones Oxidation of Lactol 13. To an ice-cold solution of lactol **13** (0.25 g, 1.4 mmol) in acetone (10 ml) was added Jones reagent (1 ml) dropwise until the yellow color persisted. The reaction mixture was stirred overnight at room temperature and then poured into water (15 ml). Extraction with ether (2 × 20 ml), washing with 10% sodium carbonate solution and brine, and removal of solvent yielded diketone **14,** 0.18 g (70%), ir (neat) 1740 (cyclopentanone), 1718 cm^{-1}.

Oxidation of Pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one (2) with Ceric Ammonium Sulfate. To a magnetically stirred slurry of ceric ammonium sulfate (3.5 g, 5.5 mmol) in water (7 ml) a solution of 1,4-bishomocubanone (0.2 g, 1.4 mmol) in acetonitrile (3.5 ml) was added. The reaction mixture was stirred at 60 °C for 3 h and worked up as described above to yield 0.2 g of a waxy solid. Direct sublimation (75 °C, 1 mm) gave 0.175 g (80%) of white crystals of **15:** mp 130–132 °C; ir (KBr) 1755, 1260, 1075 cm^{-1} (lactone); ^{1}H NMR (CCl$_4$) δ 5.0 (H–C–O–C=O, 1 H, m), 1.5–3.5 (CH ring, 10 H, envelope). Anal. Calcd for C$_{10}$H$_{10}$O$_2$: C, 74.08; H, 6.17. Found: C, 74.13; H, 6.15.

Baeyer–Villiger Oxidation of 2 with *m*-Chloroperbenzoic Acid. To a solution of 1,4-bishomocubanone (**2,** 0.1 g, 0.7 mmol) in dry benzene (10 ml) was added *m*-chloroperbenzoic acid (0.15 g, 0.87 mmol, Aldrich) and a catalytic amount of *p*-toluenesulfonic acid with gentle swirling of the flask. Reaction was complete in 2 h (TLC) and usual work-up as described in the earlier case yielded 0.095 g (86%) of lactone **15** identical with the CAS oxidation product of **2.**

Oxidation of Pentacyclo[6.2.1.0^{2,7}.0^{4,10}.0^{5,9}]undecane-3,6-dione (3) with Ceric Ammonium Nitrate. To a magnetically stirred slurry of ceric ammonium nitrate (16 g, 30 mmol) in water (30 ml) a solution of diketone **3** (1 g, 5.7 mmol) in acetonitrile (20 ml) was added. The reaction mixture was stirred at 30 °C for 1 h and worked up as described above to yield 1.1 g of a solid residue. Direct recrystallization from methylene chloride–ether gave 0.9 g (82%) of colorless crystals of **16:** mp 280–282 °C; ir (CH$_2$Cl$_2$) 1780 (δ-lactone), 1725 cm^{-1} (cyclopentanone); ^{1}H NMR (CDCl$_3$) δ 5.17 (H–C–O–C=O, 1 H, t, J = 7.5 Hz), 2.45–3.4 (CH ring, 5 H, envelope), 1.7–2.3 (CH ring, 4 H, m); MS *m/e* 190 (M$^+$), 146 (M$^+$ − CO$_2$), 145 (M$^+$ − CO$_2$H), 118 (M$^+$ − CO$_2$ − CO), 117 (M$^+$ − CO$_2$ − CO − H), 91 (C$_7$H$_7^+$), 79 (C$_5$H$_3$O$^+$ or C$_6$H$_7^+$), 66 (C$_5$H$_6^+$). Anal. Calcd for C$_{11}$H$_{10}$O$_3$: C, 69.46; H, 5.30. Found: C, 69.63; H, 5.19.

Beayer–Villiger Oxidation of 3 with *m*-Chloroperbenzoic Acid. To a solution of diketone **3** (0.25 g, 1.4 mmol) in dry benzene (15 ml) was added *m*-chloroperbenzoic acid (0.29 g, 1.4 mmol, Aldrich) and a catalytic amount of *p*-toluenesulfonic acid with gentle swirling of the flask. Reaction was complete in 2 h and usual work-up as described in the case of **1** yielded 0.28 g of dilactone **20.** Recrystallization from methylene chloride gave colorless microneedles (0.13 g, 43%): mp >300 °C; ir (CH$_2$Cl$_2$) 1760 cm^{-1} (δ-lactone); MS *m/e* 207? (M$^+$ + 1), 206 (M$^+$), 178 (M$^+$ − CO), 150 (M$^+$ − 2CO), 134 (M$^+$ − CO$_2$ − CO). The ^{1}H NMR spectrum of **20** could not be recorded owing to its insolubility in CDCl$_3$ and (CD$_3$)$_2$C=O. Anal. Calcd for C$_{11}$H$_{10}$O$_4$: C, 64.07; H, 4.89. Found: C, 63.86; H, 4.73. The mother liquor from the recrystallization of **20** showed the presence of unreacted starting material. When BV oxidation of diketone **3** (0.25 g, 1.4 mmol) was carried out with *m*-chloroperbenzoic acid (0.58 g, 2.8 mmol) as described above, dilactone **20** was obtained in 93% yield.

Registry No.—**1,** 15584-52-8; **2,** 15745-99-0; **3,** 2958-72-7; **4,** 57051-35-1; **5,** 57051-34-0; **6,** 57719-10-5; **7,** 57719-11-6; **8,** 57719-12-7; **9,** 57719-13-8; **10,** 57719-14-9; **11,** 57719-15-0; **12,** 57719-16-1; **13,** 57719-17-2; **14,** 57719-18-3; **15,** 57051-36-2; **16,** 57719-19-4; ceric ammonium sulfate, 7637-03-8; *m*-chloroperbenzoic acid, 937-14-4; lithium aluminum hydride, 16853-85-3; diazomethane, 334-88-3; methyl iodide, 74-88-4; ceric ammonium nitrate, 16774-21-3.

References and Notes

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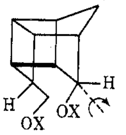
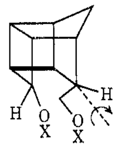
(7) W. L. Dilling and M. L. Dilling, *Tetrahedron,* **23,** 1225 (1967); W. L. Dilling, R. A. Plepys, and R. D. Kroening, *J. Am. Chem. Soc.,* **94,** 8133 (1972).

(8) Attempted base hydrolysis or methanolysis of **4** and **5** always lead to the quantitative recovery of the starting material and therefore a more circuitous degradative scheme was selected.

(9) To rationalize the different behavior of **4** and **5** toward lithium aluminum hydride, a tentative suggestion may be made. In the structures (**4a** and **5a**) of the reduction products before work-up, the substituents (H, OX in **4a** and H, CH$_2$OX in **5a**) would be displaced to a slight extent by twisting (cf. arrows) in order to minimize steric strain. This action as well as the tilting of the carbon atoms bearing these substituents upward are favored by the presence of the bond indicated in bold type. For ether formation from **4a,** the OX of the CH$_2$OX (X = H or Al) group must swing inward the molecular cavity in order to attain a good S$_N$2 transition state[10] and it is strongly opposed by steric interactions. On the other hand, the deformation of **5a** tends to align the attacking and the leaving groups in a better disposition.



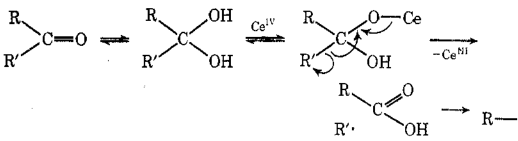
4a



5a

(10) L. Tenud, S. Farooq, J. Seible, and A. Eschenmoser, *Helv. Chim. Acta,* **53,** 2059 (1970).

(11) A referee has suggested that the ceric oxidation might preferably occur via the hydrates of the ketones as shown below:



However, we did not observe the deep red color of the solution upon mixing the oxidant with the substrates which is characteristic of ceric oxidation of alcohols.[3]

(12) We have not been able to locate experimental data in the literature to support this supposition but one can empirically analyze the situation as follows. The extracyclic bonds of cyclobutane have more s character than those of cyclopentane. Thus assuming that the free radicals have planar structures, they are more difficultly accommodated at a cyclobutane than a cyclopentane carbon.

(13) S. A. Monti and C. K. Ward, *Tetrahedron Lett.,* 697 (1971).

(14) Melting points and boiling points are uncorrected. Melting points were taken in capillaries on a Fisher-Johns melting point apparatus. Boiling points refer to bath temperature in those cases where short-path bulb-to-bulb distillations were carried out. The petroleum ether corresponds to fraction of bp 60–80 °C. All solvent extracts were dried over anhydrous sodium sulfate. Infrared spectra were recorded on a Perkin-Elmer Model 137B spectrophotometer as neat liquids or solids as KBr disks. ^{1}H NMR spectra were obtained on approximately 10–15% solutions in CCl$_4$ or CDCl$_3$ on a Varian A-60 spectrometer. The chemical shifts are reported in parts per million downfield from internal tetramethylsilane at 0.00 as internal standard. The abbreviations s, d, t, q refer to singlet, doublet, triplet, and quartet, respectively. Microanalyses were performed by Mr. A. H. Siddiqui in the microanalytical laboratory of our department.

(15) R. C. Cookson, J. Hudec, and R. O. Williams, *J. Chem. Soc. C,* 1382 (1967).

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(17) R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *J. Chem. Soc.,* 3062 (1964).