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(23) Melting points were measured on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were determined on a Perkin-Elmer 257 grating spectrophotometer in $CHCl_3$, CCl_4, or CS_2. A Varian A-60 spectrophotometer was used to record NMR spectra in CCl_4 using tetramethylsilane as an internal standard. Gas chromatographic analyses were made on a Hewlett-Packard 720 thermal conductivity gas chromatograph. Most products were determined on a 4 ft × 0.25 in. silicone rubber column on Chromosorb W. Helium flow rates of 30–40 ml/min were found optimal. Elemental analyses were carried out by Geller Laboratories, Saddle River, N.J.
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Reactions of Dicarbonyl Compounds with Dimethyl β-Ketoglutarate. 2. Simple Synthesis of Compounds of the [10.3.3]- and [6.3.3]Propellane Series[1]

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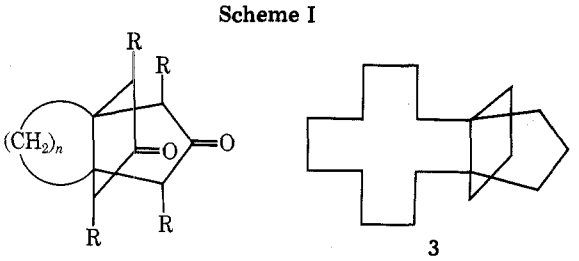
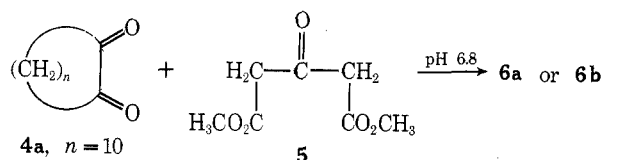
Reaction of cyclododecane-1,2-dione (**4a**) or cyclooctane-1,2-dione (**4b**) with dimethyl β-ketoglutarate (**5**) at room temperature in aqueous buffer (pH 6.8) provided good yields of tetramethyl[10.3.3]propellane-14,17-dione 13,15,16,18-tetracarboxylate (**6a**) and tetramethyl[6.3.3]propellane-10,13-dione 9,11,12,14-tetracarboxylate (**6b**), respectively. Hydrolysis and decarboxylation of **6a** and **6b** furnished the propellanediones **7a** and **7b.** The dione **7a** was converted to [10.3.3]propellane by Wolff–Kishner reduction while Clemmensen reduction of the propellanediones yielded the cyclic substituted bisnoradamantyl alcohols **11** and **12.**

Chemistry of propellanes has been given much attention in recent years.[2] In particular, a large effort has been spent upon the synthesis of propellanes containing small rings and upon the study of the bonding character of their central bond.[3] On the other hand, no propellanes with medium or large rings ($n > 6$) seem to have been prepared, presumably because of difficulties in synthesizing such compounds. However, the approach used by Weiss and Edwards[4] for the synthesis of diketo derivatives of [4.3.3]- (**1**) and [3.3.3]propellane (**2**) through reaction of cyclohexane-1,2-dione and cyclopentane-1,2-dione, respectively, with dimethyl β-ketoglutarate seemed to be capable of extension to medium-ring 1,2-diketones. This proved indeed to be the case. We wish to report here on the synthesis and properties of several compounds of the [10.3.3]- and [6.3.3]propellane series, including the parent hydrocarbon (**3**) of the former.[5]

Scheme I



1, $n = 4$; R = H
2, $n = 3$; R = H
6a, $n = 10$; R = CO_2CH_3
6b, $n = 6$; R = CO_2CH_3
7a, $n = 10$; R = H
7b, $n = 6$; R = H

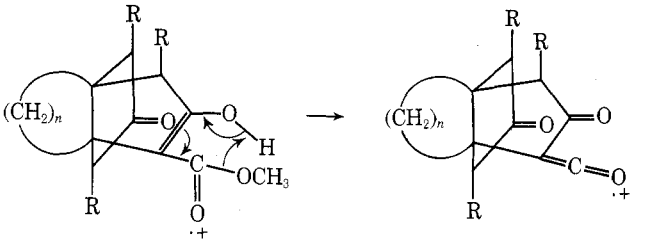


4a, $n = 10$
b, $n = 6$

5

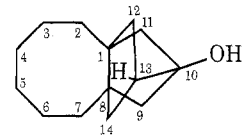
Reaction of 1 mol of cyclododecane-1,2-dione (**4a**)[6] with 2 mol of dimethyl β-ketoglutarate (**5**) in a mixture of methanol and citrate–phosphate buffer (pH 6.8) for 24 h at room temperature gave a precipitate (94%) of tetramethyl[10.3.3]propellane-14,17-dione 13,15,16,18-tetracarboxylate (**6a**), mp 156.5–158 °C (from methanol); high-resolution mass spectrum, calcd for $C_{26}H_{36}O_{10}$, 508.2308; found, 508.2300. This product of 1:2 stoichiometry was homogenous on TLC with several solvent systems; only one of the several possible stereoisomers seems to have been obtained. Structure **6a** is consistent with ir, NMR, and mass spectral data. Three successive losses of 32 units (CH_3OH) were observed from the parent ion in the mass spectrum of **6a.** This can be formulated to occur as illustrated in Scheme II to generate ketene intermediates. Similar fragmentations have been reported by

Scheme II



6a

Table I. ^{13}C Chemical Shifts for Tetracyclo[6.3.3.0.0^{10,13}]tetradecan-10-ol (11)



11

Types of carbon atoms	Chemical shift, ppm	Types of carbon atoms	Chemical shift, ppm
3 + 6	26.19[a]	13	49.63
4 + 5	27.76	11 + 9	51.30
2 + 7	28.94	1 + 8	57.10
12 + 14	44.50	10	82.11

[a] Measured from Me_4Si standard.

Biemann[7] with *cis*-crotonic acid methyl ester and are observed quite consistently in our β-keto ester derivatives. A fourth loss of 32 units was also observed but it was of very low intensity.

The tetramethyl tetracarboxylate derivative (**6a**) was hydrolyzed and decarboxylated in refluxing 6 N hydrochloric acid to furnish an oil in 90% yield which crystallized from methanol, mp 53–55 °C (CH_3OH). Spectral data unambiguously support structure **7a** for this white solid. The alicyclic protons of the 12-membered ring appeared as a singlet at δ 1.40 (20 H) in the NMR spectrum, while the cyclopentanone protons were observed as two singlets at δ 2.36 (4 H) and 2.45 (4 H), respectively. The presence of a strong band at 1741 cm^{-1} in the ir and the absence of signals from the methyl ester functions in the NMR further substantiated the structural assignment.

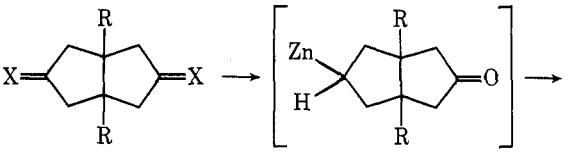
Treatment of [10.3.3]propellane-14,17-dione (**7a**) with hydrazine and base[8] furnished [10.3.3]propellane (**3**) in 54% yield. The compound was crystallized from ether, mp 33–35 °C (sublimes at 750 mmHg); high-resolution mass spectrum calcd for $C_{18}H_{32}$, 248.2504; found, 248.2499. The ir spectrum of this compound lacked carbonyl or hydroxyl bands. Two singlets (12 H and 20 H) observed in the NMR at δ 1.51 and 1.38 can be attributed to the cyclopentane and cyclododecane protons, respectively. The cyclopentane protons are somewhat deshielded compared to the cyclododecane protons because of strain in the five-membered rings.[9] A mixture of cyclopentane and cyclododecane furnished an NMR spectrum identical with that of **3**.

Reaction of cyclooctane-1,2-dione (**4b**) and **5** under conditions similar to those described above provided tetramethyl[6.3.3]propellane-10,13-dione tetracarboxylate (**6b**) in good yield. Hydrolysis with 6 N hydrochloric acid and a cosolvent (acetic acid) yielded an oil which was crystallized from methanol to furnish [6.3.3]propellane-10,13-dione (**7b**) in 85% yield, mp 80–82 °C (from CH_3OH). The similarity between the physical and spectral properties of compounds **7a** and **7b** confirmed the structural assignment of [6.3.3]propellane-10,13-dione as **7b**.

Several attempts to reduce the [6.3.3]propellane-10,13-dione (**7b**) to the parent hydrocarbon by Wolff–Kishner reduction[8] were made. None of these attempts were successful. Only traces of the oxygen-free propellane were observed and the majority of the material isolated was dimeric (see Experimental Section).

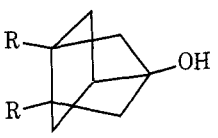
Because Wolff–Kishner reduction did not prove successful in the [6.3.3] system, it was hoped that Clemmensen reduction of the carbonyl functions would yield the parent hydrocarbon. Borden and co-workers[10] had converted 1,5-dimethylbicyclo[3.3.0]octane-3,7-dione (**8**) into 1,5-dimethylbicyclo[3.3.0]octane (**9**) by zinc amalgam reduction in aqueous solution. In addition, a small amount of the bisnoradamantyl

Scheme III

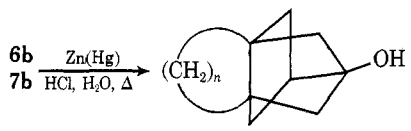


8, R = CH_3; X = O
9, R = CH_3; X = H_2
14, R = H; X = O

13



10, R = CH_3
15, R = H



11, $n = 6$
12, $n = 10$

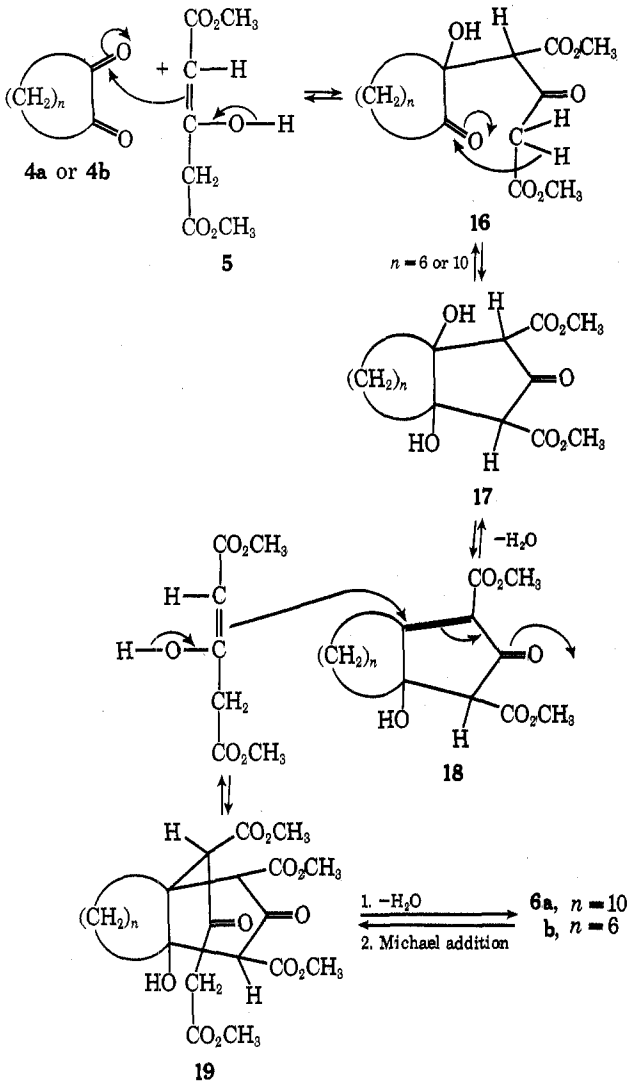
derivative 3,7-dimethyltricyclo[3.3.0.0^{3,7}]octan-1-ol (**10**) was isolated; the acetate of **10** was the major product on reduction in acetic anhydride. Consequently, this reduction was expected to be straightforward; however, when [6.3.3]propellane-10,13-dione was reduced with Zn(Hg) in aqueous HCl at reflux, a crystalline compound (mp 87–88 °C) containing one oxygen atom was isolated in 69% yield (high-resolution mass spectrum, calcd for $C_{14}H_{22}O$, 206.1670; found 206.1670). The compound was nonketonic but contained a hydroxy group (ir). Since the NMR spectrum lacked signals from methylene protons or methine protons next to oxygen the compound appeared to contain a tertiary hydroxy function analogous to compound **10** reported by Borden.[10] The structure which best fits the spectroscopic evidence is tetracyclo[6.3.3.0.0^{10,13}]tetradecan-10-ol (**11**). This structure is strongly supported by ^{13}C NMR (see Table I). The oxygen-substituted tertiary carbon (C-10) appeared at lowest field (82.11 ppm), clearly distinct from the other carbon atoms, while carbon atom 13 was observed at 49.63 ppm. The remaining 12 carbon atoms appeared as six singlets. Each of these singlets represented two carbon atoms because of the symmetry of this part of the molecule as depicted in Table I.[11] When [10.3.3]propellane-14,17-dione was allowed to react under the same conditions, a 70% yield of tetracyclo[10.3.3.0.0^{14,17}]octadecan-14-ol (**12**), mp 142–143 °C (from methanol) was realized. The structure was confirmed by comparison with data collected on **11**. In addition, the tertiary proton present on C-17 of the tetracyclooctadecanol **12** was observed as a triplet at δ 2.09 in the 220-MHz NMR spectrum. The other signals in this spectrum were also in accord with this assignment.

The reduction conditions employed in the work of Borden for conversion of **8** to **9** provided substantial amounts of 1,5-dimethylbicyclo[3.3.0]octane (**9**). We never observed any trace of the parent hydrocarbon (**3**) in our reaction. A plausible mechanism for the formation of the bridge between the two carbon atoms has been proposed;[10] the zinc-stabilized carbanion (**13**) resulting from reduction of one carbonyl function of **8** can react intramolecularly with the second carbonyl function to form the C(10–13) bridge. Our work is in agreement with this postulated mechanism but the higher temperature here may have allowed more interaction between the two carbonyls leading to substantially higher yields of the bridged tetracyclo species **11** and **12**. We then attempted to convert bicyclo[3.3.0]octane-3,7-dione (**14**) to bisnoradamantyl alcohol (**15**) at reflux, but obtained only complex mix-

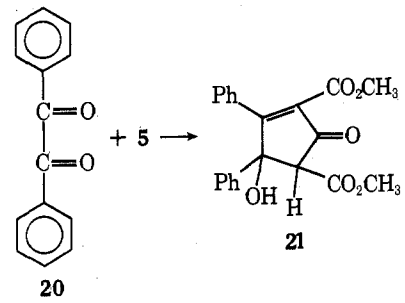
tures of products, none of which appeared to be the desired alcohol **15**.

The preferential 1:2 stoichiometry observed in the reaction of 1,2-diketones and dimethyl β-ketoglutarate including **4a** and **4b** can be explained through a sequence suggested by Weiss[12] and supported by our work.[5] It is shown for the compounds described in the present paper in Scheme IV. In this sequence aldol condensation of **4a** or **4b** and **5** is assumed to give the β-hydroxy ketones **16** and **17**; the latter would lose one molecule of water to give the 4-hydroxycyclopenten-2-one derivative (**18**). Michael addition of a second molecule of **5** would provide **19** which could then lose another molecule of water; and a second Michael reaction (intramolecularly) would generate the observed final products **6a** and **6b**.

Scheme IV



All attempts to isolate the 1:1 intermediates **17** or **18** from the reaction at pH 6.8 have been so far unsuccessful. Even when the reaction was carried out with a 10:1 excess of the 1,2-dicarbonyl compound, the product first observed by TLC, or isolated, was the propellanedione **6a**. However, a 1:1 adduct entirely analogous to **18** has been obtained already by Japp and Lander[13] from the reaction of benzil and β-ketoglutaric acid in alcoholic KOH and we have encountered several other compounds of this type. Under the conditions used by Japp and Lander, we have obtained the 1:1 adduct (**21**) closely related to their cyclopentenolone, from benzil (**20**) and dimethyl β-ketoglutarate (**5**). The same compound was prepared independently by White.[14] When cyclododecane-1,2-dione (**4a**) was treated with **5** in alcoholic KOH two compounds were



20 **21**

observed by TLC. The less polar one of these was identified as the propellanedione **6a**. All attempts to isolate the second, more polar substance have yielded only the propellanedione **6a**. We feel that this new compound may be the 4-hydroxycyclopenten-2-one (**18**) analogous to **21**. A paper which discusses the details of this mechanism and which reports on isolation of 1:1 adducts in related systems is in preparation.[15] Reaction of **4a** and **5** in methanol with sodium methoxide also provided **6a**.

In the buffer system (pH 6.8), the rate of the Michael addition of dimethyl β-ketoglutarate to the 4-hydroxycyclopenten-2-one (**18**) seems to be faster than the formation of **18** itself; consequently, only the adducts of 1:2 stoichiometry have been isolated.

We have also investigated reaction of **4a** and **5** under anhydrous acidic conditions. When cyclododecane-1,2-dione (**4a**) and dimethyl β-ketoglutarate (**5**) were allowed to react in refluxing benzene in the presence of a small amount of *p*-toluenesulfonic acid, a colorless compound was isolated in small yield, mp 85–86 °C (from CH_3OH); high-resolution mass spectrum calcd for $C_{19}H_{26}O_5$, 334.1780; found, 334.1788. This is evidently formed from one molecule each of the reactants by elimination of two molecules of water. The NMR of this 1:1 adduct is very complex and suggests that extensive rearrangement has occurred during formation of this substance.

It appears that reaction of alicyclic α-dicarbonyl compounds with dimethyl β-ketoglutarate will in general proceed with 1:2 stoichiometry to furnish tetramethylpropellanedione tetracarboxylate derivatives in good yield, and similar results are obtained in alkaline methanol. In contrast to this, the reaction in refluxing benzene appears to give a 1:1 adduct, although some rearrangement may take place and in addition, reactions of aromatic α-diketones also yield 1:1 adducts.[16] At no time did we observe the formation of a propellanedione on reaction of benzil and dimethyl β-ketoglutarate.

Experimental Section

Microanalyses were performed (UWM) on an F & M Scientific Corp. Carbon, Hydrogen, Nitrogen Analyzer Model 185; some analyses were carried out at the National Institutes of Health, Bethesda, Md. Melting points were taken on a Thomas-Hoover apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded on Varian T-60, HA-100, and CFT-20 spectrometers. Infrared spectra were taken on a Beckman Acculab-1 instrument, ultraviolet spectra were recorded on a Cary 17 spectrophotometer, and mass spectra were taken on a Finnigan 1015 or AEI MS902 instrument.

Analytical TLC plates used were E. Merck-Brinkmann uv active silica gel on plastic. The spray reagent was composed of 2,4-dinitrophenylhydrazine, ethanol, and sulfuric acid. The citrate–phosphate buffer (pH 6.8) was prepared by dissolving $Na_2HPO_4 \cdot 7H_2O$ (11.67 g) and citric acid (3.68 g) in water (900.00 ml).

Preparation of Cyclododecane-1,2-dione (4a) and Cyclooctane-1,2-dione (4b). The 1,2-dione **4a** was prepared by the method of Sharpless,[6] yield 50%, bp 90–94 °C (0.8 mmHg) [lit. 93–95 °C (1 mmHg)].[6] Cyclooctane-1,2-dione (**4b**) was prepared by the same method, albeit in very low yield. Higher yields of **4b** were obtained by acyloin condensation[17] followed by oxidation:[18] bp 68–69.5 °C (3 mmHg) [lit.[19,20] bp 68.8–69.5 °C (3 mmHg)].

Tetramethyl[10.3.3]propellane-14,17-dione 13,15,16,18-Tetracarboxylate (6a). Cyclododecane-1,2-dione (5.0 g, 0.025 mol) was dissolved in methanol (100 ml) and citrate–phosphate buffer (pH 6.8)

was added until the solution became turbid. A few additional drops of methanol were added to clarify the solution and dimethyl β-ketoglutarate (8.87 g, 0.050 mol) was added all in one portion. After stirring for several hours at room temperature, a white precipitate began to form. The reaction was continued for 3 days and then the mixture was filtered. A white, crystalline solid (11.9 g) was isolated by filtration in 94% yield. It was homogenous on TLC (R_f 0.39, 1:9 ethyl acetate/benzene). The product was recrystallized from methanol, mp 156.5–158 °C (unchanged on further recrystallization) and identified as **6a:** ir ($CHCl_3$) 2930 (C–H), 1728 (ester carbonyl), and 1653 cm^{-1} (enol form of β-keto ester); uv λ_{max} (CH_3OH) 246.8 nm; NMR δ ($CDCl_3$) 1.45 (20 H, broad singlet), 3.68–4.20 (14 H, six singlets of unequal intensity), 10.64 (1 H, s, enol proton), and 10.72 (1 H, s, enol proton), both enol protons D_2O exchangeable; mass spectrum M^+ *m/e* 508.2300 (calcd for $C_{26}H_{36}O_{10}$, 508.2308); *m/e* 508 (49, M^+), 490 (27.1, M − 18), 477 (79.2), 476 (100, M − 32), 446 (5.8), 444 [50.1, M − (2 × 32)], 443 (12.1), 442 (15.8), 414 (15.1), 412 [43.1, M − (3 × 32)], 410 (5.3), 404 21.5), 382 (17.8), 399 (5.5), 380 [6.0, M − (4 × 32)], and 300 (4.0).

Anal. Calcd for $C_{26}H_{36}O_{10}$: C, 61.40; H, 7.10. Found: C, 61.62; H, 7.18.

[10.3.3]Propellane-14,17-dione (7a). The tetramethylpropellanedione tetracarboxylate (**6a,** 5.1 g, 0.01 mol) was dissolved in 6 N hydrochloric acid (60 ml) and the solution was refluxed for 6 h. After extraction with chloroform (5 × 50 ml), washing of the combined organic layers with water, and drying (Na_2SO_4), the solution was evaporated under reduced pressure to yield a brown oil. The oil was taken up in hot methanol; on cooling, white crystals formed (2.5 g, 90% yield) of mp 53–55 °C; ir ($CHCl_3$) 2915 (C–H), 2850 (C–H), and 1741 cm^{-1} (cyclopentanone C=O); NMR ($CDCl_3$) δ 1.40 (20 H, s), 2.36 (4 H, s), and 2.45 (4 H, s); mass spectrum *m/e* 276 (100, M^+), 248 (89.6), 233 (18), 220 (73), 218 (31), 205 (14.5), 195 (16.6), 191 (8.3), 177 (16.6) 164 (10), 163 (20), 149 (40), 150 (14.5), 135 (56.2), 122 (67), and 121 (68.7).

Anal. Calcd for $C_{18}H_{28}O_2$: C, 78.30; H, 10.10. Found: C, 78.10; H, 10.28.

[10.3.3]Propellane (3). The propellanedione **7a** (0.50 g, 0.0098 mol) and hydrazine (4.5 g of 95%) were added to a mixture of diethylene glycol and potassium hydroxide pellets (2.4 g). The reaction mixture was slowly heated to 135 °C[8] until the potassium hydroxide pellets dissolved; the solution was refluxed for 1 h. The water and excess hydrazine were distilled from the mixture (750 mmHg) until the pot temperature reached 180 °C. The viscous residue was heated for 3 h at 180 °C, cooled to room temperature, and then poured into cold water (40 ml). The aqueous solution was extracted with benzene (5 × 25 ml), and the combined extracts were washed several times with small portions of water and dried (Na_2SO_4). Partial removal of solvent provided white crystals (0.24 g, 54%) of **3** with mp 33–34 °C (sublimed) and R_f 0.64 (benzene). The spectral data were as follows: ir ($CHCl_3$) 2930 and 2860 cm^{-1} (C–H); NMR ($CDCl_3$) δ 1.38 (20 H, s, cyclododecane protons) and 1.51 (12 H, s, cyclopentane protons); mass spectrum *m/e* 248 (100, M^+), 220 (51), 205 (50), 203 (4.4), 177 (4.4), 163 (8.5), 149 (20), 135 (53.3), 122 (99), 122 (100); M^+ at *m/e* 248.2499; calcd for $C_{18}H_{32}$, 248.2504.

Tetramethyl[6.3.3]propellane-10,13-dione 9,11,12,14-Tetracarboxylate (6b). This compound was prepared from **4b** under the same conditions as the preparation of **6a** above; however, the yield (9 g) of crystalline **6b** was only 80%, mp 160–163 °C (from methanol); ir ($CHCl_3$) 2940, 2850 (C–H), 1730 (ester C=O) and 1648 cm^{-1} (enol form of β-keto ester); NMR ($CDCl_3$) δ 1.3–1.7 (12 H, broad multiplet), 3.6–4.0 (14 H, several overlapping singlets of unequal intensity, 4 OCH_3 and two nonenolized β-keto ester protons); mass spectrum M^+ at *m/e* 452.1689; calcd for $C_{22}H_{28}O_{10}$, 452.1682; low-resolution *m/e* 452 (11.4, M^+), 420 (83), 388 (100), 360 (41), 356 (65.8), 329 (51.5), 328 (54.2), 319 (34), 297 (57.2), 296 (29), 287 (42), 278 (21), 272 (32), 246 (67), 229 (56), 214 (95), 202 (44); uv λ_{max} (CH_3OH) 244 nm.

Anal. Calcd for $C_{22}H_{28}O_{10}$: C, 58.40; H, 6.20. Found: C, 58.13; H, 6.50.

[6.3.3]Propellane-10,13-dione (7b). To a solution of glacial acetic acid (55 ml), concentrated hydrochloric acid (40 ml), and water (20 ml), tetramethyl[6.3.3]propellane-10,13-dione 9,11,12,14-tetracarboxylate (4.5 g, 0.010 mol) was added and the resultant mixture was refluxed for 10 h. A portion of the excess acid was removed under reduced pressure and the residue made alkaline with sodium bicarbonate. The basic solution was next extracted with chloroform (10 × 50 ml) and the extracts were combined and dried (Na_2SO_4). Evaporation of solvent furnished an oil (1.9 g, 85%) which on dissolution in a small amount of hot methanol provided white crystals of **7b,** mp 80–82 °C (R_f 0.15 in 20% ethyl acetate/benzene): ir ($CHCl_3$) 1740 cm^{-1} (cyclopentanone C=O); NMR ($CDCl_3$) δ 1.40–1.93 (12 H, broad singlet), 2.35 (4 H, s, cyclopentanone protons), and 2.38 (4 H, s, cyclopentanone protons); mass spectrum *m/e* 220 (100, M^+), 192 (12.5, M − 28), 188 (43.8), 164 [100, M − (2 × 28)], 149 (52.5), 135 (50), 136 (52.5), 123 (50), 121 (52.5), 109 (88), 108 (80), and 107 (75).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.40; H, 9.10. Found: C, 76.45; H, 9.35.

Attempted Reduction of [6.3.3]Propellane-10,13-dione (7b). A. A mixture of **7b** (0.50 g, 0.0022 mol), hydrazine (1.5 g of 95%), diethylene glycol (9.2 ml), and potassium hydroxide pellets (1.2 g) was heated slowly to 146 °C. After the liquid had refluxed (dry ice–acetone cold finger condenser) at this temperature for 1 h, the water and excess hydrazine were distilled from the solution until the pot temperature reached 200 °C. The viscous residue was heated at 200 °C another 3 h, cooled to room temperature, and poured into water (20 ml). The solution was extracted with benzene (8 × 25 ml). The combined extracts were washed several times with small portions of water and the organic layer was dried (Na_2SO_4). Evaporation of solvent afforded an oil (0.2 g, R_f 0.655, benzene): ir ($CHCl_3$) 2930 and 2870 cm^{-1} (C–H); mass spectrum *m/e* 380 (29.9, M_1+), 376 (38.4, M_2+), 361 (6.0), 351 (6), 337 (100), 295 (7), 279 (8.5), 232 (19.6), 229 (15), 215 (13), 204 (14.5), 203 (14.5), 192 (2.0), 189 (37.6), 187 (20.5), 173 (13), and 167 (32). This appears to be composed of two dimeric compounds M^+ at *m/e* 380 and M^+ at *m/e* 376.

B. When the reaction was repeated using excess hydrazine (5.5 g of 95%), diethylene glycol (200 ml), and potassium hydroxide pellets (3 g), an oil (0.2 g) was isolated which had R_f 0.47 (benzene); ir ($CHCl_3$) 2930 and 2860 cm^{-1} (C–H); mass spectrum *m/e* 376 (100, M^+), 361 (12.3), 347 (15), 334 (30), 319 (10), 276 (74), 248 (78), 239 (16), 233 (25), 229 (29), and 220 (59). None of the [6.3.3]propellane was observed in this experiment.

Tetracyclo[10.3.3.0.0^{14,17}]octadecan-14-ol (12). A mixture of zinc (2 g), mercuric chloride (0.2 g), concentrated hydrochloric acid (0.1 ml), and water (2 ml) was stirred for 5 min. The aqueous layer was then decanted to furnish the zinc amalgam. Water (1 ml), hydrochloric acid (4 ml of concentrated), glacial acetic acid (2 ml), and **7a** (1.0 g, 0.0036 mol) were added to the amalgam and the resulting mixture was refluxed for 20 h.[21] The solution was next cooled, decanted into water (30 ml), and refrigerated for 2 days. A white, crystalline solid (0.66 g, 70%) formed which was filtered off, mp 142–143 °C (from methanol). The spectral data are in accord with structure **12:** ir ($CHCl_3$) 3460 (OH) and 2490 cm^{-1} (C–H); 220-MHz NMR ($CDCl_3$) δ 1.43 (20 H, m), 1.64 (4 H, m), 1.76 (4 H, m), and 2.09 (1 H, t); mass spectrum M^+ at *m/e* 262.2295; calcd for $C_{18}H_{30}O$, 262.2296; *m/e* 262 (100, M^+), 233 (83.3), 220 (75), 244 (20), 207 (50), 191 (16.6), 177 (25), 163 (50), 151 (45), 149 (66), 135 (100). Solvent of crystallization was tightly bound in the crystals and precluded exact analysis.

Tetracyclo[6.3.3.0.0^{10,13}]tetradecan-10-ol (11). The same reduction procedure was employed to convert **7b** to **11.**[21] It furnished a 69% yield (0.52 g) of the alcohol **11:** mp 87–88 °C (benzene); R_f 0.3 (methylene chloride); ir ($CHCl_3$) 3440 (OH) and 2925 cm^{-1} (C–H); NMR ($CDCl_3$) δ 1.48–1.50 (20 H, two overlapping singlets) and 1.78–2.2 (1 H, broad multiplet); mass spectrum *m/e* 206 (43.7), 177 (62.5), 164 (73), 163 (100), 150 (25), 151 (37), 149 (75), 136 (99), 122 (69), and 121 (100); M^+ at *m/e* 206.1670; calcd for $C_{14}H_{22}O$, 206.1670. ^{13}C data are contained in the text.

Reaction of Benzil (20) and Dimethyl β-Ketoglutarate (5) in Potassium Hydroxide/Ethanol[13] to Yield 2,5-Dicarbomethoxy-4-hydroxy-3,4-diphenylcyclopent-2-enone (21). To a solution of potassium hydroxide (0.5 g) in ethanol (125 ml of absolute), benzil (10.5 g, 0.05 mol) was added with stirring. Dimethyl β-ketoglutarate (17.4 g, 0.10 mol) was then added to the solution and the reaction stirred at room temperature. White crystals formed within several hours and were filtered from the reaction mixture after 20 h. The crystals (12.8 g, 70%) were washed with water and dried: mp 136–140 °C; ir (KBr) 3460 (OH) and 1740 cm^{-1} (ester C=O), M^+ at *m/e* 366; NMR identical with that of **21** reported by White.[14]

Reaction of Cyclododecane-1,2-dione (4a) with Dimethyl β-Ketoglutarate in Potassium Hydroxide/Methanol. Cyclododecane-1,2-dione (2.0 g, 0.010 mol) and dimethyl β-ketoglutarate (0.24 g, 0.0013 mol) were dissolved in methanol. Methanolic potassium hydroxide (0.1 g of potassium hydroxide in 20 ml of methanol) was added to the reaction and the solution was stirred continuously for several hours. A new compound, R_f 0.16 (20% ethyl acetate/benzene), was observed on TLC; however, after workup and column chromatography only the propellanedione **6a** with R_f 0.40 was isolated. No trace of the new compound (R_f 0.16) could be found after column chromatography or preparative TLC.

Reaction of Cyclododecane-1,2-dione with Dimethyl β-Ketoglutarate in Sodium Methoxide/Methanol. This reaction was carried out as outlined in the preceding experiment; however, sodium methoxide was used in place of potassium hydroxide.[22] A new com-

pound (R_f 0.70, M^+ 392) precipitated from the solution while the propellanedione **6a** was observed by TLC of the mother liquor. This substance (R_f 0.70) was the product of reaction of one molecule of the 1,2-dione (**4a**) with another molecule of **4a** since it was also obtained by carrying out the same reaction in the absence of dimethyl β-ketoglutarate. No 1:1 adduct of **4a** and **5** could be found.

Acid-Catalyzed Reaction of Cyclododecane-1,2-dione and Dimethyl β-Ketoglutarate in Refluxing Benzene. Cyclododecane-1,2-dione (3.0 g, 0.015 mol), dimethyl β-ketoglutarate (**5**, 3.2 g, 0.018 mol), and *p*-toluenesulfonic acid (200 mg) were dissolved in benzene (70 ml). The solution was refluxed and water (0.4 ml) was removed by means of a Dean-Stark trap. Evaporation of the benzene afforded an oil (6 g) which was found to be a mixture of starting material and a *new compound* (R_f 0.42 in 10% ethyl acetate/benzene). The oil was chromatographed on silica gel which furnished a small quantity of the new compound (0.3 g, 6% yield). This substance was crystallized from methanol to provide white crystals: mp 85–86 °C; ir (CCl_4) 2940 and 2870 (C–H), 1740, 1715 with a shoulder at 1700 cm^{-1} (saturated and unsaturated ester functions); NMR ($CDCl_3$) δ 1.21–1.91 (12 H, broad multiplet), 2.2 (q, 2 H), 2.8 (t, 2 H), 3.62–3.7 (6 H, two overlapping singlets), 3.95 (s, 2 H), and 6.2 (m, 2 H); mass spectrum M^+ at *m/e* 334.1788; calcd for $C_{19}H_{26}O_5$, 334.1773; *m/e* 334 (100), 306 (14), 302 (57), 291 (816), 276 (20), 275 (100), 274 (40), 270 (1.4), 251 (14), 246)10.7), 245 (15), 231 (15), 228 (16), 219 (23), 218 (24), 205 (34), 203 (34), 192 (35), 191 (61.3), 189 (57), 173 (30), 159 (51), 149 (54), 145 (35), and 131 (65).

Anal. Calcd for $C_{19}H_{26}O_5$: C, 68.30; H, 7.8. Found: C, 68.00; H, 8.02. The structure of this compound is still undetermined.

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Photochemical Reactivity of Some Bridgehead Phenyl Ketones[1]

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The photochemistry of several bridgehead phenyl ketones has been investigated. Bicyclo[2.2.2]octyl, 1-adamantyl, and 1- and 3-homoadamantyl phenyl ketones undergo efficient photochemical α-cleavage in benzene solution, whereas bicyclo[3.2.1]octyl and bicyclo[2.2.1]heptyl phenyl ketones do not. The rates for α-cleavage of ketones **1–4** are dependent upon bi- and tricycloalkane structure in a manner similar to that previously reported for the thermolysis of bridgehead peresters. The rate constant for α-cleavage is accelerated for 1- or 3-homoadamantyl vs. *tert*-butyl, but retarded by the smaller bicyclic ring systems. The kinetic results are indicative of an early transition state with polar character for photochemical α-cleavage. Quantum yields for product formation are larger for the bridgehead ketones than for pivalophenone owing to a decreased cage effect. The photoreduction of these ketones has also been investigated.

Reliable prediction of reactivity of an entire class of molecules is one of the ultimate goals of the investigation of reaction mechanisms. We have studied the reactivity of phenyl ketones toward photochemical α-cleavage (eq 1) with the

$$\mathrm{PhCR} \xrightarrow{h\nu} \mathrm{PhC}\cdot + \cdot\mathrm{R} \qquad (1)$$

above goal in mind.[3–5] We have established that the stability of the product free radicals does not correlate with photochemical reactivity. For example, pivalophenone (R = *tert*-butyl) is an order of magnitude more reactive than deoxybenzoin (R = benzyl).[3] We have also found that α substituents capable of stabilizing an adjacent positive charge are far more effective in accelerating α-cleavage than are substituents ca-