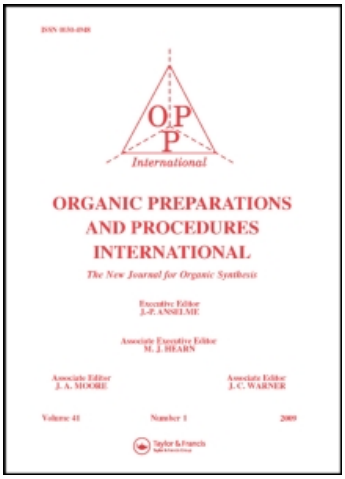

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[3.3.1]PROPELLANE-2,8-DIONE. SYNTHESIS AND STRUCTURE

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[3.3.1]PROPELLANE-2,8-DIONE. SYNTHESIS AND STRUCTURE

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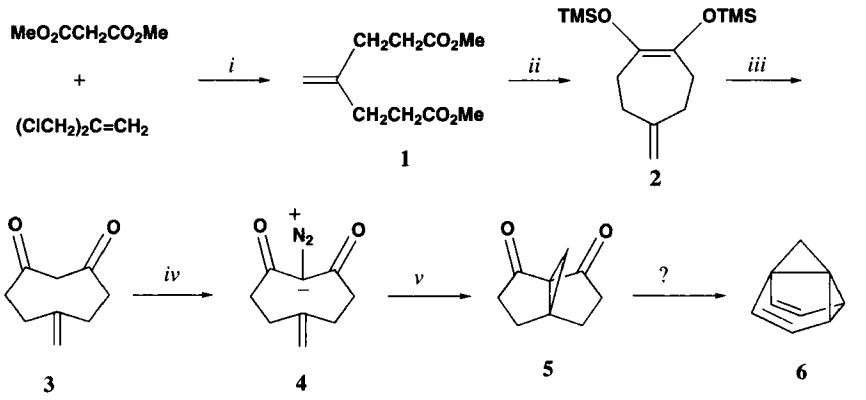
Over a decade ago, 1,5-methylenesemibullvalene (**6**) was calculated to be a symmetric molecule in which the delocalized form, normally associated with the transition state for the Cope rearrangement, was lower in energy than the localized "ground" state.[1] Thus this molecule should be an example of the elusive bishomobenzene. Recent calculations at very high levels of theory have led to the same conclusion.[2] We have been attempting to synthesize **6** for some time. Our strategy required the key intermediate [3.3.1]propellane-2,8-dione (**5**), whose synthesis was reported several years ago.[3] We have now been able to carry it out reproducibly on a significant scale, so that **5** can be obtained in gram rather than milligram quantities. The present paper reports the details of the synthesis of **5**, characterization data on it and its precursors, and its structure; its chemistry will be reported later.

The design of the synthesis has not changed significantly from that reported earlier (*Scheme 1*).[3] It was found that the preparation of the starting material **1**, previously carried out in two steps in 35% yield, can now be accomplished in one pot by using KOH as the base and N-methylpyrrolidinone as the solvent. The water and salt required for the Krapcho decarbomethoxylation[4] are thus generated *in situ*, and the product is isolated in about 60% yield after 24–36 h of heating. These conditions were found by trial and error: other polar aprotic solvents and other hydroxides did not work as well. The acyloin condensation proceeded very efficiently to afford **2** in over 95% yield. Compound **2**



i) KOH, N-Methylpyrrolidinone; ii) Na, TMSCl, toluene; iii) $CHBr_3$, Et_2Zn, CH_2Cl_2; iv)TsN_3, Et_3N, CH_3CN; v) $Rh_2(OAc)_4$

Scheme 1

was not purified but was used immediately for the ring expansion reaction. Unfortunately, the results reported earlier[3] have proved not to be reproducible, and although the desired product **3** was obtained, the best yield was about 45% yield; the remainder of the material was a complex mixture from which no identifiable product could be separated. Fortunately, while the problem with this reaction remains mysterious, yields approaching 40% are routine and reproducible. Diazo transfer to give **4** was accomplished with tosyl azide.[5] Complete purification of **4** was difficult, but proved to be unnecessary. Since propellane **5** is quite insoluble in ether, treatment of an ethereal solution of **4** (after removal of most of the tosyl amide by precipitation) with a catalytic amount of rhodium acetate dimer[6] gave beautiful crystals of **5** in 50% yield over the two steps.

Crystals of propellane **5** grown from ethyl acetate were submitted to X-ray analysis. Compound **5** crystallizes in the monoclinic system, space group $P2_1$, with two independent molecules in the unit cell ($Z = 4$) located at general positions. The molecules have approximate, but not crystallographic, mirror symmetry as expected for the rigid framework-structure. There are no unusual intermolecular interactions and the internal geometry is unremarkable. The bridgehead bond lengths in the two independent molecules are 1.513(9)Å and 1.550(8)Å which bracket the average value for similar bonds in [3.3.1]-propellanes from the Cambridge Structural Database.[7,8]

EXPERIMENTAL SECTION

Toluene was dried by distillation from calcium hydride. Bromoform was distilled before use. All other chemicals were used as received. NMR samples were prepared in $CDCl_3$, and unless otherwise noted were acquired on a Bruker AC200 Spectrometer.

Dimethyl 4-Methylenepimelate (1).- A mixture of 13.68 g (0.244 mol) of KOH, 32.31 g (0.245 mol) of dimethyl malonate, and 10.153 g (0.0812 mol) of methallyl dichloride in 300 mL of N-methylpyrrolidinone was stirred at room temperature for 30 minutes, then heated to 150°. The progress of the reaction was monitored by GC. After 36 h, the mixture was cooled and diluted with 300 mL of water. The mixture was extracted with 5 x 75 mL of ether, and the organic layer was washed with 2 x 100 mL of water, dried and concentrated to provide 14.31 g (88%) of a pale yellow oil, which was distilled under high vacuum to give 10.2 g (63%) of a colorless oil, bp. 65° (0.1 mm). ^{1}H NMR: δ 4.60 (s, 2H), 3.50 (s, 6H), 2.32 (m, 4H), 1.82 (m, 4H); ^{13}C NMR: δ 173.0 (2C) 146.0 (C), 109.4 (CH_2), 51.2 ($2CH_3$), 32.0 ($2CH_2$), 30.6 ($2CH_2$); IR (neat): 3100, 3070-2830, 1745, 1700, 1655, 1442, 1170, 994, 895 cm^{-1}; EIMS, m/z (rel intensity) 200 (M+, 0), 169 (41), 168 (49), 136 (44), 109 (63), 108 (51), 98 (50), 81 (100), 67 (42), 59 (45), 41 (41), 15 (68).

Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.83; H, 8.09

Acyloin Condensation.- A mixture of 10.2 g (0.051 mol) of diester **1**, 50 mL (0.39 mol) of chlorotrimethylsilane, and 8.86 g (0.385 mol) of sodium spheres in 500 mL of dry toluene was heated to reflux overnight under nitrogen in a dry 1L round-bottomed flask. The mixture was cooled, filtered through a pad of Celite on a dry, sintered glass funnel covered by a stream of nitrogen delivered from

an inverted funnel, rinsed with fresh, dry toluene and evaporated to give 13.61 g (96%) of **2** as a yellow oil with some solid in it. It was used without further purification.

5-Methylenecyclooctane-1,3-dione (3).- A mixture of 5.0 g (0.018 mol) of the crude acyloin product, 50 mL of dichloromethane, and 9.3 g (0.037 mol) of bromoform was cooled in a Dry-Ice/acetone bath. Diethylzinc (2.0 mL, 0.02 mol) was added dropwise over about 10 min; the cooling bath was then removed and the mixture allowed to warm up to 0°, by which time the reaction was complete. It was quenched with 25 mL of saturated ammonium chloride solution (dropwise at first!) and stirred for 30 min, then the layers were separated and the aqueous layer was extracted with 2 x 25 mL of chloroform. The combined organic layers were extracted with 3 x 25 mL of 5% sodium hydroxide solution, the yellow basic layer was washed with 25 mL of chloroform, acidified with 12M HCl and extracted with 5 x 30 mL of chloroform. The combined organic layers were dried over magnesium sulfate and concentrated to give 1.00 g (40%) of a nearly colorless oil. A portion of this oil was distilled at 50-55° (0.1 mm) to give **3** as a colorless oil. ^{1}H NMR: δ 4.75 (s, 2H), 3.28 (s, 2H), 2.35 (m, 4H), 2.20 (m, 4H); ^{13}C NMR: δ 204.5 (2C) 145.4 (C), 115.3 (CH_2), 58.9 (CH_2), 43.6 ($2CH_2$), 32.5 ($2CH_2$); IR (neat): 2942, 2910-2820, 1722, 1699, 1648, 1450, 1117, 910 cm^{-1}; EIMS, m/z (rel intensity) 152 (M+, 6), 134 (5), 124 (11), 109 (55), 95 (44), 81 (64), 67 (100), 53 (54), 43 (61), 39 (85), 27 (77), 15 (11).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.73; H, 8.03

[3.3.1]Propellane-2,8-dione (5).- A mixture of 1.62g (0.0107 mol) of undistilled diketone, 2.1g (0.0107 mol) of tosyl azide, 2.0 mL (1.45 g, 0.0145 mol) of triethylamine in 20 mL of acetonitrile was stirred at room temperature for 10 min. The solution was concentrated, taken up in 20 mL of CH_2Cl_2 and diluted with 50 mL of petroleum ether (bp. 30-60°) to precipitate the tosyl amide. The mixture was filtered and concentrated again to give the diazo compound as a yellow oil (IR: 2165 cm^{-1}). This was taken up in 30 mL ether and a small amount of $Rh_2(OAc)_4$ was added. Bubbling ensued and as the reaction proceeded, crystals grew in the solution. After standing overnight, 0.787 g (49%) of crystals deposited and were collected. Recrystallization from ethyl acetate:ether gave an analytical sample, mp. 157-159°. ^{1}H NMR (400 MHz): δ 2.05 (s, 2H), 2.14 (dt, 2H, J = 13, 10), 2.31 (dt, 2H, J = 13, 5), 2.45 (dd, 4H, J = 10, 5); ^{13}C NMR: δ 203.3 (2C) 48.1 (C), 45.1 (C), 37.8 ($2CH_2$), 27.8 (CH_2), 26.4 ($2CH_2$); IR (KBr): 2900-2820, 1760, 1735, 1702, 1692, 1365, 1330, 1036 cm^{-1}; EIMS, m/z (rel. intensity) 150 (M+, 71), 135 (8), 122 (86), 108 (44), 94 (18), 79 (100), 66 (72), 54 (71), 39 (57), 27 (39), 15 (4).

Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 72.14; H, 6.84

X-ray Analysis and Crystal Data: $C_9H_{10}O_2$, MW = 150.18, monoclinic $P2_1$; cell dimensions, a = 6.636(1) Å, b = 14.927(3) Å, c = 7.697(1) Å, β = 92.220(6)°, V = 742.12(2) Å^3; Z = 4, D_c = 1.344 g/cm^3, μ = 0.88 cm^{-1}, colorless plate 0.47 x 0.39 x 0.16 mm. **Data Collection.** The diffractometer was an Enraf-Nonius CAD4 with graphite monochromated MoKα radiation, λ = 0.71073 Å. Cell parameters were determined from the 20 reflections collected with the CAD4 Express software.[8] 1283 Reflections were measured with 5°≤ 2θ ≤ 47°. Lorentz and polarization corrections were applied, but absorption and decay corrections were not applied. **Solution and Refinement.** The structure was solved by direct methods using SHELX-86.[9] All heavy atoms were refined anisotropically and

hydrogen atoms were included at idealized positions but not refined (199 variable parameters). (901 Reflections were used with $I > 3\sigma(I)$. $R = 0.038$ and $R^w = 0.043$ where $R = \Sigma|F_o-F_c|/\Sigma F_o$ and $R_w = (\Sigma w|F_o-F_c|^2/\Sigma w\ F_o^2)^{1/2}$. The largest positive and negative peaks in the final difference Fourier maps were 0.14 e/Å^3 and -0.21 e/Å^3, respectively.

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