Synthesis and Facile Rearrangement of 10,10-Dicarbonyl-substituted [4.3.1]Propellane Derivatives

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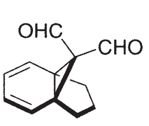
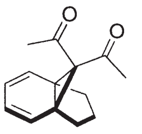
While an attempt to prepare 10,10-diformyl[4.3.1]propella-1,4-diene was not successful owing to its facial skeletal rearrangement, the corresponding diacetyl derivative was isolated, which would serve as a useful precursor of carbene sources.

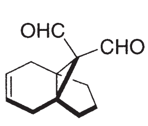
Since [4.*n*.1]propelladienes ($n = 3$, 4) and methano[10]annulenes have been shown to serve as good precursors of free carbenes,[1,2] substantial interest has been focused on the synthesis of their derivatives having a variety of substituents on the methano bridge. Although a number of alkyl substituted derivatives have been synthesized, those having unsaturated functional groups are relatively rare.[1f] Our recent interest in the generation of all carbon molecules from organic compounds[3,4] led us to design macrocycles having [4.3.1]propelladiene units as precursors of cyclo[5n]carbons.[5] In this connection, we planned to prepare 10,10-diformyl[4.3.1]propella-1,4-diene (**1a**) and the diacetyl derivative **1b** which would serve as versatile intermediates of the carbene precursors, since both functionalities can be readily converted to an ethynyl group.[6] We wish to report here our attempts to synthesize **1a** and **1b** and the corresponding olefins **2a** and **2b**, together with the extremely facile, unusual rearrangement observed during the preparation of these compounds.



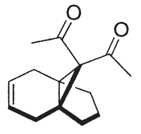
1a



1b



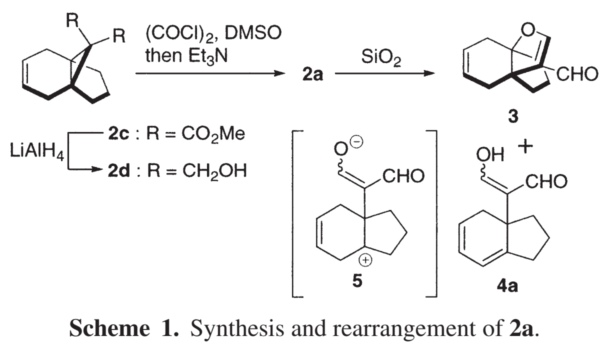
2a



2b

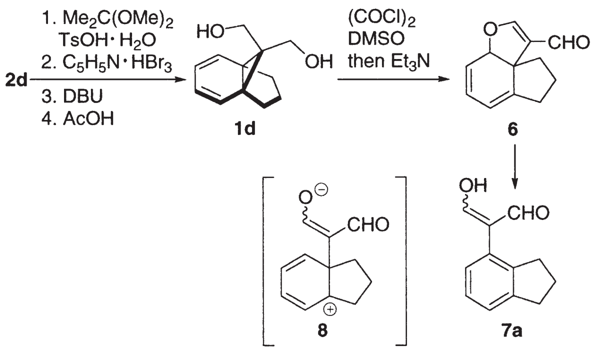
Swern oxidation (oxalyl chloride and DMSO, then Et$_3$N)[7] of diol **2d** derived from diester **2c**[8] afforded labile dialdehyde **2a**[9] in quantitative yield. However, attempted purification of **2a** with silica gel chromatography resulted in the isomerization to propellane type dihydrofuran **3**[9] and dihydroindan **4a**[9] in 17% and 52% isolated yields, respectively (Scheme 1).

The formation of **3** and **4a** can be interpreted in terms of the initial bond cleavage to form a zwitterion intermediate **5** which is stabilized by the electron-withdrawing formyl groups. Cyclization or proton transfer of **5** gives **3** or **4a**.



Scheme 1. Synthesis and rearrangement of **2a**.

The corresponding dienediol **1d** was parepared from **2d** by protection of the hydroxy groups as an acetonide followed by bromination, dehydrobromination, and deprotection in 66% yield without event. Oxidation of **1d** under similar conditions, however, resulted in the formation of angularly fused dihydrofuran **6**[9] as a single product, whose structure was elucidated on the basis of the preference of a tertiary C(sp^3) signal at 94.5 ppm. Moreover, on standing at room temperature, the product **6** isomerized to indan derivative **7a**.[9] The formation of these products is also explained in terms of the zwitterion **8**. The lability of **1a** relative to **2a** can be attributed to the presence of a pentadienyl cation structure in the intermediate **8** (Scheme 2).



Scheme 2. Attempted synthesis of **1a**.

Since the diformyl derivatives were too unstable for isolation, we next carried out the synthesis of propellanes with less electron-withdrawing acetyl groups. Toward this end, the crude dialdehyde **2a** was treated with methyllithium at room temperature to afford a 1:1 mixture of diols **2e** and **2f** (95%). The ratio changed to 9:1 when methylmagnesium iodide was employed at −78 °C. The stereochemistry of major isomer **2e** was established to be R^*, S^* by the X-ray crystallographic structure analysis of diene **1e** derived from **2e** as described below. PCC oxidation of a mixture of **2e** and **2f** (1:1) gave diketone **2b**[9] in 48% yield after purification by silica gel chromatography (Scheme 3). In order to convert diols **2e** and **2f** into the corresponding dienes, **2e** was treated with dimethoxypropane and *p*-toluenesulfonic acid to give acetonide **2g**. Since similar reaction of **2f** resulted in the formation of dihydroindan **4b**,[9] only **2e** was used for the further transformation. Thus, **2g** was transformed to **1e** by bromination, dehydrobromination, and deprotection under mild condition to afford **1e** in 27% yield, whose stereochemistry was established by the X-ray analysis (Figure 1).[10] The bond lengths of the cyclopropane bonds of **1e** (C(1)–C(6) = 1.546 Å, C(1)–C(10) = 1.530 Å, C(6)–C(10) = 1.543 Å) are longer than those reported for a 10,10-dichloro-[4.3.1]propelladiene derivative.[11] It is also worth noting that a pair of **1e** forms a dimer by complementary hydrogen bonding between the hydroxy groups. Finally, Swern oxidation of **1e**

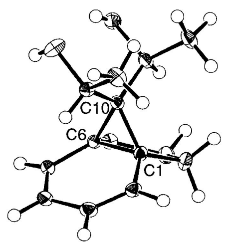
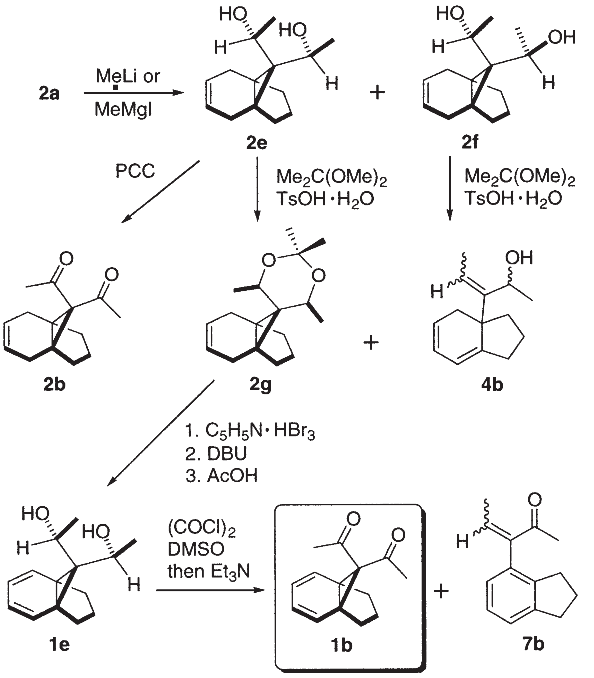


Figure 1. ORTEP drawing of **1e** with arbitary numbering.



Scheme 3. Synthesis of **1b** and **2b**.

furnished **1b**[9] in 22% yield together with indan **7b**[9] (35%) after purification.

In conclusion, though diformyl propelladiene **1a** was not obtained, we succeeded in the synthesis of diacetyl derivative **1b**. Since diketone **1b** is stable enough to tolerate chromatography, it would serve as a useful precursor of many carbene sources.

References and Notes

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8 **2c** was prepared by dicarboxylation of the corresponding dibromide (E. Vögel, W. Wiedemann, H. D. Poth, J. Eimer, and H. Günther, *Liebigs Ann. Chem.*, **759**, 1 (1972).) according to the reported procedure: D. Ginsburg, "Propellanes: structure and reactions," Verlag Chemie, Weinhein (1975), p 119.

9 All new compounds were characterized by elemental analyses or high resolution mass spectra. The characteristic NMR signals are listed below: **2a**: ^{1}H NMR (CDCl$_3$) δ 9.78 (s, 1H), 9.36 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 197.2 (d), 196.8 (d) 124.6 (d), 53.1 (s), 43.4 (s), 35.4 (t). **3**: ^{1}H NMR (CDCl$_3$) δ 9.46 (s, 1H), 7.22 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 184.8 (d), 165.6 (d), 129.7 (d), 127.4 (s), 125.7 (d), 106.2 (s), 55.7 (s). **4a**: ^{1}H NMR (CDCl$_3$) δ 14.08 (br s, 1H), 8.31 (s, 2H), 5.67–5.54 (m, 2H), 5.50 (d, $J = 2.2$ Hz, 1H), 2.88 (d, $J = 20.1$ Hz, 1H), 2.63 (d, $J = 20.0$ Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 181.2 (d), 142.8 (s), 126.3 (d), 125.1 (d), 123.4 (d), 118.1 (s), 48.0 (s), 40.1 (t). **6**: ^{1}H NMR (CDCl$_3$) δ 9.52 (s, 1H), 7.37 (s, 1H), 5.94 (ddd, $J = 9.5$, 5.4, 1.7 Hz, 1H), 5.65 (br s, 1H), 5.63 (dd, $J = 5.4$, 2.7 Hz, 1H), 5.31 (dd, $J = 9.5$, 1.7 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 184.1 (d), 165.6 (d), 144.5 (s), 130.2 (s), 125.9 (d), 122.5 (d), 114.2 (d), 94.5 (d), 52.3 (s). **7a**: ^{1}H NMR (CDCl$_3$) δ 14.24 (br s, 1H), 8.50 (s, 2H) 7.22 (d, $J = 7.0$ Hz, 1H), 7.17 (dd, $J = 7.0$, 7.0 Hz, 1H), 6.98 (d, $J = 7.0$ Hz, 1H); ^{13}C NMR (Acetone-d_6) δ 179.4 (d), 145.0 (s), 144.8 (s), 129.3 (s), 129.1 (d), 126.8 (d), 124.4 (d), 124.0 (d). **2b**: ^{1}H NMR (CDCl$_3$), δ 5.50–5.44 (m, 2H), 2.18 (s, 3H) 2.11 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 202.9 (s), 202.0 (s), 125.4 (d), 59.0 (s), 36.8 (s). **1e**: ^{1}H NMR (CDCl$_3$) δ 3.82 (q, $J = 6.9$ Hz, 1H), 3.47 (q, $J = 6.9$ Hz, 1H), 1.67 (d, $J = 6.9$ Hz, 3H), 1.34 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 127.85 (d), 127.78 (d) 121.7 (d), 120.7 (d), 68.5 (d), 66.5 (d), 49.0 (s), 46.9 (s), 29.0 (s), 23.1 (q), 22.0 (q). **1b**: ^{1}H NMR (CDCl$_3$) δ 6.09 (dd, $J = 7.4$, 2.7 Hz, 2H), 5.85 (dd, $J = 7.4$, 2.7 Hz, 2H), 2.33 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 201.3 (s), 198.9 (s), 126.3 (d), 121.4 (d), 54.6 (s), 45.0 (s), 32.5 (t), 29.3 (q), 27.3 (q), 19.8 (t).

10 X-ray data for **1e**: Crystal dimension $0.50 \times 0.70 \times 0.30$ mm^3, monoclinic, space group $P2_1/n$ (#14), $D_{\text{calcd}} = 1.251$ g cm^{-3}, $Z = 4$, $a = 7.8470(2)$ Å, $b = 7.2384(2)$ Å, $c = 20.6918(4)$ Å, $\beta = 95.7053(5)°$, $V = 1169.46(4)$ Å^3, $2\theta_{\max} = 63.0°$, MoKα radiation ($\lambda = 0.71069$ Å), $T = 100(1)$ K. Of 5178 reflections collected, 3900 were unique and 3424 were taken as observed ($I > 2.0\sigma(I)$). The structure was solved by direct methods (SIR97) and refined on F^2 by full-matrix least-squares methods, using SHELXL-97. Non-hydrogen atoms were anisotropically refined, and all hydrogen atoms were isotropically refined to converge with $R = 0.0590$, $R_w = 0.1292$. Deposited in CCDC-200307.

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