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Polycyclic Rearrangements: Novel Lewis Acid-catalysed Rearrangement of the Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane Framework; *X*-Ray Crystal Structure of 1,10-Dimethylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]-undecane-9,11-dione

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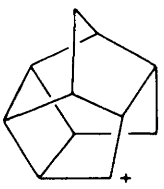
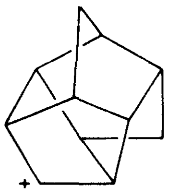
The pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione derivatives (**4**) and (**5**) on exposure to boron trifluoride–diethyl ether undergo a hitherto unknown rearrangement to the novel pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]-undecane ring system (**7**) and (**8**).

The Lewis-acid catalysed rearrangements of polycyclic systems usually proceed with thermodynamical control to the most stable carbocyclic isomer.[1] An interesting illustration is provided by the pentacycloundecane system; the pentacyclic cationic species (**1**) always rearranges to provide the most stable pentacyclic D_3 trishomocubanyl cations (**2**) *via* a facile 1,2-alkyl shift.[1c,2] We report here a deviation from this behaviour; various substituted derivatives of system (**1**) rearrange to the novel pentacycloundecane system (**3**)[3] through the intermediacy of a carbocation formally related to the most stable carbocyclic isomer (**2**).[1c]

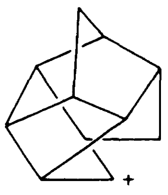
Reaction of the readily obtainable pentacycloundecanedione (**4**)[4] with BF_3–Et_2O in benzene (reflux, 8 h) and column chromatography (silica gel) furnished a 2 : 1 mixture of (**7**) and (**10**) in 80% yield. While the structure of the minor product (**10**)† could be deduced from the ^{1}H and ^{13}C n.m.r. data,



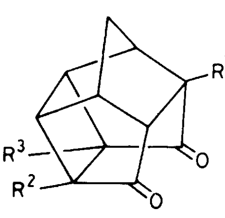
(**1**)

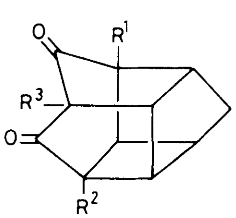


(**2**)

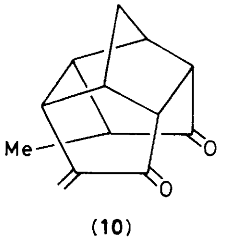


(**3**)





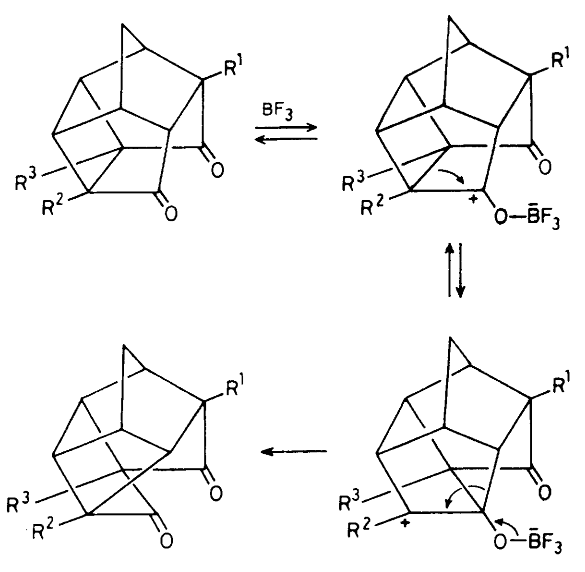
(4) $R^1 = H, R^2 = R^3 = Me$ (7)
(5) $R^1 = R^2 = Me, R^3 = H$ (8)
(6) $R^1 = R^2 = R^3 = H$ (9)



(10)

assignment of structure (7)† for the major product required an *X*-ray diffraction study (Figure 1).‡ The pentacyclic dione (5),[4] like (4), on exposure to BF_3–Et_2O rearranged essentially to a single product (8) in 50% yield. The structure of (8)† was deduced from its spectral data which closely resembled data for (7).

We propose that the diones (7) and (8) are formed from the precursors (4) and (5) *via* a Lewis acid-catalysed ketone–ketone rearrangement as depicted in Scheme 1. The role of the methyl substituents in steering the rearrangement is highlighted by the fact that the unsubstituted dione (6) did not undergo the expected rearrangement to (9).



Scheme 1

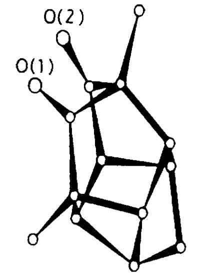


Figure 1. *X*-Ray structure of compound (7).

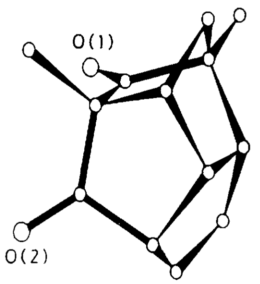


Figure 2. *X*-Ray structure of compound (12).

Since the rearrangement described here provides easy access to the novel trishomocubane ring systems (7) and (8), we have investigated the reactions of compounds (7) and (8). Flash vacuum pyrolysis (f.v.p.; 500 °C; 1 Torr; quartz tube) of (7) furnished the *cis,syn,cis*-tricyclopentane (11) and the tetracyclic ene-dione (12) in 35 and 55% yield, respectively. The structure of (11)§ was clear from its spectral parameters, but

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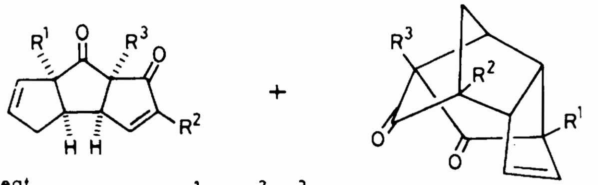
† Compound (10): m.p. 108—110 °C, λ_{max} (MeOH) 239 nm; ν_{max} (KBr) 1740, 1725, and 1645 cm^{-1}; ^1H n.m.r. ($CDCl_3$; 100 MHz), δ 6.04 (1H, s), 5.34 (1H, s), 3.18 (1H, br.d), 2.2—3 (5H, m), 1.96 (2H, ABq, *J* 11 Hz), 1.68 (1H, s), and 1.14 (3H, d, *J* 6 Hz); ^{13}C n.m.r. ($CDCl_3$; 25.0 MHz) δ 219.0 (s), 205.0 (s), 147.9 (s), 119.7 (t), 57.7 (d), 56.3 (d), 48.8, 48.0, 47.5, 46.8, 45.6, 35.2 (t), and 10.2 (q) p.p.m.; (7): m.p. 91—92 °C, ν_{max} (KBr) 1760 and 1720 cm^{-1}; ^1H n.m.r. ($CDCl_3$; 100 MHz) δ 3.43 (1H, br.s), 2.88 (1H, br.s), 2.62 (2H, m), 2.4 (2H, m), 1.74 (2H, s), 1.38 (3H, s), and 1.3 (3H, s); ^{13}C n.m.r. ($CDCl_3$; 25.0 MHz) δ 210.1 (s), 208.0 (s), 66.9 (s), 56.4 (d), 55.6 (s), 49.3 (d), 45.3 (d), 44.0 (d), 43.1 (d), 42.8 (d), 37.2 (t), 14.5 (q), and 10.9 (q) p.p.m.; (8): m.p. 79—80 °C, ν_{max} (KBr) 1760 and 1710 cm^{-1}; ^1H n.m.r. ($CDCl_3$; 100 MHz) δ 3.47 (2H, s and d, *J* 3 Hz), 2.7—3.0 (1H, m), 2.2—2.7 (2H, m), 1.96 (1H, m), 1.76 (2H, br.s), 1.36 (3H, s), and 1.0 (3H, s); ^{13}C n.m.r. ($CDCl_3$; 25.0 MHz) δ 208.6 (s), 207.6 (s), 64.8 (d), 58.8 (s), 55.1 (s), 51.6 (d), 50.8 (d), 43.2 (d), 43.0 (d), 40.9 (d), 35.6 (t), and 14.3 (q, 2C) p.p.m.

‡ *Crystal data:* (7), $C_{13}H_{14}O_2$, space group $P2_1/a$, $a = 6.276(3)$, $b = 7.747(3)$, $c = 22.272(4)$ Å, $\beta = 109.46(5)°$, $Z = 4$, $D_c = 1.316$ g cm^{-3}, Mo-K_{α_1} radiation, $\lambda = 0.70926$ Å, $\mu = 0.5$ cm^{-1}, 1773 unique reflections of which 774 had $I > 3\sigma(I)$; (12), $C_{13}H_{14}O_2$, space group $P2_1/c$, $a = 12.493(4)$, $b = 6.621(4)$, $c = 13.000(3)$ Å, $\beta = 104.44(2)°$, $Z = 4$, $D_c = 1.290$ g cm^{-3}, Mo-K_{α_1} radiation, $\lambda = 0.70926$ Å, $\mu = 0.49$ cm^{-1}. 1664 Unique reflections of which 454 had $I > 3\sigma(I)$. The data for both compounds were collected on a CAD-4 four-circle diffractometer and structures were solved by automatic centrosymmetric direct methods and refined by large-block least-squares. The final refinements converged at $R = 0.059$ for (7) and $R = 0.094$ for (12).

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ Compound (11): ν_{max} (neat): 1740, 1700, 1640 cm^{-1}; ^1H n.m.r. ($CDCl_3$; 100 MHz) δ 7.25 (1H, s with fine structure), 5.64 (2H, m), 3.5 (1H, br.s), 3.3 (2H, br.s), 2.7 (2H, br.s), 1.72 (3H, s), and 1.36 (3H, s); ^{13}C n.m.r. ($CDCl_3$; 25.0 MHz) δ 210.6 (s), 156.7 (d), 140.0 (s), 132.1 (d), 129.8 (d), 63.6 (s), 62.3 (d), 52.0 (d), 37.5 (d), 35.1 (t), 18.7 (q), and 10.6 (q) p.p.m.; (12) m.p. 161—162 °C, ν_{max} (KBr) 1750, 1715, and 1605 cm^{-1}; ^1H n.m.r. ($CDCl_3$; 100 MHz) δ 5.72 (2H, s), 3.5—3.92 (1H, ddd, J_1 8, J_2 10, J_3 6 Hz), 3.12 (2H, dt, J_1 10, J_2 2 Hz), 2.75 (1H, d, *J* 6 Hz), 2.22 (1H, dd, J_1 11, J_2 2 Hz), 1.96 (1H, ½AB, *J* 11 Hz), 1.2 (3H, s), and 1.09 (3H, s).



$(7) \xrightarrow{\text{heat}} (11)$ $R^1 = H, R^2 = R^3 = Me$ (12)
$(8) \xrightarrow{\text{heat}} (13)$ $R^1 = R^2 = Me, R^3 = H$ (14)

assignment of (**12**)§ required an *X*-ray diffraction study (Figure 2).‡ Similarly, f.v.p. of (**8**) produced the *cis,syn,cis*-tricyclopentane (**13**)¶ and the tetracycle (**14**)¶ in 35 and 25% yield, respectively. The formation of the tricyclopentanes (**11**) and (**13**) is readily understood in terms of a [2 + 2]-cycloreversion but the mechanism for the genesis of the tetracyclic ene-diones (**12**) and (**14**), products of a deep-seated reorganisation, is not yet clear. An attractive mechanism involves an intramolecular ene reaction in the folded tricyclopentane (**11**) and (**13**) followed by a [1.3] shift.

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¶ Compound (**13**): m.p. 131—132 °C, ν_{max} (KBr) 1738, 1690, and 1630 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$, 100 MHz) δ 7.35 (1H, br.s), 5.68 (1H, d), 5.42 (1H, d), 3.66 (1H, m), 3.36 (1H, d), 2.4—3 (3H, m), 1.72 (3H, m), 1.72 (3H, d, J 1 Hz), and 1.16 (3H, s); ^{13}C n.m.r. ($CDCl_3$, 100 MHz) δ 209.0 (s), 200.0 (s), 158.1 (d), 140.6 (s), 135.7 (d), 131.3 (d), 66.2 (s), 61.6 (d), 47.0 (d), 41.0 (d), 34.9 (t), 21.2 (q), and 10.5 (q) p.p.m.; (**14**): m.p. 158—159 °C, ν_{max} (KBr) 1760, 1715, and 1605 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$; 100 MHz) δ 5.7 (1H, dd, J_1 6, J_2 3 Hz), 5.48 (1H, d, J 6 Hz), 3.2—3.5 (1H, m), 3.14 (1H, d with fine structure, J 9 Hz), 2.86 (1H, dd, J_1 5, J_2 2 Hz), 2.16 (dd, J_1 10, J_2 2 Hz), 1.93 (1H, ½ABq, J 10 Hz), 1.25 (3H, s), and 1.23 (3H, s); ^{13}C n.m.r. ($CDCl_3$; 25.0 MHz) δ 210.5 (s), 208.4 (s), 138.7 (d), 133.6 (d), 65.5 (d), 62.1 (s), 59.5 (d), 56.6 (s), 56.5 (d), 44.4 (t), 37.3 (d), 18.5 (q), and 13.0 (q) p.p.m.