

Fig. 3. Bond lengths (Å). The mean standard deviation is 0.03 Å.

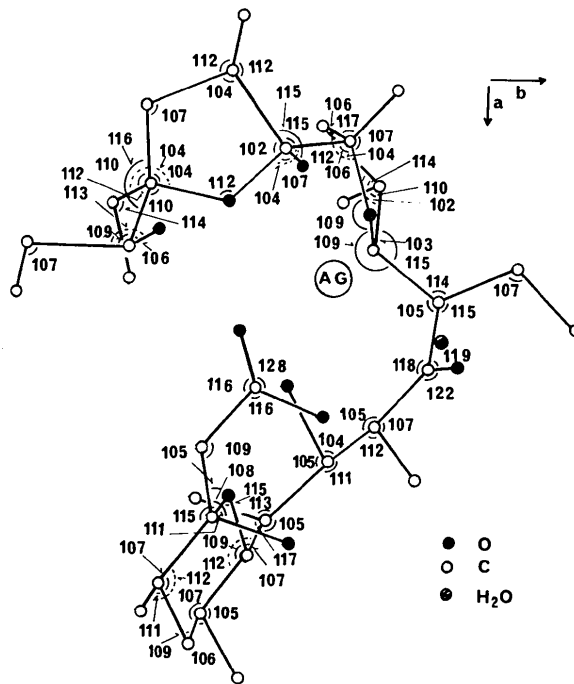


Fig. 4. Bond angles (°). The mean standard deviation is 2°.

tances ranging from 2.39 (2) to 2.99 (2) Å. The five-membered rings, *A* and *B*, take an envelope conformation and the six-membered ring *C* adopts a chair conformation. For ring *C*, the methyl groups of C(4') and C(6') along with the two substituents of C(2) and C(8) at the α -position of the tetrahydropyran function are equatorial, while the hydroxyl group of O(3) is axial. Bond lengths and angles are shown in Figs. 3 and 4, respectively. They do not differ significantly from the normal values.

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Two Acid Rearrangement Products from Substituted Pentacyclododeca-5,12-diones: $C_{18}H_{24}O_2$ and $C_{16}H_{20}O_4$

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Abstract. (II) $C_{18}H_{24}O_2$, $P2_1/c$, $a=6.818$ (4), $b=12.586$ (6), $c=17.966$ (9) Å, $\beta=106.8$ (1)°, $Z=4$, $d_{calc}=1.22$ g cm^{-3} , $\sim(0.8 \times 0.6 \times 0.2)$ mm. This molecule has a bis-

nordiadamantane ring skeleton. (III) $C_{16}H_{20}O_4$, $P2_1/n$, $a=12.247$ (7), $b=9.972$ (6), $c=12.242$ (7) Å, $\beta=102.9$ (1)°, $Z=4$, $d_{calc}=1.26$ g cm^{-3} , $\sim(0.5 \times 0.5 \times 0.8)$ mm.

Molecules of this compound are linked into pairs across a center of symmetry by $\text{OH}\cdots\text{O}=\text{C}$ hydrogen bonds.

Introduction. The products obtained from treatment of pentacyclocadiones [e.g. (I)] with trifluoroacetic acid vary significantly depending upon the substitution at the C-1, 6, 4, and 11 positions. The 1-6 dimethyl cage compound gave a bisnordiadamantane (II) through two sets of stereospecific twofold Wagner-Meerwein rearrangements (Hirao *et al.*, 1975) while the hydroxylated version of (I) [having an $-\text{OH}$ substituted for a $-\text{CH}_3$ on C(4) and C(11)] was opened to form (III) through a series of fragmentation and retro-Michael reactions which were also stereospecific. The configurations of both molecules were established by X-ray analyses.

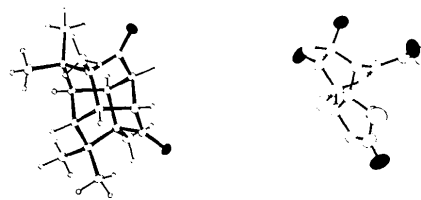
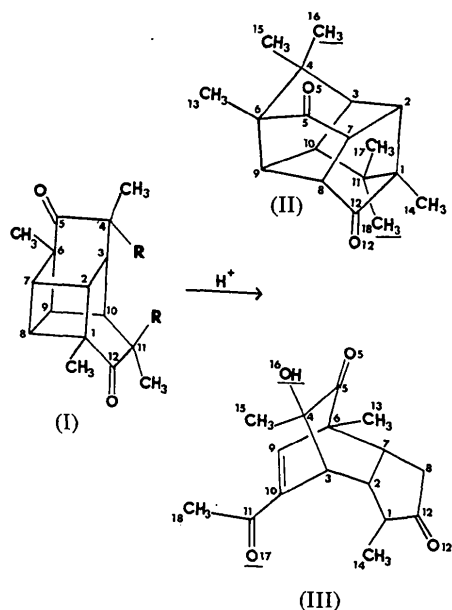


Fig. 1. Results of the X-ray analyses. Molecule II is shown on the left. The oxygen atoms have been shaded for identification.

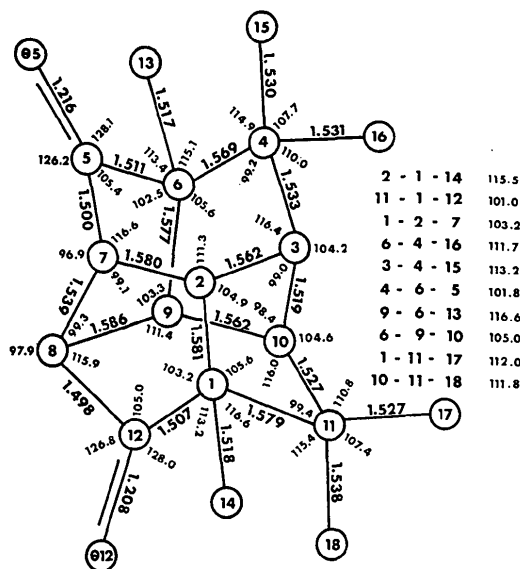


Fig. 2. Bond lengths and angles for molecule II. Standard deviations are of the order of 0.003 Å for the bond lengths and 0.3° for the angles.

Crystals of both materials were obtained from B. Witkop of the National Institutes of Health and O. Yonemitsu of Hokkaido University. Both structures were solved by the symbolic addition procedure for centrosymmetric crystals (Karle & Karle, 1966) using the normalized structure factor magnitudes $|E|$. The full-matrix least-squares program *ORXFLS3* (Busing *et al.*, 1971) was used to refine both structures. Atomic scattering factors used were those listed in *International Tables for X-ray Crystallography* (1962).

Difference maps, calculated after some anisotropic refinement on the heavier atoms, revealed the positions of all the hydrogen atoms for both molecules. The hydrogen parameters were then included as constants in the final cycles of refinement. The function minimized by the least-squares procedure was $\sum w(|F_o| - |F_c|)^2$ where the weight (w) was calculated according to Gilardi (1973). In addition, for molecule III, all data having $|F_o| < 3.0\sigma|F_o|$ were given zero weight and

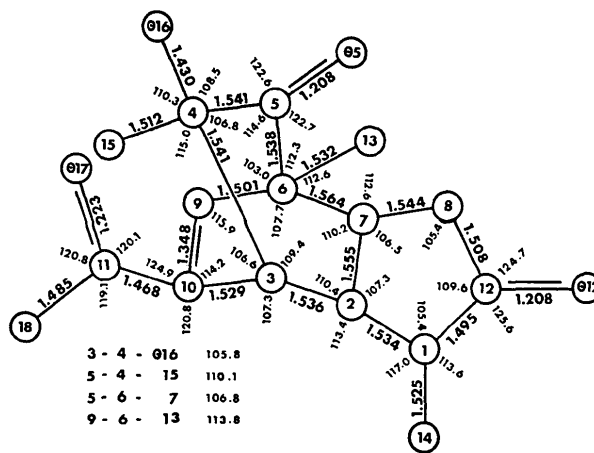


Fig. 3. Bond lengths and angles for molecule III. Standard deviations are of the order of 0.004 Å for the distances and 0.4° for the angles.

omitted from the refinement. The final R , where $R = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}$, was 5.8% for compound II and 7.3% for the 2177 reflections used in the refinement for (III) (for the full set of 2366 reflections, $R = 8.0\%$).

The final weighted R values, where $R_w = \frac{[\sum w(|F_o| - |F_c|)^2]}{\sum w F_o^2}^{1/2}$, were 6.2% for (II) and 10.2% for (III). Table 1 lists the refined coordinates and thermal parameters of the heavy atoms and the difference map

Table 1. Fractional coordinates and thermal parameters

Parameters for molecule III are listed below those for molecule II.

The thermal parameters are of the form $T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

| | x | y | z | B_{11} | B_{22} | B_{33} | B_{12} | B_{13} | B_{23} |
|-------|---------|---------|---------|----------|----------|----------|----------|----------|----------|
| C(1) | 0.2416 | 0.0293 | 0.1998 | 4.6 | 2.7 | 3.6 | 0.1 | 0.9 | 0.3 |
| | 0.6799 | -0.0128 | -0.0615 | 4.6 | 3.5 | 3.6 | -0.3 | 1.3 | -0.4 |
| C(2) | 0.1283 | 0.0683 | 0.1146 | 3.5 | 2.7 | 3.4 | -0.2 | 0.8 | -0.3 |
| | 0.7497 | 0.1072 | -0.0859 | 3.5 | 3.7 | 3.2 | -0.4 | 1.4 | -0.5 |
| C(3) | 0.0684 | 0.1861 | 0.1244 | 3.0 | 2.9 | 3.2 | 0.0 | 0.9 | -0.1 |
| | 0.8390 | 0.1529 | 0.0164 | 3.3 | 3.4 | 3.1 | -0.2 | 0.8 | 0.2 |
| C(4) | 0.0787 | 0.2632 | 0.0595 | 3.8 | 3.0 | 3.2 | 0.2 | 0.8 | 0.2 |
| | 0.9043 | 0.2725 | -0.0168 | 2.8 | 4.9 | 4.0 | -0.8 | 1.0 | 0.9 |
| C(5) | 0.3104 | 0.1510 | 0.0181 | 3.9 | 4.6 | 3.9 | 0.2 | 1.5 | -0.2 |
| | 0.8191 | 0.3864 | -0.0536 | 4.1 | 3.9 | 4.7 | -1.5 | 1.2 | 0.5 |
| C(6) | 0.3113 | 0.2511 | 0.0647 | 4.1 | 3.3 | 3.4 | -0.5 | 1.3 | 0.1 |
| | 0.6973 | 0.3497 | -0.0526 | 3.7 | 3.5 | 4.0 | -0.2 | 0.8 | 0.2 |
| C(7) | 0.3006 | 0.0612 | 0.0719 | 4.2 | 3.3 | 3.7 | 0.1 | 1.2 | -0.6 |
| | 0.6669 | 0.2236 | -0.1293 | 2.9 | 3.8 | 3.5 | -0.4 | 0.9 | 0.2 |
| C(8) | 0.4861 | 0.0951 | 0.1394 | 3.3 | 4.1 | 4.5 | 0.5 | 1.1 | -0.1 |
| | 0.5483 | 0.1697 | -0.1308 | 3.4 | 4.8 | 4.6 | -0.5 | 0.5 | 0.1 |
| C(9) | 0.4202 | 0.2136 | 0.1504 | 3.2 | 3.4 | 3.8 | -0.5 | 0.6 | -0.2 |
| | 0.7050 | 0.3060 | 0.0663 | 3.5 | 3.4 | 4.3 | -0.7 | 1.4 | -0.5 |
| C(10) | 0.2495 | 0.2171 | 0.1926 | 3.8 | 2.7 | 3.0 | -0.1 | 0.8 | -0.3 |
| | 0.7772 | 0.2054 | 0.1033 | 3.0 | 3.2 | 3.1 | -0.9 | 0.9 | 0.1 |
| C(11) | 0.2600 | 0.1306 | 0.2532 | 4.6 | 3.4 | 3.0 | 0.1 | 0.8 | 0.1 |
| | 0.7927 | 0.1418 | 0.2138 | 4.1 | 4.1 | 3.2 | -1.1 | 0.7 | 0.1 |
| C(12) | 0.4604 | 0.0165 | 0.1985 | 4.7 | 3.6 | 4.1 | 0.9 | 0.4 | -0.2 |
| | 0.5615 | 0.0199 | -0.1174 | 4.2 | 4.4 | 4.3 | -1.0 | 1.5 | -0.4 |
| C(13) | 0.4053 | 0.3457 | 0.0353 | 6.0 | 4.9 | 5.9 | -1.5 | 2.4 | 0.7 |
| | 0.6166 | 0.4668 | -0.0895 | 5.0 | 4.0 | 7.0 | 0.6 | 0.9 | 0.5 |
| C(14) | 0.1546 | -0.0703 | 0.2260 | 7.0 | 3.5 | 5.3 | -0.4 | 1.8 | 1.0 |
| | 0.7169 | -0.1517 | -0.0907 | 7.1 | 4.1 | 6.9 | 0.1 | 0.6 | -0.8 |
| C(15) | -0.0701 | 0.2347 | -0.0194 | 4.7 | 5.1 | 3.4 | 0.3 | 0.4 | 0.2 |
| | 0.9662 | 0.2434 | -0.1081 | 3.8 | 8.6 | 5.6 | 0.2 | 2.4 | 1.7 |
| C(16) | 0.0282 | 0.3761 | 0.0799 | 6.3 | 3.2 | 4.8 | 0.9 | 1.8 | 0.6 |
| C(17) | 0.0802 | 0.1399 | 0.2875 | 6.9 | 5.0 | 4.3 | 0.3 | 3.0 | 0.4 |
| C(18) | 0.4579 | 0.1381 | 0.3210 | 6.7 | 5.0 | 3.3 | 0.4 | -0.1 | -0.0 |
| | 0.7388 | 0.2027 | 0.2992 | 6.3 | 7.5 | 3.4 | -0.7 | 2.0 | -0.6 |
| O(5) | 0.3318 | 0.1428 | -0.0465 | 8.1 | 6.0 | 4.2 | 0.5 | 3.3 | -0.2 |
| | 0.8461 | 0.4965 | -0.0791 | 5.1 | 4.4 | 9.7 | -1.7 | 1.8 | 1.5 |
| O(12) | 0.5856 | -0.0472 | 0.2337 | 6.2 | 5.2 | 6.4 | 2.6 | 0.6 | 1.2 |
| | 0.4859 | -0.0600 | -0.1425 | 5.5 | 5.8 | 8.1 | -2.7 | 1.1 | -1.3 |
| O(16) | | | | | | | | | |
| O(17) | 0.9812 | 0.3129 | 0.0837 | 4.1 | 6.6 | 4.6 | -2.4 | 0.1 | 0.3 |
| | 0.8500 | 0.0406 | 0.2350 | 6.4 | 5.4 | 4.5 | 0.5 | 1.1 | 1.5 |

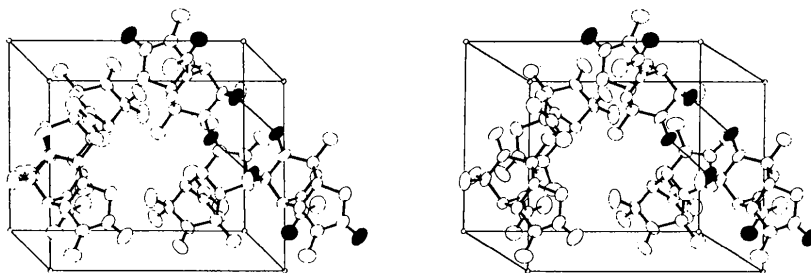


Fig. 4. Contents of one unit cell for molecule III. The intermolecular $\text{OH} \cdots \text{O}=\text{C}$ hydrogen bond, which links the molecules into pairs across a center of symmetry, is indicated in the illustration.

Table 2. *Hydrogen atom coordinates ($\times 10^3$) from difference maps*

| | Molecule II | | | Molecule III | | |
|---------|-------------|------|-----|--------------|------|------|
| | x | y | z | x | y | z |
| H(O16) | | | | 1038 | 393 | 78 |
| H(C1) | | | | 677 | -13 | 20 |
| H(C2) | -11 | 22 | 86 | 779 | 82 | -155 |
| H(C3) | -72 | 194 | 134 | 893 | 74 | 48 |
| H(C7) | 318 | -18 | 44 | 666 | 253 | -213 |
| H(C8A) | 632 | 93 | 129 | 517 | 190 | -63 |
| H(C8B) | | | | 515 | 186 | -184 |
| H(C9) | 563 | 256 | 180 | 662 | 356 | 128 |
| H(C10) | 240 | 294 | 220 | | | |
| H(C13A) | 554 | 334 | 36 | 538 | 438 | -94 |
| H(C13B) | 313 | 375 | -19 | 645 | 560 | -36 |
| H(C13C) | 447 | 414 | 72 | 621 | 496 | -171 |
| H(C14A) | 13 | -69 | 218 | 643 | -234 | -98 |
| H(C14B) | 225 | -93 | 282 | 723 | -134 | -162 |
| H(C14C) | 183 | -139 | 193 | 793 | -159 | -58 |
| H(C15A) | -58 | 158 | -38 | 1010 | 173 | -93 |
| H(C15B) | 222 | 238 | -19 | 924 | 220 | -179 |
| H(C15C) | -38 | 275 | -67 | 1011 | 324 | -121 |
| H(C16A) | 19 | 422 | 37 | | | |
| H(C16B) | -100 | 382 | 94 | | | |
| H(C16C) | 127 | 416 | 124 | | | |
| H(C17A) | -64 | 126 | 255 | | | |
| H(C17B) | 80 | 84 | 329 | | | |
| H(C17C) | 74 | 217 | 314 | | | |
| H(C18A) | 484 | 79 | 359 | 661 | 222 | 275 |
| H(C18B) | 592 | 143 | 305 | 749 | 159 | 358 |
| H(C18C) | 458 | 204 | 356 | 759 | 281 | 318 |

coordinates for the hydrogen atoms are listed in Table 2.*

Discussion. The results of the X-ray analyses on molecules II and III are illustrated in Fig. 1. Bond distances and angles for the two molecules are presented in Figs. 2 and 3 for molecules II and III respectively. Within experimental error, molecule II exhibits non-crystallographic twofold rotation symmetry. In symmetrical cedrone (Beisler & Silverton, 1972) which also has a bisnordiamantane ring skeleton, the two halves of the molecule are related by a center of symmetry which is coincident with a crystallographic center. The fused cage system of (II), made up of 4 five-membered rings and 2 six-membered rings, is severely strained. The five-membered rings all have normal envelope conformations, but the six-membered rings are quite distorted from normal chair conformations. The ideal value for a torsion angle in a six-membered ring in a normal chair conformation is 60° . In (III) the average deviation from 60° for the torsion angles in the six-membered rings is 18.5° with individual deviations of up to 33.2° (see Table 3). The strain can also be seen in several of the bond lengths and angles (see Fig. 2). Similar effects have been noted in other molecules containing similar ring systems (Alden,

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31562 (24 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Kraut & Traylor, 1968; Kobayashi, Iitaka & Shibata, 1970; Beisler & Silverton, 1972). When the ring system in the parent compound (I) was opened to form (III) most of the strain found in (II) was eliminated. The three six-membered rings have a normal boat conformation and the five-membered ring is in a C(12) envelope. The crystal packing of (II) is influenced only by van der Waals forces and there are no intermolecular approaches less than van der Waals radii. Packing in the crystal of molecule III is influenced by the presence of a pair of $\text{OH}\cdots\text{O}=\text{C}$ intermolecular hydrogen bonds ($\text{O}\cdots\text{O}=2.85 \text{ \AA}$, $\text{H}\cdots\text{O}=1.79 \text{ \AA}$, $\text{O}-\text{H}-\text{O}=168.7^\circ$) which link the molecules into dimeric pairs across centers of symmetry. The hydrogen bonds, which are illustrated in the stereodrawing (Johnson, 1965) in Fig. 4, are the only intermolecular approaches less than van der Waals separations.

Table 3. *Molecule II, ring torsion angles ($^\circ$)*

| Five-membered rings | | | |
|---------------------|-------|---------------------|-------|
| C(11)C(1)C(2)C(3) | -5.4 | C(10)C(9)C(6)C(4) | -5.6 |
| C(10)C(11)C(1)C(2) | -24.4 | C(9)C(6)C(4)C(3) | -24.7 |
| C(3)C(10)C(11)C(1) | 47.7 | C(6)C(4)C(3)C(10) | 48.4 |
| C(2)C(3)C(10)C(11) | -51.4 | C(4)C(3)C(10)C(9) | -51.9 |
| C(1)C(2)C(3)C(10) | 33.3 | C(3)C(10)C(9)C(6) | 33.9 |
| C(12)C(1)C(2)C(7) | 5.7 | C(8)C(9)C(6)C(5) | 4.8 |
| C(1)C(2)C(7)C(8) | -36.3 | C(7)C(8)C(9)C(6) | -36.4 |
| C(2)C(7)C(8)C(12) | 53.3 | C(5)C(7)C(8)C(9) | 53.5 |
| C(7)C(8)C(12)C(1) | -52.2 | C(6)C(5)C(7)C(8) | -53.4 |
| C(8)C(12)C(1)C(2) | 28.6 | C(9)C(6)C(5)C(7) | 30.0 |
| Six-membered rings | | | |
| C(7)C(5)C(6)C(4) | -79.3 | C(11)C(1)C(12)C(8) | -80.5 |
| C(5)C(6)C(4)C(3) | 82.1 | C(10)C(11)C(1)C(12) | 82.7 |
| C(6)C(4)C(3)C(2) | -59.4 | C(9)C(10)C(11)C(1) | -59.4 |
| C(4)C(3)C(2)C(7) | 33.2 | C(8)C(9)C(10)C(11) | 33.3 |
| C(3)C(2)C(7)C(5) | -28.6 | C(12)C(8)C(9)C(10) | -27.6 |
| C(2)C(7)C(5)C(6) | 50.4 | C(1)C(12)C(8)C(9) | 52.1 |

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