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PROPELLANES V.[1] [3.3.1]PROPELLANE[2]

Philip Warner,* Richard LaRose and Thomas Schleis[3]

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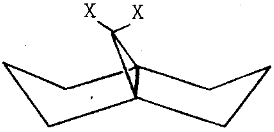
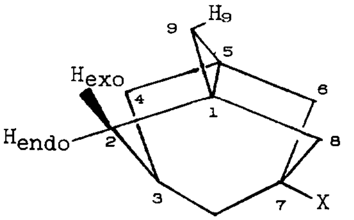
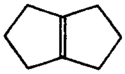
Our recent synthesis of [4.2.1]propellane[1d] and interest in solvolysis of some derivatives thereof,[1a,c] has led us to investigate the isomeric[3.3.1]propellane (Ib). Previously, some simple [3.3.1]propellane systems have been reported,[4] but apparently no study of their "propellanic" chemistry has been made. By contrast, the dehydroadamantyl-type [3.3.1]propellanes (II) have been studied with respect to their strain properties.[5]



Ia, X = Br
b, X = H



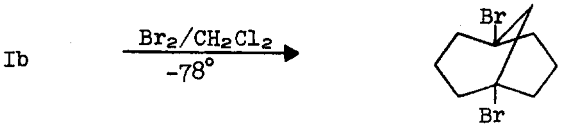
II



III

The synthesis of Ib was readily achieved via dibromocarbene ($CHBr_3$,KOtBu, 75%) addition to $\Delta^{1,5}$-bicyclo[3.3.0]octene (III)[6] to give Ia (mp 68 - 69°; nmr: ($CDCl_3$, TMS) narrow multiplet at $\delta 2.08$; mass spectrum: parent ions at m/e 278, 280, 282, base peak at m/e 91; acceptable elemental analysis), followed by reduction [$(nBu)_3SnH$, 56%] to Ib [glc purified material showed ir: (CCl_4) major peaks at 3070, 3010, 2945, 2870, 1470, 1460, 2190, 1020 cm^{-1}; nmr: ($CDCl_3$, TMS) $\delta 0.45$ (singlet, 2H), $\delta 1.65$ (center of a multiplet, 12H); mass spectrum: calc'd. for C_9H_{14}: 122.10955; observed: 122.1096 ± 0.002; and gave the correct elemental analysis]. As opposed to II, [3.3.1]propellane, Ib, was insensitive to oxygen; Ib was also recovered unchanged after heating at 180° for 22 hrs. Also, unlike the facile catalytic hydrogenation of II,[5a] Ib was recoverd unchanged after 6 hrs under 40 p.s.i. H_2 (EtOH, Pd/C).

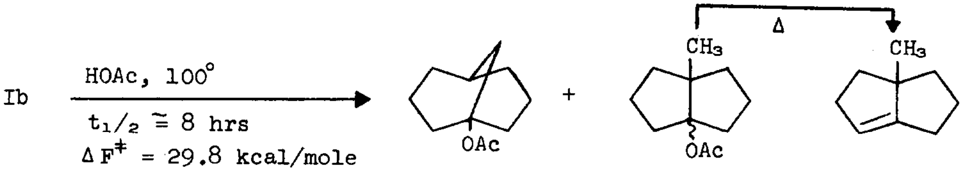
By constrast, Ib was very reactive toward Br_2/CH_2Cl_2, absorbing the reagent immediately at -78° to give, primarily, IV [mp 111 - 112°; nmr: (CCl_4, TMS)



IV

δ2.80 (singlet, 2H of methylene bridge), δ1.5 - 2.6 (multiplet, 12H); mass spectrum: parent ions at m/e 280, 282, 284, $(P-Br)^+$ at m/e 201, 203, base peak at m/e 121 $(P-HBr_2)^+$]. This reaction appears to be free radical in nature since it is inhibited by isoamyl nitrite.[7]

Ib also shows reactivity to electrophilic addition, as exemplified by its reaction with acetic acid:[8]



V VI VII

53.5% 46.5%

V was identified by comparison to the published spectral data,[9] while the minor component was identified only by its nmr spectrum [($CDCl_3$), δ1.10 (singlet, CH_3), δ2.01 (singlet, OAc), δ1.4 - 2.2 (mult.)] and further elimination (under the reaction conditions) to VII [nmr:[10b,c] δ1.05 (sing., CH_3), δ5.03 (mult., vinyl H)].[10] It can be seen that [3.3.1]propellane is much less reactive toward acetic acid than [4.2.1]propellane;[1d] part of the lessened reactivity may be due to torsional interaction between a proton attacking at the C_1 position (corner[11]) and the adjacent exo H's of Ib.

The high reactivity of II relative to Ib (particularly towards oxygen) can be ascribed to at least 2 factors. First of all, the chair conformation enforced on the bicyclohexane system of II causes four eclipsing interactions of the type between C_1-C_9 and C_2-H_{exo}.[12] Secondly, the joining of C_3 and C_7 by a methylene group pinches back the cyclopentane rings in such a way as to increase the angle strain around the cyclopropane ring.[5c] Thus II resembles, in geometry and reactivity, [3.2.1]propellane,[13] rather than [3.3.1]propellane.

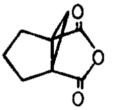
REFERENCES

1. Previous papers in this series: (a) IV: P. Warner, J. Fayos and J. Clardy, Tetrahedron Lett., 4473 (1973); (b) III: P. Warner and S. Lu, J. Amer. Chem. Soc., 95, 5099 (1973); (c) II: P. Warner, R. LaRose, C. Lee and J. Clardy, J. Amer. Chem. Soc., 94, 7607 (1972); (d) I: P. Warner and R. LaRose, Tetrahedron Lett., 2141 (1972).

2. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support of this research.

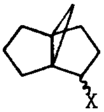
3. NSFURP participant, summer, 1973.

4. (a)



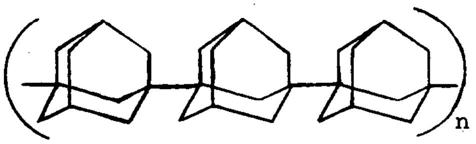
E. Vogel, W. Wiedemann, H. Roth, J. Eimer and H. Günther, Liebigs Ann. Chem., 759, 1 (1972).

(b)



P. Gassman, R. Steppel and E. Armour, Tetrahedron Lett., 3287 (1973).

5. (a) R. Pincock and E. Torupka, J. Amer. Chem. Soc., 91, 4593 (1969).
(b) W. Scott and R. Pincock, ibid., 95, 2040 (1973).
(c) The strain of II (X = CN) has been measured[5b] by scanning calorimetry, and found to be 28.6 kcal/mole, on the assumption that the adamantane polymer



is strainfree. This assumption is fallacious. In addition to the 6.5kcal/mole strain in adamantane itself [P. Schleyer, J. Williams and K. Blanchard, ibid., 92, 2377 (1970)], there is an additional 7.0 kcal/mole strain from the buttressing effects of the 2 adamantyl groups attached to any given adamantane unit in the polymer [E. Engler, J. Andose and P. Schleyer, ibid., 95, 8005 (1973)]. Thus the actual strain of II is ca. 42 kcal/mole.

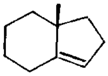
6. We synthesized III via a slight modification of Corey's procedure [E. Corey and E. Block, *J. Org. Chem.*, **34**, 1233 (1969)]. In addition to an nmr singlet at δ2.13 (benzene), III showed $\nu_{C=C}$ = 1675 cm^{-1} in the Raman spectrum.

7. Details of our studies of the mechanism of bromine addition to propellanes will be published elsewhere.

8. The yields quoted are "before work-up, nmr yields", which appear quantitative; however, the formation of VII from VI is not quantitative.

9. J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, **92**, 948 (1970).

10. (a) Since both VI and VII were quite volatile, relative to V, and the final ratio of VI:VII was 1.7, these were not isolated; hence their identification, although well grounded, must be considered "tentative". (b) for comparision, the vinyl proton of



appears at δ5.10;[10c,d]
(c) chemical shifts in glacial acetic aicd, using the solvent ^{13}C sidebands as internal standards, and taking the chemical shift of the cyclopropyl protons of Ib as δ0.45;
(d) P. Warner, unpublished results.

11. This is independent of the question of whether or not the proton first attacks edgewise and then slides to the corner [C. H. DePuy, *Fortschr. Chem. Forsch.*, **40**, 73 (1973)].

12. The effect of the 4 axial H$_{exo}$'s is probably responsible for the considerable downfield shift seen for H$_9$ in II (X = H, δ1.66) relative to the comparable H's of Ib (δ0.45) and [3.2.1]propellane (δ0.68).[11]

13. K. B. Wiberg and G. J. Burgmaier, *J. Amer. Chem. Soc.*, **94**, 7396 (1972).