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SYNTHESES OF THE TRICYCLO$[5.2.1.0^{4,8}]$DECA-2,5-DIENE SYSTEM

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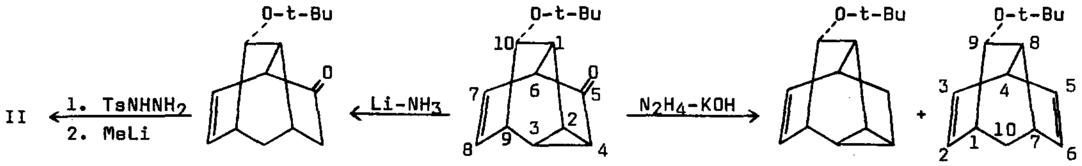
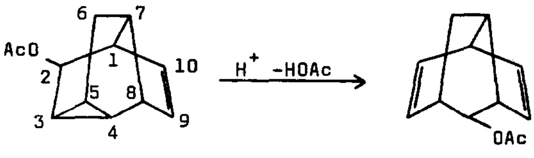
Tricyclo$[5.2.1.0^{4,8}]$deca-2,5-diene derivatives, which are of interest as rigid model systems for the study of trishomocyclopentadienyl interactions have been obtained by three routes:

- Huang-Minlon reduction of exo-10-t-butoxytetracyclo$[4.4.0.0^{2,4}.0^{3,9}]$dec-7-en-5-one (I)[1] gave ± 15% of endo-9-t-butoxytricyclo$[5.2.1.0^{4,8}]$deca-2,5-diene (II) besides the major product III.
- Li-NH_3 reduction of I yielded IV, which was converted into II via its tosylhydrazone[2].
- Treatment of exo-2-acetoxytetracyclo$[5.3.0.0^{3,5}.0^{4,8}]$dec-9-ene (V)[3] with catalytic amounts of p-toluenesulfonic acid in acetic acid led to the ring opened isomer exo-10-acetoxytricyclo$[5.2.1.0^{4,8}]$deca-2,5-diene (VI).

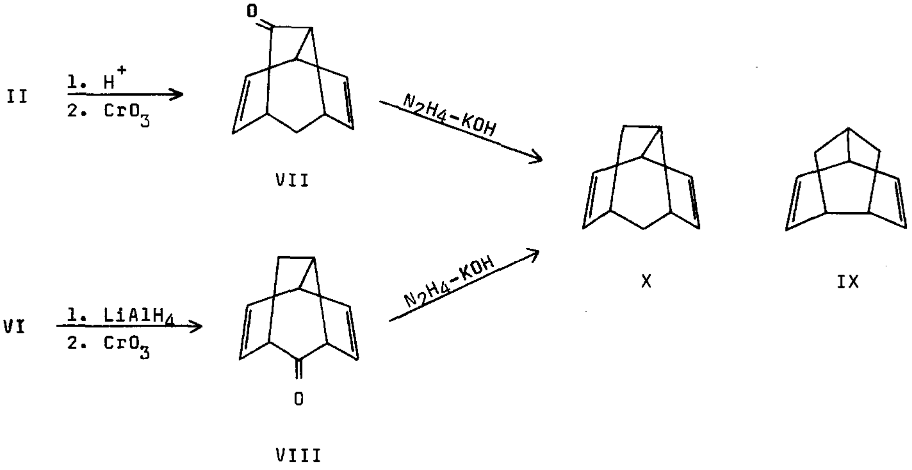


IV I III II

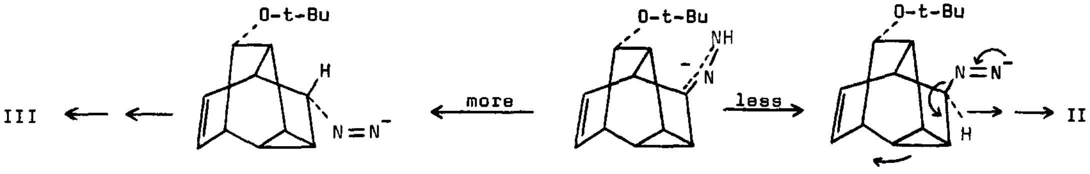


V VI

Acid cleavage of II and LAH treatment of VI gave the corresponding alcohols, which were oxidized by Jones reagent to the isomeric ketons VII ($\nu_{C=O}$: 1758 cm^{-1}) and VIII ($\nu_{C=O}$: 1740, shoulder at 1755 cm^{-1}). Both ketones were transformed by Huang-Minlon reduction into the same hydrocarbon, whose NMR spectrum (100 MHz, signals in the ratio of 3 : 1 : 1 : 2 : 1 : 3 : 1 at δ 5.9 - 5.65; 5.6 - 5.4; 3; 2.9 - 2.6; 2.35; 1.65; 1.3 - 1.1) excluded the symmetrical structure IX. Provided that ring opening during the Huang-Minlon reduction of I is not followed by further rearrangement the structure of the hydrocarbon therefore must be X, and the t-butoxy group in II must occupy the *endo*-position. Confirmation of this is obtained from the shape of the NMR signal of H-9 of II (δ 4.0, t, $J_{1,9\text{-}\underline{exo}} = J_{8,9\text{-}\underline{exo}} = 3.6$ Hz), which indicates dihedral angles around 40° in agreement with values obtained by inspection of molecular models. The *exo*-position of the acetoxy substituent in VI was also derived from the NMR spectrum, which shows no coupling between H-10 and the adjacent bridgehead protons.



The regiospecificities observed in the Li-NH$_3$ reduction of I and in the cationic transformation of V are very probably stereoelectronic in nature, that cyclopropane bond being broken, which overlaps more efficiently with the carbonyl pi system in I[4] or which is more nearly parallel to the C-OAc bond in V[5]. Product stability and steric approach control may play a role in the formation of II by Huang-Minlon reduction-rearrangement of I. According to models X is less strained than IX. Anti-periplanar fragmentation[6] to the carbanion of II may therefore still be possible in XI (formed by C-protonation of XII from the less accessible *endo*-side) but in XIII the corresponding transformation leading to the carbanion derived from IX apparently is superseded by normal reduction to III[7]. The intriguing possibility that trishomoaromaticity of the carbanion of II contributes to its formation will be elaborated in future papers[8].



XIII XII XI

Literature

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2. R.H. Shapiro and M.J. Heath, J. Amer. Chem. Soc., 89, 5734 (1967); G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, ibid., 89, 5736 (1967).

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4. W.G. Dauben and R.E. Wolf, J. Org. Chem., 35, 2361 (1970) and references cited therein.

5. For similar cases of regiospecific cyclopropylcarbinyl cation rearrangements cf.:
   a. J.J. Tufariello and D.W. Rowe, Chem. Comm., 1972, 1066 and references cited therein;
   b. A.S. Kende and J.Y.C. Chu, J. Org. Chem., 38, 2252 (1973).

6. H. Szmant, Angew. Chem., 80, 141 (1968).

7. Product stability may govern the course of the Huang-Minlon reduction of 8,9-dehydro-2-adamantanone, too. Although anti-periplanar transition states leading to protoadamantene are possible, ring opening is not observed and 2,4-dehydroadamantane is obtained as the sole product:
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8. It is noted that Huang-Minlon reduction of polycyclic cyclopropyl ketones leads to minor amounts of olefinic material in many cases [cf.: H. Musso and U. Biethan, Chem. Ber., 100, 119 (1967); H. Klusacek and H. Musso, ibid., 103, 3066 (1970)], however, with one exception [S.M. Kupchan, E. Abushanab, K.T. Shamasundar, and A.W. By, J.

Amer. Chem. Soc., 89, 6327 (1967)] production of larger amounts of olefinic material seems to be confined to those cyclopropyl ketones, which can yield a stabilized anion. Thus tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octan-3-one yielded bicyclo[3.2.1]octa-2,6-diene [N.A. LeBel and R.N. Liesemer, J. Amer. Chem. Soc. 87, 4301 (1965)], isobullvalone gave azulene and barbaralone gave bicyclo[3.2.2]nona-2,6,8-triene [W. von E. Doering, B.M. Ferrier, E.T. Fossel, J.H. Hartenstein, M. Jones, Jr., G.W. Klumpp, R.M. Rubin and M. Saunders, Tetrahedron, 23, 3943 (1967)].