Tetrahedron Letters No. 18, pp 1741 - 1742, 1972. Pergamon Press. Printed in Great Britain.

SYNTHESIS OF SOME TETRACYCLO[$4.4.0.0^{2,4}.0^{3,9}$]DECANE AND TRICYCLO[$3.3.1.0^{2,4\text{-}endo}$]NONANE DERIVATIVES

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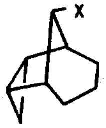
(Received in UK 3 March 1972; accepted for publication 22 March 1972)

In the course of our work on homoaromatic carbenium ions[1] we became interested in *anti*-9-tricyclo[$3.3.1.0^{2,4\text{-}endo}$]nonane derivatives (I). A stereospecific synthesis of this class of compounds is now reported.

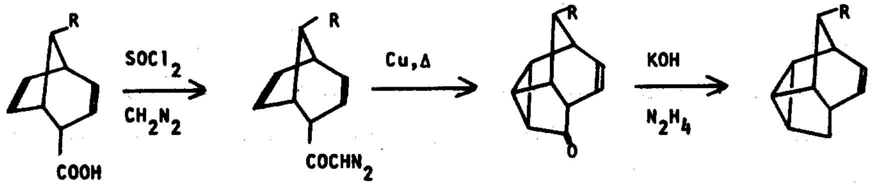


I

Because it was anticipated that reagents, which would add CH_2 to the double bond of appropriate bicyclo[3.2.1]oct-6-ene derivatives would attack preferably from the *exo*-direction, we chose to start our synthesis from the readily available *endo*-bicyclo[3.2.1]octa-2,6-dien-3-yl carboxylic acids IIa,b[2] and to prepare first the novel tetracyclo[$4.4.0.0^{2,4}.0^{3,9}$]dec-7-en-5-ones IVa,b by intramolecular addition of a ketocarbenoid. The nonenolizable cyclopropyl ketones IVa,b were expected to yield *endo*-tricyclo[$3.3.1.0^{2,4\text{-}endo}$]non-6-en-3-yl carboxylic acids by cleavage with strong base[3].

The acids IIa,b were converted by standard methods into the α-diazoketones IIIa,b (2100, 1650)[x]. Decomposition of IIIa,b in refluxing heptane or cyclohexane in the presence of copper bronze gave IVa (66.5-70.5,1725,1710,1315,1300,1196,1109,1053,1003) and IVb (84-86, heptane,1723, 1195,1130,1110,1043,997) in 5% and 50% yield based on II, respectively[xx]. Huang-Minlon reduction gave as main product Va,b in 80-85% yield (Va: 1320,1298,1075,998,980, Vb: 1250,1200,1105,1000). From treatment of IVb with KO-*t*-Bu/DME/H_2O *anti*-9-*t*-butoxy-*endo*-3-carboxytricyclo[$3.3.1.0^{2,4\text{-}endo}$] non-6-ene (VI, 145, hexane, 1690,1292,1195,1168,1110,985) was obtained in 90% yield[xxx]. VI was hydrogenated catalytically and, via the acid chloride, further converted into the *t*-butyl perester VII (93,pentane, 1775,1272,1195,1110,1058) in 80% yield. Pyrolysis (decalin, 180-200°) or photolysis (pentane, 30°) of VII gave approximately 1:1 mixtures of *anti*-9-*t*-butoxytricyclo[3.3.

1.0^{2,4}-endo]nonane (VIII, 1303,1197,1112,1093,1055,1030) and a compound, which is supposed to be anti-9-t-butoxytricyclo[3.3.1.0^{2,4}-endo]non-6-ene (IX, 1190,1103,1088,975) in 10% yield. On attempts to convert IX into VIII by catalytic hydrogenation the cyclopropane ring of IX underwent hydrogenolysis. Diimide did not affect IX.

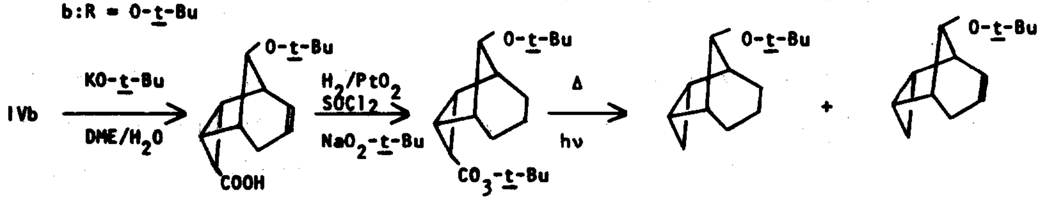


II a:R = H
b:R = O-t-Bu

IIIa,b

IVa,b

Va,b



VI

VII

VIII

IX

x) Melting point, recrystallization solvent, and an ir-fingerprint are given in parentheses.

xx) Since none of the reactions employed is known to cause rearrangement, structures are assigned on basis of the mode of synthesis.
All compounds gave satisfactory analytical and spectral data.

xxx) 1 mmol IVb, 8mmol KO-t-Bu, 2 mmol H_2O, 3 ml DME 1.5h at 60-70°C.
Under the same conditions the saturated compound H_2-IVb did not react.

References

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3) P.G. Gassman, J.T. Lumb, and F.V. Zalar, J. Amer.Chem.Soc., 89, 946 (1967).