Tetrahedron Letters,Vol.24,No.31,pp 3259-3260,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

A NEW APPROACH TO THE BICYCLO (5.2.1) DECANE SYSTEM.[1]

Yu.E. Klimko, S.D.Isaev, A.G.Yurchenko

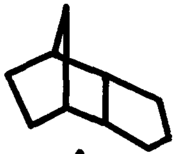
Department of Chemical Technology, Kiev
Politechnic Institute, Kiev, 252056, USSR

O.S.Chizov

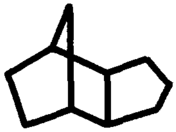
N.D.Zelinsky Institute of Organic Chemistry
Academy of Sciences of USSR, Moscow.

SUMMARY : A simple route to the bicyclo (5.2.1) decane system by oxidation of trimethylenenorbornane is demonstrated.

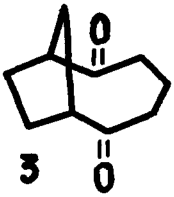
The unique properties of cage compounds containing more than seven-membered rings arouse steady interest of organic chemists.[2] The bicyclo (5.2.1) decane system as a model for mechanistic and conformational studies is quite attractive although there is no convenient synthesis of compounds with such a skeleton.[3] Here we wish to describe a simple method for the preparatione of the hitherto unknown bicyclo (5.2.1) deca-2.6-dione (3).



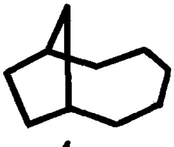
1



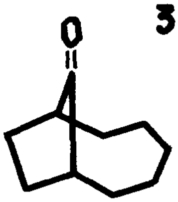
2



3



4



5

Both endo- and exo - trimethylenenorbornane (tricyclo ($5.2.1.0^{2.6}$) decane) (1 and 2, respectively) undergo oxidation with a five to ten fold excess of chromic acid or anhydride in glacial acetic acid at 20-35°C. After 4 hours the reaction mixture was diluted with water, neutralized with concentrated sodium hydroxide solution and extracted with chloroform. The diketone (3) was obtained after recrystallisation of the residue from pentane, in 65% yield, m.p. 62-65 °C; ^1H NMR ($CDCl_3$, 80 MHz : complex multiplet in δ 1.3-3.1 ppm region ; ^{13}C NMR ($CHCl_3$, 20 MHz) :

δ 21.92 ($C_{8,9}$), 23.07 (C_4), 29.26(C_{10}), 37.40($C_{3,5}$), 49.66 ($C_{1,7}$), 212.25 ($C_{2,6}$) ; IR (CCl_4) : 1710 cm^{-1} ; MS (m/z) : 166 (M^+), 131, 125, 97, 96, 55 (100 %); Calcd for $C_{10}H_{14}O_2$: C,71.13 ; H,8.83. Found : C,71.15; H,8.69

The parent hydrocarbon, bicyclo (5.2.1) decane (4) still unknown was prepared by the Huang-Minlon reduction of the diketone (3) in 50 % yield.

After chromatographic separation on silicagel and subsequent recrystallization from acetic acid, the specimen was 98% pure, containing 2% of (1) and (2) as an impurity, m.p. 52-54 °C; ^{13}C NMR ($CHCl_3$, 20 MHz) ; δ 23.92 ($C_{3,5}$), 25.92(C_4 28.72 ($C_{8,9}$), 33.51 ($C_{2,6}$), 34.67 (C_{10}), 36.06($C_{1,7}$)[4] ; MS (m/z): 138 (M^+), 110, 95, 82, 81, 67, 28 (100%); Calcd for $C_{10}H_{18}$: C, 86.89; H, 13.11. Found : C, 86.80; H, 13.09.

The final proof of structure of the hydrocarbon (4) was performed by direct comparison with the hydrocarbon obtained in 50% yield by Huang-Minlon reduction of bicyclo (5.2.1) decane-10-on (5)[3a].

The IR and NMR spectra and retention time in GLC of these two hydrocarbons are identical. Hence, the hydrocarbon has the structure of bicyclo (5.2.1) decane (4) , as proposed.

REFERENCES AND NOTES

1. Presented at the scientific conference on the organic polyhedranes chemistry, Volgograd, USSR, September, 8-11, 1981. See Abstracts, p.56.
2. N.S.Zefirov, S.S.Trach, O.S. Chizov, Cage and Polycyclic compound. Molecular design based on the isomorphic substitution, VINITI, Moscow, 1979, p.82.
3. (a) C.D. Gutsche, T.D.Smith, J.Am.Chem.Soc., 82, 4067, (1960); (b) G.Fachinetti, F. Pictra, A.Marzili , Tetr. Lett., 1971, 393, (c) C.W.Jefford, F.Delay, Tetr.Lett., 1973, 3639.
4. The signal assignment method see L.P.Lindeman, J.Q.Adams, Anal.Chem., 43, 1245 (1971).

(Received in UK 23 May 1983)