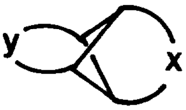
Tetrahedron Letters,Vol.23,No.26,pp 2647-2650,1982 0040-4039/82/262647-04$03.00/0
Printed in Great Britain

A SIMPLE PATH TO TRICYCLO[5.3.0.$0^{2,8}$]DECANE AND ITS DERIVATIVES

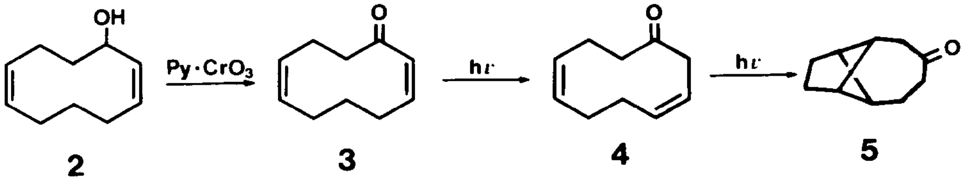
Rolf Gleiter*, Wolfram Sander, Hermann Irngartinger and
Andrea Lenz
Institut für Organische Chemie der Universität,
Im Neuenheimer Feld 270, D-6900 Heidelberg (W.-Germany)

A simple method to prepare tricyclo[5.3.0.$0^{2,8}$]decane-4-one (5) is reported. The most relevant bond lengths for the tosylhydrazone of 5 determined by X-ray crystallography are given. From 5 the parent hydrocarbon and tricyclo[5.3.0.$0^{2,8}$]deca-3,5-diene (9) have been prepared.

Tricyclic systems of the type 1 (x and y = $(CH_2)_n$ or/and $(CH)_n$) are of interest with respect to natural products$^{1)}$ and in connection with model calculations$^{2)}$. A simple access to tricyclo[5.3.0.$0^{2,8}$]decane and several derivatives can be achieved starting from 2,7-cyclodecadiene-1-ol (2)$^{3)}$. Oxidation of 2 by pyridine CrO_3 gives 2,7-cyclodecadiene-1-one (3) (74%). Irradiation of 3 in benzene with a Hannovia 450 W lamp produces (95%) 3,7-cyclodecadiene-1-one (4) which on further irradiation can be converted to tricyclo[5.3.0.$0^{2,8}$]decane-4-one (5) in 55% yield. The observation that 3 first undergoes a photoinduced hydrogen shift to 4 followed by photochemical ring closure is in accord with the rule of *Srinivasan*$^{4)}$ but at variance with the findings of *Heathcock* and *Badger*$^{5)}$ on related compounds.

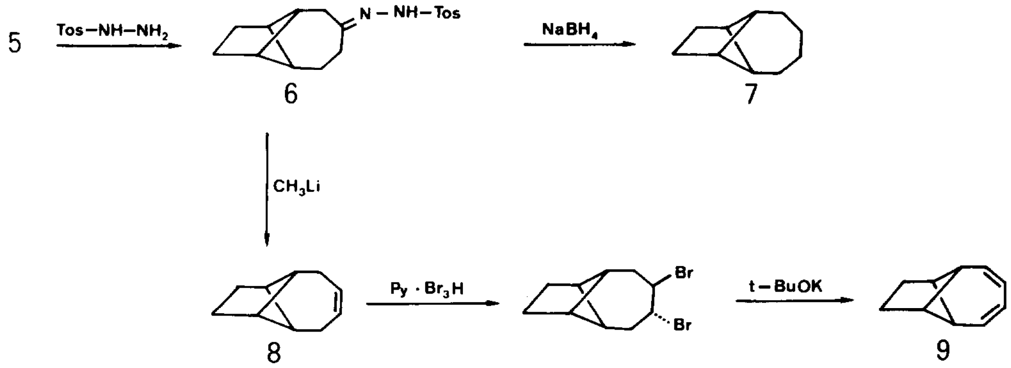


1



According to *Scheme I* we prepared from 5 the tosylhydrazone 6 which could be reduced to tricyclo[5.3.0.0^{2,8}]decane (7) in 47% yield. Treating 6 with CH_3Li leads to tricyclo[5.3.0.0^{2,8}]decene-4 (8) (70%). After addition of bromine to 8 and subsequent HBr elimination we obtained tricyclo[5.3.0.0^{2,8}]deca-3,5-diene (9) (37%). Some relevant data for 3 - 9 are collected in the table.

Scheme I



Assignment of the structures of the tricyclo[5.3.0.0^{2,8}]decane systems 5 - 9 was based on the spectroscopic data given in the table and on a X-ray analysis of 6$^{6)}$. The most relevant bond lengths are shown in Fig. 1.

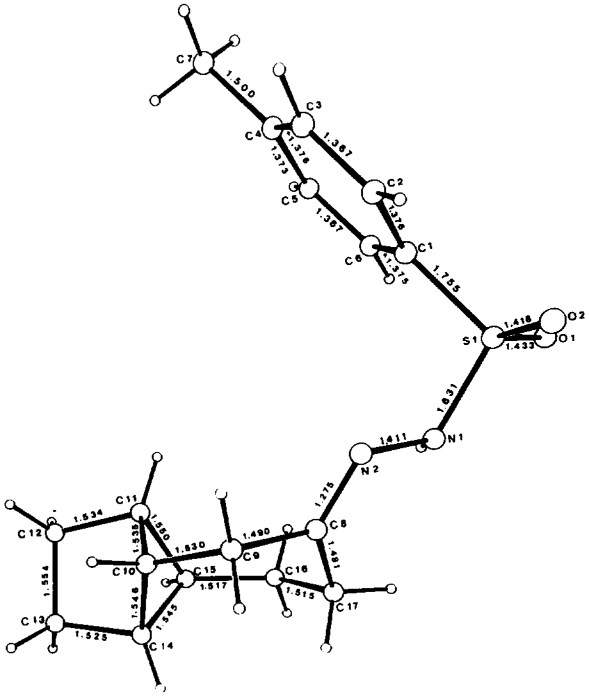


Fig. 1. Bond lengths (Å) of 6

Table All new compounds gave correct elemental analyses and showed spectra fully compatible with the structures drawn. Only selected spectroscopic data are listed.

3 m.p. 57-58°C; IR(KBr):1695 cm^{-1}; ^{13}C-NMR(20 MHz, CDCl$_3$) δ:206.58(s), 139.84(d), 131.94(d), 130.06(d), 128.41(d), 42.34(t), 26.52(t), 25.47(t), 24.32(t), 24.09(t); MS(m/z):150(M$^+$, 18%), 79(100%).

4 IR(Film):1700 cm^{-1}; ^{13}C-NMR(75.46 MHz, CDCl$_3$) δ:210.46(s), 132.14(d), 130.03(d), 129.49(d), 123.41(d), 44.29(t), 40.73(t), 26.41(t), 25.15(t), 23.77(t); MS(m/z):150(M$^+$, 6%), 54(100%).

5 IR(Film):1710 cm^{-1}; ^{1}H-NMR(300 MHz, CDCl$_3$) δ:2.72(2H, d, 4.4 Hz), 2.60(2H, t, 6.8 Hz), 2.35(2H, s), 1.94(3H, m), 1.82(1H, m, 4.4 Hz), 1.75(4H, m); ^{13}C-NMR(20 MHz, CDCl$_3$) δ:212.00(s), 50.65(d), 46.29(d), 44.89(d), 44.67(t), 41.58(t), 28.72(t), 24.15(t); MS(m/z):150(M$^+$, 5.5%).

6 m.p. 159-161°C; MS(m/z):318(M$^+$, 7%), 91(100%).

7 ^{1}H-NMR(300 MHz, CDCl$_3$) δ:2.23(2H, s), 1.76(6H, m), 1.64(4H, s), 1.58-1.55(4H, m); ^{13}C-NMR(75.46 MHz, CDCl$_3$) δ:51.89(d), 44.55(d), 29.72(t), 29.00(t), 27.28(t).

8 ^{1}H-NMR(90 MHz, CDCl$_3$) δ:5.55(2H, m), 2.47(2H, m), 2.31(2H, s), 1.81(2H, m), 1.71(4H, s); ^{13}C-NMR(75.46 MHz, CDCl$_3$) δ:126.88, 50.67, 46.10, 31.17, 29.45.

9 UV(Hexan, λ(ε)):309(1300), 295(2400), 283(2450), 272(1800); ^{1}H-NMR(300 MHz, CDCl$_3$) δ:6.05-5.98(2H, m), 5.92-5.88(2H, m), 2.45-2.39(2H, m), 1.82(4H, s), 1.27(2H, s); ^{13}C-NMR(75.46 MHz, CDCl$_3$) δ:133.61(d), 124.38(d), 51.32(d), 28.31(d), 26.93(t).

References

1 C. H. Heathcock, R. A. Badger, R. A. Starkey, J. Org. Chem. 37, 231 (1972); M. Miyashita, A. Yoshikoshi, J. Amer. Chem. Soc. 96, 1917 (1974); H. Kikuchi, Y. Tsukitani, Y. Yamada, K. Iguchi, S. A. Drexler, J. Clardy, Tetrahedron Lett. 23, 1063 (1982).

2 P. Bischof, R. Gleiter, R. Haider, J. Amer. Chem. Soc. 100, 1036 (1978).

3 J. G. Traynham, G. R. Franzen, G. A. Knesel, D. J. Northington, Jr., J. Org. Chem. 32, 3285 (1967); S. K. Taylor, C. B. Rose, J. Org. Chem. 42, 2175 (1977).

4 R. Srinivasan, K. H. Carlough, J. Amer. Chem. Soc. 89, 4932 (1967).

5 C. H. Heathcock, R. A. Badger, J. Org. Chem. 37, 234 (1972).

6 Crystallographic data of 6: a = 19.726 (3), b = 15.637 (2), c = 10.749 (1) Å; *Pbca*; Z = 8; D_c = 1.28 g/cm^3; 3935 independent reflections, 2384 observed reflections (I> 2.5 σ(I); R = 0.037). The methyl group shows disorder.

(Received in Germany 18 March 1982)

Financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the BASF Aktiengesellschaft in Ludwigshafen is acknowledged. We thank Dr. D. Krauß, Dr. P. Kunzelmann and Mrs. G. Rissmann for measurements and helpful discussions concerning the NMR and mass spectra. W. S. is grateful to the Studienstiftung des Deutschen Volkes for a stipend.