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UNUSUAL CHEMICAL REACTIVITY OF A 1,3 H-SHIFTED ISOMER OF HEXAMETHYLBENZVALENE

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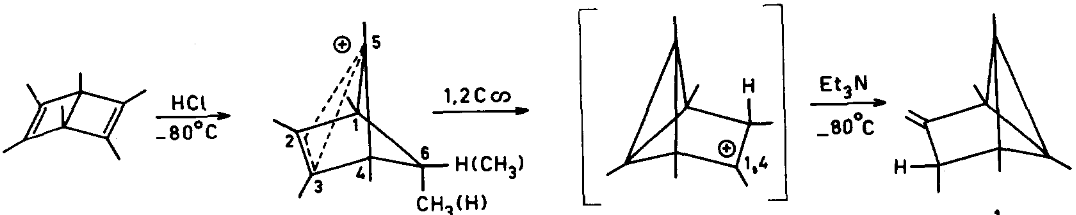
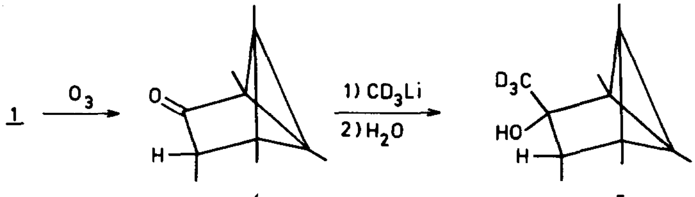
Using hexamethyldewarbenzene as starting material 1,2,4,5,6-pentamethyl-3-methylene-tricyclo$[3.1.0.0^{2,6}]$hexane (1) - an isomer of hexamethylbenzvalene - can be obtained in good yield (90%) by a protonation - deprotonation sequence at low temperatures using HCl and Et_3N, respectively.[1]

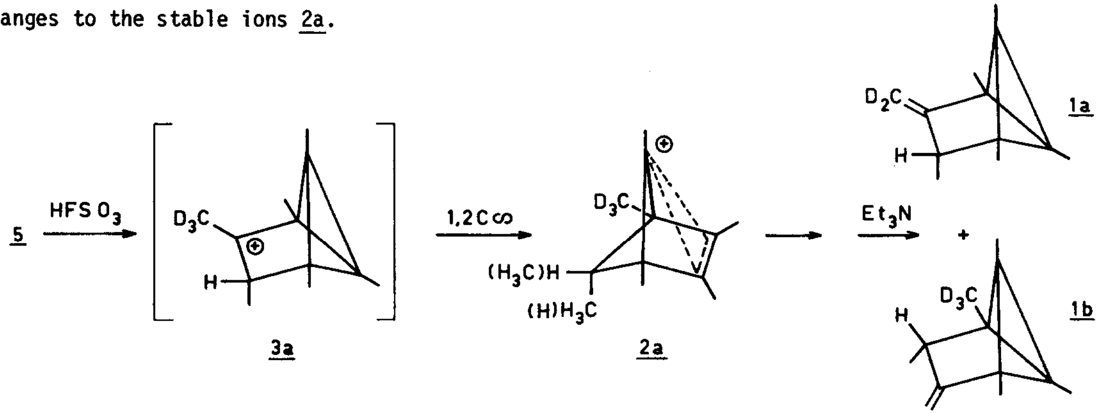


The fact that proton abstraction from ions 2 (exo-endo mixture 3:1[2]) by Et_3N seems to take place at the $C_{1,4}$ methyl groups rather than at the $C_{2,3}$ methyl groups - a rather unexpected phenomenon - made it desirable to have labelled material available in order to provide supporting evidence for the mechanistic scheme suggested.

Low-temperature ozonolysis of 1[3] afforded the corresponding ketone 4 which in turn was converted to alcohol 5[4] using CD_3Li.



In $HFSO_3/SO_2ClF$ at -70°C protonation of 5 is followed by dehydration to form ion 3a which rearranges to the stable ions 2a.



Also if 1 is treated with $DFSO_3/SO_2ClF$ at -70°C deuterium is found to be selectively incorporated in the bridgehead methyl groups. Scrambling of the CD_3-label in ions 2a over other methyl positions was not observed within 5 minutes at 0°C. Upon quenching of ions 2a with Et_3N at -70°C the deuterium distribution pattern of the products 1a and 1b (obtained in a 1:3 ratio, respectively) indicates that proton (deuterium) abstraction has taken place from the bridgehead methyl groups of 2a.

These experiments are of special importance in view of the reactions which we have discovered between 1 and tetracyanoethylene (TCNE). This uniparticulate electrophile was reported[5] to react with vinylcyclopropanes, to give a [2+2] adduct which thermally rearranges to a seven-membered ring. Although 1 contains formally a vinylcyclopropane moiety no [2+2] adduct could be observed by NMR spectroscopy in the reaction between 1 and TCNE. At room temperature a 1:1 adduct[6] was isolated to which the structure of 7,7,8,8-tetracyano-2-endo-3,4-trans-5,6-pentamethyl tricyclo $[4.3.0.0^{1,5}]$ nona-3-ene (6) was assigned using X-ray techniques.[7] On NMR spectroscopic examination of the reaction at temperatures below 0°C it was found that prior to the formation of compound 6 an intermediate adduct 7[8] from TCNE and 1 was produced.

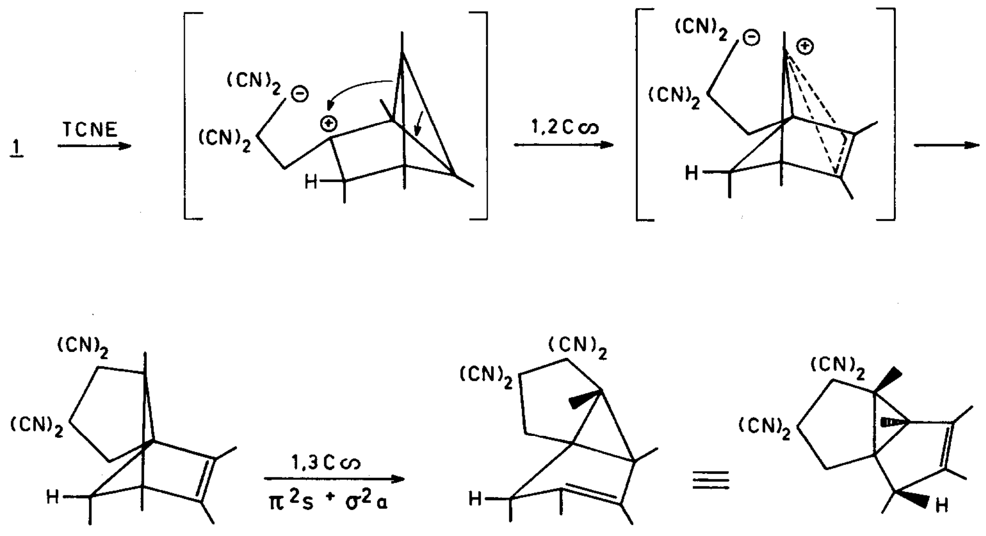
In order to obtain more information about the mechanistic details of both reactions 1 → 7 and 7 → 6 kinetic measurements were performed in solvents of different polarity as measured by E_T values[9] (see table). As can be seen the rate of reaction 1 → 7 is influenced by the solvent polarity in agreement with an ionic reaction mechanism whereas that of reaction 7 → 6 is independent of solvent polarity supporting a concerted sigmatropic process. This must proceed with inversion of configuration of the migrating C-atom according to the Woodward-Hoffmann predictions for 1,3 C shifts[10] and this is indeed observed (see Scheme).

Finally it is of interest to note that compound 6 contains a di-cis-fused cyclopropane constituting the first representative of the hitherto unsynthesized $[4.3.0.0^{1,5}]$ system[11] which according to

Gassmann should possess a twist-bend σ bond.[12]

The chemistry of compound 1 is being actively investigated.

Scheme: 1



7

6

Table Kinetic measurements[a] of reactions 1 → 7 and 7 → 6.

Solvent	E_T value	$k^{b}_{1\rightarrow 7}$ lmol^{-1}sec^{-1}(-20°C)	$k^{b}_{7\rightarrow 6}$ sec^{-1} (21°C)
C_6H_5Br	37.5	7.2 (± 0.5) x 10^{-3}	5.4 (± 0.7) x 10^{-4}
$CHCl_3$	39.1	2.1 (± 0.2) x 10^{-2}	7.5 (± 0.7) x 10^{-4}
CH_3COCH_3	42.2	5.3 (± 0.7) x 10^{-2}	3.9 (± 0.9) x 10^{-4}
CH_3CN	46.0	$\geqslant 1^c$	5.5 (± 0.4) x 10^{-4}

a) performed by integrating suitable NMR absorptions at appropriate intervals; concentrations of 1 and TCNE ranging from 5 x 10^{-2} to 20 x 10^{-2} mol.l^{-1}.

b) determined for 50-75% conversion.

c) too fast to be measured at -20°C by NMR spectroscopy.

Notes and References

1. Compound 1 has previously been assumed to possess the [2.2.0.0^{2,6}] skeleton but from independent chemical and spectroscopic evidence structure 1 has been derived unambigueously for this isomer. Generally speaking either tricyclic[2.2.0.0^{2,6}] or tricyclic[3.1.0.0^{2,6}] structures can be obtained by reaction of ions of type 2 with nucleophiles and bases. H. Hogeveen and P.W. Kwant, Tetrahedron Lett., 1972, 5357; J. Org. Chem., 39, 2624, 2626 (1974).
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3. A solution of 15.0 gr (92.6 mmol) of 1 in 1 l of CH_2Cl_2 containing 15 gr (0.19 mol) of pyridine was treated at -85°C with 1,2 eq. of ozone generated over a period of 3 hours. After work up (removal of pyridine by treatment with CH_3I) 7 gr (0.04 mol, 46%) of ketone 4 was obtained in 90% purity by distillation bp 18-22°C/0.01 mm Hg. MS: M^+ at 164 m/e,exact mass 164.124 m/e (calcd: 164.120 m/e); IR: C=O absorption at 1730 cm^{-1}; ^{1}H-NMR: 0.94 (d, J = 7 Hz, 3H) 1.05

(s, 3H), 1.12 (s, 3H), 1.46 (broad s, 6H), 1.70 (q, J = 7 Hz, 1H) ppm; ^{13}C-NMR: 2.7 (CH_3), 3.3 (CH_3), 4.3 (CH_3), 8.2 (CH_3), 12.5 (CH_3), 27.7 (C), 28.0 (C), 40.3 (C), 42.8 (CH), 51.7 (C), 221.0 (C=O) ppm.

4. At 0°C 1.0 gr (6.1 mmol) of ketone 4 was slowly added to a five-fold excess of CD_3Li in ether solution. After stirring for 30 min. the reaction mixture was quenched with water. Alcohol 5 (only 1 isomer is formed) was purified by sublimation at room temperature affording 1.1 gr (6.0 mmol, 95%); mp 48-50°C. MS: M^+ at 183 m/e, exact mass 183.174 m/e (calcd 183.170 m/e); IR: OH absorption at 3400 cm^{-1}; ^{1}H-NMR: 0.70 (d, J = 7 Hz, 3H), 0.92 (s, 3H), 0.95 (s, 3H), 1.20 (s, 3H), 1.24 (s, 3H), 1.30 (q, J = 7 Hz, 1H), 1.70 (s, 1H) ppm. When the reaction was carried out with CH_3Li an additional signal in the ^{1}H-NMR spectrum of the all-protio isomer was observed at 1.07 (s, 3H) ppm. ^{13}C-NMR (all-protio isomer): 2.1 (CH_3), 3.2 (CH_3), 4.7 (CH_3), 7.9 (CH_3), 11.0 (CH_3), 21.1 (C), 21.5 (C), 23.3 (CH_3), 44.4 (C). 49.2 (CH), 50.4 (C), 81.9 (C) ppm.
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6. To a solution (or suspension) of 790 mgr (6.2 mmol) of TCNE in 10 ml. solvent (eg. acetone, chloroform, benzene) a solution of 1000 mgr (6.2 mmol) of 1 in 20 ml solvent was added. After stirring for 1 hour at room temperature 1750 mgr (6.0 mmol, 97%) of 6 was isolated and purified by recrystallization from cyclohexane, mp 123-124°C; MS: M^+ at 290 m/e;IR: CN absorption at 2240 cm^{-1}, C=C absorption at 1660 cm^{-1}; ^{1}H-NMR: 1.06 (d, J = 7 Hz, 3H), 1.35 (s, 3H), 1.60 (broad s, 9H), 2.51 (q, J = 7 Hz, 1H), 2.90 and 3.16 (AB q, J_{AB} = 14 Hz, 2H) ppm; ^{13}C-NMR: 11.4 (CH_3), 11.6 (CH_3), 11.6 (CH_3), 12.4 (CH_3), 15.6 (CH_3), 39.6 (CH_2), 43.1 (C), 45.6 (CH), 46.8 (C), 48.3 (C), 48.8 (C), 52.8 (C), 111.6 (CN), 112.1 (CN), 112.7 (CN), 114.1 (CN), 133.6 (sp^2C), 138.8 (sp^2C) ppm; correct elemental analysis.
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8. ^{1}H-NMR of 7 at -20°C: 0.95 (d, J = 6 Hz, 3H), 1.20 (s, 3H), 1.48 (s, 3H), 1.77 (broad s, 6H) 3.05 and 3.15 (AB q, J_{AB} = 13 Hz, 2H), 3.40 (q, J = 6 Hz, 1H) ppm; ^{13}C-NMR of 7 at -20°C: 6.5 (CH_3), 8.2 (CH_3), 10.5 (CH_3), 10.5 (CH_3). 16.0 (CH_3), 38.0 (CH_2), 48.0 (C), 52.6 (C), 58.6 (C), 64.2 (CH), 71.8 (C), 84.6 (C), 111.2 (CN), 112.0 (CN), 112.8 (CN) 113.2 (CN), 133.0 (sp^2C), 146.0 (sp^2C); Nucleophilic attack on the 3-centra bond of bicyclo[2.1.1]hexenyl ions is known to occur at the back-side; H. Hogeveen and P.W. Kwant, J. Amer. Chem. Soc., 95, 7315 (1973).
9. E_T values taken from: K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, Ann. 661, 1 (1963).
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12) P.G. Gassmann, J.C.S. Chem. Commun., 1967, 793. P.G. Gassmann and F.J. Williams, J. Amer. Chem. Soc., 93, 2704 (1971).