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6-Isopropylidene-1,2,3,4,5-pentamethylbicyclo[3.1.0]hex-3-en-2-yl Cation

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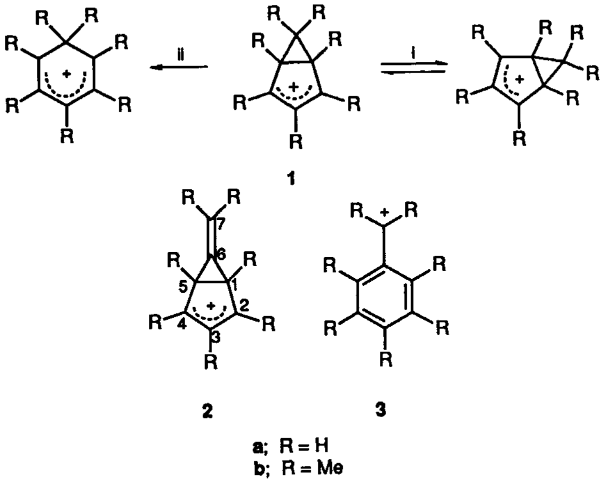
The 6-Isopropylidene-1,2,3,4,5-pentamethylbicyclo[3.1.0]hex-3-en-2-yl cation, formed as a result of the rearrangement of 4-(4′-methylpent-2′-yn-4′-yl)-1,2,3,4-tetramethylcyclobutenyl cation, shows no tendency to undergo a walk rearrangement but is capable of easy ring-opening to form the corresponding benzyl ion, 2-(2,3,4,5,6-pentamethylphenyl)-2-propyl cation.

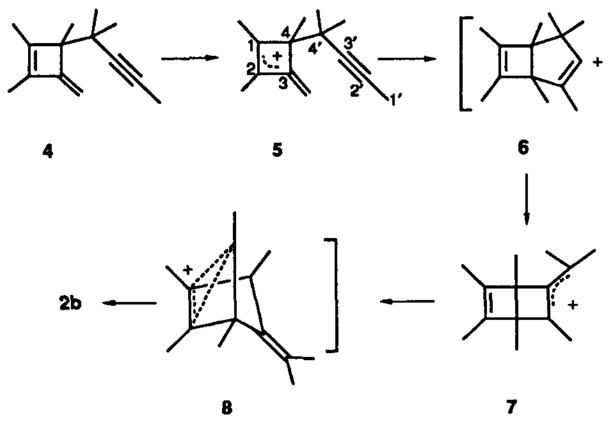
Bicyclo[3.1.0]hexenyl cations of type **1** are well known, as is their ability to undergo a walk rearrangement (path i, Scheme 1) and electrocyclic ring-opening (path ii).[1]



Scheme 1

The data available on bicyclo[3.1.0]hexenyl cations of type **2** with a terminal alkene fragment seem to be restricted to a single example, ion **2a**.[2] This has been found to undergo a degenerate walk rearrangement (at −110°C) about 10^7 times faster than ion **1a** (R = H) but shows no tendency towards ring-opening to form ion **3a**.

This Communication reports the generation of the methylated analogue of ion **2a**, 6-isopropylidene-1,2,3,4,5-pentamethylbicyclo[3.1.0]hex-3-en-2-yl cation **2b** and its chemical properties. Ion **2b** is formed along with the 4-(4′-methylpent-2′-yn-4′-yl)-1,2,3,4-tetramethylcyclobutenyl cation **5** on dissolution of 3-(4′-methylpent-2′-yn-4′-yl)-1,2,3-trimethyl-4-methylenecyclobutene **4** in $FSO_3H-SO_2ClF-CD_2Cl_2$ (1:9:2, v/v) at −120°C, apparently by Scheme 2, *cf.* refs. 3, 4. The ion **5** eventually rearranges to **2b**.†



Scheme 2

At a higher temperature (−80°C)‡ the ^{1}H NMR spectrum of ion **2b** shows no signal broadening. Hence, the free energy of activation of the expected degenerate walk rearrangement is at

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† *Spectroscopic data*: ^{1}H NMR (200 MHz, −115°C), for **2b**: δ 1.65 (s, 6H), 1.89 (s, 6H, 1,5- and 7-CH_3), 2.05 (s, 3H, 3-CH_3), 2.72 (s, 6H, 2- and 4-CH_3).

For **5**: δ 1.38 (s, 4- and 4′-CH_3), 1.79 (s, 2′-CH_3), 2.37 (s, 1,3-CH_3), 2.42 (s, 2-CH_3).

^{13}(NMR (50.323MHz, −115°C) for **2b**: δ 64.1 (s, C^1,C^5), 115.5(s,C^7), 145.7(s,C^3), 192.0 (s,C^6), 226.5(s,C^2,C^4), signals of methyl groups 9.4(q), 12.0(q,3-CH_3), 17.6(q), 20.8(q) (intensity ratio 2:1:2:2).

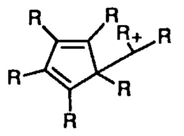
For **5**: δ, 42.1(s,$C^{4'}$), 78.5(s,C^4), 83.3(s), 88.3(s,$C^{2'}$,$C^{3'}$), 162.9-(s,C^1,C^3), 182.6(s,C^2), signals of methyl groups overlap with those of cation **2b**. Signal assignments in the NMR spectrum were made by comparison with available data for analogous ions.[2,3,5]

‡ Above this temperature the ion is unstable.

least 10.7 kcal mol^{-1},§ while that for cation **1b** is 10.1 kcal mol^{-1}.[1] Thus, on passing from ion **1b** to **2b** as opposed to the pair **1a**→**2a**, the walk rearrangement is somewhat slower rather than faster.

MNDO calculations[6] on the approximation of a model transition state for the walk rearrangement of ions **1** and **2** by ions of type **9** and **10**, respectively (*cf.* ref. 7) lead to results which are in fair agreement with those observed experimentally; the walk rearrangement barrier of ion **2b** is considerably (~16 kcal mol^{-1}) higher than that for ion **1b**, whereas for ion **2a** it is ~2 kcal mol^{-1} lower than for ion **1a**. It is interesting to note that the non-classical ions of type **8** and **11**, which might also be regarded as models of the transition state for walk rearrangement (*cf.* ref. 2), are shown by the calculations to be energetically less favourable than ions of type **10**, probably owing to greater steric hindrance.

Another feature of the chemical behaviour of ion **2b** as compared with that of **1b** is its much easier ring-opening to form the benzyl ion, the 2-(2,3,4,5,6-pentamethylphenyl)-2-propyl cation **3b** [$\Delta G^{\ddagger}$ (-70°C) < 13.9 kcal mol^{-1}¶ *vs.* $\Delta G^{\ddagger}$ (-9°C) = 19.8 kcal mol^{-1} (ref. 1)]. The driving forces of this orbital-symmetry-forbidden reaction are probably aromatization (*cf.* ref. 2) and the effect of the methyl groups in stabilizing ion **3b**. We also generated this cation by dissolving 1-isopropenyl-2,3,4,5,6-pentamethylbenzene[8] in FSO_3H–SO_2ClF–CD_2Cl_2 at −120°C, *cf.* ref. 9.‖



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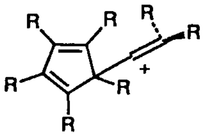

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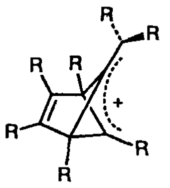

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a; R = H
b; R = Me

Signal assignments in the NMR spectra were made by comparison with the available data for the analogous benzyl cations.[10]

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§ cal = 4.184 J.

¶ Calculated from $k(-70°C) > 5 \times 10^{-3}$ s^{-1} estimated from the ^{1}H NMR spectra.

‖ *Spectroscopic data* for **3b**: ^{1}H NMR (200 MHz, −70°C) δ 2.38 (s, 6H, 3,5-CH_3), 2.56 (s, 9H, 2,4,6-CH_3), 3.36 [s, 6H, $(CH_3)_2C^+$]; ^{13}C NMR (50.323 MHz, −70°C) δ 16.1 (q, 3,5-CH_3), 19.6 (q, 4-CH_3), 22.7 (q, 2,6-CH_3), 40.3 [q, $(CH_3)_2C^+$], 139.9 (s, C^3, C^5), 147.0 (s, C^2, C^6), 149.0 (s, C^1), 162.9 (s, C^4), 250.8 (s, C^+).