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Preliminary communication

INTRAMOLECULAR FERROCENYLVINYL CATION CYCLISATION TO STABLE 9-BARBARALYL AND 8-BICYCLO[3.2.2]NONA-2,6-DIENYL CATIONS

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Protonation of 7-(ferrocenylethynyl)cycloheptatriene gives a mixture of 9-ferrocenyl-9-barbaralyl and 8-ferrocenylbicyclo[3.2.2] nona-2,6-dien-8-yl cations resulting from intramolecular cyclisation of an intermediate vinyl cation.

Although the intermediacy of vinyl cations in electrophilic addition reactions of alkynes is well established [1], the potential of such species in directed organic synthesis has been little explored. During an investigation [2] of the properties of ferrocenyl-stabilised vinyl cations, we have discovered a novel and synthetically convenient route to derivatives of barbaralol and bicyclo[3.2.2]nonatriene and we report herein the preparation and properties of these compounds and derived carbenium ions.

7-(Ferrocenylethynyl)cycloheptatriene (I) (m.p. 99-100°C) was obtained (92% yield) by the addition of tropylium tetrafluoroborate to the lithium salt of ethynylferrocene [3], prepared in ether from the reaction of the alkyne with methyllithium. On treatment of this product with trityl tetrafluoroborate, a deep green salt was formed (68% yield) whose spectroscopic properties were more in accord with a tropylium structure (II) than with representation as a salt of a mesomeric ferrocenylallenyl cation. Hydride reduction ($LiAlH_4$ /ether) of this salt gave a mixture of (ferrocenylethynyl)-cycloheptatrienes including the precursor I.

The alkyne I dissolved slowly in CF_3CO_2H giving a maroon solution containing two ferrocenylcarbenium ions in the ratio ca. 2:1 (^1H NMR). This solution was quenched with a large excess of Na_2CO_3 (aq). and the products were separated by TLC (SiO_2) giving the barbaralol VI (38%; m.p. 119-121°C), the trienol VIII (9%; m.p. 158-160°C), and the readily hydrolysed trifluoro-acetate VII (12%; gum) in addition to other unidentified minor products. Reduction ($LiAlH_4$/ether) of this ester gave a quantitative yield of the trienol VIII. The structures of the alcohols were established from their ^1H NMR

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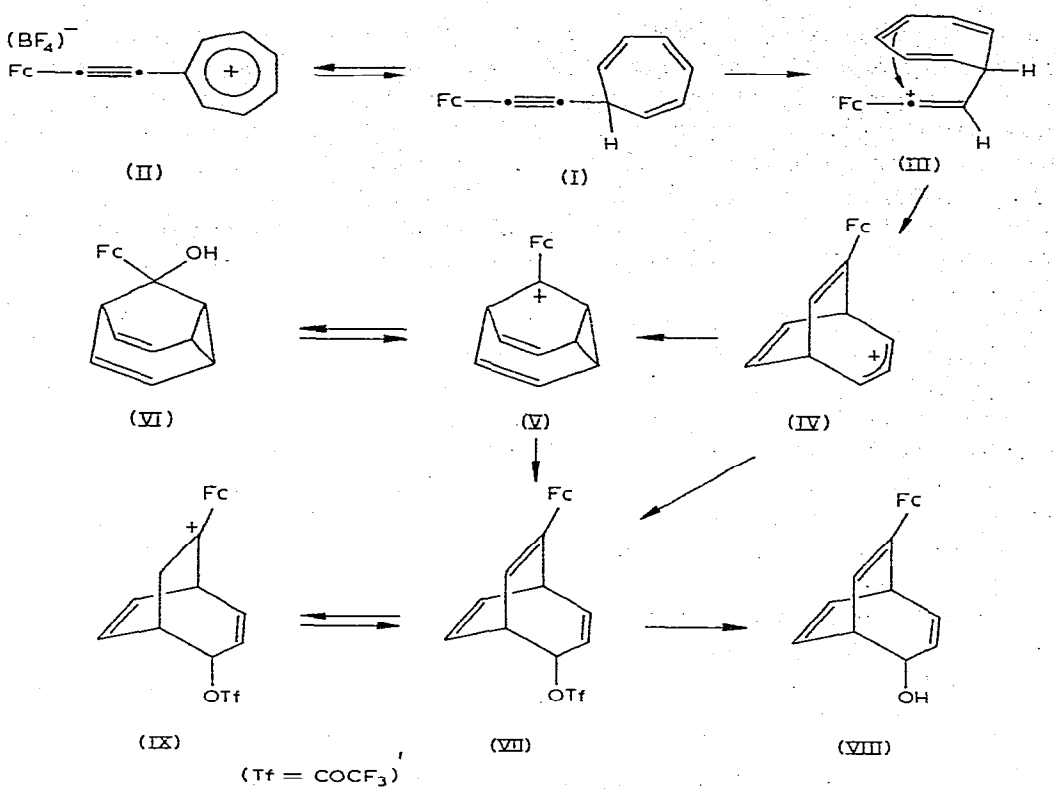

SCHEME 1

spectra* which were closely similar to those of analogous compounds: cf. 9-barbaralol [4,5], 9-methyl-9-barbaralol [6,7], and 2-methylbicyclo[3.2.2]-nona-3,6,8-trien-2-ol [7].

In CF_3CO_2H, the barbaralol VI was converted into the 9-ferrocenyl-9-barbaralyl cation V while the trienol VIII similarly afforded the bicyclic cation IX. In the latter case, immediate protonation of the ferrocenylvinyl group occurred followed by slower trifluoroacetylation of the hydroxyl function. Comparison of the ^1H NMR spectra of these cations with that of the original mixture clearly established that, in CF_3CO_2H, the alkyne I is converted into a mixture of the carbenium ions V and IX, the former predominating. The magnetic equivalence of i.a. the bridgehead protons (H(1,5)) in the spectra of the barbaralol VI and the barbaralyl cation V demands that these structures, as expected [4,6], possess a fluxional homotropilidene ring system.

Comparison of the ^1H NMR spectrum of the 9-ferrocenyl-9-barbaralyl

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*^1H NMR spectra (Me_4Si internal reference).

V: τ(CF_3CO_2H) (ppm) 3.82 and 4.99 (2t; C_5H_4); 4.00 and 4.35 (2t; H(3,7)); 5.17 (s; C_5H_5); 5.05-5.5 (m; H(2,4,6,8)); 6.53br (t; H(1,5)).

VI: τ($CDCl_3$) (ppm) 4.18 and 4.53 (2t; H(3,7)); 5.7-5.95 (m; C_5H_4, C_5H_5, and H(2,4,6,8)); 7.41 (t; H(1,5)); 7.97 (s; OH; D_2O-exchanged).

VIII: τ($CDCl_3$) (ppm) 3.0-4.0 (4H) and 4.85-5.0 (1H) (2m; vinyl); 5.65-6.05 (m; CHOH and C_5H_4); 5.82 (s; C_5H_5); 6.2-6.6 (m; H(1,5)); 8.40br (s; OH; D_2O-exchanged).

IX: τ(CF_3CO_2H) (ppm) 2.5-2.9 (1H), 3.05-3.4 (2H), and 3.5-3.6 (1H) (3m; vinyl); 3.65-3.85 (2H), 4.85-4.95 (1H), and 5.2-5.3 (1H) (3m; C_5H_4); 4.35-5.1 (m; $CHOCOCF_3$ and bridgehead); 5.22 (s; C_5H_5); 5.65-6.05 (m; CH_2).

cation V with that reported [6,7] for the 9-methyl analogue shows that positive charge delocalisation to the hydrocarbon cage is strongly attenuated by the ferrocenyl group; the cage proton shifts for V more closely correspond to those reported [6,7] for protonated barbaralone (i.e. 9-hydroxy-9-barbaralyl cation). The stability of the cation V in CF_3CO_2H at 33°C (cf. the 9-methyl analogue rearranges above —116°C) attests to the powerful electron-releasing capacity of the ferrocenyl group whose presence strongly disfavours a rearrangement process which would relocate positive charge at other carbon atoms of the system.

The assignment of the structures VII and VIII to the bicyclic products, rather than alternative allylic isomeric structures, is based of the finding that Na_2CO_3 (aq.) quenching of the cation V, generated unambiguously from the alcohol VI in CF_3CO_2H, gave (after $LiAlH_4$ reduction) a mixture of the barbaralol VI (81%) and the trienol VIII (5%), identical with the product isolated from the original reaction and resulting from opening of the cyclopropyl ring*. When a CF_3CO_2H solution of the cation IX, prepared from the trienol VIII, was similarly quenched, only the ester VII and the alcohol VIII were isolated.

The mode of formation of the products is suggested in Scheme 1. Protonation of the triple bond of the alkyne I affords the vinyl cation III which undergoes cyclisation to give the bicyclic allylic cation IV. It is remarkable that this reaction to produce an antibicycloaromatic [9] cation competes successfully with capture of the cation III by solvent (CF_3CO_2H) as found for other ferrocenylvinyl cations [2]. The bicyclic cation IV then collapses by two independent pathways, each generating a tertiary ferrocenylcarbenium ion. Intramolecular addition to the ferrocenylvinyl group leads directly to the barbaralyl cation V while, in a competing reaction, capture of trifluoroacetate by the allylic system and protonation of the ferrocenylvinyl group generates the bicyclic ester cation IX.

Support for this mechanism was provided by the observation that addition of tropylium tetrafluoroborate to ethynylferrocene in CH_2Cl_2, followed by hydrolysis, gave the barbaralol VI, albeit in low yield. The absence of the trienol VIII in the product from this reaction is understandable since the intermediate cation IV, formed via III in a non-nucleophilic medium, is diverted exclusively to the barbaralyl cation V and thence to product.

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*Simple 1-ferrocenylcyclopropylalkylium ions undergo similar ring-opening reactions (see ref. 8).