Novel Rearrangement Products from Longifolene *via* Stable Carbonium Ions

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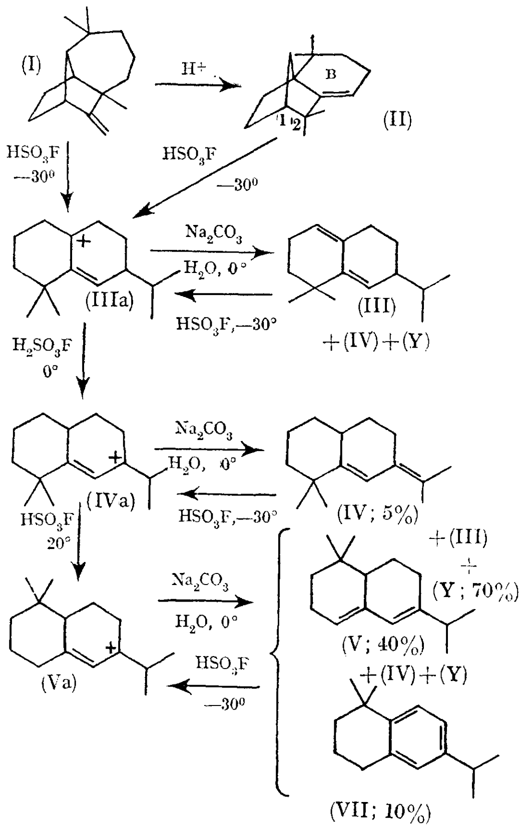
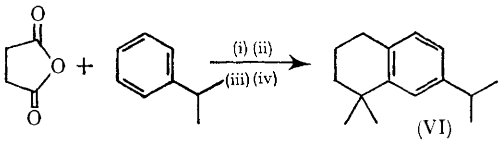
SOLUTIONS of stable carbonium ions have been used to investigate carbonium-ion structure and rearrangements.[1] The Chart summarizes some results of our investigation into the nature of stable carbonium ions obtained from the tricyclic sesquiterpene hydrocarbon longifolene (I) upon dissolution in fluorosulphonic acid at several temperatures. The value of this technique both as a means of deflecting the normal acid-catalyzed rearrangement of longifolene to isolongifolene (II),[2] and as a means of converting longifolene to other useful synthetic intermediates is evident.

When longifolene (I) or isolongifolene in Freon 114 B is added dropwise to rapidly stirred fluorosulphonic acid at temperatures below −30°, clear solutions containing up to 10% organic material can be obtained. The presence of the cation (IIIa) in these solutions was suggested by the n.m.r. spectrum, which exhibited a broad singlet signal at τ 0·78 for the terminal hydrogen of the allylic cation, a singlet at τ 8·63 for the geminal dimethyl, and a doublet (J 6 c./sec.) at τ 8·86 for the isopropyl group. Structure (IIIa) was further confirmed by formation of the olefin (III) upon quenching cation solutions in iced aqueous sodium carbonate. A 90% recovery of material containing 80% of the olefin (III) was obtained. The structure of purified olefin (SiO_2–$AgNO_3$)[3] was evident from its spectra [mass spectrum *m/e* 204; λ_{max} H (EtOH) 241 (ϵ 22,000) ν_{max} (neat) 1590, 862 cm.$^{-1}$, n.m.r., τ 4·48 (1H, broad s), 4·70 (1H, m), 8·97 (3H, s), 9·00 (3H, s), 9·10 (3H, d, *J* 6 c./sec.), 9·13 (3H, d, *J* 6 c./sec.)], and its conversion to aromatic hydrocarbon (VI) with chloranil in boiling carbon tetrachloride. Hydrocarbon (VI) [mass spectrum *m/e* 202, n.m.r., τ 2·95 (1H, s), 3·18 (2H, s), 7·05—7·50 (3H, m), 8·75 (6H, s), 8·80 (6H, d, *J* 6 c./sec.)] was easily prepared as shown below.



CHART

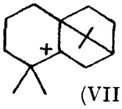


(i) $AlCl_4$; (ii) Clemmensen; (iii) MeLi
(iv) polyphosphoric acid.

At 0° the carbonium ion (IIIa) in fluorosulphonic acid rearranged to the carbonium ion (IVa) whose n.m.r. spectrum now showed a singlet at τ 2·23 for the central hydrogen of the allylic cation. The geminal dimethyl and doublet isopropyl signals appeared further downfield than in the cation (IIIa) at τ 8·50 and 8·47 (d, *J* 6 c./sec.) respectively, in accord with their terminal position on the allylic cation. Quenching the cation gave two dienes, the minor one of which (5% yield) was identified as (IV) by dehydrogenation to (VI) with chloranil, and by its spectroscopic properties [parent peak *m/e* 204, λ_{max} (EtOH) 248 (ϵ 17,000); ν_{max} (neat) 1650, 885, 870 cm.$^{-1}$, n.m.r., τ 3·83 (1H, broad s), 8·27, 8·32, 8·88, 8·95 (each 3H, s)]. The major diene (Y; 70%) is unstable and its structure is still under investigation. Both dienes gave the cation (IVa) in fluorosulphonic acid at −30°.

At room temperature under nitrogen, cation (IVa) in fluorosulphonic acid rearranges to cation (Va). The n.m.r. spectrum of cation (Va) revealed the central hydrogen on the allylic cation (τ 2·35, s), a terminal isopropyl group (τ 8·50, d, *J* 6 c./sec.), and a geminal dimethyl group with nonequivalent methyls further from the cationic centre (τ 8·75, 9·02, ss). Quenching the cation (Va) gave the aromatic hydrocarbon (VII) (10%) and the diene (V) [40% yield, identified by its spectroscopic properties; λ_{max} (EtOH) 240 mμ (ϵ 18,400); ν_{max} (neat) 1640 and 893 cm.$^{-1}$; n.m.r., τ 4·28 (1H, s), 4·70 (1H, m), 8·98 (6H, d, *J* 6 c./sec.), 9·03 and 9·23 (each 3H, s)]; and by its dehydrogenation to the aromatic hydrocarbon (VII) with *N*-bromosuccinimide. The n.m.r. spectrum of hydrocarbon (VII) (AB quartet centred at τ 3·05, $\Delta\tau$ 0·3 p.p.m., *J* 8 c./sec., and overlapping doublet, τ 3·22, *J* 3 c./sec.) evidenced the 1,2,4-trisubstitution pattern which also gave rise to its characteristic i.r. absorption at 2000—1650, 895, and 825 cm.$^{-1}$. The rest of the n.m.r. spectrum of hydrocarbon (VII) was identical to that of its isomer (VI), thus confirming the structure.

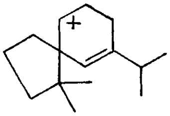
Since the cation (IIIa) arises from both longifolene and isolongifolene, it probably comes from a common cation, such as (VIII), already proposed as an intermediate in the longifolene–isolongifolene rearrangement.[4,5]



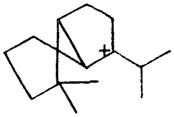
(VIII)

One reasonable interpretation of the rearrangement of (IVa) to (Va) involves the spiro-cation (IXa) as an intermediate. Although the conversion of an allylic tertiary cation to a secondary cation seems energetically unfeasable, it may be that the cation (IXa) is better represented as the more stable cyclopropyl carbinyl cation (IXb). This novel and perhaps general rearrangement appears analogous to the dienone-phenol and anthrasteroid rearrangements.

Although it is difficult to reproduce the quenching results it is possible to adjust the reaction conditions to obtain mixtures rich in a particular diene. Such equilibrium controlled formation of stable cations followed by kinetically controlled quenching may provide an interesting and useful variant on the usual synthetic uses of carbonium ion intermediates.



(IXa)



(IXb)

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