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NOVEL DITERPENE REARRANGEMENTS: DICHOTOMOUS BEHAVIOUR OF ABIETIC-TYPE RESIN ACIDS IN STRONG ACID MEDIUM

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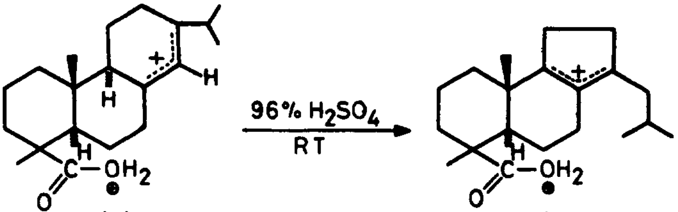
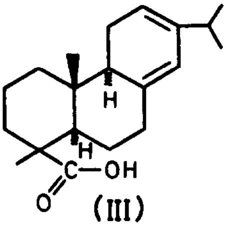
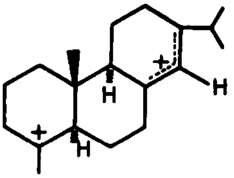
We have been interested[1] in the study of unusual terpene rearrangements of synthetic and biogenetic interest via observable carbocations in strong acid medium. In an earlier communication[1b] a facile and general rearrangement of cation(I) derived from abietic-type diterpene resin acids to the ring contracted abeoabietate cation (II) in 96% sulphuric acid was described. It was observed therein that the fate of ion (I) in chlorosulphonic acid or 99% sulphuric acid is dramatically altered. We wish to describe here a novel rearrangement of levopimaric acid(III),[2] which is initiated by the dehydration and decarbonylation of the C_4-carboxylic acid function[3] and proceeds through the formation of intermediate dication (IV).



(I) (II)

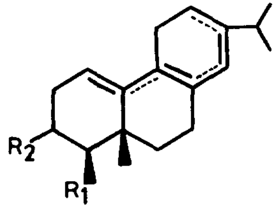


(III)



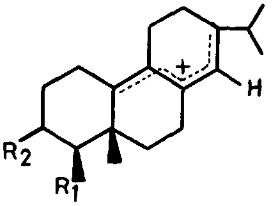
(IV)

Rapid dispersal of a 10% CH_2Cl_2 solution of LPA in $ClSO_3H$ at -25° gave a burgundy solution, whose NMR spectrum exhibited signals compatible[1b] with structure (I). When the solution of (I) was allowed to warm up to r/t profuse evolution of CO ensued and new signals emerged in the NMR spectrum of the ion. These signals consisted of an isopropyl doublet at 1.25 (J=6.5 Hz), a tertiary methyl singlet at 1.28, two doublets at 0.91 and 1.31 (J=6 Hz) due to two secondary methyl resonances and an olefinic proton singlet at 6.88 (cf. 7.61 in ion (I)). These NMR parameters along with the high field shift of the olefinic proton resonance indicating the further dispersal of the positive charge, suggested the presence of rearranged ions (V) & (VI) in $ClSO_3H$ solution. On quenching the cations (V) & (VI) in iced Na_2CO_3, a mixture of C_{19}-trienes (VII & VIII, UV: λ_{max}^{MeOH} 300 nm) was recovered in 88% yield.



(VII) $R_1=CH_3$, $R_2=H$

(VIII) $R_1=H$, $R_2=CH_3$



(V) $R_1=CH_3$, $R_2=H$

(VI) $R_1=H$, $R_2=CH_3$

The triene mixture was extremely labile & complex and furnished disproportionation products (XI), (XII) and styrene (IX) on attempted purification. However, the structure[4] of the trienes and cations (V) & (VI) can be deduced from the dehydrogenation and aromatisation products of triene mixture. The results are depicted in chart 1 and the physico-chemical characterisation of the compounds (IX)→ (XIII) is summarised below:

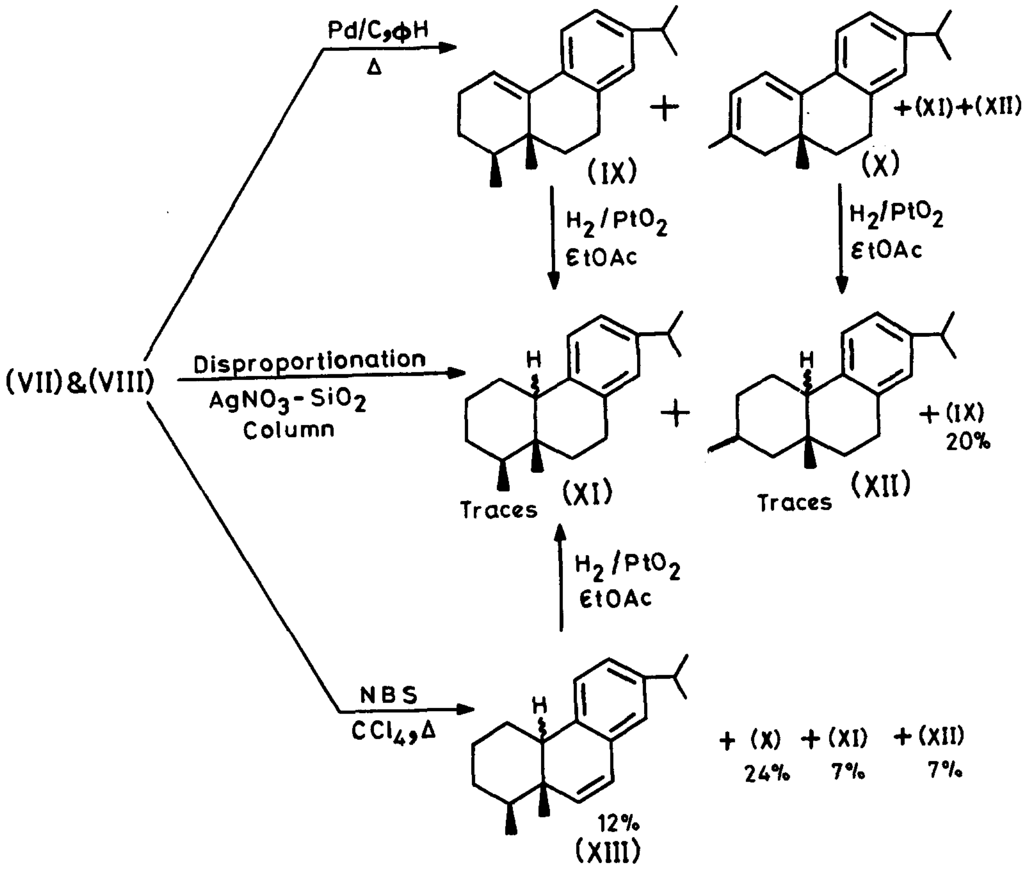
Compound (IX): $C_{19}H_{26}$, λ_{max}^{MeOH} 256 nm (ϵ=9430); ν_{max}(neat): 1630, 885, 830 cm^{-1}. NMR: δ 1.23 (6H, d, J=7 Hz, $\underline{CH_3}-\underset{CH_3}{\overset{|}{C}}-H$), 0.87 (3H, s, $\underline{CH_3}-\underset{|}{\overset{|}{C}}-$), 0.93 (3H, d, J=6.5 Hz, $H-\underset{|}{\overset{|}{C}}-\underline{CH_3}$), 2.7-3.1 (3H, m, benzylic), 6.17 (1H, t, J=4 Hz, $Ar-\overset{|}{C}=\overset{|}{C}-\underline{H}$), 7.05 (1H, d, J=9 Hz, Ar), 6.95 (1H, s, Ar), 7.51 (1H, d, J=9 Hz, Ar).

Compound (X): $C_{19}H_{24}$, λ_{max}^{MeOH} 318 nm (ϵ=7200) and 306 nm (ϵ=6900); ν_{max}(neat): 1660, 1635, 1610, 830, 795 cm^{-1}. NMR: δ 1.21 (6H, d, J=7Hz, $\underline{CH_3}-\underset{CH_3}{C}-H$), 1.19 (3H, s, $\underline{CH_3}-\underset{|}{\overset{|}{C}}-$), 1.71 (3H, s, $\underline{CH_3}-\overset{|}{C}=\overset{|}{C}-$), 2.5-3.1 (3H, m, benzylic), 6.33 (2H, ABq, J=9.5 Hz, $-\overset{|}{C}=\underset{\underline{H}}{C}-\underset{\underline{H}}{C}=\overset{|}{C}-$) 6.83 (1H, s, Ar), 6.9 (1H, d, J=9 Hz, Ar), 7.13 (1H, d, J=9 Hz, Ar).

Compound (XI): $C_{19}H_{28}$, λ_{max}^{MeOH} 280 nm (ϵ=1900) and 272 nm (ϵ=1900); ν_{max}(neat): 1612, 890, 830, 640 cm^{-1}. NMR: δ 1.21 (6H, d, J=7 Hz, $\underline{CH_3}-\underset{CH_3}{\overset{|}{C}}-H$), 1.08 (3H, s, $\underline{CH_3}-\underset{|}{\overset{|}{C}}-$), 0.93 (3H, d, J=6 Hz, $\underline{CH_3}-\underset{|}{\overset{|}{C}}-H$), 2.6-3.1 (4H, m, benzylic), 6.93 (1H, s, Ar), 7.01 (1H, d, J=8 Hz, Ar), 7.28 (1H, d, J=8 Hz, Ar).

Compound (XII): $C_{19}H_{28}$, λ_{max}^{MeOH} 280 nm (ε=1400) and 272 nm (ε=1260); ν_{max}(neat): 1615, 895, 830 cm^{-1}. NMR: δ 1.22 (6H, d, J=7 Hz, $\underline{CH_3}-\overset{H}{\underset{CH_3}{C}}-$), 0.93 (3H, s, $\underline{CH_3}-\overset{|}{\underset{|}{C}}-$), 0.78 (3H, d, J=7 Hz, $\underline{CH_3}-\overset{|}{\underset{|}{C}}-H$), 2.4-3.0 (4H, m, benzylic), 6.80 (1H, s, Ar), 6.88 (1H, d, J=8 Hz, Ar), 7.06 (1H, d, J=8 Hz, Ar).

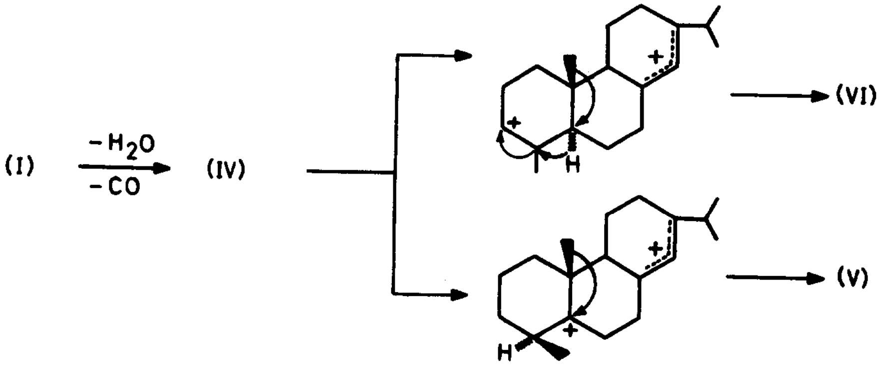
CHART 1



Compound (XIII): $C_{19}H_{26}$, λ_{max}^{MeOH} 266 nm (ε=7770); ν_{max}(neat): 1662, 1610, 830, 730, 700 cm^{-1}. NMR: δ 1.2 (6H, d, J=7 Hz, $\underline{CH_3}-\overset{|}{\underset{CH_3}{C}}-H$), 0.95 (3H, s, $\underline{CH_3}-\overset{|}{\underset{|}{C}}-$), 0.96 (3H, d, J=6 Hz, $\underline{CH_3}-\overset{|}{\underset{|}{C}}-H$), 2.6-3.1 (3H, m, benzylic), centre 6.21 (2H, ABq, J=8 Hz, $-\underset{\underline{H}}{C}=\underset{\underline{H}}{C}-$), centre 6.98 (3H, m, Ar).

The mechanism of formation of carbocations (V) & (VI) and derived products (VII)→ (XIII) is straight forward and outlined in chart 2. The novel rearrangement

CHART 2



of abietic type acids involving C_{10}-methyl migration and their dual behaviour in strong acids provides a new variant to the synthetic utility of stable carbocations in highly ionising medium. We intend to make use of this methyl migration sequence to synthesize rearranged terpenes employing model systems.

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1. (a) D.G. Farnum and G. Mehta, Chem. Comm., 1643 (1968);
   (b) G. Mehta and S.K. Kapoor, Tetrahedron Letters, 4947 (1972);
   (c) G. Mehta and B.P. Singh, Unpublished results.

2. Most of the present work was done employing (III) but it has been shown that other resin acids of abietic family also give the same ionic species.

3. For examples of decarbonylation of aliphatic carboxylic acids via acylium ions, see, G.A. Olah and A.M. White, J. Amer. Chem. Soc., 89, 3591 (1967).

4. Similar rearrangement of abietic acid in FSO_3H has been independently investigated by Dr. D.G. Farnum, Michigan State University, U.S.A. The gross carbocyclic structure of the compounds (V)– (XIII) has been further confirmed by comparison with some of his synthetic compounds and our own degradative work. We wish to thank Dr. Farnum for sending us a pre-print[5] of his paper prior to publication.

5. D.G. Farnum and R.A. Mader, J. Amer. Chem. Soc., 95, 000 (1973).