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REARRANGEMENT OF ABIETIC-TYPE RESIN ACIDS VIA STABLE CARBOCATIONS

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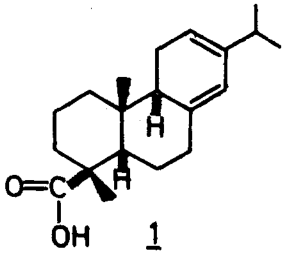
The structure, reactivity and rearrangement of carbocations as stable solutions in strong acids have been extensively studied.[1] We have been fascinated by the prospect of carrying out certain biogenetic-type transformations and rearrangements of selected terpenes[2] via observable carbocations. We describe here a new and efficient rearrangement of levopimaric acid 1, neoabietic acid 2 and abietic acid 3 through common observable carbenium ions and the preparation of a tricyclic synthon 8 of potential value in a variety of natural product synthesis.



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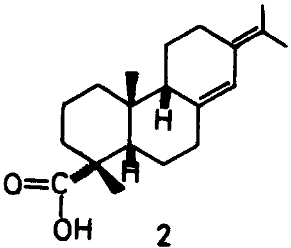

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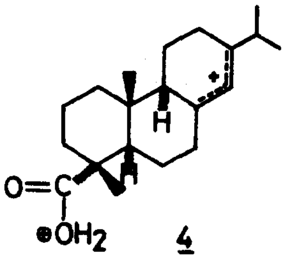

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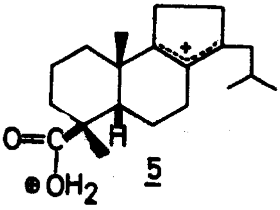
When a CH_2Cl_2 solution of levopimaric acid 1[5] was dispersed in 96% H_2SO_4 (5-10°), clear light orange solution of cation 4 was obtained. The structure of the cation 4 follows from its UV spectrum $\lambda_{max}^{H_2SO_4}$ 318 nm (ε = 14600) and its nmr spectrum, which exhibited a broad singlet at δ 7.6 for the central proton of an allylic cation, singlets at 1.61 and 1.05 for the C_4- and C_{10}-methyls and a doublet at 1.41 (J = 6.5 Hz) for the C_{13}-isopropyl group. On quenching the cation solution in iced aq. Na_2CO_3 a near quantitative recovery of abietic acid 3 resulted.

Cation 4 at 25° (2 hrs) in sulphuric acid underwent smooth rearrangement to 5 as evidenced by its UV spectrum $\lambda_{max}^{H_2SO_4}$ 312 nm (ε = 13400) and nmr spectrum which displayed singlet at δ 1.58 for the C_4- and C_{10}-methyls, a doublet at 1.13



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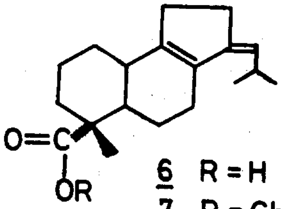
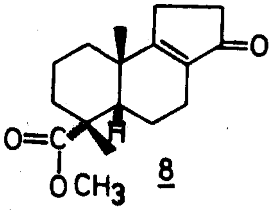


6 R = H

7 R = CH_3



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(J = 6.5 Hz) for the isopropyl group and was transparent in the olefinic proton region. Quenching the cation 5 gave an unstable dienoic acid 6 in 80% yield and was purified (SiO_2-$AgNO_3$) through its methyl ester 7. The dienoic acid 6 regenerated cation 5 on dissolution in 96% sulphuric acid. The structure of 7 follows from its spectral parameters λ_{max}^{MeOH} 248 nm (ε = 15000), ν^{neat} 1735, 1640 cm^{-1}, δ5.83 (1H, broad singlet), 3.71, 1.38, 0.91 (3H, singlets), 1.16 (3H, doublet, J = 6 Hz), 1.23 (3H, doublet, J = 6 Hz), and its conversion (75%) to tricyclic enone 8, λ_{max}^{MeOH} 240 nm (ε = 13000), $\nu^{C=O}$ 1735 (ester), $\nu^{C=O}$ 1705 (Conj.5-membered), $\nu^{C=C}$ 1650 cm^{-1}; δ3.73 ($-OCH_3$), 1.25, 1.16 (3H, singlets, C_4- and C_{10}-methyl), on selective ozonolysis and oxidative work-up. The mechanism of the rearrangement of cation 5 → 6 appears to be base catalysed[1,6] as the behaviour of the resin acids in 98% H_2SO_4 and $ClSO_3H$ is dramatically altered and only highly rearranged polyenes derived through decarbonylation are obtained.[7]

REFERENCES

1. G.A. Olah and P. von R. Schleyer, "Carbonium Ions," Vol. I & II, Interscience Publishers, London, 1968 & 1970.
2. The motivation to undertake this work came from a rearrangement observed by us[3] which is formally equivalent to a 1,2-isopropyl shift. A similar rearrangement in present study should result in abietic-type → sempervirol type[4] transformation through stable enylic cation. Also see, E. Wenkert and B.G. Jackson, J. Amer. Chem. Soc., 80, 211 (1958).
3. D.G. Farnum and G. Mehta, Chem. Commun., 1643 (1968).
4. L. Mangoni and R. Caputo, Tetrahedron Letters, 673 (1967).
5. All the three acids viz., 1, 2 & 3 gave the same cation 4 but most of our work was done with 1.
6. N.C. Deno and R.R. Lastomusky, J. Amer. Chem. Soc., 90, 4085 (1968).
7. The details of this work will be published in a separate communication.