Tetrahedron Letters Vol.24,No.23,pp 2411-2412,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

ALLOISOLONGIFOLENE, A UNIQUE ACID-CATALYZED ISOMER OF LONGIFOLENE+

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Abstract. A remarkably catalyst-specific rearrangement of longifolene 1 to a new tricyclic isomer, alloisolongifolene 3, has been discovered after more than two decades of dormancy since the first acid-catalysed isomer, isolongifolene 2, was unravelled by us.

THAT the enigmatic longifolene 1 is still not a spent force in the realm of molecular rearrangements is highlighted by our recent discovery of yet another bizarre isomer of the sesquiterpene, skeletally quite distinct from the now well-entrenched isolongifolene 2 uncovered[1] by us way back in 1960. Generation and structure elucidation of alloisolongifolene[2] 3, the new hydrocarbon, forms the essence of this communication.


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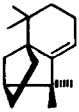
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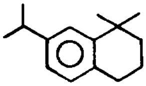
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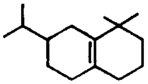
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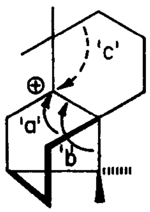

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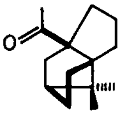

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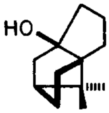

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Refluxing longifolene for several hours in the presence of certain specific catalysts (eg. XCH$_2$COOH, X = Br, I, not Cl) resulted in a binary mixture of skeletally distorted hydrocarbons, resolved by AgNO$_3$-SiO$_2$ gel chromatography into the unique alloisolongifolene 3 (75-85%) and the known isolongifolene 2 (15-25%). Most other catalysts (eg. p - TsOH), under similar conditions, furnished a disproportionated mixture of the tetralin 4 and the octalin 5.

Alloisolongifolene, $C_{15}H_{24}$, $(\alpha)_{2D}$ - 40.6°(CHCl$_3$), like its parent 1, was monoolefinic/tricyclic /CMR: two sp^2 carbons at 152.5° (s) and 109.6 ppm (t)/; on hydrogenation (PtO$_2$-AcOH), with or without added HClO$_4$, it yielded the same saturated hydrocarbon $C_{15}H_{26}$ (M$^+$ 206), suggesting also the absence of any cyclopropane ring. A distinguishing feature of the sp^3 methyl region in the PMR spectrum of the new isomer was the presence of only two 3H-singlets at 0.80, 0.92 ppm as compared to three 3H-singlets in 1/four 3H-singlets in 2; signals at 4.60, 4.67 ppm (br s, 2H, = CH$_2$) and 1.69 ppm (s, 3H, vinylic Me) also enabled elaboration of the double bond (IR: 1632, 890 cm^{-1}) into an isopropenyl moiety.

In the recently proposed and experimentally verified[3] Berson mechanistic scheme[4] for the rearrangement of longifolene, the neoisolongifolyl cation 6 (generated viathe exo-methyl shift pathway[4] involving a carbocation at the bridgehead of a bicyclo [4.3.1] decane system, more flexible[5] in comparison with a bicyclo [4.2.1] nonane- in which a planar trigonal carbon at the bridgehead causes severe distortion of its bicyclo [2.2.1] heptane component) is strategically important as the break-off point for product development into either isolongifolene 2 (syn migration route 'a')/tetralin[6] 4 (fragmentation route 'b'). While studying a framework molecular model of the carbocation 6, an anti-1,2-alkyl shift of the type 'c' appeared quite facile, thus generating structure 3, assignable to the new hydrocarbon on the basis of its excellent agreement with the aforementioned spectral data.

Isolongifolene 2 /alloisolongifolene 3 are mutually non-interconvertible when exposed to acidic reagents. Unlike in the case of 2, exposure of 3 to neat BF$_3$.OEt$_2$ does not achieve further rearrangement to the tetralin 4. Hydrolysis of the ester resulting from the Baeyer-Villiger oxidation of the methylketone 7, derived from the periodate-permanganate oxidation of alloisolongifolene, gave a tertiary alcohol 8 ($C_{12}H_{20}O$, M$^+$ 180) in conformity with the assigned structure 3 for the hydrocarbon.

References and Notes

[+] NCL Communication No. 3235.

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(Received in UK 25 March 1983)