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X-RAY STRUCTURE OF ALLOISOLONGIFOLOL-p-NITROBENZOATE : REVISION OF THE STRUCTURE OF ALLOISOLONGIFOLENE, THE PARENT HYDROCARBON[+]

H.R. Shitole, V.S. Dalavoy, V.B. Deodhar and U.R. Nayak*
K.R. Acharya, S.S. Tavale and T.N. Guru Row*
National Chemical Laboratory, Poona 411 008 (India)

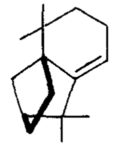
and

V.P. Kamat and S.K. Paknikar*
Centre of Postgraduate Instruction and Research
University of Bombay, Panaji 403 001 (India)

Summary. An X-ray crystal structure analysis of alloisolongifolol-p-nitrobenzoate as 4 has necessitated a revision of the earlier assigned structure 3 to 5 for alloisolongifolene, the parent hydrocarbon.

IN THE RECENT assignment[1] of the structure 3 to alloisolongifolene, the remarkably catalyst-specific isomer of longifolene 1, the overriding consideration has been the experimentally verified[2] Berson mechanistic scheme[3] for the rearrangement of longifolene 1 to isolongifolene 2 : the exo-methyl shift pathway involving a carbocation at the bridgehead of a bicyclo [4.3.1] decane, more flexible[4] in comparison with a bicyclo [4.2.1] nonane. Our attempts to provide an unambiguous proof of the complex bridged carbon framework of alloisolongifolene by the X-ray technique were foiled for a long time by the tenacious resistance of the new hydrocarbon to yield a stable crystalline derivative (dibromide, hydrobromide etc.) suitable for an X-ray study. We now describe an X-ray crystal structure analysis of alloisolongifolol-p-nitrobenzoate (via hydroboration of alloisolongifolene) as 4 for deriving the structure of the parent hydrocarbon as 5, which now overrules the previously assigned structure 3 for alloisolongifolene.

1



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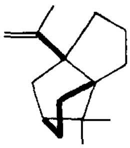

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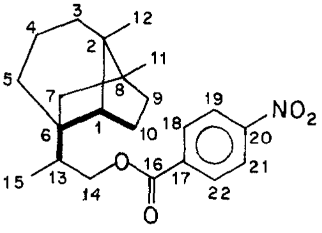

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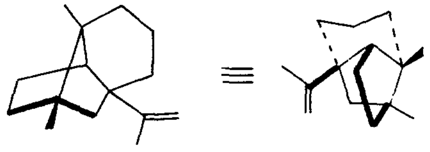
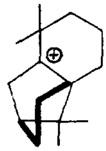


5 5



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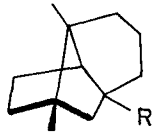
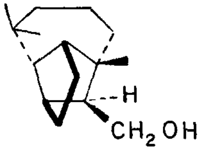


9 : R = $COCH_3$
10 : R = OH



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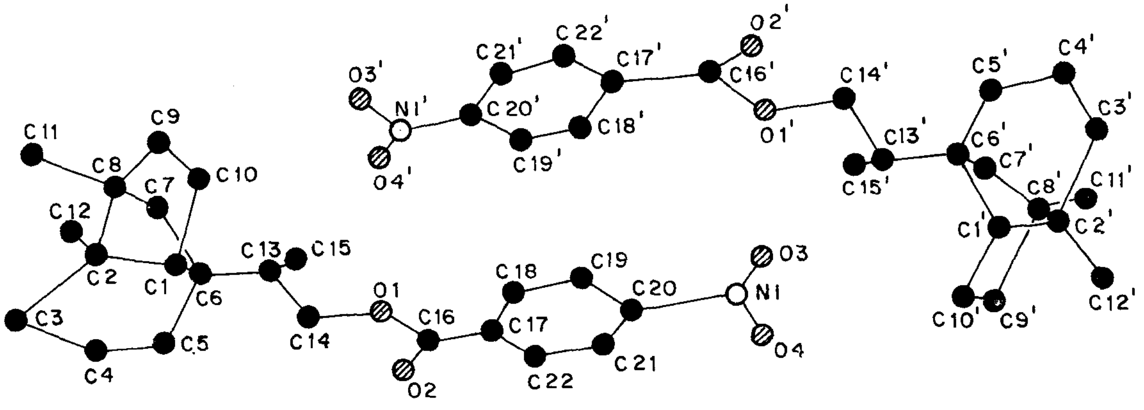

Fig. 1. Molecular structure of Alloisolongifolol-p-nitrobenzoate

The crystals of alloisolongifolol-p-nitrobenzoate belong to the space group $P2_1$ with a ≐ 7.440(5), b = 34.963(6), c = 7.909(2)Å and β = 105.42(3)°. The intensity data (3421 reflections) were collected on a CAD4F-11M diffractometer with MoK_α radiation (0.7107 Å) using the $\omega/2\theta$ scan technique. There are two molecules in the asymmetric unit (i.e. Z = 4) and the structure was solved by direct methods[5]. Refinement of the structure is in progress with the current R value[6] of 0.155 for 785 reflections with $/F_o/ > 3\sigma/(F_o)/$. A view of the molecules is shown in Fig. 1.

The carbon skeleton of the X-ray dictated structure 5 for alloisolongifolene is however different from that of the earlier structure 3 derived from the multiply rearranged neoisolongifolyl cation 6, arising from an energetically more favourable pathway from 1. The now revised structure 5 is obviously generated from the carbocation 8 (based on a relatively strained bicyclo [4.2.1] nonane, vide supra), the point of departure in the longifolene 1 → isolongifolene 2 pathway[2] occurring at the much earlier longibornyl cation stage 7 itself. Obviously, we still do not understand all the factors that influence carbocation rearrangements; further studies are necessary to reveal more details of carbocation potential energy surfaces, particularly rearrangement transition states.

In view of the revised structure 5 for alloisolongifolene, its periodate-permanganate oxidation product and the tertiary alcohol resulting from the Baeyer-Villiger/hydrolysis reaction on the methylketone should now be properly designated as 9 and 10 respectively, overriding the earlier assigned structures[1] based on 3 for the new hydrocarbon.

Following a preliminary investigation[7] of the reaction of isolongifolol 11 with $KHSO_4$, the Panaji-based group carried out a detailed analysis and demonstrated the formation of isolongifolene 2 and another hydrocarbon having spectral properties[8] characteristic of alloisolongifolene. The identity was established by a direct comparison with an authentic sample of the Poona group. On the basis of mass spectral fragmentation pattern and a close examination of molecular models of carbonium ions 6 and 8, the Panaji group favoured the alternative structure 5 for alloisolongifolene before the X-ray picture emerged. The results described above unravel yet another fascinating aspect of longifolene chemistry.

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6. This R corresponds to refinement with isotropic temperature factors for all atoms. Several interesting and noteworthy features of this X-ray crystal structure study will be detailed elsewhere after complete refinement.

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8. We are deeply indebted to Dr. R.L. Snowden of Firmenich, Geneva, for preparative GLC and spectral data on isolongifolene and alloisolongifolene, and CSIR, India, for a fellowship to VPK.

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