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DEHYDRONEOLONGIFOLENE AND DEHYDROLONGIFOLENE: TWO EXOTIC 1,4-DIENES FROM LONGICYCLENE VIA 9-IODOLONGIFOLENE[1,2]

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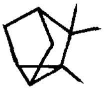
THE UTILITY of the methylcyclopropane-halogen reaction on cyclene 1/ longicyclene 2 for achieving facile, otherwise inaccessible homoallylic functionalization in camphene 3 / longifolene 4 has been described[3] by us recently: thus ICl-pyridine complex in AcOH readily transforms 1 → 5 and 2 → 6. In the generation of the homoallylic iodoolefins 5 / 6, it is important to consider the mode of cleavage of the cyclopropane ring in 1 / 2. Either of the two possible bond cleavages at the methyl-bearing carbon in cyclene 1 procreates one and the same iodocamphene 5 (≡5a). In the case of longicyclene 2, however, the same two bond cleavages can theoretically give rise to two *different* iodoolefins 6 / 7, of which only the former is realized in practice. The generation from iodolongifolene 6 (*vide infra*), what would formally constitute a β-elimination product from the isomeric iodo*neo*longifolene 7, *viz* the exotic dehydroneolongifolene 8 (with a bridgehead sp^2 carbon!), forms the essence of this communication. The formation of the more prosaic but a close relative of 8 - dehydrolongifolene 9 - by treatment of 6 with a strong base is also described.



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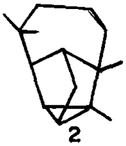

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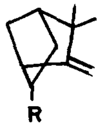

3: R=H
5: R=I

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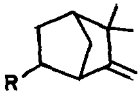

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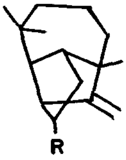
5a: R=I



4: R=H
6: R=I

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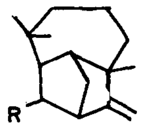
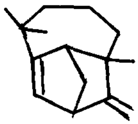


7: R=I



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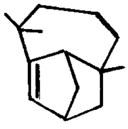
Chromatography (SiO_2/IIa) of the KOAc-DMF product (140°/40 hr) from iodolongifolene 6 furnished the pure diene 8 [4] (55%) while simple fractional distillation of the t-KOBu-DMSO product (80°/6 hr) from 6 yielded the isomeric diene 9 (91%). Meaningful spectral data of 8 and 9 are compared in Table I.

TABLE I

	Diene 8	Diene 9
PMR(CCl$_4$)	5.63* (*d*,1H,J=3 Hz, C=CHCH) 4.77,4.40 (2 *s*, 1H each, >=CH$_2$) 1.10,1.07,0.95 (3 *tert* Me singlets)	6.17* (*m*,2H, HC.CH=CHCH) 4.90, 4.58 (2*s*, 1H each, >=CH$_2$) 0.88 (3X *tert* Me singlets)
IR(smear)	3010,1650,1600,885,830 cm^{-1}	3010,1650,1570,890,760 cm^{-1}
MS	202 (M$^+$, base peak)	202 (M$^+$)

*values in ppm

The assignment of the novel bridgehead double bonded structure 8 for the KOAc-diene was dictated by the diagnostic[5] 1H doublet (J = 3 Hz) at 5.63 ppm; in the case of 10, a closely related normethylene derivative of 8, the lone olefinic proton appears[5] as a doublet at 5.67 ppm (J = 3 Hz). While formation of dehydrolongifolene 9 from 9-iodolongifolene 6 with *t*-KOBu is only to be expected (β-elimination) what is more fascinating is the generation of the skeletally-rearranged diene 8 by KOAc-DMF. Conceivably 8 can arise from 6 *via* the intermediate *pseudo*-longifolol acetate 11[6] (see below).



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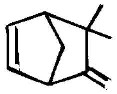

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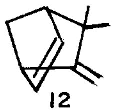

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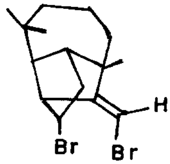

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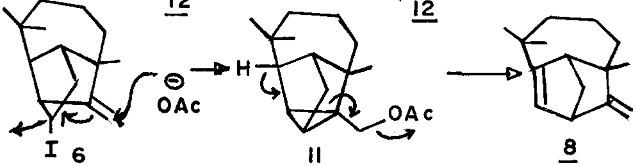

Finally, it may also be mentioned that the monoterpene analogue of 8/9 *viz*.dehydrocamphene 12 was formed in a similar manner (*t*-KOBu[7]) from the iodocamphene 5-C$_{10}$H$_{14}$ (62%); M$^+$ 134. IR(CCl$_4$):3010,1650,1580,895 cm^{-1}. PMR(CCl$_4$): 5.97 ppm (*m*, 2H, HC.CH=CH.CH); 4.73,4.48 ppm (2*s*, 1H each, >=CH$_2$); 1.18,0.95 ppm (two *tert* Me singlets).

REFERENCES AND NOTES

1 Communication No. 2360 , National Chemical Laboratory, Poona

2 Newer Aspects of Longifolene - XV

3 S.N.Suryawanshi and U.R.Nayak, *Tetrahedron Letters* (in press).

4 Dehydroneolongifolene 8 (58%) can also be prepared from the dibromide 13[3] by the action of KOAc-DMF followed by reductive elimination of the vinylic bromine from the product by treatment with Na/THF/*t*-BuOH. W.R.Dolbier Jr., D. Lomas and P. Tarrant, *J. Am. Chem. Soc*. **90**, 3594 (1968).

5 R.M.Coates and J.P. Chen, *Chem. Commun*. 1481 (1970).

6 Actually this is a major constituent of the mixture of oxygenated products (acetates/alcohols) constituting about 40% of the reaction yield.

7 In the case of iodocamphene 5 the KOAc-DMF reagent failed to give any distillable product.

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