CHEMISTRY LETTERS, pp. 963-966, 1974. Published by the Chemical Society of Japan

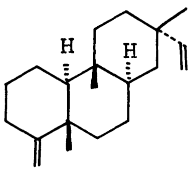
BACKBONE REARRANGEMENT IN DOLABRADIENE

Masayuki KITADANI,* Chizuko KABUTO,** Kunikazu SAKAI,**
Akira YOSHIKOSHI,*** and Yoshio KITAHARA**
*College of General Education, Kobe University, Nada-ku, Kobe 657
**Department of Chemistry, Tohoku University, Sendai 980
***Chemical Research Institute of Non-Aqueous Solutions,
Tohoku University, Sendai 980

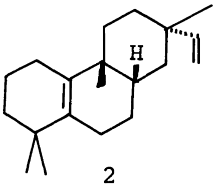
Upon heating in formic acid dolabradiene (1) gives a mixture of hydrocarbons. Five backbone rearrangement products isolated from the mixture are assigned to $\Delta^{5(10)}$-8β-rimuene (2), $\Delta^{5(10)}$-rimuene (3), $\Delta^{1(10)}$-rimuene (4), $\Delta^{8(9)}$-pimaradiene (5), and $\Delta^{1(10),5}$-rimutriene (6a), respectively. Their formation mechanisms are also discussed.

Backbone rearrangement in dolabradiene (1), a rearranged pimaradiene isolated from *Thujopsis dolabrata*1) and *Thuja standishii*,2) is of interest in relation to analogous rearrangements of steroids3a) and terpenoids.3b)

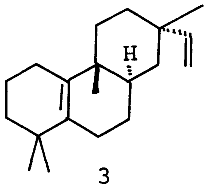
Dolabradiene was refluxed with formic acid, and a stationary ratio of products was attained after *ca*. 45 hr. No detectable amount of dolabradiene was found in this reaction mixture, which showed several glc peaks. Five rearrangement products (compound A$\sim$E)4) were separated by fractional distillation followed by silver nitrate-silica gel chromatography and preparative glc purification.



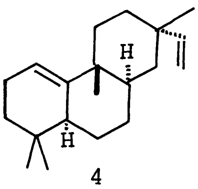
1



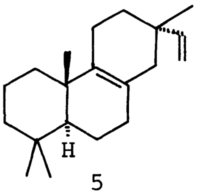
2



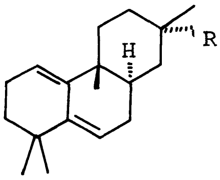
3



4



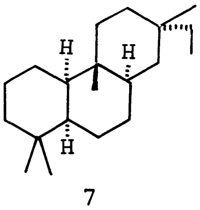
5



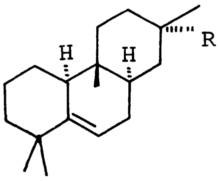
6

a; R = vinyl

b; R = Et



7



8

a; R = Et

b; R = vinyl

i) Compound A,[5] $C_{20}H_{32}$ (M^+ 272), $[\alpha]_D^{26}$ -132.5°,[6] is crystalline (m.p. 89∿90°). Four methyl groups and a vinyl group were indicated in the ir [ν (KBr) 3080, 1811, 1641, 997, and 906 cm^{-1}] and nmr spectra[7] [δ 0.96, 0.99, 1.01, and 1.03 (3H, s each), 4.6∿6.0 (3H, ABC-patterned m)]. Since neither $\Delta^{5(10)}$-rimuene (3) nor $\Delta^{8(9)}$-sandaracopimaradiene (5), however, was identical with this olefin, its structure was analyzed by X-ray crystallography.

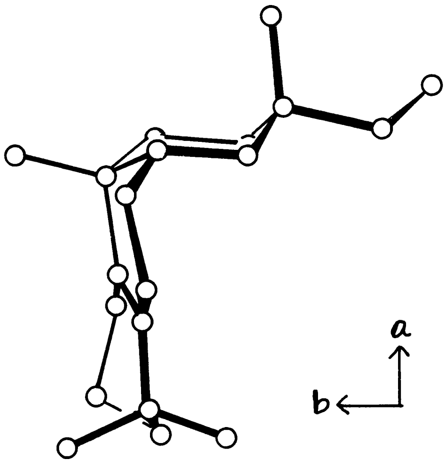


Fig. 1 The molecular structure of A viewed along c-axis.

Crystals of A belong to orthorhombic space group $P2_12_12_1$; a = 21.994, b = 10.365, c = 7.599 Å; Z = 4. A total of 1874 reflections up to 2θ = 52° were measured on a Rigaku automated four circle diffractometer using MoK_α radiation. The structure analysis was carried forward by means of the direct method[8] applying symbolic addition and tangent formula. However many attempts were necessary to accomplish this task; especially to search out the molecular position with respect to the unit cell. Translations were tried repeatedly using a structural model derived from E-map, and the confirmation was made by least-squares method. Indeed this difficulty for direct method might be attributed to the special location of the entire molecule in the unit cell as pointed out by Hauptman.[9]

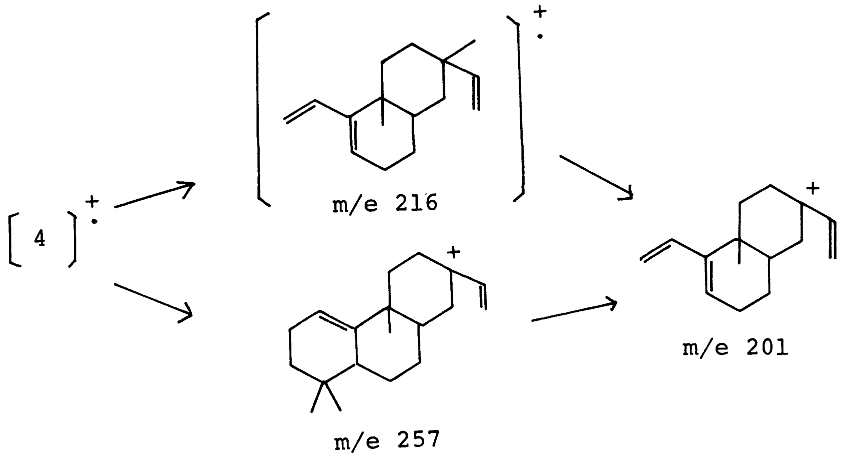
As shown in Fig. 1 where the final structure of A is viewed along c-axis, the molecule arranges parallel to this axis. There are all normal bond lengths and angles obtained from the atomic parameters after refinement converged to give the R-factor of 0.10.[10]

Thus the compound A was unambigously assigned to the structure (2).

$\Delta^{8(9)}$-Sandaracopimaradiene (5) afforded a similar equilibrated mixture under the same reaction conditions, and the compound A was separated from the mixture and identified. As the most probable pathway, hence, β-face protonation of 5 followed by methyl migration may account for the formation of A.

ii) Oily compound B was identified as $\Delta^{5(10)}$-rimuene[2,11] (3) by comparison with an authentic sample.

iii) The spectra of oily compound C, $C_{20}H_{32}$ (M^+272), $[\alpha]_D^{26}$ + 10.1°, n_D^{20} 1.492, exhibited a trisubstituted double bond [ν (liquid film) 830 cm^{-1}; δ 5.32 (1H, t, J = 4)] besides four tert. methyl groups [δ 0.85, 0.93, and 0.96 (3H, s)] and a vinyl group [ν (liquid film) 3080, 1820, 1645, 990, and 910 cm^{-1}; δ 4.8∿5.9 (3H, m)]. Fragment ions at m/e 257, 216, and 201 in the mass spectrum strongly suggested the following retro-Diels-Alder fragmentations.



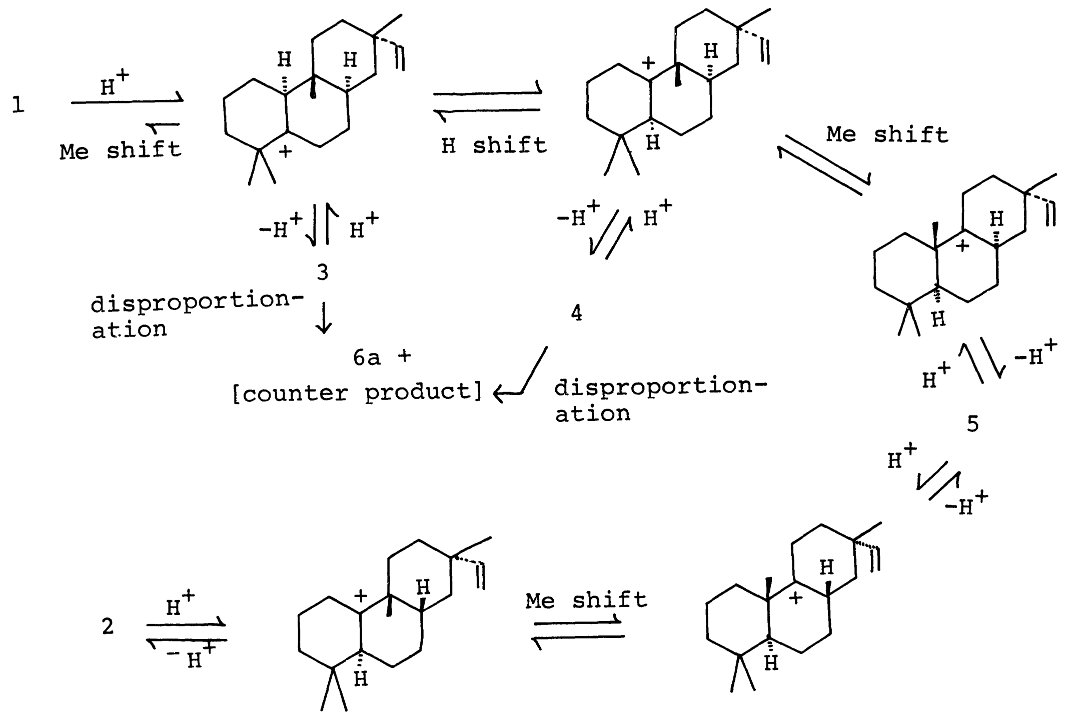
Hydrogenation of C in a mixture of acetic acid and ethanol over platinum catalyst gave rimuane[12)] (7), which was identified by comparison with an authentic sample. Thus $\Delta^{1(10)}$-rimuene (4) was assigned to the compound C.

iv) Compound D is crystalline and was identified as $\Delta^{8(9)}$-sandaracopimaradiene[2,13)] (5) by comparison with an authentic sample.

v) Compound E, $C_{20}H_{30}$(M^+ 270), $[\,\alpha\,]_D^{26}$ + 160.4°, is also crystalline (m.p. 82∿83°). The spectra showed two olefin protons [δ 5.49 (2H, br. m)] besides four tert. methyl groups [δ 0.78, 0.91, 0.96, and 1.05 (3H, s each)] and a vinyl group [ν 3080, 1810, 1645, 1625, 998, and 906 cm^{-1}; δ 4.8∿6.0 (3H, m)]. The uv spectrum [λ (MeOH) 225 (sh.), 231 (log ε 4.17), 239 (4.20), and 241 (sh.) nm] revealed it to be a heteroannular conjugated diene. Hydrogenation of E in ethyl acetate over platinum catalyst gave oily dihydrorimuene[12)] (8a), along with rimuane (7) as minor product. Both of the products were identified by comparison with authentic samples. On the other hand, hydrogenation using tris(triphenylphosphine)rhodium chloride as catalyst furnished the known dihydro derivative[12)] (6b). The results suggested the compound E to be $\Delta^{1(10),5}$-rimutriene (6a). Further support of the structure (6a) was obtained by the reaction of rimuene (8b) with selenium dioxide in acetic acid at 60∿70° affording the triene in 90% yield.

The compound E would be produced by disproportionation although no counter product has been isolated.[14)]

The equilibrium between the products may be represented as shown in Scheme 1.



Scheme 1

References and Notes

1) Y. Kitahara and A. Yoshikishi, Tetrahedeon Lett., 1755 (1964); A Yoshikoshi, Nippon Kagaku Zasshi, 85, 383, 386, 390 (1964).

2) M. Kitadani, Nippon Kagaku Zasshi, 91, 664 (1970).

3) For reviews, refer to a) N. D. Kirk and M. P. Hartshorn, "Steroid Reaction Mechanisms", Elsevier Publishing Co., Amsterdam (1968), pp. 290 ~ 294 and pp. 362 ~ 365, and b) J. F. King and P. de Mayo, "Molecular Rearrangements", Vol. 2, ed. by P. de Mayo, Interscience Publishers, New York (1960), pp. 813 ~ 834.

4) These are denoted in elution order of glc (PEG-20M column), and their approximate ratio in glc was 13:36:6:26:9.

5) Combustion analysis gave satisfactory results for new compounds.

6) Optical rotations were all measured in chloroform solutions.

7) Chemical shift values in carbon tetrachloride solutions are given in this paper.

8) I. L. Karle and J. Karle, Acta Cryst., 17, 835 (1964).

9) H. A. Hauptman, "Crystal Structure Determination" , Plenum Press, New York (1972).

10) A detailed account of the X-ray crystallography will be published later.

11) E. Wenkert and Z. Kumazawa, Chem. Commun., 140 (1968); T. McCreadie and K. H. Overton, ibid., 288 (1968).

12) R. E. Corbett and S. G. Wyllie, J. Chem. Soc. (C), 1737 (1966).

13) R. F. Church and R. E. Ireland, J. Org. Chem., 17, 28 (1967).

14) Carbonium ions have been known to possess hydrogen acceptor properties. See G. Baddeley and W. Pickles,J. Chem. Soc., 3726 (1953); P. D. Bartlett and J. D. McCollum, J. Amer. Chem. Soc., 78, 1441 (1956).

(Received June 20, 1974)