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TERPENOIDS—XLIII

BASE-CATALYSED REACTIONS WITH N-LITHIOETHYLENEDIAMINE

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Abstract—Application of N-lithio-ethylenediamine as an isomerizing and dehydrogenating reagent has been further extended. It is useful for partial aromatization of cadinenic terpenes and for conversion of selenenic compounds to heteroannular diene, optical rotation of which throws light on the absolute configuration of the parent compound. It is also useful for smooth isomerization of fatty acid.

IN a previous communication[1] certain aspects of the use of N-lithio-ethylenediamine as an isomerizing and dehydrogenating agent have been explored. The scope has been further extended and the results presented in this communication.

Cadinenic alcohols. Lithioethylenediamine* appears to be an excellent reagent for the partial aromatization of cadinenic terpenes. The crystalline alcohol khusinol[2](I) on treatment with this reagent affords the hydrocarbon (II), the purity of which is evidenced by a single peak on the VPC column. The product shows characteristic U.V. and I.R. spectra. As the formation of this hydrocarbon involves the elimination of the hydroxyl group of khusinol it must be represented by the structure II and not by III, a product which has been previously obtained by the dehydrogenation of γ_1-cadinene[1] (IV) by this reagent. The hydrocarbon (II) on dehydrogenation with selenium or sulphur gives high yield of cadalene. Similarly, on treatment with the reagent the crystalline alcohol khusol[3] (V) affords the partially aromatized alcohol (VI). Formation of such a product retaining the hydroxyl group intact is not normally possible during dehydrogenation using conventional reagents.

Selinenic compounds. When β-selinene (VII) prepared by the pyrolysis of β-eudesmol benzoate is treated with the reagent it undergoes facile transformation to the heteroannular diene (+) δ-selinene (VIII). This diene contains only one asymmetric centre with a β-oriented methyl group at C_{10} and is well known,[4,6] for its high dextro

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* The use of lithio-ethylenediamine for low temperature isomerization and the dehydrogenation of organic compounds was first initiated by Reggel *et al.*, *J. Org. Chem.* **23**, 1136; 1958, who employed the reaction in the case of a few simple hydrocarbons. He pointed out the special suitability of the ethylenediamine derivative for dehydrogenation of organic systems because of the bidentate nature of ethylenediamine, making it possible to form cyclic intermediates and helping in elimination of elemental hydrogen. Ethylene-diamine has other advantages: it has an easily workable boiling point and dissolves organic compounds easily and thus helps in carrying out reaction in a homogenous medium.

[1] B. S. Tyagi, B. B. Ghatge and S. C. Bhattacharyya, *J. Org. Chem.* **27**, 1430 (1962).

[2] (Mrs) A. Rao, (Miss) K. L. Surve, K. K. Chakravarti and S. C. Bhattacharyya, *Tetrahedron* in press.

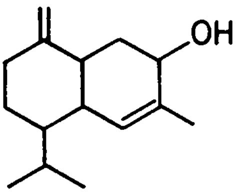
[3] P. S. Kalsi, K. K. Chakravarti and S. C. Bhattacharyya, *Tetrahedron* in press.

[4] L. Ruzicka and M. Stoll, *Helv. Chim. Acta* **6**, 846 (1923).

[5] G. Buchi, M. Schach, V. Wittenau and Dwain M. White, *J. Amer. Chem. Soc.* **81**, 1958 (1959).

[6] M. L. Maheshwari, T. C. Jain and S. C. Bhattacharyya, *Tetrahedron* in press.

CHART I



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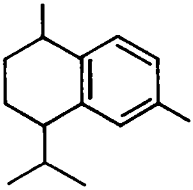

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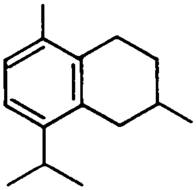

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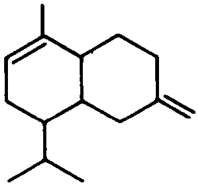

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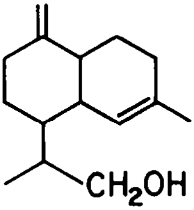

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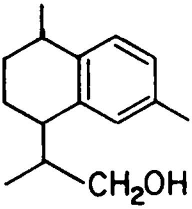

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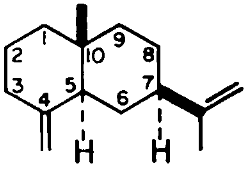

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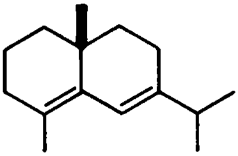

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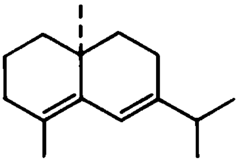

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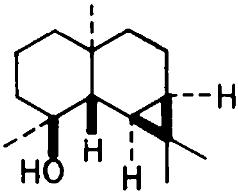

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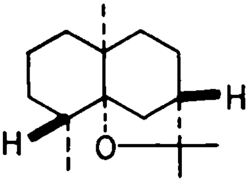

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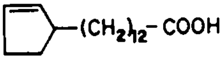

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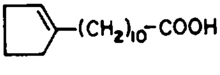

XIII

rotation, $(\alpha)_D$ +250° approximately, and characteristic triple absorption in the U.V. region. Its optical antipode (IX) having an α-oriented methyl group showing equally strong laevo-rotation can be obtained by treating maaliol (X) with formic acid[5] or dihydroagarofuran (XI) with boron-trifluoride[6]. Smooth conversion of VII to VIII is of considerable significance. From N.M.R. studies it is now possible to find out the *cis-* or *trans* nature of the ring juncture in selinenic compounds,[7] after which irrespective of the location of the double bonds, treatment with lithioethylenediamine will convert them to one of the heteroannular dienes (VIII or IX), examination of the optical rotation of which will decide the absolute configuration of the ring juncture of the parent compound. This transformation is of general applicability and has been helpful in determining the stereochemistry of elemene and elemol and several other compounds in this laboratory.

Fatty acids. One non-terpenic product was examined during this investigation. Chaulmoogric acid (XII) having di-substituted double bond is completely converted to iso-chaulmoogric acid (XIII) having tri-substituted double bond with expected loss of optical activity. The reaction product is initially obtained in the form of an amide from which free fatty acid is liberated by hydrolysis.

EXPERIMENTAL

Mp.'s are uncorrected. Rotations have been taken in chloroform unless otherwise stated. U.V. spectra were determined in alcohol solution on a DK-2 recording spectrophotometer by Miss Prabhu and I.R. spectra on a Perkin-Elmer Infracord spectrophotometer by Mr. Gopinath. Microanalyses were carried out by Mr. Pansare and colleagues.

Procedure for preparation of anhydrous ethylenediamine, treatment of different compounds with the lithioderivative and subsequent processing of the reaction products, was essentially the same as described in the previous communication.

Treatment of khusinol (I). Khusinol was obtained from a laboratory stock isolated by chromatography of Bharatpur vetiver oil. It showed the following properties: m.p. 87°, $(\alpha)_D$ − 174·4° (Found: C, 81·03; H, 11·1. Calc. for $C_{15}H_{24}O$: C, 81·76; H, 10·98%).

A mixture of khusinol (3 g), Li (2 g) in ethylene diamine (100 ml) was refluxed for 15 hr. The reaction product after isolation in the usual way was initially distilled *in vacuo*, b.p. 122°/4·5 mm and chromatographed on alumina (gr. I, 100 g) and eluted with pet. ether. It was finally distilled over sodium, b.p. 111°/4 mm, $n_D^{29.5}$ 1·5198, $(\alpha)_D$ + 0·36°, d_4^{30} 0·9318. I.R. bands (0·1 mm liquid cell) at 729, 757, 813, 888, 900, 943, 980, 1036, 1111, 1156, 1176, 1258, 1290, 1316, 1361, 1379, 1408, 1440, 1493, 1562, 1600, 1695, 1739, 1808, 1887 cm^{-1} (Fig. 1). U.V. absorption λ_{max} 269·5, 278 mμ, ϵ_{max} 768·8 and 517·4 respectively. It showed a single peak on the VPC column. (Found: C, 88·76; H, 11·22. $C_{15}H_{22}$ requires: C, 89·04; H, 10·75%).

Treatment of khusol (V). Khusol was also obtained from laboratory stock isolated from Bharatpur vetiver oil and had the following properties, m.p. 101·5°, $(\alpha)_D$ −137·6° (*c*, 4·7, ethanol) (Found: C, 81·77; H, 10·43. Calc. for $C_{15}H_{24}O$: C, 81·76; H, 10·98%).

A mixture of khusol (2·8 g), Li (2 g), ethylenediamine (100 ml) was refluxed for 16 hr. After working up in the usual way, the reaction product was purified by distillation, b.p. 170° (bath)/1 mm. The product solidified and was recrystallized from pet. ether (40–60°), m.p. 80°, $(\alpha)_D$ 20·62°. I.R. bands at 819, 875, 936, 970, 1031, 1075, 1093, 1170, 1325, 1370, 1449, 1471, 1587, 1869 cm^{-1} (Fig. 1) (Found: C, 82·37; H, 10·45. $C_{15}H_{22}O$ requires: C, 82·51; H, 10·16%).

Conversion of β-selinene to δ-selinene (VIII). Benzoate of pure β-eudesmol was prepared by treating β-eudesmol (7 g) with benzoyl chloride (9 ml) in pyridine (40 ml) initially at room temp for 24 hr and then at 100° for 3 hr. The resulting benzoyl derivative (10 g) was pyrolysed from a distillation flask with a wide side arm at 200°/100–150 mm. Crude selinene obtained was purified by chromatography over alumina (gr. I, 300 g) and eluted with pet. ether. The product was distilled over sodium

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[7] J. I. Musher, *J. Amer. Chem. Soc.* **83**, 1146 (1961); K. R. Varma, T. C. Jain and S. C. Bhattacharyya, *Tetrahedron* **18**, 979 (1962).

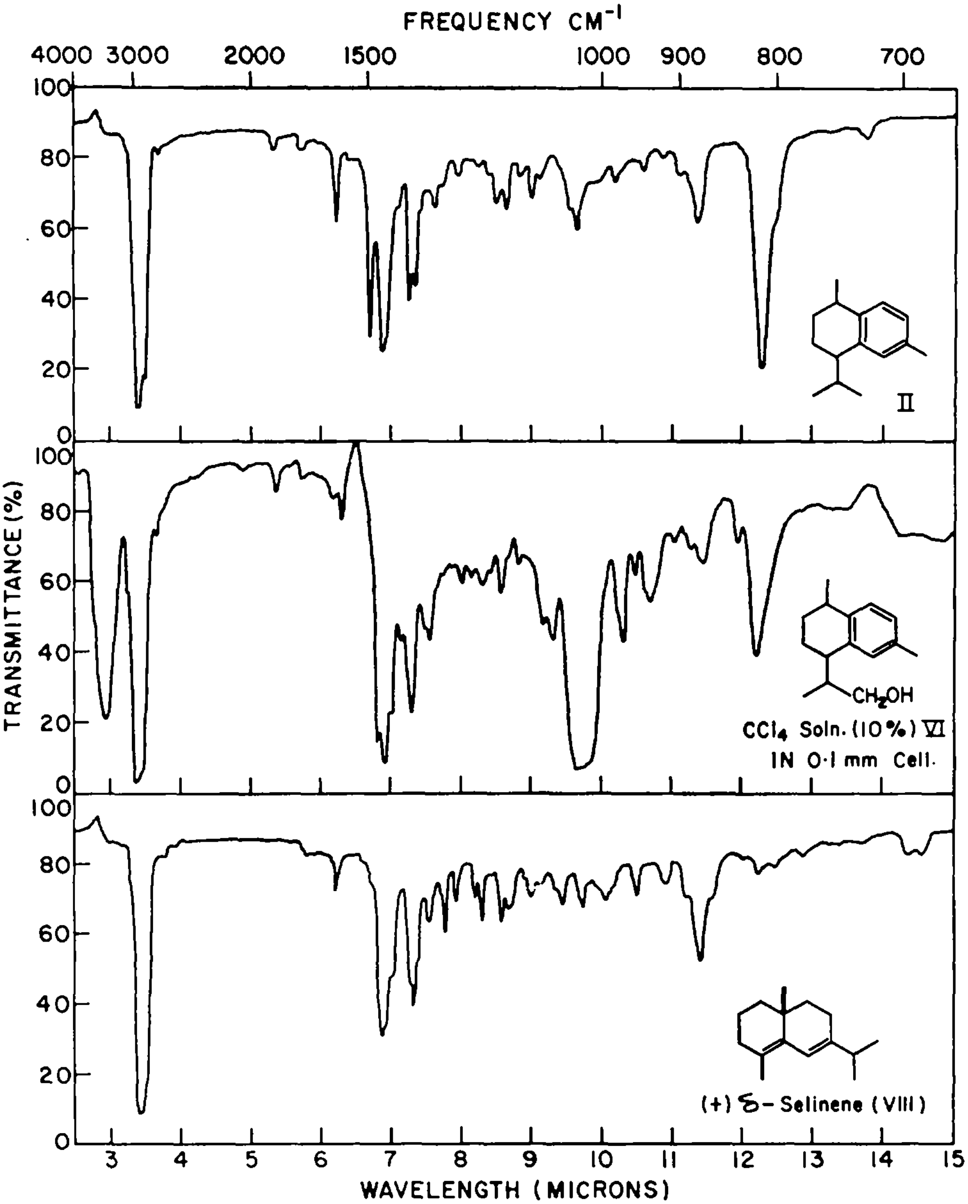
FREQUENCY CM^{-1}
4000
3000
2000
1500
1000
900
800
700
TRANSMITTANCE (%)
100
80
60
40
20
0
II
CH$_2$OH
CCl$_4$ Soln. (10%) VI
IN 0·1 mm Cell.
(+) δ-Selinene (VIII)
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)

Fig. 1.

to yield pure selinene (5 g), b.p. 120°/10 mm., n_D^{23} 1·5010, $(\alpha)_D$ +31·7°. It showed characteristic I.R. spectra for β-selinene. Bands at: 793, 885, 930, 998, 1212, 1370, 1449, 1639, 1770 cm^{-1}.

A mixture of β-selinene (3·5 g), Li (2 g), ethylenediamine (100 ml) was heated at 110° for 8 hr. After usual processing the reaction product (3·5 g) was chromatographed on alumina (gr. I, 150 g) to yield pure δ-selinene (3·1 g), b.p. 119°/10 mm, $n_D^{28 \cdot 5}$ 1·5185, $(\alpha)_D$ +235·2°. U.V. spectra, λ_{max} 241, 247, 255 mμ, ε_{max} 22626, 24035, 18436 respectively. I.R. bands at: 873, 913, 950, 990, 1026, 1053, 1111, 1149, 1163, 1205, 1258, 1282, 1325, 1366, 1449, 1613 cm^{-1} (Fig. 1) (Found: C, 87·9; H, 11·5. Calc. for $C_{15}H_{24}$: C, 88·16; H, 11·84%).

Preparation of isochaulmoogric acid (XIII). Chaulmoogric acid (XII) was obtained from chaulmoogra oil. The acid had the following properties agreeing with the literature values, m.p. 66°, $(\alpha)_D$ +60·24°. I.R. bands at : 724, 921, 1111, 1190, 1205, 1232, 1266, 1282, 1316, 1379, 1418, 1429, 1471, 1724 cm^{-1}.

A mixture of chaulmoogric acid (2·5 g), Li (1·5 g), ethylenediamine (100 ml) was heated at 110° for 9 hr. The reaction product was reddish-brown in colour. Excess of ethylenediamine was removed on the water bath under red. press. and the residual amide was hydrolysed by refluxing for 12 hr with alcoholic potash (25%, 150 ml.). After removal of alcohol, the resultant acid was isolated in the usual way and distilled at 155–160°/0·15 mm and then crystallized from pet. ether (60–80°) to yield pure isochaulmoogric acid, m.p. 51°, $(\alpha)_D$ ±0°, identical with that described in the literature. I.R. bands at: 724, 780, 816, 838, 921, 938, 950, 1031, 1075, 1111, 1190, 1205, 1232, 1266, 1282, 1316, 1379, 1418, 1429, 1471, 1724 cm^{-1} (Found: C, 77·89; H, 11·81; eq.wt. 281·5. Calc for $C_{18}H_{32}O_2$: C, 77·09; H, 11·50%; eq.wt. Calc 280·44).

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