Tetrahedron, 1964, Vol. 20, pp. 2911 to 2919. Pergamon Press Ltd. Printed in Northern Ireland

TERPENOIDS—LVIII

BASE CATALYSED REACTIONS WITH N-LITHIOETHYLENE-DIAMINE*

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Abstract—The use of lithioethylenediamine as a dehydrogenating and isomerizing reagent has been further extended and applied to new mono-, sesqui- and diterpenes. Structures of reaction products, including the phenol (XXVII), recently obtained as a degradation product of copaene, were decided on the basis of IR, UV and NMR spectral studies. Some of the transformations carried out with the help of this reagent do not appear possible with any other known reagent.

IN PREVIOUS communications,[1,2] some interesting transformation products of terpenoids by treatment with N-lithioethylenediamine have been reported. This work has been extended and the results presented in this paper.

Monoterpenic hydrocarbons containing cyclopropane and cyclobutane rings. It has been shown[1] earlier that Δ^3-carene on treatment with N-lithioethylenediamine gives a mixture of *p*-cymene and *m*-cymene in nearly equal proportions. Sabinene (I) has now been found to give only *p*-cymene. Although α-pinene (III) remains unaffected, β-pinene (II) is isomerized to α-pinene in quantitative yield.

Sesquiterpene hydrocarbons. When β-elemene (IV) is treated with N-lithioethylenediamine, 1-methyl-2,4-di-isopropyl benzene (V) is obtained.[3] During this process, the three exocyclic double bonds migrate inside the ring with simultaneous elimination of the bulky ethyl group. Tetrahydroelemene (VI) is converted to the isomeric hydrocarbon (VII), containing a trisubstituted double bond. The position of the double bond in VII was determined by its conversion to the ketone† (VIII) by epoxidation followed by isomerization with boron trifluoride ethereate. In conformity with its structure, the IR spectrum of the ketone (VIII) does not show absorption in the vicinity of 1420 cm^{-1}, indicating the absence of —CO—CH$_2$-grouping. Elemol (IX), however, remains unaffected by the use of this reagent.

Zingiberene (X) on treatment with this reagent gives dihydro-*ar*-curcumene (XI), characterized,[4] by mixed VPC and the superimposable IR spectra, as dihydro-*ar*-curcumene obtained by hydrogenation of *ar*-curcumene. The NMR spectrum also confirms this structure.

A mixture of α- and β-himachalenes[5] (XII and XIII) on treatment yields a mixture of two hydrocarbons which are stable towards ozone and peracid and do not show the presence of olefinic protons in the NMR spectra. The two constituents were identified

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* Communication No. 701 from the National Chemical Laboratory, Poona-8, India.

† Unpublished work by G. D. Joshi and collaborators from this Laboratory.

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

[2] B. S. Tyagi, B. B. Ghatge and S. C. Bhattacharyya, *Tetrahedron* **19**, 1189 (1963).

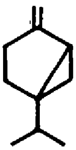
[3] V. Sýkora, V. Herout, J. Plíva and F. Šorm, *Coll. Czech. Chem. Comm.* **19**, 124 (1954).

[4] V. Herout, V. Benešová and J. Plíva, *Coll. Czech. Chem. Comm.* **18**, 248 (1953).

[5] T. C. Joseph and Sukh Dev, *Tetrahedron Letters* No 6, 216 (1961).

as dihydro-*ar*-curcumene (XI; 68%) and the bicyclic hydrocarbon (XIV; 32%) by mixed VPC with authentic samples. It has been previously shown[5] that these two hydrocarbons are also formed by the dehydrogenation of himachalenes with sulphur and selenium; although the proportion of products are different. The formation of dihydro-*ar*-curcumene, under such mild conditions, as in the present case, involving opening of the seven membered ring system is an interesting phenomenon.

Acyclic alcohols. It has been shown[1] that citronellol remains unaltered and the allylic double bond of geraniol migrates from the alcoholic group to give the conjugated diene alcohol. In conformity with this, the allylic alcohol dihydrogeraniol[6] (XV) on treatment with this reagent is smoothly converted to citronellol (XVI). This transformation has not been observed with any other reagent. Crotyl alcohol (XVII) remains unaltered, no migration of the double bond to give allyl carbinol (XVIII) being observed. On the other hand, the double bond of allyl carbinol (XVIII) partially migrates from the terminal position giving a mixture of crotyl alcohol and allyl carbinol. Thus the terminal methylene double bond has a greater tendency to migrate than the double bond allylic to an alcohol group migrating to the terminal methylene position.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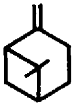
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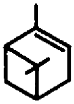
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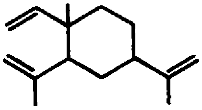
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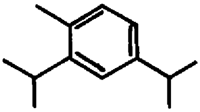
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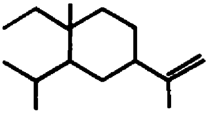
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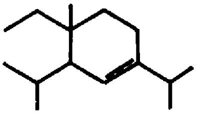
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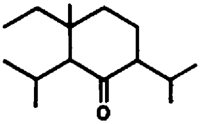
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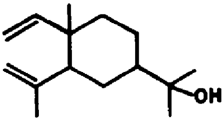
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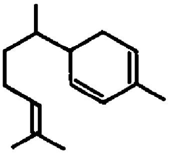
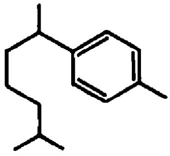

X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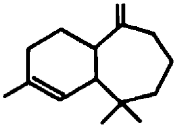
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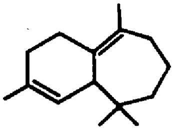
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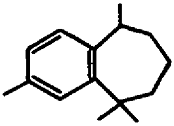
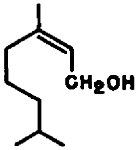

XIV



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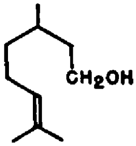

XVI

$CH_3{\cdot}CH{=}CH{\cdot}CH_2OH$

XVII

$CH_2{=}CH{-}CH_2{-}CH_2OH$

XVIII

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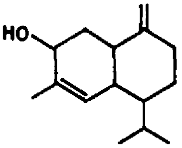
[6] Rene Heilmann and Rene Glenat, *Bull. Soc. Chim. Fr.* 1589 (1955).

Cadinenic compounds. It has been reported earlier that the crystalline alcohol khusinol[2] (XIX) on treatment with this reagent gives 1,6-dimethyl-4-isopropyl-1,2,3,4-tetrahydronaphthalene (XX; IR spectrum, Fig. 1). Its structure has now been confirmed by its NMR spectrum (Fig. 2). The structure of the crystalline alcohol (XXII), obtained from khusol[2] (XXI), has now been revised and found to be represented by XXIII. On reduction with lithium aluminium hydride, the tosyl derivative of the alcohol affords 1,6-dimethyl-4-isopropyl-5,6,7,8-tetrahydronaphthalene (XXIV; IR spectrum, Fig. 1). The NMR spectrum (Fig. 2) clearly distinguishes it from the hydrocarbon (XX), obtained from khusinol. On treatment with this reagent, (—)-γ-cadinene (XXV), prepared from khusinol, gives a mixture of the hydrocarbons (XX and XXIV), confirmed by VPC analysis.

Oxidation of khusinol* in acetone with chromic acid yields a crystalline dienone



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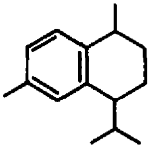

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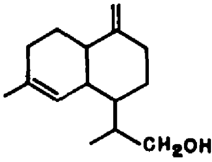
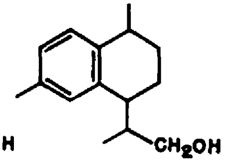


XXI



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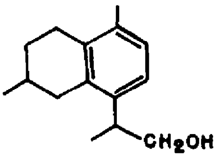
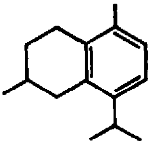
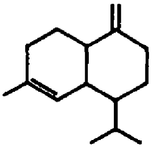


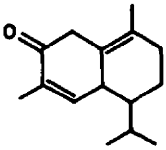
XXIII



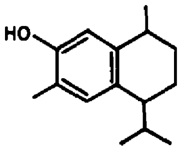
XXIV



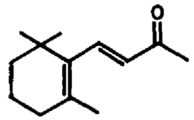
XXV



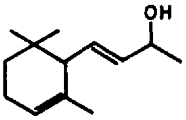
XXVI



XXVII



XXVIII



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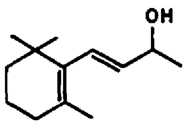
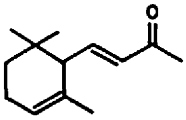
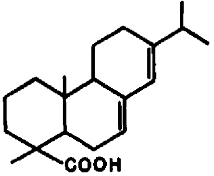


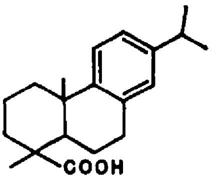
XXX



XXXI



XXXII



XXXIII

$CH_2{=}CH\cdot(CH_2)_8\cdot COOH$

XXXIV

$CH_3\cdot CH{=}CH\cdot(CH_2)_7\cdot COOH$

XXXV

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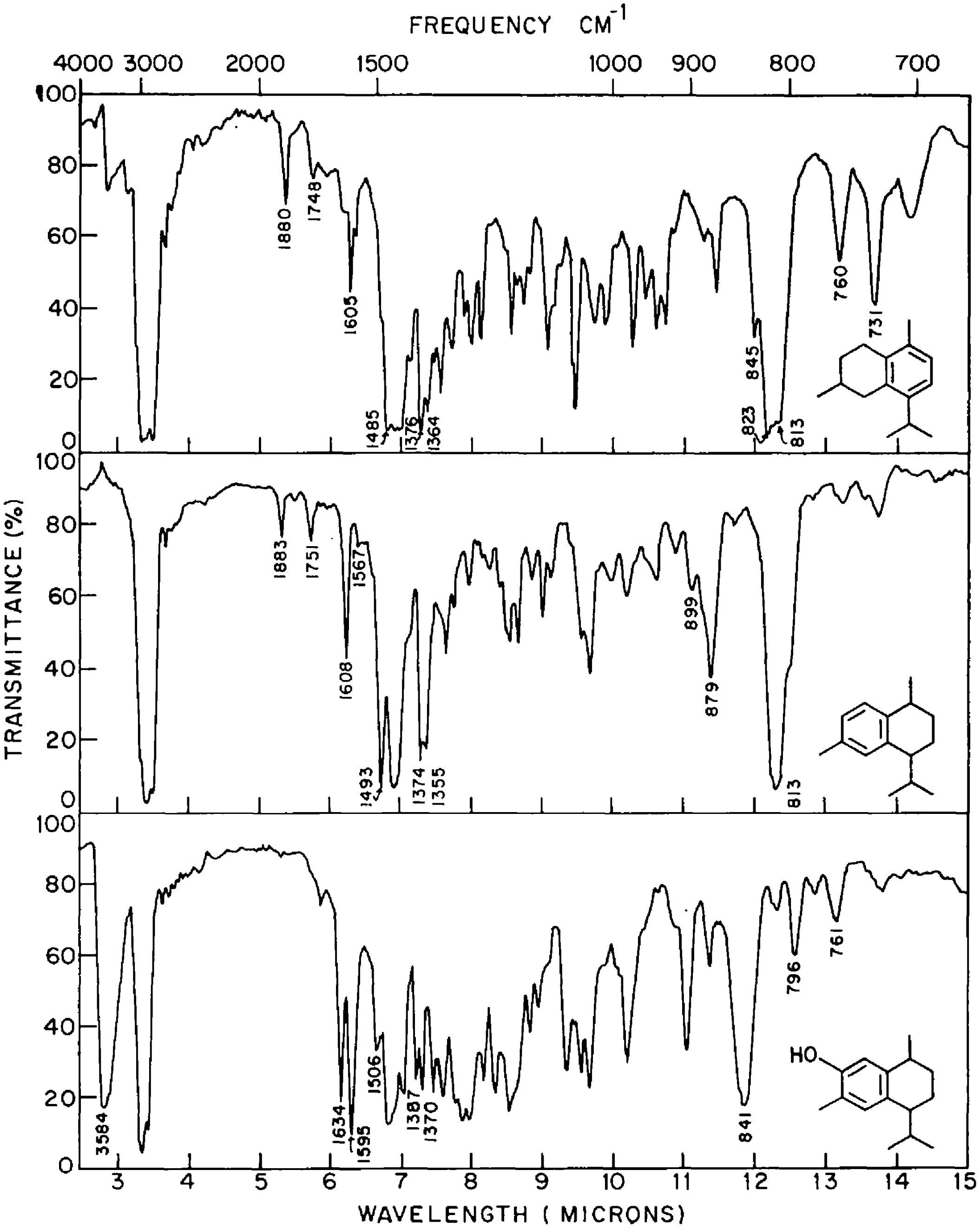
* Unpublished work of A. D. Wagh and collaborators of this Laboratory. The revised structure is based on IR and NMR spectral studies; see also the paper on the structure of khusinol by A. A. Rao, K. L. Surve, K. K. Chakravarti and S. C. Bhattacharyya, *Tetrahedron* 19, 233 (1963).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2000
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900
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TRANSMITTANCE (%)
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80
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1880
1748
1605
1485
1376
1364
845
823
813
760
731
1883
1751
1567
1608
1493
1374
1355
899
879
813
3584
1634
1595
1506
1387
1370
841
796
761
HO
3
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5
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7
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9
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11
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13
14
15
WAVELENGTH (MICRONS)

Fig. 1

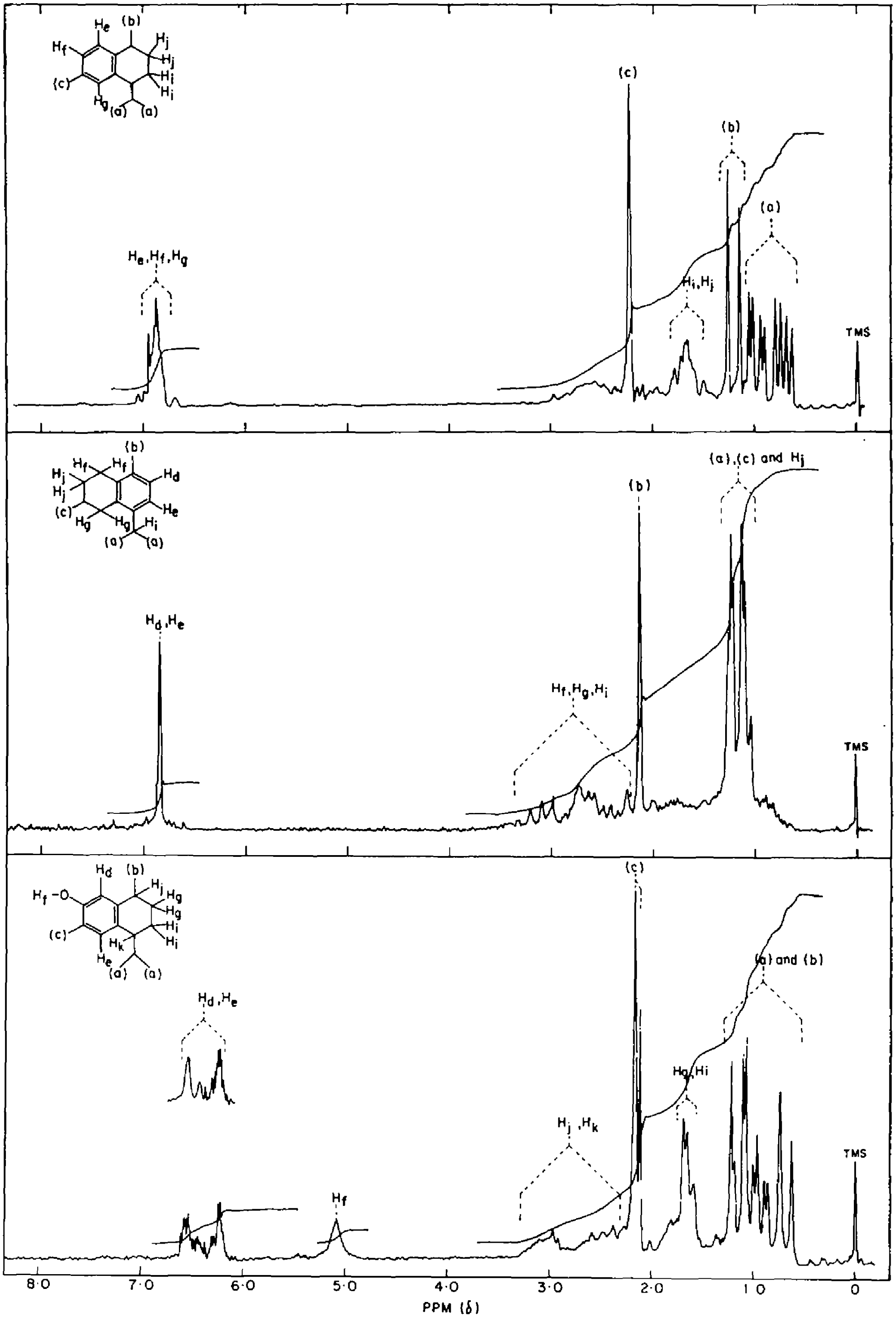
He (b)
Hf
Hj
Hj
(c)
Hi
Hi
Hg (a) (a)
(c)
(b)
(a)
He,Hf,Hg
Hi,Hj
TMS
(b)
Hf Hf
Hj
Hj
Hd
(c)
He
Hg Hg Hi
(a) (a)
(a),(c) and Hj
(b)
Hd,He
Hf,Hg,Hi
TMS
Hd (b)
Hf -O
Hj Hg
Hg
(c)
Hi
Hk
Hi
He
(a) (a)
(c)
(a) and (b)
Hd,He
Hg,Hi
Hj ,Hk
Hf
TMS
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
0
PPM (δ)

FIG. 2

(XXVI), m.p. 57° which on treatment with the reagent gives a phenol (XXVII; IR spectrum, Fig. 1), the structure of which has been confirmed by its NMR spectrum (Fig. 2). This phenol has been recently obtained by Büchi *et al.*[7] as a degradation product of copaene.

Ionones and ionols. β-Ionone (XXVIII) is stable to this reagent, but α-ionol (XXIX), β-ionol (XXX) and α-ionone (XXXI) are converted to β-ionone. Besides migration of the double bonds to the conjugated position, the alcohol group of ionols is oxidized to the ketone.

L-*Abietic acid.* L-Abietic acid[8] (XXXII) on treatment with this reagent is converted to dehydroabietic acid[9] (XXXIII) in good yield.

Fatty acids. Undecylenic acid (XXXIV) on treatment is converted to *trans*-undec-9-enoic acid (XXXV), the end methylene double bond migrating to a disubstituted position. The bands due to the vinyl group are absent but a band due to a *trans* disubstituted double bond appears in the IR spectrum of the isomerized acid. The actual location of the double bond was confirmed by oxidation with potassium permanganate of the isomerized acid to azelaic acid.

EXPERIMENTAL

M.ps are uncorrected. Rotations were taken in $CHCl_3$. UV spectra were determined in alcohol solution on a DK–2 recording spectrophotometer, and IR spectra on a Perkin-Elmer (Model 137b) Infracord spectrophotometer by Mr. Gopinath and Mr. Deshpande. NMR spectra were measured on A60 (Varian instrument set at 60 MC) by Dr. P. M. Nair and colleagues. Tetramethylsilane was used as an internal standard; CCl_4 solutions were used. Microanalyses were carried out in the microanalytical section of the laboratory by Mr. Pansare and colleagues.

The preparation of anhydrous ethylenediamine, treatment of the various compounds with the lithio derivative and subsequent processing of the reaction products were essentially the same as described in the previous communications.

Treatment of monoterpenes

(a) D-Sabinene (I) was isolated by careful fractionation of the oil of *Cupressus macrocarpa.* It showed the following properties; b.p. 155–157°/710 mm, α_D^{20} +47° (neat); n_D^{20} 1·4608; VPC single peak. A mixture of D-sabinene (2·5 g), Li (0·6 g) in ethylenediamine (25 ml) was refluxed for 9 hr. The reaction product (2·15 g) after isolation in the usual way was distilled over Na; b.p. 175–176°/710 mm, n_D^{20} 1·4850. The product was identified as pure *p*-cymene by comparison of VPC analysis and IR spectra with an authentic sample. (Found: C, 89·35; H, 10·48. $C_{10}H_{14}$ requires: C, 89·49; H, 10·51%).

(b) *β-pinene* (II) was freshly distilled; b.p. 55–57°/10 mm, n_D^{20} 1·4630, α_D^{20} −21° (neat); VPC single peak; IR bands at: 826, 852, 875, 890, 945, 1050, 1120, 1368, 1383, 1640, 1760, 2962, 3025, 3080 cm^{-1}.

β-pinene (5 g) on treatment in the usual way with Li (1·0 g) and ethylenediamine (30 ml) for 7 hr gave the reaction product (4·7 g) which was distilled over Na; b.p. 70–72°/12 mm, n_D^{20} 1·4645; α_D^{20} −47·25° (neat); characterized as α-pinene by comparison of VPC (single peak) and IR spectra with an authentic sample. (Found: C, 88·08; H, 11·73. $C_{10}H_{16}$ requires: C, 88·16; H, 11·84%).

Treatment of β-elemene (IV), *tetrahydroelemene* (VI) *and zingiberene* (X)

(a) β-Elemene (IV) was prepared by pyrolysis of elemol benzoate; b.p. 150–154° (bath)/33 mm, n_D^{20} 1·4934; $(\alpha)_D^{20}$ −8·7° (*c*, 4·2) (Found: C, 88·30; H, 12·00. $C_{15}H_{24}$ requires: C, 88·16; H, 11·84%).

β-Elemene (1·5 g) was treated in the usual way with Li (1·0 g) and ethylenediamine (50 ml) for 6 hr. The product, after isolation, was subjected to ozonolysis to remove unreacted olefin. The final

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[7] G. Büchi and S. H. Feairheller and P. de Mayo and R. E. Williams, *Proc. Chem. Soc.* 214 (1963).

[8] S. Palkin and T. H. Harris, *J. Amer. Chem. Soc.* **56**, 1935 (1934).

[9] Louis F. Fieser and William P. Campbell, *J. Amer. Chem. Soc.* **60**, 167 (1938).

product (1·0 g) was distilled and identified as 1-methyl-2,4-di-isopropylbenzene (V, 1·0 g); b.p. 135–140° (bath)/25 mm, $n_D^{27\cdot5}$ 1·4940; α_D ±0°; λ_{max} 273, 264, 257 mμ; ε_{max} 342, 425, 380 respectively; IR bands (liq. cell, 0·1 mm) at: 733, 819, 924, 992, 1029, 1053, 1079, 1105, 1176, 1205, 1258, 1311, 1355, 1374, 1495, 1567, 1608, 1757, 1878 cm^{-1} (Found: C, 88·90; H, 11·50. $C_{13}H_{20}$ requires: C, 88·56; H, 11·44%).

(b) *Tetrahydroelemene* (VI) was prepared by pyrolysis of tetrahydroelemol benzoate; b.p. 128–129°/9 mm, n_D^{26} 1·4748; α_D −7·59° (neat) (Found: C, 86·80; H, 13·50. $C_{15}H_{28}$ requires: C, 86·46; H, 13·54%).

Tetrahydroelemene (2 g) on treatment with Li (1·0 g) and ethylenediamine (50 ml) for 16 hr gave VII (1·9 g) which was distilled over Na; b.p. 105–110° (bath)/6 mm, $(\alpha)_D$ −20·9° (*c*, 2·3); VPC single peak; IR bands at: 807, 856, 885, 916, 1015 cm^{-1}. A solution of the product (0·6 g) in chloroform (5 ml) was treated with the requisite amount of a chloroform solution of perbenzoic acid (24 hr). The epoxide formed was isomerized with boron trifluoride ethereate to the ketone (VIII) which did not show any IR band at 1420 cm^{-1} and did not form any semicarbazone (Found: C, 86·30; H, 13·27. $C_{15}H_{28}$ requires: C, 86·46; H, 13·54%).

(c) *Zingiberene* (X; 3 g) [b.p. 94–95°/4·0 mm, n_D^{28} 1·4968, α_D −74° (clean), λ_{max} 232, 261 mμ, ε_{max} 12,360, 1,687], was refluxed with lithioethylenediamine (Li, 1·5 g; ethylenediamine 70 ml; 10 hr). The product (2·8 g) after isolation was distilled over Na; b.p. 100–105° (bath)/3 mm, $n_D^{22\cdot5}$ 1·4862; $(\alpha)_D$ +2·82° (*c*, 4·60); λ_{max} 247, 250, 256, 264, 272 mμ; ε_{max} 633, 621, 604, 549, 371 respectively. It was identified as dihydro-*ar* curcumene (XI) by comparison of VPC analysis and IR spectra with an authentic sample. NMR spectrum shows the presence of an isopropyl group (9·24, 9·22, 9·16, 9·13 τ); a methyl group (8·89, 8·79 τ); a methyl group on a double bond (7·73 τ); a benzylic proton (7·30 τ) and four aromatic protons (3·06 τ). (Found: C, 87·98; H, 11·66. $C_{15}H_{24}$ requires: C, 88·16; H, 11·84%).

Treatment of himachalenes (XII *and* XIII)

The mixture containing α and β-himachalenes (70:30 by VPC) were isolated by chromatography and distillation of Indian deodar oil; b.p. 110–115° (bath)/5 mm, $(\alpha)_D$ +54° (*c*, 4·3), n_D^{28} 1·5095; IR bands at: 826, 861, 869, 891, 1361, 1374, 1630, 1665 cm^{-1} (Found: C, 88·24; H, 11·55. $C_{15}H_{24}$ requires: C, 88·16; H, 11·84%). Himachalene (5 g) on treatment with Li (3·0 g) and ethylenediamine (150 ml) for 16 hr gave the reaction product which was filtered through alumina and distilled over Na; b.p. 115–125° (bath)/2 mm, $(\alpha)_D$ +5·5° (*c*, 4·33), n_D^{25} 1·4998; IR bands at: 816, 1370, 1382, 1497, 1522, 1916 cm^{-1}; λ_{max} 259, 265, 267, 273 mμ; ε_{max} 487, 487, 472, 411 respectively; mixed VPC analysis with authentic samples showed the presence of two constituents (XI, 68%; XIV, 32%).

Treatment of dihydrogeraniol (*3,7-dimethyl-2-octene-1-ol*, XV), *crotyl alcohol* (XVII) *and allyl carbinol* (XVIII)

(a) *Dihydrogeraniol* (XV), b.p. 101–102°/11 mm, n_D^{27} 1·4530; VPC single peak; IR bands at: 1050, 1260, 1365, 1450, 1670, 3025, 3400 cm^{-1} (Found: C, 76·80; H, 13·40. $C_{10}H_{20}O$ requires: C, 76·86; H, 12·90%), was prepared according to the known procedure.[6]

Dihydrogeraniol (2·5 g) on treatment with Li (0·6 g) and ethylenediamine (50 ml) for 12 hr gave the reaction product (1·87 g) which was isolated by the usual method and distilled; b.p. 110–112°/15 mm, n_D^{30} 1·4560; VPC single peak. On ozonolysis acetone was formed (iodoform test and 2,4-DNP derivative, m.p. 128°). The product was further characterized as citronellol (XVI) by VPC analysis and superimposable IR spectra with that of an authentic sample. (Found: C, 77·1; H, 13·2. $C_{10}H_{20}O$ requires: C, 76·86; H, 12·90%).

(b) *Crotyl alcohol* (XVII) was prepared by reducing crotonaldehyde with aluminium isopropoxide; b.p. 116–117°/715 mm, n_D^{25} 1·4145; VPC single peak; remained unchanged on treatment with the reagent.

(c) *Allyl carbinol* (XVIII) was prepared by reducing ethylvinyl acetate with $LiAlH_4$; b.p. 120–121°/715 mm, n_D^{25} 1·4142; VPC single peak. Allyl carbinol (5·5 g) on treatment with Li (1·5 g) and ethylenediamine (100 ml) for 10 hr gave a mixture of crotyl alcohol (65%) and allyl carbinol (35%) as determined by VPC analysis.

Treatment of cadinenic compounds

(a) 1,6-*Dimethyl*-4-*isopropyl*-1,2,3,4-*tetrahydronaphthalene* (XX; IR spectrum, Fig. 1; NMR spectrum Fig. 2) was obtained by treating khusinol (XIX) by the method described earlier; b.p.

106–108° (bath)/1·4 mm; $(\alpha)_D$ +0·88° (*c*, 4·5); n_D^{27} 1·5205; λ_{max} 269, 278 mμ; ε_{max} 633, 517 respectively; VPC analysis showed 95% purity. (Found: C, 88·51; H, 10·94. $C_{15}H_{22}$ requires: C, 89·04;H, 10·96%).

(b) *Khusol* (XXI, 1·7 g), on treatment with Li (2·2 g) and ethylenediamine (100 ml) for 6 hr, gave the alcohol (XXIII) which was crystallized from pet. ether, m.p. 95–96°; $(\alpha)_D$ −25·77° (*c*, 1·2); single spot in silica gel TLC; IR bands at: 810, 819, 970, 1015, 1031, 1587, 3333 cm^{-1}; λ_{max} 264 mμ; ε_{max} 195·4 (Found: C, 82·71; H, 10·18. $C_{15}H_{22}O$ requires: C, 82·51; H, 10·16%).

The tosyl derivative (0·8 g) of the alcohol was reduced with $LiAlH_4$ (0·3 g), to XXIV (0·3 g; IR spectrum Fig. 1; NMR spectrum, Fig. 2); b.p. 130–135° (bath)/2·5 mm, $(\alpha)_D$ −14·45° (*c*, 1·00); λ_{max} 267 mμ; ε_{max} 325·4; purity 95% (VPC) (Found: C, 88·31; H, 10·92. $C_{15}H_{22}$ requires: C, 89·04; H, 10·96%).

(c) *(−)-γ-Cadinene* (XXV) was prepared from khusinol and had the following properties; b.p. 135–140° (bath)/4 mm, $(\alpha)_D$ −151·2° (*c*, 2·1); VPC single peak; IR bands at: 791, 833, 885, 1357, 1374, 1639, 1664, 2874, 3096 cm^{-1}.

(−)-γ-Cadinene (2 g), on treatment with Li (1·0 g) and ethylenediamine (50 ml) for 8 hr, gave the reaction product (1·8 g) which was distilled over Na; b.p. 120–140° (bath)/2 mm, n_D^{29} 1·5210; $(\alpha)_D$ −5·8° (*c*, 6·00); λ_{max} 267·5, 276 mμ; ε_{max} 451, 348 respectively; IR bands at: 813, 1359, 1377, 1493, 1608 cm^{-1}. The product was a mixture of XX (53%) and XXIV (47%) as determined by mixed VPC analyses with authentic samples.

(d) *Dienone* (XXVI) was prepared from khusinol by the procedure of Wagh *et al.*, m.p. 57°; $(\alpha)_D$ +79·95° (*c*, 3·33); λ_{max} 244, 278 mμ; ε_{max} 10,480, 7498 respectively; IR bands at: 862, 877, 901, 1073, 1110, 1142, 1239, 1277, 1302, 1355, 1389, 1609, 1669 cm^{-1}. (Found: C, 82·73; H, 10·07. $C_{15}H_{22}O$ requires: C, 82·51; H, 10·16%).

A mixture of dienone (1·2 g), ethylenediamine (70 ml) and Li (1·8 g) was refluxed for 8 hr. After removal of ethylenediamine by distillation *in vacuo*, the reaction product was acidified with dil. HCl and extracted with ether. After removal of ether, the product was distilled, when the phenol (XXVII; 0·9 g) was obtained; b.p. 140–145° (bath)/0·2 mm, $(\alpha)_D$ −24·2° (*c*, 2·5); λ_{max} 274, 281 mμ; ε_{max} 1956, 1846 respectively; (IR spectrum, Fig. 1 and NMR spectrum, Fig. 2). (Found: C, 82·55; H, 10·15. $C_{15}H_{22}O$ requires: C, 82·51; H, 10·16%).

Treatment of ionones and ionols

(a) *β-Ionone* (XXVIII) obtained by regeneration from the semicarbazone (m.p. 149°) showed the following properties; b.p. 95–97°/1·5 mm, n_D^{27} 1·5180, λ_{max} 295 mμ; ε_{max} 10400; VPC single peak. It remained unaffected by treatment with the reagent for 12 hr.

(b) *α-Ionone* (XXXI), obtained by regeneration from its semicarbazone (m.p. 147°), showed the following properties; b.p. 95–97°/1·5 mm, n_D^{27} 1·5010; λ_{max} 228 mμ; ε_{max} 14287; VPC single peak.

α-Ionone (5 g), on treatment with Li (1·5 g) and ethylenediamine (75 ml) for 12 hr, gave β-ionone (4·7 g) which was identified by VPC, UV and IR spectra.

(c) *α-Ionol* (XXIX) was obtained by reduction of α-ionone with aluminium isopropoxide in isopropylalcohol; b.p. 90–92°/1·5 mm, n_D^{30} 1·4870; VPC single peak; IR bands at: 825, 970, 1160, 1270, 1310, 1365, 1370, 3025, 3400 cm^{-1}.

α-Ionol (5 g), on treatment with Li (1·5 g) and ethylenediamine (50 ml) for 12 hr, gave the reaction product which was chromatographed over neutral alumina (grade III, 150 g). The first fraction (2·1 g; eluted with pet. ether) and the second fraction (2·43 g; eluted with ether) were identified as β-ionone and β-ionol respectively by elemental analyses, VPC, UV and IR spectra.

(d) *β-Ionol* (XXX) was prepared from β-ionone by reduction with aluminium isopropoxide and had the following properties; b.p. 85–87°/1·5 mm, n_D^{28} 1·5001; λ_{max} 234 mμ; ε_{max} 5099; VPC single peak; IR bands at: 975, 1150, 1310, 1365, 1675, 3025, 3400 cm^{-1}.

β-Ionol (5 g), on treatment with Li (1·5 g) and ethylenediamine (50 ml) for 12 hr, was converted to β-ionone (3·82 g), identified as previously.

Treatment of abietic acid (XXXII)

Abietic acid was isolated according to the method of Palkin and Harris[8] from rosin and showed the following properties; m.p. 172–74°, $(\alpha)_D^{30}$ −103·5° (alcohol; *c*, 0·305); λ_{max} 235, 240, 252 mμ; ε_{max} 12,300, 13,400, 10,825 respectively; eq. wt. 301 (required 302·4); IR bands at: 1025, 1270, 1365, 1383, 1450, 1670, 2600, 2962, 3025 cm^{-1}.

The reaction mixture of abietic acid (3·5 g), Li (1·5 g) in ethylenediamine (75 ml) was refluxed for 18 hr and on working up as in the case of undecylenic acid yielded dehydroabietic acid (XXXIII, 2·85 g) which was crystallized from n-hexane, m.p. 172–73°; $(\alpha)_D^{30}$ +66·1° (alcohol, *c*, 0·518); λ_{max} 268, 272 mμ; ε_{max} 5990, 6120 respectively; IR bands at: 820, 1025, 1050, 1070, 1175, 1270, 1365, 1383, 1450, 1510, 2600, 2962, 3025 cm^{-1}; eq. wt. 299·2 (required 300·42). (Found: C, 80·23; H, 9·52. Calc. for $C_{20}H_{28}O_2$ C, 79·95; H, 9·39%).

Treatment of undecylenic acid (XXXIV)

The acid had the following properties; b.p. 121–122°/5 mm, n_D^{25} 1·4465; IR bands at: 910, 990, 1270, 1710, 2660, 3085 cm^{-1}.

Undecylenic acid (10 g) was treated with the reagent (Li 7 g; ethylenediamine 150 ml for 9 hr). Excess ethylenediamine was removed by distillation on a water bath under red. press. The residual amide was hydrolysed by refluxing for 12 hr with alcoholic potash (25%, 300 ml). After removal of alcohol, the residual product was acidified and the resultant acid (XXXV) isolated in the usual way and distilled; b.p. 121–22°/5 mm, n_D^{28} 1·4458; IR bands at: 950, 1270, 1310, 1710, 2600, 3025 cm^{-1} (Found: C, 71·56; H, 11·12. $C_{11}H_{20}O_2$ requires: C, 71·69; H, 10·94%); eq. wt. 184·7 (required 184·27). The product on oxidation with $KMnO_4$ gave azelaic acid, m.p. 104–105°.