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PREPARATION OF (-)-cis-CAR-4-ENE

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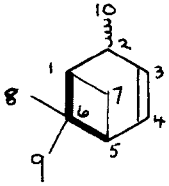
A recent publication[1] describes the preparation of *cis*- and *trans*-pin-3-ene (δ-pinene) (I) by a method that we have used to prepare (-)-*cis*-car-4-ene (II). Earlier[2,cf.3] we described the formation of (II) by the pyrolysis of the methylxanthogenate of (-)-*cis*-caran-*trans*-4-ol (III). In this reaction, however, (+)-car-3-ene (IV) was the major product. We have since found that when the toluene *p*- sulphonylhydrazone of (-)-*cis*-caran-4-one (V) is treated with methyl lithium,[cf.4] (-)-*cis*-car-4-ene (II) is the only volatile product. Similar treatment of the derivative of (+)-*cis*-caran-5-one (VI) affords a mixture of (-)-*cis*-car-4-ene (II) (80%) and (+)-*m*-mentha-3(8),4-diene[5] (VII) (20%).

In a typical preparation, the toluene *p*- sulphonylhydrazone of (-)-*cis*-caran-4-one, m.p. 134°, $[\alpha]_D^{20}$- 192° (*c* 1.31 in $CHCl_3$) (7.6 g.) was stirred for 12 hr. with methyl lithium (lithium, 2.1 g.; methyl iodide, 17 c.c.; ether, 150 c.c.). The mixture, worked up in the usual way, gave (-)-*cis*-car-4-ene (II) (3.1 g.), b.p. 29°/0.5 mm., $[\alpha]_D^{20}$- 155° (0.75 in $CHCl_3$), n_D^{20} 1.4664 (lit.,[2] $[\alpha]_D^{20}$- 146°, n_D^{20} 1.4665), ν_{max} (liquid) 1639, 713 cm^{-1}; τ 9.10 (d., *J* 6Hz., Me-10), 9.10 (s, Me-8), 8.92 (s, Me-9), 4.5 (H-4 and H-5).

The toluene *p*- sulphonylhydrazone of (+)-*cis*-caran-5-one, m.p. 122°, $[\alpha]_D^{20}$+ 189.8° (*c* 0.5 in $CHCl_3$) (1.8 g.) similarly treated, gave an oil (0.94 g.) containing (-)-*cis*-car-4-ene (II) (80%) and (+)-*m*-mentha-3(8),4-diene[5] (VII) (20%) as shown by g.l.c. on a Carbowax column (20 ft.) at 100°. Separation by preparative g.l.c. gave (VII) whose n.m.r. spectrum showed signals at τ 9.02 (d, *J* 6Hz., Me-7), 8.26 (Me-9,10), 4.4 (m, H-5), and 3.66 (d, *J* 10 Hz., H-4), identical with that of an authentic specimen.[5]

Satisfactory analyses were obtained for the new compounds.



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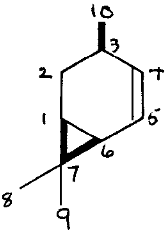

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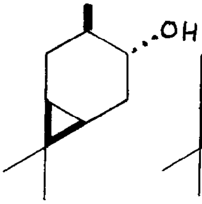

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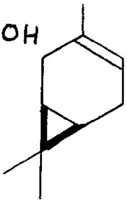

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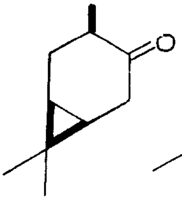

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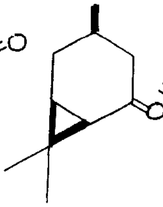

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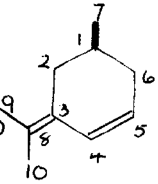

VII

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