

Methylpropylmaleimide (1) was prepared from urea and methylpropylmaleic anhydride (cf. Ref. 2), m.p. 55–56° (sublimed) (lit.⁴ 56–57°). NMR (CDCl₃, δ-units relative to tetramethylsilane as internal standard): 0.95 (t, C–CH₃), 1.3–1.7 (m, C–CH₂), 1.97 (s, C=C–CH₃), 2.32 (t, C=C–CH₂). (Found: C 62.4; H 7.1. Calc. for C₈H₁₁NO₂: C 62.7; H 7.2).

Cis-2-methyl-3-propylsuccinimide (2). The maleimide (1, 1.01 g) in ethanol (60 ml) was reduced catalytically using palladium on charcoal (Engelhardt, 10% Pd, 0.06 g) as catalyst. The reduction was very slow, the theoretical amount of hydrogen being absorbed only after 12 h. Isolation of the product in the usual manner followed by recrystallisation from light petroleum gave *cis-2-methyl-3-propylsuccinimide (2)*, 0.91 g, m.p. 49–50°. Tschugaeff⁷ gives m.p. 51–53° for a product which is probably predominantly the *trans*-isomer of (2). NMR: 0.95 (m, C–CH₃), 1.22

(d, C–CH₃), 1.5 (m, CH₂), 2.88 (m, O=C–CH–). (Found: C 61.8; H 8.5. Calc. for C₈H₁₃NO₂: C 61.9; H 8.4).

Erythro-2-methyl-3-propylsuccinic acid. The *cis*-imide (2, 0.086 g) was refluxed in concentrated hydrochloric acid (1 ml) for 1 h. The hydrochloric acid was removed using a rotatory evaporator to give methylpropylsuccinic acid (0.090 g), m.p. 135–148° in an *erythro:threo* ratio of 9:1. Recrystallisation from dilute hydrochloric acid gave *erythro-2-methyl-3-propylsuccinic acid (3)*, 0.040 g, m.p. 158–160°. Lit. m.p. for the high melting isomer of methylpropylsuccinic acid 156–158°⁴ (cf. Ref. 7). (Found: C 55.4; H 8.0. Calc. for C₈H₁₄O₄: C 55.2; H 8.1).

The *erythro:threo* ratio was determined by gaschromatography of the methyl esters.

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Formation of Dibenzofuran from 2,2'-Dihydroxybiphenyl via the Cyclic Phosphorane

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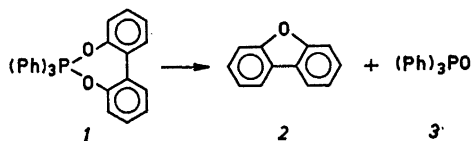
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During experiment aimed at the synthesis of lichen acids of the dibenzofuran type, the following observation was made.

2,2'-Dihydroxybiphenyl reacted with dibromotriphenylphosphorane to give the cyclic phosphorane (1). When this compound was heated under reduced pressure, rapid decomposition occurred and a fair yield of dibenzofuran (2) was obtained.

This reaction appears to be of some interest in connection with the synthesis of carboxylated dibenzofurans, e.g. the lichen acids pannaric acid¹ and porphyritic acid,² which are decarboxylated under the strongly acidic conditions generally required for the ringclosure of 2,2'-dihydroxybiphenyls to dibenzofurans.^{3,4}

The formation of dibenzofuran from the phosphorane (1) is probably related to the reactions whereby bromobenzene derivatives are produced by thermal decomposition of bromophenoxytriphenylphosphoranes⁵ and chlorobenzene by decomposition of dichlorotriphenoxyphosphorane.⁶ The replacement of hydroxyl by halogen by boiling with phosphorus oxychloride or phosphorus pentachloride, frequently used for heterocyclic compounds, appears also to be a related reaction.



Experimental. Dibromotriphenylphosphorane was prepared by bromination of triphenylphosphine (7.45 g) in benzene solution⁷ (100 ml). 2,2'-Dihydroxybiphenyl (5.20 g) was added followed by triethylamine (10 ml). The mixture was refluxed for 1 h and then allowed to cool. The clear solution was decanted from a dark precipitate, which was not investigated further. The solvent was evaporated to give a viscous sirup, presumably the phosphorane (1). This was decomposed by heating to 250–300° at reduced pressure. Dibenzofuran (2, 2.00 g) distilled during the decomposition and was collected in essentially pure state, m.p. 80–83° (lit.⁸ m.p. 87°). The residue from the decomposition (6.8 g) was mainly triphenylphosphine oxide (3). If moisture was not rigorously excluded during the formation and decomposition of (1), lower yields of dibenzofuran was obtained and the residue from the decomposition contained unchanged 2,2'-dihydroxybiphenyl.

No attempt was made to purify the phosphorane (1) since it was very hygroscopic. An analysis showed that the crude material contained about 2% of bromine. The IR-spectrum and the chromatographic behaviour were similar to those of diphenoxytriphenylphosphorane.⁷

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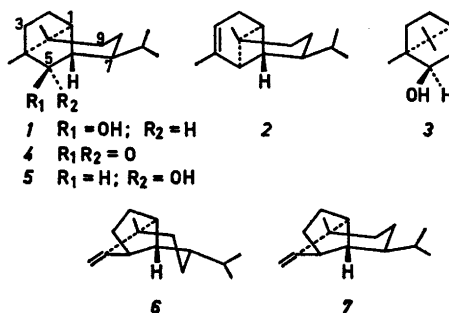
Copaborneol, the Major Sesquiterpene Alcohol in *Pinus silvestris* Wood and Sulphate Turpentine*

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The major sesquiterpene alcohol occurring in the wood of *Pinus silvestris* L.¹ and in Swedish sulphate turpentine² has been found to possess structure (1). The name copaborneol is proposed for the alcohol on the basis of its structural relationship both to copaene (2) and to borneol (3).

Copaborneol (1) has m.p. 47.5–48°, $[\alpha]_D + 27.4^\circ$ and the molecular formula $C_{15}H_{24}O$.³ On dehydrogenation no cadalene or azulene was obtained. Copaborneol was shown to be a saturated secondary alcohol by tetranitromethane test and by ozonolysis at -80° , which gave copacamphor (4), $C_{15}H_{24}O$, $[\alpha]_D + 98.7^\circ$ (c 1.7),** as the main product. Copacamphor was also obtained, in higher yield, when the alcohol was oxidized with chromic acid according to Jones.³



Reduction of copacamphor with sodium in ethanol gave copaborneol (1). However, on lithium aluminium hydride reduction, an isomeric alcohol, copaisoborneol (5), $[\alpha]_D + 15.3^\circ$ (c 2.0) was obtained as the main product.

* The Chemistry of the Order Pinales, Part 44. Part 43: *Arkiv Kemi* **26** (1967) 539.

** Rotations were taken in chloroform.