

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

Acknowledgements. I would like to thank Professor H. Erdtman for his interest and for stimulating discussions.

- Åkermark, B., Erdtman, H. and Wachtmeister, C. A. *Acta Chem. Scand.* **13** (1959) 1855.
- Wachtmeister, C. A. *Acta Chem. Scand.* **10** (1956) 1404.
- Elderfield, R. C. (Ed.), *Heterocyclic Compounds*, Wiley 1951, vol 2, p. 126.
- Stjernström, N. E. *Svensk Kem. Tidskr.* **75** (1963) 184.
- Wiley, J. A., Hershkovitz, R. L., Rein, B. M. and Chung, B. C. *J. Am. Chem. Soc.* **86** (1964) 964.
- Autenrieth, W. and Geyer, A. *Ber.* **41** (1908) 146.
- Horner, L., Oediger, H. and Hoffmann, H. *Ann.* **626** (1959) 26.
- Hodgman, C. D. (Ed.), *Handbook of Chem. and Phys.* 44 Ed. 1962, p. 956.

Received January 23, 1967.

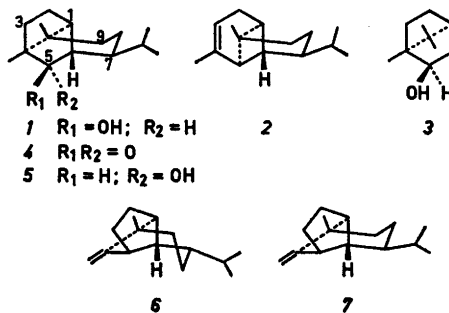
Copaborneol, the Major Sesquiterpene Alcohol in *Pinus silvestris* Wood and Sulphate Turpentine*

MARGARET KOLBE and
LARS WESTFELT

Organisk-kemiska Institutionen, Kungl. Tekniska Högskolan, Stockholm, Sweden

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.

The IR and NMR * spectra of copaborneol (1), copaisoborneol (5) and copacamphor (4) were in agreement with the above results, and the NMR spectra also provided additional evidence for the assigned structures. In the 60 Mc/s NMR spectrum of copaborneol a broad singlet at δ 3.41 was assigned to the proton attached to the same carbon as the hydroxyl group. It was broadened, probably due to the combined effects of weak coupling to the proton at C-6 and long-range coupling to the *exo*-proton at C-3 (for similar long-range coupling in borneol, cf. Ref. 4). The corresponding signal in the NMR spectrum of copaisoborneol appeared as a doublet at δ 3.58. The relatively large coupling constant, 8 cps, must be due to vicinal coupling between the protons at C-5 and C-6.

In the 100 Mc/s NMR spectrum ** of copaborneol, the signals originating from the methyl groups were relatively well resolved. The proton signals of the two quaternary methyl groups overlapped and appeared as a singlet at δ 0.82. The methyl protons of the isopropyl group gave rise to a pair of doublets at δ 0.84 and 0.90, respectively, each representing three protons. A decoupling experiment was performed, which confirmed the presence of an isopropyl group in the molecule.

When copacamphor (4) was refluxed with sodium deuterioxide in deuterium oxide-dioxane, no deuterium was incorporated. This demonstrated that C-6 constituted a bridgehead.

Copaborneol was treated with brosyl chloride in pyridine at room temperature for 15 h to give a brosylate, m.p. 68°. When a pyridine solution of this product was heated at 90° for 2 h, a mixture of hydrocarbons was obtained. Gas-liquid chromatography (GLC) and argentative thin layer chromatography (Ag-TLC) indicated that it consisted mainly of two components. Two hydrocarbon fractions were isolated by argentative column chromatography. The first fraction eluted appeared to be pure according to GLC and Ag-TLC. However, the IR and NMR spectra revealed that it was a mixture, probably consisting of compounds containing cyclopropane rings and a compound with a tetrasubstituted double bond.

* Instrument: Varian A 60; solvent carbon tetrachloride, internal standard tetramethylsilane.

** Instrument: Varian HA 100.

The second, major fraction appeared to consist of a pure hydrocarbon, $C_{15}H_{24}$, $[\alpha]_D + 28.9^\circ$ (c 1.2). It showed IR absorption bands at 3075, 1657, and 877 cm^{-1} indicating the presence of an exocyclic double bond. The NMR spectrum could be interpreted as follows. The presence of an isopropyl group was indicated by a doublet at δ 0.89 (J 6 cps, 6 H) and a methyl group attached to a carbon bearing no hydrogens by a singlet at δ 1.00 (3 H). The compound appeared to contain an exocyclic double bond (singlets at δ 4.50 and 4.78, 1 H each) with only one proton in an allylic position (unresolved multiplet at δ 2.47, 1 H).

These spectral data are very similar to those reported for sativene (6) $[\alpha]_D - 186^\circ$.⁵ However, the hydrocarbons were not identical as shown by the difference in optical rotations and by the fact that different diols were obtained on osmium tetroxide oxidation. Sativene was reported to give a diol, m.p. 64°, $[\alpha]_D - 68^\circ$,⁵ while the diol derived from copaborneol, $C_{15}H_{26}O_2$, had m.p. 46–47° and $[\alpha]_D - 30^\circ$ (c 0.5).^{*} Apparently, the hydrocarbons only differ by being epimeric at C-7. The configuration of sativene at C-7 as shown in formula (6), "ylangocamphene", is obvious from the manner it has been synthesized from longifolene.⁵ Thus, the hydrocarbon derived from copaborneol should possess the copacamphene structure (7).

The course of the elimination reaction of copabornyl brosylate is apparently analogous to similar transformations of bornyl and isobornyl derivatives. Bornyl naphthalene- β -sulphonate has been reported to give mainly camphene on heating in various solvents.⁶ Also the reductions of copacamphor described above proceed analogously to those of the corresponding ketonic monoterpene, camphor. With sodium in ethanol predominantly the most stable alcohols, copaborneol (1) and borneol,⁷ respectively, are formed, while lithium aluminum hydride reduction involves attack from the least hindered side of the carbonyl group to give copaisoborneol (5) and isoborneol,⁸ respectively.

Added in proof. We have synthesized copaisoborneol from α -santalol.⁹

* It is essential to use proper conditions for the decomposition of the osmate ester. We thank Prof. P. de Mayo, who kindly let us know the unpublished details of preparation of the diol from sativene.

Acknowledgements. We thank Professor Holger Erdtman for his kind interest in this work and *Cellulosaindustriens Stiftelse, 1959 års Fond*, for financial support.

1. Westfelt, L. *Acta Chem. Scand.* **20** (1966) 2829.
2. Westfelt, L. *Acta Chem. Scand.* **20** (1966) 2841.
3. Bowden, K., Heilbron, I. M., Jones, E. R. H. and Weedon, B. C. L. *J. Chem. Soc.* **1946** 39.
4. Flautt, T. J. and Erman, W. F. *J. Am. Chem. Soc.* **85** (1963) 3212.
5. de Mayo, P. and Williams, R. E. *J. Am. Chem. Soc.* **87** (1965) 3275.
6. Patterson, T. S. and McAlpine, I. M. *J. Chem. Soc.* **1928** 2464.
7. Jackson, C. J. and Menke, A. E. *J. Am. Chem. Soc.* **5** (1883) 270.
8. Trevo, L. W. and Brown, W. G. *J. Am. Chem. Soc.* **71** (1949) 1675.
9. Kolbe, M. and Westfelt, L. *To be published.*

Received January 25, 1967.

Torsional Motion in Non-ortho Substituted Biphenyls

O. BASTIANSEN and A. SKANCKE

Department of Chemistry, University of Oslo, Oslo 3, Norway

Biphenyl and its non-ortho substituted derivatives have a planar structure in the crystalline phase,¹ whereas a non-planar structure has been observed in the vapour phase.²⁻⁴ In this case the angle α between the two benzene planes was determined to be 42°, and the work indicated that the molecules are far from being rigid. This is in accordance with theoretical calculations combining non-bonded interaction and conjugation energy. The theoretically calculated potential curve exhibits a flat and shallow minimum at $\alpha \simeq 40$ °.⁵

The purpose of the present work was to estimate the magnitude of the torsional amplitude around the central C—C' bond. The idea was to study the 3,3'-Br...Br distance contribution to the electron-diffraction radial-distribution curve for the

two molecules, 3,3'-dibromobiphenyl and 3,5,3',5'-tetrabromobiphenyl.

The angle between the ring planes is calculated by studying several distances that vary with the angle. The tetrabromo-substituted compound was found to be best suited for this study because of the double weight of the angle dependent Br₃...Br₃' distances, but the angle seems to be identical in the two compounds. The value $\alpha = 45$ ° was found by averaging the value calculated from different peaks in the radial distribution curve. The shift of the maximum position of the peak in the radial distribution curve with the rotational and vibrational motions is estimated and taken into account.

In a molecular model with an inter-ring angle of 45° two Br₃...Br₃' distances exist. It appears that only the longer one is suited for studies of torsional amplitudes. The peak in the radial distribution curve of the shorter one is badly overlapped by peaks from other angle-dependent distances. The longer distance peak is influenced by the angle independent Br₃...H₄' distance only, the contribution of which may easily be subtracted from the curve. In the present work, all calculations of intra-molecular motion are therefore based upon the long Br₃...Br₃' distance peak only.

The Br₃...Br₃' distances of the di- and tetrabromo-substituted compounds depend upon the angle of twist. The corresponding root-mean-square amplitude, u , depends upon the rotational amplitude, σ_α , as well as the non-rotational vibration, here called framework vibration, u_f . We assume these two types of motion to be separable. But even with an exact knowledge of the shape of the Br...Br' peak, it is impossible to obtain both σ_α and u_f without additional information. If one wants to estimate σ_α , assumptions have to be made concerning u_f . In order to obtain a basis for an evaluation of the framework vibration, 3,5,4'-tribromobiphenyl was chosen as a reference substance. The inter-ring angle, α , for this compound was identical with that of the other compounds. The Br₃...Br₄' distance is not very different from the Br₃...Br₃' distance of the other compounds. But as the Br₄' atom lies on the axis of rotation, the Br₃...Br₄' distance is independent of α . Consequently the corresponding u value is due to framework vibration only. This is the basis for using the u value for the two other compounds, though it can be nothing but a rather rough approximation.