
Terpenoids and Steroids—Volume 4

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Terpenoids and Steroids

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Introduction

While following the pattern established in previous Reports of this series, we have this year added two chapters of a new kind. It seemed to us that areas of terpenoid and steroid chemistry not normally included in our coverage should be reviewed in occasional chapters. These will cover periods of about five years while otherwise preserving the detailed character of our annual Reports. The first results of this decision are Chapters 2 and 3 of Part II of this volume.

In 'Microbiological Reactions with Steroids' Professor L. L. Smith gives a comprehensive account of the very large amount of work that has appeared in this field since the last review was published in 1967. The chapter 'Steroid Conformations from X-Ray Analysis Data' by Professor C. Romers and Dr. C. Altona and their colleagues goes somewhat beyond the usual scope of Specialist Periodical Reports. The authors have in part used data recorded in the literature to recalculate equilibrium geometries for a large number of steroids. In their critical survey based on these geometries, they provide a most illuminating analysis of the way in which steroid conformations respond to functionality and configuration. This will be of interest to organic chemists and biochemists alike.

Because of a change in authorship which we were not able to implement in time for this Report, the chapter on Steroid Synthesis has regretfully been held over for Volume 5, which will cover a two-year period. Finally, we have included a list of selected reviews of terpenoid chemistry that have appeared in the period 1968—1973, to fill what to us seemed a regrettable gap in the tertiary literature.

K. H. OVERTON

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Part I

TERPENOIDS

This year, the section on general chemistry has been enlarged, and some reactions that are not specific to monoterpenoids have been included. Physical methods are given a separate section. Unfortunately it must be noted that *Chemical Abstracts* contains an increasing number of errors, as well as frequently citing insufficient information for the abstract to be useful. So far as possible, attention has been drawn to these points in each individual case.

The abstracts of the Proceedings of the 4th Congress on Essential Oils (Tbilisi, 1968) have appeared, but much of this work is now out of date.

1 Physical Measurements: Spectra etc., Chirality

The ^{13}C n.m.r. spectra of citronellol, citronellal, and related substances have been discussed,¹ and a study of the shifts of the alkene signals induced by Ag^{I} in the ^{13}C n.m.r. spectra of a number of substances including the pinenes has been made.² A very full discussion of the effect of shift reagents on the ^1H and ^{13}C n.m.r. spectra of borneol and isoborneol has shown that the complexes formed with the reagents are effectively axially symmetric, the magnetic axis being practically collinear with the oxygen-metal bond;³ an estimate of the contact contribution has been made.⁴ Coupling constants in 7,7-dimethylnorborneols have been examined using the $[\text{Eu}(\text{dpm})_3]$ shift agent.⁵

In a study of the u.v. spectra of the complexes between boron trifluoride and unsaturated ketones, monoterpenoids are particularly unlucky: piperitone (1) does not fit the attempted correlation, and carvone (2) polymerizes under the conditions of measurement!⁶

The mass spectra of monoterpenoids have been discussed,⁷ and the loss of EtCONH_2 in the mass spectrum of (3) (a retro-Ritter reaction) has given rise to

¹ A. K. Bose and R. J. Brambilla, *J. Agric. Food Chem.*, 1972, **20**, 1013.

² C. D. M. Beverwijk and J. P. C. M. van Dongen, *Tetrahedron Letters*, 1972, 4271.

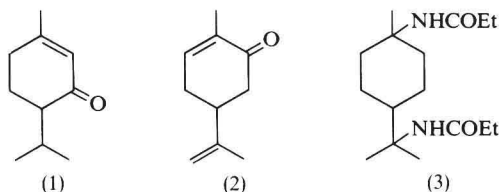
³ G. E. Hawkes, D. Leibfritz, D. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1973, **95**, 1659.

⁴ G. E. Hawkes, C. Marzin, S. R. Johns, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1973, **95**, 1661.

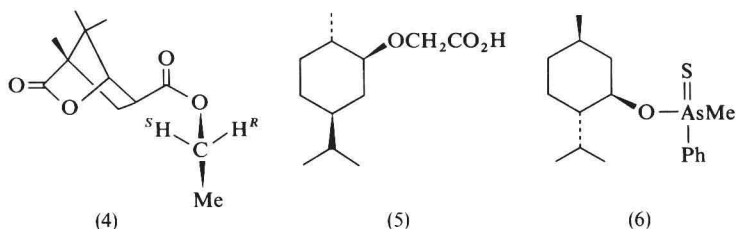
⁵ K.-T. Liu, *Tetrahedron Letters*, 1973, 2747.

⁶ J. Torri and M. Azzaro, *Tetrahedron Letters*, 1973, 3251.

⁷ M. Sakaguchi, A. Hirakata, and H. Yamada, *Kogyo*, 1972, No. 102, p. 41 (*Chem. Abs.*, 1973, **78**, 84 555).



speculations, without the support of labelling studies.⁸ The Raman 'circular dichroism' of a number of optically active monoterpenoids has been examined. Circular intensity differentials (CID), $\Delta_\alpha = I_\alpha^R - I_\alpha^L / (I_\alpha^R + I_\alpha^L)$, where I_α^R , I_α^L are the scattering intensities with α -polarization in right and left circularly polarized incident light, have been measured in the low-frequency Raman spectra of (+)- and (-)- α -pinene, (-)- β -pinene, (-)-borneol, and carvone.⁹ The circular differential Raman spectrum of carvone has been reported elsewhere.¹⁰



Monoterpenoids are the most common of the chiral agents used for inducing asymmetry. Measurement of the n.m.r. spectra of esters of camphanic acid, such as (4), has been used to find the enantiomeric purity and absolute configuration of α -deuteriated primary alcohols,¹¹ and separations of various alcohols and amines using esters of chrysanthemic acid are reported.¹² An interesting mutual resolution can be effected with (\pm)-camphorsulphonic acid and α -(\pm)- $\text{Me}_2\text{NCH}_2\text{CHMeCPh(OH)CH}_2\text{Ph}$.¹³ (+)-Carvomenthol and chloroacetic acid give carvomethylacetic acid (5), which is useful for resolving alanine.¹⁴ Mislow *et al.* have used menthyl methylphenylthioarsenite (6) in an extension to arsenic of their earlier method (see Vol. 2, p. 28) of making optically active phosphine oxides.¹⁵

Probably the most interesting work taking advantage of the chirality of monoterpenoids has involved the attempts to induce asymmetry in organic

⁸ S. Blum and S. Sarel, *J. Org. Chem.*, 1972, **37**, 3121.

⁹ L. D. Barron and A. D. Buckingham, *J.C.S. Chem. Comm.*, 1973, 152.

¹⁰ M. Diem, J. L. Fry, and D. F. Burrow, *J. Amer. Chem. Soc.*, 1973, **95**, 253.

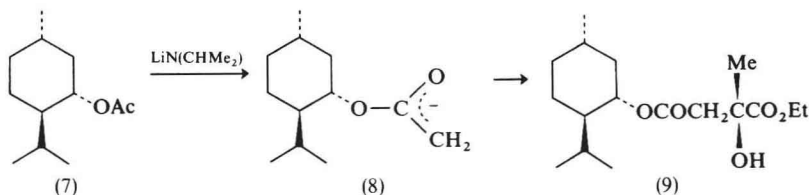
¹¹ H. Gerlach and B. Zagalak, *J.C.S. Chem. Comm.*, 1973, 274.

¹² C. J. W. Brooks, M. T. Gilbert, and J. D. Gilbert, *Analyt. Chem.*, 1973, **45**, 896.

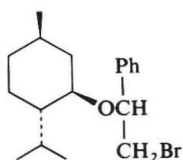
¹³ W. E. Thompson and A. Pohland, *Ger. Offen.* 2 230 838.

¹⁴ F. Rulko, K. Witkiewicz, and Z. Chabudziński, *Diss. Pharm. Pharmacol.*, 1972, **24**, 297.

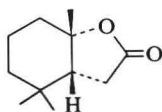
¹⁵ J. Stackhouse, R. J. Cook, and K. Mislow, *J. Amer. Chem. Soc.*, 1973, **95**, 953.



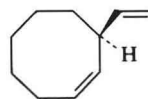
synthesis. As a simple example, the rate of esterification of D-amino-acids with (–)-menthol is greater than that of L-acids, and this has led to a proposal for menthyl ester formation.¹⁶ The anion (8), obtained when menthyl acetate (7) is metallated, reacts with ethyl pyruvate to yield the menthyl ester of (S)-citramalic acid (9) in 26% optical yield.¹⁷ Kergomard *et al.* found no asymmetric induction in the reaction between styrene, t-butyl hypobromite, and menthol [leading to (10)].¹⁸ Oxidation of (±)-borneol with (R)-(+)-menthyl *p*-tolyl sulphoxide and dicyclohexylcarbodi-imide in the presence of phosphoric acid in benzene gave (–)-camphor in 7% optical yield,¹⁹ and the cyclization of homogermanic (–)-menthyl ester with stannic chloride to *cis*-tetrahydroactinidiolide (11) occurred with only *ca.* 12% optical yield, although this rose to 20.8% when the 1,2:5,6-di-*O*-isopropylidene- α -D-glucofuranose ester was used.²⁰ Asymmetric reductions of diphenylmethyl alkyl ketones by complexes of lithium aluminium hydride and *cis*-pinane-2,3-diol and benzyl alcohol gave up to 20% optical yields,²¹ but far more successful was the reaction of ethylene and cyclo-octa-1,3-diene [to (12)], catalysed by certain π -allyl complexes of nickel where one ligand is a monoterpene phosphine, in which 70% optical purity was achieved.²²



(10)



(11)



(12)

King and Sim have described a useful method for demonstrating the presence of a reactive intermediate in reactions involving chiral diastereomeric transition

¹⁶ T. Hayakawa, H. Yamamoto, Y. Murakami, Y. Yobiko, and S. Mitani, *Bull. Chem. Soc. Japan*, 1972, **45**, 3556; see also Vol. 3, p.6.

¹⁷ S. Brandänge, S. Josephson, and S. Vallén, *Acta Chem. Scand.*, 1973, **27**, 1084.

¹⁸ G. Dauphin, A. Kergomard, and A. Scarset, *Bull. Soc. chim. France II*, 1973, 1104.

¹⁹ M. H. Benn, P. Christensen, D. Kjersgaard, and C. Watanatada, *Canad. J. Chem.*, 1973, **51**, 1977.

²⁰ T. Kato, S. Kumazawa, and Y. Kitiyara, *Synthesis*, 1972, 573.

²¹ R. Haller and H. J. Schneider, *Chem. Ber.*, 1973, **106**, 1312.

²² B. Bogdanović, B. Henc, B. Meister, H. Pauling, and G. Wilke, *Angew. Chem. Internat. Edn.*, 1972, **11**, 1023.

states; it provided a new piece of evidence for the intermediacy of a sulphene in the reaction between camphor-10-sulphonyl chloride and menthylamine.²³

The Reporter is ill-placed to criticize a chapter on the synthesis of monoterpenoids in a recently published book on the total synthesis of natural products.^{23a} However, a delay of three years between the latest reference quoted and publication of a book is deplorable.

2 General Chemistry

Sukh Dev has reviewed alumina- and silica gel-induced rearrangements, many of which involve monoterpenoids.²⁴ The Prins reaction of monoterpenoid hydrocarbons has also been reviewed.²⁵

Microwave discharge of carbon dioxide can function as a singlet oxygen source; photo-oxygenation by this means has been accomplished using limonene and γ -terpinene as substrates.²⁶ A two-phase solvent system is useful for epoxidizing sensitive olefins (e.g. 6-methylhept-5-en-2-one) with *m*-chloroperbenzoic acid, but limonene gave the same epoxide in the same yield as with the single-phase system.²⁷

Several novel methods for the reduction and oxidation of oxygenated terpenoids have appeared. Potassium metal in graphite can be used to reduce camphor (a 60:40 *exo:endo* mixture is obtained), and oxidations of primary alcohols are effected by chromic oxide in graphite (citronellol yields 90% of the aldehyde in 24 h),²⁸ but the preparation of the reagent can be dangerous.²⁹ Potassium metal in hexamethylphosphoramide, with or without a co-solvent, has also been used to reduce terpenoid ketones; with camphor, more *endo*-product is formed than in the potassium-graphite reduction.³⁰ Hindered saturated secondary alcohols are oxidized by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; thus borneol and isoborneol are 96% and 95% oxidized in 8 h and neoisomenthol (*i.e.* the all-*cis*-isomer) and neoisocarvomenthol are 48% and 40% oxidized in the same time, whereas the all-equatorial alcohols menthol and carvomenthol are hardly affected in this time.³¹ Reduction of camphor with various silanes (Ph_2SiH_2 , PhSiH_3 , PhMeSiH_2 , and Et_2SiH_2) in the presence of tris(triphenylphosphine)chlororhodium gives 73–90% of isoborneol (*exo*), but triethylsilane gives only 30% of isoborneol and phenyldimethylsilane does not reduce. Analogous results were obtained for menthone,³² but pulegone (13) presented some irregularities, mixtures of menthone (14) and pulegol (15) being

²³ J. F. King and S. K. Sim, *J. Amer. Chem. Soc.*, 1973, **95**, 4448.

^{23a} A. F. Thomas, in 'The Total Synthesis of Natural Products', ed. J. W. ApSimon, Wiley, New York, 1973, Vol. 2, p. 1.

²⁴ Sukh Dev, *J. Sci. Ind. Res.*, 1972, **31**, 60.

²⁵ J. Chlebicki, *Wiadomosci Chem.*, 1972, **26**, 629.

²⁶ K. Gollnick and G. Schade, *Tetrahedron Letters*, 1973, 857.

²⁷ W. K. Anderson and T. Veysoglu, *J. Org. Chem.*, 1973, **38**, 2267.

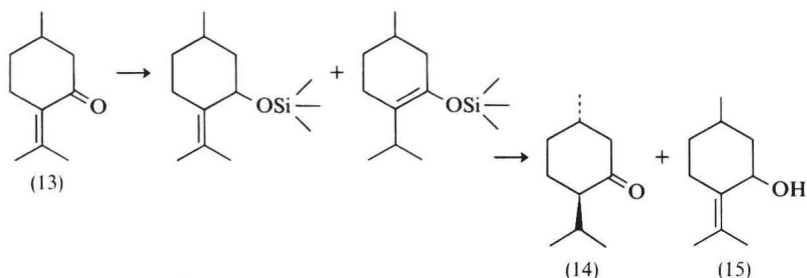
²⁸ J.-M. Lalancette, G. Rollin, and P. Dumas, *Canad. J. Chem.*, 1972, **50**, 3058.

²⁹ Communication from the manufacturers, Ventron Corp., Beverly, Mass.

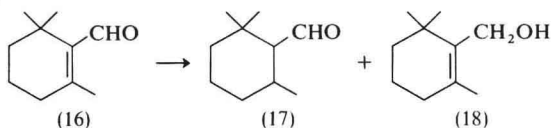
³⁰ M. Larcheveque and T. Cuvigny, *Bull. Soc. chim. France II*, 1973, 1145.

³¹ J. Iwamura and N. Hirao, *Tetrahedron Letters*, 1973, 2447.

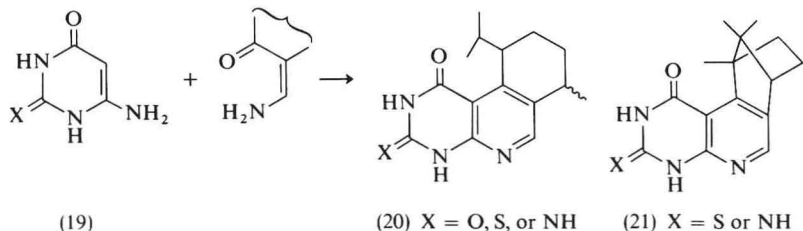
³² I. Ojima, M. Nihonyanagi, and Y. Nagai, *Bull. Chem. Soc. Japan*, 1972, **45**, 3722.



produced in different amounts depending on the reagent.³³ The rate of Meerwein-Ponndorf reduction (propan-2-ol-aluminium isopropoxide) for a variety of terpenoid ketones is unexpectedly high. The half-life of camphor, for example, (the slowest of those measured) was 145.8 min at 82 °C.³⁴ Triphenyltin hydride reduces the conjugated double bond of unsaturated aldehydes; thus citral gives citronellal, but in the case of β -cyclocitral (16), the reaction works less specifically, leading to a 1:1 mixture of the saturated aldehyde (17) and the unsaturated alcohol (18).³⁵



4-Dimethylaminopyridine is a useful catalyst in acylations; an 80% yield of linalyl acetate can be obtained (without rearrangement—see Vol. 3, p. 15) with its aid, using triethylamine as solvent and (presumably, for it is omitted from the experimental details!) acetic anhydride at room temperature for 14 h. Only catalytic amounts are needed, as was demonstrated by the preparation of menthyl monophthalate.³⁶ Reaction of aminomethylene ketones with 4-aminouracil (19; X = O), the thio-analogue (20; X = S), or 2,4-diamino-6-hydroxypyrimidine (the enolized imino-analogue), yields '5-deazapteridines'; those corresponding to menthone (20) and camphor (21) have been reported³⁷ (see Vol. 3, p. 42).



³³ I. Ojima, T. Kogure, and Y. Nagai, *Tetrahedron Letters*, 1972, 5035.

³⁴ V. Hach, *J. Org. Chem.*, 1973, **38**, 293.

³⁵ H. R. Wolf and M. P. Zink, *Helv. Chim. Acta*, 1973, **56**, 1062.

³⁶ G. Höfle and W. Steglich, *Synthesis*, 1972, 619.

³⁷ E. Stark and E. Breitmaier, *Tetrahedron*, 1973, **29**, 2209.