stretching vibration, in accord with a one-minimum potential.[15]

The present discussion is relevant not only in the context of the geometrical structure of benzene, it has even more general implications in connection with questions as to the CC bond length alternation and double bond localization (and the related aromaticity problems), respectively, in annulenes of arbitrary ring size, bridged annulenes, and polycyclic π systems with condensed rings. In particular, this holds for analyses of such problems by means of routine X-ray diffraction studies: *Caution is obviously called for!*[3, 16]

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CAS Registry number:
C_6H_6, 71-43-2.

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[4] Series of 21 publications; in particular see: W. R. Angus, C. R. Bailey, J. B. Hale, C. K. Ingold, A. H. Leckie, C. G. Raisin, J. W. Thompson, C. L. Wilson, *J. Chem. Soc. 1936*, 966, 971; C. R. Bailey, C. K. Ingold, H. G. Poole, C. L. Wilson, *ibid. 1946*, 222; N. Herzfeld, C. K. Ingold, H. G. Poole, *ibid. 1946*, 316; cf. [5].

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[6] K. Kuchitsu, S. J. Cyvin in S. J. Cyvin (Ed.): *Molecular Structures and Vibrations*, Elsevier, Amsterdam 1972, p. 206. Regarding the D_{6h}/D_{3h} resolution problem of benzene, cf. also: I. L. Karle, *J. Chem. Phys. 20* (1952) 65.

[7] The one-dimensional distance distributions resulting from electron diffraction analyses may be compared to one-dimensional Patterson functions. From single crystal X-ray and neutron diffraction measurements one obtains three-dimensional Patterson functions (vector density distributions), such that in the absence of disorder and the usually sufficiently high reflection orders no resolution problems are encountered.

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[10] A. Cabana, J. Bachand, J. Giguère, *Can. J. Phys. 52* (1974) 1949.

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[15] J. Paldus, M. Takahashi, *Int. J. Quantum Chem. 25* (1984) 423; R. C. Haddon, K. Raghavachari, *J. Am. Chem. Soc. 107* (1985) 289. A collection of benzene calculations which almost always *presuppose* D_{6h} symmetry, may be found with R. S. Mulliken, W. C. Ermler: *Polyatomic Molecules (Results of ab initio Calculations)*, Academic Press, New York 1981, p. 331. Theoretical interpretations of the benzene structure have recently sparked off controversy which is of some interest in the present context: N. C. Baird, *J. Org. Chem. 51* (1986) 3907; P. C. Hiberty, S. S. Shaik, G. Ohanessian, J.-M. Lefour, *ibid. 51* (1986) 3908; S. S. Shaik, P. C. Hiberty, J.-M. Lefour, G. Ohanessian, *J. Am. Chem. Soc. 109* (1987) 363. Finally some very recent quantum-mechanical calculations are pointed out which throw new light on the electronic structure of benzene: D. L. Cooper, J. Gerratt, M. Raimondi, *Nature London 323* (1986) 699; however, a critical reply has already appeared: W. H. E. Schwarz, *Nachr. Chem. Tech. Lab. 35* (1987) 178; see also P. A. Schultz, R. P. Messmer, *Phys. Rev. Lett. 58* (1987) 2416.—For demonstration purposes, a geometry optimization of benzene on a good quantum-mechanical basis would be desirable which starts out from a D_{3h} geometry with markedly different, alternating C–C and C=C bond lengths, and which shows smooth convergence towards the D_{6h} minimum. Newton-Raphson procedures should be applied for this optimization and the minimum nature of the optimal D_{6h} structure should be clearly assessed by diagonalization of the second-derivative matrix of the potential energy. At least for didactical purposes, such a calculation which is not documented in the literature, would be useful.

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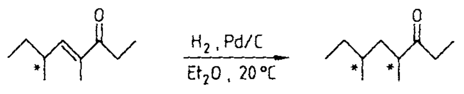
The Absolute Configuration of the Ant Alarm Pheromone Manicone**

By *Hans Jürgen Bestmann,** *Athula B. Attygalle*, *Jürgen Glasbrenner*, *Roland Riemer*, and *Otto Vostrowsky*

Manicone, (4*E*)-4,6-dimethyl-4-octen-3-one **1**, had been identified 15 years ago as an active pheromone constituent of the mandibular glands in two North American species of ants *Manica mutica* and *M. bradleyi* (Hymenoptera: Formicidae).[2] However, the absolute configuration of this chiral natural product was not determined. We have also been able to identify **1** as the main pheromone (2–3 μg/insect) in the mandibular gland secretion of the only known Euroasiatic Manica species, *Manica rubida* Latr.[3, 4] Assignment of the configuration of the chiral ketone **1** has now been accomplished, in an indirect way, by means of complexation gas chromatography[5] on a chiral phase. In total, only ten insects were required in order to elucidate the stereochemistry of **1**. The method employed is outlined below.

Hydrogenation of the double bond of synthetic, racemic manicone, *rac*-**1**, with Pd/activated carbon led to the formation of a new chiral center; as a result two diastereomeric pairs of dihydromanicone, *rac*-**2**, were produced. These four isomers could be separated by complexation gas chromatography[5] on nickel(II) bis[3-heptafluorobutyryl-(1*R*)-camphorate] (Fig. 1A).[6] *rac*-**1** could not be separated.



rac-**1** *rac*-**2**

The same reaction was carried out with natural manicone **1**. The constituents of two heads of *M. rubida* female workers were hydrogenated by reaction gas chromatography (solid sample injector,[illegible] H_2 as carrier gas, 1% Pd catalyst in the GC injection block) and the dihydromanicone **2** thus formed was isolated, after GC separation, in cooled

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[**] Pheromones, Part 61. This work was supported by the Deutsche Forschungsgemeinschaft. *A. B. A.* thanks the Alexander-von-Humboldt Stiftung for a grant.—Part 60: [1].

glass capillaries.[9] The condensate was subsequently rechromatographed on an optically active Ni^{II}-phase. Only two diastereomeric hydrogenation products **2** appeared in the gas chromatogram (Fig. 1B); these corresponded to the isomers 1 and 4 in Figure 1A.

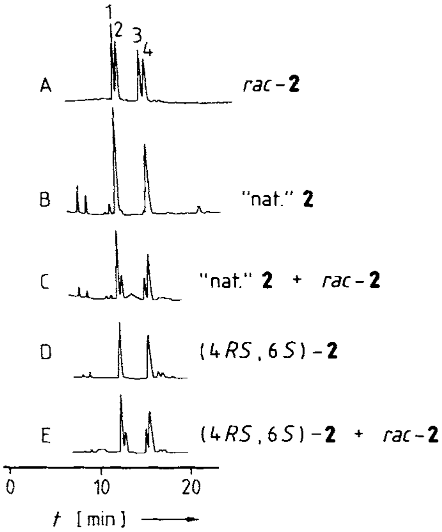
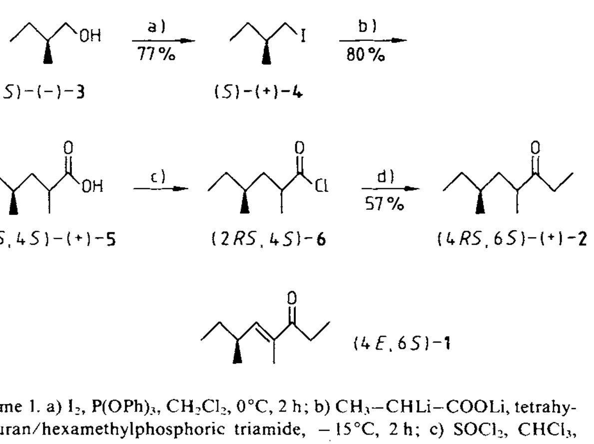


Fig. 1. Gas chromatographic separation of A) synthetic racemic dihydromanicone *rac*-**2**, B) "natural" **2**, obtained from the heads of *M. rubida* by hydrogenation, C) co-injected "natural" **2** and *rac*-**2**, D) synthetic (4*RS*,6*S*)-**2**, E) co-injected synthetic (4*RS*,6*S*)-**2** and *rac*-**2**.—Optically active GC phase: nickel(II) bis[3-heptafluorobutyryl-(1*R*)-camphorate] [5, 6]. The signals 1 and 4 correspond to the pair of diastereomers (4*RS*,6*S*)-**2**, the signals 2 and 3 correspond to (4*RS*,6*R*)-**2**.

The pair of diastereomers of dihydromanicone **2**, having (*S*)-configuration on C-6 (Fig. 1D), could be synthesized, as shown in Scheme 1, starting from commercially available (*S*)-(−)-2-methylbutanol **3**, via (*S*)-(+)-2-methylbutyl iodide **4**, (2*RS*,4*S*)-(+)-2,4-dimethylhexanoic acid **5** and its chloride **6** (for analytical data and spectra of **2** and **5**, see Table 1). This (4*RS*,6*S*)-(+)-**2** corresponded to the isomers 1 and 4 of the racemic dihydromanicone **2**, as could be demonstrated by a co-injection of the two samples into the gas chromatograph (Fig. 1E; cf. Fig. 1C). The GC-mass spectra of the synthetic diastereomeric dihydromanicones (4*RS*,6*S*)-(+)-**2** were identical to those of the hydrogenation products of racemic manicone *rac*-**1** as well as to those of the diastereomeric reduction products of natural manicone, **1**, obtained from the insect heads (Table 1).



Scheme 1. a) I_2, $P(OPh)_3$, CH_2Cl_2, 0°C, 2 h; b) $CH_3{-}CHLi{-}COOLi$, tetrahydrofuran/hexamethylphosphoric triamide, −15°C, 2 h; c) $SOCl_2$, $CHCl_3$, 70°C, 2 h; d) $LiCuEt_2$, ether, −78°C, 45 min.

Table 1. Physical data of (4*RS*,6*S*)-**2** and (2*RS*,4*S*)-**5** [a].

2: IR (film): $\tilde{\nu} = 1735\ cm^{-1}$ (s); ^1H-NMR ($CDCl_3$): $\delta = 0.60$-2.00 (m, 17 H), 2.10-2.85 (m, 3 H); MS (70 eV): *m/z* 156 ($M^\oplus$, 0.3%), 127 (2), 99 (5), 86 (52), 71 (2), 69 (4), 57 (100), 43 (12), 41 (15); $[\alpha]_D^{25} = +10.3°$ ($c = 4.90$ in pentane); b.p. 76-78°C/18 torr (Kugelrohr)

5: IR (film): $\tilde{\nu} = 1710\ cm^{-1}$ (s); ^1H-NMR ($CDCl_3$): $\delta = 0.80$-2.10 (m, 14 H), 2.20-2.90 (m, 1 H), 12.25 (s, 1 H); MS (70 eV): *m/z* 144 ($M^\oplus$, 2), 129 (2), 126 (4), 115 (23), 101 (24), 71 (98), 74 (100); $[\alpha]_D^{25} = +13.3°$ ($c = 6.00$ in CH_3OH); b.p. 81-83°C/0.5 torr (Kugelrohr)

[a] Correct elemental analyses.

Therefore it can be concluded that manicone **1** from *M. rubida* has (*S*)-configuration at C-6 and thus is present as (4*E*,6*S*)-4,6-dimethyl-4-octen-3-one.

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[6] Packard United Technologies 438A, 25 m × 0.2 mm FSCC OV101 with 0.1% nickel(II) bis[3-heptafluorobutyryl-(1*R*)-camphorate], 80°C isotherm, carrier gas N_2. Retention times of the four isomers of *rac*-**2**: 12.2, 12.47, 14.75, and 15.21 min. We thank Prof. Dr. *V. Schurig* (Tübingen) for lending us the GC column.

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Reduction of 2-Enoates and Alkanoates with Carbon Monoxide or Formate, Viologens, and *Clostridium thermoaceticum* to Saturated Acids and Unsaturated and Saturated Alcohols[**]

By *Helmut Simon*,[*] *Hiltrud White*, *Herbert Lebertz*, and *Iordanes Thanos*

All the hitherto reported biological reductions of carboxylates to aldehydes proceed via an activation of the carboxy group. The carboxylate/aldehyde pair (with $E_0' \approx -550$ mV) has a large negative redox potential. The cosubstrates or prosthetic groups usually used by reductases have redox potentials of $E_0' = -320$ mV (pyridine nucleo-

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