pane, 109-64-8; 2-phenyl-1,2-oxaphospholane 2-oxide, 16324-19-9; isopropylmethylphenylphosphine oxide, 36032-81-2; isopropyl bromide, 75-26-3; tribenzylphosphine oxide, 4538-55-0; triethyl phosphate, 78-40-0; benzyl chloride, 100-44-7; methylphenylphosphine oxide, 19315-13-0; (*S*)-(−)-menthyl methylphenylphosphinate, 16934-92-2; (±)-benzylmethylphenylphosphine oxide, 51153-50-5.

## References and Notes

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) For a preliminary communication, see R. B. Wetzel and G. L. Kenyon, *J. Amer. Chem. Soc.*, **94**, 1774 (1972).

(3) Address correspondence to this author at the Department of Pharmaceutical Chemistry, School of Pharmacy.

(4) A. E. Arbusov, *J. Russ. Phys. Chem. Soc.*, **42**, 395 (1910); *Chem. Abstr.*, **5**, 1397 (1911); A. E. Arbusov and K. V. Nikonorov. *Zh. Obshch. Khim.*, **18**, 2008 (1948); *Chem. Abstr.*, **43**, 3801 (1949).

(5) N. Collie, *J. Chem. Soc.*, **42**, 724 (1881); W. E. McEwen, K. F. Kumli, A. Blade-Font, M. Zanger, and C. A. Vanderwerf, *J. Amer. Chem. Soc.*, **86**, 2378 (1964).

(6) K. D. Berlin, T. Austin, M. Peterson, and M. Nagabhushanam, *Top. Phosphorus Chem.*, **1**, 17 (1965).

(7) O. Korpium, A. Lewis, J. Chickos, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4842 (1968).

(8) T. H. Chan and K. T. Nwe, *Tetrahedron Lett.*, 3601 (1973).

(9) A. Michaelis and T. Becker, *Ber.*, **30**, 1003 (1897).

(10) W. B. Farnham, R. K. Murray, Jr., and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 5809 (1970).

(11) G. M. Kosolopoff, *J. Amer. Chem. Soc.*, **72**, 4292 (1950).

(12) A. K. Hoffman and A. G. Tesch, *J. Amer. Chem. Soc.*, **81**, 5519 (1959).

(13) H. D. Zook and W. L. Gumby, *J. Amer. Chem. Soc.*, **82**, 1386 (1960).

(14) L. Horner and H. Hoffman, *Chem. Ber.*, **91**, 1583 (1958).

(15) T. L. Emmick and R. L. Letsinger, *J. Amer. Chem. Soc.*, **90**, 3459 (1968).

(16) In one experiment the conversion of methyl methylphenylphosphinate to benzylmethylphenylphosphine oxide (see Experimental Section) was carried out with the modification that the phosphinate was added to the $NaAlH_2(OCH_2CH_2OCH_3)_2$ solution, followed, after bubbling had ceased, with addition of benzyl chloride, to give a 43% yield of the phosphine oxide.

(17) Similarly, Chan and Nwe[8] have recently reported obtaining an anomalous product in an attempt to convert an open-chain phosphonate to a cyclic phosphinate.

(18) R. Tang and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 5645 (1969).

(19) N. K. Bliznyuk, Z. N. Kvasha, and A. F. Kolomiets, *J. Gen. Chem. USSR*, **37**, 1726 (1967).

(20) R. Kluger and F. H. Westheimer, *J. Amer. Chem. Soc.*, **91**, 4143 (1969).

(21) G. M. Kosolopoff and W. F. Huber, *J. Amer. Chem. Soc.*, **69**, 2020 (1947).

(22) Eastman Organic Chemical Bulletin, Vol. 42, No. 3, Kodak Publication No. JJ60-703, Rochester, N. Y., 1970, p 1.

(23) J. Meisenheimer, J. Casper, M. Höring, W. Lauter, L. Lichtenstadt, and W. Samuel, *Justus Liebigs Ann. Chem.*, **449**, 213 (1926).

(24) J. H. Davies, J. D. Downer, and P. Kirby, *J. Chem. Soc. C.*, 245 (1966).

(25) F. Fleissner, *Ber.*, **13**, 1665 (1880).

---

# Two Syntheses of Optically Pure (1*R*,2*R*)-1,2-Dimethylcyclopentane

W. C. M. C. Kokke* and Frans A. Varkevisser

*Department of Theoretical Organic Chemistry, University of Leiden, P.O. Box 75, Leiden, The Netherlands*

*Received January 19, 1973*

Three syntheses of *trans*-1,2-dimethylcyclopentane are described, *viz.*, two syntheses of (1*R*,2*R*)-1,2-dimethylcyclopentane (*trans*-**12** $\equiv$ **20**) and one of the racemic hydrocarbon. In the first synthesis (+)-pulegone was converted into (3*R*)-2,3-dimethylcyclopentanone, whose semicarbazone on Wolff reduction afforded a mixture of *trans*-**12** and *cis*-1,2-dimethylcyclopentane (*cis*-**12**). Formation of *cis*-**12** cannot be prevented because epimerization occurs during Wolff reductions of semicarbazones of $\alpha$-alkyl ketones. In the second synthesis the title compound (**20**) was prepared from resolved 4-cyclohexene-1,2-dicarboxylic acid. One of the steps in this route was the $LiAlH_4$ reduction of (1*R*,2*R*)-4-cyclohexene-1,2-dimethanol ditosylate. Use of *N*-methylmorpholine instead of THF as a solvent saved labor and increased the yield considerably. **20** was found to have $[\alpha]_D$ −51.5° ($CHCl_3$), in disagreement with a literature value of −35.2°. Racemic 2,3-dimethylcyclohexanone was used for the preparation of racemic **1** (and **2**) *via* 2,3-dimethylcyclopentanone.

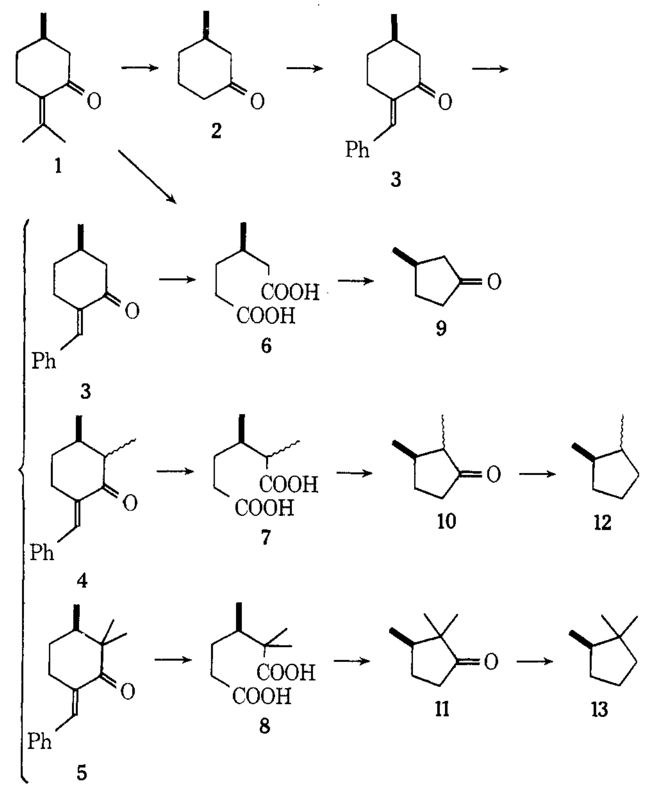
Recently optically active *trans*-1,2-dimethylcyclopentane has been discovered in a crude oil.[1] The specific rotation found was 5.8° but a theoretical estimate made many years ago in this department resulted in a much higher value.[2] Therefore it became of interest to synthesize this substance. When we had completed the synthesis from (+)-pulegone (Scheme I) we became aware of a paper by Hill, *et al.*,[3] which we had overlooked before. In their work on the absolute configuration of the antibioticum sarcomycin they also prepared *trans*-1,2-dimethylcyclopentane from (+)-pulegone, but by a route different from ours. Taking absolute values, the angle of rotation we found was 45% higher than the highest value reported by Hill.[3] Therefore it became of importance to follow a second route to the same substance. The absolute configurations of the compounds are depicted in the schemes.[4]

The route we chose was an obvious extension of a synthesis used by Walborsky, *et al.*,[5] for the determination of the absolute configuration of resolved 4-cyclohexene-1,2-dicarboxylic acid (Scheme II). Both syntheses led to compounds with nearly identical values of the angle of rotation. Therefore it can be stated that the specific rotation of optically pure (1*R*,2*R*)-1,2-dimethylcyclopentane is $[\alpha]_D$ −51.5° ($CHCl_3$).

**Dimethylcyclopentane from Pulegone (Scheme I).** Pulegone was hydrolyzed to give 3-methylcyclohexanone. The 6 position in this ketone was blocked by condensation with benzaldehyde, yielding $\alpha$-benzylidene ketone.[6] Methylation of this compound gave a mixture of mono- and dimethylated product, together with unreacted $\alpha$-benzylidene ketone. Oxidation of this mixture and decarboxylation of the acids obtained yielded a mixture of 3-methylcyclopentanone, 2,3-dimethylcyclopentanone, and 2,2,3-trimethylcyclopentanone. The ketones were separated by distillation. The semicarbazone of 2,3-dimethylcyclopentanone gave on Wolff reduction a mixture of optically active and meso dimethylcyclopentane (83.3:16.7). Corrected to chemical purity, *trans*-1,2-dimethylcyclopentane showed $[\alpha]_D$ −51.2° ($CHCl_3$). Hill[3] reported $[\alpha]_D$ −35.2° ($CHCl_3$). In the course of this investigation it became also of interest to study possible epimerization during Wolff-Kishner reductions. The results are described in the Experimental Section.

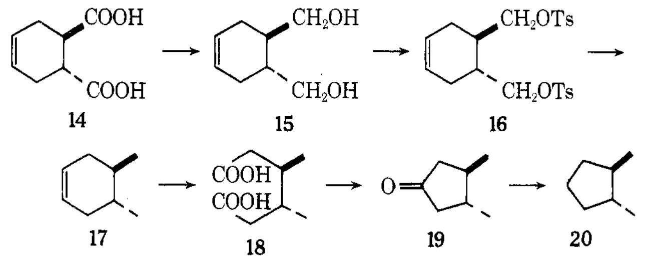
**Dimethylcyclopentane from 4-Cyclohexene-1,2-dicar-**

Scheme I



**boxylic Acid (Scheme II).** Two steps in Walborski's synthesis of 3,4-dimethylhexanedioic acid[5] could be improved.

Scheme II



We recommend *N*-methylmorpholine[7] as a solvent for the preparation of low molecular weight hydrocarbons by LiAlH$_4$ reduction of sulfonic esters because the hydrocarbon is easily obtained pure and in high yield when the reaction mixture is worked up by steam distillation.[8]

The resolution of 4-cyclohexene-1,2-dicarboxylic acid was reinvestigated. It was found that the best results are obtained when quinidine is used.

The angle of rotation of 3,4-dimethylcyclopentanone, $[\alpha]_D$ −241° (CHCl$_3$), appeared to be much higher in absolute value than was recorded by Carnmalm,[9] $[\alpha]_D$ −160° (CHCl$_3$); in contrast the angle of rotation of the corresponding semicarbazone was found to be in reasonable agreement with his results.

We also tried to resolve racemic 3,4-dimethylcyclopentanone with the Woodward reagent menthydrazide,[10] but our efforts were not rewarding.

## Experimental Section

Melting and boiling points are not corrected. Angles of rotation were determined with a Bendix-NPL photoelectric polarimeter, or with a Perkin-Elmer polarimeter (Model 141) at room temperature. Nmr spectra were recorded with a Jeol 100-MHz nmr spectrometer. The solutions used for the nmr measurements contained 5–15% (by weight) of the solute. Nmr shifts are with respect to TMS. Concentrations are given in grams of solute per 100 ml of solution. New compounds gave satisfactory elemental analyses.

**Pulegone (1)** was isolated from pennyroyal oil (Dragoco, Holzminden, West Germany) as the sodium bisulfite adduct,[11] prepared at pH 7. After distillation over an efficient column it had $[\alpha]_D$ +23.8° (*c* 2.8, MeOH); $[\alpha]_D$ +24.1° (*c* 1.5, CHCl$_3$) [lit. $[\alpha]_D$ + 22.8° (*c* 20, CHCl$_3$);[12] $[\alpha]_D$ +31.6° (*c* 0.1, CHCl$_3$)].[3] This latter value seems to be erroneous.

**(3*R*)-3-Methylcyclohexanone (2)**, $[\alpha]_D$ +8.60° (*c* 1.9, MeOH), was prepared by hydrolysis of **1** in 65% yield.[13] Nmr data of **2** (CDCl$_3$) include a doublet at $\delta$ 1.02 ppm ($J$ = 5.93 Hz, methyl group).

**(3*R*)-3-Methyl-6-benzylidenecyclohexanone (3)** was prepared by Wallach[14] by condensation of **2** with benzaldehyde in alcohol. To prevent the formation of dibenzylidene ketone it is convenient to use water instead of alcohol.[15] A mixture of **2** (152 g), benzaldehyde (152 g), and 4% KOH solution (1520 g) was vigorously boiled for 3 hr. After neutralization the unreacted ketone and aldehyde were removed by steam distillation. The yellow residue in the steam flask crystallized on cooling in ice. The crude product was distilled and the distillate was recrystallized from petroleum ether to give 208 g (72.5%) of **3**, mp 61.5–63.0° (lit.[14] mp 62°), $[\alpha]_D$ −151.6° (*c* 0.45, MeOH), after recrystallization from THF-hexane. Racemic **3**, prepared in the same manner from racemic **2** (Fluka), had mp 38–41°. Nmr data of **3** (CDCl$_3$) include a quartet at $\delta$ 7.48 ppm ($J_1$ = 2.61 Hz, $J_2$ = 1.70 Hz, vinylic proton), a multiplet at $\delta$ 7.34 ppm (5 aromatic protons), and a doublet at $\delta$ 1.00 ppm ($J$ = 6.07 Hz, methyl group).

**Methylation of 3.** After various attempts on the basis of the procedure of Johnson[16] for the methylation of 2-methyl-6-benzylidenecyclohexanone it was found that the following procedure gave the highest yield of distillable reaction product. In a 2-l. flask, provided with an efficient stirrer,[17] potassium (23.0 g) was dissolved in *tert*-butyl alcohol (1.5 l., dried on sieves) under nitrogen. This solution was placed in an ice–salt mixture, and when it was cooled to 22° a solution of **3** (100 g) in methyl iodide (213 g) was added at once. The temperature then rose to 31–34°. When the mixture was cooled to 25° the bath was removed and the solution was refluxed for 1.5 hr; then the solvent was removed with suction and water and ether were added to the residue. Part of the reaction product crystallized. These crystals had mp 101.0–102.5°, $[\alpha]_D$ −70.5° (*c* 0.4, MeOH), after recrystallization from hexane and ether. It was found to be (mass spectroscopy) almost pure (3*R*)-2,2,3-trimethyl-6-benzylidenecyclohexanone (**5**), the impurity being (3*R*)-2,3-dimethyl-6-benzylidenecyclohexanone (**4**). The part of the reaction product which dissolved in ether was worked up by distillation. Yield (distillate + crystals) 68 g. Mass spectroscopy showed **5** to be the main product; there was more starting material **3** in the mixture than monomethylated product **4**, which was not surprising because Conia[18] has shown an $\alpha$-alkyl ketone to be more reactive in alkylation than a ketone without an $\alpha$-alkyl group. Nmr data of **5** (CDCl$_3$) include a multiplet at $\delta$ 7.31 ppm (5 aromatic protons + 1 vinylic proton), complex multiplets at $\delta$ 2.45–3.13 ppm (2 protons) and at $\delta$ 1.37–2.05 ppm (3 protons), singlets at $\delta$ 1.20 and 1.03 ppm (methyl groups), and a doublet at $\delta$ 0.99 ppm ($J$ = 6.52 Hz, methyl group).

**Oxidation of the Methylation Products.** The procedure of Johnson[19] for the oxidation of *cis*-2-benzylidene-9-methyldecalone was used. In our case the isolation of the products was simple because the methyl-substituted adipic acids **6**, **7**, and **8** are much more soluble in water than benzoic acid, and most of the latter could be removed by filtration. **3** (450 g) gave after methylation and oxidation a mixture of **6**, **7**, and **8** (175.5 g, a dark brown oil).

**A mixture of cyclopentanones 9, 10,** and **11** (74.65 g) was prepared by heating the crude mixture of dicarboxylic acids **6**, **7**, and **8** (175.5 g) with Ba(OH)$_2$.[20] The ketones were separated by distillation, using a Nester-Faust spinning band column, to yield **9**, 7.8 g, bp 106° (175 mm); **10**, 3.6 g, bp 115–117° (175 mm); **11**, 20.4 g, bp 124–145° (175 mm).

**(3*R*)-3-Methylcyclopentanone (9)**, bp 144–146°, $[\alpha]_D$ +154.8° (*c* 0.6, MeOH), was prepared by ozonization[21] of **1** to give (3*R*)-3-methylhexanedioic acid (**6**), decarboxylation[20] with Ba(OH)$_2$ and purification *via* the semicarbazone, mp 177.5–178.5° after recrystallization (three times) from alcohol, $[\alpha]_D$ +44.7° (*c* 0.82, CHCl$_3$) (lit.[22] mp 185–186°). Corroborating Tétry's result[6] we found for the methylcyclopentanone fraction of the distillation of the mixture of **9**, **10**, and **11** physical constants in agreement with the data of this reference compound, prepared by ozonization of **1** etc. Nmr data of **9** (CDCl$_3$) include a doublet at $\delta$ 1.13

ppm (*J* = 6.17 Hz, methyl group). Nmr data of 9 semicarbazone ($CF_3COOH$) include a doublet at $\delta$ 1.25 ppm (*J* = 5.09 Hz, methyl group).

**(3*R*)-2,2,3-Trimethylcyclopentanone (11)**, bp 162–164°, $[\alpha]_D$ +79.6° (*c* 0.48, MeOH), which has not been described before, was obtained by purification of the corresponding fraction of the distillation of the mixture of **9**, **10**, and **11** as the semicarbazone, $[\alpha]_D$ +24.1° (*c* 0.5, $CHCl_3$). This semicarbazone (recrystallized from alcohol) turns yellow at 210°; on rapid heating mp 216–218° is found. Nmr data of **11** ($CDCl_3$) include singlets at $\delta$ 0.81 and 1.00 ppm (methyl groups) and a doublet at $\delta$ 1.00 ppm (*J* = 6.45 Hz, methyl group). Nmr data of **11** semicarbazone ($CF_3COOH$) include singlets at $\delta$ 1.46 and 1.26 ppm (methyl groups) and a doublet at $\delta$ 1.10 ppm (*J* = 6.06 Hz, methyl group).

**(2*R*)-1,1,2-Trimethylcyclopentane (13).** Using the conditions of Kohlrausch[23] for the reduction of 3-methylcyclopentanone semicarbazone, the semicarbazone of **11** gave **13** on Wolff reduction. We always isolated the reaction products of Wolff reductions by steam distillation. The hydrocarbon layer of the distillate was then shaken with an equal volume of concentrated $H_2SO_4$, washed with water, dried on sodium, and distilled from sodium. **13** thus prepared was found to be contaminated with 2.32 mol % of (−)-**12** and 0.48 mol % of *meso*-**12** (glc, SE-30 column), yield 66%. **13** was purified by preparative glc (OV-210 column). Pure **13** showed $[\alpha]_D$ −7.74° (*c* 1.2, $CHCl_3$). Nmr data of **13** ($CDCl_3$) include two singlets at $\delta$ 0.72 and 0.94 ppm (methyl groups) and a doublet at $\delta$ 0.82 ppm (*J* = 6.30 Hz, methyl group).

**(1*R*,2*R*)-1,2-Dimethylcyclopentane [(−)-12].** The semicarbazone of **10**, prepared from the corresponding fraction of the distillation of **9**, **10**, and **11**, after recrystallization from alcohol, had $[\alpha]_D$ +94.1° (*c* 0.43, $CHCl_3$), mp 200–202°; the crystals turn yellow between 195 and 200°. The chemical purity of this semicarbazone was not 100% because on reduction[23] it gave (−)-**12**, contaminated with 16.3 mol % of *meso*-**12**, 1.52 mol % of **13**, and 0.40 mol % of methylcyclopentane (glc, SE-30 column) in 59% yield. This impure (−)-**12** showed $[\alpha]_D$ −41.9° (*c* 1.3, $CHCl_3$). Corrected to chemical purity (−)-**12** had $[\alpha]_D$ −51.2° ($CHCl_3$) [lit.[3] $[\alpha]_D$ −35.2° (*c* 0.2, $CHCl_3$)].

**Racemic *trans*-4-Cyclohexene-1,2-dicarboxylic Acid (Racemic 14).** In a refrigerator at −15° an autoclave was filled with diethyl fumarate (364 g, Merck) and butadiene (272 ml, excess). The mixture was kept at 140–150° for 24 hr,[24] yield 90% after distillation. This Diels–Alder adduct was saponified[5] to give racemic **14**, mp 166.0–168.5° after recrystallization from water (lit.[25] mp 172°).

**Resolution of *trans*-4-Cyclohexene-1,2-dicarboxylic Acid (14).** Walborsky's procedure[5] for the resolution of **14** is cumbersome, and that was for us an inducement to reinvestigate the resolution. Bases used were ephedrine, quinine,[26] strychnine, brucine, cinchonidine, cinchonine, and quinidine. The latter gave the best results.

**A. Preparation of the Quinidine Salt.** In a 1-l. flask were refluxed until homogeneous anhydrous quinidine (Brocades, The Hague, The Netherlands, or Lamers & Indeman, Bois-le-Duc, The Netherlands) (81 g), **14** (21.2 g) (2 mol of base to 1 mol of acid), and alcohol (500 ml). In case the mixture was not homogeneous after 30 min, it was filtered. The alcohol was removed with a rotatory evaporator, and to the residue were added water (500 ml) and alcohol (150 ml); on heating a clear solution was obtained which was left to cool. Every time it became turbid, the turbidity was removed by the addition of some alcohol (about 60 ml of alcohol was necessary). Seeding is recommended. After standing for 2 days at room temperature the crystals were removed by filtration and recrystallized. We used water (6.5 l.) and alcohol (2.5 l.) for the recrystallization of quinidine salt from **14** (292 g) and quinidine (1120 g), seeded the mixture and left it to crystallize for 2 days, and obtained 486.25 g of salt.

**B. Regeneration of the Quinidine Salt.** Recrystallized quinidine salt (108 g) was stirred with $CHCl_3$ (340 ml) and a solution of NaOH (20 g) in water (120 ml) for 1.5 hr. Then the $CHCl_3$ layer containing the alkaloid was separated from the alkaline layer containing the sodium salt of (1*R*,2*R*)-**14**. The latter solution was acidified with concentrated HCl, and the dicarboxylic acid was isolated by ether extraction. From quinidine salt (486.25 g from 292 g of racemic **14**) was thus obtained (1*R*,2*R*)-**14** (98.0 g, 67.1% of one antipode), $[\alpha]_D$ −161° (*c* 0.5, absolute EtOH) [lit.[5] $[\alpha]_D$ −161° (*c* 2.7, EtOH).

The mother liquor of the resolution of **14** (292 g) with anhydrous quinidine (1120 g) was evaporated to dryness to give an oil, which was treated with NaOH solution and $CHCl_3$, etc., as indicated above to give optically impure (1*S*,2*S*)-**14** (166.5 g), $[\alpha]_D$ +90° (*c* 0.5, absolute EtOH).

Quinidine can be recovered in high yield by evaporating its $CHCl_3$ solution to dryness and recrystallizing the residue from MeOH (~30 g of alkaloid to 1 l. of MeOH).

**(1*R*,2*R*)-4-Cyclohexene-1,2-dimethanol (15)** was prepared by $LiAlH_4$ reduction of (1*R*,2*R*)-**14** in THF in 94% yield.

**(1*R*,2*R*)-4-Cyclohexene-1,2-dimethanol ditosylate (16)** was prepared from **15** with A.R. *p*-toluenesulfonyl chloride in A.R. pyridine, yield 84% after recrystallization from alcohol, mp 107–108°, $[\alpha]_D$ −43.7° (*c* 1.1, $CHCl_3$).

**(1*R*,2*R*)-1,2-Dimethyl-4-cyclohexene (17).** A mixture of *N*-methylmorpholine (Merck or EGA, 1630 ml) and $LiAlH_4$ (77 g) was heated to 60°. Caution: this starting temperature is necessary because **16** is not reduced at room temperature (possibly as a consequence of the low solubility of **16** in cold *N*-methylmorpholine). Then **16** (395 g) was added in few-gram portions at a time at such a rate that the temperature was kept at <75°. Because the mixture became viscous, an efficient stirrer[17] was necessary. After the completion of the addition the mixture was kept at 70° for 1.5 hr, then heated to 100°, left to cool, and worked up by careful addition of water (500 ml) and steam distillation. The upper layer of the distillate was washed with dilute HCl and water, and dried on sodium, yield 83.3 g (84.5%), $[\alpha]_D$ −143.8° (*c* 0.52, $CHCl_3$) [lit.[5] $[\alpha]_D$ −138° (*c* 2.58, $CHCl_3$).

Nmr data of **17** ($CDCl_3$) include doublets at $\delta$ 5.61 ppm (*J* = 2.80 Hz, 2 vinylic protons) and at $\delta$ 0.93 ppm (*J* = 5.40 Hz, 2 methyl groups).

**(3*R*,4*R*)-3,4-Dimethylhexanedioic acid (18)** was prepared from **17** using Cope's procedure[27] for the oxidation of bicyclo[6.1.0]nonene. The crude product, obtained in 57.3% yield, was an oil which solidified on standing.

**(3*R*,4*R*)-3,4-Dimethylcyclopentanone (19).** Crude **18** was decarboxylated[20] with $Ba(OH)_2$ to give crude **19** in 88.8% yield. After purification as the semicarbazone, it had mp 205–208° (yellow melt); $[\alpha]_D$ −73.4° (*c* 0.92, $CHCl_3$) [lit.[9] mp 203.0–204.5°, $[\alpha]_D$ −76° (*c* 0.74, $CHCl_3$)]. **19** had $[\alpha]_D$ −241° (*c* 0.46, $CHCl_3$) [lit.[9] $[\alpha]_D$ −160° (*c* 0.7, $CHCl_3$)], *g* factor 0.152 (cyclohexane).

Nmr data of **19** ($CDCl_3$) include quartets at $\delta$ 2.44 ppm ($J_1$ = 22.3, $J_2$ = 11.3 Hz, two protons) and at $\delta$ 1.82 ppm ($J_1$ = 21.3, $J_2$ = 10.0 Hz, 4 protons) and a doublet at $\delta$ 1.13 ppm (*J* = 5.55 Hz, 2 methyl groups).

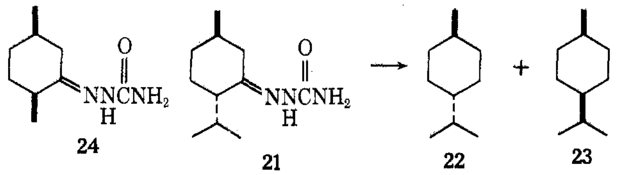
Nmr data of **19** semicarbazone ($CF_3COOH$) include doublets at $\delta$ 1.23 ppm (*J* = 5.37 Hz, 2 methyl groups) and at $\delta$ 3.29 ppm (*J* = 20.5 Hz, 2 protons), a singlet at $\delta$ 1.98 ppm (2 protons), and a quintet at $\delta$ 2.59 ppm ($J_1$ = 19.4, $J_2$ = $J_3$ = 9.7 Hz, 2 protons).

**(1*R*,2*R*)-1,2-Dimethylcyclopentane (20)** was prepared by reduction[23] of the semicarbazone of **19** in 50% yield: $[\alpha]_D = [\alpha]_{589}$ −51.5°; $[\alpha]_{578}$ −53.6°; $[\alpha]_{546}$ −61.0°; $[\alpha]_{436}$ −102.7°; $[\alpha]_{365}$ −158.0° (*c* 1.1, $CHCl_3$) [lit.[3] $[\alpha]_D$ −35.2° (*c* 0.1, $CHCl_3$)]. Nmr data of **20** ($CDCl_3$) include a doublet at $\delta$ 0.95 ppm (*J* = 5.19 Hz, methyl groups).

**Attempted Resolution of Racemic 19.** Racemic **19**, prepared from racemic **14** in the same manner as (3*R*,4*R*)-**19**, was treated with "menthydrazide"[10] under conditions as used for the preparation of the corresponding derivative of $\alpha$-ionone.[28] The solution was evaporated to dryness, and the residue was recrystallized from *n*-heptane. Neither melting point nor angle of rotation changed on further recrystallization. Regeneration of the derivative, mp 124.5–126.0°, $[\alpha]_D$ −63.0° (*c* 1.25, MeOH), after the third recrystallization then gave the ketone, small negative Cotton effect around 290 nm, *g* factor 0.0097 (cyclohexane), *i.e.*, optical purity 6.4%. The semicarbazone of this ketone gave optically impure **20**, $[\alpha]_D$ −3.77° (*c* 1.25, $CHCl_3$), on reduction.[23]

**Epimerization during the Wolff Reduction.** As already mentioned, Wolff reduction of the semicarbazone of 2,3-dimethylcyclopentanone yielded a mixture of (−)- and *meso*-dimethylcyclopentane. We found it worthwhile to investigate whether the observed cis–trans ratio was due to careless purification of the semicarbazone, or to epimerization during the reduction, or both. Epimerization during Wolff–Kishner reductions has been frequently observed,[29] but in those cases a hydrazone was decomposed without intermediate purification; so it has not been established whether epimerization occurred during the preparation of the hydrazone or during its decomposition. Epimerization clearly is a limitation of the Wolff reduction, for we found that menthone semicarbazone (**21**), which is easily obtained free from its epimer isomenthone semicarbazone (**24**),[30] gave a 1:1 mixture of *cis*- and *trans*-*p*-menthane (Scheme III) on reduction.[23] After this experiment it was not surprising that the semicarbazone of racemic

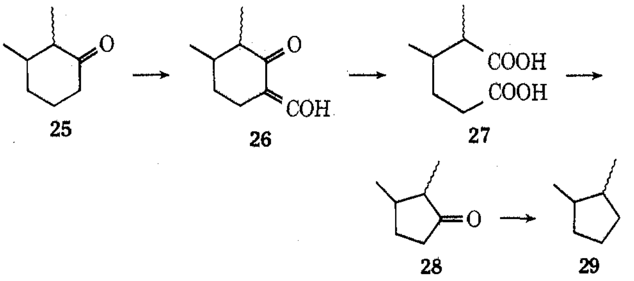
Scheme III



2,3-dimethylcyclopentanone gave on reduction[23] the same cis-trans ratio as was found when working with the corresponding optically active compound.

Racemic 2,3-dimethylcyclopentanone was prepared according to Scheme IV.[31]

Scheme IV



**Menthone Semicarbazone (21).** Menthone, prepared by oxidation[32] of (−)-menthol (Fluka), was converted into its semicarbazone, mp 186–189° (lit.[30] mp 188°), after two recrystallizations from alcohol. Reduction[23] then gave a 1:1 mixture of two compounds (glc, SE-30 column), which were identified as 22 and 23 because the nmr spectrum of this mixture was a superposition of the nmr spectra of pure 22 and 23, and because of gas chromatographic identification. Nmr data of 21 ($CF_3COOH$) include a doublet at $\delta$ 1.15 ppm ($J$ = 5.8 Hz, 3 methyl groups). The nmr spectrum produces no evidence for the presence of a large percentage of 24 in 21.

*trans-p*-**Menthane (22)**, for use as a reference, was made available by Mr. J. C. A. Windhorst in this department. He prepared sterically pure 22 from menthyl tosylate[33] by $LiAlH_4$ reduction in *N*-methylmorpholine.[7] Nmr data of 22 ($CDCl_3$) include a multiplet at $\delta$ 1.68 ppm (4 protons), which looks like a doublet ($J$ = 6.4 Hz) under low resolution, and a complex multiplet at $\delta$ 0.70–1.05 ppm (16 protons). Two peaks of this latter multiplet have a high intensity, which suggests that these peaks are caused by the three methyl groups of 22 ($\delta$ 0.85 ppm. $J$ = 6.70 Hz).

*cis-p*-**Menthane (23)** was obtained for use as a reference. Redistilled (+)-limonene (Fluka) was hydrogenated [125 g of limonene, 125 g of ethanol or methanol, 1.6 g of Pd/C (10% Pd, Fluka), 150 atm $H_2$, no external heating (the reaction is exothermic[34])] to give a mixture of three components. Part of this mixture was carefully distilled using a Nester-Faust spinning band column (20 cm/1 ml of distillate per hour). Boiling points of the components were in the order 22 < 23 < unknown compound. The molar ratio of 22 and 23 in the mixture after the hydrogenation was 75:25; about 10% of this mixture (an average of two hydrogenation experiments) consisted of the unknown compound. A comparison of the mass spectrum of this unknown compound with literature data[35] indicated that this compound probably was either *p*- or *m*-cymene. Nmr data supported the *p*-cymene structure: a singlet at $\delta$ 7.14 ppm (4 aromatic protons), a quintet at $\delta$ 2.78 ppm ($J_1$ = 13.0 Hz, $J_2 = J_3$ = 6.5 Hz, proton attached to the quaternary carbon atom of the isopropyl group), a singlet at $\delta$ 2.30 ppm (methyl group), and a doublet at $\delta$ 1.22 ppm ($J$ = 7.20 Hz, two equivalent methyl groups). Note: *p*-cymene was not an impurity of the limonene used for the hydrogenation (glc, Carbowax column). Nmr data of 23 ($CDCl_3$) [freed from 22 and *p*-cymene by preparative glc (SE-30 column)] include a complex multiplet at $\delta$ 1.39 ppm (11 protons) and doublets at $\delta$ 0.91 ppm ($J$ = 6.63 Hz, 1 methyl group) and at $\delta$ 0.86 ppm ($J$ = 6.36 Hz, 2 equivalent methyl groups).

**2,3-Dimethylcyclohexanone (25).** Chromic acid oxidation[36] of 2,3-dimethylcyclohexanol (Aldrich) gave 25 in 94% yield.

**2,3-Dimethyl-6-hydroxymethylenecyclohexanone (26).** A procedure for the preparation of hydroxymethylenecyclohexanone[37] was used to give 26 in 70.7% yield.

**2,3-Dimethylhexanedioic Acid (27).**[31] Because 1 can be ozonized to give 6 in high yield,[21] it was worthwhile trying to prepare 27 from 26 in the same manner. 26 (55.0 g) dissolved in $CCl_4$ (300 ml) and cooled in ice was ozonized. To the solution of the ozonide, water (300 ml) was added, and while vigorously stirring the $CCl_4$ was distilled off. The aqueous solution, made alkaline, was extracted with ether, then made acid, and 27 was isolated by ether extraction. From 26 (159.9 g) was obtained in this manner crude 27 (149 g, 82.4%) as an orange-red oil.

**2,3-Dimethylcyclopentanone (28).** Crude 27 (149 g) was decarboxylated[20] with $Ba(OH)_2$ to give pure 28 (62.0 g, 64.6%) after distillation. It was shown by glc that 28 was an 84:16 mixture of two components. Nmr data of *trans*-28 (main component of this mixture) include doublets at $\delta$ 1.16 ppm ($J$ = 5.28 Hz, methyl group) and at $\delta$ 1.05 ppm ($J$ = 6.43 Hz, methyl group). Nmr data of *cis*-28 (minor component of the mixture) include doublets at $\delta$ 0.94 ppm ($J$ = 6.22 Hz, methyl group) and at $\delta$ 0.97 ppm ($J$ = 6.62 Hz, methyl group).

**1,2-Dimethylcyclopentane (29).** 28 was converted into its semicarbazone. Part of the crude semicarbazone was kept; the remainder was recrystallized three times from *n*-butyl alcohol. The purified semicarbazone had mp 210.0–214.5° dec on rapid heating. Reduction[23] of both crude and purified semicarbazone gave a mixture of *cis*-29 (16.5%) and *trans*-29 (83.5%). Nmr data of three times recrystallized 28 semicarbazone ($CF_3COOH$) include doublets at $\delta$ 1.25 ppm ($J$ = 6.00 Hz, methyl group), $\delta$ 1.46 ppm ($J$ = 6.55 Hz, methyl group) and $\delta$ 1.09 ppm ($J$ = 7.0 Hz). The intensity of this latter doublet is ~2% of the intensity of the other doublets, which suggests that the sterical purity of 28 semicarbazone used for the reduction was ~98%.

**Acknowledgment.** One of the authors (Kokke) is indebted to the Netherlands Organization for the Advancement of Pure Research (Z. W. O.) for the sponsoring of this work. A NATO grant for the purchase of quinidine is gratefully acknowledged. The authors owe their gratitude to Professor L. J. Oosterhoff, who proposed to do the work reported in this paper, and to Professor H. Wynberg (Groningen) for reading and commenting on the manuscript.

**Registry No.**—**1,** 89-82-7; (3*R*)-**2,** 13368-65-5; (±)-**2,** 625-96-7; (3*R*)-**3,** 7577-00-6; (±)-**3,** 51096-05-0; **5,** 50987-10-5; **6,** 623-82-5; **9,** 6672-30-6; **9** semicarbazone, 50987-11-6; **10,** 51096-06-1; **10** semicarbazone, 50986-97-5; **11,** 50987-12-7; **11** semicarbazone, 50987-13-8; (−)-**12,** 13012-46-9; **13,** 50987-14-9; (±)-**14,** 51096-07-2; (1*R*,2*R*)-**14,** 50987-15-0; (1*S*,2*S*)-**14,** 51096-08-3; **15,** 15679-28-4; **16,** 20246-03-1; **17,** 51025-14-0; **18,** 51063-79-7; (±)-**19,** 50987-16-1; (3*R*,4*R*)-**19,** 51096-09-4; (3*R*,4*R*)-**19** semicarbazone, 50987-17-2; **21,** 51051-09-3; **22,** 1678-82-6; **23,** 6069-98-3; **27,** 50986-96-4; **28,** 14845-37-5; **28** semicarbazone, 50986-97-5.

## References and Notes

(1) E. D. Engelhardt, Koninklijke/Shell Exploration & Production Laboratory, Rijswijk (Z. H.), The Netherlands, to be published.
(2) R. Deen, unpublished results.
(3) R. K. Hill, P. J. Foley, and L. A. Gardella, *J. Org. Chem.*, **32**, 2330 (1967).
(4) The absolute configuration of the compounds in this paper follows from the work in ref 3 and 5.
(5) H. M. Walborsky, L. Barash, and T. C. Davis, *Tetrahedron*, **19**, 2333 (1963).
(6) For a proof of the structure of this condensation product see L. Tétry, *Bull. Soc. Chim. Fr.*, [3] **27**, 302 (1902).
(7) We borrowed the idea to use *N*-methylmorpholine from R. R. Sauers and J. A. Wittle, *J. Org. Chem.*, **34**, 3579 (1969).
(8) For representative yield in $LiAlH_4$ reductions of sulfonates in THF or ether to give simple hydrocarbons, *cf.* ref 3 and 5 and J. F. Bussert, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Amer. Chem. Soc.*, **78**, 6076 (1956).
(9) B. Carnmalm, *Acta Chem. Scand.*, **10**, 477 (1956); *Chem. Ind. (London)*, 1093 (1956); *Ark. Kemi*, **15**, 215 (1960).
(10) R. B. Woodward, T. P. Kohman, and G. C. Harris, *J. Amer. Chem. Soc.*, **63**, 120 (1941).
(11) E. Gildemeister and F. Hoffmann, "Die Etherischen Oele," 4, Aufl. (4th ed), Akademie-Verlag, West Berlin, 1963, Bd IIIc, p 228.
(12) Y.-R. Naves, *Helv. Chim. Acta*, **26**, 162 (1943).
(13) H. Rupe, *Justus Liebigs Ann. Chem.*, **436**, 202 (1924).
(14) O. Wallach, *Ber.*, **29**, 1596 (1896).
(15) R. Poggi and P. Saltini, *Gazz. Chim. Ital.*, **62**, 680 (1932).
(16) W. S.Johnson, *J. Amer. Chem. Soc.*, **65**, 1320 (1943).
(17) A Vibro-mix stirrer was used (A. G. für Chemie-Apparatebau, Zürich, Switzerland).
(18) F. G. Gault, J. E. Germain, and J.-M. Conia, *Bull. Soc. Chim. Fr.*, 1064 (1957).

(19) W. S. Johnson, *J. Amer. Chem. Soc.*, **66**, 216 (1944).

(20) J. F. Thorpe and G. A. Kon, "Organic Syntheses," Collect. Vol. I, 2nd ed, Wiley, New York, N. Y., 1961, p 192.

(21) H. Neresheimer, Dissertation Kiel, 1907.

(22) M. Godchot, G. Cauquil, and R. Cales, *Bull. Soc. Chim. Fr., Ser. 5*, **6**, 1358 (1939).

(23) K. W. F. Kohlrausch, A. W. Reiz, and W. Stockmair, *Z. Physik. Chem. (Leipzig)*, **B32**, 234 (1936). We found it convenient to carry out the reduction in a small autoclave instead of in a sealed tube.

(24) For references to other procedures for this Diels–Alder reaction see A. S. Onishchenko, "Diene Synthesis," Israel Program for Scientific Translations, Jerusalem, 1964, p 111.

(25) K. Alder and M. Schuhmacher, *Justus Liebigs Ann. Chem.*, **564**, 96 (1949).

(26) G. Abati and C. De Horatiis, *Gazz. Chim. Ital.*, **39**(1), 553 (1909).

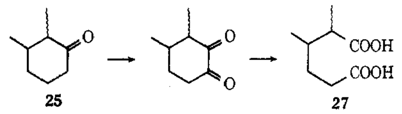
(27) A. C. Cope, S. Moon, and C. H. Park, *J. Amer. Chem. Soc.*, **84**, 4843 (1962).

(28) Y.-R. Naves, *Helv. Chim. Acta*, **30**, 769 (1947).

(29) C. Djerassi, T. T. Grosnickle, and L. B. High, *J. Amer. Chem. Soc.*, **78**, 3166 (1950); W. S. Johnson, A. van der Gen, and J. J. Swoboda, *ibid.*, **89**, 170 (1967); W. S. Johnson, G. A. Harbert, and R. D. Stipanovic, *ibid.*, **90**, 5279 (1968); N. S. Crossley and H. B. Henbest, *J. Chem. Soc.*, 4413 (1960); R. K. Hill, J. G. Martin, and W. H. Stouch, *J. Amer. Chem. Soc.*, **83**, 4006 (1961).

(30) M. Delépine and M. Badoche, *C. R. Acad. Sci.*, **228**, 19 (1949); M. Badoche, *Ann. Chim. (Paris)*, **4**, 449 (1949); *Ind. Parfum.*, **10**, 180, 238 (1955).

(31) A plan for the preparation of **27** by $SeO_2$ oxidation of **25** followed by $H_2O_2$ oxidation of the diketone obtained (see below) was rejected because cyclohexanedione can be prepared from cyclohexanone by $SeO_2$ oxidation only in low yield based on ketone: 10.4% [C. C. Hach, C. V. Banks, and H. Diehl, *Org. Syn.*, **32**, 35 (1952)], 19.6% (A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., New York, N. Y., 1957, p 975).



**25** **27**

(32) E. Beckmann, *Justus Liebigs Ann. Chem.*, **250**, 322 (1889).

(33) E. R. Alexander and A. G. Pinkus, *J. Amer. Chem. Soc.*, **71**, 1787 (1949).

(34) W. F. Newhall, *J. Org. Chem.*, **23**, 1274 (1958).

(35) A. Cornu and R. Massieu, "Compilation of Mass Spectral Data," Heyden and Sons Ltd., London, 1966, Part B, p 42.

(36) A. Killen Mabeth and J. A. Mills, *J. Chem. Soc.*, 709 (1945).

(37) C. Ainsworth, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1962, p 536.

---

# Unsaturated Organosilicon Heterocycles

Karl E. Koenig, Raymond A. Felix, and William P. Weber*

*Department of Chemistry, University of Southern California, Los Angeles, California 90007*

*Received October 23, 1973*

The photolytic addition of $H_2S$ to dimethyldiallylsilane yields 1,1-dimethyl-1-sila-5-thiacyclooctane. Oxidation of the sulfide yields the corresponding sulfone, which can be directly converted *via* a modified Ramberg–Backlund reaction into 1,1-dimethyl-1-sila-4-cycloheptene. This reaction sequence has also been used to prepare 1,1-diphenyl-1-sila-4-cycloheptene from diphenyldiallylsilane. An alternate synthesis of 1,1-dimethyl-1-sila-4-cycloheptene and 1,1-diphenyl-1-sila-4-cycloheptene is also reported.

We have been concerned with improving synthetic routes to seven- and eight-membered organosilicon heterocycles.[1] The modified acyloin reaction[2,3] on suitable organosilicon diesters has been the best entry into these ring systems. For instance, dimethyl 4,4-dimethyl-4-sila-1,7-heptanedioate can be cyclized to 1,1-dimethyl-4,5-bis(trimethylsiloxy)-1-sila-4-cycloheptene in good yield.[1] However, two problems remain. One is that the synthesis of suitable organosilicon diester substrates for the acyloin reaction often involves many steps from commercially available dichlorosilanes. The second is that the heterocycle formed after hydrolysis of the trimethylsilyl ether protecting groups contains an $\alpha$-hydroxy ketone functionality which requires several steps to transform into a carbon–carbon double bond. To solve these problems we have developed a new synthetic entry into these heterocyclic systems.

There are several recent examples of the use of organosulfur compounds to establish both carbon–carbon single[4,5] and carbon–carbon double bonds. The conversion of a sulfide to a carbon–carbon double bond by a double Stevens rearrangement is one example from the latter category.[6,7] The Ramberg–Backlund reaction, which converts an $\alpha$-chloro sulfone into an alkene, is another.[8-12]

We decided to attempt to prepare cyclic compounds containing silicon and sulfur by addition of $H_2S$ to dimethyldiallylsilane and to diphenyldiallylsilane owing to the ready availability of these organosilicon compounds.[1,13] We find that $H_2S$ adds to dimethyldiallylsilane in a dilute pentane solution at −78° upon irradiation through a quartz photolysis well with a 450-W medium-pressure Hanovia lamp to form 1,1-dimethyl-1-sila-5-thiacyclooctane in 25% isolated yield.[14] Similarly, $H_2S$ adds to diphenyldiallylsilane upon irradiation at −78° to form 1,1-diphenyl-1-sila-5-thiacyclooctane in 10% isolated yield.

This is remarkable considering the problems involved in synthesis of medium-sized ring compounds from alicyclic precursors. For instance, closure of $\omega$-chloro sulfides $RS(CH_2)_nCl$ to form cyclic sulfonium salts fails for $n$ = 6–11.[15] The fact that both C–Si (1.87 Å) and C–S (1.82 Å) bonds are longer than C–C single bonds may make formation of 1,1-dimethyl-1-sila-5-thiacyclooctane more like cyclization of a nine-membered than an eight-membered all-carbon ring system.[16] Ring closure reactions are usually most difficult to accomplish for ring sizes from $C_9$ to $C_{11}$. For example, the Ziegler ring closure reaction of $\alpha,\omega$-dinitriles with base fails for rings from $C_9$ to $C_{11}$ even under high dilution conditions.[17]

Our yields are also remarkable considering the variety of competing pathways open to a thiyl radical intermediate. A thiyl radical must be involved to account for the anti-Markovnikov sense of the addition, since the addition of $H_2S$ to diallyl ether under ionic conditions yields 2,6-dimethyl-1,4-thioxane.[18,19] Clearly the intramolecular radical addition of the S–H bond of dimethylallyl-3-mercaptopropylsilane (**1**) to the carbon–carbon double bond of the allyl group is critical to the success of the reaction. To substantiate this point we prepared **1** independently by the photochemical addition of thiolacetic acid to dimethyldiallylsilane followed by hydrolysis of the thiolace-