Journal of Organometallic Chemistry, 63 (1973) C5–C6
© Elsevier Sequoia S.A , Lausanne – Printed in The Netherlands

Preliminary communication

Optically active bis(methyl-1-naphthylphenylgermyl)mercury

V.M. VODOLAZSKAYA, B.V. FEDOT'EV, Yu I. BAUKOV, O.A. KRUGLAYA and N.S VYAZANKIN
Institute of Chemistry of the Academy of Sciences of the USSR, Gorky (U.S.S.R.) and Chemistry Department, M V. Lomonosov State University, Moscow (U.S.S R.)

(Received October 9th, 1973)

SUMMARY

(–)-Bis(methyl-1-naphthylgermyl)mercury has been synthesised through the action of optically active (+)-methyl-1-naphthylphenylgermane on di-tert-butylmercury. The germylmercury compound enters into an exchange reaction with $Hg(CH_2COOMe)_2$. This includes a demercuration step and is stereospecific.

The reaction of (+)-methyl-1-naphthylphenylgermane (I) with di-tert-butylmercury has given us (–)-bis(methyl-1-naphthylphenylgermyl)mercury (II), the first example of an optically active germylmercury derivative.

$$\underset{(I)}{2\,(+)\text{-}R_3Ge^*H} + t\text{-}Bu_2Hg \rightarrow \underset{(II)}{(-)\text{-}(R_3Ge^*)_2Hg} + 2\ t\text{-}BuH \qquad (1)$$

$R_3Ge^* = Me\text{-}(1\text{-}C_{10}H_7)PhGe^*$

This reaction, like all the reactions described for optically active (I), may involve predominant retention of configuration at germanium. It proceeds via either a four-centre transition state or a pyramidal organogermyl radical[1] and resembles the reaction of (–)-methyl-1-naphthylphenylsilane with dibenzylmercury resulting in (+)-bis(methyl-1-naphthylsilyl)mercury[2].

The compound (+)-(I) (1 g, 0.0034 mole, $[\alpha]_D$ + 16.1°) was heated with di-tert-butylmercury (0.59 g, 0.0019 mole, m.p. 56–58°) at 80° in 3 ml hexane in an evacuated system for eight hours, to give colourless crystals of (–)-(II), 0.84 g (63%) m.p. 139.5°, $[\alpha]_D$ –0.6° (benzene). (Found: C 51.85, H 3.90, Hg 25.40. $C_{34}H_{30}Ge_2Hg$ calcd.: C 52.06, H 3.86, Hg 25.27%).

The reaction of (–)-(II) with methylmercury bisacetate goes under mild conditions and yields (+)-$R_3Ge^*CH_2COOMe$ (III) which retains the configuration at germanium (the stereochemical assignment is based on the fact that (+)-R_3Ge^*H and (+)-(III) have identical configurations)[3].

$$(-)\text{-}(R_3Ge^*)_2Hg + Hg(CH_2COOMe)_2 \rightarrow 2\,Hg + 2\,(+)\text{-}R_3Ge^*CH_2COOMe \qquad (2)$$

$$\text{(II)} \qquad\qquad\qquad\qquad \text{(III)}$$

1.26 g (0.0016 mole) of (–)-(II) (synthesised from (+)-(I) (1.3 g, 0.0044 mole, $[\alpha]_D$ +16.1°) and di-tert-butylmercury (0.71 g, 0.0023 mole)) were treated with methylmercury bisacetate (0.73 g, 0.0021 mole) in 4 ml tetrahydrofuran in an evacuated system at room temperature for nine days, to give 0.56 g (87%) of mercury and 1.1 g of (+)-(III) containing ca. 20% $(R_3Ge^*)_2O$. Chromatography on silica gel gave pure (+)-(III) (oil, 0.59 g (50%), $[\alpha]_D$ +1.88° (cyclohexane)). Its IR and PMR spectra correspond to those reported earlier[3].

REFERENCES

1 H. Sakurai and K. Mochida, *Chem. Commun.*, (1971) 1581.
2 C. Eaborn, R.A. Jackson and M.T. Rahman, *J Organometal. Chem.*, 34 (1972) 7.
3 V.M. Vodolazskaya and Yu.I. Baukov, *Zh. Obshch. Khim.*, 43 (1973) 1410.