

## NOTE

### CORRELATION OF THE ABSOLUTE CONFIGURATIONS OF R-(+)-METHYL(1-NAPHTHYL)PHENYLGERMANE AND (+)-ETHYL(1-NAPHTHYL)PHENYLGERMANE

C. EABORN, R. E. E. HILL, P. SIMPSON,

*School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)*

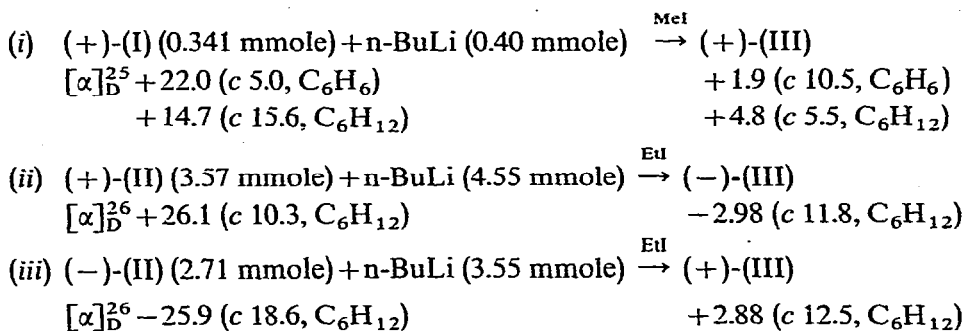
A. G. BROOK AND D. MACRAE

*Department of Chemistry, University of Toronto, Toronto 5 (Canada)*

(Received July 23rd 1968)

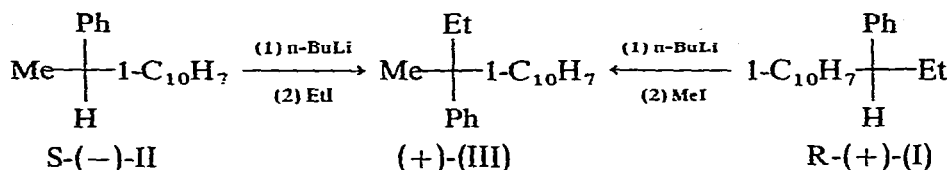
Eaborn *et al.*<sup>1,2</sup> have reported the optical resolution of ethyl(1-naphthyl)phenylgermane, (I), and Brook *et al.*<sup>3</sup> have reported the resolution of methyl(1-naphthyl)phenylgermane, (II), the absolute configuration of the (+)-enantiomer of which has been shown to be identical to that of R-(+)-methyl(1-naphthyl)phenylsilane<sup>4-6</sup>. It seemed appropriate to relate the configurations of the two germanes, and this has been accomplished through stereospecific metallation to give the germyllithium reagents followed by their reaction with either methyl or ethyl iodide to give optically-active ethylmethyl(1-naphthyl)phenylgermane, (III).

The results were as follows:



Since (+)-(III) was obtained from both (+)-(I) and S-(-)-(II), and since we can assume with reasonable certainty that the metallations and couplings involved have the same stereochemical consequences in both cases, we conclude that (-)-(I) and (-)-(II) have the same configuration; this is what would be predicted by Brewster's rules<sup>8</sup>, which appear to be applicable to these systems<sup>5,9,10</sup>.

The following stereochemical representations are based on the assumptions that metallation involves retention and the coupling with the alkyl iodides involves inversion of configuration<sup>10</sup>:



The differing rotations of (+)-(III) obtained from the (+)-I and (-)-II may arise mainly from differing degrees of loss of optical activity in the reactions of the germyllithium compounds with the alkyl iodides.

#### EXPERIMENTAL

##### *Characterisation of ethylmethyl(1-naphthyl)phenylgermane*

To ( $\pm$ )-ethyl(1-naphthyl)phenylgermane (0.510 g, 1.73 mmoles) in anhydrous ether (40 ml) under dry nitrogen, was added *n*-butyllithium in hexane (2.5 ml of 1.7 M solution) and the mixture was stirred for 1 h. An excess of methyl iodide (0.8 ml) in ether (5 ml) was then added, and the mixture was stirred for 1 h then refluxed for a further 1 h. The resulting suspension was washed with water and dried ( $\text{MgSO}_4$ ), and the solvent was then removed *in vacuo* to leave an oil (0.534 g), which on distillation at low pressure gave ( $\pm$ )-ethylmethyl(1-naphthyl)phenylgermane,  $n_D^{21}$  1.6228 (0.265 g, 50%) (Found: C, 70.7; H, 6.2.  $\text{C}_{19}\text{H}_{20}\text{Ge}$  calcd.: C, 71.0; H, 6.3%).

##### *Reactions with optically-active compounds*

(i). *n*-Butyllithium (0.40 mmole) in hexane was added by syringe through a serum cap to (+)-ethyl(1-naphthyl)phenylgermane (0.10 g, 0.34 mmole) in anhydrous diethyl ether (20 ml) under nitrogen. The mixture was swirled for 30 min, then excess of methyl iodide (*ca.* 0.1 ml) was added all at once, causing a rapid loss of colour. The ether was taken off, the residue was extracted with light petroleum (b.p. 40–60°), the extract filtered to remove lithium iodide, and the solvent again taken off, the residue being kept for a short time at 120°/0.5 mm to remove the last traces of solvent. The resulting clear oil (obtained *ca.* 85% yield) had  $n_D^{25}$  1.6228; its IR spectrum was identical with that of an authentic specimen of ethylmethyl(1-naphthyl)phenylgermane, and showed no Ge–H stretch at 4.9  $\mu$ .

(ii). To methyl(1-naphthyl)phenylgermane (*ca.* 1 g) in 50–60 ml of freshly distilled anhydrous ether under nitrogen a slight excess of *n*-butyllithium in hexane was added by syringe through a serum cap. The mixture was stirred for one hour, then excess of ethyl iodide (2 ml) was added by syringe. After a few minutes' stirring, the ether was removed under reduced pressure by rotary evaporation, the product dissolved in petroleum ether (b.p. 40–60°), and the lithium iodide removed by filtration. Evaporation of the solvent left an oil which showed no Ge–H stretch in the IR spectrum. The oil was distilled in a Kugelrohr apparatus at 180° (50  $\mu$  pressure), giving 76 and 79% yields of ethylmethyl(1-naphthyl)phenylgermane,  $n_D^{25}$  1.6245.

## REFERENCES

- 1 R. W. BOTT, C. EABORN AND I. D. VARMA, *Chem. Ind. (London)*, (1963) 614.
- 2 C. EABORN, P. SIMPSON AND I. D. VARMA, *J. Chem. Soc.*, (1966) 1133.
- 3 A. G. BROOK AND G. J. D. PEDDLE, *J. Amer. Chem. Soc.*, 85 (1963) 1869.
- 4 A. G. BROOK AND G. J. D. PEDDLE, *J. Amer. Chem. Soc.*, 85 (1963) 2338.
- 5 A. G. BROOK AND G. J. D. PEDDLE, *J. Amer. Chem. Soc.*, 85 (1963) 3051.
- 6 Y. OKAYA, *Reports of Meeting of American Crystallographic Association*, Minnesota, August 1967, p. 60.
- 7 H. M. WALBORSKY, F. J. IMPASTATO AND A. E. YOUNG, *J. Amer. Chem. Soc.*, 86 (1966) 3283.
- 8 J. H. BREWSTER, *J. Amer. Chem. Soc.*, 81 (1959) 5475.
- 9 A. G. BROOK AND W. M. LIMBURG, *J. Amer. Chem. Soc.*, 85 (1963) 832.
- 10 C. EABORN, R. E. E. HILL AND P. SIMPSON, *J. Organometal. Chem.*, 15 (1968) P1.

*J. Organometal. Chem.*, 15 (1968) 241-243