Tetrahedron Letters,Vol.26,No.40,pp 4949-4950,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

ALKYLMETAL ASYMMETRIC REDUCTION. XVI.[1]
TRIS(CIS-MYRTANYL)GALLIUM: AN UNUSUAL ORGANOMETALLIC COMPOUND AS ENANTIOSELECTIVE REDUCING AGENT OF KETONES

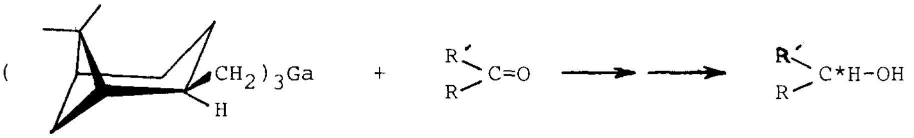
Massimo Falorni, Luciano Lardicci and Giampaolo Giacomelli*

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Centro di Studio del CNR per le Macromolecole Stereordinate ed Otticamente Attive,
via Risorgimento 35, I-56100 PISA

Summary: Tris[[(1S,2R)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl]methyl]-gallium was found to react with ketones above room temperature: optically active reduction carbinols were recovered as main products.

Recently, it has been reported the use of organoaluminium, organoboron and organoberyllium compounds, containing alkyl groups derived from 2-pinene, as enantioselective reducing agents of prochiral ketones.[1-3] As the first contribution to the study of the reactivity of β-branched organogallium derivatives towards carbonyl compounds, herein we report the preliminary results obtained with tris(cis-myrtanyl)gallium. The chemical behaviour of organogallium derivatives has been examined some years ago,[4-6] but very little is known about this kind of reactivity.[4]

We have noted that the reactivity of tris(cis-myrtanyl)gallium[7] is roughly the same of that of the corresponding aluminium alkyl.[2] Under the experimental conditions adopted for the reaction between ketones and beryllium and aluminium alkyls,[1,2] the trialkylgallium did not react with carbonyl compounds: in fact, after 48 h at room temperature, the conversion of the reaction was practically negligible. However, in the absence of solvents and at 50°C, the organogallium derivative reacted slowly with the ketones employed affording, after hydrolysis, the corresponding carbinols. In all the cases examined, the carbinols, recovered and purified by "flash chromatography", were optically active (Table 1).



On the basis of these preliminary results, the steric hindrance of the substituent of the carbonyl carbon atom seems to hinder the transfer of the hydrogen atom in the 2-position with respect to the metal atom, the reduction rate dropping significantly on passing from ethyl phenyl to i-propyl phenyl ketone. The dependence of the enantioselectivity from the structure of the ketone seems to be more complex: however, the tris(cis-myrtanyl)gallium has about the same enantioselectivity degree as the analogous aluminium derivative[2] and is more enantioselective than the beryllium alkyl.[1] In all cases, the absolute configuration of the carbinols is (R), the same as that of those from reductions by beryllium and aluminium alkyls.[1,2]

Table 1. Reduction of ketones by tris(cis-myrtanyl)gallium

Substrate	Carbinol %Conv.	Time (h)	$[\alpha]^{25}_D$, deg	%ee
Ethyl phenyl ketone	77	24	+ 5.9 (neat)	21(R)
i-Propyl phenyl ketone	58	48	+24.5 (ether)	51(R)
2-Methyl-4-nonyn-3-one	79	24	+ 6.0 (ether)	75(R)
2,2-Dimethyl-4-nonyn-3-one	89	24	+ 8.7 (neat)	54(R)

The absolute configurations of the phenyl alkyl carbinols are different from that reported for the reduction of acetophenone by cis-myrtanyl borane.[3] On the basis of the present evidences, we think that the stereochemistry of the reduction processes strongly depends on the metallic character of the metal atom. In this respect, a possible explanation of the different behaviour of the boron compound should be related to its low Lewis acid strength, which might affect the transition states of the reduction itself. Extension of these reductions to the use of organogallium derivatives having different optically active alkyl groups is presently under study in this laboratory.

ACKNOWLEDGEMENT: We wish to thank the "Ministero della Pubblica Istruzione", Rome, for partial support of this research.

REFERENCES AND NOTES

1. Giacomelli,G.; Falorni,M.; Lardicci,L., Gazz. Chim. Ital., **1985**, 115, 289.
2. Giacomelli,G.; Lardicci,L.; Palla,F., J. Org. Chem., **1984**, 49, 310.
3. Midland,M.M.; McLoughlin,J.I., J. Org. Chem., **1984**, 49, 4101.
4. Gilman,H.; Jones,R.G., J. Am. Chem. Soc., **1940**, 62, 980.
5. Eisch,J.J., J. Am. Chem. Soc., **1962**, 84, 3830.
6. Lardicci,L.; Salvadori,P.; Palagi,P., Ann. Chim. (Rome), **1966**, 56, 1043.
7. The organogallium derivative, prepared by reacting cis-myrtanylmagnesium chloride with $GaCl_3$, was characterized as diethyl etherate.

(Received in UK 5 August 1985)