*Journal of Organometallic Chemistry*, 285 (1985) 65–69
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# LITHIUM TRIS(PHENYLTHIO)METHANE FOR THE HOMOLOGATION OF TRIALKYLBORANES: CONVENIENT SYNTHESES OF KETONES AND t-CARBINOLS

ANDREW PELTER and J. MADHUSUDHANA RAO
*Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP (Great Britain)*

(Received October 31st, 1984)

## Summary

Lithium tris(phenylthio)methane is a readily available, cheap reagent for the production of ketones and t-carbinols from trialkylboranes. The scope and limitations of the reactions are indicated as are some of its unique features.

---

The conversion of triorganylboranes to trialkylcarbinols (eq. 1) is a unique and useful process that may be accomplished by the oxidation of intermediates resulting from interaction of trialkylboranes with carbon monoxide [1,2], sodium cyanide [1,3] or lithium dichloromethoxymethane [1,4]. Each of the reagents has its uses, but also drawbacks either in terms of the requirement for high pressures or due to toxicity. The conversion of trialkylboranes to ketones (eq. 2) is of particular use and the same homologating reagents, with modification of conditions [1,5] or substrate [6] may be used for this purpose.

$$R_3B \xrightarrow[\text{(2) Oxidation}]{\text{(1) One carbon unit}} R_3COH \qquad (1)$$

$$R^1R^2_2B \rightarrow R^2_2CO \qquad (2)$$

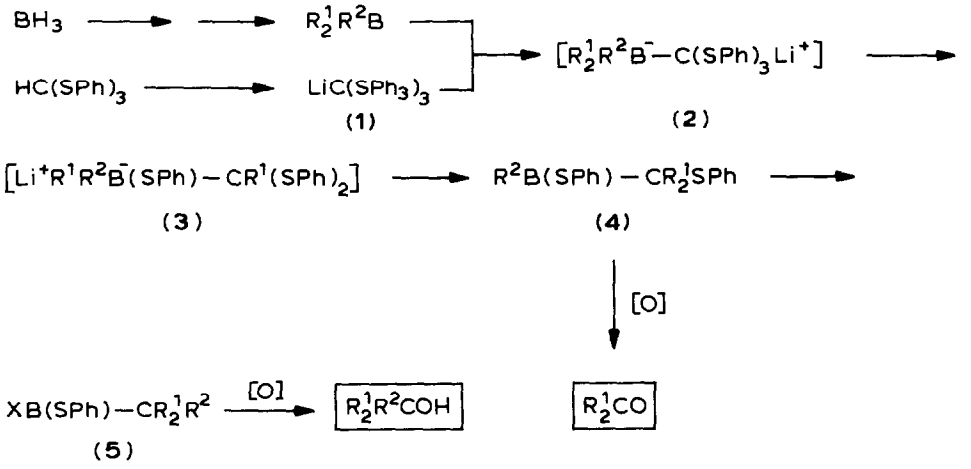
We have reported the use of acyl carbanion equivalents 1-lithio-1,1-bis(phenylthio)alkanes [7], and 2-lithio-2-alkyl-1,3-benzodithioles [8], for the conversion of trialkylboranes into either t-carbinols or ketones. In this process one alkyl group of the product is derived from the acyl carbanion equivalent.

We now provide details of the use of readily available [10] lithium tris(phenylthio)methane (**1**) as an acyl carbanion equivalent for the homologation of trialkylboranes. The starting material, tris(phenylthio)methane, is cheap and readily handled, and the reactions are readily controlled to give two or three migrations from boron to carbon.

Based on previous experience [7,8] we envisaged that we could bring about the reactions shown in Scheme 1. We felt that migrations should be spontaneous from

0022-328X/85/$03.30 

the ate complex **2** to the ate complex **3** and then to **4**. This would be of lowered Lewis acidity so that further ate complex formation would not occur and oxidation should yield ketones. Addition of a thiophilic reagent ($Hg^{II}$, methylating agents) should, however, induce a third migration to give **5** which should then give trialkylcarbinols on oxidation.




SCHEME 1

## Production of ketones

Mixing simple trialkylboranes ($R^1 = R^2$, Scheme 1) with **1** and allowing the temperature to warm to 25°C led to intermediates (presumably **4**) which on oxidation give ketones in isolated yields of ca. 80% (Table 1). The reaction of

TABLE 1

KETONE SYNTHESIS FROM ORGANOBORANES AND LITHIUM TRIS(PHENYLTHIO)-METHANE (**1**)

| Experiment | Trialkylborane | | Product [a] | Yield (%) [b] |
|---|---|---|---|---|
| | $R^1$ | $R^2$ | | |
| 1 | Hexyl [c] | Hexyl | $(C_6H_{13})_2CO$ | 82 |
| 2 | Heptyl | Heptyl | $(C_7H_{13})_2CO$ | 80 |
| 3 | Cyclopentyl | Cyclopentyl | $(cyclo\text{-}C_5H_9)_2CO$ | 81 |
| 4 | Cyclohexyl | Cyclohexyl | $(cyclo\text{-}C_6H_{11})_2CO$ | 80 |
| 5 | Cyclohexyl | Pentyl | $(cyclo\text{-}C_6H_{11})CO(C_5H_{11})$<br>$(cyclo\text{-}C_6H_{11})_2CO$ | 35 [d]<br>41 |
| 6 | 1-Methylcyclohexyl | Hexyl | – | 0 |
| 7 | n-Hexyl | Thexyl [e] | $(C_6H_{13})_2CO$<br>$C_6H_{13}CO$ Thexyl [f] | 11 [d]<br>61 |

[a] All products except from exp. 7 identified by direct comparison with authentic samples. [b] Yields are of isolated purified products and are based on borane and tris(phenylthiomethane). [c] All organic groups are straight chain primary except where otherwise stated. [d] Ratio established by quantitative GLC analysis. [e] Thexyl is 1,1,2-trimethylpropyl. [f] This product, 2,3,3-trimethyldecan-4-one is new and was characterised fully (see Experimental section).

TABLE 2

SYNTHESIS OF t-CARBINOLS FROM ORGANOBORANES AND 1

| Experiment | Trialkylborane | | Product [a] | Yield (%) [b] |
|---|---|---|---|---|
| | $R^1$ | $R^2$ | | |
| 8 | Hexyl [c] | Hexyl | $Hexyl_3COH$ | 91 |
| 9 | Heptyl | Heptyl | $Heptyl_3COH$ | 79 |
| 10 | Cyclopentyl | Cyclopentyl | $(cyclo\text{-}C_5H_9)_3COH$ | 82 |
| 11 | Cyclohexyl | Cyclohexyl | $(cyclo\text{-}C_6H_{11})_3COH$ | 43 [d] |
| 12 | Cyclohexyl | Hexyl | $(cyclo\text{-}C_6H_{11})_2HexylCOH$ | 83 |
| 13 | n-Hexyl | Thexyl [e] | $(n\text{-}C_6H_{13})_2ThexylCOH$ | 71 |

[a-d] Same meaning as in Table 1. [e] $MeO_2SF$ in glyme to induce third migration.

triphenylborane under standard conditions gave only 15% yield of benzophenone though much triphenylborane was unused.

We had expected, as in the case of other one carbon homologating reagents, that primary alkyl groups would migrate preferentially to secondary or to tertiary alkyl groups. However, this was not the case. In experiment five the relative migratory aptitude * of cyclohexyl as compared with an n-pentyl group is 1.5 and the thexyl group has a relative migrating aptitude of 2.2 as compared with an n-hexyl group (exp. 7). Thus the hindered ketone 2,3,3-trimethyldecan-4-one was readily prepared and isolated for the first time (exp. 7) and this would seem to be a feature of this new reaction that has unique promise. These results suggested that the low polarity of the intermediate (as with 1,2-migrations of alkynylborates) might be responsible for the differences in migratory aptitude as compared with homologation with sodium cyanide, carbon monoxide or lithium dichloromethoxymethane. Radical reactions do not seem to be involved as the processes of Scheme 1 are completely inhibited (for the components of exp. 7) by the radical initiator azobis(isobutyronitrile), and the ratio of ketones remained unchanged by the addition of galvinoxyl. Reaction six failed to give products, presumably due to steric inhibition of the formation of ate complex **2** in this case.

Attempts to hydrolyse intermediates **4** with dry, degassed isobutyric acid to give $R^1_2CHSPh$ were unsuccessful.

*Preparation of trialkylcarbinols*

Addition of mercuric chloride in THF at $-78°C$ to the reaction mixture resulting from two migrations served, in most cases, to give intermediates (**5**, X = Cl or SPh) that gave trialkylcarbinols on oxidation. The yields are good and the three groups migrating can include a very hindered group such as a thexyl group (Table 2, exp. 11). In the case of tricyclohexylborane the use of mercuric chloride was not successful in inducing a third migration, but methyl fluorosulphonate gave the required product in an unoptimised experiment. The overall process of carbinol

* As the products of the first migration cannot be isolated, the relative migratory aptitudes quoted are defined as the average over the two migrations, no assumptions being made with respect to the individual steps. If the migratory aptitude of $R^1/R^2 = x/y$ in $R^1R^2B$, then the ratio of product ketones, $R^1_2CO/R^1R^2CO$ is given by $2x^2/(3xy + y^2)$. Putting $y = 1$ gives the relative migratory aptitudes quoted.

production is efficient and uses cheap and readily available reagents that are easily manipulated without recourse to special equipment and without special precautions.

## Experimental

Ether solvents were distilled from calcium hydride or lithium aluminium hydride under nitrogen prior to use. Diborane was kept as a $BF_3$-free solution in THF and standardised prior to use [11]. All manipulations prior to work up were carried out in dry glassware under nitrogen, dry syringes being used for the transfer of liquids. Hydroborations were carried out according to published procedures [11]. GLC analyses were carried out on a 2 m column of 8% PEGA on 60–80 Chromsorb A using a programmed run up to 190°C.

*Production of ketones. Typical procedure*

*Reaction of thexyldihexylborane with lithium tris(phenylthio)borane.* Thexyldihexylborane (1 mmol) is prepared by a standard procedure [5,11]. A 50 ml two-neck round-bottomed flask is fitted with a magnetic follower and a septum cap and connected to a nitrogen-vacuum line, and flushed with nitrogen. The flask is charged with dry tris(phenylthio)methane (340 mg, 1 mmol) dissolved in THF (5 ml) by syringe, and cooled to −78°C. A solution of n-BuLi in hexane (0.7 ml of 1.50 *M* solution, 1.05 mmol) is added dropwise by syringe to the stirred solution and the reaction left stirring at −78°C for 2.5 h. Dry THF (2 ml) is added to the trialkylborane, the solution cooled to −78°C and added through a double-ended needle under nitrogen pressure to the reaction flask, also at −78°C. The reaction mixture is allowed to come to room temperature over 3 h, and left stirring for 20 h.

The reaction mixture is cooled in ice and oxidised by addition first of aqueous sodium hydroxide (4 ml of 5 *M* solution) and hydrogen peroxide (2 ml, 50%). The reaction mixture is allowed to stir for 8 h at 25°C, then extracted with ether (2 × 50 ml), the combined organic extract washed with water (3 × 50 ml), dried ($MgSO_4$) filtered and evaporated. The ketones are purified by passage through a column of silica gel, 60–120 mesh (30 g), eluting first with pentane and then with a mixture of dichloromethane-pentane (1/3) (300 ml), followed by a 1/1 mixture of the same solvents (400 ml). The first ketone fractions are pure 2,3,3-trimethyldecan-4-one (99 mg, 50%), $n_D^{25}$ 1.4495, $M^+$ 198.1983, C, 78.42; H, 13.14, $C_{13}H_{20}O$ calcd.: $M^+$ 198.19835, C, 78,78; H, 13.13%. $^1H$ NMR shows methyl groups at $\delta$ 0.75, 0.85, 1.00 (15H), methylene groups at 1.25 (m, 8H), and signals at 1.7–2.1 (m, 1H tertiary), and 2.40 ppm (t, 2H, $CH_2CO$). The later fractions are a mixture of 2,3,3-trimethyldecan-4-one and tridecan-7-one (44 mg, 22%). The total yield is 72% consisting of an 85/15 mixture (quantitative GLC) of the two ketones.

*Production of t-carbinols. Typical procedure*

*Synthesis of tri-n-hexylcarbinol.* Tri-n-hexylborane (1 mmol) is produced by the standard procedure [5,11] and reacted as described above with lithium tris(phenylthio)methane (1 mmol) produced in situ. The reaction mixture is cooled to −78°C and dry mercuric chloride (2.17 g, 8 mmol) in THF (6 ml) also at −78°C is added dropwise by double-ended needle to the stirred solution. The reaction mixture is allowed to stir for 24 h at 25°C and then oxidised by addition of sodium hydroxide (4 ml, 5 *M* solution) and then hydrogen peroxide (2 ml, 50%) at 0°C. Oxidation is

allowed to proceed overnight, the mercury salts filtered off and the organic product taken into ether ($2 \times 50$ ml). The combined ethereal extract is washed with water ($3 \times 50$ ml), dried ($MgSO_4$), filtered and evaporated. The residue is then thoroughly washed with pentane to leave residual mercury salts and the residue from the pentane extract placed on a short column of silica gel (10 g, 60–120 mesh). Elution with pentane is followed by dichloromethane/pentane. The carbinol is eluted with a 1/1 mixture of the solvents to give pure 7-n-hexyltridecan-7-ol(tri-n-hexylcarbinol) (258 mg, 91%), $n_D^{23}$ 1.4446, identical in all respects with an authentic sample.

## Acknowledgement

We thank the University of Wales for the award of a Fellowship to J.M.R.

## References

1 A. Pelter and K. Smith, Organic Boron Compounds, in D.H.R. Barton, W.D. Ollis (Eds.), Comprehensive Organic Chemistry, vol. 3, p. 689–940 contains exhaustive bibliography to the end of 1976.
2 H.C. Brown, Acc. Chem. Res., 2 (1969) 65.
3 A. Pelter, M.G. Hutchings, K. Rowe and K. Smith, J. Chem. Soc. Perkin I, (1975) 138.
4 H.C. Brown and B.A. Carlson, J. Org. Chem., 38 (1973) 2422.
5 A. Pelter, K. Smith, M.G. Hutchings and K. Rowe, J. Chem. Soc. Perkin I, (1975) 129.
6 B.A. Carlson and H.C. Brown, J. Am. Chem. Soc., 95 (1973) 6876.
7 R.J. Hughes, S. Ncube, A. Pelter, K. Smith, E. Negishi and T. Yoshida, J. Chem. Soc. Perkin I, (1977) 1172.
8 S. Ncube, A. Pelter and K. Smith, Tetrahedron Lett., (1977) 225; (1979) 1893, 1895.
9 A. Pelter and J. Madhusudhana Rao, J. Chem. Soc. Chem. Comm., (1981) 1149.
10 D. Seebach, Angew. Chem. Internl. Edition, (1967) 442.
11 H.C. Brown, Organic Synthesis via Boranes, Wiley Interscience, New York, 1975.