*Journal of Organometallic Chemistry*, 205 (1981) C4—C6
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

---

# REACTIONS OF DIORGANOYTTERBIUM COMPOUNDS WITH KETONES AND ALDEHYDES

G. B. Deacon and T. D. Tuong

Chemistry Department, Monash University, Clayton, Victoria 3168 (Australia)

(Received October 27th, 1980)

## Summary

Reactions of the diorganolanthanoids $R_2Yb$ (R = PhCC or $C_6F_5$) with aldehydes (R′CHO) and ketones ($R'_2CO$) (R = Me or Ph) followed by hydrolysis generally gives the alcohols RR′CH(OH) or $RR'_2COH$, but, with benzophenone, reduction giving benzopinacol either competes (R = PhCC) or is predominant (R = $C_6F_5$).

---

Syntheses of several novel diorganolanthanoids by the transmetallation reaction (1) (R = $C_6F_5$, M = Yb or Eu; R = *p*-$HC_6F_4$ or PhCC, M = Yb) have been reported [1-3],

$$R_2Hg + M \rightarrow R_2M + Hg\downarrow \qquad (1)$$

but, apart from their extreme air and water sensitivity, little is known of their reactivity. We now report that in reactions of bis(pentafluorophenyl)- and bis(phenylethynyl)-ytterbium with some aldehydes and ketones, these reagents are effective carbanion sources and can also act as reducing agents.

Solutions of the diorganoytterbium compounds in tetrahydrofuran were prepared by reaction (1), filtered to remove precipitated mercury, and treated with the aldehydes or ketones (Table 1) for 16h at room temperature. After hydrolysis with aqueous ammonium chloride and extraction with chloroform, the products (Table 1) were identified by g.l.c., g.c./m.s., t.l.c. and u.v. spectroscopy, using authentic samples for comparison, or by spectroscopic methods in the case of $(PhCC)Ph_2COH$ and $[Ph_2C(OH)]_2$. In most cases, an alcohol was obtained [reaction (2), R = PhCC or $C_6F_5$; R′ = Me or Ph; R″ = H, Me, or Ph].

$$R_2Yb + 2R'R''CO \rightarrow (RR'R''CO)_2Yb \xrightarrow{H^+} RR'R''COH \qquad (2)$$

TABLE 1

REACTIONS OF DIORGANOLANTHANOIDS WITH CARBONYL COMPOUNDS

| $R_2Yb$[a] | Initial Reagents | | Carbonyl | | Product | Yield[b] |
|---|---|---|---|---|---|---|
| R | Yb(mg at) | $R_2Hg$(mmol) | Compound | mmol | | (%) |
| PhCC | 4.67 | 1.26 | MeCHO | 25 | (PhCC)MeCH(OH) | 63 |
| PhCC | 4.47 | 1.28 | $Me_2CO$ | 2.4 | $(PhCC)Me_2COH$[c] | 34 |
| PhCC | 4.73 | 1.25 | PhCHO | 1.9 | (PhCC)PhCH(OH) | 71 |
| PhCC | 4.63 | 1.25 | $Ph_2CO$ | 2.5 | $(PhCC)Ph_2COH$ | 42 |
| | | | | | $[Ph_2C(OH)]_2$ | 14 |
| $C_6F_5$ | 2.00 | 1.45 | MeCHO | 24 | $(C_6F_5)MeCH(OH)$ | 57 |
| $C_6F_5$ | 2.00 | 1.45 | $Me_2CO$ | 1.9 | $(C_6F_5)Me_2COH$ | 24 |
| $C_6F_5$ | 2.00 | 1.49 | PhCHO | 1.5 | $(C_6F_5)PhCH(OH)$ | 43 |
| $C_6F_5$ | 1.90 | 1.48 | $Ph_2CO$ | 1.3 | $[Ph_2C(OH)]_2$ | 84 |

[a] Formed 'in situ' by reaction of the reagents (columns 2 and 3) in tetrahydrofuran at room temperature [reaction (1)].

[b] Yields of products, based on the initial mercurial, were determined by g.l.c. analysis, except for $(PhCC)Ph_2COH$ and $[Ph_2C(OH)]_2$, which were estimated by u.v. spectroscopy after separation by t.l.c.

[c] Other products discussed in text.

However, benzopinacol was a significant product from reaction of bis(phenylethynyl)ytterbium with benzophenone, and the major product from the corresponding reaction of bis(pentafluorophenyl)ytterbium [reaction (3), R = PhCC or $C_6F_5$].

$$2Ph_2CO + 2R_2Yb \longrightarrow (R_2\overset{III}{Yb})_2[Ph_2C(O^-)]_2 \xrightarrow{H^+} [Ph_2C(OH)]_2 \qquad (3)$$

Intermediate formation of the radical anion $Ph_2\overset{\bullet}{C}O^-$ is likely, and indeed a blue colour similar to that of $Na/Ph_2CO$ in tetrahydrofuran was observed on treatment of $(PhCC)_2Yb$ with benzophenone. The behaviour of the organoytterbium compounds in reaction (3) resembles that of ytterbium(II) iodide, which also reduces benzophenone to benzopinacol (this work). It is surprising that reduction products are not more prevalent in view of the reported reducing capacity of ytterbium(II) towards organic substrates [4]. Moreover, the species $(RR'R''CO)_2Yb$ formed [reaction (2)] by carbanion transfer are potential reducing agents in addition to the initial diorganoytterbium compounds. However, even using an excess of acetaldehyde (Table 1), there is no evidence of reduction. Similarly, no reduction was observed on reaction of $(PhCC)_2Yb$ with an excess of dry acetone. Removal of the volatiles before hydrolysis revealed the presence of some phenylacetylene, diacetone alcohol, and 4-methylpent-3-en-2-one. Protonation of the organolanthanoid by the enol of acetone accounts for the formation of phenylacetylene whilst the other products can be explained by a subsequent aldol condensation and dehydration.

Thus, diorganoytterbium compounds are predominantly carbanion transfer reagents in reactions with aldehydes and ketones, but they can act as reducing agents. Their behaviour with the majority of substrates (Table 1) resembles that of organolithium reagents, but the reaction of bis(pentafluorophenyl)ytterbium with benzophenone contrasts with the formation of pentafluorophenyldiphenylmethanol in the corresponding reaction of pentafluorophenyllithium [5].

## Acknowledgement

We are grateful to the Australian Research Grants Committee and the Monash Special Research Grant for support, and to Dr. D. Kelly and Dr. C.G. Barraclough, University of Melbourne for spectroscopic assistance.

## References

1. G.B. Deacon and D.G. Vince, J. Organometal. Chem., 112 (1976) C1; G.B. Deacon, W.D. Raverty, and D.G. Vince, J. Organometal. Chem., 135 (1977) 103.
2. G.B. Deacon and A.J. Koplick, J. Organometal. Chem., 146 (1978) C43.
3. G.B. Deacon, A.J. Koplick, W.D. Raverty, and D.G. Vince, J. Organometal. Chem., 182 (1979) 121.
4. F. Girard, J.L. Namy, and H.B. Kagan, J. Amer. Chem. Soc., 102 (1980) 2693.
5. N.N. Vorozhtsov, V.A. Barkhash, T.N. Gerasimova, E.G. Lokshina, and N.G. Ivanova, J. Gen. Chem. U.S.S.R., 37 (1967) 1223.