CHEMISTRY LETTERS, pp. 221-222, 1980. © The Chemical Society of Japan 1980

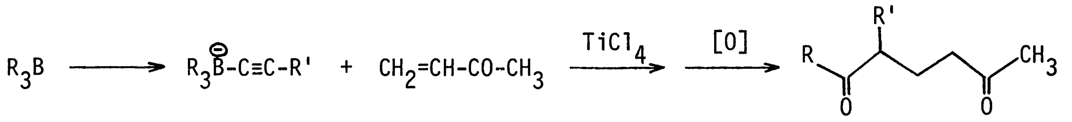
THE MICHAEL-TYPE REACTION OF LITHIUM 1-ALKYNYLTRIALKYLBORATES WITH METHYL VINYL KETONE IN THE PRESENCE OF TITANIUM TETRACHLORIDE. A NEW SYNTHESIS OF δ-DIKETONES FROM ORGANOBORANES

Shoji HARA, Kotaro KISHIMURA, and Akira SUZUKI*
Department of Applied Chemistry, Faculty of Engineering,
Hokkaido University, Sapporo 060

1-Alkynyltrialkylborates readily available from trialkylboranes and lithium acetylides react with methyl vinyl ketone in the presence of titanium tetrachloride followed by hydrogen peroxide oxidation under neutral conditions to give corresponding δ-diketones.

Although lithium 1-alkynyltrialkylborates are well-known to react with various types of electrophiles such as H^+,[1] RX,[2] and iodine[3] to give a variety of organic compounds, such ate-complexes do not react with aldehydes, ketones, and α,β-unsaturated carbonyl compounds.[4]

We wish to report here a new δ-diketone synthesis by the reaction of lithium 1-alkynyltrialkylborates with methyl vinyl ketone in the presence of titanium tetrachloride, which is the first Michael-type addition reaction of the ate-complexes to α,β-unsaturated carbonyl compounds to provide a novel synthetic procedure of δ-diketones from organoboranes (eq. 1).

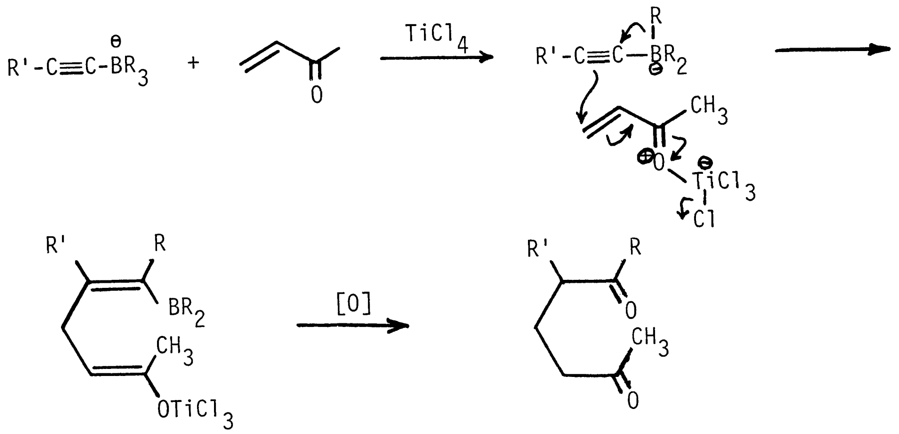


(1)

A typical procedure is as follows: Treatment of phenylethyne (0.306 g, 3 mmol) in anhydrous tetrahydrofuran (5 ml) with butyllithium in ether (1.5 ml of a 2 M solution, 3 mmol) at 0°C gave the corresponding lithium acetylide. After stirring for 30 min at the temperature, tributylborane in tetrahydrofuran (2 ml of a 1.5 M solution, 3 mmol) was added to give a pale yellow solution of the ate-complex. The reaction mixture was stirred for 30 min at 0°C, and then cooled to -78°C. Methyl vinyl ketone (0.315 g, 4.5 mmol) and titanium tetrachloride in dichloromethane[5] (2.25 ml of a 2 M solution, 4.5 mmol) were added to give a dark brown heterogeneous solution. The mixture was stirred for 1 h at -78°C and then allowed to warm to room temperature. Finally the reaction mixture was oxidized with 30% hydrogen peroxide (3 ml) under neutral conditions.[6] Analysis of the organic layer by glpc indicated that 5-phenyldeca-2,6-dione had been formed in a 83% yield. Representative results are summarized in Table 1.

Although other Lewis acids were examined in the reaction of lithium phenylethynyltributylborate with methyl vinyl ketone, the highest yield of 5-phenyldeca-2,6-dione was obtained by using titanium tetrachloride as a Lewis acid. The results are as follows: $AlCl_3$ (yield of the diketone, 21%), $AlBr_3$ (23%), $BF_3 \cdot Et_2O$ (trace), $SnCl_4$ (trace), and $ZnCl_2$ (trace).

The reaction should be considered to proceed through the following reaction path (eq. 2). Methyl vinyl ketone activated by co-ordination with $TiCl_4$[7] reacts with lithium 1-alkynyltrialkylborate via a Michael-type addition fashion to give the intermediate (I), which is then oxidized to form the corresponding δ-diketone.



I

(2)

Table 1. The Synthesis of δ-Diketones via the Reaction of 1-Alkynyltrialkylborates with Methyl Vinyl Ketone in the Presence of $TiCl_4$

Alkyne $R'\text{-}C\equiv CH$	Organoborane R_3B, R	Yield (%)[a] of δ-diketone[b] $R\text{-}CO\text{-}CHR'CH_2CH_2\text{-}CO\text{-}CH_3$
Phenylethyne	Propyl	52
	Butyl	83
	Isobutyl	68
	Hexyl	53
1-Heptyne	Propyl	36
	Butyl	58
	Isobutyl	61
	Hexyl	38

a) Glpc yield based on the organoborane used. b) Satisfactory IR and ^1H-NMR spectra and elemental analyses were obtained for all compounds.

References and Notes

1) (a) A.Pelter,C.R. Harrison, and D.Kirkpatrick, Chem.Comm., 1973, 544. (b) N. Miyaura,T.Yoshinari, M.Itoh, and A.Suziki, Tetrahedron Lett., 1974, 2961. (c) H.C. Brown,A.B.Levy, and M.M.Midland,J.Am. Chem.Soc.,95,5017 (1975). (d) G.Zweifel and R.P.Fisher, Synthesis,1975,376. (e) M.M.Midland and H.C.Brown,J.Org.Chem. 40,2845(1975). (f) A.Pelter,C.R.Harrison,C.Subrahmanyam,and D.Kirkpatrick,J.Chem.Soc.Perkin I,1976, 2435. 2) (a) 1a. (b) A.Pelter,C.R.Harrison, and D.Kirkpatrick, Tetrahedron Lett., 1973, 4491. (c) A. Pelter and C.R.Harrison, Chem.Comm., 1974, 828. (d) A.Pelter,K.J.Gould, and C.R.Harrison, Tetrahedron Lett., 1975, 3327. (e) K.Utimoto,M.Kitai,M.Naruse, and H.Nozaki, ibid., 1975, 4233. (f) J.Hooz and Mortimer, ibid., 1976, 805. (g) A.Pelter,T.W.Bentley,C.R.Harrison,C.Subrahmanyam, and R.J.Laub, J.Chem.Soc.Perkin I, 1976, 2419. (h) A.Pelter,K.J.Gould, and C.R.Harrison, ibid., 1976, 2428. 3)(a) A.Suzuki,N.Miyaura,S.Abiko,M.Itoh,H.C.Brown,J.A.Sinclair,M.M.Midland, J.Am.Chem.Soc., 95, 3080(1973). (b) E.Negishi,G.Lew, and T.Yoshida, Chem.Comm., 1973, 874. (c) K.Yamada,N.Miyaura,M.Itoh,A.Suzuki, Tetrahedron Lett., 1975, 1961. (d) A.Pelter,R.Hughes,K.Smith, and M.Tabata, ibid., 1976, 4385.

4) Pelter and Hughes have reported that α,β-unsaturated nitro compounds and sulfoxides react with lithium 1-alkynyltrialkylborates in the absence of additives: A.Pelter and L.Hughes, Chem.Comm., 1977, 913. 5) Methyl vinyl ketone and $TiCl_4$ should be added in this turn. 6) A buffer solution(3 ml of 2.2 M aqueous NaH_2PO_4 and K_2HPO_4 solution) was added to keep the mixture neutral: H.C.Brown and R.A.Colemam, J.Am.Chem.Soc., 91,4606(1969). 7) T.Mukaiyama, Angew.Chem., 89, 858 (1977).

(Received December 12, 1979)