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OLEFINATION OF KETONES USING 1,1-DIMETALLOALKANES DERIVED FROM $i\text{-}Bu_2AlCH=CHR - Cl_2TiCp_2$ SYSTEM

Tadao YOSHIDA
Central Research Laboratories, Toagosei Chemical Industry Co., Ltd.
Funami-cho, Minato-ku, Nagoya 455

The alkylidenation of ketone carbonyls using 1,1-dimetalloalkanes prepared by the reaction of 1-alkenyldiisobutylalanes with titanocene dichloride afforded the corresponding olefins in good yields.

1,1-Dimetalloalkanes have been attracted much attention of organic chemists as a reagent for alkylidene transfer$^{1)}$ or as models for intermediates in the olefin metathesis reaction$^{2)}$ or the Fischer-Tropsch process.$^{3)}$

On studying the utilization of a combination system of organoaluminum compounds with transition metal complexes for synthetic reagents, author has discovered that 1-alkenyldiisobutylalanes react with titanocene dichloride to produce 1,1-dimetalloalkanes. At this stage, the alkanes have not yet characterized in detail, but it has been found that they act as active Wittig type reagents for ketone carbonyls. Here the preparative methods of the reagents and olefination of ketones with them are described.

Treatment of titanocene dichloride in CH_2Cl_2 for 1 hr at room temperature with 1 equivalent of 1-heptenyldiisobutylalane prepared by the action of 1-heptyne on diisobutylaluminum hydride$^{4)}$ results in the formation of n-heptane in 47% yield after hydrolysis of the reaction mixture with 3N HCl (Table 1). On the other hand, its deuterolysis with D_2O gives 1,1-dideuterioheptane ($\geqslant$95% pure) in 47% yield, which indicates the formation of ca. a half equivalent of a 1,1-dimetalloheptane to the starting materials (equation 1). The yield of the 1,1-dimetallo species obtained under the other reaction condition is summarized in Table 1.

The complex is very sensitive to moisture and oxygen. This has prevented the identification. So this species was used as an unisolated entity for the carbonyl olefination reaction.

The above species reacted smoothly with 1 equivalent of ketones to afford the corresponding olefins in good yields (Table 2), as shown in equation 1.

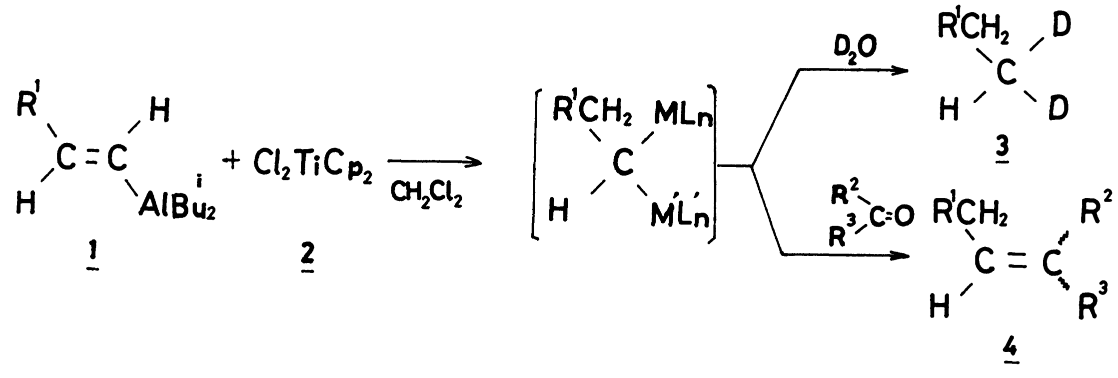
Table 1. Reaction of i-$Bu_2AlCH=CH(n-C_5H_{11})$ with Cl_2TiCp_2

Run	Solvent	Al/Ti Ratio	Temp.	Time(hr)	Yield of n-heptane(%)$^{a)}$
1	CH_2Cl_2	1	r.t.	1	47
2	$C_6H_5CH_3$	1	r.t.	1	30
3	CH_2Cl_2	1	0°C	3	42
4	CH_2Cl_2	0.5	r.t.	1	37$^{b)}$
5	CH_2Cl_2	2	r.t.	1	20$^{b)}$
6$^{c)}$	CH_2Cl_2	1	r.t.	1	11

a) By protonolysis of the reaction mixture with 3N HCl. GLC yields.

b) Based on i-$Bu_2AlCH=CH(n-C_5H_{11})$.

c) A (1:1:1) mixture of 1-heptyne with i-Bu_2AlH and Cl_2TiCp_2.



(1)

For example, to a suspension of 2 (4.98 g, 20 mmole) in 80 ml of CH_2Cl_2 was added a n-hexane solution of 1 (R^1= n-C_5H_{11}) (2.5 M, 8 ml, 20 mmole)$^{4)}$at 0°C under a nitrogen atmosphere. After stirring for 1 hr at room temperature, the reaction mixture was added to acetone (0.058 g, 10 mmole) in 5 ml of THF at -50°C under a nitrogen atmosphere. The mixture was allowed to warm to 0°C over a 30 min period, and the reaction was quenched with a large excess of water. The organic materials were extracted with ether. The organic layer was washed with 3N HCl, saturated $NaHCO_3$ solution and water, and dried over $MgSO_4$. 2-Methyl-2-nonene (0.09 g, 64 %) was isolated by distillation. Bp 81-82°C/40 mmHg (Lit.$^{5)}$, 171°C/760 mmHg) ; n_D^{25} 1.4263 (Lit.$^{5)}$, n_D^{25} 1.4264) ; ^1H NMR ($CDCl_3$) δ 0.86 (t,3H,J=7Hz), 1.1-1.45 (m,8H), 1.57 (m,3H), 1.65 (m,3H), 1.75-2.1 (m,2H), 4.95-5.2 (m,1H) ; IR (neat) 2960, 2900, 2840, 1460 cm^{-1}.

In this reaction, the stereoselectivity is not so good (Table 2). It would be noted, however, that the Z isomer of 2-phenyl-2-heptene is obtained predominantly by the reaction of the 1,1-dimetallopentene with acetophenone, whereas steric reasons may be advanced for the prefered formation of the E isomer.

Table 2. Olefination of Ketones with 1,1-Dimetalloalkanes Derived from $i\text{-}Bu_2AlCH{=}CHR^1$- Cl_2TiCp_2 System

R^1	R^2	R^3	Yield of 4 (%)[a)]	E/Z Ratio[b)]
$n\text{-}C_5H_{11}$	Me	Me	64 (73)	
	Me	Et	62 (72)	61/39
	$-(CH_2)_5-$		61 (74)	
$n\text{-}C_3H_7$	Me	Ph	70 (82)	33/67
	Ph	Ph	61 (70)	

a) Yields after isolation by distillation. GLC yields are given in parentheses.

b) Determined by GLC analysis, comparing with the authentic sample.

The above-mentioned reaction presents a new route for the preparation of olefins from alkynes and ketones, and various olefins would be synthesized by this reaction, as a replacement of 1-heptyne or 1-pentyne by the other alkyne allows a structural variation in the alkylidene unit.

Similarly, a (1:1) mixture of zirconocene dichloride and 1 (R^1= $n\text{-}C_5H_{11}$) in CH_2Cl_2 afforded 1,1-dideuterioheptane ($>$94% pure) in 79% yield after stirring for 20 hr at room temperature and then its deuterolysis with D_2O. However, the reaction of this dimetallic species with acetone did not give 2-methyl-2-nonene in any more than 1% yield. Thus the aluminum-zirconium combination displayed a marked contrast with the analogous titanium system in the reactivities towards ketones. The similar behaviour has been observed on 1,1-dimetalloalkenes of the type $Cp_2ClM(Me_2Al)C{=}CMe(R)$ (M = Ti or Zr).[6)]

The mechanism for the formation of such a 1,1-dimetalloalkane is ambiguous, but it is possible to be formed by the addition of a metal hydride species which would be produced via a β-elimination reaction from the metal-i-Bu bond, to the double bond of a metal alkenyl compound.

Work is in progress to characterize the 1,1-dimetalloalkane and to investigate the scope of this olefination reaction.

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