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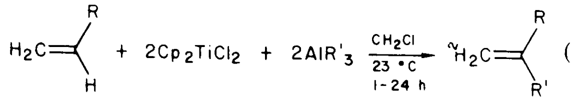
Conversion of Monoalkyl Olefins to 1,1-Dialkyl Olefins by Reaction with Bis(cyclopentadienyl)titanium Dichloride–Trialkylaluminum

Summary: Reaction of certain monoalkyl olefins with a reagent generated by mixing bis(cyclopentadienyl)titanium dichloride and a trialkylaluminum compound provides a single-step procedure for preparing 1,1-dialkyl olefins.

Sir: We wish to report that the reaction of certain monoalkyl olefins with a reagent generated by mixing bis(cyclopentadienyl)titanium dichloride and a trialkylaluminum compound provides a single-step procedure for preparing the corresponding 1,1-dialkyl olefins (eq 1).[2,3]



(1)

This reaction proceeds most cleanly using a twofold molar excess of both titanium and aluminum components. Smaller excesses result in lower yields of alkylated olefin and increased yields of byproducts (CH_3CH_2R, CH_3CHR^1R, $CH_3CR^1{}_2R$, and higher molecular weight compounds). Use of methylene chloride as solvent gives more rapid reaction than toluene. Table I summarizes results obtained at room temperature using 1:2:2 molar ratios of olefin/Cp_2TiCl_2/$AlR^1{}_3$. Reactions were followed by GLC, and the indicated times are those giving the maximum yield of alkylated product.

In a representative reaction, $AlMe_3$ (24 mL of a 3 M solution in hexanes, 72 mmol) was added under argon to a vigorously stirred solution of Cp_2TiCl_2 (18 g, 72 mmol), 1-decene (6.8 mL, 36 mmol), and ethyl acetate (3.5 mL, 36 mmol) in CH_2Cl_2 (125 mL).[4,5] After 14 h at room temperature, the reaction mixture was carefully poured onto a 3 M aqueous HCl–ice slush. The organic layer was separated and solvent was removed by rotary evaporation in the presence of neutral alumina (15 g). Rapid elution of the product mixture with 300 mL of pentanes from a 2 × 30-cm column of neutral alumina and evaporation of solvent afforded a clear oil (4.06 g) composed of 2-methyl-1-decene (92%), *n*-decane (5%), and 1-decene (3%).

The reaction appears to be sensitive to steric effects: the larger the alkyl group of the trialkylaluminum compound, the lower the yield of alkylated olefin; bis(ethyltetramethylcyclopentadienyl)titanium dichloride[6] gives a slower reaction and lower yields than Cp_2TiCl_2; branched primary olefins give lower yields than unbranched; internal olefins are unreactive. Lewis bases slow the reaction and, frequently, lower the product yield: ethers (1:1 molar ratio of diethyl ether/olefin) suppress the reaction almost

(1) Supported by the National Science Foundation, 7711282 CHE, and by Hercules Inc.

(2) Alkylation of unfunctionalized olefins is a recognized side reaction in Ziegler–Natta polymerization but has not been exploited in organic synthesis. Dyachkovskii, F. S. in "Coordination Polymerization"; Chien, J. C. W., Ed.; Academic Press: New York, 1975; pp 199–222, and references cited therein.

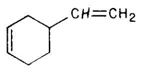
(3) Variously substituted olefins have been prepared via alkyl metalation of acetylenes with organoaluminum–transition metal reagents: Negishi, E.; Van Horn, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 3170–3171. Van Horn, D. E.; Negishi, E. *Ibid.* **1978**, *100*, 2252–2254. Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *Ibid.* **1978**, 2254–2256. Mixtures of organoaluminum and -titanium compounds have been used to alkylate terminal acetylenes and olefins activated by proximate hydroxyl groups: Youngblood, A. V.; Nichols, S. A.; Coleman, R. A.; Thompson, D. W. *J. Organomet. Chem.* **1978**, *146*, 221–228, and references cited therein. Organoaluminum reagents add to substituted benzonorbornadienes and acetylenes: Eisch, J. J.; Burlinson, N. E. *J. Am. Chem. Soc.* **1976**, *98*, 753–761. Eisch, J. J.; Damasevitz, G. A. *J. Org. Chem.* **1976**, *41*, 2214–2215.

(4) Reactions were carried out using unexceptional inert atmosphere techniques: Brown, H. C. "Organic Syntheses via Boranes"; Wiley: New York, 1975; Chapter 9. Methylene chloride (reagent grade) was purged with argon before use. Solutions of trialkylaluminum compounds were obtained from Ethyl Corporation.

(5) **Caution.** Although solutions of trialkylaluminum compounds are claimed to be nonpyrophoric, they will ignite spontaneously if exposed to oxygen while dispersed on a high-surface support. Concentrated or neat trialkylaluminum compounds are strongly pyrophoric.

(6) Feitler, D.; Whitesides, G. M. *Inorg. Chem.* **1976**, *15*, 466–469.

Table I. Conversion of $RCH{=}CH_2$ to $RCR'{=}CH_2$[a]

olefin	mmol	R′	additive, mmol[b]	time, h	% yield $RCR'{=}CH_2$[c,d]	% recovered $RCH{=}CH_2$[d]
n-$C_8H_{17}CH{=}CH_2$	1.0	Me		1	65	
	36		EtOAc, 36	14	80 (74)[e,f]	
	1.0		EtOAc, 2.0	20	0	92
	1.0		Et_2O, 1.0	35	6	90
	1.0		$(CH_3)_2CHOH$, 1.0	5	65	35
	1.6	Et		1	45	
	1.0		EtOAc, 1.0	24	35	30
	1.0	n-Bu[g]		2	34	55
	1.0	i-Bu		11	0	87
	1.0	Me		15	50	36
	1.0		EtOAc, 1.0	23	10	87
	1.0	Et		2	10	75
$CH_3CO_2CH_2(CH_2)_3CH{=}CH_2$	1.0	Me		20	85	
$BrCH_2(CH_2)_3CH{=}CH_2$	1.0			3	70	
$(CH_3)_3SiOCH_2(CH_2)_3CH{=}CH_2$	1.0			6	33	34
$N{\equiv}C(CH_2)_4CH{=}CH_2$	1.0			6	12	60
$EtO_2CCH{=}CH_2$	1.5			3	0	

[a] Reactions were run on a scale corresponding to 1 mmol of olefin, 2 mmol of AlR'_3, and 2 mmol of Cp_2TiCl_2 in 25 mL of CH_2Cl_2 at room temperature, unless specified otherwise. [b] No additive was present if this column contains no entry. [c] The product is that derived by substitution of the italicized olefin hydrogen by alkyl; yield is based on olefin. [d] GLC yields, unless indicated otherwise. [e] Isolated yield. [f] The solvent volume was 125 mL. [g] Prepared by reaction of $AlCl_3$ with BuLi at −50 °C in toluene and used without purification.

entirely and nitriles (e.g., 6-heptenenitrile) lower the rate of production formation and the yield. The effect of esters on the reaction is not straightforward. Ethyl acetate in a 2:1 molar ratio of ester/olefin inhibits the reaction entirely. In a 1:1 molar ratio (ethyl acetate/olefin) the reaction is slowed, but the yield of dialkyl olefin depends on the particular trialkylaluminum and olefin involved. Yields are increased in the least sterically hindered case (1-decene–$AlMe_3$), but are lowered in other cases.

The reaction is compatible with alkyl bromide, hydroxyl, and ester functionality present in, but not directly attached to, the olefinic reactant. Ketones and epoxides are destroyed during the reaction. Ethyl acrylate is unreactive. One experiment (utilizing n-butyllithium) suggests that the organoaluminum component of the mixture can be generated by reaction of $AlCl_3$ and the corresponding organolithium reagent and used without purification.

The mechanism of this reaction is no better understood than that of Ziegler–Natta polymerization. It probably involves initial alkylation of titanium by the organoaluminum reagent, insertion of olefin into the titanium–alkyl bond, and elimination of titanium hydride. The fate of the hydride equivalent and other details of the transformation are obscure.[7]

The reaction has the attractive characteristics that it effects in one step a type of carbon–carbon bond formation which is difficult to accomplish by other procedures, it is compatible with several useful functional groups, and it shows high selectivity for monosubstituted olefins. It has the disadvantages that it uses organoaluminum and -titanium equivalents inefficiently. We will describe further development of the reaction in subsequent papers.

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Registry No. n-$C_8H_{17}CH{=}CH_2$, 872-05-9; 4-ethenylcyclohexene, 100-40-3; $CH_3CO_2CH_2(CH_2)_3CH{=}CH_2$, 5048-26-0; $BrCH_2(CH_2)_3CH{=}CH_2$, 2695-47-8; $(CH_3)_3SiOCH_2(CH_2)_3CH{=}CH_2$, 71138-63-1; $NC(CH_2)_4CH{=}CH_2$, 5048-25-9; $EtO_2CCH{=}CH_2$, 140-88-5; trimethylaluminum, 75-24-1; triethylaluminum, 97-93-8; tributylaluminum, 1116-70-7; triisobutylaluminum, 100-99-2; n-$C_8H_{17}CCH_3{=}CH_2$, 13151-27-4; n-$C_8H_{17}C(C_2H_5){=}CH_2$, 71138-64-2; n-$C_8H_{17}C(n\text{-}C_4H_9){=}CH_2$, 51655-65-3; n-$C_8H_{17}C(CH_2CH(CH_3)_2){=}CH_2$, 71138-65-3; 4-isopropenylcyclohexene, 26325-89-3; 4-(1-ethylethenyl)cyclohexene, 71138-66-4; $CH_3CO_2CH_2(CH_2)_3CCH_3{=}CH_2$, 71138-67-5; $BrCH_2(CH_2)_3CCH_3{=}CH_2$, 1974-89-6; $(CH_3)_3SiOCH_2(CH_2)_3CCH_3{=}CH_2$, 71138-68-6; $NC(CH_2)_4CCH_3{=}CH_2$, 6887-97-4; $EtO_2CCH_3{=}CH_2$, 97-63-2; Cp_2TiCl_2, 1271-19-8.

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(7) The predominant oxidation state of titanium in the product appears to be Ti(III). This observation is compatible with a stoichiometry for the reaction in which: $Ti^{IV}H + Ti^{IV} \rightarrow 2Ti^{III} + H^+$.

(8) Halcon Fellow, 1978–1979.