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CARBOALUMINATION OF ALKYNES WITH DIALKYLCHLOROALANES IN THE PRESENCE OF ZIRCONOCENE DICHLORIDE. AN IMPROVED METHOD FOR CARBOALUMINATION OF ALKYNES

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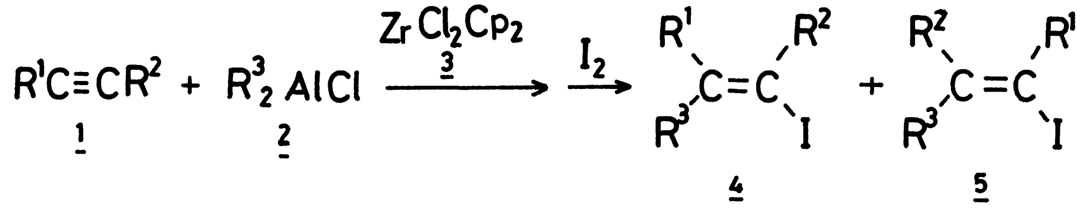
In the presence of zirconocene dichloride, treatment of alkynes with dialkylchloroalanes followed by iodination gave the corresponding alkenyl iodides in good yields.

Recently, it has been reported the carboalumination of terminal alkynes with trimethylalane and zirconocene dichloride.[1] This reaction can serve as a useful synthetic method of trisubstituted olefins.[2] However, the similar reaction using tri-n-propylalane instead of trimethylalane lowers the yield of the carboaluminated product, becauce a hydrometallation of the alkynes occurs competitively.[1,3] The hydrometallation reaction is induced by the Schwartz reagent[4] produced via a β-elimination reaction from the complex $Cp_2Zr(n\text{-}Pr)Cl$ which is formed by the action of tri-n-propylalane on zirconocene dichloride.[3] On the other hand, the nature of the above carboalumination reaction has been shown to be a Zr-assisted direct addition of the aluminum-carbon bond to the triple bond of alkyne.[5] On these grounds, it was to be expected that only a carboalumination reaction would proceed in the related system which does not produce the complex of type $Cp_2Zr(R)Cl$.

This hypothesis has now been actualized by using dialkylchloroalanes in place of trialkylalanes, as shown in the following equation.



For example, to a suspension of 3 (2.92 g, 10 mmole) in 20 ml of $(CH_2Cl)_2$ was added a solution of 2 (R^3 = Et) (2.41 g, 20 mmole) in 20 ml of $(CH_2Cl)_2$ at room temperature under a nitrogen atmosphere. After stirring the mixture for 10 min at room temperature, 5-decyne (1.38 g, 10 mmole) was added to a yellow solution obtained at room temperature. After stirring for 15 hr at room temperature, to the solution was added a solution of I_2 (3.30 g, 13 mmole) in 30 ml of Et_2O at 0°C. A yellow precipitate appeared and the sludgy solution was filtered off. The filtrate was washed with 3N HCl, saturated $NaHCO_3$ solution and water, and dried over $MgSO_4$. After removal of the solvent under reduced pressure, (E)-5-ethyl-6-iodo-5-decene (2.35 g, 80 %) was isolated by distillation. Bp 75-76°C/0.35 mmHg ; ^1H NMR ($CDCl_3$) δ 0.91 (t,3H,J=7Hz), 0.96 (t,6H,J=7Hz), 1.1-1.7 (m,8H), 2.20 (t,4H,J=7Hz), 2.47 (q,2H,J=7Hz) ; ^{13}C NMR ($CDCl_3$) δ 12.13, 13.97, 14.06, 21.73, 22.80, 31.03, 31.15, 32.14, 35.82, 41.01, 104.20, 145.02 ; IR (neat) 2960, 2920, 2860, 1625, 1460 cm^{-1}.

Table 1. Carboalumination of $R^1C{\equiv}CR^2$ with $R^3{}_2AlCl$ in the presence of Cp_2ZrCl_2

R^1	R^2	R^3	2/1 Ratio	Time(hr)	Yields of alkenyl iodides(%)[a)]	4/5 Ratio[b)]	E/Z Ratio[b)]
n-C_5H_{11}	H	CH_3	1	48	(48)	98/2	
		CH_3	2	6	73 (87)	98/2	>99/1
		C_2H_5	2	3	82 (91)	76/24	
n-C_4H_9	n-C_4H_9	C_2H_5	2	15	80 (95)		>99/1
n-C_5H_{11}	H	n-C_3H_7	1	20	(60)	78/22	
		n-C_3H_7	2	3	75 (84)	80/20	
		n-C_4H_9	2	6	71 (80)	84/16	

a) By iodinolysis of the carboaluminated products. Yields isolated by distillation. GLC yields are presented in parentheses. b) Determined by GLC analysis.

In this reaction, the undesirable hydrometallation of alkynes was not observed, and after iodinolysis of the carboaluminated products were obtained the corresponding alkenyl iodides in good yields. This reaction presents a route to the preparation of olefins from alkynes.

As expected, 2 (R^3 = Me, Et or n-Pr) did not react with 3 to afford the complex of type $Cp_2Zr(R)Cl$, as judged by ^1H NMR.[6)]

References

1) D. E. Van Horn and E. Negishi, J. Am. Chem. Soc., 100, 2252 (1978). 2) E. Negishi, L. F. Valente and M. Kobayashi, ibid., 102, 3298 (1980). 3) E. Negishi and T. Yoshida, Tetrahedron Lett., 1980, 1501. 4) For a review, see J. Schwartz, J. Organomet. Chem. Library, 1, 461 (1976). 5) T. Yoshida and E. Negishi, J. Am. Chem. Soc., 103, 4985 (1981). 6) The ^1H NMR of a 1:1 mixture of 2 (R^3 = Me, Et or n-Pr) and 3 in $(CH_2Cl)_2$ showed a singlet at δ 6.45 ppm due to π-C_5H_5 groups of 3 and signals due to the corresponding R^3 groups of 2.

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