NEW METHOD OF β-ALKYLATION OF α-OLEFINS USING DIALKYLALUMINUM CHLORIDES WITH CATALYTIC AMOUNTS OF Ti, Zr, AND Hf COMPLEXES

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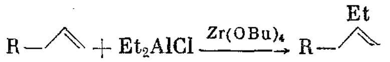
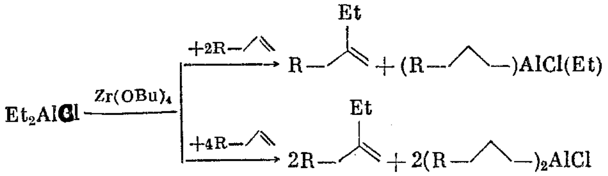
In [1] a new reaction was described between Et_2AlCl and α-olefins in the presence of catalytic amounts of $Zr(OBu)_4$, leading to the corresponding methylenealkanes.



With the goal of a more detailed investigation of the method of ethylation of α-olefins by Et_2AlCl, and also a clarification of the possible existence of this reaction with participation by other dialkylaluminum chlorides, we studied the interaction of Et_2AlCl, $(n\text{-}Pr)_2AlCl$, and $(n\text{-}C_6H_{13})_2AlCl$ with various olefins and dienes.

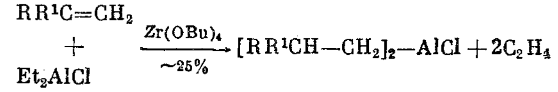
Upon the reaction of Et_2AlCl with 1-hexene (1:2) in the presence of a catalytic amount of $Zr(OBu)_4$ (Zr:Al = 1:100), 3-methyleneheptane (I) [1] and ethylhexylaluminum chloride (II) are formed in different ratios with a total yield of 95%. The structure of (II) is supported by physicochemical methods, and also by its quantitative transformation by H_2O into hexane and ethane. An increase in the proportion of olefin in the reaction of Et_2AlCl with 1-hexene (Al: olefin = 1:4) leads to the production along with (I) of a stoichiometric amount of dihexylaluminum chloride (III). Compound (III) was identified by comparison with a preparation obtained by the reaction of $AlCl_3$ with $(C_6H_{13})_3Al$ as in [2]. In addition, upon interaction of (III) with water, hexane was quantitatively formed.

As a result of the investigation of the β-ethylation of 1-octene, 1-decene, 1-dodecene, and 1,4-Z-hexadiene by diethylaluminum chloride (Al:olefin = 1:4) in the presence of $Zr(OBu)_4$, the C_8-C_{14} methylenealkanes (IV)-(VII) and higher dialkylaluminum chlorides (VIII)-(XI) were obtained in high yields (Table 1). Thus, the presence of a disubstituted double bond in an α-olefin (1,4-Z-hexadiene) does not influence the direction of the reaction; however, the yield of (VII) is somewhat lower since part of the original diene isomerizes to the unreactive 2,4-hexadiene.



The β-disubstitued α-olefins, 3-methyleneheptane and 5-methyleneundecane, and not alkylated by Et_2AlCl. In these experiments, only the higher dialkylaluminum chlorides (XII), (XIII), and C_2H_4 were formed. The yields of (XII) and (XIII) were $\leqslant$ 25%. The reaction mixture contained a significant amount (~75%) of the unreacted initial methylenealkane.

It should be expected that the methylenealkanes tested had low activity under the reaction conditions of β-ethylation by alkylzirconium complexes which were synthesized by the reduction of $Zr(OBu)_4$ by diethylaluminum chloride [1].



$$\begin{matrix} RR^1C{=}CH_2 \\ + \\ Et_2AlCl \end{matrix} \xrightarrow[\sim 25\%]{Zr(OBu)_4} [RR^1CH{-}CH_2]_2{-}AlCl + 2C_2H_4$$

$R = C_4H_9$, $R^1 = C_2H_5$ (XII); $R = C_4H_9$, $R^1 = C_6H_{13}$ (XIII).

Disubstituted olefins (2-E-hexene, 2-Z-hexene, 2-E-octene) or 1,3-dienes (2,4-hexadiene) do not participate in reactions with Et_2AlCl. Conjugated dienes (butadiene, isoprene), and also

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TABLE 1. $Zr(OBu)_4$ Catalyzed Interaction of α-Olefins with $AlEt_2Cl$ (3 h, toluene solvent, Zr:Al - 1:100, Al:olefin = 1:4)

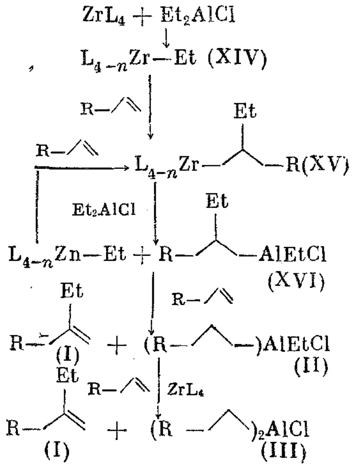
Original olefin	Reaction T., °C	Reaction product			
		hydrocarbon	yield, %	organoaluminum compound	yield, %
1-Hexene	20	3-Methyleneheptane (I)	95	Di(n-hexyl)aluminum chloride (III)	95
1-Octene	20	3-Methylenenonane (IV)	90	Di(n-octyl)aluminum chloride (VIII)	90
1-Decene	20	3-Methyleneundecane (V)	85	Di(n-decyl)aluminum chloride (IX)	85
1-Dodecene	20	3-Methylenetridecane (VI)	80	Di(n-dodecyl)aluminum chloride (X)	80
1,4,-Z-Hexadiene	20	2-Ethyl-1,4-Z-hexadiene (VII)	65	Di(n-1-hexenyl)aluminum chloride (XI)	65
		2,4-Hexadiene	35		
3-Methyleneheptane	40	Ethylene	25	(3-Methylheptyl)ethylaluminum chloride (XII)	20
5-Methyleneundecane	60	»	20	(2-Butyloctyl)ethylaluminum chloride (XIII)	25

TABLE 2. Comparative Catalytic Activity of Ti, Zr, and Hf Alcoholates (Al:M:olefin = 50:1:200, 25°, 10 h)

Catalyst	Composition of catalyst after hydrolysis of organoaluminum compound, %				
	hexane	hexenes	2-ethyl-hexene	dimeric products	higher oligomers
$Ti(OBu)_4$	3,5	10,5	35,5	9,5	41
$Zr(OBu)_4$	40	4,5	44	6,5	5
$Hf(OBu)_4$	10	69	11	–	10

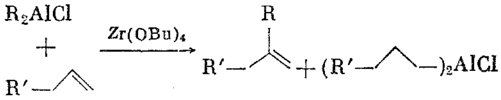
styrene, are easily polymerized under conditions of β-ethylation, with the formation of high-molecular-weight products whose identification is quite difficult.

Obtaining these results made possible the proposal of a more probable mechanistic scheme for the β-ethylation of α-olefins by Et_2AlCl, according to which in the first step, $Zr(OBu)_4$ reacts with Et_2AlCl giving the alkylated complex (XIV) which carbometalates the α-olefin (hexene in the scheme) producing compound (XV). Et_2AlCl transmetalates (XV) into (XVI). The latter, on exposure to an excess of α-olefin, is converted into (I) and (II). The participation of (II) in the alkylation of the Zr complex and transmetalation of the latter in the presence of the α-olefin gives (I) and (III).



$R = C_3H_7$, $L = OC_4H_9$.

The scheme which we propose provides for the possibility of the involvement of yet other dialkylaluminum chlorides in the β-alkylation reaction of α-olefins. Actually, $(n\text{-}Pr)_2AlCl$ and $(n\text{-}C_6H_{13})_2AlCl$ alkylate 1-hexene in the presence of $Zr(OBu)_4$ at ∿50°C with the formation of the methylenealkanes (XVII), (XVIII) in yields ⩾70%. Diisobutylaluminum chloride does not alkylate olefins even under more rigid conditions.



$R = C_3H_7$(XVII), C_6H_{13}(XVIII), $R' = C_3H_7$.

Along with $Zr(OBu)_4$, other transition-metal compounds were studied as catalysts. It appears that $Zr(acac)_4$ and $(cyclopentadienyl)_2ZrCl_2$ were not active in the β-alkylation of α-olefins. $ZrCl_4$, $TiCl_4$, $(C_5H_5N)_2ZrCl_2$, and $Ti(OBu)_4$ facilitated the last transalkylation of Et_2AlCl by products of ethylation and dimerization of the original α-olefins. $HfCl_4$ and $Hf(OBu)_4$ have low activity in the β-alkylation process, and the yields of methylenealkanes in these experiments was ⩽30%.

The catalytic activities of the tested transition-metal complexes in the β-alkylation reaction are in the order Ti > Zr > Hf (Table 2).

EXPERIMENTAL

The olefins used were ⩾95% pure, and were first distilled over triisobutylaluminum. The Zr and Hf alcoholates were synthesized according to [3], and 1,4-Z-hexadiene by the method in

[4]. PMR spectra were recorded on a "Tesla BS-480" apparatus (CCl_4 solutions, hexamethyldisiloxane internal standard), IR spectra on a UR-20 spectrophotometer (film), and mass spectra on an MKh-1306 instrument (electron ionization energy 70 eV). GLC analysis was conducted on a Chrom-41 instrument with a flame-ionization detector, 3.7 × 3 mm column of Carbowax-1500 on Chromaton N-AW for hydrocarbons up to C_{16}, Carbowax-6000 on Chromaton N-AW for hydrocarbons C_{16} and higher, He carrier gas at 60 ml/min.

General Method of Ethylation of α-Olefins with Diethylaluminum Chloride. To a solution of 0.1 mole Et_2AlCl and 0.001 mole of Zr, Ti, or Hf compound in heptane or toluene (50 ml) was added under a stream of Ar, dropwise over 1 h, 0.4 mole of olefin, after which it was stirred at ∿20° for another 3 h. The catalyzate was cooled with dry ice and hydrolyzed in an inert atmosphere, adding water dropwise. The hydrolyzate was washed with 5% HCl, then water, dried with $MgSO_4$, and analyzed by GLC. The experimental results are presented in Table 1.

Upon ethylation of 8.2 g (0.1 mole) of 1,4-Z-hexadiene, 2.8 g (35%) of 2,4-hexadiene was obtained [5] and 5.4 g (65%) 2-ethyl-1,4-Z-hexadiene, bp 30-32° (30 mm), n_D^{20} 1.4330. IR spectra (ν, cm^{-1}): 740, 3030 (cis-CH=CH), 890, 3080 (CH_2=C). PMR spectra (δ, ppm): 0.96 m (3H, CH_3), 1.6 d (3H, CH_3C=), 1.81 m (2H, CH_2=C), 2.66 m (2H, =CCH_2C=), 4.60 s (2H, CH_2=C), 5.45 m (CH=CH), M^+ 110.

For isolation of the dialkylaluminum halide, the catalyzate was distilled at high vacuum without decomposition. Obtained were dihexylaluminum chloride (III) [8] and ethylhexylaluminum chloride (III), bp 120° (1 mm). Found: C 55.1; H 9.9; Cl 19.5; Al 15.3%. $C_8H_{18}AlCl$. Calculated: C 54.39; H 9.80; Al 15.29; Cl 20.11%. Hydrolysis of the isolated organoaluminum compounds was conducted analogously.

Alkylations of 1-hexene by $(n-Pr)_2AlCl$ and $C_6H_{13}AlCl$ were conducted by the general method at 50°. From 8.4 g (0.1 mole) of 1-hexene and 0.025 mole of $(n-C_6H_{13})_2AlCl$, 12.6 g (70%) of 5-methyleneundecane (XVIII) was obtained [6]. Analogously, upon the interaction of 1-hexene with $(n-Pr)_2AlCl$, 4-methyleneoctane (XVII) [7] was obtained in a 75% yield.

Reaction of Methylenealkanes with Et_2AlCl in the Presence of Zr Compounds. To a solution of 0.1 mole Et_2AlCl and 0.001 mole $Zr(OBu)_4$ in dry toluene was added 0.4 mole 3-methyleneheptane or 5-methyleneundecane, and it was mixed 5 h, sealed, at the temperature stated in Table 1. Analysis of the gas phase showed the presence of ethylene. The catalyzate was hydrolyzed with H_2O, and after the treatment described above, was analyzed by GLC by comparison with the original olefins and their hydration products.

Upon substitution of $ZrCl_4$ for $Zr(OBu)_4$, the content of saturated hydrocarbons in the hydrolyzate reached 60-80% even at 25°.

CONCLUSIONS

1. The possibility of β-alkylation of α-olefins by higher dialkylaluminum chlorides in the presence of $Zr(OBu)_4$ was shown.

2. A single step catalytic method was proposed for the synthesis of higher dialkylaluminum chlorides from Et_2AlCl and α-olefins.

3. The catalytic activity of various Ti, Zr, and Hf compounds was studied in the alkylation reaction of α-olefins by diethylaluminum chlorides.

LITERATURE CITED

1. U. M. Dzhemilev, O. S. Vostrikova, A. G. Ibragimov, and G. A. Tolstikov, Izv. Akad. Nauk SSSR, Ser. Khim., 1979, 2626.
2. T. Mole and E. A. Jeffery, Organoaluminum Compounds, Amsterdam (1972), p. 31.
3. B. Bradley, F. M. Abd'el Halim, E. Sadek, and W. Wardlaw, J. Chem. Soc., 1952, 2032.
4. N. M. Seidov, M. A. Geidarov, and L. M. Pershina, Azerb. Khim. Zh., 1969, No. 1, 70.
5. Beilstein's Handbuch der Organischen Chemie, B. 1, Berlin (1918), S. 254.
6. Beilstein's Handbuch der Organischen Chemie, B. 1, Berlin (1928), S. 195.
7. Beilstein's Handbuch der Organischen Chemie, B. 1, Berlin (1941), S. 204.
8. Houben-Weyl, Methoden der Organischen Chemie, 13/4, Stuttgart (1970), S. 64.