

TRANSALKYLATION OF AROMATIC HYDROCARBONS
BY A METATHESIS CATALYST ($WCl_6-C_2H_5AlCl_2$)

Léonard HOCKS, A.J. Hubert and Ph. Teyssié

Laboratory of Macromolecular Chemistry and Organic Catalysis
UNIVERSITE DE LIEGE, SART TILMAN - B. 4000 LIEGE - BELGIQUE.

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Recent publications^{1,2,3}) on the alkylation of benzene and toluene by the $WCl_6-C_2H_5AlCl_2$ system prompt us to report our observations stressing the difference between the behaviour of this metathesis catalyst and that of a simple Lewis acid such as $C_2H_5AlCl_2$ for the alkylation of benzene.

$C_2H_5AlCl_2$ alone is indeed an effective alkylating reagent^{4,5}) (A), but it gives a mixture of mono-, di- and higher alkylated products, while the WCl_6 -containing catalyst promotes the formation of monoalkylated derivatives (B); on the other hand, a small but definite difference is observed in the distribution of monoalkylated isomers. Moreover, the catalyst is a highly active species : in most cases, the reaction is complete in a matter of seconds.

Interestingly, small amounts of dialkylated products (7 %) which could be detected after a few seconds disappeared very rapidly. This prompted us to treat, with the metathesis catalyst in benzene, a mixture of mono- and polyalkylated benzenes (prepared from oct-4-ene and benzene with $C_2H_5AlCl_2$ alone as catalyst) : the di- and polyalkylated products disappeared rapidly to form exclusively monoalkylated products (C).

A common feature of these reactions is the subsequent isomerization of the monoalkylated products to give a constant isomeric composition, obtained from oct-1-ene as well as from oct-4-ene; this behaviour is also illustrated by the conversion, under the same conditions, of 2-phenylhexane into a 60 : 40 mixture of 2- and 3-phenylhexane.

Catalyst ^{a)}	Time (minutes)	Monoalkylated Products (x-Phenyloctanes) (%) ^{b)}			Dialkylated Products (%) ^{b)}	Polyalkylated Products (%) ^{b)}
		2-	3-	4-		
$C_2H_5AlCl_2$ (A)	1-1440	22	18	24	29	7
$WCl_6-C_2H_5AlCl_2$ (B)	0.5	31	32	30	7	-
	1	37	29	34	-	-
	10-1440	42	27	31	-	-
$WCl_6-C_2H_5AlCl_2$ ^{c)} (C)	0	18	17	20	33	12
	15	24	17	27	25	7
	24	29	20	33	16	2
	45	33	24	35	8	-
	80	40	29	31	-	-
	120	44	30	26	-	-

a) Experimental Conditions : Benzene, $2 \cdot 10^{-1}$ mole; oct-4-ene, 10^{-2} mole, WCl_6 , $1,5 \cdot 10^{-4}$ mole; $C_2H_5AlCl_2$, $6 \cdot 10^{-4}$ mole; T = 25° C.

b) % of products calculated versus the initial amount of octene, using an internal g.l.c. standard; the different types of alkylated products mentioned in this table account for a quantitative conversion of the initial olefin : the corresponding values were standardized to 100 %.

c) In this experiment, oct-4-ene was replaced by alkylated products isolated after 24 hrs from former experiment involving oct-4-ene and $C_2H_5AlCl_2$ alone.

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