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

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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, 2.10^{-1} mole; oct-4-ene, 10^{-2} mole, WCl_6, $1,5.10^{-4}$ mole; $C_2H_5AlCl_2$, 6.10^{-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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STABLE CYCLIC SULFENOCARBOXYLIC ACID ANHYDRIDES DERIVATIVES OF 1,2-OXATHIOLE-5-ONE

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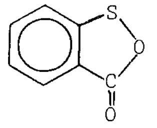
Previously Field and collaborators[1] have given evidence for the unstable cyclic o-sulfenobenzoic acid anhydride (I), which also has been proposed as an intermediate by D'Silva[2] and Danehy[3].

We now wish to report two stable 3-substituted 4-carboxy-1,2-oxathiole-5-ones (IIa,b), whose structures have been determined by spectroscopic data, elemental analysis and by means of chemical reactions.



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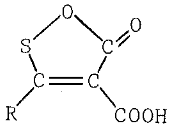
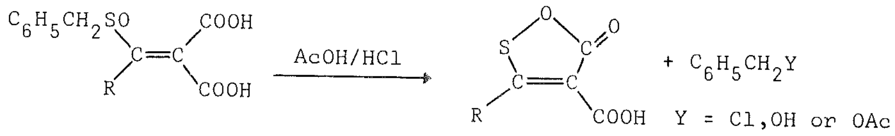


II

IIa R = Ph
IIb R = Me

The compounds (II) have been prepared by treatment of the corresponding benzylsulfinylmalonic acids (III)[4] in a mixture of acetic and hydrochloric acid at 45° C. Under these conditions the compounds (III) underwent a benzylic carbon-sulfur bond cleavage according to Scheme 1.



III II

Scheme 1

The benzylic part was isolated and identified as benzyl chloride, benzyl alcohol and benzyl acetate.

The other part (II) was isolated as white crystalline solids. The product derived from IIIa was shown to be the most stable one and could be kept at room temperature for several months. The proposed structures (II) are supported by the following data.

The mass spectrum of IIa gave a M^+-peak at m/e (rel int) 222(96), M^++1 (11.4) M^++2 (5.5) and for IIb m/e: M^+ 160(82), M^++1 (5.3), M^++2 (4.5). IR-spectrum of the crude product IIa shows two strong bands in the carbonyl region at 1786 and 1675