Tetrahedron Letters No. 27, pp 2268 - 2270, 1975. Pergamon Press. Printed in Great Britain.

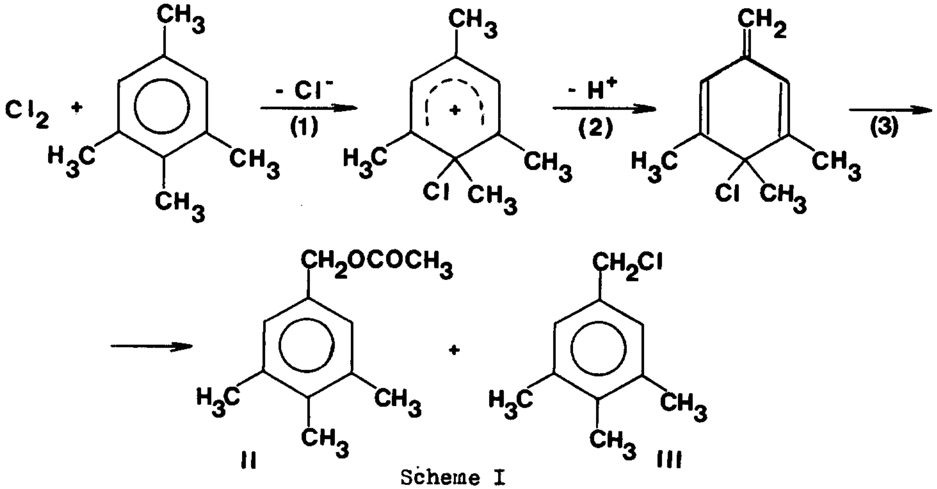
# NON CONVENTIONAL PATHS IN ELECTROPHILIC AROMATIC REACTIONS.
# XIV. INTERVENTION OF ION PAIRS IN THE MECHANISM OF THE SIDE-CHAIN CHLORINATION OF POLYALKYLBENZENES[1].

Enrico Baciocchi*, Luigi Mandolini**, and Amedeo Patara**

* Dipartimento di Chimica, Università di Perugia, 06100 Perugia (Italy)
** Centro C.N.R. dei Meccanismi di Reazione, Istituto Chimico, Università di Roma, 00185 Roma (Italy)

(Received in UK 19 May 1975; accepted for publication 22 May 1975)

The mechanism of electrophilic side-chain reactions of alkylbenzenes with chlorine in acetic acid appears quite well established with respect to both the steps concerning the attack of chlorine and the proton loss[2,3,4] (steps 1 and 2 in scheme I where the reaction shown is that of isodurene). In contrast, we have no definite information on the routes through which the side-chain substituted products (acetates and chlorides) are formed from the intermediate I (step 3). The following possibilities can be considered:



Scheme I

a) both II and III derive by ionization of I to an ion pair which can either give III or react with the solvent to form II; b) III and II are formed by an $S_N2'$ reaction of $Cl^-$ and of the solvent acetic acid, respectively, on I; c) III may be produced by an electrophilic attack of a molecule of chlorine at the exocyclic methylene group of I (with expulsion of $Cl^+$) whereas II is still formed through one of the possibilities previously mentioned.

In order to clarify on this problem we have studied the effect of the chlorine concentration and of the presence of salts (LiCl, $LiClO_4$, $LiOCOCH_3$) on the side-chain acetate: side-chain chloride product ratio (II/III product ratio) obtained in the chlorination of isodurene in acetic acid at room temperature.

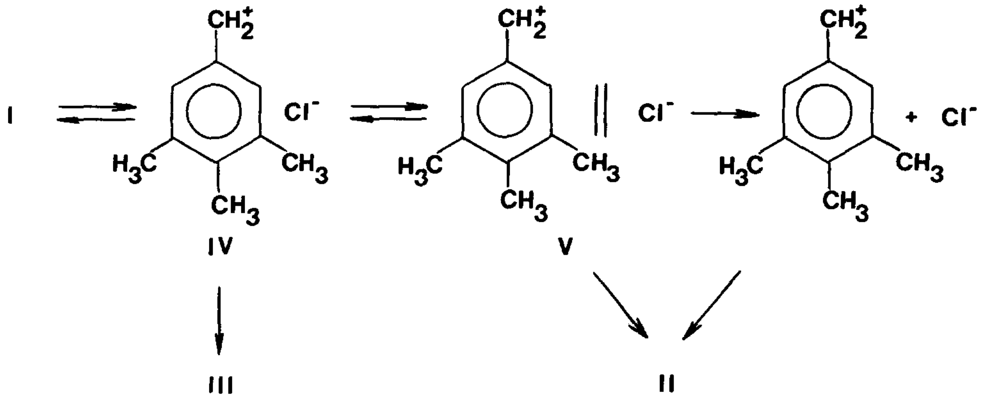
The results, reported in the Table, show that the II/III product ratio is practically unaffected by a 7 fold increase in the chlorine concentration. This leads to exclude that III is produced by attack of $Cl_2$ on I, since, in such a case, an increase of the $Cl_2$ concentration is expected to produce a significant increase in the relative yield of III and therefore a decrease in the II/III product ratio, which is not observed.

Table

II/III Product ratio in the reaction of chlorine with isodurene in acetic acid

| Isodurene, M | $Cl_2$,M | Salt added,M | | II/III[a] product ratio |
|---|---|---|---|---|
| 0.010 | 0.010 | | | 0.21 |
| 0.011 | 0.011 | | | 0.22 |
| 0.022 | 0.022 | | | 0.25 |
| 0.071 | 0.070 | | | 0.23 |
| 0.013 | 0.010 | LiCl, | 0.051 | 0.28 |
| | | | 0.044 | 0.29 |
| | | | 0.103 | 0.27 |
| | | | 0.200 | 0.35 |
| | | | 0.290 | 0.34 |
| 0.013 | 0.010 | $LiClO_4$, | 0.012 | 0.29 |
| | | | 0.050 | 0.39 |
| | | | 0.101 | 0.41 |
| | | | 0.205 | 0.43 |
| 0.013 | 0.010 | $LiOCOCH_3$, | 0.05 | ~0.4[b] |

a) Determined by glc; b) In this case a product other than II and III was observed in the analysis of the reaction mixture. No attempt was made to identify this product.



Scheme II

A very significant observation is also that the presence of LiCl does not increase the relative yield of the side-chain chloro derivative (III); in fact the II/III product ratio increases as the LiCl concentration increases. This finding clearly enables to reject the $S_N2'$ mechanism for the formation of III (in this case a decrease of the II/III product ratio on icreasing the LiCl concentration would have been expected) and indicates that the rearrangement of I to III is intramolecular. It is most probable that the rearrangement occurs as described in Scheme II where IV is a tight ion pair and III is formed by the collapse of IV (internal return) without any intervention of an external return from fully separated ions. In competition with the internal return IV can be converted to the solvent separated ion pair V leading to II. Both $LiClO_4$ and $LiOCOCH_3$ increase the II/III product ratio in a similar way than LiCl. Presumably in the presence of salts the ion solvating ability of the medium increases and the formation of V, and therefore of II, is slightly favoured with respect to the internal return[5].

We wish to thank Prof. G. Illuminati for discussion.

## References

1. Part XIII in ref. 2.
2. E. Baciocchi and G. Illuminati, preceding communication.
3. G. Illuminati, L. Mandolini, A. Patara, and E. Baciocchi, Tetrahedron Letters, 4161 (1972).
4. Hartshorn in his review (Chem.Soc.Rev., 3, 167 (1974)) states that product studies are ambiguous with respect to the mechanism of electrophilic side-chain chlorination. However this is not completely correct since the absence of a partitioning isotope effect clearly shows that all the side-chain derivatives come from the intermediate I. See ref.3.
5. S. Winstein and G.C. Robinson, J.Amer.Chem.Soc., 80, 169 (1958).