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CHLORINE EXCHANGE IN ArSCl AND ITS DRASTIC ACCELERATION BY THE o-NO_2 GROUP

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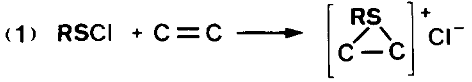
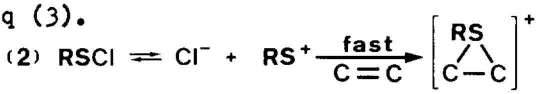
Summary - Exchange process $ArSCl + Li^{36}Cl \xrightarrow{AcOH} ArS^{36}Cl + LiCl$ occurs rapidly only for the sulphenyl chlorides, containing o-NO_2 group.This finding was rationalized by postulating a sulphurane structure due to participation of the o-NO_2 group.

The addition of sulphenyl halides to olefins is generally considered to follow an Ad_E2 mechanism [2,3](eq(1)). Indeed,while a vast body of data show sulphenyl chlorides undergo polarization in the sense $RS^{\delta+}$——$Cl^{\delta-}$,there is no evidence that these reagents could dissociate along this line in the usual solvents. The second order of the additions [2] and especially the absence of the effect of added chloride ion[3] seem to rule out any reasonable mechanisms involving a preliminarily ionization of RSCl (e.g. eq(2)). To the best of our knowledge the ionization has been observed either in H_2SO_4 [3] or in the presence of Lewis acids [2b,c,3,4].

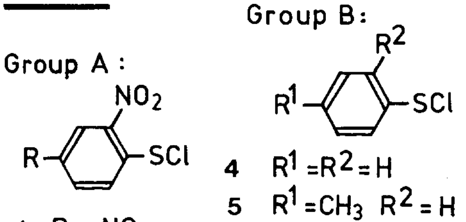
Recent investigations of the ArSCl additions revealed the important role of ion-pairing phenomena which determine both the structure and stereochemistry of products [2b,c,5]. Having in mind the investigation of these features by tracer methods we decided first to study the exchange process of a number of ArSCl (Chart 1) with $Li^{36}Cl$ in accordance with eq (3).





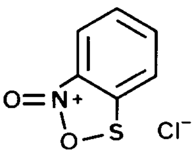
(3) $ArSCl + Li^{36}Cl \rightleftharpoons ArS^{36}Cl + LiCl$

Chart 1



1 R = NO_2
2 R = H
3 R = CH_3

4 $R^1 = R^2 = H$
5 $R^1 = CH_3$ $R^2 = H$
6 $R^1 = Cl$ $R^2 = H$
7 $R^1 = NO_2$ $R^2 = H$
8 $R^1 = NO_2$ $R^2 = Cl$



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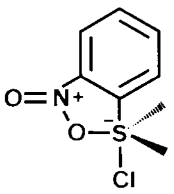

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The isotopic exchange experiments have been carried out as following: 1 mmol Li^{36}Cl was dissolved in 2 ml of CH_3COOH at 20° and 1 mmol of ArSCl was added. The sample of the mixture(with total radioactivity at least by two orders of magnitude exceeding background level)was chromatographed on SiO_2[6].The spots of ArSCl and of LiCl were cut off and their radioactivity(n-hexane:ether)was measured using SL-4000 liquid scintillation counting system.

The main result of the present work is the observation of the drastic dependence of the rate of exchange (eq(3)) on the structure of ArSCl. All sulphenyl chlorides investigated are divided into two groups (Chart 1).The compounds of the group A,which contain o-NO_2 substituent show *extremely rapid exchange*, which proceeds too fast to be measured by the method used[7].On the opposite,the ArSCl of the group B(Chart 1) even containing electron withdrawing groups(*e.g.* **6**,**7** and especially **8**) *do not undergo appreciable exchange* during 24 h.

The natural explanation of such a sharp difference of exchange behaviour of ArSCl of the group A *vs*.B is the acceptance of o-NO_2 participation either for dissociative process (ion pair **9**) or even for starting sulphenyl chlorides(hypothesis of the sulphurane structure of type **10**). These ideas have been occasionally advanced by a number of authors(*e.g.*[8])but still have not received unambigous structural proof (*cf*.[9]).

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6 "Silufol" plates were used; ratios of hexane:ether have been carefully selected for every particular ArSCl.

7 The use of AcOH:CCl_4 mixtures with minimal content of the acid has not also permitted to decrease a rate of the exchange to a measureable level.

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