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ADDITION OF SULPHENYL CHLORIDES TO ACETYLENES - VI - ADDITION OF p-TOLYL-SULPHENYL CHLORIDE TO SUBSTITUTED TOLANES: ORIENTATION AND KINETIC EFFECT OF SUBSTITUENTS.

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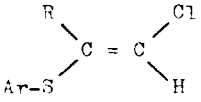
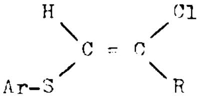
In the preceeding letter[1] it was shown that the orientation of the addition of p-nitro-benzene-sulphenyl chloride to phenyl-acetylene is affected by the solvent since in ethyl acetate the main reaction product was, in agreement with our previous findings[2], the antiMarkownikoff adduct I, while in acetic acid the Markownikoff adduct II is preferentially formed in agreement with Kharasch's results[3].



I

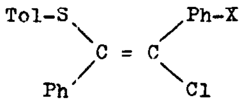


II

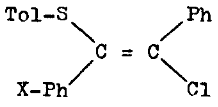
As we have already suggested[1], the solvent is not the only factor affecting the orientation, and the results of the addition to substituted tolanes, hereafter reported, support this hypothesis.

The addition of p-tolyl-sulphenyl chloride to tolane in ethyl acetate gives in almost quantitative yields a single product: 1,2-diphenyl-1-chloro-2-p-tolylmercapto-ethylene [m.p. 91° (ethanol); sulphone, m.p. 140° (ethanol)] of a probable trans configuration[4].

The same reaction carried out with p-metoxy-tolane yields almost exclusively the 1-chloro-1-methoxyphenyl-2-phenyl-2-p-tolylmercapto-ethylene-III [m.p. 154-5° (ethylacetate); sulphone, m.p. 165° (ethanol)] . The isomer IV has not yet been isolated



III



IV

and it should be, if present, not more than 5% of the products of the reaction.

On the contrary the addition to m-chloro-tolane yields as major product (~ 80%) the isomer IV [1-chloro-1-phenyl-2-m-chlorophenyl-2-p-tolylmercapto-ethylene, m.p. 83-84° (methanol); sulphone, m.p. 158-160° (ethanol)] , and as minor one the isomer III [1-chloro-1-m-chlorophenyl-2-phenyl-2-tolylmercapto-ethylene, m.p. 112° (methanol); sulphone, m.p. 173-174° (ethanol)] .

With p-chloro-tolane both compounds are formed in similar amounts: III ~ 60; IV ~ 40% [1-chloro-1-p-chlorophenyl-2-phenyl-2-p-tolylmercapto-ethylene-III, m.p. 83-84° (hexane), sulphone, m.p. 141-142° (ethanol); 1-chloro-1-phenyl-2-p-chlorophenyl-2-p-tolylmercapto-ethylene-IV, m.p. 126°-127° (ethanol), sulphone, m.p. 179-181° (ethanol)] .

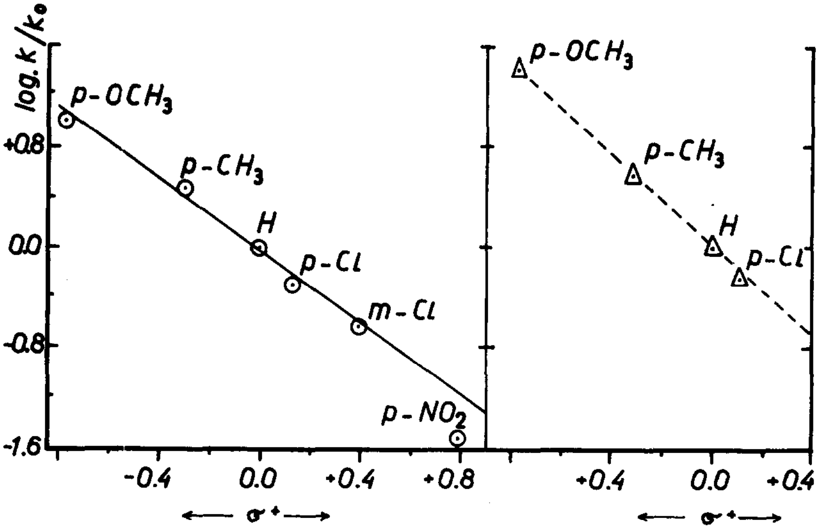
Quite clearly the addition to tolanes are directed regularly by polar effects even in ethylacetate. In this case, therefore, our results are in substantial agreement with those of Kharasch[3].

The rates of addition of a series of substituted benzenesulphenyl chlorides to tolane in chloroform and of p-tolyl-sulphenyl chloride to a series of substituted tolanes in chloroform and ethyl acetate have also been measured (see table 1 and Figure).

Table 1

Rates of addition of substituted phenylsulphenyl chlorides to tolane in chloroform at 25°

X =	p-OCH_3	p-CH_3	H	p-Cl	p-NO_2
k x 10^3 ($sec^{-1} mol^{-1}$ l)	170	190	159	77	6.9



⊙ Reactions in chloroform at 25°; "rho" = - 1.3

△ Reactions in ethyl-acetate at 25°; "rho" = - 1.8

The substituents in sulphenyl chloride, as previously observed in the addition to 1-butyne[5], neither affect significantly the rates nor present a definite trend. This is at variance to what Hogg[6] found in the addition of 2-nitro-4-X-benzene-sulphenyl chloride to cyclohexene and suggests that the two formally equivalent reactions substantially differ in the details of the reaction mechanism.

On the other hand electron-donor substituents in tolanes accelerate the additions[7]. The effect of substituents in both solvents follows the Hammett relationship, when the σ^+ constants are used, with fairly high values of "*rho*" (see Figure). It reconfirms the highly polar character of the transition state and the nucleophilic role played by the acetylene derivative.

The kinetic effect of the solvent is similar to that observed in the addition to alkyl-acetylenes[5] but it is even greater (see table 2). The energy and entropy of activation of the addition of p-tolyl-sulphenyl chloride to tolane in chloroform are also reported in table 2.

Table 2

Rates of addition (k in $sec^{-1}mol^{-1}$ l) of p-tolylsulphenyl chloride to tolane and to 1-hexyne.

		$k \cdot 10^3$	E(Kcal/mol)	log A	ΔS(u.e.)
Addition to tolane in:					
Chloroform	t = 0°	116			
	t = 15°	154			
	t = 25°	190	3.1	1.6	- 53
Ethyl acetate	t = 25°	0.093			
Addition to 1-hexyne[5] in:					
Chloroform	t = 25°	199	4.8	2.9	- 47
Ethyl acetate	t = 25°	9.07	7.4	3.4	- 45

The very low energy of activation and the large negative value of ΔS parallel our previous results on the addition to alkylacetylenes[5] and together with the effect of substituents in sulpheryl chloride suggest that the reaction follows a complex mechanism and that at least one relatively stable intermediate should be in the reaction path. The same explanation seems to be valid for the different orientations observed in different solvents or with different reactants.

All the new compounds gave satisfactory analyses. The full details of the experimental with the identification of the reaction products will be given at a later date as well as the techniques used in the kinetic experiments which are substantially the same as previously described[5].

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5) Nota III, A. Dondoni, G. Modena and G. Scorrano, Ric. Sci., 34 (II-A), 665 (1964).

6) Personal communication. In the mentioned case, electron withdrawing substituents increase the reaction rates following the Hammett relationship with σ^+ constants.

7) Similar results have been obtained in the alkyl-acetylenes reactions[5].