Tetrahedron Letters No.8, pp. 661-663, 1971. Pergamon Press. Printed in Great Britain.

ADDITION OF SULFONYL CHLORIDES TO ACETYLENES

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(Received in UK 12 December 1970; accepted for publication 19 January 1971)

Additions of sulfonyl chlorides to olefinic compounds are known.[1,2] However, additions of sulfonyl chlorides to acetylenes have not been reported in the prior literature. We have discovered that such addition reactions take place with terminal and non-terminal acetylenes, in the presence of a copper catalyst, such as Cu (I or II) chloride or cyanide, to yield β-chlorovinyl sulfones.

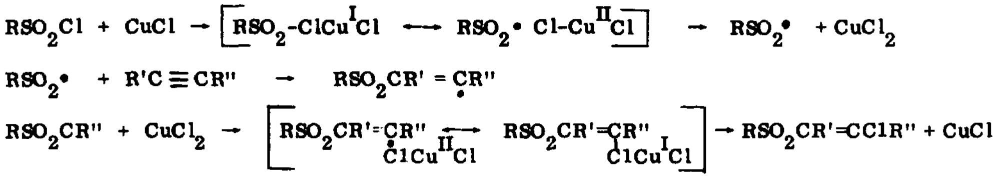
$$RSO_2Cl + R'C\equiv CR'' \rightarrow RSO_2CR'=CClR''$$

(R = alkyl, substituted alkyl, aryl and substituted aryls; R'R" = H, alkyl or aryl).

Previously reported syntheses leading to β-chlorovinyl sulfones are based on at least two steps. These methods include the preparation of β-chlorovinyl sulfides, as intermediate compounds, which are then oxidized to the corresponding sulfones.[3]

The reaction of sulfonyl chlorides to acetylenes could be performed at reflux temperatures in solution, or preferably, in a sealed tube where reaction could be conveniently followed by dilatometry. We suggest that this reaction, which is carried out under similar conditions as described for the redox-transfer addition of sulfonyl chlorides to olefins,[2] is also of a free-radical nature.

The present reaction may similarly be described as follows :

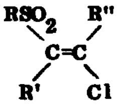


$$RSO_2Cl + CuCl \rightarrow \left[RSO_2\text{-}ClCu^{I}Cl \longleftrightarrow RSO_2{\bullet}\ Cl\text{-}Cu^{II}Cl\right] \rightarrow RSO_2{\bullet} + CuCl_2$$

$$RSO_2{\bullet} + R'C\equiv CR'' \rightarrow RSO_2CR'=\underset{\bullet}{C}R''$$

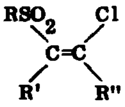
$$RSO_2CR'' + CuCl_2 \rightarrow \left[RSO_2CR'=\underset{ClCu^{II}Cl}{\underset{\bullet}{C}}R'' \longleftrightarrow RSO_2CR'=\underset{ClCu^{I}Cl}{C}R''\right] \rightarrow RSO_2CR'=CClR'' + CuCl$$

This reaction was found to be stereoselective and very dependent on polar factors, such as polarity of solvent and presence of additional chloride ions. Course of addition could be controlled to give preferentially either cis or trans addition products. Solvents having high and low dielectric constants favor trans and cis additions respectively. Acetonitrile exhibits an anomalous behavior, being different from other aprotic, dipolar solvents, in favoring somewhat the formation of the latter addition products. Added hydrochloride salts were shown to have a marked influence, leading predominantly to trans addition products, as shown in Table 1.



I

<u>trans</u>-addition
product



II

<u>cis</u>-addition
product

Table 1

Reaction of sulfonyl chlorides with phenylacetylene in the presence of cupric chloride and triethylammonium chloride (if indicated) at 100°.

Run No.	Sulfonyl Chloride	NEt_3HCl	Solvent	Time (hr)	Conversion (%)*	Yields(%) of I	II
1	benzene	+	acetonitrile	4	84	92	8
2	benzene	-	nitrobenzene	12	69	94	6
3	benzene	-	acetonitrile[4]	6	92	43	57
4	benzene	+	carbon disulfide	16	88	82	18
5	benzene	-	carbon disulfide	16	81	16	84
6	methane	+	acetonitrile	16	73	96	4
7	methane	-	acetonitrile	16	75	7	93

* Calc'd on consumed sulfonyl chloride.

Similar stereoselective additions to phenylacetylene, giving predominantly either <u>trans</u>- or <u>cis</u> -addition products (I) or (II) , were performed with a variety of sulfonyl chlorides yielding the following adducts (see Table 2).

Table 2.

Sulfonyl Chloride - Phenylacetylene Addition Products

(I and II, R'=H, R''=C_6H_5)

	I			II		
R	mp °C	λ_{max}	ϵ	mp °C	λ_{max}	ϵ
C_6H_5	80	262	10,000	84	275	20,000
CH_3	59-60	253	8,000	53-54	264	16,000
p-MeC_6H_4 (3)	102-103	246	12,500	123-124	276	20,000
p-ClC_6H_4	114-115	241	14,500	111-112	276	20,500
p-$NO_2C_6H_4$ (3)	127-128	256	15,500	157-158	286	20,000

Addition of benzene- and chloromethanesulfonyl chlorides to terminal alkynes (n-hexyl- and n-butylacetylene), as well as to a non-terminal alkyne (3-hexyne) gave liquid β-chlorovinyl sulfones.

Structural assignments for all isolated products were based on : (a) elemental analysis (b) catalytic reduction, where both I and II afforded the same saturated sulfone (c) comparison of adducts and their reduction products with known sulfones[3] (d) ultraviolet spectra showed bathochromic shifts, indicating planarity in II (R"=aryl) (e) infrared spectra, where the 6.18, 10.76 and 11.04 μ absorptions indicated I, and 10.72 and 10.92 μ indicated II (f) nmr, where planarity of II was evident by deshielding of the vinylic proton at δ 7.16 compared to I having δ 6.92 .

References.

(1) F.W. Stacey and J.F. Harris Jr., Organic Reactions, **13**, 150 (1963).

(2) M. Asscher and D. Vofsi, J. Chem. Soc., 4962 (1964).

(3) V. Caló, G. Modena, and G. Scorrano, J. Chem. Soc. (C), 1339, 1344 (1968).

(4) The amount of acetonitrile used also influences the course of the reaction. this will be fully described in a later publication.