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SOME CARBANIONIC REACTIONS OF α-CHLOROALLYL SULFONES[1]

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The chlorination of 3-methyl-2-butenyl phenyl sulfone with either hexachloroethane or 1,1-dichloro-3-methyl-2-butenyl phenyl sulfone in basic medium gives rise to 1-chloro-3-methyl-2-butenyl phenyl sulfone which in turn reacts in situ with electrophilic compounds to give a variety of products in good yields.

While the carbanionic reactions of allyl sulfones have been well studied,[2,3] the preparation of α-haloallyl sulfones and potentially attractive reactions of their carbanions have been evidently neglected. A few papers[4,5] describe a low-yield preparation of the parent compounds by the reaction of allyl sulfones with a base-solvent system followed by the action of a halogenating agent, usually $BuLi/C_6H_6/C_2Cl_6$[4] or $LDA/THF/C_2Cl_6$.[5] Chlorination of allyl sulfones, which possess an α' hydrogen, with solid $KOH/t\text{-}BuOH/CCl_4$ results in the formation of polyenes via the Ramberg-Bäcklund reaction of the α-monochlorinated species.[6]

We have recently reported[3] that both α-chloro- and α,α-dichloroallyl aryl sulfones can be easily prepared via the reaction of the corresponding allyl aryl sulfones with C_2Cl_6 carried out in the presence of concentrated aqueous NaOH solution and a quaternary ammonium salt as a catalyst (so called catalytic two-phase, CTP, system[7]).

We now wish to present our results on the application of α-chloroallyl sulfonyl carbanions in organic synthesis.

Thus stirring sulfone 1 (1.05 g, 5 mmol) and C_2Cl_6 (1.18 g, 5 mmol) in CH_2Cl_2 or C_6H_6 (2-5 ml) with 50% aq NaOH solution (5-7.5 ml) and a catalytic amount of tetrabutylammonium bromide (TBABr, 0.08 g, 0.25 mmol) results in the formation of α-chlorosulfone 2. Alternatively sulfone 2 can be generated from equimolar amounts of 1 and dichlorosulfone 3[8] in the CTP system (Scheme 1). Sulfone 2 generated by any of the two reported methods, reacts in situ with alkyl halides (6-10 mmol), electrophilic alkenes (5.5-7.5 mmol) or aromatic aldehydes (6-7.5 mmol) to give products 4-8 respectively in high yields.[9-12] Some products 4 easily undergo dehydrohalogenation to give dienes, e.g. the one-pot reaction of 2 with benzyl chloride at 80-85°C for 5 h results in the formation of diene 7[13] via chlorosulfone 4c. Amongst the compounds prepared the unknown hitherto compounds 6 represent a reactive class of oxiranes, e.g. the crude oxirane 6 ($Ar=4\text{-}CH_3OC_6H_4$) passed through a column with silica gel rearranges to ketosulfone 8[14] (Scheme 1, Table 1).

A new process of "vicarious" nucleophilic substitution of hydrogen in aroma-

Scheme 1.

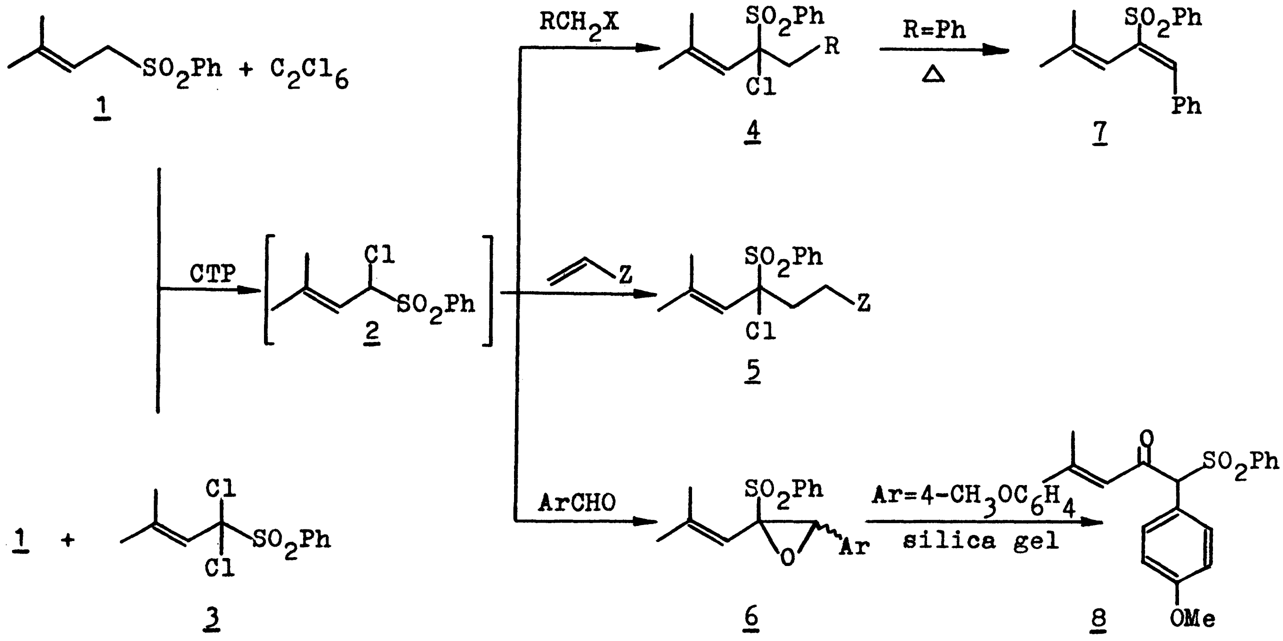

Table 1.

Product	Substituent	Yield (%)[a)]	Mp (°C), solvent for cryst
4a	R = CH_3[b)]	78	74-76, hexane-EtOH
4b	C_3H_7[b)]	61	oil
4c	C_6H_5	70	111.5-112, hexane-EtOH
7		70	104.5-106, hexane-EtOH[c)]
5a	Z = CN	74	114.5-115.5, hexane-EtOH
5b	SO_2Ph	84	108-109.5, hexane-EtOH
5c	COOH[d)]	84	119-120.5 dec, hexane-$CHCl_3$
6a[e)]	Ar = C_6H_5	94	oil
6b[e)]	4-$CH_3C_6H_4$	86	oil
6c[e)]	2-$C_{10}H_7$	95	oil
8[f)]		68	113-114, hexane-EtOH

a) The yields correspond to the products isolated by column chromatography. b) Bromides were used; the alkylation was carried out with a small amount of HMPT. c) Lit.[13)] mp 106 °C. d) t-Butyl acrylate was used; the crude product was hydrolyzed with conc. hydrochloric acid in aqueous solution of dioxane. e) One geometrical isomer of unknown stereochemistry. f) The crude reaction mixture contains oxirane 6 (Ar = 4-$CH_3OC_6H_4$) and no product 8 (from ^{1}H-NMR spectrum).

tic nitro compounds by carbanions derived from α-haloalkyl phenyl sulfones has been reported.15) We have found that sulfone 2 generated from 1 and 3 in t-BuOK/DMSO reacts with nitroaromatic compounds to give the products of "vicarious" nucleophilic substitution 9a-c16) in moderate yields (Scheme 2, Table 2).

Scheme 2.

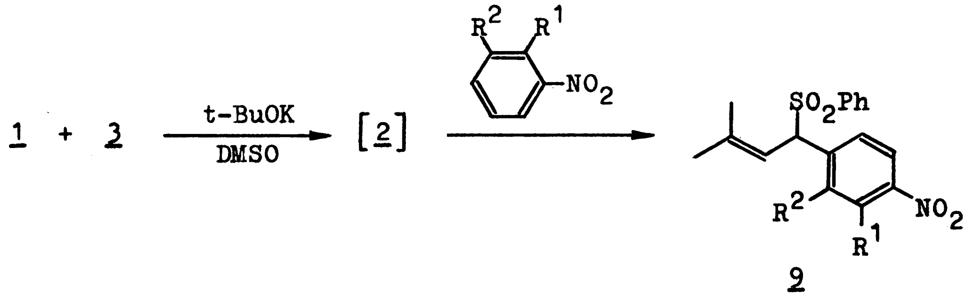

Table 2.

Product	Substituents	Yield (%)a)	Mp (°C), solvent for cryst
9a	$R^1= R^2= H$	49	136-137, EtOH-hexane
9b	$R^1= Cl; R^2= H$	51	134-135, EtOH-hexane
9c	$R^1= SPh; R^2= H$	51	126-126.5, EtOH-hexane
9db)	R^1=R^2= CH=CH-CH=CH	31	139-139.5 dec, EtOH

a) The yields correspond to the products isolated by column chromatography.
b) Pure 23) was used; no 9d was formed if 2 was generated from 1 and 3 as described above.

Thus our preliminary experiments with α-chloroallyl sulfones and α-chloroallyl sulfonyl carbanions provide usefull access to some interesting structures. This method is especially usefull for the preparation of compounds 6-9, formation of which engages both the carbanionic centre as well as the chlorine atom in 2.

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3) A. Jończyk and T. Radwan-Pytlewski, J. Org. Chem., 48, 910 (1983).
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1847 (1980); Heterocycles, 14, 1739 (1980).

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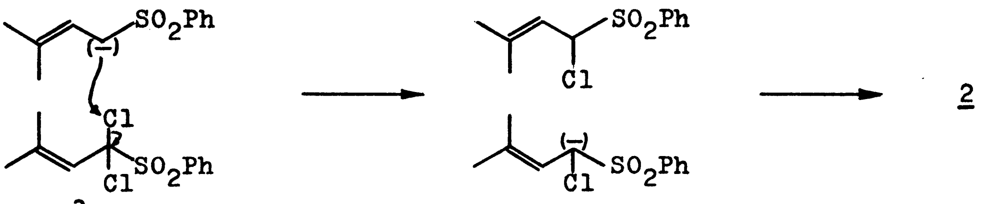
7) E. V. Dehmlow and S. S. Dehmlow, "Phase Transfer Catalysis", Verlag Chemie, Weinheim (1980); M. Mąkosza, "Survey of Progres in Chemistry", ed by A. F. Scott, Academic Press, New York (1980), Vol. 9, p. 1.

8) This reaction presents a unique example of a halogen transfer via the attack of a carbanion on the halogen atom in 3:



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Similar transformations are known as halogenophilic reactions, S_NX: N. S. Zefirov and D. I. Makhon'kov, Chem. Rev., 82, 615 (1982).

9) The reactions were carried out at 15-35 °C, until 2 disappeared (TLC). The reaction mixtures were conventionally worked up.3) Experimental details will be reported in a full paper.

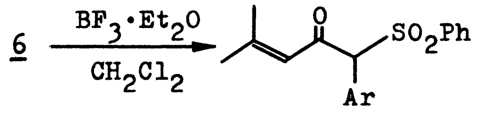
10) A similar approach using solid NaOH/DMF/CCl_4 was recently applied for chlorination and alkylation of benzyl sulfones: R. R. Regis and A. M. Doweyko, Tetrahedron Lett., 23, 2539 (1982).

11) A reverse sequence of reactions e.g. alkylation of 1 than chlorination of the alkylated sulfones, gives impure products 4 in low yields.

12) The ^1H-NMR and IR spectra were consistent with the assigned structure. Satisfactory elemental analyses were obtained for all compounds except of 6a-c; their structures were additionaly supported by chemical transformations.14)

13) The diene 7 was prepared by condensation of benzaldehyde with 1 in the CTP system (yield 25%): G. Cardillo, D. Savoia, and A. Umani-Ronchi, Synthesis, 1975, 453.

14) Other oxiranes 6 rearrange in the presence of BF_3 to ketosulfones in satisfactory yields:



yield 45-75%

This reaction is typical for sulfonyloxiranes: T. Durst, K.-C. Tin, F. de Reinach-Hirtzbach, J. M. Decesare, and M. D. Ryan, Can. J. Chem., 57, 258 (1979).

15) J. Goliński and M. Mąkosza, Tetrahedron Lett., 19, 3495 (1978).

16) To the stirred solution of t-BuOK (0.72 g, 6.2 mmol) in DMSO (12 ml) was added dropwise a solution of 1 (0.31 g, 1.5 mmol), 3 (0.42 g, 1.5 mmol) and $ArNO_2$ (3.1 mmol)in DMSO (5 ml) at 15-20 °C (ice-bath). The mixture was stirred at 15-20 °C for 5 min, poured into the mixture of ice with HCl aq and conventionally worked up (Table 2).

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