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**Preliminary communication**

# VARIABLE STEREOCHEMICAL COURSE IN THE REACTION OF 1-BENZENESULPHONYL-2-BROMO- AND -2-FLUORO-ETHENES WITH DIALKYL AND DIPHENYL CUPRATES

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## Summary

The nature of the cuprate has been found to exert a marked influence upon the stereochemical course of the coupling with sulphonyl-activated halogenoethylenes.

We recently [1] reported a study of the reactions between lithium dimethylcuprate, and *cis*- and *trans*-1-benzenesulphonyl-2-bromo-, or -2-fluoroethylenes (I)—(IV) or the corresponding chloro derivatives (eq. 1).

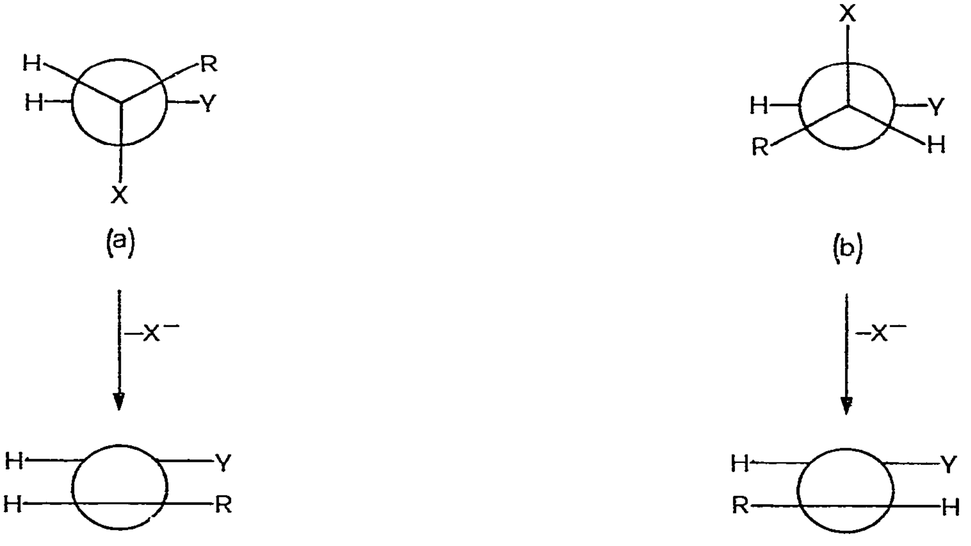
$$\underset{\text{(I)—IV)}}{PhSO_2CH{=}CHX} \xrightarrow{R_2CuLi} PhSO_2CH{=}CHR \qquad (1)$$

(I, *cis* X = Br; II, *trans* X = Br; III, *cis* X = F; IV, *trans* X = F)

The stereochemical course was found to depend upon the nature of the leaving group and substrate configuration. *trans*-Isomers gave complete retention, and retention also predominated (~90%) in the case of the bromo compound (I). The stereospecificity was lost when the fluoro derivative (III) was used. Finally, in the case of the bromoethylene (I) reductive dehalogenation was an important competitor, leading to phenylvinylsulphone.

With this background an investigation on the effects of the nature of the cuprate appeared warranted, and we now report the results of a study with di-n-butyl-, di-sec-butyl-, di-t-butyl- and diphenyl-cuprates. With these reagents the product of reduction (phenylvinylsulphone [1]) was not detected. In the reactions of the *cis*-isomer (I) variations in the stereochemical course were observed on changing the nature of the cuprate. The inversion component was rather low with di-n-butyl cuprate, but increased when the di-sec-butyl and the diphenyl reagents were used, while complete inversion was observed with di-t-butyl cuprate. Control experiments showed that *cis*→*trans* isomerization was not important either for the reagents or for the products. For the reactions involving di-t-butyl cuprate the complete absence of the *cis* product prevented evaluation of the possibility of a rapid *cis*→*trans* isomerization of the produced olefin but it was shown that the retention product is not formed even in reaction conducted at −78°C with an insufficient amount of cuprate for very short times (15 sec). Furthermore, since the behaviour of this reagent fitted well into the overall picture, it seems reasonable to assume that we are dealing largely or completely with a genuine inversion pathway. This type of stereochemical course was also followed by the fluoro olefin (III). Only in the case of di-n-butyl cuprate was a significant amount of retention (~20%) detected. Compounds II and IV reacted with complete retention (see Table 1).

The results reported can be contained within the framework previously discussed [1] in the light of current views on cuprate chemistry [2,3] and nucleophilic substitution at the ethylenic carbon [4]. At present we need only recall that independently of the model chosen, a crucial feature of the addition—elimination pathway proposed for these reactions [1] is the ejection of $X^-$ either from $sp^3$ or $sp^2$ carbanions. If we accept Miller's [4b] suggestion that the sulphonyl group is likely to lead to planarity in the anionic site, we can see that starting from *cis* isomers retention and inversion would respectively result from elimination of $X^-$ from the carbanionic intermediates (see Scheme 1 (a) and (b)).



SCHEME 1. R = alkyl or phenyl; X = halogen; Y = $PhSO_2$.

When large R groups are used, steric interference with the bulky $PhSO_2$ would occur during the elimination leading to *cis* products and therefore the route to the *trans* derivatives, which avoids $PhSO_2$/R eclipsing [5] would be preferred.

In conclusion, our results show the reaction between sulphonylhaloethylenes and cuprates to be a convenient route to vinylic sulphones. Reductive

TABLE 1

REACTIONS BETWEEN 1-BENZENESULPHONYL-2-HALOETHENES AND CUPRATES ($R_2CuLi$) AT —30°C IN ETHER[a]

| Substrate | R | Products[b] | | Overall yield (%) |
|---|---|---|---|---|
| | | *cis*-$PhSO_2CH{=}CHR$ | *trans*-$PhSO_2CH{=}CHR$ | |
| I[c] | Me | 90 | ~ 10 | — |
| I | n-Bu | 90 | 10 | 70 |
| I[d] | sec-Bu | 76 | 24 | 75 |
| I[d] | t-Bu | — | 100 | 70 |
| I[d,e] | t-Bu | — | 100 | 73 |
| I | Ph | 45 | 55 | 82 |
| II[c] | Me | — | 100 | — |
| II | n-Bu | — | 100 | 70 |
| II[d] | sec-Bu | — | 100 | 75 |
| II[d] | t-Bu | — | 100 | 78 |
| II | Ph | — | 100 | 73 |
| III[c] | Me | 65 | 35 | — |
| III | n-Bu | 22 | 78 | 73 |
| III[e] | n-Bu | 20 | 80 | 70 |
| III[d] | sec-Bu | 5 | 95 | 85 |
| III[d] | t-Bu | — | 100 | 73 |
| III[d,e] | t-Bu | — | 100 | 75 |
| III | Ph | 5 | 95 | 95 |
| IV[c] | Me | — | 100 | — |
| IV | n-Bu | — | 100 | 73 |
| IV[d] | sec-Bu | — | 100 | 85 |
| IV[d,e] | sec-Bu | — | 100 | 80 |
| IV[d] | t-Bu | — | 100 | 78 |
| IV | Ph | — | 100 | 83 |

[a] Unless otherwise indicated substrates and cuprates were $6\times10^{-2}$ *M*. Reactions times of 1—2 min. were used. [b] Satisfactory NMR spectra and elemental analyses were obtained for the new compounds here reported. [c] Data extrapolated from those obtained at —60—0°C and reported in ref. 1. [d] Cuprate was $2\times10^{-1}$ *M*. [e] THF was used as solvent.

dehalogenation seems to be restricted to dimethyl cuprate, and it does not compete significantly when the other reagents are used. The stereochemical pattern, is not complete enough to permit exact predictions, but is useful in devising syntheses. Finally, it appears that caution has to be used in regarding the reaction of cuprates with vinylic halides as stereospecific, at least when activated systems are used.

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