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MONO- AND BIS-ADDITION OF CUPRATES TO BENZENESULPHONYLACETYLENE.

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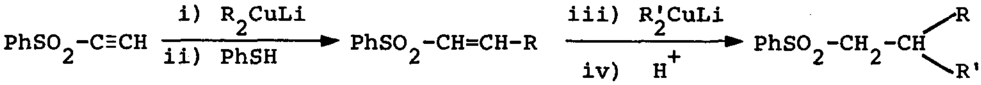
Addition of copper(I) reagents to acetylenes represents an useful stereoselective route to olefins.[1] In spite of the synthetic interest of the resulting ethylenic products[2] ethynyl sulphones have been used as substrates only in a few instances[3,4] involving mainly RCu type organometallics. Furthermore, when a dialkylcuprate was used an *anti*-addition was followed.[4] We report here pertinent stereochemical results concerning the mono-addition of dialkyl- and diphenyl-cuprates to benzenesulphonylacetylene which occurs according to equation(1).

$$PhSO_2\text{-}C{\equiv}CH \; + \; R_2CuLi \; \xrightarrow[-78-0^0]{ether} \; \underline{E} \text{ and } \underline{Z} \; PhSO_2\text{-}CH{=}CH\text{-}R \qquad (1)$$

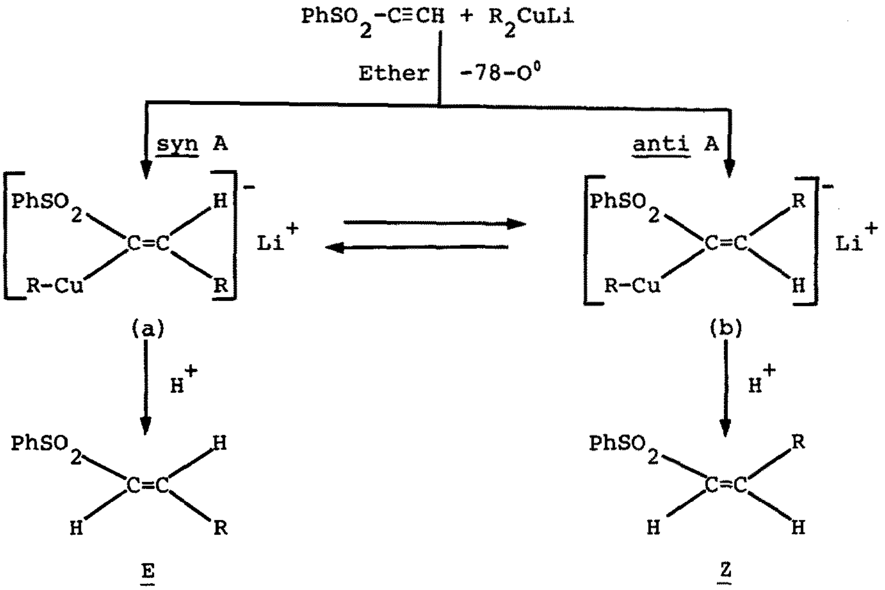
Also, we have devised a route which permits a facile double addition of cuprates with the consecutive formation of *two* C-C bonds according to equation(2).



$$PhSO_2\text{-}C{\equiv}CH \xrightarrow[\text{ii) } PhSH]{\text{i) } R_2CuLi} PhSO_2\text{-}CH{=}CH\text{-}R \xrightarrow[\text{iv) } H^+]{\text{iii) } R'_2CuLi} PhSO_2\text{-}CH_2\text{-}CH\begin{matrix} R \\ R' \end{matrix} \qquad (2)$$

MONO-ADDITION.- We have found that lithium dimethyl- and diphenyl-cuprates at 0° add to benzenesulphonylacetylene with complete *syn*-stereoselectivity leading to *E* olefins (See Scheme). In the case of the di-*n*-butyl- and di-*sec*-butyl-cuprates 5-20% of *Z* olefin was also formed. Furthermore, the data reported in Table reveal that by working at lower temperature the *syn*-stereoselectivity is lost, a relevant competition of the *anti*-course being observed. Only in the case of the di-*tert*-butyl reagent the *Z* isomer was not detected. An explanation of the temperature dependence is not straightforward. Actually, addition of cuprates to α-β acetylenic esters shows a higher *syn*-stereoselectivity at the lower tempera-

SCHEME



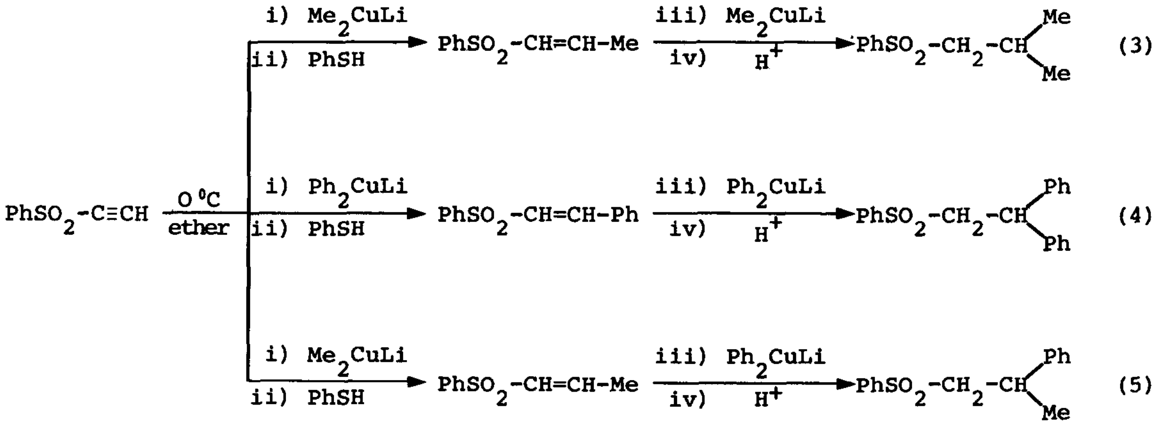
TABLE

R	T °C	Time (minutes)	Configuration of products[a]	
			Z%	E%
Me	0	30	-	100
Me	0	-[b]	20-30	80-70
Me	-78	0.5	38	62
Me	-78—0[c]	10—30	31	69
Ph	0	15	-	100
Ph	-78	0.5	10	90
n-Bu	0	40	5	95
n-Bu	0	0.5	5	95
n-Bu	-78	0.5	42	58
sec-Bu	0	30	22	78
sec-Bu	-30	0.5	34	66
sec-Bu	-78	0.5	42	58
tert-Bu	-30	10	-	100
tert-Bu	-30	40	-	100
tert-Bu	-78	0.5	-	100

a) Gas-chromatographic analysis (Cf.also ref.7). Overall yields for reactions which had reached completion were in the range 80-90%. b) Reactions quenched rapidly soon after mixing reagent with substrate(See text). c) 10' at -78° and then 30' at 0°(See text).

tures whereas at the higher temperatures the degree of stereoselectivity decreases.[5] As explanation of our data one could suggest the operation of two different pathways with different activation energies and/or an isomerization (b→a) of the likely intermediates. With the aim of finding out the importance of the latter process we performed two types of experiments using lithium dimethylcuprate as reagent. In one type reactions at 0° were quenched soon after mixing and 20-30% of the Z isomer was present in the products. Other reactions were performed at -78° for 10' and then the temperature was risen slowly to 0°. In these cases, even after **half** hour at 0°, the amount of Z isomer was found to be similar to that measured at -78°, but occasionally upon warming the mixture became dark and eventually only a small (<5%) amount of the Z isomer could be detected. In view of this complex pattern it seems more safe to postpone any conclusion on the role of isomerization process to a wider investigation which should also include experiments with the other cuprates.

BIS-ADDITION.-When benzenethiol was used as a quenching acid and the mixture was dropped into an additional solution of cuprate saturated sulphones were obtained according to equations (3)-(5).



$$PhSO_2\text{-}C{\equiv}CH \xrightarrow[\text{ether}]{0\,^{\circ}C} \xrightarrow[\text{ii) PhSH}]{\text{i) } Me_2CuLi} PhSO_2\text{-}CH{=}CH\text{-}Me \xrightarrow[\text{iv) } H^+]{\text{iii) } Me_2CuLi} PhSO_2\text{-}CH_2\text{-}CH(Me)(Me) \quad (3)$$

$$\xrightarrow[\text{ii) PhSH}]{\text{i) } Ph_2CuLi} PhSO_2\text{-}CH{=}CH\text{-}Ph \xrightarrow[\text{iv) } H^+]{\text{iii) } Ph_2CuLi} PhSO_2\text{-}CH_2\text{-}CH(Ph)(Ph) \quad (4)$$

$$\xrightarrow[\text{ii) PhSH}]{\text{i) } Me_2CuLi} PhSO_2\text{-}CH{=}CH\text{-}Me \xrightarrow[\text{iv) } H^+]{\text{iii) } Ph_2CuLi} PhSO_2\text{-}CH_2\text{-}CH(Ph)(Me) \quad (5)$$

It is worth noting that lithium alkyls could replace the cuprates during the second step very likely due to the formation *in situ* of hetero-cuprates. However, when this procedure was used lower yields were obtained.

In a typical procedure benzenesulphonylacetylene (0.22 g,1.32 mmol) in 20 ml of ether was allowed to react with lithium dimethylcuprate[6] (20 ml,6.6 10^{-2}M) for 40' at 0°. After quenching with thiophenol (20 ml,0.13 M) the mixture was added to a solution of diphenylcuprate (20 ml,6.6 10^{-2} M) at 0°, all the operations being performed under argon. After one hour, addition of aqueous NH_4Cl and extraction with ether yielded 0.24 g of phenyl 2-phenylpropylsulphone (yield 70%; m.p.87-88°C, from n-hexane).[7] Similar yields were obtained in the other cases.

REFERENCES AND NOTES

1) For reviews see, J.F.Normant, 'Organocopper Reagents in Organic Synthesis', in 'New Applications of Organometallic Reagents in Organic Synthesis, ed. D.Seyferth, Elsevier, Amsterdam,p.219(1976); G.H.Posner, Org.Reactions, 19,1(1972); W.Carruthers, Chem.and Ind.,931(1973). For recent work see, a) A.Alexakis, G.Cahiez, J.F.Normant, and J.Villieras, Bull.Soc.Chim. (France), 693(1977); b) H.Westmijze, H.Kleijn, and P.Vermeer, Tetrahedron Lett.,2023(1977); c) P.R.McGuirk, A.Marfat, and P.Helquist, ibid.,2465(1978).

2) P.D.Magnus, Tetrahedron, 33,2019(1977).

3) J.Meijer and P.Vermeer, Recueil Trav.Chim.Pays-Bas, 94,14(1975).

4) W.E.Truce and M.J.Lusch, J.Org.Chem., 39,3174(1974).

5) E.J.Corey and J.A.Katzenellenbogen, J.Amer.Chem.Soc., 91,1851(1969); J.B. Siddall, M.Biskup, and J.H.Fried, ibid., 91,1853(1969).

6) Cuprates were prepared from CuI and salt-free solution of RLi.

7) Satisfactory elemental analysis and N.M.R. spectra were obtained for the new compounds here reported.

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