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AN EASY ROUTE TO SOME α - AND β- ALLENIC ALCOHOLS VIA ORGANOCOPPER(I) INDUCED 1,3- SUBSTITUTION IN PROPARGYLIC METHANESULFINATES .

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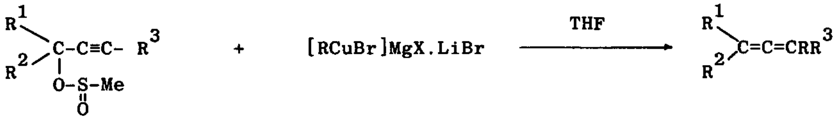
Recently [1] we reported on the efficient synthesis of various alkyl and aryl substituted allenic hydrocarbons 3 by interacting propargylic methanesulfinates 1 with organocopper(I) compounds of type 2 (eq. 1). Homocuprates , $R_2CuMgX.LiBr$, could not be used for the conversion of 1 into 3 as these reagents also attacked the sulfur atom in 1 .

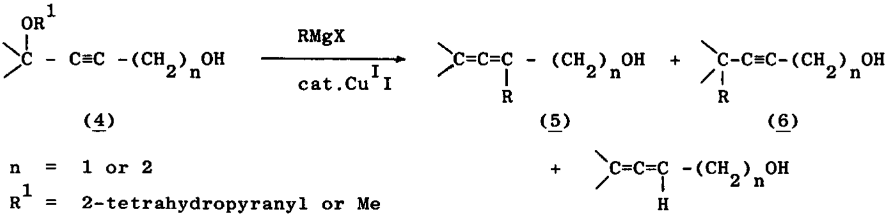


(1)

(1) (2) (3)

R^1,R^2 and R^3 : H , alkyl or aryl
R : alkyl or aryl
X : Cl or Br

The present work concerns the application of the reaction principle of eq. 1 for the synthesis of a number of α- and β - allenic alcohols. Some years ago [2] α - and β - allenic alcohols were prepared by copper(I) halide promoted 1,3-substitution in substrates of type 4 , but in most cases the produced α - and β - allenic alcohols 5 were contaminated with substantial amounts of compounds 6 and / or 7 (eq. 2) :



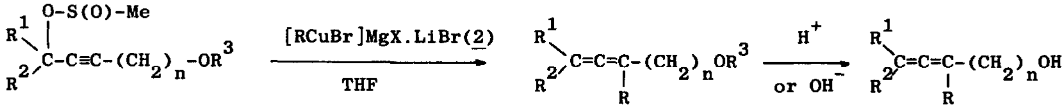
(4) (5) (6) (2)

n = 1 or 2
R^1 = 2-tetrahydropyranyl or Me

(7)

In this paper we shall show that pure α - and β - allenic alcohols 5 are easily accessible via a route similar to the one depicted in equation 1 (see eq. 3)[3].
Thus reaction of the hydroxy protected methanesulfinates 8 (0.030 mol)with the organobromocuprates 2 (0.030 mol , R = alkyl or aryl)[4] in dry tetrahydrofuran (THF , 100 ml)

for 15 min.at $-50^{\circ}C$ followed by allowing the reaction temperature to rise to $+20^{\circ}C$ and subsequent aqueous work-up (cf[1]) , furnished in all cases allenes 9a-f in excellent yields (>90%). Without further purification allenes 9 were deprotected to yield pure α- and β -allenic alcohols 5 by treating with p-toluenesulfonic acid in methanol (R^3 = EtOCH(Me)- ; 9a-d ⇒ 5a-d) or with sodium hydroxide in aqueous methanol (R^3 = Me_3Si- ; 9e-f ⇒ 5e-f)[5].The table summarizes the results .



(8) (9) (5) (3)

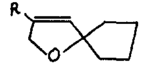
In contrast with the reaction of 8 (R^1,R^2 = $-(CH_2)_4-$, R^3= Me_3Si , n = 1) with phenylbromocuprate (2 ; R = Ph,X = Br) a non-selective reaction was observed when the same copper(I) compound was reacted with $MeS(O)O-CH_2-C≡C-CH_2OR^3$ (8;R^3 = EtOCH(Me)-).In this case the desired allene $H_2C=C=C(Ph)CH_2OR^3$ and $PhCH_2C≡C-CH_2OR^3$ were obtained in a ratio 35:65. This ratio was improved up to 90 : 10 when the corresponding tosylate $p-CH_3-C_6H_4SO_2OCH_2C≡C-CH_2OR^3$ was reacted with the cuprate but hitherto no conditions have been found under which the allene was free from the isomeric product. For most purposes , however , the presented method will be suitable .

Table

Starting compound 8[6]				Cuprate 2		Product[a]	B.p.	n_D^{20}	Yield[b]
R^1	R^2	R^3	n	R	X	5	°C/mmHg		(%)
H	H	EtOCH(Me)	1	Et	Br	5a	67-68/25	1.4753	60
H	H	EtOCH(Me)	1	t-Bu	Cl	5b	74-75/22	1.4721	73
Pr	H	EtOCH(Me)	2	Me	Cl	5c	91-93/17	1.4748	77
Pr	H	EtOCH(Me)	2	Et	Br	5d	106-108/18	1.4737	75
$-(CH_2)_4-$		Me_3Si	1	Me	Cl	5e	110-112/10	1.5111	70
$-(CH_2)_4-$		Me_3Si	1	Ph	Br	5f	80-81(m.p.)	-	90

a) Purity of 5 : >95% (based on ^1H NMR,IR and GLC analysis) b) Yields refer to distilled products and are calculated on the starting compound 8 .

References and notes.

1. P.Vermeer,H.Westmijze,H.Kleijn and L.A.van Dijck,Recl.Trav.Chim.Pays-Bas,97,56 (1978).
2. A.Claesson,L.Tåmnefors and L.I.Olsson,Tetrahedron Lett. , 1975 , 1509.
3. The preparation of α-allenic alcohols from acetylenic oxiranes and organocopper(I) compounds has also been described: P.R.Ortiz de Montellano,Chem.Comm.,1973,709; P.Vermeer,J.Meijer, C.de Graaf and H.Schreurs , Recl.Trav.Chim.Pays-Bas , 93 , 46 (1974).
4. The cuprates 2 were prepared as indicated in ref. 1 .
5. When in these cases for R^3 EtOCH(Me)- was used , tarry products and presumably the spiro compound  (yield : 30 %) were obtained upon acidic deprotection .
6. Compounds 8 were prepared from $R^1R^2C(OH)-C≡C-(CH_2)_nOR^3$ and $CH_3S(O)Cl$ according to ref. 1.

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