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ADDITION OF SULPHENIC ACIDS TO UNACTIVATED ALKYNES TO GIVE ALKENYL SULPHOXIDES

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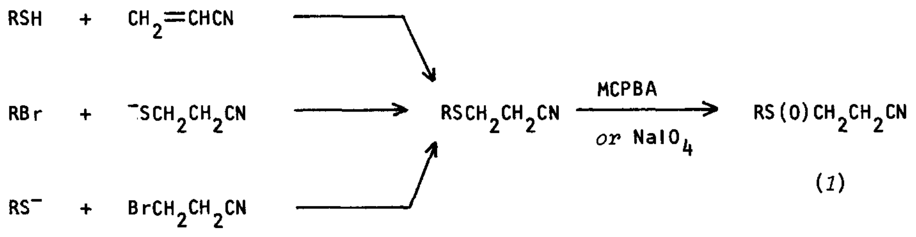
Summary. Sulphenic acids, conveniently generated by thermolysis of readily available β-cyanosulphoxides, added regiospecifically in good yield to 1-alkynes to provide synthetically useful alkenyl sulphoxides.

The increasing synthetic utility of alkenyl sulphoxides, particularly as dienophiles[1] and Michael acceptors,[2] has stimulated interest in convenient methods for their preparation.[3] The addition of sulphenic acids to alkynes provides in principle a simple method of making alkenyl sulphoxides (equation 3) but it has found little use up to now because it appeared to be limited in scope.[4,5] Methyl propiolate and ethynyl benzene were shown to be good substrates,[4] but simple alkynes were considered to be unreactive,[4,5] despite a brief mention of the addition of ethanesulphenic acid to 1-heptyne in low yield.[5] The ephemeral nature of most sulphenic acids may also have been an inhibiting factor. With few exceptions[6] they cannot be isolated because they readily undergo intermolecular dehydration and other transformations, so when required for a specific reaction they have been generated in situ by thermolysis of dialkyl or alkyl aryl sulphoxides,[4] thiosulphinates,[5] or N-alkylidenesulphinamides.[7] Some of these compounds are inconvenient to prepare and handle, and we have found the best precursors to be 1-cyano-2-aryl (or alkyl)sulphinylethanes (*1*). They are easily prepared by oxidation of the readily available sulphides[8] (equation 1) and they thermolyse cleanly above 100°C to give the corresponding



$$\begin{tikzcd}
\mathrm{RSH} + \mathrm{CH_2{=}CHCN} \arrow[dr] & & \\
\mathrm{RBr} + {}^{-}\mathrm{SCH_2CH_2CN} \arrow[r] & \mathrm{RSCH_2CH_2CN} \arrow[r, "\mathrm{MCPBA}", "or\ \mathrm{NaIO_4}"'] & \mathrm{RS(O)CH_2CH_2CN} \\
\mathrm{RS^-} + \mathrm{BrCH_2CH_2CN} \arrow[ur] & &
\end{tikzcd} \quad (1)$$

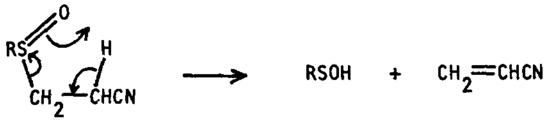
(*1*)

sulphenic acids and acrylonitrile (equation 2). The cyanosulphoxides (*1*) were chosen because the ease of thermal decomposition of sulphoxides is facilitated by the presence of an activated hydrogen atom on a β-carbon atom.[4]

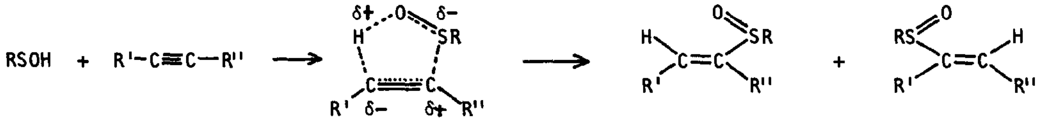
Thermolysis of 1-cyano-2-phenylsulphinylethane (*1a*) in 1-octyne (5 equiv.) at 126°C for 30 minutes gave 2-phenylsulphinyloct-1-ene (*3a*) (94%) after evaporation of the octyne and chromatography on silica. Evidently thermal decomposition of (*1a*) gave acrylonitrile and benzenesulphenic acid (*2a*) (equation 2) which in turn added regioselectively to 1-octyne (equation 3). Methanesulphenic acid (*2b*) and ethoxycarbonylmethanesulphenic acid (*2c*), generated by thermolysis of (*1b*) and (*1c*) respectively in 1-octyne, also added efficiently to the solvent. Results for the addition of the sulphenic acids (*2a–c*) to various alkynes by this simple procedure are recorded in the Table. It is clear that, contrary to previous opinion,[4,5] alkynes need not be conjugated with activating groups in order to undergo efficient and regioselective addition to sulphenic acids. The NMR spectral characteristics of the vinyl protons in the minor isomers (*4b*) (J 15 Hz), (*4c*) (J 16 Hz), and (*4m*) (J 14 Hz) indicated stereospecific cis addition, as expected for a pericyclic mechanism.[9] However, the regioselectivity of addition suggests that the partial carbon-sulphur bond in the transition state (*A* in equation 3) is polarized such that the carbon atom has some cationic character. This rationale finds analogy in the interpretation of the regioselectivity of addition of sulphenic acids to ethynylbenzene and to olefins.[4,10] The greater stabilization by phenyl than methyl of the polarized transition state (*A*) (cf. ref. 11) may also contribute to the higher degree of regioselectivity of addition of benzenesulphenic acid than methanesulphenic acid to the alkynes.

The synthetic potential of alkenyl sulphoxides is enhanced by the ready accessibility of functionalized derivatives by this method. For example, the selective addition of benzenesulphenic acid to the triple bond in 1-ethynylcyclohexene to give (*3k*) is of interest in relation to the use of butadienes bearing sulphur containing groups in Diels-Alder reactions;[12] the oxidation of hydroxy alkenyl sulphoxides (*3f*, *3g*) provides keto alkenyl sulphoxides which are excellent Michael acceptors,[13,14] and which are potentially capable of other transformations;[15] and the use of (*3n*) as an alkylating agent provides a new method of introducing an alkenyl sulphoxide group into a molecule.[14]

Hydrolysis and displacement accompanied addition of benzenesulphenic acid to 3-bromopropyne, the products being (*3n*) (36%), (*3d*) (11%), and 2,3-di(phenylsulphinyl)prop-1-ene



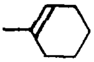
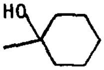
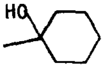
(*1*) (*2*) (2)



(*A*) (and with R',R" interchanged) (*3*) (*4*) (3)

TABLE

Products from thermolysis of β-cyanosulphoxides (*1*) in alkynes

				Reaction conditions		Products (%)[a]	
	R	R'	R''	Temp (^{o}C)	Time (h)	(*3*)	(*4*)
a	Ph	H	$(CH_2)_5CH_3$	126	0.5	94	0
b	Me	H	$(CH_2)_5CH_3$	126	9	86	3
c	CH_2CO_2Et	H	$(CH_2)_5CH_3$	126	1	83	0.5
d	Ph	H	CH_2OH	114	2	82	3
e	Me	H	CH_2OH	114	24	75	9
f	Ph	H	$CH(OH)CH_3$	107	3	85	0
g	Me	H	$CH(OH)CH_3$	107	4	75	9
h	Ph	H	CH_2SMe	109	2	52	0
i	Me	H	CH_2SMe	109	4	50	0
j	Ph	Br	$(CH_2)_5CH_3$	126	0.5	94	0
k	Ph	H		126	0.5	91	0
l	Ph	H		126	0.5	94	0
m	Me	H		126	1.5	74	18
n	Ph	H	CH_2Br	90	12	36[b]	0

a Yield % of isolated products

b Together with (*3d*) (11%) and (*3*, R = Ph, R' = H, R'' = S(O)Ph) (11%)

(11%). The water for hydrolysis presumably arose from some intermolecular dehydration of the sulphenic acid.[4] Accordingly, hydrolysis of (*3n*) in boiling wet acetone gave (*3d*) quantitatively, whilst thermolysis of (*1a*) in a boiling benzene solution of (*3n*) over molecular sieves gave 2,3-di(phenylsulphinyl)prop-1-ene (49%) together with a trace of (*3d*). This direct conversion of an allylic bromide into an allylic sulphoxide is unprecedented.

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