"Ene-type" Addition of Alkenes to Phenyl Vinylsulfoxide

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Abstract - Phenyl vinylsulfoxide reacts under acylating conditions (TFA, TFAA) with isobutene to give double "ene" α,β -adduct. Propene and other alkenes examined afford a β -"ene" alkylation accompanied by trifluoroacetoxylation at the same carbon atom.

Due to their unsaturation, vinylsulfoxides are even more versatile than their saturated counterparts¹. They undergo more complex Pummerer-type reactions leading to the functionalization of *both* carbons of the C-C double bond by identical or different substituents. As we found, the process can also be accompanied by sulfur migration which results in an apparent β , β -double functionalization. Phenyl vinylsulfoxide 1 is known to undergo double trifluoroacetoxylation upon reaction with trifluoroacetic anhydride². More significantly, C-C bond formation was observed with very reactive ketene O,O-acetals using Lewis acid catalysis³. The outcome depends on the *bulkiness* of substituents on the silicon atom (scheme 2).



We report here on the behaviour of phenyl vinylsulfoxide 1 under acidic conditions (trifluoroacetic acid, TFA and its anhydride, TFAA) in the presence of non-activated olefins. As we found, isobutene affords the corresponding double "ene" adduct 4, most probably according to the mechanism proposed in scheme 2.



Accordingly, the initially formed electron-poor vinyl sulfoxonium cation 5 undergoes the first "ene" addition in the β -position, followed by the second alkylation of the next electrophilic species 6. This second step is fully analogous to the well-known addition of alkenes to alkyl sulfoxides under the classical Pummerer rearrangement conditions³. One isolated example, recently presented in the literature, has revealed double alkylation products upon addition of allyl magnesium bromide to several phenyl vinylsulfoxides, which proceeds via a different mechanism⁴.

A completely different outcome is encountered with propene and other olefins. A β -alkylation and a β -trifluoroacetoxylation take place thereby leading to 7 (Scheme 3). The results are summarized in Table 1.



Scheme 3	3
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Entry	R ¹	R ²	Yield of 7(%)
1	Н	н	7 a, 72
2	н	C ₂ H ₅	7b, 65
3	н	n-C3H7	7c, 68
4	н	n-C5H11	7d , 61
5	CH3(E)	н	7e, 69
6	(CH ₂)3		7f , 62

The formation of 7, which seems to derive from a β , β -dication appears to be highly uncommon. The clue to this reaction is inferred from the fact that the isolated α , β -bistrifluoroacetate 8 affords the same product 7b with pentene. This in turn permits to conclude that the reactive species is the episulfonium cation 9 which reacts at the more hindered carbon (Scheme 4). Attack at the other possible reaction site was not observed.



Inasmuch as the process apparently involves a 1,2 migration of the phenylsulfenyl group, we have chosen a more dissymmetrical case, namely 10 which derives from 1-phenylsulfinyl propene. When 10 is exposed to excess pentene in TFA for 2 days, the expected rearranged product 12 is indeed formed through the episulfonium intermediate 11a (Scheme 5).



Scheme 5

The presence of about equal amounts of the "normal" Pummerer adduct 14, i.e. without migration of the phenylthio group, is intriguing. In fact, it seems that only the diastereoisomer 10a reacts through an episulfonium ion 11a which leads to sulfur migration. On the other hand, the more hindered isomer cis 11b is apparently not formed at all and the reaction would proceed through an α -thiocarbonium ion 13 instead, i.e. without sulfur migration.

Isobutene does not react with double trifluoroacetoxylation products 8 or 10, which implies that the sequential pathway 5 to 6 is operating. Further investigations about the mechanism of this reaction are under study.

This work illustrates further the versatile behaviour of vinylsulfoxides and more specifically, it describes interesting "ene-type" functionalizations of non-activated olefins by phenyl vinylsulfoxides.

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