PREPARATION AND CHEMISTRY OF VINYL TRIFLATES. XV.
ALKYLATION OF AROMATIC SUBSTRATES[1]

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One of the oldest and most extensively employed reactions in organic chemistry is the Friedel-Crafts alkylation, where aromatic substrates undergo substitution by a wide variety of alkyl derivatives in the presence of Lewis acid catalysts.[2] In the case of highly reactive derivatives, such as fluorosulfonate esters, aromatic alkylation occurs even in the absence of catalysts.[3] It is, of course, well established that these reactions proceed by electrophilic processes via carbonium ions or carbonium ion-like species.[2]

Recently, besides normal carbonium ions, there has been considerable interest and activity in vinyl cations[4] yet little is known about possible electrophilic aromatic alkylation with such species. A few intramolecular alkylations and formation of benzothiophenes and benzofurans from appropriate vinylic substrates and perhaps via vinyl cations have been reported,[5] but with the exception of a recent report by Roberts and Baset[6] on alkylation with styryl bromide and AlBr$_3$, there are very few reports on intermolecular aromatic alkylations with vinyl derivatives. Hence, we decided to investigate the feasibility of using vinyl triflates 1-5 in aromatic alkylations.
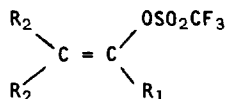
1: R$_1$=R$_2$=C$_6$H$_5$

2: R$_1$=C$_6$H$_5$,R$_2$=CH$_3$

3: R$_1$=R$_2$=CH$_3$
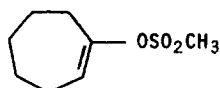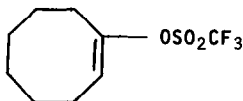
Vinyl triflates 1-5 were prepared in good yields from the appropriate ketones; in the case of 1 and 2 by trapping the KH derived enolate[7] with triflic anhydride, and triflates 3-5 via the Dueber method.[8] Alkylations were carried out in sealed tubes with 2-5 mmoles of triflate in a

20-30 fold excess of aromatic substrate and with 1-2 equivalents of 4-methyl-2,6-di-tert-butylpyridine, a non-nucleophilic hindered base.[9] The base was used in order to prevent protonation and possible polymerization of both the starting vinyl triflates and the product styrenes by the triflic acid formed in the reaction. Reaction mixtures were worked up by dilution with pentane, filtration of the precipitated pyridinium triflate, evaporation of the solvent and vacuum distillation of the residual oil in a micro-still. Products were identified by spectral means[10] and/or comparison with authentic samples where available. The results are given in Table I.
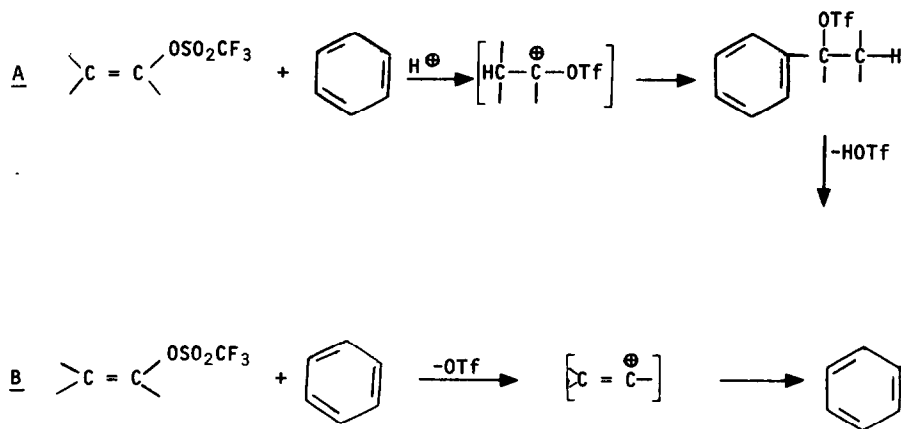
Table I. Alkylation of Aromatic Substrates with Vinyl Triflates

Starting Triflate	Aromatic Substrate and Rxn. Cond.	Product, Yield[a]
1	C_6H_6, 150°, 24 hrs.	$(C_6H_5)_2C=C(C_6H_5)_2$, 54%
2	$C_6H_5OCH_3$, 120°, 24 hrs.	$(CH_3)_2C=CC_6H_5(C_6H_4OCH_3)$, 79%
2	$C_6H_5CH_3$, 120°, 24 hrs.	$(CH_3)_2C=CC_6H_5(C_6H_4CH_3)$, 66%
2	C_6H_5Cl, 120°, 24 hrs.	$(CH_3)_2C=CC_6H_5(C_6H_4Cl)$, 80%
2	C_6H_5F, 120°, 24 hrs.	$(CH_3)_2C=CC_6H_5(C_6H_4F)$, 87%
3	C_6H_6, 80°, 48 hrs.	No Rxn., 3 recovered
3	C_6H_6, 80°, BF_3, 48 hrs.	No Rxn., 3 recovered
3	C_6H_6, 150°, 12 hrs.	Tar
4	$CH_3OC_6H_5$, 155°, 20 hrs.	1-(methoxyphenyl)cyclooctene, 20%
5	$CH_3OC_6H_5$, 170°, 24 hrs.	1-(methoxyphenyl)cycloheptene, 30%

[a]Isolated yields, > 98% pure by gc.

Perusal of the data in Table I reveals a number of interesting facts. Aklylation of aromatic substrates and formation of styrenes from vinyl triflates occurs in good yields (for small scale reactions), even in the absence of the usual Friedel-Crafts catalysts and in the presence of the amine base. Alkylation takes place not only of activated substrates like anisole and toluene, but also of benzene and deactivated substrates like chlorobenzene. However, as shown by the behavior of triflates 3 and 4, alkylation only occurs with vinyl triflates that cannot eliminate a β-proton to give an acetylene or allene. In fact, both triflates 4 and 5 give only 20% and 30% of alkylation products, respectively, and substantial amounts of allenes, 1,2-cyclooctadiene and 1,2-cycloheptadiene, as determined by the mass spectrum of their respective dimers.[11] Triflate 3 does not react with benzene under mild conditions, in the presence or absence of BF_3 catalyst, and gives only tar under more vigorous‚conditions. The tar presumably arises from elimination of CF_3SO_3H, allene formation and subsequent polymerization.

Vinyl triflate alkylations can occur by one of two possible mechanisms:

$$\underline{A} \quad \text{>C = C<}^{OSO_2CF_3} \; + \; \bigcirc \; \xrightarrow{H\oplus} \; \left[HC-\overset{\oplus}{C}-OTf \right] \; \longrightarrow \; \bigcirc-\overset{OTf}{\underset{}{C}}-\overset{}{\underset{}{C}}-H$$

$$\downarrow -HOTf$$

$$\underline{B} \quad \text{>C = C<}^{OSO_2CF_3} \; + \; \bigcirc \; \xrightarrow{-OTf} \; \left[\text{>C} = \overset{\oplus}{\text{C}}- \right] \; \longrightarrow \; \bigcirc-\overset{}{\underset{}{C}} = C<$$

Path $\underline{A}$ involves protonation of the starting triflate by traces of acid, followed by normal
Friedel-Crafts type alkylation, and then elimination of triflic acid to give the observed products.
Path $\underline{B}$ involves formation of a vinyl cation, and electrophilic aromatic substitution by this
vinyl cation to give the products directly. Although we do not have any direct
evidence for either mechanism, we favor Path $\underline{B}$ on the basis of the following considerations.
Alkylation occurs even in the presence of the amine base, which should neutralize any acid present.
At least qualitatively, these reaction conditions are similar to those observed for the solvolysis
of vinyl triflates $\underline{1}$-$\underline{5}$ that have clearly been shown to proceed via vinyl cations.[4] Moreover,
it is known that vinyl halides do not condense with benzene in the presence of catalytic amounts
of sulfuric acid.[12] Since the triflate group is more deactivating[13] than a halide, a vinyl
triflate is even less likely to be protonated than a vinyl chloride.

In summary, we have shown that alkylation of aromatic substrates by a variety of vinyl
triflates is possible resulting in good yields of substituted styrenes under moderate reaction
conditions. The full scope, exact mechanism, relative reactivity, selectivity, etc., of these
novel vinyl triflate aromatic alkylations are under active investigation and will be reported in
future papers.

References and Notes

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