

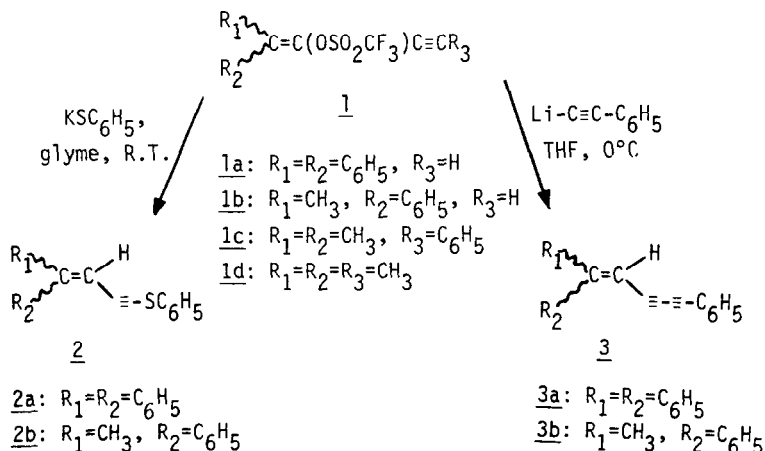
REACTION OF ENYNE TRIFLATES WITH NUCLEOPHILES

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**Abstract:** Reaction of nucleophiles with enyne triflates,  $R_1R_2C=C(OTf)C\equiv CR_3$ , via an  $S_N-2'$  process, results in functionalized enynes by way of a 1,3-hydride shift from the initially formed butatrienes.

Bimolecular nucleophilic substitution with allylic rearrangement ( $S_N-2'$ ) has been of considerable mechanistic and synthetic interest<sup>1</sup> since the days it was first proposed by Bergmann,<sup>2</sup> Hughes<sup>3</sup> and Winstein<sup>4</sup> and first reported by Kepner, Winstein and Young.<sup>5</sup> Likewise the reaction of propargyl halides with nucleophiles proceeds through an  $S_N-2'$  process and gives rise to the formation of functionalized allenes.<sup>6-8</sup> Therefore, it was of interest to explore the feasibility of an  $S_N-2'$  type reaction with enyne triflates, 1, and the possible formation of functionalized butatrienes. Triflates, 1, can be easily made in good overall yields by adoption of previously reported<sup>9</sup> methods. Treatment of these triflates with certain nucleophiles in glyme or THF results in the formation of enyne products as shown in Scheme 1.

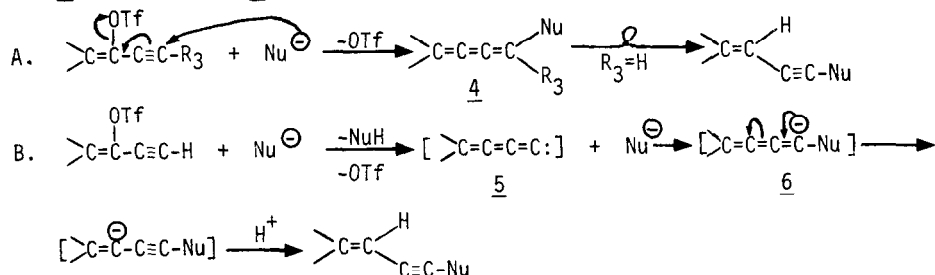


Scheme 1.

Specifically treatment of triflates 1a and 1b with potassium thiophenoxide ion in glyme under argon at 25°C gave, upon concentration of the solvent and flash column chromatography<sup>10</sup> on silica gel (hexane as eluent), a 55-65% yield of pure eneyne products 2a and 2b.

Likewise, treatment of triflates 1a or 1b with  $\text{LiC}\equiv\text{CC}_6\text{H}_5$  in THF at 0°C gave a 50% isolated yield of pure enediynes 3a and 3b respectively. The product enynes 2a and 2b and enediynes 3a and 3b were identified by spectral means as summarized in the Table. Particularly characteristic are the  $\text{C}\equiv\text{C}$  absorptions in the infrared and the acetylenic chemical shifts in the C-13 nmr along with the mass spectra.

Enynes 2 and enediynes 3 may arise by two different processes as shown:



In path A, a nucleophilic  $\text{S}_{\text{N}}-2'$  process gives butatriene 4 that, when  $\text{R}_3=\text{H}$ , undergoes a 1,3 hydrogen shift to give the observed products. Path B involves formation of carbene 5, with the nucleophile acting as base, followed by an ylide complex 6, that upon protonation yields the observed products.<sup>11</sup>

Path B can be ruled out on the basis of the following evidence. The known  $\text{pK}_a$  values of the conjugate acids, (i.e.  $\text{C}_6\text{H}_5\text{SH} = 6.5$  vs  $\text{C}_6\text{H}_5\text{C}\equiv\text{CH} = 21$  in methanol) mitigate against the possibility of  $\text{C}_6\text{H}_5\text{S}^-$  being sufficiently basic to abstract the acetylenic proton in 1 ( $\text{R}_3=\text{H}$ ) to give carbene 5. Furthermore, with 1a a small amount of cumulene 4a could be detected, albeit not isolated, by the very characteristic ir absorption<sup>12</sup> at  $2040\text{ cm}^{-1}$ . Moreover, formation of butatrienes,  $[(\text{CH}_3)_2\text{C}=\text{C}=\text{C}(\text{SC}_6\text{H}_5)\text{R}_3; \text{R}_3=\text{CH}_3 \text{ and } \text{C}_6\text{H}_5]$  were clearly observed in the infrared (at  $2070$  and  $2060\text{ cm}^{-1}$  respectively) in the reaction of 1c and 1d respectively with  $\text{C}_6\text{H}_5\text{S}^-$ . Unfortunately, these butatrienes were too unstable to isolate. Since triflates 1c and 1d are incapable of forming carbene 5 this speaks strongly in favor of path A, an  $\text{S}_{\text{N}}-2'$  process, for the reaction of enyne triflates with  $\text{C}_6\text{H}_5\text{S}^-$ . Base catalyzed 1,3-hydrogen migration and butatriene-enyne isomerization is well known.<sup>13</sup>

In contrast acetylide ions are clearly sufficiently basic to form carbenes 5 by abstracting a proton from enyne triflates 1a and 1b. All attempts to observe cumulenes in these reactions or to react triflates 1c and 1d with  $\text{C}_6\text{H}_5\text{C}\equiv\text{C}^-$  failed. With 1a and 1b only the enediynes 3a and 3b were isolated, with 1c and 1d only polymeric materials were observed. This suggests, but does not prove, that these reactions also occurred via an  $\text{S}_{\text{N}}-2'$  like process.

In summary, we have shown that enyne triflates readily react with organic nucleophiles, such as  $C_6H_5S^-$  and  $C_6H_5C\equiv C^-$ , to give enyne and enediyne products respectively, most likely via an  $S_N-2'$  type process.

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Table. Summary of Spectral Data of Enynes 2 and 3.

Compound	IR, $cm^{-1}$ , ( $CCl_4$ ) ( $C\equiv C$ )	$^1H$ -NMR, $CDCl_3$ TMS	$^{13}C$ -NMR $CDCl_3$	Mass Spec. m/z (%)
<u>2a</u>	2140	7.0-7.65 (m, 15 H), 6.2(S, 1H)	80.08, 99.00, 107.49, 126.63, 127.04, 128.50, 128.94, 128.99, 129.13, 129.90, 130.67, 133.69, 140.18, 141.69, 152.42	312.0( $M^+$ , 4.3), 202.0( $M^+$ -PhS, 2.1), 121.0(30.3), 118.9(100), 116.9 (97.8), 109.0(2.5)
<u>2b</u>	2150	7.0-7.6(m, <sup>b</sup> 10H), 5.75(q, 1H, $J=1.48Hz$ ), 2.05 (d, 3H, $J=1.38Hz$ ), 7.0-7.6(m, 10H), 6.1(q, 1H, $J=1.07Hz$ ), 2.3(d, 3H, $J=0.99Hz$ )	18.32, 23.69, <sup>b</sup> 76.10, 80.48, 97.25, 97.87, 105.96, 106.10, 125.40, 125.60, 125.90, 126.40, 126.60, 127.44, 128.12, 128.25, 128.40, 128.50, 129.20, 129.40, 133.20, 140.10, 148.90	252.0( $M^+$ +2, 2.57), 235.0( $M^+$ -15, 13.9), 173.0( $M^+$ -77, 65.8), 121.0(100), 109.0 (2.4), 77.0(33.8)
<u>3a</u>	2200, 2130	7.15-7.6(m, 15H), 6.15(s, 1H)	74.34, 77.61, 80.96, 82.17, 105.68, 121.90, 128.08, 128.33, 128.61, 128.77, 129.02, 129.90, 132.405, 138.75, 140.980, 156.24	305.0( $M^+$ +1, 5.5), 304.0( $M^+$ , 22.0), 303.0( $M^+$ -1, 22.4), 302.0( $M^+$ -2, 22.4), 227.0( $M^+$ -77, 0.4), 57.0(100)
<u>3b</u>	2210, 2140 <sup>a</sup>	7.15-7.7(m, 10H), <sup>b</sup> 5.7(q, 1H), 2.15 (d, 3H, $J=1.14Hz$ ), 7.15-7.7(m, 10H), 5.95(q, 1H), 2.35 (d, 3H, $J=0.71Hz$ )		244.0( $M^+$ +2, 9.4), 243.0( $M^+$ +1, 57.3), 242.0( $M^+$ , 100), 241.0( $M^+$ -1, 50.8)

a) neat; b) mixture of two isomers

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