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A Convenient Preparation of 2-Fluoro-3-alkoxy-1,3-butadienes

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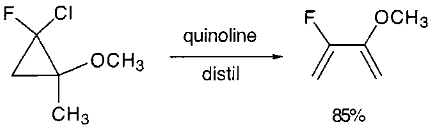
ABSTRACT



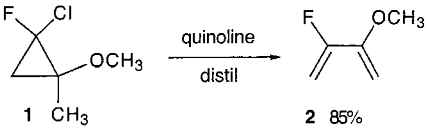
1-Chloro-1-fluoro-2-methoxy-2-methylcyclopropane eliminates HCl on heating in quinoline solution above 50 °C to give 2-fluoro-3-methoxy-1,3-butadiene in high yield. If an alcohol is added to the reaction then a 2-fluoro-3-alkoxy-1,3-butadiene is obtained in high yield. The dienes give smooth 4 + 2 cycloaddition reactions.

Methodology for the preparation of monofluoro 1,3-butadienes consists of fluorocyclopropane ring opening,[1−4] palladium(0) crossed coupling reactions of fluorinated alkenyl stannanes,[5,6] and Wittig olefination of fluorinated α,β-unsaturated aldehydes.[7]

In 1993, Johnson and co-workers proposed a fluorodiene intermediate in the preparation of fluorinated polyenes from reaction of 1-fluoro-1-chloro-2-methoxy-2-methylcyclopropane (**1**)[8] with a dienol in a solution of toluene and pyridine at 115 °C for 10 h.[4]

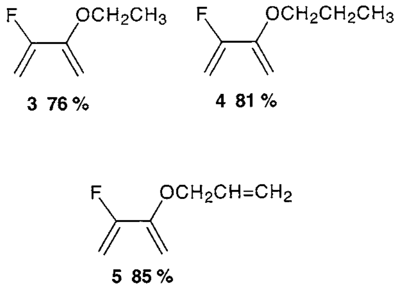
We report here that when **1** is heated in pyridine solution a clear colorless distillate of 2-fluoro-3-methoxy-1,3-butadiene (**2**)[9] is obtained around 50−80 °C in 85% yield. Pyridinium hydrochloride is obtained from the reaction mixture on cooling. The product is obtained with a small contamination with pyridine, but when the solvent is changed to quinoline **2** is obtained pure as seen in Scheme 1.

Scheme 1



When the reaction is performed in the presence of an excess of alcohol (ethanol, propanol, or allyl alcohol), then 2-fluoro-3-ethoxy-1,3-butadiene (**3**), 2-fluoro-3-*n*-propyl-1,3-

Scheme 2



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[9] All new compounds (**2**−**8**) gave spectral data consistent with the assigned structure. Compound **2**: ^{1}H NMR ($CDCl_3$, TMS) δ 3.62 (s, CH_3), 4.2−5.0 (m, vinyl); ^{19}F NMR (TFA═O, 76.6 relative to $CFCl_3$) δ −40.0; ^{13}C NMR δ 57.5 (CH_3), 84.1 (C4), 90.5 (d, C1), 153.8 (d, C3), 158.3 (d, C2, J = 189 Hz). Compound **6**: ^{1}H NMR δ 2.38 (m, 4H, CH_2), 4.9−6.05 (m, 5H, vinyl); ^{19}F NMR −116.2; ^{13}C NMR δ 27.1 (C4), 43.1 (d, C3), 100.5 (C1), 114.9 (C7), 136.5 (C6), 159.5 (d, J = 259 Hz), 206 (d, C1). Compound **7**: ^{1}H NMR δ 4.1 (m, CH_2), 4.21 (m, CH_2), 7.25 (m, aromatic); ^{19}F NMR −71; Compound **8**: ^{1}HNMR δ 2.84 (s, OCH_3), 3.63, 4.00 (two multiplets, CH_2 next to F), 3.85 (m, CH_2 next to OCH_3); ^{19}F NMR −58.6.

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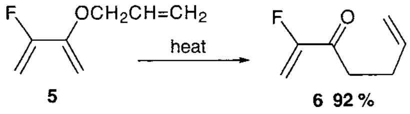
butadiene (**4**), and 2-fluoro-3-allyloxy-1,3-butadiene (**5**) are obtained in good yields. (Scheme 2).

When compound **5** was heated above 80 °C for 30 min, the product from Claisen rearrangement (**6**) was obtained in 92% yield (Scheme 3).

Scheme 3



When diene **2** is subjected to reaction with reactive dienophiles such as *N*-phenyl-1,2,4-triazoline-3,5-dione and tetracyanoethylene, the 4 + 2 cycloaddition products **7** and **8** were obtained respectively in good yield (Scheme 4). Reaction of **2** with maleic anhydride furnished the cycloadduct **9** in a mixture of products. These reactions were performed in $CDCl_3$ solvent at room temperature over 6 h.

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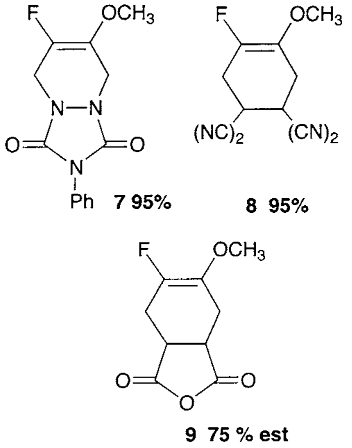
Scheme 4



Supporting Information Available: ^{1}H NMR and analytical data for **2**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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