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SHORT COMMUNICATIONS

Stereoselective Synthesis of Methyl 3,3-Diarylpropenoates

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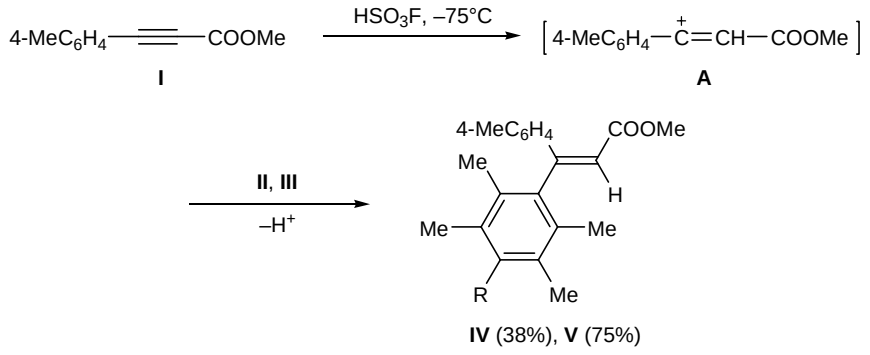
We recently reported on an unusual low-temperature dimerization of methyl 3-(4-methylphenyl)propynoate (**I**), which involved intermediate formation of cation **A** [1]. It seemed reasonable to estimate the scope of the revealed reaction as applied to other acetylene compounds, and (what is the most important) to use the vinyl-like cations generated therefrom by the action of HSO_3F as addends to foreign organic substrates. Such processes would provide a simple synthetic route to various practically important compounds. For this purpose, we examined reactions of cation **A** with 2,3,5,6-tetramethylbenzenesulfonyl fluoride (**II**, R = FSO_2) and (2,3,5,6-tetramethylphenyl)acetonitrile (**III**, R = $NCCH_2$). These substrates do not react with HSO_3F but are characterized by considerably different reactivities in electrophilic substitution processes.

Despite the presence of two *ortho*-methyl groups, compounds **II** and **III** readily reacted with cation **A** generated *in situ* from methyl 3-(4-methylphenyl)propynoate (**I**). The reactions were stereoselective, and the products were the corresponding *E* isomers of methyl 3,3-diarylpropenoates **IV** and **V**. However, the yields of compounds **IV** and **V** differed considerably due to difference in electron-acceptor properties of the substituents in the aromatic substrates.

The structure of compounds **IV** and **V** was determined on the basis of their IR, ^1H and ^{19}F NMR, and mass spectra with account taken of published data for structurally related compounds [1]. The reaction mixtures were separated by column chromatography on silica gel using a 2–5% solution of ethyl acetate in hexane as eluent. In the reaction of cation **A** with compound **II**, the mixture contained dimerization products of ester **I**.

Methyl (*E*)-3-(4-methylphenyl)-3-(4-fluorosulfonyl-2,3,5,6-tetramethylphenyl)propenoate (IV). Ester **I**, 0.050 g (0.287 mmol), was added over a period of 30 min to a solution of 0.068 g (0.316 mmol) of compound **II** in 1.5 ml of HSO_3F, cooled to –75°C. After 15 min, the mixture was poured into 15 ml of concentrated hydrochloric acid cooled to –60°C. The mixture was extracted with chloroform (3×5 ml), the combined extracts were washed with water, a saturated aqueous solution of $NaHCO_3$, and water again, dried over Na_2SO_4, and evaporated under reduced pressure (water-jet pump), and the residue was subjected to column chromatography on silica gel. Yield 0.042 g (38%), mp 130–132°C. IR spectrum, ν, cm^{-1}: 1620 (C=C), 1720 (C=O). ^1H NMR spectrum, δ, ppm: 2.22 s (6H, 2Me), 2.33 s (3H, Me), 2.57 d (6H, 2Me, J_{HF} = 2.0 Hz), 3.71 s (3H, OMe), 5.77 s (1H, CH=), 7.09–



IV (38%), **V** (75%)

IV, R = FSO_2; **V**, R = $NCCH_2$.

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7.13 m (4H, H_{arom}). ^{19}F NMR spectrum: δ_F 49.59 ppm, m (1F, SO_2F, J_{HF} = 2.0 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 390 (88) M^+, 375 (29) $[M - Me]^+$, 359 (25) $[M - OMe]^+$, 343 (27), 330 (100), 316 (49), 315 (52), 307 (22), 306 (21), 292 (14), 275 (23), 247 (59), 234 (26), 218 (19), 203 (25), 115 (33), 91 (22), 66 (14), 59 (24). Found, %: C 64.40; H 5.97. *M* 390. $C_{21}H_{23}FO_4S$. Calculated, %: C 64.60; H 5.94. *M* 390.

Methyl (*E*)-3-(4-cyanomethyl-2,3,5,6-tetramethylphenyl)-3-(4-methylphenyl)propenoate (V) was synthesized in a similar way from 0.033 g (0.19 mmol) of compound **I** and 0.030 g (0.172 mmol) of nitrile **III** in 0.5 ml of HSO_3F (ester **I** was added over a period of 10 min, and the mixture was kept for 30 min). Yield 0.0445 g (75%), mp 136.5–137.5°C. IR spectrum, ν, cm^{-1}: 1615 (C=C), 1715 (C=O), 2250 (C≡N). ^1H NMR spectrum, δ, ppm: 2.17 s (6H, 2Me), 2.29 s (6H, 2Me), 2.32 s (3H, Me), 3.70 s (3H, OMe), 3.71 s (2H, CH_2), 5.79 s (1H, CH=), 7.09 d (2H, H_{arom}, *J* = 8.1 Hz), 7.15 d (2H, H_{arom}, *J* = 8.1 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 347 (100) M^+, 332 (38) $[M - Me]^+$, 316 (28) $[M - OMe]^+$, 330 (30), 287 (80), 273 (80), 272 (58), 247 (58), 234 (45), 115 (23), 91 (20). Found, %: C 79.29; H 7.17. *M* 347. $C_{23}H_{25}NO_2$. Calculated, %: C 79.51; H 7.25. *M* 347.

The IR spectra were recorded from solutions in $CHCl_3$ using a Specord 75IR spectrophotometer. The ^1H and ^{19}F NMR spectra were measured on a Bruker AM-500 spectrometer at 500 and 470.7 MHz, respectively, using $CDCl_3$ as solvent; the chemical shifts were measured relative to residual $CHCl_3$ (^1H, δ 7.25 ppm) or $CFCl_3$ (^{19}F). The mass spectra (electron impact, 70 eV) were run on an MKh-1321 instrument.

REFERENCE

1. Savechenkov, P.Yu., Rudenko, A.P., and Vasil'ev, A.V., *Russ. J. Org. Chem*., 2004, vol. 40, p. 1065.