

SHORT
COMMUNICATIONS

A Novel Dimerization of Methyl *p*-Tolylpropynoate in Fluorosulfonic Acid with Conservation of the Triple Bond

P. Yu. Savechenkov, A. P. Rudenko, and A. V. Vasil'ev

St. Petersburg State Academy of Forestry Engineering, Institutskii per. 5, St. Petersburg, 194021 Russia

Received January 23, 2004

According to the ^1H and ^{13}C NMR data, dissolution of methyl *p*-tolylpropynoate (**I**) in fluorosulfonic acid at low temperature is accompanied by protonation of the carbonyl oxygen atom with formation of a relatively stable ion which gradually undergoes further transformations [1]. We performed this reaction on a preparative scale at a HSO_3F -to-**I** molar ratio of 60:1 (-75°C). The solution was kept for 0.5 h and treated with concentrated hydrochloric acid at -60°C . As a result, two compounds were formed (**II** and **III**), which can be separated by column chromatography on silica gel (eluent 2–5% of ethyl acetate in hexane). The structure of the isolated products was established on the basis of their IR, ^1H and ^{13}C NMR, and mass spectra.

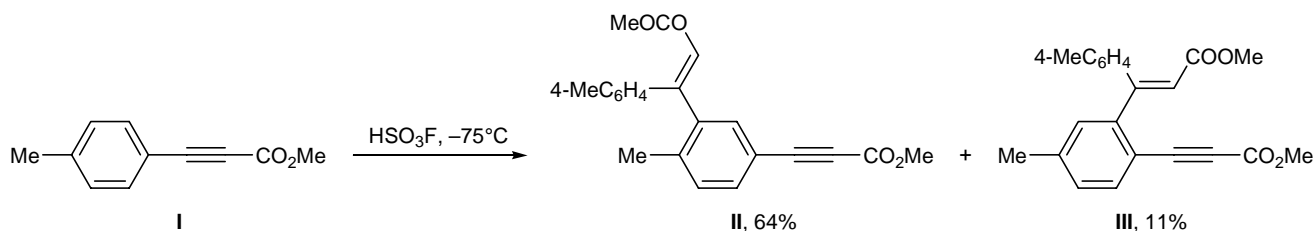
The process is likely to involve slow generation of vinyl-type cation $\text{ArC}^+=\text{CHCO}_2\text{Me}$ and stereoselective attack by the latter on the aromatic ring in substrate **I**. Deprotonation of intermediate ions gives final regioisomeric products **II** and **III** (Scheme 1). The unexpected inactivity of the triple bond in **II** and **III** toward HSO_3F may be interpreted in terms of reduced basicity of the carbon atoms at the triple bond due to the presence of electron-acceptor $\text{C}(\text{Ar})=\text{CHCO}_2\text{Me}$ moiety.

Methyl (*E*)-3-(5-methoxycarbonylethynyl-2-methylphenyl)-3-(4-methylphenyl)-2-propenoate (II). Yield 64%, mp $102\text{--}103^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 1695, 1710, 2215. ^1H NMR spectrum, δ , ppm: 2.08 s

(3H, Me), 2.34 s (3H, Me), 3.67 s (3H, OMe), 3.82 s (3H, $\text{MeO}_2\text{CC}\equiv$), 5.94 s (1H, $\text{HC}=\text{C}$), 7.08–7.12 m (4H, H_{arom}), 7.15 d (1H, H_{arom} , $J = 7.8$ Hz), 7.43 s (1H, H_{arom}), 7.45 d (1H, H_{arom} , $J = 7.8$ Hz). ^{13}C NMR spectrum (CDCl_3), δ_{C} , ppm: 20.48 q.d ($J = 127.6$, 4.5 Hz), 21.32 q.t ($J = 126.0$, 4.0 Hz), 51.37 q ($J = 147.0$ Hz), 52.76 q ($J = 147.9$ Hz), 80.41 s and 86.23 t ($J = 5.5$ Hz), 116.94 d ($J = 8.9$ Hz), 119.68 d ($J = 162.3$ Hz), 128.60 d.q ($J = 158.1$, 4.5 Hz), 129.07 d.d ($J = 159.0$, 4.5 Hz), 131.07 d.q ($J = 159.5$, 5.0 Hz), 132.66 d.d ($J = 163.0$, 6.0 Hz), 133.85 d.d ($J = 163.0$, 6.5 Hz), 134.75 m ($J = 6.0$ Hz), 138.93 m ($J = 5.0$ Hz), 139.56 m ($J = 5.0$ Hz), 142.59 q ($J = 4.0$ Hz), 154.41 q ($J = 4.0$ Hz), 155.38 m ($J = 4.0$ Hz), 166.36 m ($J = 2.0$ Hz). Mass spectrum, m/z (I_{rel} , %): 348 (72) M^+ , 333 (25) $[M - \text{Me}]^+$, 317 (100) $[M - \text{OMe}]^+$, 301 (36), 288 (55), 274 (91), 257 (13), 243 (15), 229 (19), 215 (23), 202 (15), 143 (11), 139 (10), 115 (15), 59 (11). Found, %: C 75.61; H 5.85. $\text{C}_{22}\text{H}_{20}\text{O}_4$. M 348. Calculated, %: C 75.84; H 5.79. M 348.39.

Methyl (*E*)-3-(2-methoxycarbonylethynyl-5-methylphenyl)-3-(4-methylphenyl)-2-propenoate (III). Yield 11%, mp $94\text{--}97^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 1700, 1715, 2225. ^1H NMR spectrum, δ , ppm: 2.34 s (3H, Me), 2.35 s (3H, Me), 3.65 s (3H, OMe), 3.74 s (3H, $\text{MeO}_2\text{CC}\equiv$), 6.15 s (1H, $\text{HC}=\text{C}$), 7.05 s (1H, H_{arom}), 7.10–7.15 m (5H, H_{arom}), 7.47 d (1H, H_{arom} , $J = 8.9$ Hz). Mass spectrum, m/z (I_{rel} , %): 348 (50) M^+ ,

Scheme 1.



333 (18) [$M - \text{Me}$]⁺, 320 (18) [$M - \text{CO}$]⁺, 317 (23) [$M - \text{OMe}$]⁺, 290 (100), 289 (91), 277 (30), 259 (59), 245 (23), 231 (23), 230 (36), 229 (45), 228 (27), 216 (55), 215 (75), 203 (41), 202 (50), 189 (25), 101 (27), 59 (39). Found, %: C 75.93; H 5.95. M 348. $\text{C}_{22}\text{H}_{20}\text{O}_4$. Calculated, %: C 75.84; H 5.79. M 348.39.

The IR spectra were measured from solutions in chloroform using a Specord 75 IR spectrometer. The ¹H and ¹³C NMR spectra were obtained on a Bruker AM-500 instrument at 500 and 125.76 MHz, respectively; chloroform-*d* was used as solvent and reference

(CHCl_3 , δ 7.25 ppm, δ_{C} 77.0 ppm). The mass spectra (electron impact, 70 eV) were run on an MKh-1321 mass spectrometer.

REFERENCE

1. Rudenko, A.P., Vasil'ev, A.V., Savechenkov, P.Yu., Sommer, Zh., Khauas, M., and Val'spurzhe, S., *Intermediaty. Sintez, protonirovanie i okislenie atsetilenovykh soedinenii* (Intermediates. Synthesis, Protonation, and Oxidation of Acetylenic Compounds), St. Petersburg: Gos. Lesotechn. Akad., 2003, no. 2, p. 232.