

SHORT  
COMMUNICATIONS

**Oxidative Heterocyclization of 4-(4-Methoxy-3-fluorophenyl)-1,1,1-trifluorobut-3-yn-2-one in a System  $\text{CF}_3\text{CO}_2\text{H}-\text{CH}_2\text{Cl}_2-\text{PbO}_2$**

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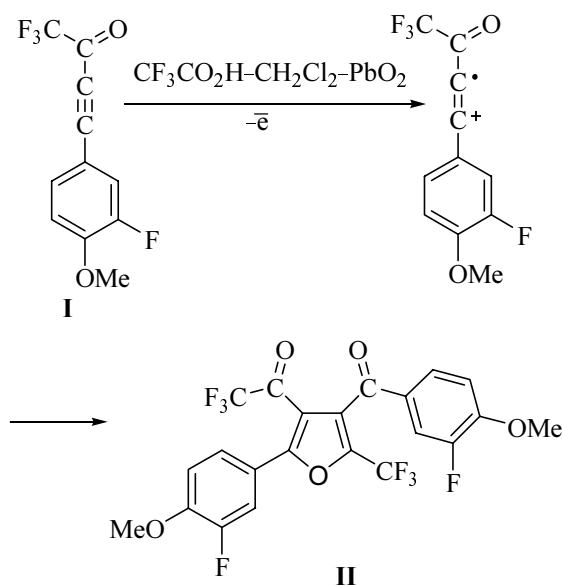
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By oxidation of 1,3-diarylpropynones in a system  $\text{CF}_3\text{CO}_2\text{H}-\text{CH}_2\text{Cl}_2-\text{PbO}_2$  we succeeded to synthesize in one preparative stage tetraketones of unsaturated series, 1,1,2,2-tetraaroyl ethenes [1].

With acetylene ketone **I** containing a trifluoromethyl group the oxidative process in the same system at  $-10^\circ\text{C}$  occurred less deeply (with overall transfer of two electrons) and was accompanied by cyclization of the insufficiently oxidized dimer intermediate into a substituted furan **II**.

The structure of furan **II** was established from IR,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  NMR, and mass spectra. The sum of spectral data permitted the rejection of alternative structures.

**2-(4-Methoxy-3-fluorophenyl)-4-(4-methoxy-3-fluorophenylcarbonyl)-5-trifluoromethyl-3-trifluoromethylcarbonylfuran (II)**. Yield 52%, mp.



124–124.5°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1690, 1720.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 3.96 s (3H, OMe), 3.97 s (3H, OMe), 7.00–7.08 m (2H arom), 7.45–7.49 m (2H arom), 7.62–7.68 m (2H arom).  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 56.3 q (OMe,  $J$  147.0 Hz), 56.4 q (OMe,  $J$  145.8 Hz), 112.5 d ( $J$  162.4 Hz), 113.2 d ( $J$  161.7 Hz), 115.0 q ( $\text{CF}_3\text{CO}$ ,  $J$  289.9 Hz), 116.0 s, 116.2 d.d.d ( $J$  164.5, 21.2, 7.4 Hz), 116.5 d.d.d ( $J$  164.0, 19.3, 7.2 Hz), 118.0 q ( $J$  163.8, 3.0 Hz), 127.1 s, 127.5 d.d ( $J$  162.8, 4.1 Hz), 129.4 d ( $J$  4.9 Hz), 138.6 q ( $J$  43.2 Hz), 150.8 d ( $J$  10.6 Hz), 152.0 d.m ( $J$  248.6 Hz), 152.2 d.m ( $J$  249.7 Hz), 153.3 d ( $J$  11.0 Hz), 158.8 s, 178.6 q ( $\text{CF}_3\text{CO}$ ,  $J$  39.0 Hz), 184.7 s (CO).  $^{19}\text{F}$  NMR spectrum,  $\delta$ , ppm:  $-129.75$  t (1F arom,  $J$  10.0 Hz),  $-129.64$  t (1F arom,  $J$  10.0 Hz),  $-70.37$  s (3F,  $\text{CF}_3\text{CO}$ ),  $-57.28$  s (3F,  $\text{CF}_3$ ). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 509 (14)  $[M+1]^+$ , 508 (48)  $M^+$ , 489 (2)  $[M-F]^+$ , 439 (26)  $[M-\text{CF}_3]^+$ , 419 (18), 254 (5), 153 (100)  $[(\text{MeO})\text{FC}_6\text{H}_3\text{CO}]^+$ , 125 (12)  $[(\text{MeO})\text{FC}_6\text{H}_3]^+$ , 110 (9), 95 (14), 77 (7). Found, %: C 51.7; H 2.61.  $\text{C}_{22}\text{H}_{12}\text{F}_8\text{O}_5$ . Calculated, %: C 51.98; H 2.38.  $M$  508.23.

IR spectrum was recorded on spectrophotometer Specord 75 IR from solution of compound in  $\text{CHCl}_3$ .  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra were registered on spectrometer Bruker AM-500 (at operating frequencies 500, 125.76, and 470.7 MHz respectively) from solutions in  $\text{CDCl}_3$ . As internal references were used the residual proton signal of chloroform ( $^1\text{H}$ ,  $\delta_{\text{H}}$  7.25 ppm), the carbon signal of solvent ( $^{13}\text{C}$ ,  $\delta_{\text{C}}$  77.0 ppm), and the signal of  $\text{C}_6\text{F}_6$  ( $^{19}\text{F}$ ,  $\delta_{\text{F}}$   $-162.9$  ppm). Mass spectra were measured on MKh-1321 instrument, ionizing electrons energy 70 eV.

REFERENCES

1. Vasil'ev, A.V., Rudenko, A.P., and Grinenko, E.V., *Zh. Org. Khim.*, 2000, 36, p. 1193.