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SHORT COMMUNICATIONS

Dedicated to the 100th Anniversary of Corresponding Member of the Russian Academy of Sciences A.A. Petrov

Oxidation of 3,3,3-Trifluoro-1-(4-methoxyphenyl)propyne in the System PbO_2–CF_3COOH–CH_2Cl_2

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We previously showed [1] that one-electron oxidation of acetylenic compounds ArC≡CX in the system PbO_2–CF_3CO_2H–CH_2Cl_2 leads to the formation of different products, depending on the nature of electron-withdrawing X substituent. If X = CO_2R, COAr, COR, $PO(OEt)_2$ (medium-strength acceptors), tetrasubstituted ethenes X(ArCO)C=C(COAr)X are formed, whereas stronger acceptor groups (X = $COCF_3$, $COCO_2R$, CN) give rise to furan derivatives.

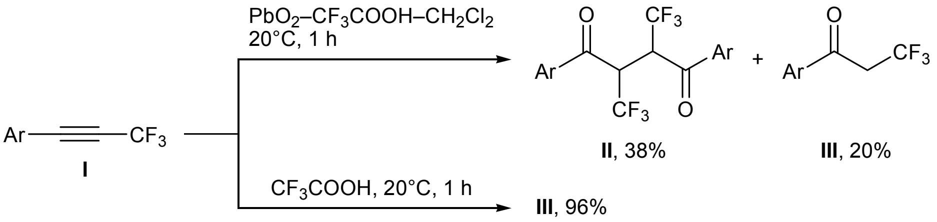
The present communication reports on the oxidation and electrophilic reactions of 3,3,3-trifluoro-1-(4-methoxyphenyl)propyne (**I**) in the system PbO_2–CF_3CO_2H–CH_2Cl_2. Trifluoromethyl-substituted acetylenes constitute an interesting class of highly reactive compounds that are promising due to their specific properties arising from the presence of an electron-withdrawing CF_3 group [2].

When the oxidant (PbO_2) was added to a solution of compound **I** in a mixture of trifluoroacetic acid and methylene chloride, the major product was ketone **III** (Kucherov reaction). Electrophilic addition of trifluoroacetic acid molecule to the triple C≡C bond of **I** gives vinyl trifluoroacetate which undergoes hydrolysis upon treatment of the reaction mixture with water to afford compound **III** [3, 4]. In this reaction we detected only a small amount of diketone **II** resulting from oxidative dimerization of alkyne **I**.

The reverse order of addition of the reactant, i.e., addition of **I** to preliminarily prepared oxidation system, ensures sharp increase of the yield of **II** (to 38%), though ketone **III** is also formed as a result of concurrent electrophilic reaction (Scheme 1).

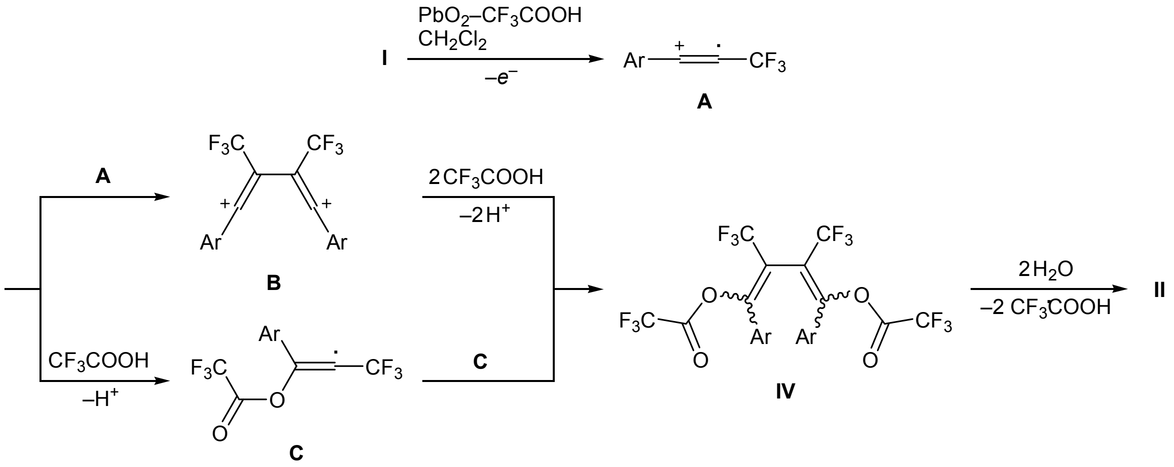
The ^1H, ^{19}F, and ^{13}C NMR spectra of **II** contained only one set of signals, indicating stereoselective formation of a single diastereoisomer among two possible for structure **II** (*meso* form or racemate). We plan to elucidate the steric structure of **II** by X-ray analysis.

Scheme 1.



Ar = 4-$MeOC_6H_4$.

Scheme 2.



Ar = 4-$MeOC_6H_4$.

Two alternative mechanisms may be proposed for the formation of diketone **II**. The first one implies dimerization of initially generated radical cation **A** to give dication **B** which takes up two trifluoroacetic acid molecules with formation of buta-1,3-diene-1,4-diyl bis(trifluoroacetate) (**IV**). An alternative path of the transformation of radical cation **A** is the reaction with CF_3CO_2H with formation of vinyl radical **C** and its dimerization to bis(trifluoroacetate) **IV** (Scheme 2). Hydrolysis of the latter yields bis-enol which tautomerizes to diketone **II**. It should be noted that the presence of two electron-withdrawing CF_3 groups in **IV** prevent it from undergoing further oxidation.

1,4-Diketones like **II** are difficultly accessible compounds. The only known representative of this class of compounds was obtained previously as an inseparable mixture with two other products by radical addition of propionaldehyde to bis(trifluoromethyl)acetylene [5]. Such 1,4-diketones are very promising from the viewpoint of their use in the synthesis of various trifluoromethyl-substituted five- and six-membered heterocyclic compounds.

Oxidation of 3,3,3-trifluoro-1-(4-methoxyphenyl)propyne (I). Compound **I**, 200 mg (1 mmol), was added at 20°C under vigorous stirring to a suspension of 239 mg (1 mmol) of PbO_2 in a mixture of 0.38 ml (5 mmol) of CF_3CO_2H and 3 ml of CH_2Cl_2. The mixture was stirred for 1 h at 20°C and poured into 100 ml of chloroform. The resulting solution was washed with water (2×20 ml), a saturated aqueous solution of $NaHCO_3$ (2×20 ml), and water again (20 ml) and dried over Na_2SO_4, the solvent was distilled off, and the residue was subjected to chromatographic separation on a column charged with silica gel using petroleum ether (bp 40–70°C)–diethyl ether as eluent. We isolated 82 mg (38%) of **II** and 44 mg (20%) of **III**. 3,3,3-Trifluoro-1-(4-methoxyphenyl)propan-1-one (**III**) was described in [3, 4].

1,4-Bis(4-methoxyphenyl)-2,3-bis(trifluoromethyl)butane-1,4-dione (II). mp 190–192°C. IR spectrum (KBr): ν 1670 cm^{-1} (C=O). ^1H NMR spectrum, δ, ppm: 3.91 s (6H, MeO), 5.13 br.m (2H, CH), 7.01 d (4H, H_{arom}, J = 8.7 Hz), 8.04 d (4H, H_{arom}, J = 8.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 46.5 q (CH, J_{CF} = 25.8 Hz), 55.7 (OMe), 114.4 q, 123.6 q (CF_3, J_{CF} = 280.6 Hz), 128.9, 131.5, 164.9, 189.1 (C=O). ^{19}F NMR spectrum: δ_F –59.18 ppm, d (CF_3, J_{HF} = 6.1 Hz). Mass spectrum, m/z (I_{rel}, %): 434 (60) $[M]^+$, 432 (42), 299 (7), 281 (12), 279 (10), 135 (100), 107 (43), 92 (62). Found, %: C 55.39; H 3.68. $C_{20}H_{16}F_6O_4$. Calculated, %: C 55.31; H 3.71. M 434.09.

The ^1H, ^{13}C, and ^{19}F NMR spectra were measured at 20°C on a Bruker AM-500 spectrometer at 500, 125.76, and 470 MHz, respectively, using $CDCl_3$ as solvent and reference (for ^1H and ^{13}C; $CHCl_3$, δ 7.26 ppm; $CDCl_3$, δ_C 77.0 ppm); the ^{19}F chemical shifts were determined relative to $CFCl_3$ (δ_F 0.0 ppm). The IR spectra were recorded on an FSM-1201 spectrometer. The mass spectra were obtained on a Agilent Technologies 6850s G2570A GC/MSD instrument (HP-5MS capillary column, 3 m×0.25 mm, film thickness 0.25 μm; oven temperature programming from 50 to 290°C at a rate of 5 deg/min; injector temperature 290°C; electron impact, 70 eV). Elemental analysis was performed on a EuroVector EA-300 analyzer.

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REFERENCES

1. Vasil'ev, A.V., Aristov, S.A., Fukin, G.K., Kozhanov, K.A., Bubnov, M.P., and Cherkasov, A.V., *Russ. J. Org. Chem.*, 2008, vol. 44, p. 791.
2. Rulev, A.Yu., Ushakov, I.A., Kondrashov, E.V., Muzalevskiy, V.M., Nenajdenko, V.G., and Shastin, A.V., *J. Fluorine Chem.*, 2011, vol. 132, p. 945; Nenajdenko, V.G., Muzalevskiy, V.M., Balenkova, E.S., Shastin, A.V., Kondrashov, E.V., Ushakov, I.A., and Rulev, A.Yu., *J. Org. Chem.*, 2010, vol. 75, p. 5679; Muzalevskiy, V.M., Nenajdenko, V.G., Balenkova, E.S., Shastin, A.V., and Haufe, G., *Synthesis*, 2009, no. 13, p. 2249; Rulev, A.Yu., Muzalevskiy, V.M., Kondrashov, E.V., Ushakov, I.A., Shastin, A.V., Balenkova, E.S., Haufe, G., and Nenajdenko, V.G., *Eur. J. Org. Chem.*, 2010, p. 300; Goldberg, A.A., Muzalevskiy, V.M., Shastin, A.V., Balenkova, E.S., and Nenajdenko, V.G., *J. Fluorine Chem.*, 2010, vol. 131, p. 384; Nenajdenko, V.G., Muzalevskiy, V.M., Shastin, A.V., Balenkova, E.S., and Haufe, G., *J. Fluorine Chem.*, 2007, vol. 128, p. 818; Nenajdenko, V.G., Varseev, G.N., Korotchenko, V.N., Shastin, A.V., and Balenkova, E.S., *J. Fluorine Chem.*, 2004, vol. 125, p. 1339; Korotchenko, V.N., Shastin, A.V., Nenajdenko, V.G., and Balenkova, E.S., *Tetrahedron*, 2001, vol. 57, p. 7519.
3. Alkhafaji, H.M.H., Ryabukhin, D.S., Muzalevskiy, V.M., Osetrova, L.V., Vasilyev, A.V., and Nenajdenko, V.G., *Russ. J. Org. Chem.*, 2013, vol. 49, p. 327.
4. Alkhafadji, H.M.H., Ryabukhin, D.S., Muzalevskiy, V.M., Vasilyev, A.V., Fukin, G.K., Shastin, A.V., and Nenajdenko, V.G., *Eur. J. Org. Chem.*, 2013, p. 1132.
5. Chambers, R.D., Jones, C.G.P., and Silvester, M.J., *J. Fluorine Chem.*, 1986, vol. 32, p. 309.