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SHORT COMMUNICATIONS

New Reaction of Terminal Acetylenes with Nitrates in the Presence of Sulfur Trioxide: Heterocyclization into 3-Acyl-5-Aryl(Alkyl)Isoxazoles*

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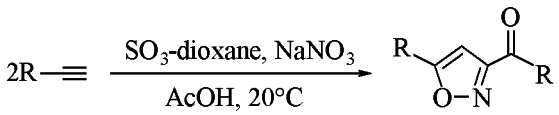
We showed formerly that phenylacetylene when treated with sulfuric acid or sulfur trioxide gave rise to an unsaturated δ-sultone, 4,6-diphenyl[1,2]oxathiyne-2,2-dioxide [1]. On the other hand, nitrates in the presence of iodine or KI in acetic acid afford with acetylenes 1-iodo-2-nitroalkenes [2].

However at combined treatment of phenylacetylene (**Ia**) in glacial acetic acid with SO_3 and sodium, potassium, or ammonium nitrates we obtained under mild conditions 3-benzoyl-5-phenylisoxazole (**IIa**) in 55% yield. The reaction discovered is of a general character: under similar conditions 1-hexyne (**Ib**) furnishes 5-butyl-3-pentanoylisoxazole (**IIb**) in 53% yield.



Ia, b **IIa, b**

R = Ph (**a**), Bu (**b**).

The traditional procedure for isoxazoles preparation consists in condensation of phosphorus ylides or acetylenes with ω-halo-ω-isonitroso derivatives [3]. Isoxazoles **IIa, b** were previously obtained in up to 40% yield at treating compounds **Ia, b** in nitromethane with nitric acid in the presence of tetrabutylammonium tetrachlorourate [4]. The reaction we found is obviously easier synthetic approach to this class compounds.

General procedure for heterocyclization of acetylenes Ia, b. A mixture of 4.55 mmol of acetylene **Ia, b**, 0.77 g (9.1 mmol) of fine powder of sodium nitrate, and 0.8 g (4.76 mmol) of a complex SO_3–dioxane in 10 ml of the glacial acetic acid was vigorously stirred for 3 h at 20°C. The reaction mixture was diluted with 40 ml of cold water, neutralized with Na_2CO_3, and extracted with ether. The extract was dried with Na_2SO_4, the solvent was removed in a vacuum, and the residue was subjected to chromatography on a column packed with silica gel (40–100 μ, eluent hexane, hexane–benzene, 5 : 1).

3-Benzoyl-5-phenylisoxazole (IIa). Yield 55%. mp 86–87°C (hexane). IR spectrum (KBr, ν, cm^{-1}): 1660 (C=æ). ^1H NMR spectrum (200 MHz, $CDCl_3$, δ, ppm): 7.35 s (1H, H^4), 7.50 m (5H arom), 7.64 t (1H arom), 7.83 m (2H arom), 8.33 d (2H arom). ^{13}C NMR spectrum (50 MHz, $CDCl_3$, δ_C, ppm): 100.10 (C^4); 125.84, 126.54, 128.44, 129.00, 130.55, 130.58, 133.91, 135.58; 162.27 (C^3); 170.62 (C^5); 185.64 (Cæ). Mass spectrum, *m/z* (I_{rel}, %): 249 (40) M^+, 105 (100) $[PhCO]^+$, 77 (60) $[Ph]^+$, 51 (20) $[M–PhCO–Ph–O]^+$, 28 (12) $[CO]^+$. Found, %: C 76.52; H 5.29; N 5.56. $C_{16}H_{11}NO_2$. Calculated, %: C 77.10; H 4.45; N 5.62.

5-Butyl-3-pentanoylisoxazole (IIb). Yield 53%. Light-yellow oily substance. IR spectrum (KBr, ν, cm^{-1}): 1704 s (Cæ). ^1H NMR spectrum (200 MHz, $CDCl_3$, δ, ppm): 0.94 m (6H, $2CH_3$), 1.40 m (4H, $2CH_2$), 1.70 m (4H, $2CH_2$), 2.80 t (2H, CH_2), 3.03 t (2H, CH_2), 6.35 s (1H, H^4). ^{13}C NMR spectrum ($CDCl_3$, δ_C, ppm): 13.60 (CH_3), 13.82 (CH_3), 22.07 (CH_2), 22.29 (CH_2), 25.81 (CH_2), 26.34 (CH_2), 29.42 (CH_2), 39.56 (CH_2), 99.27 (C^4), 161.83 (C^5), 175.38 (C^3), 195.24 (CO). Mass spectrum, *m/z* (I_{rel}, %): 194 (1) $[M–Me]^+$, 180 (1) $[M–Et]^+$, 167 (9) $[M–Et–CH]^+$, 152 (22) $[M–Bu]^+$, 139 (8)

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$[M–Bu–CH]^+$, 124 (8) $[M–BuCO]^+$, 109 (4) $[M–BuCO–N–H]^+$, 85 (100) $[BuCO]^+$, 68 (10) $[M–2Bu–CO+H]^+$, 67 (5) $[M–2Bu–CO]^+$, 57 (91) $[Bu]^+$, 55 (14) $[PrC]^+$, 43 (6) $[Pr]^+$, 42 (7) $[EtCH]^+$, 41 (39) $[EtC]^+$, 39 (12) $[M–2BuCO]^+$, 29 (24) $[Et]^+$, 28 (6) $[MeCH]^+$, 27 (12) $[MeC]^+$.

IR spectra were recorded on spectrophotometer Nicolet 205 from KBr pellets. ^1H and ^{13}C NMR spectra were registered on spectrometer Bruker ASP-300 at 300.13 and 75.48 MHz respectively, internal reference TMS, solvent $CDCl_3$. Mass spectra were measured by GC-MS method on spectrometer Hewlett Packard MSD 5972 (ionizing electrons energy 70 eV) combined with a chromatograph Hewlett Packard 5890.

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