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SHORT COMMUNICATIONS

Reactions of Acetylenic Hydrocarbons with Various CH Acids

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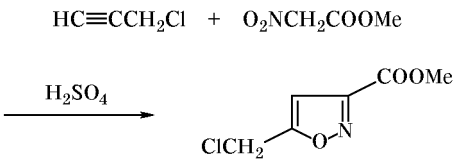
Only a few published data are available on vinylation of acetylenic compounds with CH acids. Nucleophilic addition reactions with formation of a C–C bond were reported mainly for alkynes having electron-acceptor substitutents [1, 2]. Electrophilic attack on the triple bond is more difficult to occur, and special catalysts are to be used [3].

We have previously studied electrophilic addition of CH acids, such as benzoylnitromethane, *p*-nitrobenzoylnitromethane, *m*-nitrobenzoylnitromethane, methyl nitroacetate, nitromethane, and acetylacetone, to acetylenic systems: acetylene, phenylacetylene, 2-propynyl chloride, and trimethylsilylacetylene in the presence of a catalytic amount of sulfuric acid and found that these reactions take various pathways. We were the first to reveal [4] that acetylene, phenylacetylene, trimethylsilylacetylene, and 2-propynyl chloride react with benzoylnitromethane, *p*-nitrobenzoylnitromethane, and *m*-nitrobenzoylnitromethane in the presence of acid catalyst (H_2SO_4) to give heterocyclic compounds of the isoxazole series. Like α-nitro ketones, methyl nitroacetate (α-nitro ester) reacts with acetylene derivatives, following the 1,3-dipolar cycloaddition pattern (Scheme 1).

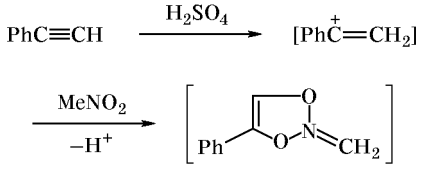
Scheme 1.



I

Under similar conditions, nitromethane failed to react with phenylacetylene, and the initial compounds were recovered from the reaction mixture. Increase in the amount of sulfuric acid in the reaction mixture led to formation of α-substituted ketone **II**, presumably through intermediate carbocation and unstable nitronate [5] (Scheme 2).

Scheme 2.

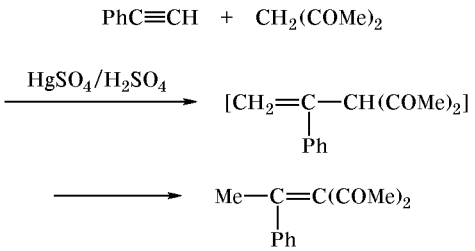


II

No desired results were obtained when 2-propynyl chloride or 3-trimethylsilyl-2-propynyl chloride was used as substrate. In all cases, only the initial compounds were isolated from the reaction mixtures despite wide variation of the conditions. Obviously, electron-acceptor substituents at the C_{sp} atom hamper the reaction [6].

Aliphatic β-diketone, acetylacetone, reacted with phenylacetylene in the presence of $HgSO_4/H_2SO_4$ as catalyst. The reaction was accompanied by prototropic rearrangement, and the product was β-dicarbonyl compound **III** with a longer conjugation chain (Scheme 3).

Scheme 3.



III

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The structure of compound **III** was unambiguously confirmed by the IR and ^{1}H NMR data and by its hydrolysis to acetophenone.

Methyl 5-chloromethylisoxazole-3-carboxylate (I). Concentrated sulfuric acid, 0.41 g (0.004 mol), was added to a mixture of 0.3 g (0.004 mol) of 2-propynyl chloride and 0.48 g (0.004 mol) of methyl nitroacetate in 30 ml of dry benzene. The mixture was kept for 5 h at 60°C, cooled, and evaporated to isolate 0.3 g (42%) of methyl 5-chloromethylisoxazole-3-carboxylate (**I**). mp 61°C (from ethanol). ^{1}H NMR spectrum, δ, ppm: 3.91 s (3H, CH_3), 5.02 s (2H, CH_2Cl), 7.00 s (1H, =CH). Found, %: C 40.95; H 3.39; N 7.75. $C_6H_6ClNO_3$. Calculated, %: C 41.03; H 3.42; N 7.98.

2-Methyleneaminooxy-1-phenyl-1-ethanone (II). Concentrated sulfuric acid, 1.00 g (0.10 mol), was added to 11.38 g (0.187 mol) of nitromethane, cooled to –20°C. A solution of 1.02 g (0.010 mol) of phenylacetylene in 4.50 g (0.074 mol) of nitromethane was added with stirring, and the mixture was kept for 25 min at –20°C, treated with a 5% solution of Na_2CO_3, and extracted with ether. The extract was dried over $CaCl_2$ and evaporated, and the residue was distilled in a vacuum to obtain 0.33 g of product **II** (yield 20%), bp 72°C (3 mm), n_D^{20} = 1.5362. ^{1}H NMR spectrum, δ, ppm: 4.68 s (2H, $COCH_2O$), 7.27 s (2H, $=CH_2$), 7.66 m (5H, C_6H_5). Found, %: C 65.87; H 5.28; N 8.21. $C_9H_9NO_2$. Calculated, %: C 66.26; H 5.52; N 8.59.

3-Acetyl-4-phenyl-3-penten-2-one (III). Phenylacetylene, 10.00 g (0.098 mol), was added to a mixture of 9.80 g (0.098 mol) of acetylacetone, 0.044 g of HgO, and 0.5 ml of concentrated sulfuric acid. The mixture was stirred for 3 h at 50°C. Vacuum distillation gave 4.50 g (23%) of product **III**, bp 116°C (2 mm). ^{1}H NMR spectrum, δ, ppm: 1.83 s (3H, CH_3), 2.42 s (6H, CH_3CO), 7.50 m (5H, C_6H_5). IR spectrum, ν, csm^{-1}: 1685 (C=O), 1610 (C=C). Found, %: C 76.91; H 6.91; H 6.81. $C_{13}H_{14}O_2$. Calculated, %: C 77.23; H 6.93.

The IR spectra were recorded on an IKS-29 spectrometer in chloroform. The ^{1}H NMR spectra were obtained on a Tesla BS-587A instrument at 80 MHz in $CDCl_3$ using TMS as internal reference.

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