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LETTERS TO THE EDITOR

Chemoselective Deoxygenation of 4,5-Dinitroacenaphthenequinone with Hexaethyltriamidophosphite

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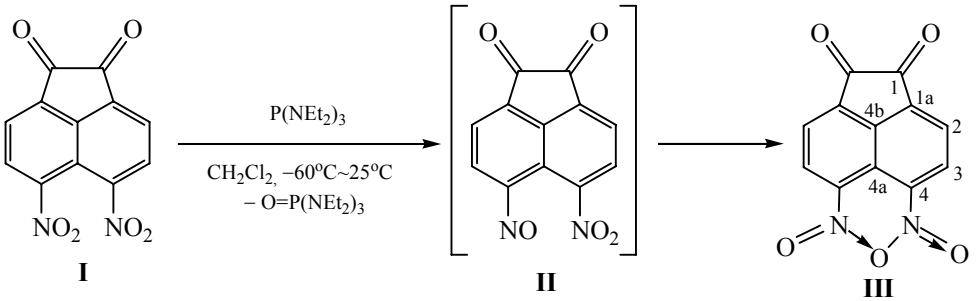
Deoxygenation under the action of the P(III) derivatives is widely used in organic chemistry [1, 2]. Among the variety of reactions a separate group includes the deoxygenation of nitro compounds with the P(III) derivatives resulting in the nitrogen-containing heterocycles of different structures [3]. The tertiary phosphines and phosphites are most commonly used as the P(III) derivatives. One of the most studied reactions of this type is the cyclization of nitroarenes to form the corresponding nitrogen-containing heterocycles (indoles, pyrrolopyrimidines, carbazoles, quinolines) under the action of the phosphorous acid esters. Presumably, the reaction proceeds through the intermediate formation of nitrenes. If 2-nitrobiaryls were used, the nitrene inserts on the C–H bond adjacent to the aryl moiety, to give the corresponding carbazoles [4, 5] or δ-carbolines [6]. The reaction of 2-nitrophenylsulfide with an excess of triethyl phosphite, resulting in phenothiazine, can be attributed to the same type of the reactions [7, 8]. If the aryl contains a double bond *ortho*-positioned relative to the nitro group (*o*-nitrostyrene), the nitrene inserts on the β-C–H bond of the vinyl moiety to give the substituted indoles [9–11]. The reactions of *o*-dinitrobenzene with the P(III) derivatives should be specially noted. For example, under the action of triethyl phosphite, diphenylethylphosphinite, or methyldiethylphosphonite one of the nitro groups is substituted by the phosphorus moiety and ethyl nitrite is eliminated [12]. At the same time, the reduction of 2,2'-dinitrobiphenyl with the gaseous PH_3 stops when benzocinnoline-2,2'-dioxide forms [13].

We have previously shown that acenaphthenequinone can be deoxygenated with hexaethyltriamidophosphite under mild conditions to give the known dye, diacenaphthylidenedione, in a nearly quantitative yield [14]. This synthetic approach was successfully applied to some isatin derivatives. As a result the new symmetrically substituted isoindigos were obtained [15–17].

In this work we investigate the chemoselectivity of the reaction of hexaethyltriamidophosphite with 4,5-dinitroacenaphthenequinone **I**, whose NO_2-groups are able to be reduced with the P(III) derivatives.



I **II** **III**

The reaction (1:1, –50°C, CH_2Cl_2) results in 1,2,6-oxadiazine-2,6-dioxide **III** and hexaethyltriamidophosphate (δ_P 24 ppm), i. e. the deoxygenation occurs chemoselectively involving only one nitro group. The reaction proceeds apparently via the intermediate formation of 4-nitro-5-nitrosoacenaphthenedione **II** followed by cyclization into the compound **III**. The symmetrical structure of the latter was unambiguously confirmed by the $^{13}C–\{^1H\}$ and ^1H NMR spectra. The mass spectrum (EI) of **III** contains a peak with *m*/*z* 226 (*M* 256), corresponding to the $[M – NO]^+$ ion.

The obtained data on a high chemoselectivity of oxidation of one nitro group indicate the advisability of further studies of the effect of the nature and position of the substituent in the α-diketone molecule on the possibility of generating the functionalized keto-carbenes in the described systems.

Compound III. To a slurry of 4,5-dinitroacenaphthenequinone **I** (0.80 g, 2.94 mmol) [18] in 10 ml of CH_2Cl_2 was added dropwise under argon atmosphere at –50°C a solution of 0.77 ml of hexaethyltriamidophosphite in 5 ml of CH_2Cl_2. When the reaction temperature rose to room temperature (1.5 h), the reaction mixture was evaporated in a vacuum of 18 mm Hg to a volume of 5 ml. To the residue 5 ml of anhydrous hexane was added. The dark brown precipitate (0.70 g, 92%) was filtered off and dried in a vacuum, mp > 350°C. IR spectrum, ν, cm^{-1}: 1748, 1699, 1617, 1540, 1508, 1352, 1209, 1157, 1023, 869, 738. ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 8.30 d (1H, H^2, $^3J_{HC}$ 7.3), 7.95 d (1H, H^3, $^3J_{HH}$ 7.3). ^{13}C ($^{13}C–\{^1H\}$) NMR spectrum (100.6 MHz, DMSO-d_6), δ_C, ppm (*J*, Hz): 184.21 br. s (s) (C^1), 133.69 d (s) (C^{1a}, $^3J_{HC}$ 7.8), 129.02 d (s) (C^2, $^1J_{HC}$ 171.2), 122.24 d (s) (C^3, $^1J_{HC}$ 173.6), 145.62 d (s) (C^4, $^3J_{HC}$ 7.2), 113.24 br. t (s) (C^{4a}, $^3J_{HC}$ 6.0–6.6), 143.62 t (s) (C^{4b}, $^3J_{HC}$ 7.2–7.8). Found, %: C 56.18; H 1.45; N 10.74. $C_{12}H_4N_2O_5$. Calculated, %: C 56.26; H 1.57; N 10.94.

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