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LETTERS TO THE EDITOR

Regiochemistry of the Reaction of Deoxygenation of 1-Tosylisatin with Hexaethyltriamidophosphite

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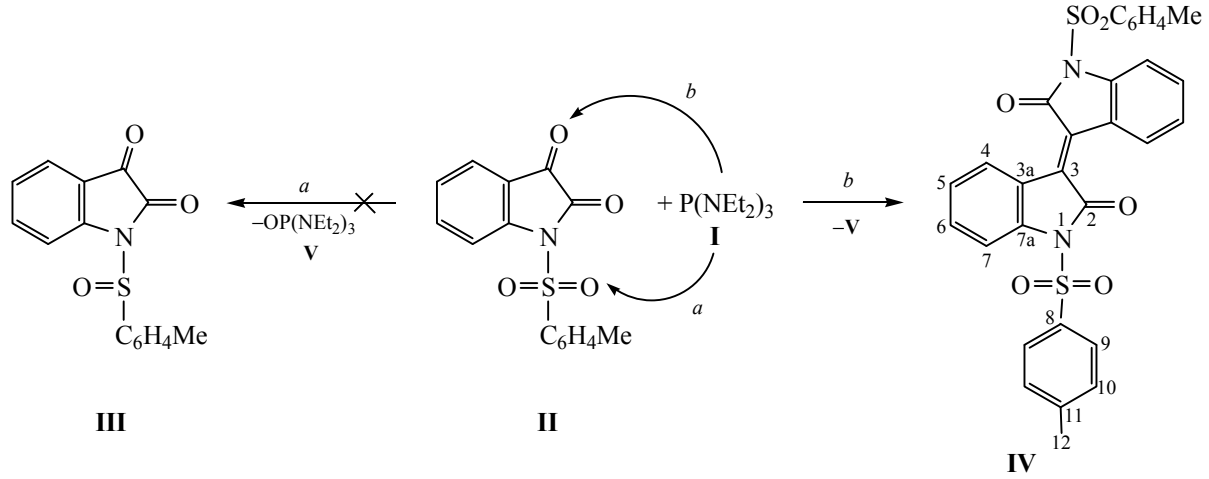
Deoxygenation and desulfonation of organic compounds by the action of trivalent phosphorus derivatives are widely used in organic chemistry [1, 2]. Among the various transformations occurring in this case a group of processes can be separated that are realized in the reactions of carbonyl compounds with P(III) derivatives. For example, the reaction of trialkylphosphites or sodium diethylphosphite with various benzaldehyde derivatives gives rise to the corresponding ethylenes including stilbenes [3, 4] in moderate yields. 2,2'-Diformylbiphenyl and its derivatives undergo the intramolecular cyclization to the corresponding 1,2-diphenyloxiranes under the action of tris(dimethylamino)phosphine [5]. It is assumed that the deoxygenation of 1,3-dicarbonyl compounds (the cyclic anhydrides or thioanhydrides) proceeds through the stage of the carbene formation [6, 7]. In the reactions of aroyl- and hetaroylphosphonates with trialkylphosphites the formed intermediate of carbene nature is added intramolecularly to the multiple bond [8–14]. Nevertheless, in a considerable number of the studies the intermediate formation of carbenes is only postulated, and other versions of explanation of these synthetic results may be offered. Unlike the deoxygenation of ketones and carboxylic acid anhydrides, similar processes with α-dicarbonyl compounds are described in only few works [4, 15, 16].

In this study the reaction of tris(diethyltriamino)-phosphine **I** with 1-tosylizatin **II** containing two reaction center (C=O and S=O) capable of reacting with an atom P(III) was first investigated. The deoxygenation reaction can proceeds by two routes: at the S=O bond to form 1-sulfinylisatin **III** (*a*) and at the carbonyl group to give 1,1'-ditosylisoindigo **IV** (*b*). Based on the IR and ^{13}C NMR data, we unambiguously established the regiochemistry of deoxygenation reaction: The process occurs exclusively with the participation of the oxygen of C^3=O moiety (*b*).



1,1'-Bis(4-methylphenylsulfonyl)-1*H*,1'*H*-[3,3']-biindolylidene-2,2'-dione (IV). To a pale yellow suspension of 0.5 g (1.66 mmol) of 1-tosylisatin **I** in 10 ml of methylene chloride was added dropwise 0.44 ml (1.66 mmol) of hexaethyltriamidophosphite at –60°C while bubbling argon. A sharp change occurred in the reaction mixture color: from dark green to brown, then to orange, and after the phosphite addition, to dark orange. When temperature rises to 25°C (after 1 h), the precipitate was filtered off, washed thrice with hot hexane, and dried in a vacuum (12 mm Hg). Yield 0.43 g (86%), mp 269–271°C (decomp.). IR spectrum, ν, cm^{-1}: 1727, 1597, 1320, 1298, 1244, 1194, 1171, 1099, 1085, 950, 775, 707, 660, 565. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J,* Hz): 8.78 d (H^4, $^3J_{HCCH}$ 8.1), 7.17 m (H^5, $^3J_{HCCH}$ 8.0–8.4), 7.46 m (H^6, $^3J_{HCCH}$ 8.3–8.6, $^4J_{HCCCH}$ 1.0–1.1), 7.98 d (H^7, $^3J_{HCCH}$ 8.8), 7.96 d (H^9, $^3J_{HCCH}$ 8.1), 7.29 d (H^{10}, $^3J_{HCCH}$ 8.1), 2.39 s (H^{12}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz) [signal type of the $^{13}C-\{^1H\}$ NMR spectrum is given in the brackets]: 165.61 br.s (s) (C^2), 132.06 br.s (s) (C^3), 121.99 m (s) (C^{3a}, $^3J_{HCCC}$ 7.0–7.3), 129.29 d. d (s) (C^4, $^1J_{HC}$ 168.7, $^3J_{HCCC}$ 7.7), 124.68 d.d (s) (C^5, $^1J_{HC}$ 162.9–163.2, $^3J_{HCCC}$ 7.3–7.7), 134.04 d.d (s) (C^6, $^1J_{HC}$ 162.1, $^3J_{HCCC}$ 7.7), 113.34 d.d (s) (C^7, $^1J_{HC}$ 169.5, $^3J_{HCCC}$ 8.1), 145.90 m (s) (C^{7a}), 140.66 m (s) (C^8, $^3J_{HCCC}$ 9.7–9.9), 129.87 d.d (s) (C^9, $^1J_{HC}$ 166.9, $^3J_{HCCC}$ 5.1), 127.98 d.m (s) (C^{10}, $^1J_{HC}$ 162.1, $^3J_{HCCC}$ 5.1), 135.00 m (s) (C^{11}, $^3J_{HCCC}$ 8.8), 21.68 q.t (s) (C^{12}, $^1J_{HC}$ 127.3, $^3J_{HCCC}$ 4.0).

The ^1H (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded on a Bruker Avance-400 instrument. The IR spectrum was registered on a Bruker Vector-22 spectrometer in mineral oil.

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