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LETTERS TO THE EDITOR

Deoxygenation of Acenaphthenequinone with Hexaethylphosphorous Triamide: An Efficient Method of Synthesis of Biacenaphthylidenedione

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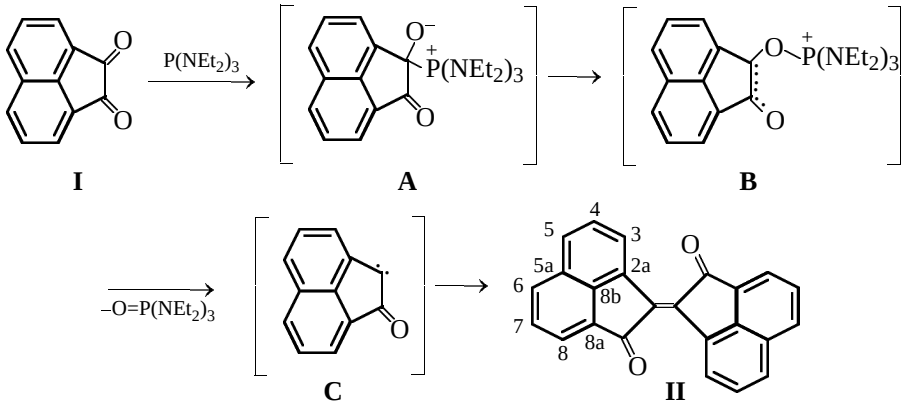
Carbenes are reactive species which are widely used in organic synthesis; they can be generated by various methods [1]. Published data on carbene generation with the aid of organic phosphorus(III) compounds are scanty and contradictory. On the other hand, many P(III) derivatives are well known to act as deoxygenating agents in reactions with carbonyl compounds; however, this property of P(III) compounds was not utilized in further development of carbene generation procedures. Ramirez *et al*. [2] showed that acenaphthenequinone (**I**) readily oxidizes 2-(1-pyrrolidinyl)- and 2-dimethylamino-1,3-dimethyl-1,3,2-diazaphospholanes and that the oxidant is thus converted into an oligomer with unidentified structure. Acyclic amides derived from P(III) acids are stronger nucleophiles. They react with carbonyl compounds to afford as a rule phosphonium derivatives. Taking the above-stated into account, we believe that acyclic phosphorous triamides should be more promising reagents for carbene generation via deoxygenation.

In fact, the deoxygenating action of phosphorous triamides was confirmed experimentally by studying the reaction of hexaethylphosphorous triamide with quinone **I**. The reaction occurred under mild conditions (–70°C, CH_2Cl_2) and afforded hexaethylphosphoric triamide (δ_P 24 ppm) and 1,1'-bis(acenaphthenylidene)-2,2'-dione (**II**) in quantitative yield. Insofar as 2-R_2N-1,3-dimethyl-1,3,2-diazaphospholanes are less reactive than hexaethylphosphorous triamide, the first step of the process may be nucleophilic attack by the phosphorus atom on the carbonyl carbon atom of acenaphthenequinone to give dipolar intermediate **A** which is then transformed into structure **B** possessing a P–O–C bond. The subsequent elimination of hexaethylphosphoric triamide gives rise to carbene species **C**. The latter undergoes quantitative dimerization to the known dye biacenaphthylidenedione (**II**). Compound **II** was synthesized previously by treatment of acenaphthenequinone with PCl_5 in the presence of $Na_2S \cdot H_2O$ in boiling ethanol [3]. An alternative procedure [4] is based on thermolysis of 2-diazoacenaphthenone in boiling toluene in the presence of copper powder; in both cases, the yield of **II** was 40–50%.



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The structure of compound **II** was confirmed by the spectral data (NMR and IR) which were consistent with those reported in [3]. Our results suggest prospects in further development of the proposed procedure for generation of functionalized carbenes.

1,1'-Bis(acenaphthenylidene)-2,2'-dione (II). A solution of 2.8 g of hexaethylphosphorous triamide in 5 ml of methylene chloride was added dropwise under stirring at –70°C to a suspension of 2.05 g of quinone **I** in 20 ml of methylene chloride. The mixture was allowed to warm up to 20°C over a period of 1.5 h, and it turned from orange to yellow, red, violet, dark blue, and (at 20°C) again red. After 48 h, the brick-red precipitate (1.68 g, 90%) was filtered off and dried under reduced pressure. mp 298–301°C. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 9.45 d (1H, 8-H, $^3J_{HH}$ = 7.5), 8.13 br.d.d (1H, 6-H, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.0), 8.07 d.d (1H, 5-H, $^3J_{HH}$ = 7.0, $^4J_{HH}$ = 1.0), 8.00 d (1H, 3-H, $^3J_{HH}$ = 8.1), 7.77 d.d (1H, 7-H, $^3J_{HH}$ = 7.9, $^3J_{HH}$ = 7.5), 7.74 d.d (1H, 4-H, $^3J_{HH}$ = 8.1, $^3J_{HH}$ = 7.0). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$–DMSO-d_6, 2 : 1; in parentheses is given the appearance of a signal in the ^{13}C–{^{1}H} spectrum), δ_C, ppm (*J*, Hz): 188.12 br.s (s) (C^1); 150.24 br.s (s) (C^2); 132.43 br.d.m (s) (C^6, $^1J_{HC}$ = 167.9); 130.58 m (s), 130.24 m (s), 129.33 m (s), 114.27 br.d (s) (C^{5a}, C^{8b}, C^{2a}, C^{8a}, $^3J_{HC}$ = 7.6); 128.68 d (s) and 127.95 d (s) (C^4, C^7, $^1J_{HC}$ = 157.8, 163.3); 126.81 d.m (s) (C^5, $^1J_{HC}$ = 166.7); 124.45 d.d (s) (C^3, $^1J_{HC}$ = 167.8, $^3J_{HC}$ = 7.6); 121.91 d.d (s) (C^8, $^1J_{HC}$ = 167.2, $^3J_{HC}$ = 7.6). Found, %: C 86.58; H 3.52. $C_{24}H_{12}O_2$. Calculated, %: C 86.74; H 3.61.

The NMR spectra were recorded on a Bruker MSL-400 spectrometer.

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