

ESR of a Cyclic Phosphahydrazidinyl

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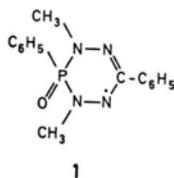
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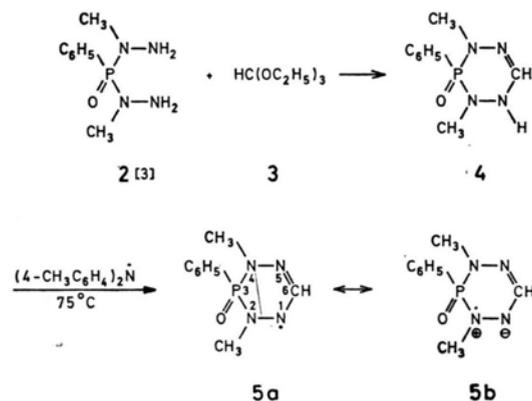
Hydrazidinyl Radicals, ESR, ENDOR

The cyclic phosphahydrazidinyl (**5**) was generated and studied by ESR. The results are discussed in connection with the properties of other hydrazidinyl radicals.

Kornuta *et al.* [1] reported the generation of the cyclic phosphahydrazidinyl radical (**1**) by dehydrogenation of the corresponding leuco compound with PbO_2 . The radical state of the blue (λ_{max} 590 nm) species **1** was confirmed by ESR: $g = 2.003$, ~ 27 hfs lines. In connection with our hydrazidinyl studies [2] we were interested in the ESR data of this radical type, particularly in those of the more basic compound **5**.



Cyclization of 1,1'-dimethyl-P-phenyl-phosphonic-dihydrazide (**2**) with 1,1,1-triethoxymethan (**3**) gave the leuco compound **4** (30%). Hydrogen abstraction from **4** by bis(4-methylphenyl)aminyl in benzene yielded stable solutions of **5** (λ_{max} 499 nm, $\log \epsilon > 3.2$). Our attempts to isolate the orange radical failed. The dehydrogenation of **4** can also



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be performed with other reagents, *e.g.* PbO_2 , Ag_2O *etc.*, one obtains, however, less stable solutions of **5**. Dilution experiments indicate a monomeric state of **5**.

The ESR spectrum of **5** in benzene is shown in Fig. 1. The simulation of this spectrum requires: $a(\text{N}) = 6.40$ G (2N); $a(\text{N}) = 4.60$ G (2N); $a(\text{P}) = 4.90$ G; $a(\text{H}_{\text{CH}_3}) = 4.60$ G (6H); and $a(\text{H}_{\text{CH}}) = 1.05$ G. The proton hfs data are confirmed by the ENDOR spectrum of **5** in toluene, which yielded $a(\text{H}_{\text{CH}_3}) = 4.48$ G and $a(\text{H}_{\text{CH}}) = 1.00$ G [4]. In other cyclic hydrazidinyl radicals, *e.g.* verdazyls, tetrazolinyls [5], electron acceptor substituents at the terminal nitrogens of the hydrazidinyl system reduce the corresponding $a(\text{N}_{2,4})$ with respect to $a(\text{N}_{1,5})$. The phosphor bridge in **5**, which represents a derivative of the phosphonic acid, should give rise to a similar effect. Therefore we attribute the smaller nitrogen splitting of 4.60 G to the terminal 2,4-nitrogens. Likewise the ESR spectrum of **1** in benzene (λ_{max} 580 nm, generated from the corresponding leuco compound by hydrogen abstraction with bis(4-methylphenyl)aminyl) can be analyzed to give: $a(\text{N}) = 6.40$ G (2N); $a(\text{N}) = 4.45$ G (2N); $a(\text{P}) = 4.70$ G; $a(\text{H}_{\text{CH}_3}) = 4.65$ G (6H). The measurement of the g -factor yielded 2.0038 for **1** and **5**. The g -values of hydrazidinyl radicals are all in the range 2.0034–2.0037 [2]. The slightly larger value of **1** and **5** is apparently caused by the phosphor atom in the system. The phosphor bridge is interacting with two nitrogen sites bearing relatively large spin densities. For a group interacting with two spin sites Whiffen [6] has proposed within the framework of simple π -electron theory, that the hfs coupling constant is proportional to the square of the sum of the π -orbital coefficients rather than the sum of the corresponding squared terms. The π -orbital coefficients of the terminal nitrogens in the hydrazidinyl system are equal but of opposite sign. Therefore one might expect a zero or a very small hfs splitting for the phosphor bridge. In agreement with this prediction the phosphor split-

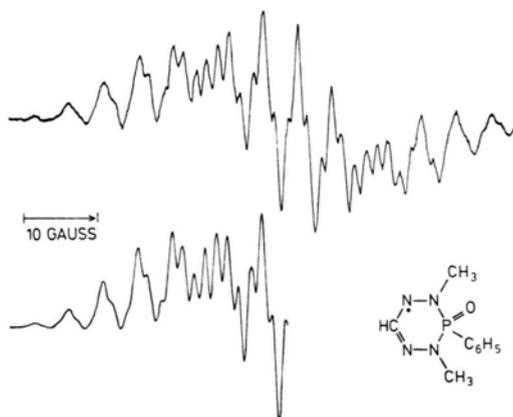


Fig. 1. ESR spectrum of **5** in benzene at 22 °C, and the simulation using the splittings given in the text.

ting of **1** and **5** is significantly smaller than those of comparable species, e.g. $R_2P(O)\dot{C}HR'$, $a(P) = 36$ G [7], but far from zero. The finding $a(P) \approx 4.8$ G may indicate, that the phosphor bridge is in some way incorporated in the π -electron system and/or the studied cyclic phosphahydrazidinyls are not planar.

Because of the hydrazyl resonance (**5a**, **5b**), the free electron pairs of the terminal nitrogens are included in the π -electron system. The observed ratio $a(N_1)/a(N_2) \approx 1.4$ reflects the relative weights of the resonance structures **5a** and **5b**, the unpolar form being preferred to some extent. Considering this ratio the cyclic phosphahydrazidinyls **1** and **5** can be ranked between verdazyls and tetraazapentenyls [2].

Experimental

1,2,3,4-Tetrahydro-2,4-dimethyl-3-oxide-3-phenyl-1,2,4,5,3-tetraazaphosphorinyl (4)

The solution of 1,1'-dimethyl-P-phenyl-phosphonic-dihydrazide [3] (3.6 g; 17 mM) and 1,1,1-triethoxymethan (2.8 ml; 17 mM) in ethanol (20 ml) was refluxed for 3 h. After evaporation in vacuum the residue was purified by chromatographing on

silica gel 60 (Merck), using methylene chloride as eluent, to yield from ethyl acetate/ethanol (19:1) colourless crystals (1.15 g; 30%); m.p. 165–166 °C. 1H NMR (80 MHz, DMSO- d_6): δ 2.70 (3H; d; $J_{P,H} = 10$ Hz; CH_3); δ 2.96 (3H; d; $J_{P,H} = 6$ Hz; CH_3); δ 6.65 (1H; CH); δ 7.3–7.8 (5H; m; C_6H_5); δ 8.20 (1H; d; $J_{P,NH} = 11$ Hz; NH). – IR (Kl): 3200 ($\nu NH_{ass.}$); 2960 (νCH), 1430 (νC_6H_5), 1210 cm^{-1} ($\nu P=O$). – UV (dioxane): λ_{max} (log ϵ) = 240 s (3.69), 218 nm (4.02).

$C_9H_{13}N_4OP$ (224.2)

Calcd C 48.21 H 5.84 N 24.99,

Found C 48.16 H 6.15 N 24.92.

$m/e = 224$ (M^+).

Generation of 1,2,3,4-tetrahydro-2,4-dimethyl-3-oxide-3-phenyl-1,2,4,5,3-tetraazaphosphorinyl (5)

Tetrakis(4-methylphenyl)hydrazine (5 mg) and **4** (5 mg) in benzene (5 ml) were heated for about 1 min until the solution developed an orange colour (λ_{max} 499 nm, log $\epsilon > 3.2$).

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