round-bottomed flask, dried and cooled under N_2, was maintained at 0 °C using an ice bath and was charged with 10.0 M borane–dimethyl sulfide complex (50 mmol). A total of 4.25 g of 2,3-dimethyl-2-butene (50 mmol) was added slowly and the mixture was sitrred for 1 h. Ethylene glycol (3.1 g, 50 mmol) was added dropwise with vigorous stirring with control of the H_2 evolution at 25 °C and the mixture was stirred for 1 h. Removal of the volatiles by water aspirator followed by distillation yielded 7.4 g of 2-thexyl-1,3,2-dioxaborolane (95%, **5a**): ^{11}B NMR δ 35.4; ^{1}H NMR δ 0.77–0.90 (s and d, 12 H), 1.35–1.65 (m, 1 H), 4.08 (s, 4 H); bp 70 °C/19 mm; n^{20}_D 1.4272; IR ν_{B-O} 1310, 1160 cm^{-1}; yield, 95%. 2-Thexyl-4,5-dimethyl-1,3,2-dioxaborolane (**5b**): ^{11}B NMR δ 35.1; ^{1}H NMR δ 0.80–0.90 (s and d, 12 H), 1.10–1.30 (d and d, 6 H), 1.60–1.90 (m, 1 H), 4.00–4.50 (m, 2 H); bp 70–73 °C/14 mm; n^{20}_D 1.4204; IR ν_{B-O} 1310, 1160 cm^{-1}; yield, 92%; MS, *m/e* M$^+$ 184/185. Anal. Calcd for $C_{10}H_{21}BO_2$: C, 65.23; H, 11.52; B, 5.87. Found: C, 65.57; H, 11.36; B, 5.60. 2-Thexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5c**): ^{11}B NMR δ 34.7; ^{1}H NMR δ 0.77–0.90 (m, 12 H), 1.18 (s, 12 H), 1.35–1.65 (m, 1 H); bp 87 °C/17 mm; n^{20}_D 1.4274; IR ν_{B-O} 1300, 1140 cm^{-1}; yield, 94%; MS, *m/e* M$^+$ 211/212. Anal. Calcd for $C_{12}H_{25}BO_2$: C, 67.92; H, 11.90; B, 5.09. Found: C, 68.27; H, 12.25; B, 4.79. 2-Thexyl-1,3,2-dioxaborinane (**5d**): ^{11}B NMR δ 31.4; ^{1}H NMR δ 0.77–0.85 (s and d, 12 H), 1.23–2.03 (m, 3 H), 3.90 (t, 4 H); bp 79–80 °C/16 mm [lit.[18] bp 74–75 °C/13 mm]; n^{20}_D 1.4368; IR ν_{B-O} 1300, 1180 cm^{-1}; yield, 92%.

General Procedure for the Reaction of Potassium Hydride with Cyclic Boronic Esters. A preparation of potassium 2-thexyl-4,5-dimethyl-1,3,2-dioxaborolane hydride is representative. To an oven-dried, 100-mL, round-bottomed flask, cooled and maintained under N_2 as usual, was added 3.5 g of KH (30 mmol) as an oil dispersion with the aid of a double-ended needle. The mineral oil was removed by washing with pentane (3 × 30 mL). To the suspension of KH in 40 mL THF kept at 25 °C by a water bath was added a total of 3.68 g of 2-thexyl-4,5-dimethyl-1,3,2-dioxaborolane (20 mmol) with vigorous stirring. The reaction was slightly exothermic and complete within 1 h. The ^{11}B NMR spectrum of the clear supernatant after the settling of excess KH showed a broad singlet at δ 9.8 and the solution IR of the product exhibited a strong B–H stretching absorption at 2010 cm^{-1}, indicating the formation of potassium 2-thexyl-4,5-dimethyl-1,3,2-dioxaborolane hydride. The hydride concentration was measured, 0.42 M (93% yield), by the number of moles of H_2 evolved when the reagent was hydrolyzed with THF–glycerine–2 N HCl (1:1:1). The reagent was analyzed for its potassium and boron contents, which were measured as potassium hydroxide (by a standard acid titration) after hydrolysis and as 2,3-dimethyl-2-butanol after oxidation with $NaOH-H_2O_2$ by GC analysis, respectively. Concnetrations of K:B:H 0.42 M:0.41 M:0.42 M were clearly establishing K:B:H 1:1:1 stoichiometry. The solution was stored over excess KH under a positive pressure of N_2 for a month and showed no disproportionation in ^{11}B NMR and no decrease in its hydride concentration.

Reduction of 2-Methylcyclohexanone. The reaction of 2-methylcyclohexanone with potassium 2-thexyl-4,5-dimethyl-1,3,2-dioxaborolane hydride (**5b**) is representative. To a 50-mL, round-bottomed flask fitted with a side arm and capped by a rubber septum were placed 0.8 mL of THF and 5.2 mL of solution of potassium 2-thexyl-4,5-dimethyl-1,3,2-dioxaborolane hydride (0.42 M, 2.2 mmol) in THF and the flask was maintained at 0 °C by an ice bath. To this was added 2.0 mL of THF solution of 2-methylcyclohexanone (1.0 M, 2.0 mmol) cooled to 0 °C, and the mixture was stirred for 3 h. The reaction was quenched with H_2O and organoborane was oxidized with $NaOH-H_2O_2$. The aqueous layer was saturated with anhydrous K_2CO_3 and the GC analysis of the organic layer after addition of cyclopentanol as an internal standard revealed 84% *cis*- and 16% *trans*-2-methylcyclohexanol.

Acknowledgment. The support of this work by the United States Army Research Office (Grants ARO DAAG-29-79-C-0027, ARO DAAG-29-82-K-0047, and ARO DAAG-29-85-K-0062) is gratefully acknowledged. We also acknowledge several earlier exploratory experiments by Drs. Ramachandra G. Naik and V. Somayaji.

Phosphinylhydrazyls $R_2\dot{N}NP(O)L_2$, an ESR Study. Influence of the Captodative Effect on the Three-Electron NN π Bond

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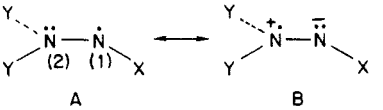
1,1-Dimethyl-2-phosphinylhydrazyls and 1-*tert*-butyl-2-phosphinylhydrazyls have been generated from the corresponding hydrazines. Their radical structures have been assigned on the basis of their ESR spectral parameters. In contrast with the behavior of trialkylhydrazyls or 1,2-dialkylhydrazyls it has been shown that in the phosphinylhydrazyls the larger nitrogen splitting is due to the tervalent nitrogen. Phosphinylhydrazyls have been shown to exist in equilibrium with their dimer form. The radical $Me_2\dot{N}NP(O)(OEt)_2$ is particularly persistent, and the free activation energy for the rotation about the NN bond has been measured ($\Delta G^{\ddagger}$ = 9.8 ± 0.5 kcal/mol).

The solution ESR spectra of a large number of triarylhydrazyls have been studied for many years.[3] More recently, Ingold et al.[4] reported the first solution spectra for some mono- and dialkyl-substituted hydrazyls as well as the spectrum of hydrazyl, $H\dot{N}NH_2$, itself.

The electronic distribution in the three-electron π bond of hydrazyls appears to be very sensitive to the electronic effect of the groups attached to the nitrogens. Thus, for 1,1-dialkylhydrazyls, Y = R, X = H, it has been shown by ^{15}N labeling that the smaller nitrogen spliting comes from the divalent N (1) nitrogen.[4a] This observation was rationalized as being due to the inductive effect of the alkyl groups which stabilize resonance structure B relative to A. The same argument accounts for the reversal of the nitrogen splittings in the case of 1-alkylhydrazyls,[4b] Y = H, X = R.



In a continuing study of aminyl radicals bearing an α- or β-phosphorus substituent,[5] we decided to investigate the

(1) Visiting scholar. University of Teheran.
(2) On leave from the Pakistan Council of Scientific and Industrial Research, 1982–1983.
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Table I. ESR Parameters[a] for Some Hydrazyls[b] $R_2N(2)$-$\dot{N}(1)P(O)L_2$ in Solution

hydrazyl	T[d] °C	soln	$a_{N(1)}$	$a_{N(2)}$	a_p	a (other)
$Me_2N\dot{N}P(O)(OEt)_2$ (**1a**·)	21	$PhCH_3$	7.17	13.5	10.2	11.0 (3H), 11.95 (3H)
	126[c]		7.75	13.44	8.85	10.98 (6 H)
$Me_2N\dot{N}P(O)(Et)_2$ (**1b**·)	0	Cy	7.75	13.15	11.25	11.25 (3H), 9.90 (3 H)
	70	C_6H_6	7.90	13.05	10.15	10.70 (6 H)
t-BuN(H)$\dot{N}P(O)(OEt)_2$ (**1c**·)	25	C_6H_6	8.22	12.30	12.90	9.06 (1 H)
	25	MeOD	8.0	12.25	12.25	1.50 (1 D)
t-BuN(H)$\dot{N}P(O)(OPh)_2$ (**1d**·)	25	C_6H_6	7.75	12.52	11.52	10.28 (1 H)
	25	MeOD	7.60	12.60	11.00	1.62 (1 D)
t-BuN(H)$\dot{N}P(O)(Et)_2$ (**1e**·)	−55	$PhCH_3$	8.60	11.91	16.97	9.1 (1 H), 1.6 (2 H)
	25	MeOD	8.79	11.95	16.48	1.4 (2 H), 1.4 (1 D)
$Me_2N\dot{N}M_e$[4b] (**2**·)	rt	(*t*-BuO)$_2$	11.7	10.5		5.9 (3 H), 8.2 (3 H)
t-BuN(H)$\dot{N}$-*t*-Bu[13] (**3**·)	rt	(*t*-BuO)$_2$	12.8	9.45		3.0 (1 H)
$H_2N\dot{N}C(O)OEt$[4d] (**4**·)	0	(*t*-BuO)$_2$	7.8	10.2		1.3 (2 H), 9.6 (2 H)

[a] Hyperfine splittings in gauss were obtained by computer simulation. [b] $2.0035 \leq g \leq 2.0037$. [c] Toluene–*tert*-butylbenzene (50/50). [d] Room temperature = rt.

influence of a phosphinyl substituent on the electronic distribution in a three-electron π bond by studying some phosphinylhydrazyls, i.e., $R_2N\dot{N}P(O)L_2$ (**1**·, R = H, alkyl).

It was found that the radicals could be successfully generated by hydrogen atom abstraction from the corresponding phosphinylhydrazines **1H** with *tert*-butoxyl radicals. The present work reports the first ESR studies of **1**.[6]

Experimental Section

Materials. Di-*tert*-butyl diperoxyoxalate was prepared by the published method.[7] Phosphinylhydrazines, $RR'NN(H)P(O)L_2$, were prepared as follows.

$RR'NN(H)P(O)L_2$: R = R′ = Me; L = EtO (1aH).[17] To a solution of *N,N*-dimethylhydrazine (0.2 mol) in dry ether (30 mL) was added dropwise, at 20–30 °C, with stirring, 0.1 mol of diethylchlorophosphite. Stirring at this temperature was continued for 2 h. Hydrazine hydrochloride was then filtered off and washed with ether. The combined ether solutions were evaporated, and the residue was distilled under reduced pressure: bp 73–75 °C (0.5 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.35 (t, J = 7 Hz, 6 H), 2.45 (s, 6 H), 4.14 (quint, J = 7 Hz, 4 H), 5.15 (d, J = 34 Hz, 1 H).

R = R′ = Me; L = Et (1bH). This compound was prepared by the same method as that for **1aH**: bp 80–83 °C (0.1 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.2 (d of t, J = 20, 7 Hz, 6 H), 1.4–2.2 (br m, 4 H), 2.5 (s, 6 H), 3.9 (d, J 23 Hz, 1 H). Anal. Calcd for $C_6H_{17}N_2OP$: C, 43.89; H, 10.44; N, 17.07. Found: C, 43.17; H, 10.51; N, 17.27.

R = H; R′ = *t*-Bu; L = Et (1eH). To a solution of *N*-*tert*-butylhydrazine hydrochloride (0.1 mol) and triethylamine (0.2 mol) in dry benzene (100 mL) was added dropwise, at 20–30 °C, with stirring, 0.1 mol of diethylphosphinic chloride. Aftr being refluxed for 4 h, the reaction mixture was filtered and evaporated. The crude **1eH** was recrystallized from chloroform: mp 104–105 °C; ^{1}H NMR ($CDCl_3$) δ 1.06 (s, 9 H), 1.19 (d of *t*, J = 19.55 Hz, J = 7.43 Hz, 6 H), 1.76–2.14 (m, 4 H), 3.15 (br s, 1 H), 3.72 (d, J = 15.68 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 6.39 (d, J = 4, 15 Hz, O=PCH_2CH_3) 22.29 (d, J = 66.34 Hz, O=PCH_2CH_3), 27.14 (s, $(CH_3)_3CNH$), 53.85 (d, J = 8.59 Hz, $(H_3C)_3CNH$). Anal. Calcd for $C_8H_{21}N_2OP$: C, 49.98; H, 11.01; N, 14.58. Found: C, 50.08; H, 11.21; N, 14.91.

R = H; R′ = *t*-Bu; L = EtO (1cH). This waxy yellow compound was obtained by the same method as that for **1eH**: ^{1}H NMR ($CDCl_3$) δ 1.1 (s, 9 H), 1.18–1.40 (m, 6 H), 3.1 (br s, 1 H), 3.8–4.3 (m, 4 H), 5.1 (d, J = 28 Hz, 1 H). Anal. Calcd for $C_8H_{21}N_2O_3P$: C, 42.85; H, 9.44; N, 12.50. Found: C, 43.10; H, 9.27; N, 12.61.

R = H; R′ = *t*-Bu; L = PhO (1dH). This crystalline compound was obtained by the same method as that for **1eH** and **1cH**: mp 80–82 °C; ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 9 H), 2.84 (br s, 1 H), 5.32 (d, J = 35 Hz, 1 H), 7.12–7.28 (m, 10 H). Anal. Calcd for $C_{16}H_{21}N_2PO_3$: C, 59.99; H, 6.61; N, 8.74. Found: C, 59.57; H, 6.80; N, 8.58.

Generation of Radicals. Hydrazyl radicals **1**· were generated (a) by thermolysis of a mixture of **1H** (20–30 mg) and di-*tert*-butyl diperoxyoxalate (20 mg) in degassed solvent (benzene, toluene, MeOH, EtOH, MeOD) and (b) direct photolysis of a degassed solution containing **1H** and di-*tert*-butyl peroxide in situ in the ESR cavity with a 1000-W (ORIEL) super high-pressure mercury-xenon lamp.

The radical **1a**· was also generated during the electrochemical oxidation of a solution (H_3CCN) of **1aH**, probably via the deprotonation of the hydrazinium radical **1aH**$^+$·.

Results and Discussion

ESR Parameters. The ESR parameters for radicals **1**· and related radicals are listed in Table I. The hyperfine splittings (hfs) for the new phosphinylhydrazyls were obtained by computer simulation. For hydrazyls **1c**·, **1d**·, and **1e**·, the distinctions between the phosphorus and the hydrogen (N–H) hfs were established by studying the corresponding N-deuterated hydrazyls.

For **1eH** the presence of the prochiral phosphorus atom causes the hydrogens of the α-methylene groups to be magnetically nonequivalent. Accordingly the small hfs with two equivalent hydrogens observed for **1e**· suggests the existence of a preferred conformation for which only one hydrogen of each methylene group gives rise to the observed long-range coupling.

^{15}N-labeling experiments[4b] have shown that in trialkylhydrazyls like **2**· (Table I), $a_{N(1)} > a_{N(2)}$. Comparison of the hfs for radicals **2**· ($a_{N(2)}/a_{N(1)}$ = 0.89) and **1a**· ($a_{N(2)}/a_{N(1)}$ = 1.88) clearly shows that on changing the alkyl substituent of the divalent nitrogen to a phosphinyl group, $a_{N(2)}$ becomes much larger than $a_{N(1)}$ while $a_H^{MeN(2)}$ is also strongly increased ($\Delta\langle a_H\rangle$ = 4.42 G).

These dramatic changes in the electron density distribution of the three-electron π N–N bond are, we suggest, a consequence of the electron-withdrawing effect of the phosphinyl group. As a result, resonance structure B will be stabilized relative to A, and the unpaired electron density on N(2) will be increased and on N(1) decreased, relative to **2**·.

Two different kinds of hydrazyl radicals could be generated by hydrogen abstraction from **1cH**, **1dH**, and **1eH**; moreover, restriction of rotation about the N–N bond could give rise to conformational isomers. Nevertheless, in each case, only one spectrum was observed.

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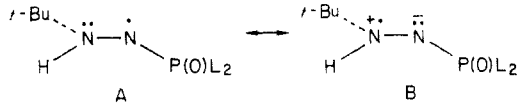
The comparison between the hyperfine splitting constants of hydrazyls **1c·**, **1d·**, **1e·**, and those of hydrazyl **3·** (Table I) clearly indicated that hydrogen abstraction on **1cH**, **1dH**, and **1eH** has occurred at N(1).

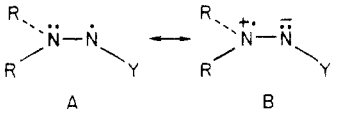
As for **1a·** and **1b·**, the electron-withdrawing phosphinyl group should stabilize resonance structure B relative to A. This implies that N(2) will now produce the larger splitting, and, as a consequence of its increased spin density, the splitting by the hydrogen attached to N(2) will also increase (from 3.0 G for **3·** and **4·** to 9–10 G for **1c·**, **1d·**, or **1e·** (Table I)).



As expected, because of the electron-withdrawing effect of the carboethoxyl group, the changes observed between the hfs of **1c·**, **1d·**, and **1e·** and those of **3·** are comparable to those observed between **3·** and **4·**. This analogy confirms the tentative assignment of Malatesta et al.[4d] for the hfs of radical **4·**.

Examination of the series of phosphinylhydrazyls, shows that the difference between $a_{N(1)}$ and $a_{N(2)}$ is reduced by reducing the number of alkyl groups attached to N(2) (compare $a_{N(2)}/a_{N(1)}$ for **1a·** and **1c·**) or by reducing the electron-withdrawing effect of the phosphinyl substituent (compare $a_{N(1)}$ for **1d·** and **1e·**). These observations are easily rationalized by considering the influence of the inductive effect of the alkyl (+I) or the phosphinyl (–I) groups on the relative weight of resonance structures A and B.

Finally, it is worth noting that the phosphorus splitting constant increases when $a_{N(1)}$ increases, in agreement with the proposed attachment of the phosphorus atom to N(1). The three-electron bond in hydrazyls is expected to become stronger when structures A and B become closer in energy. When Y = alkyl, structure A is more stable than



structure B, but when Y = $P(O)L_2$, the two structures are expected to be closer in energy and the three-electron bond should be stronger.

These electronic effects can be rationalized in terms of the captodative[8] structure of phosphinylhydrazyls, which can also be considered aminyl radicals bearing both a good electron-donor (R_2N) and a good electron-acceptor ($P(O)L_2$) group.

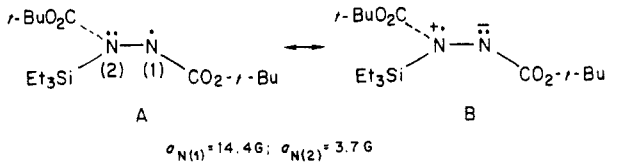
The properties of captodative hydrazyls (push–pull aminyls) were first studied by Balaban,[9] who pointed out the great stability of these species. However, most of the captodative hydrazyls described by Balaban possess aryl groups at the tervalent nitrogen. As a consequence, the donor character of the R_2N group is strongly reduced, and the two nitrogen atoms have equivalent or near equivalent coupling constants. As in 2,2-diphenylpicrylhydrazyl (DPPH), the enhanced stability of these species should be primarily attributed to a large electron and charge delocalization.

Table II. Temperature Influence on the Hyperfine Splittings[a] of Radical $Me_2N(2)$–$NP(O)(OEt)_2$ (1a)

$a_{N(1)}$, G	$a_{N(2)}$, G	a_p, G	T, °C
7.0	13.6	11.0	–32
7.17[b]	13.5	10.2	+20
7.3	13.5	9.8	+40
7.4	13.5	9.1	+86
7.75[b]	13.45	8.85	+126[c]

[a] In toluene. [b] Obtained by computer simulation (Figure 1). [c] In toluene–*tert*-butylbenzene (50/50).

On the other hand, B. P. Roberts[10] studied hydrazyls which can be considered aminyl radicals bearing two electron-withdrawing substituents. The nitrogen coupling constants are in agreement with the large difference in energy expected between structures A and B. Furthermore, these species are very short-lived compared to the phosphinylhydrazyls.

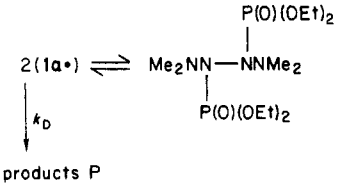


Temperature Effects. A significant change in the magnitude of the hfs of **1a·** is observed by varying the temperature (Table II), and the trend of these changes supports our hfs assignments.

The insensitivity of $a_{N(2)}$ to temperature changes in the –32 to +126 °C region compared with the sensitivity of $a_{N(1)}$ is in accord with a far greater resistance to bending expected around the cationic N(2).[11] On the other hand, the significant decrease of the phosphorus hfs in the –32 to +126 °C region indicates that the phosphorus is attached to the nitrogen atom whose pyramidal character increases during an increase in the temperature.[12]

Hydrazyls **1a·** and **1b·** are particularly persistent, and their ESR signals were easily detected over an unusually large temperature range (–30 to +126 °C for **1a·** and –30 to +100 °C for **1b·**). The highest concentration of **1a·** was observed in the temperature range 20–40 °C. Radical **1a·** is destroyed irreversibly by greater warming, but its concentration can be reversibly decreased and increased by lowering and raising the temperature between 20 and –20 °C.

These observations are in agreement with the existence of an equilibrium such as



and also to a relatively low value for k_D, the rate of the irreversible decay of **1a·** to give the products P.

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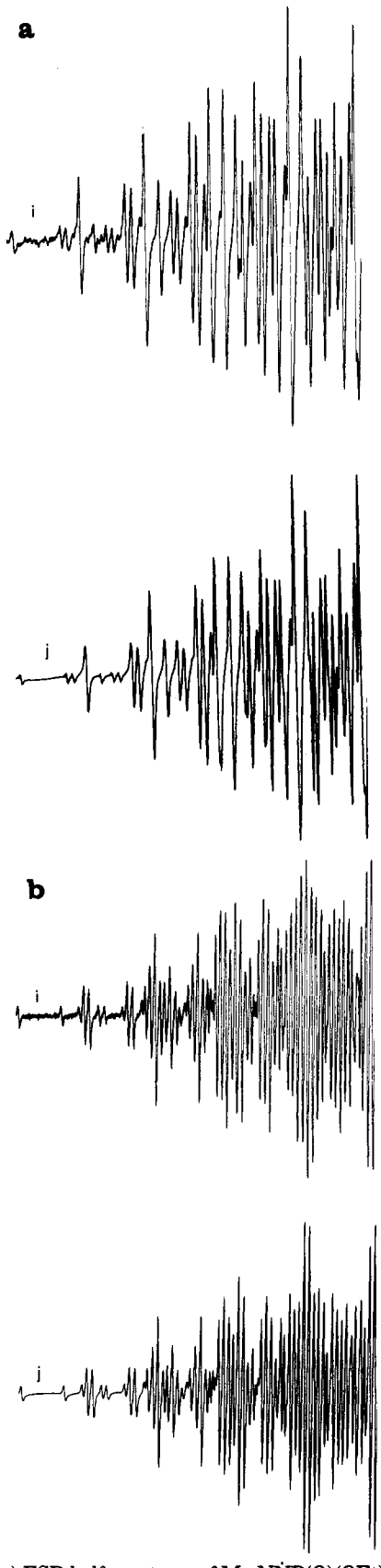


Figure 1. (a) ESR half-spectrum of $Me_2NNP(O)(OEt)_2$ in toluene at 20 °C: (i) experimental; (j) calculated. (b) ESR half-spectrum of $Me_2NNP(O)(OEt)_2$ in toluene–*tert*-butylbenzene (50/50) at 126 °C: (i) experimental; (j) calculated.

As mentioned above, the enhanced stability of **1a·** and **1b·** compared to that of a trialkylhydrazyl is certainly attributable to their captodative structure. Furthermore, the absence of hydrogen atoms in β-position relative to the

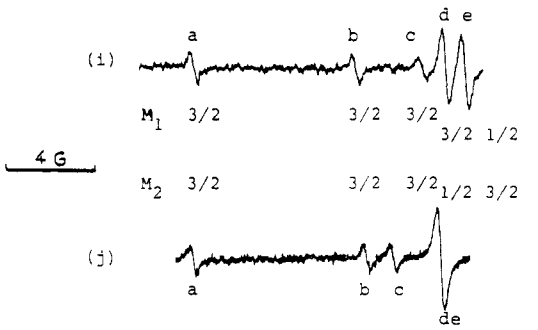
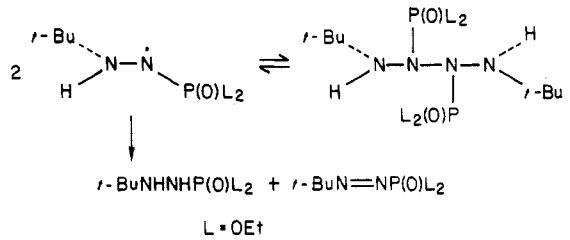


Figure 2. First five lines of the spectrum of **1a·** and the different spin states to which they belong (i) at 20 °C; (j) at 126 °C.

divalent nitrogen prevents a disproportionation process.[13] Hydrazyls **1c·**, **1d·**, and **1e·** are less persistent than **1a·** and **1b·**, and their ESR spectra become undetectable above ca. 70 °C. The highest concentration of **1e·** was detected at ca. −50 °C, and it also can be reversibly decreased and increased by lowering and raising the temperature between −70 and −50 °C. As mentioned above, this behavior is evidence for the existence of a monomer–dimer equilibrium. The lesser persistence of radical **1e·** relative to that of **1a·** may be reasonably attributable to the occurence of a disproportionation involving the amino hydrogen. An-



other interesting observation is that the the ESR spectra of **1a·** and **1b·** undergo marked and reversible changes on varying the temperature (Figure 1).

For radical **1a·** at 100 °C and above, tentative simulations with "static" parameters show that the spectra can be satisfactorily simulated assuming that the two methyl groups are equivalent (Figure 1a). Below 40 °C, the spectra were satisfactorily simulated assuming that the two methyl groups are nonequivalent (Figure 1b). In the temperature range +40 to +100 °C, owing to a distinct broadening of different lines, the spectra cannot be satisfactorily simulated using static parameters. The line broadening effects can be explained in terms of the rotation[14] around the N–N bond, which exchanges the coupling constants, a_1 and a_2, of the CH_3 group protons and the following considerations apply. One individual line of the spectrum has the relative resonance position as in eq 1, where $M_{1,2} = {}^3/_2, {}^1/_2, {}^{-1}/_2,$

$$H_r = -a_1M_1 - a_2M_2 - \sum_k a_kM_{I_k} \quad (1)$$

$-{}^3/_2$ are the total magnetic spin quantum numbers of the two groups of CH_3 protons. An exchange not affecting the M_i but the coupling constants a_i shifts the line to that given by eq 2, i.e., by a distance given by eq 3. According to

$$H_r' = -a_1M_2 - a_2M_1 - \sum_k a_kM_{I_k} \quad (2)$$

$$\Delta H_r = -(a_1 - a_2)(M_1 - M_2) \quad (3)$$

eq 3 only the lines with different M_i will be affected by

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(14) An in-plane vibrational mechanism is expected to have a large activation energy and to produce line broadening at higher temperature. Stassinopolou, C. I.; Zioudrou, C.; Karabatsos, G. J. *Tetrahedron* **1976**, *32*, 1147.

Table III. Variation of k_r vs. Temperature for Radical $Me_2NNP(O)(OEt)_2$ in Toluene-*tert*-Butylbenzene (50/50)

T, K	$10^{-6}k_r$, s^{-1}	$\Delta G^{\ddagger}$
339	3.2_7	9.8_3
344	3.8_1	9.8_8
349	5.7_0	9.7_5
355	7.6_3	9.7_3

the rotation around the N–N bond.

The first five lines of the spectrum of **1a·**, recorded at different temperatures, and the spin state to which they correspond are shown in Figure 2, assuming that the two methyl groups have coupling constants with like signs. The lines a, b, and c (Figure 2) belong to the same M_i and thus are not broadened by the exchange between the two methyl groups, while lines d and e have different M_i and are connected by the exchange process. At temperatures

$$\Delta\partial = \frac{\pi}{2^{3^{1/2}}k_r}\Delta H_r^2 \quad (\Delta H_r \text{ in frequency units}) \qquad (4)$$

above ca. 60 °C, lines d and e coalesce and the resulting line de has an excess width[15] given by eq 4. At 126 °C, $\Delta\partial = 0$, and the lines a and de have the expected $^1/_6$ intensity ratio.

In the temperature range ca. 65–100 °C the spectra can be described by the fast exchange limit, and analysis of the width of lines b and de by eq 4 leads to the k_r values reported in Table III. The free activation energy of the rotation, ΔG, was determined from Eyring's relationship, and the results of these calculations are presented in Table III.

Hindered rotation around the NN bond has been observed for a large number of hydrazyls.[4,9] However, for most of the hydrazyls studied, the ESR spectrum cannot be observed in the temperature range corresponding to a fast exchange between the substituents of the tervalent nitrogen, thus making difficult the measure of the free activation energy of the rotation process.

As far as we know, only the barrier of rotation for 1-benzoyl-2,2-bis(2,5-di-*tert*-butylphenyl)hydrazyl (**5·**) has been determined and was reported[16] to have a free activation energy of ca. 7.4 kcal mol^{-1}. As already mentioned, the higher $\Delta G^{\ddagger}$ observed for **1a·** (ca. 9.8 kcal mol^{-1}) compared to that observed for **5·** is certainly a consequence of electron delocalization which hampers the captodative effect and reduces the NN bond order in **5·**.

Registry No. **1a·**, 99657-86-0; **1aH**, 10269-98-4; **1b·**, 99657-87-1; **1bH**, 99657-91-7; **1c·**, 99657-88-2; **1cH**, 75063-52-4; **1d·**, 99657-89-3; **1dH**, 99657-93-9; **1e·**, 99657-90-6; **1eH**, 99657-92-8; Me_2NNH_2, 57-14-7; *t*-BuNHNH$_2$·HCl, 7400-27-3; $ClP(O)(OEt)_2$, 589-57-1; $ClP(O)Et_2$, 1112-37-4; $ClP(O)(OPh)_2$, 5382-00-3.

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Pyran Annelation: An Effective Route to a Tricyclic Dienone

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A new pyran annelation reaction was investigated. 2,6-Dimethyl-4*H*-pyran-4-one (**2**) was converted to 2-[(*p*-tolylsulfonyl)methyl]-6-methyl-4*H*-pyran-4-one (**7**) which was alkylated at the C-2 methylene position regioselectively, and the *p*-tolylsulfonyl group can be easily eliminated with an aluminum amalgam reduction. On the other hand, the pyran-4-one ring was easily transformed into a 1,5-diketone derivative. By joining and applying these selective alkylations and transformations, tricyclic dienone **22** was effectively synthesized from **2**.

The development of the synthetic methods of polycyclic natural products such as steroids and terpenes has been carried out by many organic chemists for 50 years. Among the many excellent synthetic procedures, isoxazole[1] and pyridine[2] annelations appear to be the predominant methods for this purpose.

On the other hand, functionalized heterocycles[3] are often used for the synthesis of the target organic compounds. These functionalized heterocycles are used not only as a masking group but also as the controlled reactive site. These functionalized heterocycles must have the following properties; i.e., a newly formed heterocycle, whose starting material has many reactive sites, must be entirely protected from some kinds of reactions and/or reagents and only one site should react with the reagent regioselectively. Moreover, by suitable treatment these heterocycles cannot only regenerate the compounds having the original partial structure but also they can be transformed into other useful synthetic intermediates.

In the course of our seeking novel synthetic methods using heterocycles, we selected 2,6-dimethyl-4*H*-pyran-4-one (γ-pyrone) (**2**) as a functionalized heterocycle and investigated a new annealation reaction.

In order to do this we required that (1) various substituents can be introduced regioselectively at the C-2 methyl position and (2) the 4*H*-pyran-4-one ring is convertable into a 1,5-diketone derivative.

We have already reported that 2-methyl-6-phenyl-4*H*-pyran-4-one (**1**) was regioselectively metalated at the C-2

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