The crude mixture (30 ml), consisting mainly of 1,4- and 1,5-cyclooctadiene, was converted to a mixture of 1,3- and 1,5-cyclooctadiene by treatment for 12 hr at 140° with a solution of sodium (20 g) in *tert*-amyl alcohol (150 ml).

The dienes were recovered from the purified silver nitrate complexes by steam distillation and distillation at atmospheric pressure in purity greater than 99% by glpc on a silicone column. Each sample was identified by ir and nmr spectra: cycloocta-1,3-diene, bp 141.0°, λ_{max} 227 nm (ϵ_{max} 6160); cycloocta-1,4-diene, bp 143.0°; cycloocta-1,5-diene, bp 148.5°.

Cycloocta-1,3,5-triene was prepared according to Jones.[49] It was freed of bicyclo[4.2.0]octa-2,4-diene by treatment with maleic anhydride according to the procedure of Cope, *et al.*[50]

Cycloocta-1,3,6-triene was prepared by the procedure of Sanne and Schlichting.[51] The substance was separated from accompanying cycloocta-1,3,5-triene by distillation in a 1-m spinning band column. Any bicyclo[4.2.0]octa-2,4-diene was removed by shaking at 50° with maleic anhydride.

cis- and *trans*-Hexa-1,3,5-triene were prepared according to Hwa, DeBenneville, and Svens.[52]

Professor E. Vogel and Dr. E. Dinne kindly supplied samples of *cis,cis*- and *cis,trans*-cyclonona-1,5-diene.

Samples of *cis,cis*- and *trans,trans*-cyclodeca-1,6-dienes were prepared in the laboratory of Professor W. R. Roth, Cologne, according to the procedure of Heimbach.[53]

Calorimetric Measurements. Heats of hydrogenation were measured in the apparatus, and by the general procedure, described earlier.[2a] The solvent consisted in all runs of 225 ml of prereduced acetic acid. Samples of olefins sufficient to provide for an uptake of approximately 3 mmol of hydrogen were introduced in evacuated, sealed ampoules. Hydrogenation was initiated by breaking an ampoule containing approximately 100 ml of PtO_2 catalyst, which had been calibrated previously with respect to hydrogen absorption and heat evolution. Although calculations are based on the amount of hydrogen absorbed, there was essentially quantitative absorption of hydrogen in all cases.

Acknowledgments. We express our gratitude to the Norman Foundation, Inc., for the award of a Sylvan E. Weil Postdoctoral Fellowship in organic chemistry to Dr. G. Schröder (Sept 1959–Oct 1960) and an Aaron E. Norman fellowship to Dr. W. R. Roth (July 1960–March 1962) and to the National Science Foundation for its support of the Texas part of this work.

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(52) J. C. H. Hwa, P. L. DeBenneville, and H. J. Svens, *J. Amer. Chem. Soc.*, 82, 2537 (1960).

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Calorimetric and Equilibrium Studies on Some Stable Nitroxide and Iminoxy Radicals. Approximate O–H Bond Dissociation Energies in Hydroxylamines and Oximes

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Contribution from the Chemistry Department, Scientific Research Staff, Ford Motor Company, Dearborn, Michigan 48121. *Received August 4, 1973*

Abstract: The differences in the heats of formation in solution of the stable free radicals, 2,2,6,6-tetramethylpiperid-4-one 1-oxyl (**1a**), 2,2,6,6-tetramethylpiperdine *N*-oxyl (**1b**), and di-*tert*-butyliminoxy (**2**), and their hydrogenated precursors have been determined by a direct calorimetric technique. The equilibrium constants for the hydrogen atom transfer reactions of these radicals with certain hydroxylamines and oximes were then determined by the epr spectroscopic method. The analysis of the results of these experiments leads to the predictions that the O–H bond strengths of unhindered dialkylhydroxylamines are in the range of 72–74 kcal/mol while the O–H bond strengths of simple unhindered oximes are equal to approximately 86 kcal/mol.

Since bond dissociation energies of organic molecules are normally determined by experiments in the gas phase, the types of molecules for which reliable values are available cover only a small fraction of the molecules of interest to organic chemists. An important extension of bond dissociation energy data to larger and less volatile molecules was the first direct calorimetric determination of the differences in the heats of formation in solution of a radical, 2,4,6-tri-*tert*-butylphenoxy ($A\cdot$), and its parent, 2,4,6-tri-*tert*-butylphenol (AH), reported by one of us in 1969.[3] This difference, *i.e.*, $(\Delta H_f)_{A\cdot}{}^{solvent} - (\Delta H_f)_{AH}{}^{solvent}$, yields the O–H bond strength in the phenol *provided* the difference in the heats of formation of the radical in the gas phase and in solution at infinite dilution is equal to the difference in the heats of formation of the phenol in the same two states, *i.e.*, provided that

$$(\Delta H_f)_{A\cdot}{}^{gas} - (\Delta H_f)_{A\cdot}{}^{solvent} = (\Delta H_f)_{AH}{}^{gas} - (\Delta H_f)_{AH}{}^{solvent}$$

In the absence of a *specific* interaction involving *either* the radical *or* the phenol and the solvent this equality is expected to be true to within ±2 kcal/mol and few bond dissociation energies of polyatomic molecules are known with much greater precision. There is not likely to be any specific solvent effect particular to the highly hindered $A\cdot$ or AH in the solvents employed (CCl_4, benzene, and chlorobenzene). We can therefore calculate an approximate bond dissociation energy for AH from the relation

$$D[A-H] \approx (\Delta H_f)_{A\cdot}{}^{solvent} - (\Delta H_f)_{AH}{}^{solvent} + (\Delta H_f)_{H\cdot}$$

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(3) L. R. Mahoney, F. C. Ferris, and M. A. DaRooge, *J. Amer. Chem. Soc.*, 91, 3883 (1969).

and be confident that the value so obtained is as reliable as the majority of gas phase data.

For certain other compounds with bond energies, D[B–H], similar to that for tri-*tert*-butylphenol it is possible to calculate values of $(\Delta H_f)_{B\cdot}{}^{\text{solvent}} - (\Delta H_f)_{BH}{}^{\text{solvent}}$ (and hence D[B–H] when appropriate) from the equilibrium constants and/or heats of reaction for the process

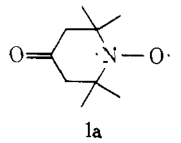
$$\text{A}\cdot + \text{BH} \rightleftharpoons \text{AH} + \text{B}\cdot$$

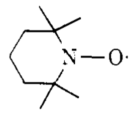
For compounds yielding stable B· radicals such as certain other 2,6-di-*tert*-butylphenols[4,5] and diphenylpicrylhydrazyl[6] the equilibrium constant can be obtained by direct measurement. For less stable radicals such as most phenoxy[7,8] and peroxy[9] radicals, the equilibrium constant must be obtained indirectly by measurement of the rates of hydrogen transfer in the forward and reverse directions.

The calorimetric technique requires that the radical be stable for many hours in concentrated solutions at room temperature.[3] In addition, the radical must react in a rapid, exothermic, and irreversible manner with a suitable hydrogen donor and this reaction must go to completion without any side products.[3] The hydrogen donor of choice is hydrazobenzene. When this compound is added to a solution containing an excess of tri-*tert*-butylphenoxy it is rapidly converted in 100% yield to *trans*-azobenzene.[3] In this paper we

$$2\text{A}\cdot + \text{PhNHNHPh} \longrightarrow 2\text{AH} + \textit{trans}\text{-PhN{=}NPh}$$

describe the results of an analogous calorimetric study on two more stable radicals, 2,2,6,6-tetramethylpiperid-4-one 1-oxyl (**1a**), 2,2,6,6-tetramethylpiperidine *N*-oxyl (**1b**), and di-*tert*-butyliminoxy (**2**). The results of a few equilibrium studies involving these two radicals and certain hydroxylamines and oximes are also reported.


1a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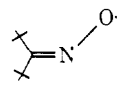
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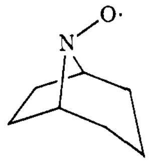
Experimental Section

Materials. 2,2,6,6-Tetramethylpiperid-4-one 1-oxyl (**1a**) was prepared by the method of Briere, *et al.*,[10] and was recrystallized from hexane, red crystals, mp 35.5–36°. 2,2,6,6-Tetramethylpiperidine *N*-oxyl was prepared by the method of Briere, *et al.*;[10] purification by sublimation yielded red transparent prisms, mp 40.0°. The two bicyclic nitroxides, nortropane *N*-oxyl (**3**) and 9-azabicyclo[3.3.1]nonane *N*-oxyl (**4**), were prepared from the corresponding bicyclic amines, hydrogen peroxide, and phosphotungstic acid.[11,12] Di-*tert*-butyl ketoxime **2H** was prepared from *tert*-butyllithium, pivalonitrile, and hydroxylamine hydrochloride.[13a] Oxidation of **2H** with silver oxide yielded the di-*tert*-butyliminoxy radical, **2**.[13b] 1-Adamantyl *tert*-butyl ketoxime (mp 203° subl. *Anal.* Calcd for $C_{15}H_{25}NO$: C, 76.54; H, 10.71; N, 5.95. Found: C, 76.41; H, 10.27; N, 5.87) was prepared by the same route from 1-cyanoadamantane. 1-Adamantyl-*tert*-butyliminoxy could be prepared by Ag_2O oxidation of the oxime as an unstable blue solid, mp 45–47°, that was characterized in this work by its solution epr spectrum: $a_N = 31.2$ G, $g = 2.0051$ in benzene at 25°. *tert*-Butyl isopropyl ketoxime was prepared by the high pressure method of Jones, *et al.*[14] Hydrazobenzene was prepared from *trans*-azobenzene according to the procedure of Corey, *et al.*[15]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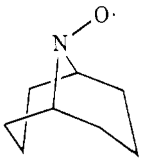
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Calorimetry. The calorimetric measurements were carried out as described in the earlier study of 2,4,6-*tert*-butylphenoxy[3] except that an inert atmosphere was unnecessary.

Equilibrium Measurements. Measured quantities of a radical, *e.g.*, **3**, and an oxime, *e.g.*, **2**H (or hydroxylamine), were dissolved in benzene and the concentrations of the two radicals, **2** and **3**, present at 25° were determined by epr spectroscopy with double integration of resolved peaks of the two radicals. The equilibrium constant was then calculated from the relation where [**2**H] and [**3**H] were obtained by difference.

$$K = [\mathbf{3}][\mathbf{2}\text{H}]/[\mathbf{3}\text{H}][\mathbf{2}]$$

Results

Calorimetry. In carbon tetrachloride solution an excess of the nitroxide **1a** reacts rapidly and exothermically with solid hydrazobenzene to yield *trans*-azobenzene in 100% yield (Table I). The heat evolved in several experiments is listed in Table II. Similar data for the iminoxy **2** in benzene are listed in Tables I and III. Due to the limited availability of the radical **1b**, only two determinations of the heat of reaction of the radical in benzene solution with solid hydrazobenzene was carried out. The measured heat of the reation was equal to −6.5 ± 0.5 kcal/mol.

Table I. Yield of *trans*-Azobenzene from the Reaction of 1 and 2 with Solid Hydrazobenzene

Moles of radical × 10^3	Moles of hydrazobenzene reacted × 10^4	Moles of *trans*-azobenzene formed × 10^4 [a]	Yield, %
1[b]			
0.893	1.73	1.76	102
2.362	4.61	4.55	98
2.362	4.85	4.85	100
2.373	6.57	6.57	100
2[c]			
0.256	0.646	0.638	99
0.256	0.575	0.573	100

[a] Spectrophotometric analysis.[3] [b] In 205 ml of CCl_4. [c] In 25 ml of benzene.

Equilibrium Measurements. Equilibrium constants

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(13) (a) G. D. Mendenhall and K. U. Ingold, *ibid.*, **95**, 6395 (1973); (b) J. L. Brokenshire, G. D. Mendenhall, and K. U. Ingold, *ibid.*, **93**, 5278 (1971).

(14) W. H. Jones, E. W. Tristram, and W. E. Benning, *ibid.*, **81**, 2151 (1959).

(15) E. J. Corey, W. L. Mock, and D. S. Pasto, *Tetrahedron Lett.*, 347 (1967).

Table II. Observed Heat of Reaction of **1** with Solid Hydrazobenzene in Carbon Tetrachloride

Moles of **1** × 10^3	Moles of H_2Az × 10^4	Cal evolved	$(\Delta H_{obsd})^{CCl_4}$, kcal/mol
0.893	1.683	1.839	10.93
2.362	1.694	1.844	10.89
2.362	4.30	4.365	10.15
2.362	4.61	4.802	10.46
2.362	6.57	6.760	10.29
			Av 10.54 ± 0.16

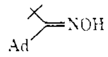
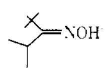
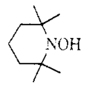
Table III. Observed Heat of Reaction of **2** with Solid Hydrazobenzene in Benzene[a]

Moles of **2**[b] × 10^3	Moles of H_2Az × 10^4	Cal evolved	$(\Delta H_{obsd})^{C_6H_6}$, kcal/mol
2.23	0.727	2.03	27.92
2.23	1.162	3.51	30.21
2.23	1.346	3.86	28.68
2.03	2.535	7.32	28.88
			Av 28.92 ± 0.48

[a] The enthalpy of solution of **2H** in benzene at infinite dilution $(\Delta H_{sol})_{2H}^{C_6H_6} = 7.66 \pm 0.05$ kcal/mol. [b] In 200 ml of solution.

for some radical–molecule reactions in benzene at 25° are listed in Table IV. In no case did the total radical concentration decrease during the course of an experiment and therefore each pair of radicals is relatively unreactive toward one another, as are each of the individual radicals. The concentrations were such that reversible dimerization of the nitroxides was not significant.

Table IV. Equilibrium Constants for Some Radical–Molecule Reactions in Benzene at 25°

Radical	Molecule	K_{eq}[a]	$-\Delta G$, kcal/mol[a] $(2.3RT \log K)$
3	**2H**	700 ± 150	3.9
4	**2H**	2900 ± 800	4.7
3		780[d]	3.9[d]
2		390 ± 70[e]	3.4[e]
3		⩽0.00012[f]	⩽ −5.9[f]
DPPH·	**2**	~1[g]	~0[g]

[a] Mean of at least five separate determinations unless otherwise noted. [b] 1-Adamantyl *tert*-butyl ketoxime. [c] The orientation of the OH group is not known. [d] Single determination. [e] Some difficulty was encountered in measuring K_{eq} because of overlap of the two epr spectra. The equilibrium was also approached from the direction *tert*-butylisopropyliminoxy + **2H** (*cf.* G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6390 (1973). [f] The equilibrium lies too strongly in favor of **3H** for K_{eq} to be measured accurately. [g] Exchange was too slow to measure the equilibrium constant conveniently. Data from ref 3 imply that K_{eq} should be ~0.1.

Thermochemistry. The thermochemical relationships applicable to a system in which a solid sample of hydrazobenzene, H_2Az, is dissolved in a solution containing an excess of a radical, R·, and is thereby entirely converted to *trans*-azobenzene have been derived previously.[3] From the viewpoint of bond dissociation energies the quantity of interest is $(\Delta H_f)_{R\cdot}^{solution} - (\Delta H_f)_{RH}^{solution}$ where these heats of formation refer to the state of infinite dilution. This quantity is given by

$$0.5\{(\Delta H_f)^{\circ}_{Az} - (\Delta H_f)^{\circ}_{H_2Az} + (\Delta H_{solution})_{Az}^{solvent} - (\Delta H_{obsd})^{solvent}\}$$

where $(\Delta H_f)^{\circ}_{Az} = 76.49$ kcal/mol[16] and $(\Delta H_f)^{\circ}_{H_2Az} = 52.9$ kcal/mol[16] are the heats of formation of azobenzene and hydrozobenzene in their standard states as solids at 298°K, $(\Delta H_{solution})_{Az}^{solvent}$ is the partial molal enthalpy of solution of azobenzene in the solvent at infinite dilution, and $(\Delta H_{obsd})^{solvent}$ is the measured enthalpy of reaction at infinite dilution. In CCl_4 $(\Delta H_{solution})_{Az}^{CCl_4} = 5.28 \pm 0.02$ kcal/mol,[3] hence

$$(\Delta H_f)_{1a}^{CCl_4} - (\Delta H_f)_{1aH}^{CCl_4} = \frac{(10.54 \pm 0.16) + (28.87 \pm 0.7)}{2} = 19.7 \pm 0.43 \text{ kcal/mol}$$

and in benzene $(\Delta H_f)_{Az}^{C_6H_6}) = 5.04 \pm 0.05$ kcal/mol,[3] hence

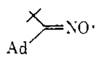
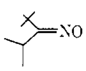
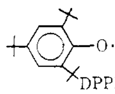
$$(\Delta H_f)_{1b}^{C_6H_6} - (\Delta H_f)_{1bH}^{C_6H_6} = \frac{(6.5 \pm 0.6) + (28.6 \pm 0.7)}{2} = 17.5 \text{ kcal/mol}$$

and $(\Delta H_f)_2^{C_6H_6} - \Delta H_{f2H}^{C_6H_6} = 28.8 \pm 0.6$ kcal/mol. Combining this quantity with the equilibrium constants from Table IV yields values for

$$(\Delta H_f)_{R\cdot}^{C_6H_6} - (\Delta H_f)_{RH}^{C_6H_6}$$

that are summarized in Table V. In calculating these quantities it has been assumed that ΔS for the hydrogen atom transfer equilibrium is negligible.

Table V. Summary of Values of $(\Delta H_f)_{R\cdot}^{solvent} - (\Delta H_f)_{RH}^{solvent}$ for Some Stable Radicals in Benzene at 25°

Solvent	Radical	$(\Delta H_f)_{R\cdot}^{solvent} - (\Delta H_f)_{RH}^{solvent}$	D[R–H]
CCl_4	**1a**	19.7	71.8
C_6H_6	**1b**	17.5	69.6
C_6H_6	**2**	28.8	80.9
C_6H_6	**3**	24.9	77.0
C_6H_6	**4**	24.1	76.2
C_6H_6		28.8	80.0
C_6H_6		32.2	84.3
C_6H_6		29.1[a]	81.2
C_6H_6	DPPH·	27.5[a]	79.6

[a] From ref 3.

Discussion

The O–H bond strength found for **1a** in the present work (71.8 kcal/mol) is in quite remarkable agreement

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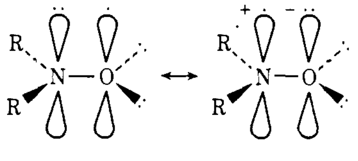
(16) L. G. Cole and E. C. Gilbert, *J. Amer. Chem. Soc.*, 73, 5423 (1951).

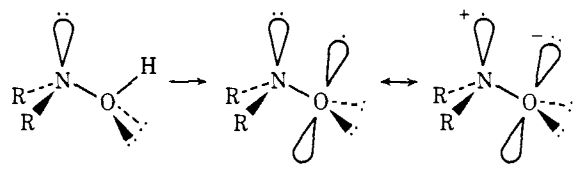
with a value of 71.9 ± 2.7 kcal/mol that can be calculated from Lebevev, *et al.*'s,[17] data on the heats of combustion and sublimation of **1** and **1H**. It would appear therefore that solution calorimetry can give bond strengths that are just as accurate as those obtained by other techniques *provided* specific solvent effects are absent (see below). The bond strengths in Table V are, we believe, reliable to within ±3 kcal/mol.

Solvent Effects. In the earlier study[3] it was concluded that with 2,4,6-tri-*tert*-butylphenoxy solvent interactions amounted to less than 0.5 kcal/mol. Solvent effects are probably larger in dialkyl nitroxides because the N–O group is fairly polar.[18] This is indicated by the rather large influence of solvents on the visible spectra of nitroxides and on the nitrogen hyperfine splittings in their epr spectra.[19,20] On the other hand, measurement of the heats of solution of di-*tert*-butyl nitroxide and hydroxylamine in several solvents showed that enthalpy differences were $\leqslant 1$ kcal/mol (at infinite dilution) between the two compounds when they were transferred from cyclohexane to other solvents such as CCl_4 and benzene.[21] The observed enthalpy differences were attributed to specific solvation of the radical or hydroxylamine. Of course, these two compounds may be rather poorly solvated by all solvents for steric reasons. It is possible, therefore, that specific solvent effects will be somewhat greater in the case of the unhindered nitroxides **3** and **4** and their hydroxylamines.

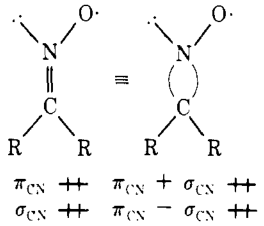
The importance of specific solvation of iminoxy radicals or oximes has received little study. From the absence of solvent effects on the spectral properties of **2**[13] it would appear that this radical interacts very slightly with its surroundings. Unless oximes are similarly inert the *apparent* O–H bond strength will differ in different solvents because interaction of the oxime with the solvent will not be compensated by a corresponding interaction of the iminoxy radical.

Structural Effects on O–H Bond Strengths. The O–H bond strengths of the hydroxylamines and oximes studied can be largely rationalized in terms of the hybridization of the orbital at the nitrogen atom. At one extreme we can imagine an sp^2 hybridized nitrogen with a planar geometry[22] and a 2p lone pair hybridized with a largely p oxygen orbital in the radical giving the configuration $(\pi)^2(\pi^*)^1$. At the other extreme, exemplified by the geometry of a hydroxylamine, the nitrogen is sp^3 hybridized and tetrahedral. The actual situation will usually lie between these two extremes. Thus, the angle between the C–N–C plane and the N–O bond (which will be 0 and 55° in the two limiting cases) is very close to 0° in di-*tert*-butyl nitroxide,[23] it is 31° in a nitroxide derived from **3**,[24] and 15.8 ± 0.8° in the alcohol[25] derived from **1**.[26]

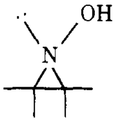




Any factor that increases the degree of p character in the two C–N bonds in the nitroxide will tend to decrease the p, and hence increase the s character of the nitrogen lone pair. As a consequence, the overlap between the N lone pair orbital and the oxygen 2p unpaired electron orbital will decrease.[27] Since this overlap stabilizes the nitroxide, any decrease in the extent of the overlap will destabilize the radical and cause the O–H bond strength to increase.[28] For the nitroxides in Table V there is a regular increase in *D*(O–H) with decreasing ring size, since this forces the C–N–C angle to assume smaller values with the consequences noted above. We may emphasize this continuity into the iminoxy radicals by drawing bent bonds to connect the carbon and nitrogen atoms.



The three-membered ring of an aziridinoxyl radical lies between the geometrical constraints of **2** and **3**. The O–H bond strength in the corresponding hydroxylamine should therefore lie between 76 and 81 kcal/mol.



D(O—H) ~ 78 kcal/mol

The fact that such radicals have not, apparently, been observed[29] is consistent with the higher reactivity expected of them compared with less strained nitroxides.[30]

A second consequence of orbital overlap that is a potential cause of radical stabilization arises from alkyl–

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alkyl and alkyl–oxygen nonbonding interactions that are greater in the hydroxylamines and oximes than in the corresponding radicals, since the latter have a more open geometry. In addition, nonbonding interactions involving the hydrogen that is removed are eliminated.

These steric effects on the O–H bond strength should be at a maximum with di-*tert*-butyl nitroxide[23] in which the relevant CNC angle is 136° and the CNO angle is 112°. In the hydroxylamine, if the nitrogen is tetrahedral, the angles will be 108°. Unfortunately di-*tert*-butyl nitroxide reacted so slowly with hydrazobenzene in CCl_4 and in benzene that the heat of the reaction could not be determined. The slowness of reaction suggests that the O–H bond strength in this compound is several kcal/mole less than in **1**, since the sterically more hindered but thermoneutral hydrogen transfer from di-*tert*-butylhydroxylamine has a rate constant of over $10^2\ M^{-1}\ \mathrm{sec}^{-1}$ in CCl_4 at room temperature.[31]

The importance of steric factors in determining the O–H bond strength in **1** is difficult to estimate. However, the six-membered ring should inhibit any large changes in the CNC angle on going from the hydroxylamine to the radical, so steric effects are probably small. It is interesting to note that the nitrogen hyperfine splitting for **1** in most solvents is similar to the values found for many less substituted and unstable, dialkyl nitroxides. In these radicals the alkyl groups are free to adopt a conformation minimizing steric interactions. We would accordingly predict that the O–H bond strengths in unhindered dialkylhydroxylamines are in the range 72–74 kcal/mol.

Steric effects should be absent in the bicyclic nitroxides **3** and **4**.

Replacement of a methyl group in **2** by a hydrogen atom increases the O–H bond strength in the oximes by *ca.* 3.4 kcal/mol (see Table V). This change must be steric in origin and has been attributed[13] to greater alkyl–alkyl and alkyl–oxygen repulsions in **2H** compared with **2** than in *tert*-butyl isopropyl ketoxime compared with its iminoxy radical. It is unlikely that a change of similar magnitude would accompany the replacement of additional methyls. We therefore expect that simple unhindered oximes will have O–H bond strengths of about 86 kcal/mol.

Radical Stability. The widespread use of nitroxides as spin labels in biological systems[32] depends critically upon their stability under the conditions of study. Although the "intrinsic stability" of the nitroxide group is sometimes cited, the very concept of stability requires some reference point. Hindered nitroxides of the kind used as spin labels have no kinetically feasible pathways for decomposition. Steric hindrance must be directly responsible for the lack of dimerization of **1** and of di-*tert*-butyl nitroxide since the less hindered radicals **3** and **4** dimerize reversibly.[12,33] The low O–H bond strength of hydroxylamines means that hydrogen abstraction from most organic substrates by the nitroxide will be a highly endothermic, and hence slow, process. Other potential reactions, such as addition to the terminii of double bonds, are even more strongly retarded than hydrogen abstractions because nonbonding repulsions in the product will be even greater than in the hydroxylamine.

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Flash Photolytic Decomposition of Aryl Azides. Measurement of an Intramolecular Closure Rate

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Abstract: We have studied the formation of carbazole from flash photolysis of 1-azidobiphenyl. The reaction proceeds through the formation of 2-nitrenobiphenyl. The first-order rate coefficient at 300°K is $2.18 \times 10^3\ \mathrm{sec}^{-1}$ and ΔH of activation is 11.46 kcal/mol (± 0.76) in cyclohexane solution. These quantities were measured from the rate of appearance of carbazole and confirmed by the rate of disappearance of the nitrene, in ultraviolet absorption spectra. The reaction in the gas phase was too fast for us to measure; a lower limit for the rate constant in the gas, at 75°, is $1.4 \times 10^6\ \mathrm{sec}^{-1}$. The mechanism in solution is inferred to be an addition of nitrene to the neighboring phenyl ring, followed by hydrogen migration. Together with the evidence presented by Swenton, Ikeler, and Williams, our results imply that both singlet and triplet states of the nitrene are involved in carbazole formation, in that sequence. We also report the confirmation of the gas-phase near-ultraviolet spectrum of phenyl nitrene and the measurement of the rate coefficient for the reaction $C_6H_5N + C_6H_5N_3 \rightarrow C_6H_5N{=}N\,C_6H_5 + N_2$, the observation of the near-ultraviolet absorption spectrum of 1-naphthyl nitrene, and the observation of the formation, in the gas phase, of the dimer of 2-nitrenodiphenylmethane from photolysis of 2-azidodiphenylmethane.

The decomposition reaction of 2-azidobiphenyl has been well studied. In solution, excited either photochemically or thermally, the reaction proceeds smoothly to give carbazole in high yield.[2,3] In fact, the yield is sufficiently high to allow the use of the reaction as a synthetic pathway to various substituted

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