spectra of Nor$_4$Ti through Nor$_4$Co were negligibly changed on substituting pyridine for isooctane as solvent, indicating that at least pyridine is too bulky to fit in among four norbornyls. A greater transition metal ionic radius, as in the cases of Nor$_4$Zr and Nor$_4$Hf compared to fourth period tetravalent compounds, or three bicycloheptyl ligands instead of four, as in the case of (4-Cam)$_3$Cr compared to (1-Cam)$_4$Cr or Nor$_4$Cr, would give a sterically more open coordination sphere and tend to favor attack of sufficiently small reagents on the metal–carbon bonds.

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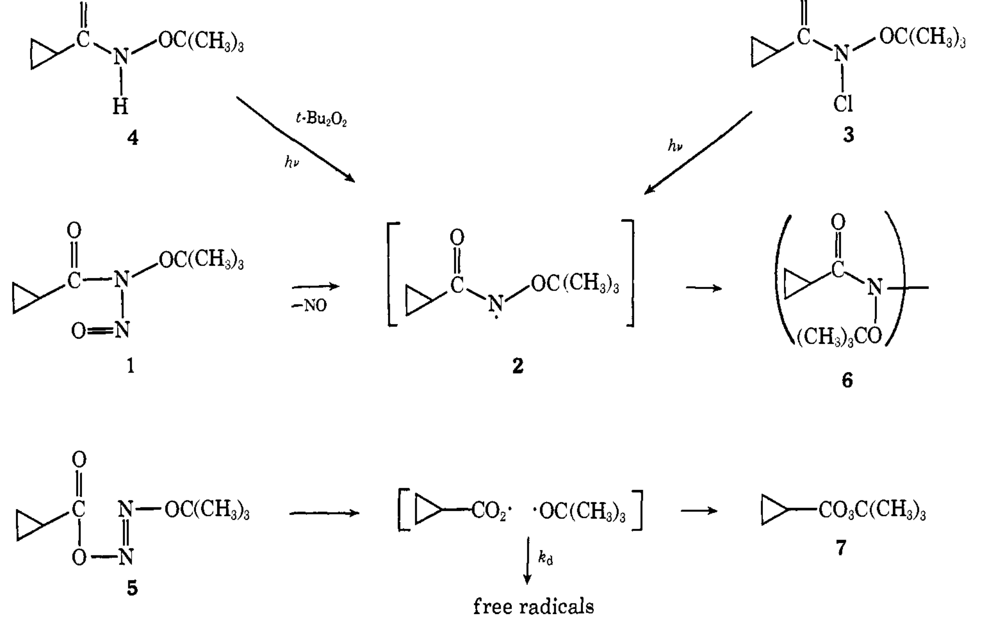
Thermal Decomposition of *N*-Nitrosohydroxylamines. V. Denitrosation and *N*-*tert*-Butoxyamido Radicals

Sir:

We wish to report the direct observation of the esr spectra of several *N*-*tert*-butoxyamido radicals. The *N*-cyclopropanecarbonyl member of this series, **2**, has been observed by warming the corresponding *N*-nitrosohydroxamate (**1**), by direct photolysis of the corresponding *N*-chloro compound **3**, and by photolysis of di-*tert*-butyl peroxide in the presence of the hydroxamate (**4**) itself.



In the foremost case, the denitrosation is in competition with rearrangement to the corresponding *O*-acyl *O'*-*tert*-butyl hyponitrite[1] (**5**) which is the major (78%) reaction pathway. The products, isolated from the overall decomposition of **1** after 1.5 hr at 32° in carbon tetrachloride solution (0.2 *M*), include a 14% yield (0.07 mol/mol of **1**) of the dimeric hydrazine[2] **6** and a 15% yield of the perester **7**. When this product mixture is allowed to stand at room temperature overnight, the dimer **6** is partially converted to *tert*-butyl cyclopropanecarboxylate.[3] When 1 *M* styrene is added initially, the yield of dimer is 22% (by nmr) after 1.5 hr and subsequent decomposition is slow. The perester yield for the present case is greater (18%) than that previously found for the benzoyl analog (13%)[1] when the 22% side reaction is taken into account. This result indicates that factors such as the rate constants for the combination process are more important than the radius of the diffusing species in determining the diffusion–combination ratio.

Direct confirmation of the presence of the *N*-*tert*-butoxyamido radical **2** was obtained when the reaction was carried out in the cavity of a Varian E-3 spectrometer. Warming cold solutions of the nitroso compound **1** in the cavity immediately gave a three-line (1:1:1) spectrum which grew in intensity as the temperature increased. Essentially identical spectra were obtained when the corresponding *N*-chloro compound **3** was photolyzed directly or when solutions containing di-*tert*-butyl peroxide and the parent hydroxamate **4** were irradiated with a focused 100-W high-pressure mercury light source using quartz or thin-wall Pyrex sample tubes. The latter method was used to obtain spectra of a series of such amido radicals. The results are summarized in Table I.

The observed *g* values are slightly larger than those recently reported[4] for *N*-alkoxyamino radicals (2.006 *vs.* 2.005). The a_N values are somewhat smaller (~10 *vs.* ~14 G). The magnitude of the reduction compares with changes observed when an acyl group replaces an alkyl group in nitroxides.[5] Both variations are in the direction expected for a π-amido radical

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[1] T. Koenig, M. Deinzer, and J. A. Hoobler, *J. Amer. Chem. Soc.*, **93**, 938 (1971).

[2] J. H. Cooley, M. Mosher, and M. A. Kahn, *ibid.*, **90**, 1867 (1968).

[3] If the 1.5-hr product solution is washed with dilute aqueous hydroxide and dried, the dimer no longer disappears so rapidly. Cooley[2] has already reported on the synthesis and acid-catalyzed reactions of this class of substituted hydrazines. We have found that **6** is formed in essentially quantitative yield through treatment of the *N*-chloro compound **3** with an ether solution of the sodium salt of **4**. The *N*-chloro compound **3** is readily obtained from **4** and *tert*-butyl hypochlorite over solid potassium carbonate.

[4] W. C. Danen and C. T. West, *J. Amer. Chem. Soc.*, **93**, 5582 (1971).

[5] (a) A. Mackor, Th. A. J. W. Wajer, and Th. J. De Boer, *Tetrahedron*, **24**, 1623 (1968); (b) A. M. Vasserman, Yu. A. Baskakov, and A. L. Buchachenko, *J. Struct. Chem.*, **10**, 620 (1969).

Table I. Observed[e] Nitrogen Hyperfine Coupling Constants and g Values for $RCO\dot{N}OC(CH_3)_3$

R	Conditions	a_N, G[f]	g value[g]
Cyclopropyl	*a*	10.50	2.0060
Cyclopropyl	*b*	10.50	2.0060
Cyclopropyl	*c*	10.30	2.0060
Isopropyl	*c*	10.35	2.0058
Phenyl	*c*	10.10	2.0058
p-Methoxyphenyl	*d*	10.20	2.0057
m-Nitrophenyl	*c*	9.60	2.0060
p-Nitrophenyl	*c*	9.60	2.0059
Ethoxy	*c*	11.95	2.0056

[a] Warming **1** in carbon tetrachloride (0.2 *M*). [b] Photolysis of **3** (0.1 *M*) in chloroform at room temperature. [c] Photolysis of di-*tert*-butyl peroxide in *tert*-butyl alcohol (0.1 *M*) in the presence of $RCONHOC(CH_3)_3$. [d] Same as footnote *c* except for the solvent which was $CHCl_3$. [e] Degassing had no important effect other than to sharpen the peaks slightly. [f] Estimated accuracy of ±0.05 G. [g] Relative to DPPH (g = 2.0036) with estimated accuracy of ±0.002.

center where the carbonyl oxygen atom shares some of the spin density. The variations in a_N for the aryl series are in the direction expected of substituent effects. The relative contributions from the dipolar resonance forms, which place a formal negative charge (and no spin) on the nitrogen atom **8b**, should respond to the remote substituents to produce this pattern.

INDO[6] calculations, for the *N*-hydroxyformamido species with the structure shown, **9**, give an unprojected nitrogen hyperfine coupling constant of 9.5 G in good agreement with the observed values. Calculations were carried out on a number of other nuclear structures;[7] all were predicted to be of higher energy and none predicted hyperfine coupling constants close to those observed here.[8]

We believe these observations strongly support the conclusion that these *N*-alkoxyamido radicals are π radicals. They also provide direct support for the suggestions made previously by Cooley[2] and his coworkers concerning possible mechanisms of denitrosation and ester formation from nitrosohydroxamates. The denitrosation process becomes an important contributor for **1** because of its slow rate of rearrangement (less than one-tenth that of the benzoyl compound). Such processes contribute to a much smaller extent with aryl or acyclic secondary alkyl side chains.

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(6) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 90, 4201 (1968).

(7) The INDO calculations were not minimized with respect to geometry. The assumed bond lengths and bond angles were taken from "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, 1965, or from ref 5.

(8) Professor W. Danen has privately communicated to us that his group has observed the esr spectrum of the *N*-*tert*-butoxypropionamido radical in *tert*-butyl alcohol. The observed a_N was 10.98. The reasons for the discrepancy in a_N between their laboratories and ours are not apparent at the present time.

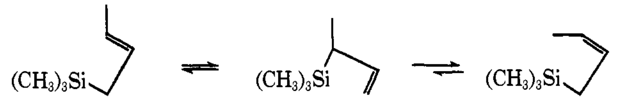
Unimolecular Thermal Rearrangement of Allylsilanes. A Sigmatropic 1,3 Migration of Silicon

Sir:

The thermal thiallylic rearrangement of allyl phenyl sulfides has been reported[1] to occur both unimolecularly and bimolecularly *via* a well-defined reaction intermediate involving development of negative charge on sulfur and positive charge on the β carbon of its allyl substituent. Such an intermediate could arise through utilization of a 3d orbital of the sulfur, or alternatively a three-center four-electron bonded structure[2] or what has been designated as a hypervalent structure.[3] It seemed appropriate, therefore, to inquire into the possibility that the periodic system neighbors of sulfur could also employ analogous reaction pathways.

A thermally induced 1,5 rearrangement of silicon has been discovered[4] but no established example of an uncatalyzed, thermal 1,3 silallylic rearrangement exists in the literature. On the other hand, carbon, which has no "available" d orbitals, has been reported[5] to undergo both 1,3 and 1,5 sigmatropic changes. The missing 1,3 rearrangement mode in silicon has now been identified and characterized as one of common occurrence *via* a relatively low-energy route, when allylsilanes are heated (either) to *ca.* 500° in the gas phase[5] for very short reaction times, or to *ca.* 275° in the liquid phase[5] for somewhat longer periods. The kinetic factors controlling the course of this reaction and their mechanistic implications are considered in the following preliminary account of the studies conducted.

Heating α-methylallyltrimethylsilane (**1**) for less than 1 min at about 500° in a helium stream converted it to a mixture consisting mostly of the γ (crotyl) isomer, whose composition was not altered significantly on prolonged heating. When the pure *trans*-crotyltrimethylsilane (**1a**) was thermolyzed under similar conditions, the same "equilibrium" composition (*ca.* 5:95) of α and γ isomers was quickly realized, but continued heating resulted in a gradual increase of **1b**, the *cis*-crotyl. Moreover, heating the pure *cis*-crotyl **1b** produced the same "equilibrium" concentration of the α-isomer **1** and a gradual increase of the *trans*-crotyl component **1a**, all of which suggested the scheme



1a (trans) 34%   1 5%   **1b** (cis) 61%

The kinetics of the rearrangement were studied in the gas phase in a flow system utilizing a gold coil reactor known[6] to entail only negligible wall effects. The reac-

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(1) H. Kwart and N. Johnson, *J. Amer. Chem. Soc.*, **92**, 6064 (1970).

(2) E. E. Havinga and E. H. Wiebinga, *Recl. Trav. Chem. Pays-Bas*, 78, 724 (1959).

(3) J. I. Musher, *J. Amer. Chem. Soc.*, 90, 7371 (1968); *Angew. Chem., Int. Ed. Engl.*, 8, 54 (1969); "Conformational Analyses," G. Chiurdoglu, Ed., Academic Press, New York, N. Y., 1971, p 177.

(4) H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.*, **4**, 313 (1965); A. Davison and P. E. Rakita, *Inorg. Chem.*, **9**, 289 (1970); A. J. Ashe III, *Tetrahedron Lett.*, 2105 (1970).

(5) See, for examples: (i) J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **89**, 5305 (1967); (ii) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968); and (iii) R. B. Woodward and R. Hoffmann, "Conservation of Orbital Symmetry," Verlag Chemie GmbH–Academic Press, Weinheim/Bergstr., Germany, 1970.

(6) H. Kwart, S. F. Sarner, and J. H. Olson, *J. Phys. Chem.*, 73, 4056 (1969).