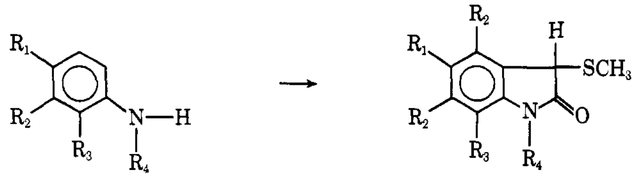
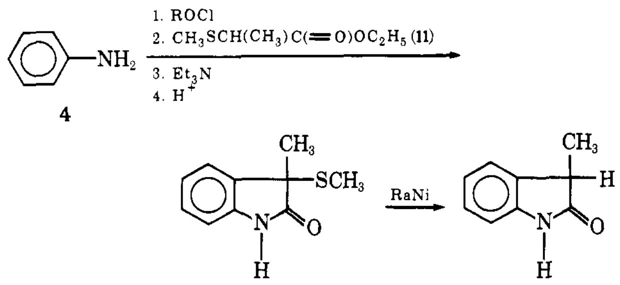
Scheme II



		% yield
9a, R$_1$ = CH$_3$; R$_2$ = R$_3$ = R$_4$ = H	**10a**	34
b, R$_1$ = R$_2$ = R$_4$ = H; R$_3$ = CH$_3$	**b**	67
c, R$_1$ = R$_2$ = R$_3$ = H; R$_4$ = CH$_3$	**c**	46
d, R$_1$ = NO$_2$; R$_2$ = R$_3$ = R$_4$ = H	**d**	51
e, R$_1$ = R$_3$ = R$_4$ = H; R$_2$ = NO$_2$	**e**	61
f, R$_1$ = CO$_2$C$_2$H$_5$; R$_2$ = R$_4$ = H; R$_3$ = CH$_3$	**f**	66



4

12 **13**

arrangement. Finally, on acid-catalyzed ring closure, we obtained **12** in 64% yield. Raney nickel desulfurization of **12** gave **13** in 70% yield.

The transformations described above illustrate the versatility of our method of preparing oxindoles. The ease of carrying out these preparations, and the normally good yields obtained, make this method superior to many of the procedures which are currently available.[1] The mild conditions, under which our oxindole synthesis occurs, will permit the construction of this ring system in the presence of reasonably sensitive substituent groups.

Acknowledgment. We are indebted to the National Cancer Institute of the Public Health Services for a grant which partially supported this investigation.

(6) Fellow of the Netherlands Organization for the Advancement of Pure Research (Z.W.O., 1972–1973).

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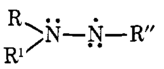
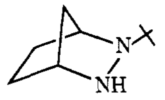
Autoxidation of 2-*tert*-Butyl-2,3-diazanorbornane to 3-*tert*-Butyl-2,3-diazanortricyclene. A γ Elimination of Hydrogen

Sir:

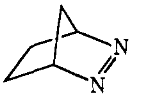
Although triarylhydrazyl radicals, such as diphenylpicrylhydrazyl,[1] are among the stablest radicals known, alkyl hydrazyls (**1**) have proven elusive. Wood, *et al.*,[2] have recently obtained esr spectra of 1,1-dialkyl hydrazyl radicals by γ irradiation of the hydrazines in adamantane matrices, but no alkyl hydrazyls have been detected in solution. Since alkyl hydrazyls are isoelectronic with nitroxides, they might be expected to show similar chemistry and disproportionate easily. Since Dupeyre and Rassat[3] have demonstrated that the bridgehead hydrogens of nitroxides are unreactive in disproportionation reactions, we chose **2** as a precursor of a trialkyl hydrazyl radical which would not disproportionate rapidly.[4]



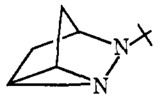
1



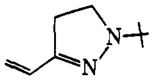
2



3



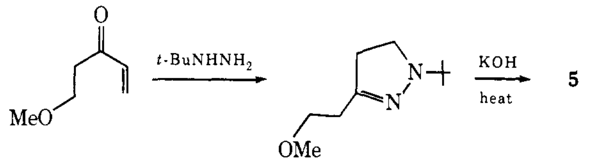
4



5

We have perpared **2** in greater than 90% yield by the addition of *tert*-butyllithium to the azo compound **3** in THF at −78°, followed by quenching with ammonium chloride.[5] We characterized **2** by its spectral properties (nmr (CDCl$_3$) δ 0.95 (s, 9 *t*-Bu H), 1.04 and 1.20 (br m, 2 H), 1.53 (br m, 4 H), 3.43 (br m, two bridgehead H); ir 2.96 μ (br NH)) and by conversion to **8a** (see below). Although **2** is reasonably stable in the absence of air, it decomposes rapidly at room temperature in the presence of oxygen to give mainly the 2,3-diazanortricyclene derivative **4**, which was identified on the basis of spectral and degradation information. The mass spectrum of **4** showed a parent peak at m/e 152 (36%), base peak at 137 (P − CH$_3$, 100%); nmr (C$_6$D$_6$) δ 0.78 and 1.27 (each a doublet of multiplets, J_{gem} = 11 Hz, 4 H total), 1.16 (s, 9 H, *t*-Bu H), 1.99 (approximate triplet, $J \simeq 1$ Hz, H$_1$, H$_6$) 3.09 (m, H$_4$). Although **4** could be purified by vpc,[6] injector temperatures above 200° or brief heating at 130° result in almost total destruction of **4**, and formation of the monocyclic diene **5** along with variable amounts of its oxidation product, 1-*tert*-butyl-3-vinylpyrazole. The dihydropyrazole **5** was independently prepared by condensation of *tert*-butylhydrazine with β-methoxyethyl vinyl ketone, and elimination of methanol from the product (Scheme I), the literature route to 1-alkyl-3-vinyl-4,5-dihydropyrazoles.[7]

Scheme I



Formation of **5** seems most simply formulated as an

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(1) For a review of arylhydrazyl chemistry, see A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, p 137.

(2) D. E. Wood, C. A. Wood, and W. A. Latham, *J. Amer. Chem. Soc.*, **94**, 9278 (1972).

(3) R. M. Dupeyre and A. Rassat, *J. Amer. Chem. Soc.*, **88**, 3130 (1966).

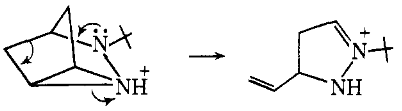
(4) G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 7166 (1972), have shown that slow loss of bridgehead hydrogen does occur for nortropane-*N*-oxyl at room temperature.

(5) The closest analogy for this addition of which we are aware of is the addition of aromatic, primary, and secondary alkyllithium compounds to azobenzene: L. A. Carpino, P. H. Terry, and J. Crowley, *J. Org. Chem.*, **26**, 4336 (1961); E. M. Kaiser and G. J. Bartling, *Tetrahedron Lett.*, 4357 (1969).

(6) XF-1150 column, flow rate 120 ml/min, column 70°, injector 120°, detector 105°.

(7) S. G. Matsoyan, *Khim. Geterotsikl. Soedin.*, 378 (1967); R. Jaquier and G. Maury, *Bull. Soc. Chim. Fr.*, 306 (1967).

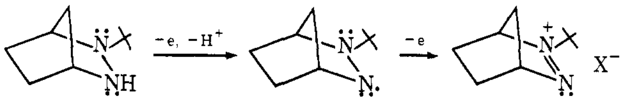
acid-catalyzed process in which protonated **4** cleaves to **6**, which can be transformed to **5** by deprotonation and a series of tautomeric shifts.



4–H$^+$ 6

The autoxidation of **2** to **4** is more interesting, and seemed to be most readily rationalized as a deprotonation of the deprotonated, two-electron oxidation product of **2**, the diazenium cation[8] **8**, by analogy with the deprotonation of norbornyl cation, the formal hydrocarbon analog of **8**, to nortricyclene.[9] Since the hydrazyl radical **7** formed by oxidation and deprotonation of **2** ought to be readily oxidized to **8**, this would seem to be a viable pathway (Scheme II) for formation of **4**.

Scheme II



2 7 8a, $X^- = BF_4^-$

We prepared **8a** in 88% yield by treatment of **3** with silver fluoroborate and *tert*-butyl iodide: mp 208–209° (CH_2Cl_2–ether); nmr (DMSO-d_6) δ 1.40 (br d, J = 9, 2 H, H_5, H_6 exo), 1.64 (s, 9 *t*-Bu H), 2.10 (br s, 2 H, H_7 syn and anti), 2.32 (br d, J = 9 Hz, 2 H, H_5, H_6 endo), 5.90 and 6.20 (two br s, 2 H, bridgehead). *Anal.* Calcd for $C_9H_{17}N_2BF_4$: C, 45.13; H, 7.14; N, 11.67. Found: C, 45.01; H, 7.20; N, 11.79.

Oxidation of **2** with benzoquinone gave a salt which was isolated as **8a** after treatment with sodium fluoroborate (the original counterion appeared to be mainly monodeprotonated hydroquinone from the nmr spectrum), and a salt of **8** with an unknown counterion was also isolated from the autoxidation of **2** as a minor product. Since **8a** is not only isolable, but also is not detectably deprotonated to **4** upon treatment with Dabco or 1,8-bis(dimethylamino)naphthalene in DMSO-d_6, **8** cannot be the direct precursor of **4** in the autoxidation of **2**.

In contrast, experiments designed to generate the hydrazyl **7** do lead to **4**. For example, photolysis of a degassed solution of **1** in 15% di-*tert*-butyl peroxide–pentane leads to a rather unstable radical which shows an esr spectrum consisting of five groups of multiplets with an average separation of 9 G, which we attribute to **7**, where $a(N_2) \approx a(N_3)$ as expected.[2] The nortricyclene analog **4** was isolated from the decomposition mixture by vpc.

Our experiments suggest that odd electron density at N_3 activates hydrogen abstraction from C_5, resulting in three-membered ring formation. We do not know of a good analogy for such a process. Investigations of the stereochemistry and generality of the transformations are continuing.

Acknowledgment. We thank the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for partial support of this work, and the National Science Foundation Major Instrument program for funds used in purchasing the nmr, mass spectral, and esr spectrometers used.

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Received December 27, 1972

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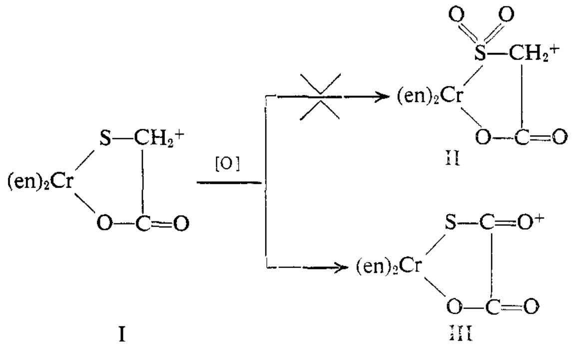
[8] For information on diazenium cations, which are well characterized, see S. Hunig, *Helv. Chim. Acta*, **54**, 1721 (1971).

[9] C. J. Collins in "Carbonium Ions," G. A. Olah and P. von R. Schleyer, Ed., Vol. I Wiley-Interscience, New York, N. Y., 1968, p 232.

Oxidation of Coordinated Thiol at Carbon Rather Than Sulfur. A Possible Reaction Pattern for the Action of Aldehyde Dehydrogenase

Sir:

The fundamental significance of reactions of coordinated ligands[1] as well as the intense current interest in reactions related to the functioning of nonheme iron–sulfur proteins in biological electron transfer processes[2] prompt us to report the novel oxidation of a coordinated thiol ligand. The following observations serve to define the oxidation of *O,S*-mercaptoacetatobis(ethylenediamine)chromium(III)[3] (I) by the one-equivalent oxidants Np(VI) and Ce(IV): the chromium-containing product of these reactions is shown not to be the anticipated[4] sulfinic acid derivative II but rather III, the first monothiooxalato complex to be reported.



I II III

(1) When excess Np(VI) is added to I in 0.0100 *F* $HClO_4$ at 25°, 3.95 ± 0.05 mol of Np(V) is produced per mole of I initially present (average of eight independent experiments, error is standard deviation, $([Np^{VI}]/[I])_{initial}$ = 4.00–31.1, $[I]_{initial} \simeq 5 \times 10^{-4}$ *F*). Under all conditions studied, the reaction of I with either Ce(IV) or Np(VI) is complete within the time of manual mixing.

(2) Ion exchange separation of the product mixture on Dowex 50W-X2 resin results in one major chromium-containing product. The elution chracteristics of

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[1] For general surveys, see (a) M. M. Jones, "Ligand Reactivity and Catalysis," Academic Press, New York, N. Y., 1968; (b) "Reactions of Coordinated Ligands," *Advan. Chem. Ser.*, No. 37 (1963).

[2] For general surveys see specific articles in (a) T. P. Singer, Ed., "Biological Oxidations," Interscience, New York, N. Y., 1968; (b) "Bioinorganic Chemistry," *Advan. Chem. Ser.*, No. 100 (1971).

[3] The preparation, characterization and single-crystal X-ray structure determination of this complex are described in papers that have been submitted for publication.

[4] (a) R. D. Gillard and R. Maskill, *Chem. Commun.*, 160 (1968); (b) R. V. G. Ewens and C. S. Gibson, *J. Chem. Soc.*, 431 (1949); (c) M. P. Schubert, *J. Amer. Chem. Soc.*, **55**, 3336 (1933).