undergo several hundred collisions during their residence times. There is no indication of reaction of any observed ions with these alkanes. Cycloheptatriene and norbornadiene showed no change in their photodissociation spectra in going from 11 to 15 eV ionizing energy.

The strikingly different photodissociation curves for these three isomeric ions make it obvious that there is no important degree of interconversion or conversion to a common structure on a time scale of seconds. The curves of Figure 1 rule out the possibility that any one of the ions converts on this time scale to one of the other two observed structures to the extent of more than a few per cent, except that conversion of about half the norbornadiene cations to the cycloheptatriene structure would not be inconsistent with the data (although this does not appear very likely). Conversion of either of the other cations to the most stable toluene structure does not occur to more than 10% (2% for cycloheptatriene).

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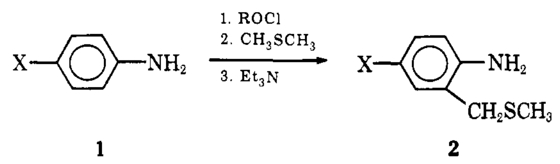
A General Method for the Synthesis of Oxindoles

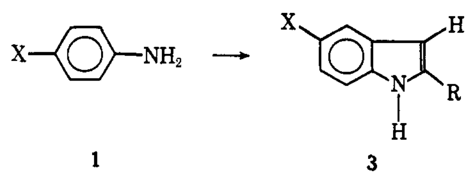
Sir:

We wish to report a general method for the synthesis of oxindole and its derivatives.[1]

Recent reports from our laboratory have provided the details of a simple, stereospecific method for the ortho alkylation of aromatic amines.[2] This procedure involved the addition of dialkyl sulfides to the mono-N-chlorinated amine to give an azasulfonium salt, followed by ylide formation and intramolecular attack of the ylide at the ortho position. In this way, 1 could be converted into 2 in good to excellent yields.

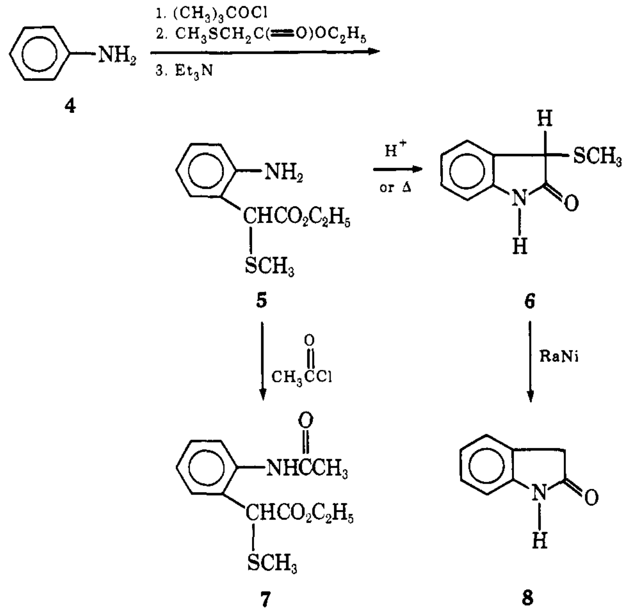


Raney nickel desulfurization then produced the desired alkyl side chain. We have also found that use of a β-keto sulfide in place of a dialkyl sulfide provided a simple process for the conversion of aniline 1 to the 2-substituted indole 3.[3] We have now discovered that the use of certain sulfur-containing esters in place of the dialkyl sulfides provides a valuable modification of our method, which leads directly to oxindoles.



In a typical procedure, 1 equiv of aniline (4) in methylene chloride at −65° was treated with 1 equiv of *tert*-butyl hypochlorite (see Scheme I). After 5–10 min,

Scheme I



1 equiv of the appropriate ethyl methylthioacetate was added (slight exotherm) and stirring was continued for 1 hr. One equivalent of triethylamine was then added and the reaction mixture was allowed to warm to room temperature. Careful workup of the reaction mixture at this stage gave a 62% yield of the very unstable amino ester 5. Acetylation of the crude reaction mixture gave a 60% yield of 7.[4] Treatment of 5 with dilute acid gave the oxindole 6 in 84% yield.[5] When the crude reaction mixture derived from 4 was treated directly with acid, the overall yield of 6 was 63%. Raney nickel reduction of 6 resulted in the formation of oxindole (8) in 76% yield.

The conversions described above were found to be quite general when applied to substituted anilines. As shown in Scheme II, a variety of functional groups, which differ considerably in electronic character, can be tolerated. Raney nickel reduction of **10a**, **10b**, **10c**, and **10f** gave the corresponding desulfurized oxindole in 55, 72, 77, and 67% yields, respectively. The formation of **10e** from **9e** represents an interesting case. In principle, either a 4- or 6-substituted oxindole could be formed. In practice, the 4-nitrooxindole derivative **10e** was the overwhelming product.

When the nature of the sulfide was changed by substituting the active methylene, a route to 3-substituted oxindoles was provided. When **4** was treated first with *tert*-butyl hypochlorite, then with ester **11**, and subsequently with base we observed base-catalyzed re-

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[1] For detailed discussions of the presently known methods of oxindole synthesis see: R. J. Sundberg, "The Chemistry of Indoles," Academic Press, New York, N. Y., 1970.

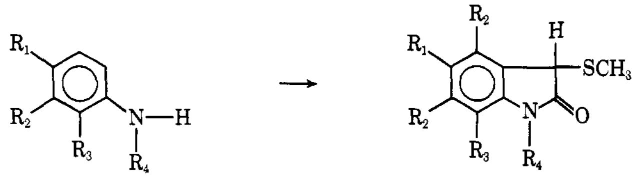
[2] P. G. Gassman, G. Gruetzmacher, and R. H. Smith, *Tetrahedron Lett.*, 497 (1972); P. G. Gassman and G. Gruetzmacher, *J. Amer. Chem. Soc.*, **95**, 588 (1973).

[3] P. G. Gassman and T. J. van Bergen, *ibid.*, **95**, 590, 591 (1973).

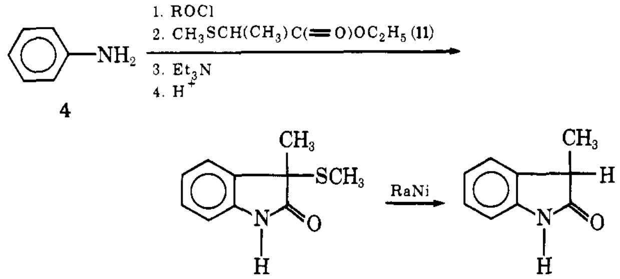
[4] Satisfactory elemental analyses have been obtained on all new compounds except 5.

[5] The conversion of 5 into 6 could also be accomplished by heating 5 or by allowing 5 to stand at room temperature.

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, $R_1 = CO_2C_2H_5$; $R_2 = R_4 = H$; $R_3 = CH_3$	**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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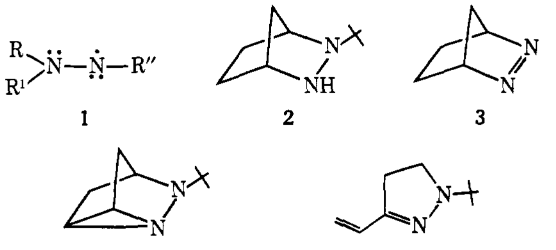
Autoxidation of 2-*tert*-Butyl-2,3-diazanorbornane to 3-*tert*-Butyl-2,3-diazanortricyclene. A γ Elimination of Hydrogen

Sir:

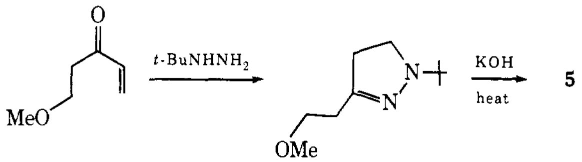
Although triarylhydrazyl radicals, such as diphenylpicrylhydrazyl,[1] are among the stablest radicals known, alkyl hydrazyls (**1**) have proven elusive. Wood, *et al.*,[2] have recently obtained esr spectra of 1,1-dialkyl hydrazyl radicals by γ irradiation of the hydrazines in adamantane matrices, but 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_6D_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),

Scheme I



the literature route to 1-alkyl-3-vinyl-4,5-dihydropyrazoles.[7]

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).