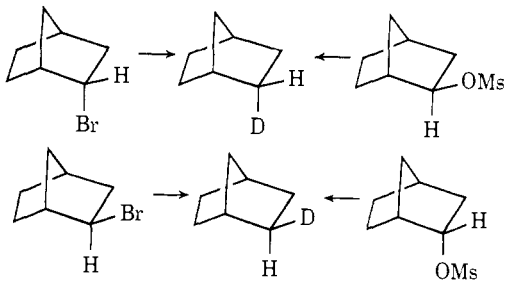
reagent and the reaction mixture was worked up with H_2O. Interestingly we found that the reduction of both *exo*- and *endo*-2-bromonorbornane[7] proceeded with 100% retention, whereas the corresponding mesylates[8,9] underwent complete inversion of stereochemistry (see Scheme I and Table I, entries 7, 8, 20, and 21). Nmr

Scheme I



and ir spectral analyses[1b,5b,10] distinguished between *exo*- and *endo*-2-deuterionorbornane and demonstrated the stereospecificity of the Cu(I) reduction.

The above results suggest that the Cu reagent may attack the bromides from the front side to form Cu complexes which in turn undergo ligand reorganization and finally release the deuterated product. In contrast, the reaction with the mesylates appeared to be categorized as the SN2 type.

Finally, some observation on the reduction of *trans*-1-bromooct-1-ene deserves comment. Use of the deuterated Cu reagent with an H_2O work-up led to no deuterium incorporation in the product, whereas an approximately 1:1 mixture of *cis*- and *trans*-1-deuteriooct-1-ene resulted upon treatment with the nondeuterated reagent and then D_2O. Clearly, hydrogen (or deuterium) was introduced into the product at the work-up stage, H_2O (or D_2O) serving as a source but not the reagent. Although the stereochemical integrity is lost in the reaction[3a,11] apparently there form thermally (room temperature) stable Cu complexes which are not prone to undergo ligand reorganization under the reaction conditions. This inference provides a clue to understanding why the cyclization of a δ-iodo-γ,δ-unsaturated ketone proceeded in excellent yield with lithium dibutyl cuprate but a similar reaction with the corresponding saturated compound met with little success.[12,13]

Acknowledgment. The authors thank the Defense Research Board of Canada and Hoffmann-La Roche, Inc., for financial support.

(7) H. C. Brown and C. F. Lane, *Chem. Commun.*, 521 (1971).
(8) H. C. Brown and H. R. Deck, *J. Amer. Chem. Soc.*, **87**, 5620 (1965).
(9) H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967).
(10) (a) A. Nickon and J. H. Hammons, *ibid.*, **86**, 3322 (1964); (b) A. P. Marchand and N. W. Marchand, *Tetrahedron Lett.*, 1365 (1971).
(11) The stereochemical stability of vinyl copper complexes (not ate complexes) was examined; G. H. Whitesides and C. P. Casey, *J. Amer. Chem. Soc.*, **88**, 4541 (1966).
(12) E. J. Corey and I. Kuwajima, *ibid.*, **92**, 395 (1970).
(13) A referee's suggestion implies that we should provide information on tosylates. Reduction of cyclohexyl tosylate under the standard conditions specified in the table proceeded to afford cyclohexane in 98% yield.
(14) 1967 National Research Council (Canada) Science Scholarship Awardee.

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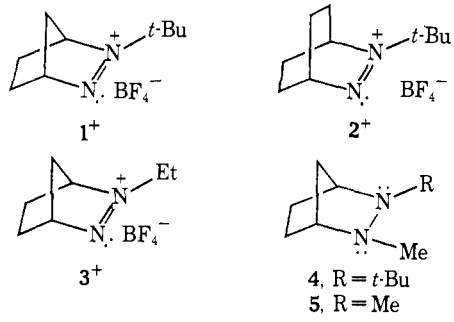
Trialkylhydrazyl Radicals in Solution

Sir:

Although diphenylpicrylhydrazyl and other triarylhydrazyls are among the stablest known radicals and have received an immense amount of study,[1] hydrazyls with alkyl substituents are nearly unknown. Although the esr spectra of 1,1-dialkylhydrazyls[2a] and hydrazyl[2b] in solid matrices have recently been determined, almost no work with alkylhydrazyls in solution has yet been reported.[3] We have found that bicyclic trialkylhydrazyls **1**·–**3**· are conveniently generated in solution by electrolytic reduction of the diazenium salts **1**$^+$–**3**$^+$, which are easily prepared by



alkylation of the related azo compounds.[4] Since reversible one-electron reduction waves were observed using cyclic voltametry from **1**$^+$ and **2**$^+$ in acetonitrile, even at 100 mV/sec scan rates, **1**· and **2**· do not disappear appreciably in a few seconds. In contrast, no reoxidation wave corresponding to **3**· → **3**$^+$ could be discerned at 190 mV/sec, although a small reoxidation wave was visible at 380 mV/sec, and the wave appeared reversible at 19 V/sec. Since **3**· has abstractable α hydrogens, we attribute its lack of stability to rapid hydrogen atom transfer disproportionation, as might be expected by analogy with the behavior of nitroxide radicals, which are isoelectronic with hydrazyls. The $E_{1/2}$ values appear in Table I. Also included in Table I

Table I. $E_{1/2}$ Values for Some Hydrazines and Diazenium Salts

Starting Compd	Process	$E_{1/2}$[a]
1$^+$	Reduction	−0.72
2$^+$	Reduction	−0.79
3$^+$	Reduction	−0.70
4	Oxidation	+0.17
5	Oxidation	+0.10
6	Oxidation	+0.10

[a] Determined by cyclic voltametry acetonitrile containing 0.1 *M* *n*-Bu_4NClO_4, sce reference.

are the $E_{1/2}$ values for oxidation of the hydrazines **4** and **5** to their radical cations. It is seen that substitution of

(1) For a review, 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) (a) D. E. Wood, C. A. Wood, and W. A. Latham, *J. Amer. Chem. Soc.*, **94**, 9278 (1972); (b) R. Fantechi and G. A. Helcke, *J. Chem. Soc., Dalton Trans. 2*, 924 (1972).
(3) R. W. West and B. R. Bichlmeir of this department have been studying silylated hydrazyl radicals in solution (private communication), and we recently discovered that Professor K. U. Ingold's group has been studying dialkylhydrazyls in solution (private communication).
(4) S. F. Nelsen and R. T. Landis, II, *J. Amer. Chem. Soc.*, **95**, 2719 (1973).

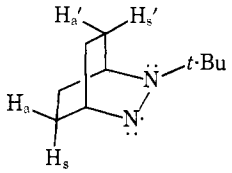
Table II. Esr Splittings for Hydrazyl and Related Radicals

Radical	a(N)	a(N′)	Other Splittings	g
1·	11.03	10.25	Complex; unanalyzed	2.0035
2·	11.44	10.61	3.00 (2 H_a), 2.13 (2 H_a'), 0.47 (2 H_s), 0.37 (2 H_s')[a]	2.0035
6·$^+$	13.61	13.61	13.06 (6 Me–H), 2.62 (4 H_a), 0.60 (4 H_s)	
1-O·	20.58		3.01 (1 H), 2.65 (1 H), 1.15 (1 H)	2.0058
2-O·	20.95	1.60	3.98 (1 H), 0.85 (2 H)	2.0060
7	14.92		2.73 (1 H), 0.80 (4 H)	2.0065
8	15.26		2.50 (1 H), 0.85 (4 H)	2.0065

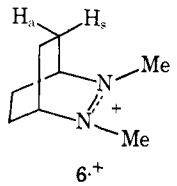
[a] Patterns complex and centers ill resolved. These splittings are probably not better than ±0.2 G. Assignments of the larger hydrogen splittings paired with the larger nitrogen splittings are only on the basis of reasonability. We cannot assign which nitrogen is which. This is particularly true since labeling work by V. Malatesta and K. U. Ingold[3] has reversed the previous assignment[2a] for 1,1-dialkylhydrazyls. We thank Professor Ingold for communicating these results prior to publication.

tert-butyl for methyl (comparing **4** to **5**) results in only a slightly more difficult oxidation, presumably because of increased strain in the radical cation.[5] It can be noted that $E_{1/2}$ for reduction of **4**·$^+$ is 0.89 V (+0.17 to −0.72) anodic of that of **1**$^+$. It is, therefore, 20 kcal/mol (23.06 kcal/mol per eV × 0.89 eV = 20.5) "harder" to force a single antibonding electron into the two-electron–two-center π bond of **1**$^+$ than it is to add an electron to the three-electron–two-center π system of **4**·$^+$ to give the neutral hydrazine, which has adjacent lone pairs. Turning the argument around, it "costs" 20 kcal/mol more to remove an electron from the hydrazine **4** than it does to remove one from the hydrazyl **1**·, since the product cation from **4** still has an antibonding electron, while that from **1**· does not.

Coulometric reduction of both **1**$^+$ and **2**$^+$ gave n values of 1.0 (at −1.0 V *vs.* sce), and transfer of the solutions to esr tubes allowed recording of the esr spectra of the hydrazyls. The spectrum of **2**· was sufficiently resolved for analysis of the splittings, under these conditions. Similar (though less resolved) spectra were observed for both hydrazyls using *intra muros* electrolytic reduction in the esr cavity and by photolysis of hydrocarbon solutions of the related hydrazines in the presence of di-*tert*-butyl peroxide.[6] The splittings for **2**· are compared with those of the isoelectronic hydrazine radical cation **6**·$^+$[7] in Table II.



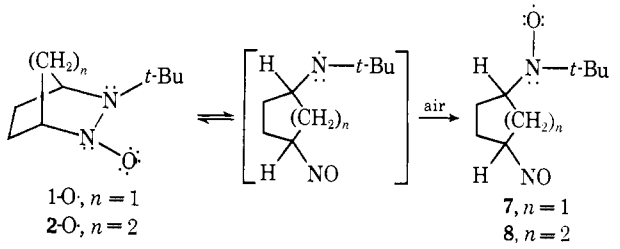
2·



6·$^+$

We failed to observe the esr spectrum of **3**·, even using *intra muros* reduction, as might have been expected from the instability of this radical, as revealed by the cyclic voltametric work. Sealed tubes containing **2**· had not decreased appreciably in radical concentration after 1 day and **2**· was still easily detectable after 3 months at room temperature. In contrast, **1**· was noticeably less stable, since the radical content could be observed to decrease quite noticeably in a few hours. The products obtained by vpc from a solution of **1**· which had been allowed to decompose at room temperature were those of hydrogen atom transfer, the related hydrazine (**1**-H) and 3-*tert*-butyl-2,3-diazanortricyclene, which was previously isolated along with **1**$^+$ from the autoxidation of 2-*tert*-butyl-2,3-diazabicyclo-[2.2.1]heptane (**1**-H).[4] Decreasing the temperature to −80° (in butyronitrile) did not result in a measured decrease in radical concentration for either **1**· or **2**· solutions at 5 × 10^{-3} *M*; no evidence was observed for dimer formation, as has been the case with some bicyclic nitroxides.[8]

Both **1**· and **2**· are rapidly destroyed by air, and their esr spectra are replaced by those of a radical with a single large nitrogen splitting (Table II). We attribute these spectra to the related hydrazyl oxides (amino-nitroxides) **1**-O· and **2**-O· both on the basis of their esr spectra, which are consistent with those of the known acylamino nitroxides,[9] and because fairly stable amino radicals, such as the diphenylamino radical, are known to give nitroxides in the presence of air. Neither amino nitroxide was very stable, and their esr



spectra faded in a few hours and were replaced by those characteristics of dialkyl nitroxides. We suggest that these nitroxides are most likely to be **7** and **8**, derived from **1**-O· and **2**-O· by N–N cleavage and oxygen scavenging. The N–N cleavage is an intramolecular analog of the reverse of spin trapping of an amino radical by an alkylnitroso compound;[10] the forward direction spin trapping reaction has been recently reported.[11]

Acknowledgment. We thank the National Science Foundation for financial support of this work, and the

(5) S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, **94**, 7108 (1972).

(6) Our greater success at resolving the esr of **2**· using complete reduction of **2**$^+$ as compared to using *tert*-butoxy abstraction from **1**-H is believed to be caused by the ease of varying radical concentration until the optimum is obtained in the former experiment.

(7) S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, **92**, 6215 (1970), report earlier data on this system; increased resolution was obtained at lower temperatures, and the data quoted are for CH_2Cl_2 solution at −80°.

(8) G. D. Mendenhall and K. U. Ingold, *ibid.*, **94**, 7166 (1972).

(9) E. F. Ullman, L. Call, and S. S. Tseng, *J. Amer. Chem. Soc.*, **95**, 1677 (1973), and references therein.

(10) For a review of spin trapping see E. G. Janzen, *Accounts Chem. Res.*, **4**, 31 (1971).

(11) O. E. Edwards, D. H. Paskovitch, and A. H. Reddoch, *Can. J. Chem.*, **51**, 978 (1973).

major instrument program of the National Science Foundation for funds used in purchase of the nmr and esr spectrometers used. We thank J. M. Buschek for building the cyclic voltametry apparatus used.

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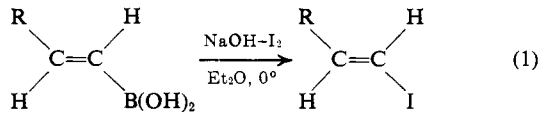
A Stereospecific Conversion of Alkenylboronic Acids into Alkenyl Bromides with Inversion of Configuration. Striking Differences in the Stereochemistry of the Replacement of the Boronic Acid Substituent by Bromine and Iodine and Its Significance in Terms of the Reaction Mechanism

Sir:

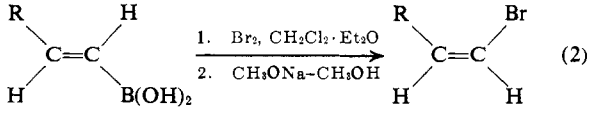
Alkenylboronic acids add bromine readily at low temperatures to produce intermediates which are converted by base into alkenyl bromides of 99% isomeric stereochemical purity in essentially quantitative yields. The replacement of the boronic acid substituent by bromine proceeds with inversion of configuration. This is in striking contrast to the retention of configuration observed in the base-induced iodination of alkenylboronic acids.[1] The catechol esters of alkenylboronic acids, readily synthesized *via* the hydroboration of alkynes with catecholborane,[2] can be converted directly into these alkenyl bromides. Consequently, this procedure provides a remarkably simple means for the conversion of alkynes into alkenyl bromides of high stereochemical purity.

We recently reported that *trans*-1-alkenylboronic acids are converted by iodine under the influence of base into the corresponding *trans*-1-alkenyl iodides of >99% stereochemical purity in almost quantitative yields[1] (eq 1). We undertook to synthesize the corresponding bromide by a similar procedure utilizing bromine. However, the results proved unsatisfactory. For example, the addition of bromine to a solution of *trans*-1-octenylboronic acid in the presence of aqueous sodium hydroxide at 0° provided a 65:35 mixture of *cis*- and *trans*-1-octenyl bromide in a yield of ~50%.[3] However, when the bromine was added first to the boronic acid, followed by the base, an essentially quantitative yield of the isomerically pure *cis*-1-octenyl bromide[4] was obtained (eq 2).



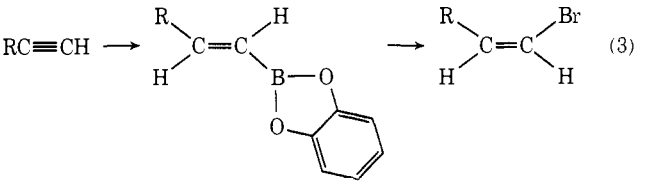
(1)

The observation that the replacement of the boronic acid group by bromine proceeds with inversion of configuration, whereas the earlier replacement by iodine proceeds with retention of configuration, was of major interest and stimulated a detailed study. The reaction appears to be general. Thus, *trans*-2-cyclohexylethenylboronic acid also undergoes substitution with inversion (eq 2).

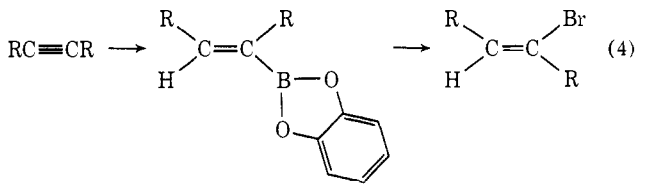


(2)

The catechol esters of *trans*-1-alkenyl- and internal *cis*-alkenylboronic acids are conveniently prepared by the hydroboration of the corresponding alkynes with catecholborane.[2] There would be an obvious advantage in utilizing these catechol esters directly. Use of 1 molar equiv of bromine resulted in a low yield. Evidently the catechol moiety was reacting competitively with the bromine. However, use of 2 molar equiv of bromine solved this problem. Consequently, treatment of the catechol esters of the alkenylboronic acids with 2 molar equiv of bromine in methylene chloride, followed by treatment with base, provides a simple, practical procedure for the conversion of both terminal and internal alkynes into stereochemically pure vinyl bromides (eq 3 and 4).



(3)



(4)

Representative results are summarized in Table I. The following experimental procedure was utilized. The alkyne, 25.0 mmol, was hydroborated with 25.0 mmol of catecholborane as described previously[2] to produce the catechol ester of the alkenylboronic acid. The product was dissolved in 25 ml of methylene chloride and cooled to the appropriate reaction temperature (Table I), and 50 mmol of bromine was added. The reaction mixture was stirred for 1 hr, and then 50 mmol of base (aqueous sodium hydroxide or sodium methoxide in methanol) was added. The mixture was stirred for 1 hr and then brought to room temperature. Water, 25 ml, was added and the organic phase was separated. The aqueous phase was extracted twice with methylene chloride and the combined organic phase was dried over magnesium sulfate. Distillation yielded the vinyl bromide. Thus, from 25.0 mmol of 1-octyne, there was obtained 3.94 g of *cis*-1-octenyl bromide [bp 90–91° (35 mm); n^{20}D 1.4619], a yield of 82%. The product was characterized by ir (700 cm^{-1}), pmr (δ 5.8–6.4 (2 H, m), 1.8–2.9 (2 H, m), 0.8–1.8 (11 H, m)), and mass spectrometry [*m/e* 192 (100), 190 (100)].

It is possible to account for the inversion of configuration in the present reaction in terms of the usual trans addition of bromine to the double bond,[5] followed by a

(1) H. C. Brown, T. Hamaoka, and N. Ravindran, *J. Amer. Chem. Soc.*, **95**, 5786 (1973).
(2) H. C. Brown and S. K. Gupta, *ibid.*, **94**, 4370 (1972).
(3) Another product, more volatile than the bromides, was noted in the gas chromatogram. The reaction mixture revealed strong >C=O absorption in the ir spectrum. Possibly octanal is formed *via* oxidation of the vinylboronic acid by hypobromite (from bromine and the base).
(4) Hydroalumination–bromination of alkynes gives vinyl bromides of opposite stereochemistry: see G. Zweifel and C. C. Whitney, *ibid.*, **89**, 2753 (1967).
(5) (a) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, pp 150, 523; (b) S. Winstein, *J. Amer. Chem. Soc.*, **64**, 2792 (1942); (c) D. H. R. Barton and E. Miller, *ibid.*, **72**, 1066 (1950); (d) E. L. Eliel and R. G. Haber, *J. Org. Chem.*, **24**, 143 (1959).