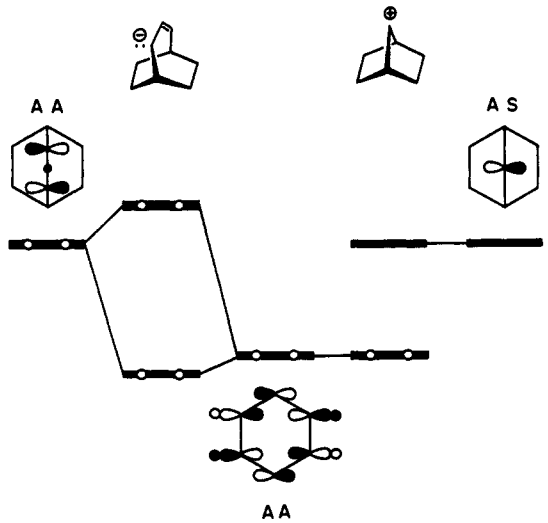

Figure 1. Destabilization and nonstabilization of bicyclic ions.

Table I. Temperature Dependence of k_{obsd}[a]

Temp, °C	$10^6 k_{obsd}$, sec^{-1} Triene **1b**	Diene **2b**
25.0	93 ± 2	0.62 ± 0.02
34.9	206 ± 10	
44.0	424 ± 9	
55.0	906 ± 21	12 ± 1
65.3		28 ± 2
75.6		62 ± 4
85.1		127 ± 4
$\Delta H^{\ddagger}$, kcal/mol[b]	14.0 ± 0.2	18.0 ± 0.1
$\Delta S^{\ddagger}_{0.057\,M}$, cal/(mol deg)	−25.6 ± 0.6	−22.0 ± 0.3

[a] 0.057 *M* KO-*t*-Bu–Me_2SO; uncertainties are standard deviations. [b] Negligibly different from those at infinite dilution.

Incorporation of deuterium or tritium into the corresponding monoene **3b**[15] proved to be much more difficult. Quantitative detritiation data were achieved only in competition with concurrent (and heterogeneous) decomposition of the basic solvent. Zero time and base dependence estimates thus provided only an upper limit to the homogeneous k_{obsd} ($<4.27 \times 10^{-7}$ sec^{-1} at 0.057 *M* and 95°). The reasonable assumption that $\Delta S^{\ddagger}_{0.057\,M}$ approximates a lower limit of −24 cal/(mol deg) (*cf.* Table I and ref 13b,c) then sets $\Delta H^{\ddagger}$ as >23.6 kcal/mol.

The 4.0 kcal/mol discrepancy between $\Delta H^{\ddagger}$ for **1** and **2** is most economically attributed to longicyclic[1b] π-electron delocalization throughout all three unsaturate bridges of the trienyl anion. The expected[1c] and observed greater discrepancy between **2** and **3** (>5.6 kcal/mol) is similarly attributed to bishomoaromatic stabilization of **2a**.

More disconcerting, **3b** is also less reactive than any other simple olefin (whether bicyclic,[4c,11,13d] monocyclic,[11,13c,d] or acyclic[13a]) previously studied in this medium.[16] This behavior recalls that of 7-norbornyl tosylate, the abnormally unreactive reference substrate of the bicyclo[2.2.1]heptyl system.[18] And it can be understood in an entirely analogous way.[19]

Within the framework of naive theory,[1b] cations are stabilized by an occupied, high-lying orbital—anions by a vacant low-lying one—but only if these are of appropriate symmetry. Figure 1 shows that the electron-occupancy and the symmetry conditions cannot both be satisfied, either for the allylic anion of **3a** or for the 7 cation of norbornyl. In the case of **3a**, as elsewhere,[1] interaction between fully occupied orbitals of corresponding symmetry necessarily leads to destabilization. In the case of the 7-norbornyl cation, electron occupancy is appropriate but the symmetry is not; this cation is therefore better described as abnormally nonstabilized.[19]

Although the originally anticipated reactivity pattern remains intact, its quantitative dissection into σ and π contributions thus becomes unresolved, if not indeed unresolvable. Conventional references, such as we and others[4b,c,e,6,7] have used, are clearly inappropriate for such finer distinctions. We therefore content ourselves with the now demonstrated semiquantitative reliability of the original π-electron approach, whatever the ultimate origins of its success.

Acknowledgment. We are grateful to R. Hoffmann for his critical comments, to M. Jones, Jr., for copies of spectra, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Professor Grutzner graciously agreed to delay publication of ref 4e until this manuscript was available.

(15) Obtained by methyllithium treatment of the *p*-toluenesulfonylhydrazone of bicyclo[3.2.2]nonan-2-one: mp 108°; *m/e* 122; nmr τ (CCl_4) 4.11 (m, 0.99), 4.56 (d of t, 0.99), and 7.54–8.60 (m, 12.02) ppm. *Anal.* Found: C, 87.84; H, 11.81.

(16) More quantitative comparisons must await the reconciliation of different treatments of base dependence[4c,e,11,13] and of conflicting data[11,13c,d] as well as the more frequent study of temperature dependence.[13b,c] Correction for isotope effects should be less important.[17]

(17) J. R. Jones, *Progr. Phys. Org. Chem.*, **9**, 241 (1972); I. O. Shapiro, F. S. Yakushin, I. A. Romanskii, and A. I. Shatenshtein, *Kinet. Kat.*, **9**, 1011 (1968).

(18) J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Amer. Chem. Soc.*, **76**, 5692 (1954); W. G. Woods, R. A. Carboni, and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 5653 (1965); P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 182 (1961); P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1854 (1964); C. S. Foote, *J. Amer. Chem. Soc.*, **86**, 1853 (1964).

(19) R. Hoffmann, P. D. Mollère, and E. Heilbronner, *J. Amer. Chem Soc.*, **95**, 4860 (1973).

(20) NDEA Title IV Fellow, 1966–1969; U. S. Public Health Service. Fellow, 1969–1970, and Trainee, 1970–1971.

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Reductive Removal of Halo and Mesyloxy Groups with a Copper(I) Complex

Sir:

A rather general synthetic problem encountered in another study has necessitated us to search for a method that effects reductive removal of halo and mesyloxy and thus indirectly hydroxy groups.[1] Required of the method are high efficiency, stereospecificity, operational simplicity, and mild conditions. We have found that a reducing system consisting of some Cu(I) species satisfies virtually all those requirements with a

(1) Methods recently developed for this purpose are: (a) $NaBH_3CN$–HMPA: R. O. Hutchins, B. E. Maryanoff, and C. A. Milewski, *Chem. Commun.*, 1097 (1971); (b) C. W. Jefford, D. Kirkpatrick, and F. Delay, *J. Amer. Chem. Soc.*, **94**, 8905 (1972); (c) $LiBH(C_2H_5)_3$: H. C. Brown and S. Krishnamurthy, *ibid.*, **95**, 1669 (1973); (d) Li–$C_2H_5NH_2$ reduction of diethyl phosphates or tetramethylphosphorodiamides of alcohols: R. E. Ireland, D. C. Muchmore, and U. Hengartner, *ibid.*, **94**, 5098 (1972).

Table I. Reduction with the Cu(I) Reagent[a]

Entry	Substrate	Product	Yield, %	Time, hr
1	1-Bromooctane	*n*-Octane	98	1.0
2	1-Bromononane	*n*-Nonane	98	2.0
3	1-Bromononane	*n*-Nonane	95[b]	2.0
4	1-Chlorooctane	*n*-Octane	96[c]	15
5	2-Bromononane	*n*-Nonane	100	1.25
6	2-Bromoadamantane	Adamantane	99	1.5
7	*exo*-2-Bromonorbornane	Norbornane	92	1.0
8	*endo*-2-Bromonorbornane	Norbornane	93	1.0
9	1-Bromoadamantane	Adamantane	100	1.75
10	3-Bromocyclohexene	Cyclohexene	99	0.5[d]
11	Geranyl chloride[e]	*trans*-2,6-Dimethylocta-2,6-diene	85	0.5[f]
12	*cis*-1-Bromooct-1-ene[g]	Oct-1-ene	96	2.5
13	*trans*-1-Bromooct-1-ene[h]	Oct-1-ene	98	2.5
14	1-Bromocyclooctene	Cyclooctene	99	2.5
15	1-Bromonaphthalene	Naphthalene	100	2.0
16	1-Bromo-2,2-dimethylhexane[i]	2,2-Dimethylhexane	97	2.0
17	9,9-Dibromobicyclo[6.1.0]nonane	Bicyclo[6.1.0]nonane	85[c]	1.0
18	1-Octanol mesylate	*n*-Octane	95	1.5
19	2-Nonanol mesylate	*n*-Nonane	99	1.0
20	*exo*-2-Norbornanol mesylate	Norbornane	99[c]	2.0
21	*endo*-2-Norbornanol mesylate	Norbornane	75[c]	5.0
22	Cyclohexene oxide	Cyclohexanol	100	1.5

[a] All runs were performed on a 2.72 mmol scale with 1 molar equiv of reagent which was prepared at 0° and the reaction was run at room temperature. All yields are based on relative glpc peak areas, corrected for the sensitivity of the detector, using octane or decane as reference. [b] Preparative scale (27.2 m*M*); product isolated. [c] Two molar equivalent of reagent used. [d] Reaction performed at −30°. [e] J. Calzada and J. Hooz, *Org. Syn.*, submitted for publication. [f] Reaction performed at 0°. [g] H. C. Brown, D. H. Bowman, S. Misumi, and M. K. Unni, *J. Amer. Chem. Soc.*, **89**, 4531 (1967). [h] G. Zweifel and C. C. Whitney, *ibid.*, **89**, 2753 (1967). [i] B. Stephenson, G. Solladié, and H. S. Mosher, *ibid.*, **94**, 4184 (1972).

wide variety of substrates. Synthetic utilities of the reagent and the stereochemical course of reaction are summarized below.

$$2LiAlH(OCH_3)_3 + CuI \longrightarrow \text{reagent I}$$
$$R\text{-}X + \text{reagent I} \longrightarrow RH$$
$$X = \text{Br, Cl, or MsO}$$

Addition of 2 molar equiv of $LiAlH(OCH_3)_3$[2] (LTMA) to a suspension of 1 equiv of CuI in THF provided a dark brown mixture, reagent I, which was utilized for the reduction throughout this investigation. Evidently the preparation of I is analogous to that of well-known lithium dialkyl cuprates,[3] assuming that LTMA is serving as a source of lithium hydride.[4] Table I shows that the reduction proceeded with primary (entries 1–3), secondary (5–8), tertiary (9), allyl (10 and 11), vinyl (12–14), aryl (15), neopentyl bromides (16), and a cyclopropyl geminal dibromide (17). In all these cases tested, the yields of reduced products were excellent and the reactions were complete in <2 hr at room temperature. Primary (18) and secondary (19–21) mesylates and an epoxide (22) underwent equally smooth reductive cleavage but a chloride (4) required a longer reaction time and an excess amount of I to achieve a 96% yield of product. The near-quantitative cleavage was only realized with 2 molar equiv of LTMA with respect to CuI (or a substrate) and when 1 molar equiv of LTMA was utilized to prepare the reagent, the reduction proceeded only to an extent of 50% completion or less. This result suggests that the reducing species appears to be an ate complex and that CuH[5] is only partially responsible for the reaction if at all.

The following preparative scale experiment illustrates the procedure. In an ice-cooled, 500-ml flask equipped with two pressure-equalizing dropping funnels containing 150 ml of THF and 54.5 mmol of concentrated (0.9–1.1 *M*)[6] LTMA solution were placed 5.18 g (27.2 mmol) of CuI and 10 ml of dry THF under an argon atmosphere. With the dropwise addition of the LTMA solution at 0°, the stirred suspension became gelatinous and the THF was added in 5-ml portions to facilitate stirring (a total of 150 ml was usually required).[6] After the addition was completed, the resulting brown mixture was stirred 30 min at 0° and then 6.54 g (27.2 mmol) of 1-bromononane was added all at once. After 15 min the cooling bath was removed, and the mixture vigorously stirred for 2 hr at room temperature. On several occasions a gel formed and enough THF was added to allow efficient stirring. Methanol (20 ml) was slowly added. The mixture was diluted with 250 ml of ether, filtered through Celite, and washed with saturated aqueous ammonium chloride, and finally the organic layer separated. The solvent was removed *in vacuo* after drying, and the residue was distilled to provide 3.3 g (95%) of pure *n*-nonane.

In order to investigate the stereochemistry of the reaction, $LiAlD(OCH_3)_3$ was employed to prepare the

(2) H. C. Brown and C. Shoaf, *J. Amer. Chem. Soc.*, **86**, 1079 (1964); H. C. Brown and P. Weissman, *ibid.*, **87**, 5614 (1965).

(3) For a review, see: (a) G. H. Posner, *Org. React.*, **19**, 1 (1972); (b) J. F. Normant, *Synthesis*, 63 (1972).

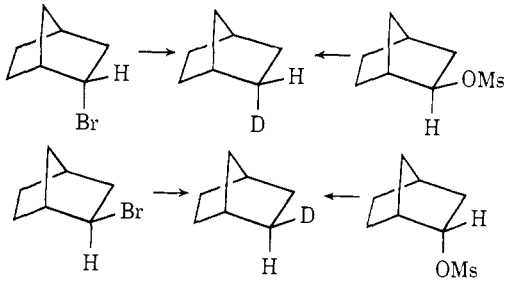
(4) H. C. Brown and S. Krishnamurthy, *J. Amer. Chem. Soc.*, **94**, 7159 (1972). A few preliminary attempts to prepare reagent I by alternate routes failed. These are: (i) 2LiH + CuI(THF), (ii) 2LiH + $CuI2[(CH_3)_2N]_3P$, and (iii) $2LiAlH[OC(CH_3)_3]_3$ + CuI(THF). Extensive studies to characterize the reagent are underway.

(5) (a) M. A. Kazankova, J. G. Malykhina, M. B. Terenina, and I. F. Lutsenko, *J. Gen. Chem. USSR*, **42**, 2129 (1972); (b) G. M. Whitesides, J. S. Filippo, Jr., E. R. Stredronsky, and C. P. Casey, *J. Amer. Chem. Soc.*, **91**, 6542 (1969); these authors noted some reducing power of CuH (see footnote 9); (c) S. A. Bezman, M. R. Churchill, J. A. Osborn, and J. Wormald, *ibid.*, **93**, 2063 (1971).

(6) Use of dilute solutions of LTMA leads to unsatisfactory results. Forcing gelatinous material [presumably $Al(OCH_3)_3$] out of the solution by mixing in this way appears to be essential. The color of the final solution before the addition of bromides must be dark brown. Purified CuI purchased from Fisher Scientific Co. is dried at 100° *in vacuo* prior to use.

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 non-deuterated 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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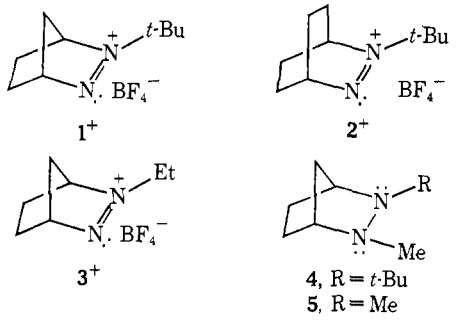
Trialkylhydrazyl Radicals in Solution

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).