(6) Previously we thought that the free alkenylcopper derived from the ate complexes underwent dimerization.[4] However, there is a possibility that some interaction between the alkenylcopper (RCu) and the borane (RBBu$_2$) is operating and the dimer is produced from this complex (RCu·BRBu$_2$).

(7) (a) Bergbreiter, D. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 4937; only one type of configurationally stable sp$^3$-hybridized R group has been reported (RCu·R'HgX). (b) Posner, G. H. *Org. React.* **1975**, *22*, 253; Normant, J. F. *Synthesis*, **1972**, 63; many examples of configurationally stable sp$^2$-hybridized R groups are known in which R is not enolizable.

(8) Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1978**, *100*, 3240; *J. Organomet. Chem.* **1978**, *156*, C9.

(9) It is recently reported that $\alpha,\beta$-acetylenic nitriles[9a] and sulfoxides[9b] undergo the stereospecific conjugate addition; (a) Westmijze, H.; Kleijn, H.; Vermeer, P. *Synthesis*, **1978**, 454. (b) Truce, W. E.; Lusch, M. J. *J. Org. Chem.* **1978**, *43*, 2252.

(10) CuI was purified by the standard procedure; Posner, G. H.; Whitten, C. E.; Sterling, J. J. *J. Am. Chem. Soc.* **1973**, *95*, 7788.

(11) If trace amounts of air were introduced into the reaction mixture, the conjugate addition of ethyl group was observed and the olefin thus obtained was stereochemically homogeneous. See also, Suzuki, A.; Nozawa, S.; Itoh, M.; Brown, H. C.; Kabalka, G. W.; Holland, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 3503.

(12) The copper boron ate complex, R$_3$B$^-$Me Cu$^+$, transfers both R and Me groups to ethyl propiolate; Yamada, K.; Miyaura, N.; Itoh, M.; Suzuki, A. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3431.

(13) For a stable chiral copper reagent, see Periasamy, M. P.; Walborsky, H. M. *J. Am. Chem. Soc.*, **1975**, *97*, 5930.

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## New Method for Direct Conversion of Amides to Amines

*Summary:* The reagent *I,I*-bis(trifluoroacetoxy)iodobenzene is found to bring about the conversion of carboxylic acid amides to amines under extremely mild conditions (room temperature, 2–5 h, 1:1 acetonitrile–water) without the necessity of isolating or trapping the intermediate isocyanate.

*Sir:* We wish to report a new reagent for carrying out the Hofmann rearrangement (RCONH$_2$ → RNH$_2$) without the necessity of trapping the intermediate isocyanate.

The decarboxylative rearrangement of organic compounds at the carboxylic acid level of oxidation has been carried out in a number of ways, including the Hofmann rearrangement, Curtius rearrangement, Schmidt rearrangement, or various modifications of these.[2] In particular, the direct rearrangement of amides to isocyanates has been typically carried out by the Hofmann hypobromite reaction or, more recently, by the rearrangement brought about by lead tetraacetate.[3] In the latter reaction, it is obligatory for best results that the isocyanate which results from the rearrangement be trapped as an intermediate carbamate by running the reaction in benzyl alcohol or *tert*-butyl alcohol. In addition, Pb(OAc)$_4$ sometimes reacts with other functionality.[3b]

We have found that *I,I*-bis(trifluoroacetoxy)iodobenzene (1) [iodobenzene bis(trifluoroacetate), or bis(trifluoroacetato)-*O*-phenyliodine] is a superb reagent for carrying out the amide-to-amine conversion to yield the amine directly in high yield without the need for isolation or trapping of the intermediate isocyanate (eq 1). Some results are presented in Table I.
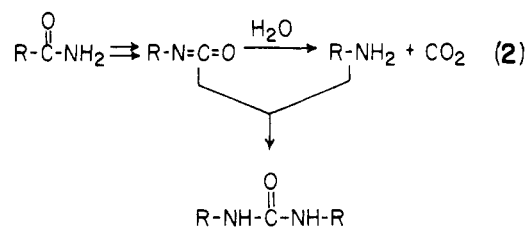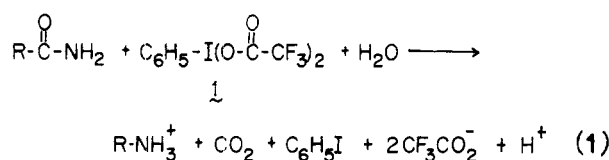


In some methods, the isocyanate will be trapped by the amine produced in the reaction to give a symmetrical urea (eq 2). Indeed, the use of the commercially available *I,I*-diacetoxyiodobenzene (iodobenzene diacetate, or phenyliodosyl acetate) in this conversion resulted in mixtures of amines and ureas.[4] The production of trifluoroacetic acid in this reaction (eq 1) can both catalyze the attack of water on the isocyanate[5] and protonate the product amine, thereby removing it from participation in the side reaction of eq 2.[6]

Only primary amides are affected during reaction with 1; secondary and tertiary amides do not react. In particular, the reagent has been used to prepare *N*-(aminomethyl)benzamide (2) in excellent yield from hippuramide (eq 3). Compounds
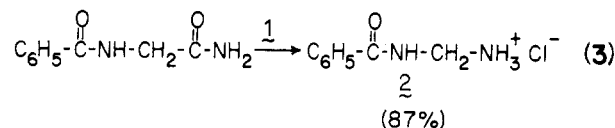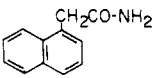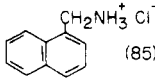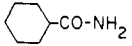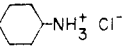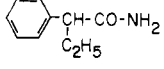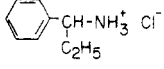


of the *N*-(1-aminoalkyl)amide type, 3, are extremely interesting in the context of the development of the retro-inverso peptide concept[7] as well as in the evolution of a carboxyl-terminal sequential peptide degradation.[8]
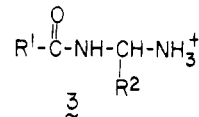


Because reagent 1 seems to be a weaker oxidizing agent than lead tetraacetate,[9] it is expected to be compatible with a wide variety of functionality. The last two entries in Table I are our initial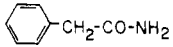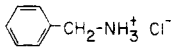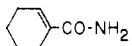 realizations of this expectation. One limitation both anticipated[4,10] and realized in practice, however, is that the reagent cannot be used in the Hofmann rearrangement of aromatic carboxylic acids to the corresponding amines, since

**Table I. Results of the Reaction of Carboxylic Acid Amides with *I,I*-Bis(trifluoroacetoxy)iodobenzene**

| amide | product (yield, %)[a] |
|---|---|
|  |  (85) |
|  |  (96) |
| CH$_3$-(CH$_2$)$_4$-CO-NH$_2$ | CH$_3$-(CH$_2$)$_4$-NH$_3^+$ Cl$^-$ (86) |
|  |  (92) |
|  |  (92) |
|  |  (55)[b] |
| C$_6$H$_5$-CO-NH-CH$_2$-CO-NH$_2$ | C$_6$H$_5$-CO-NH-CH$_2$-NH$_3^+$ Cl$^-$ (87) |

[a] The yields reported are those of isolated, recrystallized material, except for the entry described by footnote *b*. The melting points and NMR spectra of all compounds agree with those of authentic material. [b] Yield by gas chromatography.

the latter are oxidized further. However, benzylic amines are prepared in excellent yield.

A typical procedure follows. The reagent 1 is conveniently prepared by dissolution of *I,I*-diacetoxyiodobenzene[11] (Aldrich) in trifluoroacetic acid and crystallization [mp 124–126 °C (lit.[12] 119–122, 122–124 °C)], taking only the first crop of crystals (53% yield). The amide to be rearranged (typically 4 mmol) is added to a solution of 1.5 equiv of 1 in 12 mL of acetonitrile–water (1:1 v/v) and is stirred at room temperature. The reaction time depends on the migrating group in the reaction; hexanamide required 5.5 h for complete reaction, whereas cyclohexanecarboxamide required only 2.25 h for reaction. These minimum reaction times were determined by actual product isolation. The reaction mixture is then diluted with 75 mL of water, acidified with 8 mL of concentrated HCl, and the iodobenzene and unreacted 1 are then extracted into ether. The ether layer is back-extracted with 20 mL of 10% HCl solution, and the combined aqueous layers are concentrated to yield the amine hydrochloride which, in the cases studied here, can be recrystallized from ethanol–ether. Alternately, nonvolatile amines could be isolated in free base form by extraction into ether from the aqueous layer, which has been made basic with NaOH.

Further studies of the functional group compatibility and the mechanism of this reaction are in progress.

### References and Notes

(1) (a) We gratefully acknowledge support of this work by the National Institute of General Medical Sciences (GM 25143) and the National Science Foundation (CHE 77-22493). We also acknowledge the helpful comments of Professor H. E. Baumgarten cited below in ref 6 and 9c. (b) Undergraduate Research Participant, Summer, 1978. Participant, Summer, 1978.
(2) (a) T. Shioiri and S. Yamada, *Chem. Pharm. Bull.*, **22**, 855 (1974); (b) T. Shioiri, K. Ninomiya, and S. Yamada, *J. Am. Chem. Soc.*, **94**, 6203 (1972); (c) H. R. Kricheldorf, G. Schwarz, and J. Kaschig, *Angew. Chem., Int. Ed. Engl.*, **16**, 550 (1977); (d) L. E. Overman, G. F. Taylor, C. B. Petty, and P. L. Jessup, *J. Org. Chem.*, **43**, 2164 (1978).
(3) (a) B. Acott and A. L. J. Beckwith, *Chem. Commun.*, 161 (1965); (b) B. Acott, A. L. J. Beckwith, A. Hassanali, and J. W. Redmond, *Tetrahedron Lett.*, 4039 (1965); (c) H. E. Baumgarten and A. Staklis, *J. Am. Chem. Soc.*, **87**, 1141 (1965); (d) H E. Baumgarten, H. L. Smith, and A. Staklis, *J. Org. Chem.*, **40**, 3554 (1975).
(4) The first use of iodobenzene diacetate for oxidation of amides was reported by K. Swaminathan and N. Venkatasubramanian, *J. Chem. Soc., Perkin Trans. 2*, 1161 (1975). We have found, however, that certain conclusions of this paper are open to question, a point which we shall consider in the full report.
(5) A. Williams and W. P. Jencks, *J. Chem. Soc., Perkin Trans. 2*, 1753 (1974).
(6) Professor H. E. Baumgarten (unpublished work) has indicated to us that in situ formation of 1 from the commercially available iodobenzene diacetate and 5 equiv of trifluoroacetic acid works well in this reaction. In view of the urea formation which we encountered with iodobenzene diacetate alone, we preferred to work with a reagent of well-defined composition for our initial investigations. Professor Baumgarten's procedure may well turn out to be the method of choice for most applications, however.
(7) (a) M. Chorev, C. G. Wilson, and M. Goodman, *J. Am. Chem. Soc.*, **99**, 8075 (1977); (b) M. Goodman and M. Chorev, *Acc. Chem. Res.*, **12**, 1 (1979).
(8) (a) G. M. Loudon and M. E. Parham, *Tetrahedron Lett.*, 437 (1978); (b) M. E. Parham and G. M. Loudon, *Biochem. Biophys. Res. Commun.*, **80**, 1 (1978).
(9) (a) A. Spyroudis and A. Varvoglis, *Synthesis*, 445 (1975); (b) T. Takaya, H. Enyo, and E. Imoto, *Bull. Chem. Soc. Jpn.*, **41**, 1032 (1968); (c) Professor H. E. Baumgarten (unpublished work) has found from cyclic voltammetry that 1 is a stronger oxidizing agent than iodobenzene diacetate, but weaker than lead tetraacetate.
(10) G. B. Barlin, K. H. Pausacker, and N. V. Riggs, *J. Chem. Soc.*, 3122 (1954).
(11) J. G. Sharefki and H. Saltzman, "Organic Syntheses", Collect Vol. 5, Wiley, New York, 1973, p 660.
(12) (a) I. I. Maletina, V. V. Orda, and L. M. Yagupol'shii, *J. Org. Chem. USSR*, **10**, 294 (1974); (b) S. S. Makarchenka, A. S. Moskal'chuk, V. V. Glushkova, T. I. Kogai, and L. G. Polyakova, *ibid.*, **11**, 1246 (1975).

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## 2,6-Diboraadamantane, a Novel Structure with Unusual Characteristics, via Cyclic Dihydroboration of 1,3,5,7-Cyclooctatetraene

*Summary:* Cyclic dihydroboration of 1,3,5,7-cyclooctatetraene with monochloroborane–methyl sulfide yields 2,6-dichloro-2,6-diboraadamantane, easily reduced to the corresponding dihydrido derivative with unexpected properties.

*Sir:* The cyclic dihydroboration of 1,3,5,7-cyclooctatetraene with the newly discovered reagent, monochloroborane–methyl sulfide ($H_2BCl\cdot SMe_2$),[1] gives an exclusively polymeric material which, on thermal depolymerization under reduced pressure, affords 2,6-dichloro-2,6-diboraadamantane in the form of its methyl sulfide adduct (1). This represents a novel



1
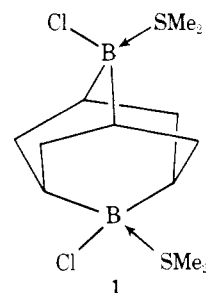
construction of a tricyclic molecule, the adamantane ring system, from a monocyclic precursor in a simple two-step reaction. The chemical properties of this tricyclic organoborane proved unexpected, indicating the need for a better understanding of the chemical effects of such structures.

A number of boraheterocycles have been conveniently prepared in the past via cyclic hydroboration of dienes and trienes.[2] These include boracycloalkanes (2), borabicyclanes (3, 4), and even a boratricyclane (5).[2] Moreover, it has proved



2    3



4    5
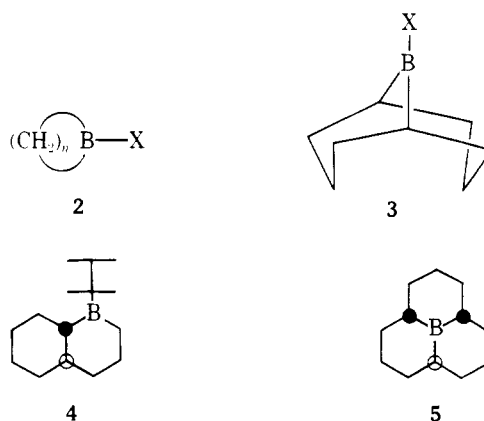
possible to achieve the transannular dihydroboration of 1,5-cyclooctadiene to synthesize 9-borabicyclo[3.3.1]nonane (9-BBN)[3] and its *B*-halo derivatives[4] by such cyclic hydroborations (eq 1).
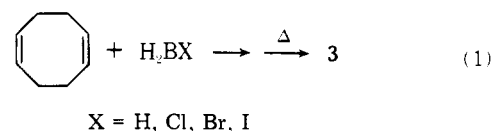


X = H, Cl, Br, I

Recently, the successful syntheses of 1-boraadamantane (6) and 2-boraadamantane (7) have been achieved by a series



6    7