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A New, Simple Procedure for the Generation and Addition of HI to Alkenes and Alkynes using BI_3:N,N-Diethylaniline complex and Acetic acid

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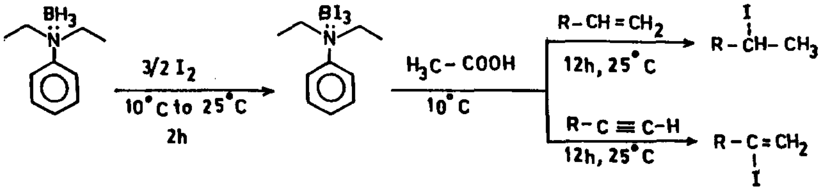
Abstract: Hydroiodic acid generated in situ from BI_3:N,N-diethylaniline complex and acetic acid, readily adds to alkenes and alkynes in Markovnikov fashion to form alkyl and alkenyl iodides in good yields under mild conditions.

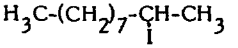
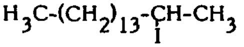
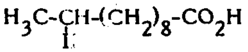
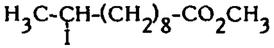
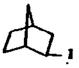
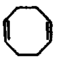
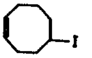
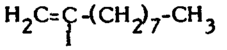
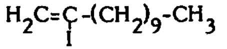
Markovnikov addition of hydrogen halides to alkenes and alkynes is one of the most important reactions in organic chemistry. Classically, this reaction is carried out with gaseous hydrogen halides.[1] However, there is still interest on the development of more convenient procedures for this reaction. For example, recently it has been reported that the reaction can be more advantageously accomplished by stirring at 115°C a heterogenous mixture of alkene (1 mol), hexadecyltributylphosphonium bromide (0.1 mole) and aqueous hydrohalogenic acid[2] (3-15 mole). More recently, it has been reported that HI addition to some alkenes and 1-hexyne can be achieved using activated Al_2O_3-I_2 in refluxing petroleum ether.[3] We wish to report that the HI addition to alkene and alkyne can be achieved under relatively mild conditions using BI_3:N,N-diethylaniline, generated using I_2,$NaBH_4$ and the amine in the presence of acetic acid.[4-6]

The report utilizing the phase transfer catalyst/alkene/HX[2] for hydroiodination indicates that the efficient transformation requires the presence of the hydrogen iodide in hydrocarbon solvents. It occurred to us that this can be achieved readily by the addition of acetic acid to BI_3 - amine complex[7] reagent prepared in benzene by the following sequence of reactions in a single pot.



The alkenes and alkynes give the corresponding Markovnikov alkyl and alkenyl iodides in good yields, on reaction with the reagent generated in this way in 12h at 25°C. The following is the general procedure. Borane-N,N-diethylaniline complex was prepared in situ by bubbling diborane, generated by dropwise addition of iodine (10 mM) in diglyme (40 ml) to $NaBH_4$ (20 mM) in diglyme (5 ml) at 25°C, into a solution of N,N-diethylaniline (5 mM) in dry benzene (60 ml) for 1h.[4-6] Iodine (7.5 mM) in benzene (20 ml) was added at 10°C in order to convert the borane-amine complex into triiodoborane-amine complex. The contents were stirred for 2h at 25°C. Acetic acid (15 mM) was added at 10°C. The alkene or alkyne (10 mM) was added under nitrogen and the contents were stirred for 12h, at 25°C. Water (30 ml) was added and the organic layer was separated. The aqueous layer was extracted with ether (50 ml). The combined organic extract was washed with saturated aqueous NaCl solution (50 ml) and dried over $MgSO_4$. The solvent was removed and the iodocompound was isolated by column chromatography on silica gel using hexane as eluent. The results are summarized in the Table. The mild nature of the reagent system is illustrated by several entries in the Table. The reagent system tolerates an ester group (entry 4) and the 1-alkynes give only the mono hydroiodination products (entries 7 and 8). These features should make this reagent attractive in transformations in which a mild reagent is required for hydroiodination.

Table: Hydroiodination using N,N-diethylaniline:BH_3, I_2 and Acetic acid system.

Entry No.	Substrate[a]	Product[b]		Yield(%)
1	$H_3C\text{-}(CH_2)_7\text{-}CH{=}CH_2$	 $H_3C\text{-}(CH_2)_7\text{-}\underset{I}{C}H\text{-}CH_3$	[1]	82
2	$H_3C\text{-}(CH_2)_{13}\text{-}CH{=}CH_2$	 $H_3C\text{-}(CH_2)_{13}\text{-}\underset{I}{C}H\text{-}CH_3$	[2]	83
3	$H_2C{=}CH\text{-}(CH_2)_8\text{-}CO_2H$	 $H_3C\text{-}\underset{I}{C}H\text{-}(CH_2)_8\text{-}CO_2H$	[3]	76
4	$H_2C{=}CH\text{-}(CH_2)_8\text{-}CO_2\text{-}CH_3$	 $H_3C\text{-}\underset{I}{C}H\text{-}(CH_2)_8\text{-}CO_2CH_3$	[4]	80
5			[5]	74
6			[6]	82
7	$HC{\equiv}C\text{-}(CH_2)_7\text{-}CH_3$	 $H_2C{=}\underset{I}{C}\text{-}(CH_2)_7\text{-}CH_3$	[7]	84
8	$HC{\equiv}C\text{-}(CH_2)_9\text{-}CH_3$	 $H_2C{=}\underset{I}{C}\text{-}(CH_2)_9\text{-}CH_3$	[8]	84

a) For entries 1-5, 7 and 8, the unsaturated hydrocarbons (10 mM), triiodoborane-amine complex (5 mM) and acetic acid (15 mM) were utilized. For entry 6, the unsaturated hydrocarbon (30 mM), triiodoboraneamine complex (5 mM) and acetic acid (15 mM) were utilized. After work-up the product separated from the starting diene by fractional distillation under reduced pressure (0.5 mm/80°C). Optimum results are obtained when 10 mM of alkenes or alkynes are utilized for 5 mM of BI_3:amine complex and the yields are based on this ratio of reagents. (b) Products were isolated by column chromatography (silica gel/hexane) and identified by spectral data (IR, ^1H NMR and ^{13}C NMR) and comparison with the data reported in the literature. The ^{13}C NMR data (δ in ppm/$CDCl_3$) are as follows: [1] 14.1, 22.6, 28.8, 28.9, 29.2, 29.4, 29.7. 29.8, 31.8, 42.9. [2] 14.1, 22.7, 27.8, 28.7, 28.9, 29.3, 29.7, 30.7, 31.9, 43.0. [3] 24.3, 28.4, 28.8, 28.9, 29.4, 30.2, 33.9, 42.7 180.5. [4] 24.8, 28.5, 29.0, 29.6, 30.6, 34.0, 42.8, 51.4, 174.3. [5] 28.3, 28.6, 29.8, 36.2, 37.8, 45.0, 47.8. [6] 25.0, 27.0, 28.8, 34.8, 38.3, 42.0, 129.2, 129.6. [7] 14.1, 22.7, 28.1, 29.1, 29.2, 31.9, 45.4, 112.8, 125.0. [8] 14.2, 22.8, 28.2, 29.2, 29.4, 29.6, 32.0, 45.4, 112.9, 125.1.

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References: (1) For reviews of addition of hydrogen halides to carbon-carbon double bonds, see (a) J. March "Advanced Organic Chemistry" 4th Edition, Willey, New York, **1985**. (b) F.W. Stacey; J.F. Harris, Org. React. **1963**, 13, 150. (2) D. Landini and F. Rolla, J. Org. Chem., **1980**, 45, 3527. (3) L.J. Stewart, D. Gray, R.M. Pagni, and G.W. Kabalka, Tetrahedron Letters, **1987**, 4497. (4) C. Narayana and M. Periasamy, J. Organomet. Chem., **1987**, 323, 145. (5) C. Narayana and M. Periasamy, J. Chem. Soc., Chem. Commun. **1987**, 1857. (6) Ch. Kishan Reddy and M. Periasamy, Tetrahedron Letters, **1989**, 5663. (7) A mixture of N,N-diethylaniline:BH_3 (1 eq) and I_2(1.5 eq) in benzene does not exhibit any $>$B-H absorption in the infrared spectrum. Using I_2 (1 eq) and the amine borane (1 eq), B-H absorption is observed at 2500 cm^{-1}, corresponding to the presence of BHI_2-amine complex, and wth I_2 (0.5 eq), the $>$B-H absorptions are observed at 2400 and 2450 cm^{-1} corresponding to the presence of BH_2I-amine complex (also see Ref. 6).

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