Table II. Temperature-Dependent Kinetic Isotope Effect (TDKIE) for the Reduction of Nitrosobenzene by DBDN[a]

temp, K	289.0	292.4	297.6	301.5	307.6	313.0	318.1
k_{HD}[b]	93.7	111.0	131.6	148.4	188.7	232.7	275.9
temp, K	289.0	292.4	297.6	302.0	307.8	313.2	318.8
k_{HH}[b]	160.8	184.9	239.8	287.1	347.2	391.5	497.7

[a] [Nitrosobenzene] = 1.24×10^{-3} M; [DBDN-4H$_2$] and [DBDN-4H,4D] = 1.48×10^{-4} M in dry methanol, anaerobic conditions. [b] Rate constants in M^{-1} min^{-1}.

of DBDN-4H, 4D,[5] the ratio of frequency factors (A_{HH}/A_{DD}) for hydride vs deuterium transfer were calculated:

$$E_a^{HH} - E_a^{HD} = 0.1 \pm 1.6 \text{ kJ/mol}$$

$$A_{HH}/A_{DD} = 9.5 \pm 2.2$$

A large kinetic isotope effect (KIE) indicated that reactions 1 and 2 occurred by a direct hydride transfer from the C4 atom of the dihydronicotinamide ring to the nitroso nitrogen of the substrate[6] and excluded the radical mechanism in Scheme I.

The estimation of ΔE_a and A_{HH}/A_{DD} is sensitive to the secondary KIE and to the isotopic impurity of DBDN-4H,4D;[7-10] the estimation of the primary KIE at different temperatures helps to minimize the random errors but does little to eliminate the systematic errors. Therefore, although the data reflect a substantial primary KIE around room temperature, the sources of inaccuracy in its estimation remain the secondary KIE and the isotopic impurity of DBDN-4H,4D.

Experimental Section

Care has been taken to obtain NADH and NAD$^+$ of the highest commercial purity. N_1-(2,6-Dichlorobenzyl)nicotinamide bromide was synthesized according to Kröhnke and Ellegast.[11] N_1-(2,6-Dichlorobenzyl)-1,4-dihydronicotinamide was synthesized according to the method of Wallenfels et al.[12] DBDN-4H,4D was synthesized in an analogous manner in D$_2$O (99.8%); care was taken to recrystallize the product several times to maximize its purity.

Absorption spectra and kinetic measurements were taken in a SPECORD UV-Vis spectrophotometer (Carl Zeiss, Jena, Federal Republic of Germany), in the thermostated cuvettes (±0.1 °C). Anaerobic conditions were obtained essentially as described by Wallenfels and Gerlach.[13] The concentrations of reactants were calculated from their absorption spectra: NADH, $\epsilon_{340nm} = 6200$ cm^2/mol; nitrosobenzene, $\epsilon_{305nm} = 9570$ cm^2/mol; 1-nitroso-2-naphthol, $\epsilon_{380nm} = 6970$ cm^2/mol; all in 0.1 M sodium phosphate buffer, pH 7.5; DBDN-4H$_2$, $\epsilon_{357nm} = 7255$ cm^2/mol in dry methanol. Concentrations of NAD$^+$ were estimated analytically as previously described.[14] In measuring the TDKIE (Table II), we took extreme care to bring the reactants to the desired temperature before the reaction and to start the reactions with very small aliquots of nitrosobenzene; reactions were performed anaerobically, as rapidly as possible (10 min), in order to minimize the influence of oxygen[2] and hydrolytic reactions[15] and the photodecomposition of reactants. Repetitive scanning of the absorption spectra (250-800 nm) indicated the photostability of reactants. The secondary KIE was assumed to be equal to unity.[7]

Registry No. NADH, 58-68-4; DBDN-4H$_2$, 13502-54-0; nitrosobenzene, 586-96-9; 1-nitroso-2-naphthol, 131-91-9; deuterium, 7782-39-0.

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(5) $k_{DD} = 2k_{HD} - k_{HH}$.

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Mild Oxidative Cleavage of Alkynes Using [Bis(trifluoroacetoxy)iodo]pentafluorobenzene

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Hypervalent iodine reagents react with alkynes to give various products depending upon the type of reagent and the reaction conditions, e.g., (i) [hydroxy(tosyloxy)iodo]benzene reacts with terminal alkynes in chloroform to yield alkynyliodonium tosylates,[1] which are important synthetic intermediates,[2,3] (ii) reaction of [hydroxy(tosyloxy)iodo]benzene with terminal and internal alkynes in methanol proceeds with oxidative rearrangement resulting in the formation of carboxylic acid esters,[4] (iii) reaction of [(perfluoroalkyl)phenyl]iodonium salts with terminal alkynes yields a mixture of substitution and addition products,[5] (iv) internal alkynes are converted to α-diketones by oxidation with iodosobenzene in the presence of ruthenium(II) catalyst, while terminal alkynes afford carboxylic acids,[6] and (v) [bis(trifluoroacetoxy)iodo]benzene reacts with internal alkynes to give α-diketones;[7] with terminal alkynes, α-hydroxy ketones are obtained.[7,8] Other methods for the oxidation of alkynes to dicarbonyl compounds using metal-based reagents include OsO$_4$,[9] KMnO$_4$,[10] RuO$_4$,[11] or Tl(NO$_3$)$_3$.[12] Ozone also yields di-

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Table I. Oxidative Cleavage of Alkynes with $C_6F_5I(OCOCF_3)_2$

entry	compd no.	substrate, R	R^1	reagent[a]	products (2)[b]	% yield[c]	mp, °C
1	**1a**	C_6H_5	H	i (3equiv)	C_6H_5COOH	79	122–123[d]
2	**1b**	C_6H_5	C_6H_5	i (3equiv)	C_6H_5COOH	41	122–123[d]
3	**1c**	$CH_3(CH_2)_3$	H	i (3equiv)	$CH_3(CH_2)_3COOH$	54	liquid
4	**1d**	$CH_3(CH_2)_5$	H	i (3equiv)	$CH_3(CH_2)_5COOH$	61	liquid
5	**1e**	$CH_3(CH_2)_6$	H	i (3equiv)	$CH_3(CH_2)_6COOH$	59	liquid
6	**1f**	$C_6H_5CH_2CH_2$	H	i (3equiv)	$C_6H_5CH_2CH_2COOH$	56	47–49[d]
7	**1g**	cyclopentyl	H	i (3equiv)	cyclopentanecarboxylic acid	70	liquid
8	**1h**	C_6H_5	CH_3	i (3equiv)	C_6H_5COOH	85	122–123[d]

[a] Reagent i = $C_6F_5I(OCOCF_3)_2/C_6H_6/H_2O$. [b] Products were characterized by IR and NMR data with comparison of known sample (Aldrich Catalog). [c] Isolated yields are not optimized. [d] Aldrich Catalog literature.

Scheme I[a]

$$\underset{\mathbf{1a\text{–}h}}{RC{\equiv}CR'} \xrightarrow[\text{(3 equiv)}]{\text{i}} \underset{\mathbf{2a\text{–}h}}{RCOOH} + R'COOH$$

[a] (i) $C_6F_5I(OCOCF_3)_2/C_6H_6/H_2O$ at reflux temperature overnight.

Scheme II[a]

$$\underset{\mathbf{3}}{p\text{-}NO_2C_6H_4COCH_2OH} \xrightarrow[\text{(2 equiv)}]{\text{i}} \underset{\mathbf{4}}{p\text{-}NO_2C_6H_4COOH}$$

[a] (i) = $C_6F_5I(OCOCF_3)_2/C_6H_6/H_2O$.

carbonyl compounds with alkynes.[13]

We have recently found that the pentafluorophenyl group as in [bis(trifluoroacetoxy)iodo]pentafluorobenzene greatly increases the oxidizing capability of this hypervalent iodine reagent,[14] and we report now a novel application, namely, carbon–carbon triple-bond cleavage of alkynes.

Fair to very good yields of the corresponding carboxylic acids (**2a–h**) are obtained upon cleavage of phenylacetylene (**1a**), diphenylacetylene (**1b**), 1-hexyne (**1c**), 1-octyne (**1d**), 1-nonyne (**1e**), 4-phenyl-1-butyne (**1f**), cyclopentylacetylene (**1g**), and 1-phenyl-1-propyne (**1h**) (entries 1–8, respectively, Table I) after refluxing overnight with [bis(trifluoroacetoxy)iodo]pentafluorobenzene in wet benzene (Scheme I).

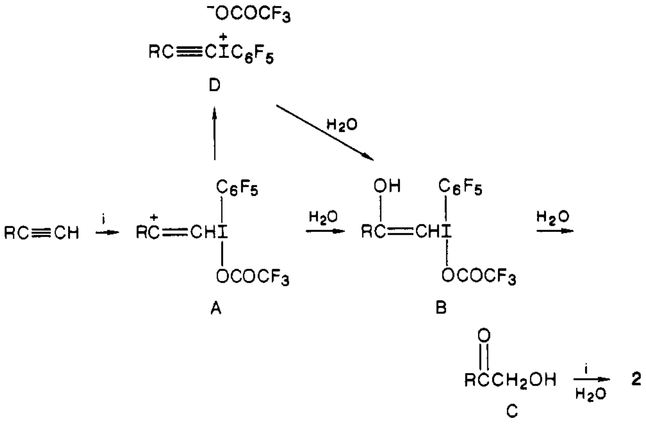
It is possible that the first equivalent of oxidant yields the α-hydroxy ketone, which may cleave with a second oxidizing equivalent to the corresponding aldehyde and acid. The third equivalent oxidizes the aldehyde to the second carboxylic acid equivalent. Thus α-hydroxy-p-nitroacetophenone (**3**) with 2 equiv of $C_6F_5I(OCOCF_3)_2$ yields p-nitrobenzoic acid (**4**) in 90% yield (Scheme II).

A possible mechanistic pathway is presented in Scheme III for both terminal and internal alkynes.

Initial electrophilic addition of (i) to the alkyne yields A followed by capture of the vinyl cation by H_2O (A → B) yields the α-hydroxy ketone C by addition of H_2O and reductive elimination of C_6F_5I (B → C). Intermediacy of the α-hydroxy ketone is reasonable (Scheme II) and terminal alkynes have been converted to α-hydroxy ketone with $C_6H_5I(OCOCF_3)_2$.[8] Intermediacy of alkynylphenyliodonium salts[1] must also be considered A → D since it has been shown that these compounds yield α-hydroxy ketones upon hydration.[7]

To summarize, the oxidative cleavage of alkynes by [bis(trifluoroacetoxy)iodo]pentafluorobenzene is of importance to synthetic organic chemists because it represents the mildest and most specific method for this transformation. In a more general sense, the work further indicates the application of hypervalent iodine to organic chemistry and the possibility of replacing toxic reagents such as ruthenium compounds with the safer ecologically acceptable iodine-based reagents.

Scheme III[a]



[a] (i) = $C_6F_5I(OCOCF_3)_2/C_6H_6$.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. The IR spectra were obtained on a Unicam SP 1000 IR spectrophotometer. ^1H NMR spectra were recorded in $CDCl_3$ at 60 MHz with a Varian EM-360 or at 200 MHz with WP-Bruker spectrometer using TMS as internal standard. All alkynes, iodopentafluorobenzene, and trifluoroacetic anhydride were obtained from Aldrich Co.

[Bis(trifluoroacetoxy)iodo]pentafluorobenzene was synthesized from iodopentafluorobenzene and trifluoroacetic anhydride by the method of Schmeisser et al.[15]

General Procedure for the Oxidative Cleavage of Alkynes. In a typical experiment, the alkyne (0.01 mol) was dissolved in benzene (50 mL) and water (5–10 drops) was added. [Bis(trifluoroacetoxy)iodo]pentafluorobenzene (0.03 mol) was added with stirring to the above reaction mixture and then it was refluxed overnight. After cooling, the reaction mixture was extracted with aqueous $NaHCO_3$ (3 × 50 mL). The aqueous solution was then neutralized with 2 N HCl and then this acidified solution was extracted with ether (5 × 50 mL). The combined ether extracts were dried over anhydrous $MgSO_4$ and then concentrated in vacuo to afford the crude mixture of carboxylic acids. Pure products were obtained by crystallization in case of solids and column chromatography in case of liquids (using ether as eluent).

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Registry No. **1a**, 536-74-3; **1b**, 501-65-5; **1c**, 693-02-7; **1d**, 629-05-0; **1e**, 3452-09-3; **1f**, 16520-62-0; **1g**, 930-51-8; **1h**, 673-32-5; **2a**, 65-85-0; **2c**, 109-52-4; **2d**, 111-14-8; **2e**, 124-07-2; **2f**, 501-52-0; **2g**, 3400-45-1.

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