

Mechanism and Scope of the Base-Induced Dehalogenation of (*E*)-Diiodoalkenes

Daniel Resch,^[a] Chang Heon Lee,^[a] Siew Yoong Tan,^[a] Liang Luo,^[a] and Nancy S. Goroff^{*[a]}

Keywords: Reaction mechanisms / Lewis bases / Iodine / Elimination

A wide range of nucleophiles have induced the elimination of iodine from (*E*)-diiodoalkenes to form alkynes under surprisingly mild conditions. The iodide anion is particularly efficient, and can drive the reaction to completion in less than 1 hour at room temperature in a polar aprotic solvent. Detailed investigations have suggested the reaction has a bimolecular polar mechanism. The diiodination reaction can be driven to completion with 1 equiv. of nucleophile and is partially catalytic with substoichiometric amounts of diiodinating reagent. Kinetic analysis of the stoichiometric iodide-in-

duced reaction indicated an overall pseudo-first-order behavior. The reaction exhibited strong solvent effects, with much slower reactions observed in protic solvents than in polar aprotic solvents. The substrate dimethyl (2*E*)-2,3-diiodobutene-2-dioate demonstrated orthogonal reactivity for either elimination or hydrolysis, depending on the solvent and nucleophile used. This reaction is a major pathway for all the diiodoalkenes examined, and represents a challenge and an opportunity for using these substrates in organic synthesis.

Introduction

Recently our group reported the elimination of iodine from poly(diiododiacetylene) (PIDA, Figure 1) under mild conditions using Lewis basic pyrrolidine^[1] or under more extreme conditions such as pyrolysis.^[2] We also demonstrated that the pyrrolidine-induced diiodination, previously unreported, is general for (*E*)-diiodoalkenes. Base-catalyzed dehalogenation of saturated vicinal dihaloalkanes is well known and has been extensively studied, especially with the iodide anion as the nucleophile.^[3–12] Yet there are only a few reports of the dehalogenation of vicinal dihaloalkenes, and the known reactions involve much harsher conditions. Miller and Noyes first reported the elimination of iodine from diiodoethene using excess sodium iodide in superheated methanol at temperatures of 109 °C and above.^[13] Kosower and Ben-Shoshan more recently reported the elimination of bromine from a dibromostilbene using NaI in acetone at reflux.^[14]

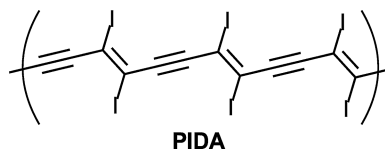


Figure 1. Molecular structure of poly(diiododiacetylene) (PIDA).

[a] Department of Chemistry, Stony Brook University, Stony Brook, NY 11794-3400, USA
E-mail: nancy.goroff@stonybrook.edu
<http://www.chem.stonybrook.edu/faculty/goroff.shtml>
Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ejoc.201402992>.

Dihaloalkenes are popular substrates for transition-metal-catalyzed coupling reactions, and have been used to prepare a variety of carbon-rich compounds such as tetraethynylethenes,^[15–17] but there have been relatively few reports on the chemistry of diiodoalkenes. Organ et al. studied the coupling reactions of iodoethenes (CHI=CHX, X = Cl, Br, or I), and carried out Suzuki and Negishi reactions with iodochloro- and iodobromoethene, but not diiodoethene.^[18] Organ and co-workers also observed dehalogenation when mixing iodoethenes with potassium hydroxide and [Pd(PPh₃)₄]. Other groups have tried similar coupling reactions and have had similar problems.^[19,20] Each of these systems involved a palladium catalyst. However, our studies suggest that diiodination happens quite readily, and may not require the presence of palladium.

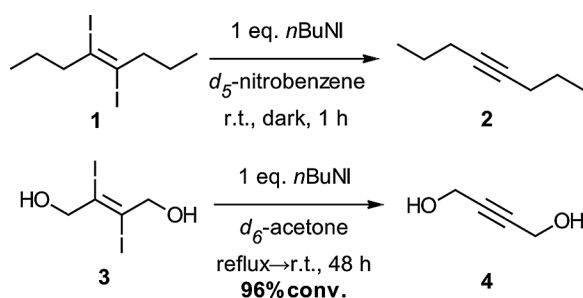
The elimination of iodine from PIDA is particularly intriguing because it makes PIDA a potential precursor to new all-carbon materials such as carbyne. In recent years, all-carbon and carbon-rich polymers have attracted interest in the areas of organic electronics and clean energy, as well as for their fundamental science.^[21–23] An understanding of the mechanism and scope of iodine elimination will help us identify conditions for complete diiodination to prepare ordered all-carbon materials. The work presented here demonstrates that the dehalogenation of diiodoalkenes occurs under mild conditions and is very broad in scope. The diiodination of simple vicinal diiodoalkenes occurs at room temperature with nucleophiles that are weak Brønsted bases, including halide salts and amines. This previously unrecognized reaction has significant consequences for chem-

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ists who wish to use dihaloalkenes as precursors to carbon-rich materials.

Results and Discussion

We previously reported that pyrrolidine induces deiodination in simple 1,2-diiodoalkenes such as compounds **1** and **3** in polar solvents such as THF.^[1] In this work we found that deiodination also occurred when compounds **1** and **3** were treated with tetrabutylammonium iodide (Scheme 1). Compound **1** readily underwent deiodination with *n*Bu₄NI in [D₅]nitrobenzene in about 1 hour, significantly faster than the reaction with pyrrolidine. Diol **3** has poorer solubility than alkene **1**, but if the reaction mixture in [D₆]acetone was first heated to reflux to dissolve compound **3**, the deiodination with *n*Bu₄NI reached 96% conversion in 48 hours.



Scheme 1. Elimination of iodine from diiodoalkene.

We investigated a wide range of solvents for the deiodination of alkene **1** (Table 1). Polar aprotic solvents promoted the deiodination, whether induced by pyrrolidine, triethyl-

amine, or iodide, whereas in protic solvents, the reaction rate was greatly reduced (Table 2). In nonpolar solvents such as toluene or cyclohexane, compound **1** remained stable and did not react with pyrrolidine over a 2-day period. Tetrabutylammonium iodide has very poor solubility in nonpolar solvents, and no reaction was observed when it was mixed with compound **1** in cyclohexane or diethyl ether. These observations are consistent with a polar mechanism, in which hydrogen bonding in protic solvents and ion-pairing in nonpolar solvents reduce the nucleophilicity of the Lewis base.

Table 2. Iodine elimination from alkene **1** in [D₄]methanol.

Days	Conversion [%]	
	1 equiv. <i>n</i> Bu ₄ NI ^[a]	1 equiv. pyrrolidine ^[b]
1	46	5
2	59	12
3	66	28
5	75	63

[a] Reagents and conditions: 0.275 M **1**, 0.275 M *n*Bu₄NI, room temp., dark. [b] Reagents and conditions: 0.275 M **1**, 0.275 M pyrrolidine, room temp., dark.

To gain a more detailed insight into the mechanism of deiodination, ¹H NMR spectroscopy was used for a kinetic analysis. Monitoring the peaks for the protons α to the double bond in diiodoalkene **1** or to the triple bond in alkyne **2**, at δ = 2.53 and 2.13 ppm, respectively, allowed the direct observation of both the starting material and the product. Compound **1** reacts with tetrabutylammonium iodide at the same rate in both [D₅]nitrobenzene and [D₃]acetonitrile (see Figures S1 and S2 in the Supporting Information). When equimolar amounts of *n*Bu₄NI and alkene **1** react, the plot of the natural log of concentration versus time (Figure 2) is linear throughout most of the reaction, which indicates that the reaction follows first-order kinetics.

Unfortunately, neither the iodide nucleophile nor I₂ could be observed directly in the NMR experiments. Iodine and triiodide could be observed by UV/Vis spectroscopy, however, as long as the solvent used was acetonitrile rather than nitrobenzene. By combining the UV/Vis absorption and NMR spectroscopic data measured under the same conditions, we obtained information on the relative concentrations of both the reactants and products. The kinetic data in Figure 3 shows that triiodide is formed more slowly than alkene **1** is consumed or alkyne **2** is formed. (The triiodide signal dominates the UV spectrum, in part due to its three-fold greater molar absorption coefficient as compared with that for iodine.^[24]) These data imply a two-step process in which iodide first reacts with alkene **1** to form alkyne **2** and molecular iodine, and at the same time release an iodide ion, and then a second reaction between iodide and I₂ leads to the consumption of iodide and the formation of I₃[−]. As the elimination reaction occurs, the concentration of alkene **1** decreases faster than the concentration of iodide, giving rise to pseudo-first-order behavior. The overall process is summarized in Scheme 2.

Table 1. Iodine elimination from alkene **1**.^[a]

Solvent	Nucleophile	Elimination/completion ^[b]
Acetonitrile ^[c,d]	I [−]	yes/1 h
Nitromethane ^[d,e]	I [−]	yes/2 h
Nitrobenzene ^[d]	I [−]	yes/1 h
Methanol	I [−]	yes/no
2-Propanol	I [−]	yes/no
1,2-Dichloroethane	I [−]	yes/3 d
Dichloromethane	I [−]	yes/3 d
1,2-Dimethoxyethane	I [−]	yes/3 d
Ethyl acetate	I [−]	yes/4 d
Diethyl ether ^[f]	I [−]	none
Cyclohexane ^[f]	I [−]	none
THF ^[g]	pyrrolidine	yes/15 h
Toluene	pyrrolidine	none
Cyclohexane	pyrrolidine	none
Nitrobenzene ^[h]	triethylamine	yes/24 h

[a] Reagents and conditions: 0.137 M **1**, 0.164 M *n*Bu₄NI, room temp., dark. [b] By TLC [silica/hexanes, *R*_f of **1** = 0.75, then silica/hexanes/ethyl acetate (3:1), *R*_f of **2** = 0.65]. [c] See Figure S2 in the Supporting Information. [d] By NMR. [e] Reagents and conditions: 0.275 M **1**, 0.330 M *n*Bu₄NI, room temp., dark. [f] Poor solubility of *n*Bu₄NI. [g] Reagents and conditions: 0.209 M **1**, 0.418 M pyrrolidine, room temp., dark. [h] Reagents and conditions: 0.137 M **1**, 0.137 M triethylamine, room temp., dark.

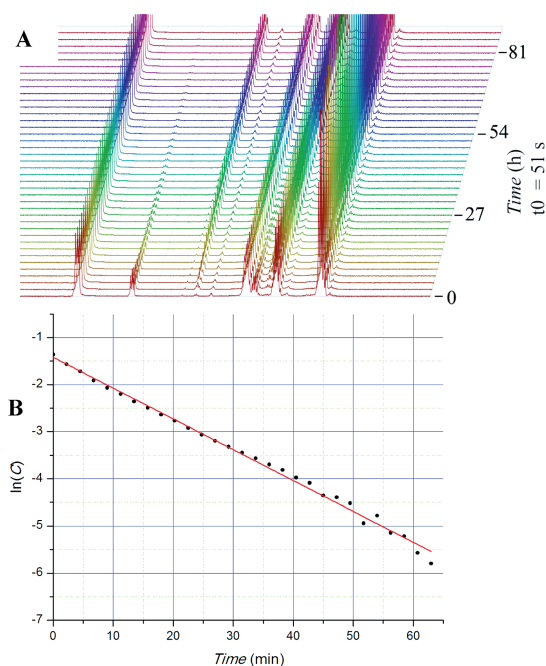


Figure 2. Kinetic plot of 0.275 M alkene **1** on reaction with 1 equiv. of $n\text{Bu}_4\text{NI}$ in CD_3CN versus time. A) NMR spectra. B) Rate law analysis of the concentration (C) of alkene **1** from data in (A). Concentrations were calculated relative to the initial concentration of alkene **1**. The red line indicates the linear least-squares fit ($R^2 = 0.994$).

To further understand the nature of the reactive species in the iodide-induced deiodination, we examined the reactivity of the triiodide ion formed during the elimination. A stoichiometric equivalent of tetrabutylammonium triiodide was pre-formed by mixing tetrabutylammonium iodide and molecular iodine for 10 min and then alkene **1** was added to the mixture. After 7 days, no deiodination of compound **1** was observed. Slator^[3] found, in saturated diiodides, that the rate of elimination slows as iodide complexes to iodine to form triiodide. Our results further confirmed that triiodide does not compete with iodide for reaction with alkene **1**. An additional control experiment, performed with 1.2 equiv. iodine and 2.4 equiv. $n\text{Bu}_4\text{NI}$, also indicated that the presence of triiodide does not inhibit the reaction (see Figure S4 in the Supporting Information).

We also examined reactions with an excess of alkene **1** to probe further the role of the iodide/triiodide equilibrium (Table 3). These studies were carried out with two different concentrations of alkene **1** (0.275 or 0.137 M) and either 0.25 or 0.5 equiv. of iodide. More than one turnover per iodide was observed in these experiments, but the deiodination did not go to completion. These results are consistent with the alkyne forming in a separate step from triiodide. The more concentrated mixtures gave higher conversions, which suggests an increased rate of elimination relative to the formation of triiodide. The complexation with iodine is thus not instantaneous. To test for salt effects, the non-nucleophilic salt tetrabutylammonium perchlorate was added to increase the ionic strength of the reaction mixture. The addition of this salt had no effect on the rate or conver-

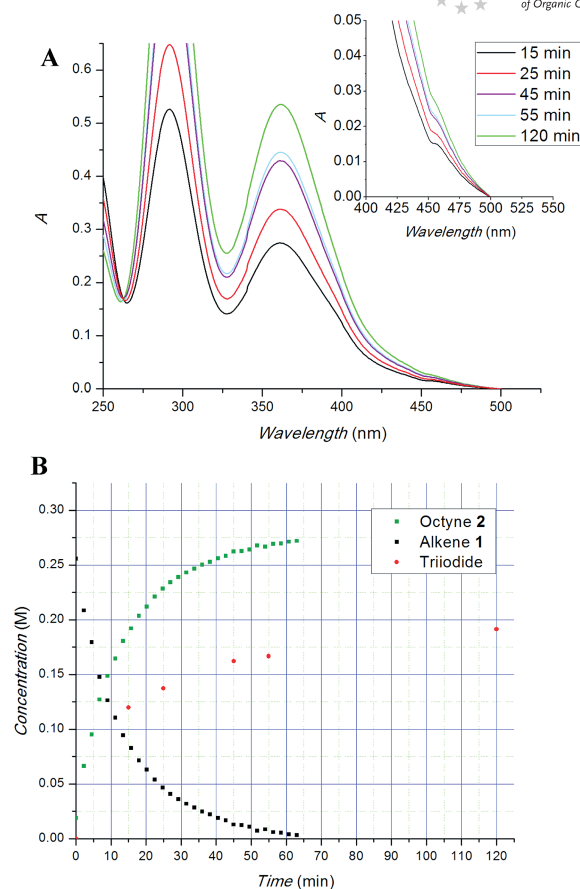
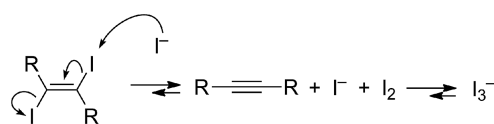


Figure 3. Kinetic data for the reaction of 0.275 M diiodoalkene **1** and 0.275 M Bu_4NI in acetonitrile. A) UV/Vis absorption spectra showing triiodide absorption at 362 nm and I_2 absorption at 457 nm. B) Kinetic plot of the concentrations of reactants and products based on data from (A) and Figure 2. Absolute concentration of I_3^- was calculated based on the standard curve shown in Figure S10 in the Supporting Information.



Scheme 2. Proposed mechanism for the deiodination of diiodoalkenes.

Table 3. Elimination of iodine from alkene **1** in the presence of substoichiometric $n\text{Bu}_4\text{NI}$.^[a]

[I] [M]	$[n\text{Bu}_4\text{NI}]$ [M]	$[n\text{Bu}_4\text{NClO}_4]$ [M]	Conv. [%]
0.275	0.069	—	32
0.275	0.103	—	61
0.275	0.138	—	86
0.137	0.034	—	26
0.137	0.069	—	57
0.137	0.034	0.034	25
0.137	0.069	0.069	60

[a] Reagents and conditions: $[\text{D}_5]\text{PhNO}_2$, 1 day, room temp., dark.

sion of the deiodination of alkene **1**, consistent with Dillon's observation in the case of vicinal dibromoalkanes that neutral substrates are not susceptible to salt effects.^[5]

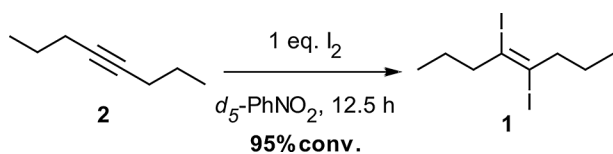
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The data in Figure 3 and Table 3 are consistent with two separate steps: 1) The consumption of alkene **1** and 2) the reaction of iodide with iodine to form triiodide, as shown in Scheme 2. The relevant rates are described by the following equations:

$$\begin{aligned} \frac{-d[\text{alkene}]}{dt} &= k_{\text{elim}}[\text{alkene}][\text{I}^-] \\ \frac{-d[\text{I}^-]}{dt} &= k_{\text{I}_3^-}[\text{I}_2][\text{I}^-] \end{aligned}$$

Because the concentration of I_2 does not build up appreciably over time, as indicated in Figure 3A, the concentration of I^- changes only slowly. Thus, the elimination reaction follows pseudo-first-order kinetics, and in the substoichiometric experiments, each iodide nucleophile is available, on average, to react with multiple diiodoalkenes. Doubling the concentration of tetrabutylammonium iodide in CD_3CN while maintaining the alkene concentration constant (see Figures S2 and S3 in the Supporting Information) led to a doubling of the reaction rate, consistent with a first-order behavior in $n\text{Bu}_4\text{NI}$. Thus, the elimination appears to be a bimolecular transformation involving one molecule of iodide and one molecule of the alkene.

To test the reversibility of the reaction, tetrabutylammonium iodide was mixed with iodine for 24 hours to form a stoichiometric equivalent of triiodide, and then alkyne **2** was added to this mixture; the mixture was monitored for 3 days, but no detectable amount of diiodoalkene **1** was observed. This experiment suggests that when iodine is fully complexed as triiodide, the deiodination reaction is irreversible. In the absence of iodide, however, molecular iodine did react with oct-4-yne (**2**) under these conditions (Scheme 3). Monitoring the reaction by NMR spectroscopy indicated 95% conversion to alkene **1** in 12.5 hours.



Scheme 3. Iodination of alkyne **2** in $[\text{D}_5]\text{nitrobenzene}$.

The pyrrolidine-induced dehalogenation has a more complicated reaction profile, with multiple possible nucleophiles. Changes in the ^1H NMR spectra show the formation of a pyrrolidinium species as the reaction progresses (Figure 4). Amines are known to react with I_2 and ICl to form iodoammonium species,^[12,25] but here we postulate that the iodypyrrolidinium ion forms directly from the reaction with the alkene. However, this reaction also yields the iodide ion, which may then react with the diiodoalkene, leading to multiple turnovers per pyrrolidine (Scheme 4). Kinetic studies with a 1:1 ratio of pyrrolidine and alkene **1** demonstrated higher than first-order kinetics for compound **1** (see Figure S5 in the Supporting Information). After 4 days of reaction, the same mixture showed only 88% conversion.

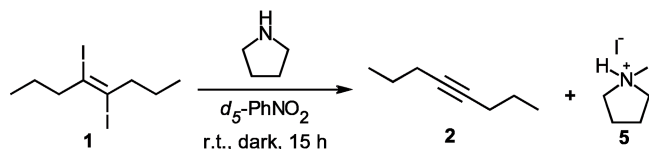
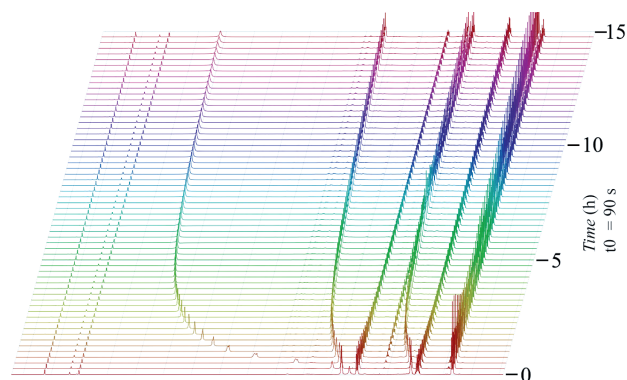
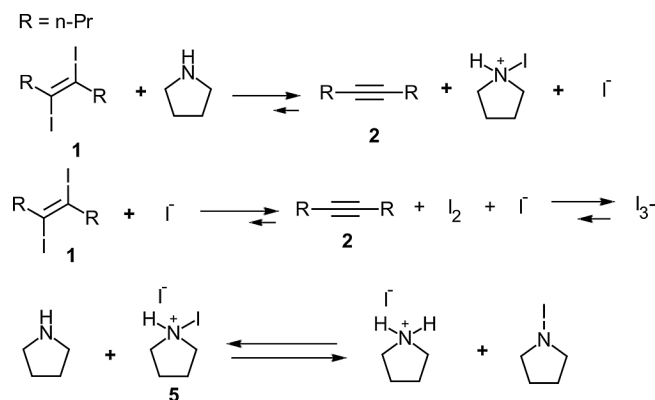


Figure 4. NMR kinetic profile showing the formation of the pyrrolidinium species. Reaction conditions: 0.275 M **1**, 0.275 M pyrrolidine, room temp., dark, 15 h. See Figure S5 in the Supporting Information for the kinetic analysis.



Scheme 4. Proposed equilibria for the reaction of pyrrolidine with diiodoalkene **1**.

The role of the iodypyrrolidinium iodide (**5**) was studied further by pre-forming it from a mixture of pyrrolidine and I_2 . NMR studies of this reaction showed that the formation of iodypyrrolidinium is completed in 3 hours (see Figure S6 in the Supporting Information). Once formed, complex **5** did not induce diiodination, which suggests that iodypyrrolidinium iodide is a tightly bound, perhaps partially covalent, complex. However, when alkene **1** was treated with substoichiometric quantities of pyrrolidine, more than one turnover per pyrrolidine was observed (Table 4), which suggests that the iodypyrrolidinium cation and iodide anion do not immediately combine to form complex **5** (Scheme 4).

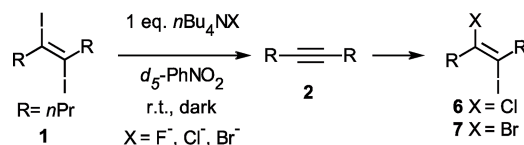
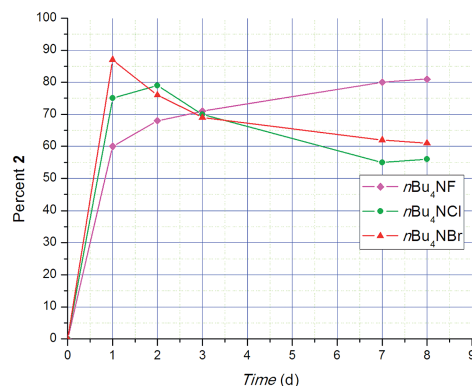
Nucleophiles other than iodide and pyrrolidine, such as tetrabutylammonium fluoride, chloride, and bromide, can also induce the deiodination of compound **1** (Figure 5). As indicated by ^1H NMR spectroscopy, the reaction of diiodoalkene **1** with tetrabutylammonium chloride or bromide resulted in the formation of the byproduct 4-chloro-5-iodo-4-octene (**6**) or 4-bromo-5-iodo-4-octene (**7**), respec-

Base-Induced Dehalogenation of (*E*)-DiiodoalkenesTable 4. Elimination of iodine from alkene **1** in the presence of substoichiometric pyrrolidine.^[a]

Days	Conversion [%]	
	0.25 equiv. ^[b]	0.5 equiv. ^[c]
0	0	0
1	50	68
2	58	75
3	58	75

[a] Reagents and conditions: 0.275 M alkene **1**, [D₅]PhNO₂, dark, room temp. [b] 0.137 M pyrrolidine. [c] 0.069 M pyrrolidine.

tively, with a corresponding reduction in the yield of alkyne **2**. These products indicate reversible dehalogenation, with a much lower reactivity of the chloriodo- and bromiodoalkenes. The reaction with tetrabutylammonium fluoride did not lead to the formation of the fluoroiodoalkene, but the deiodination under these conditions was much slower than with the other halides. Of all the nucleophiles tested, the iodide ion promotes the fastest reaction.

Figure 5. Quantity of alkyne **2** produced by fluoride, chloride, and bromide-induced deiodination.

The use of potassium halide salts in place of tetrabutylammonium halides resulted in identical behavior, as long as 18-crown-6 was added to the reaction mixture to solubilize the salt (Table 5). On the other hand, as expected, the non-nucleophilic salts KPF₆ and KClO₄ did not induce deiodination in **1**. The deiodination of compound **1** by potassium hydroxide in the presence of 18-crown-6 in [D₅]nitrobenzene was rapid and went to completion. However, in [D₄]methanol, there was no reaction with KOH after 2 days, consistent with the results for both pyrrolidine and tetrabutylammonium iodide in protic solvents.

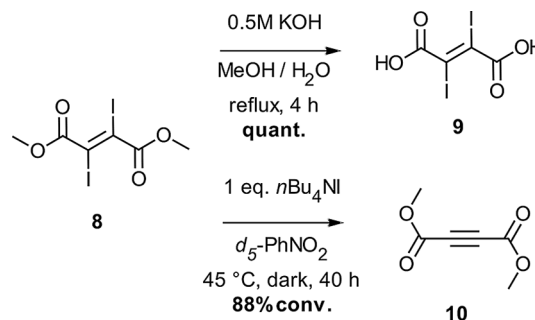
Diester **8** presents a particularly interesting case of orthogonal reactivity. Shah et al.^[26] reported the nearly quantitative hydrolysis of **8** in an aqueous alcohol hydroxide system with no observed deiodination, a result that we have

Table 5. Elimination of iodine from alkene **1** by using potassium salts.^[a]

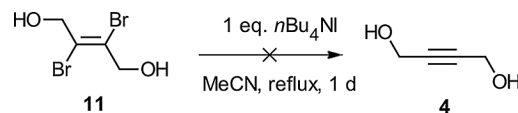
Salt	Equiv.	Solvent	Elimination	Completion	Time [d] ^[b]
KI	1	[D ₅]PhNO ₂	yes	yes	1
KI	1	toluene	no	no	7 ^[c]
KBr	1	[D ₅]PhNO ₂	yes	no	3 ^[d]
KBr	1	toluene	no	no	5
KClO ₄	1.1	MeNO ₂	no	no	7
KPF ₆	1	MeNO ₂	no	no	7
KOH	1.1	[D ₅]PhNO ₂	yes	yes	1

[a] Reagents and conditions: *x* equiv. salt, *x* equiv. 18-crown-6, room temp., dark. [b] By TLC [silica/hexanes, *R_f* of **1** = 0.75, then silica/hexanes/ethyl acetate (3:1), *R_f* of **2** = 0.65]. [c] Approximately half the KI remained dissolved. [d] Observation of **7** by NMR spectroscopy.

reproduced in our laboratory. However, compound **8** underwent complete deiodination to give the alkyne diester **10** when heated with tetrabutylammonium iodide in [D₅]nitrobenzene (Scheme 5).

Scheme 5. Orthogonal reactivity of diiododiester **8**.

In contrast to the diiodoalkenes tested, dibromoalkene **11** did not undergo dehalogenation under the conditions studied here. Mixing dibromide **11** with tetrabutylammonium iodide in acetonitrile resulted in no reaction, even when heated at reflux for a full day (Scheme 6).

Scheme 6. Probing the reaction between dibromoalkene **11** and tetrabutylammonium iodide.

Computational modeling of reactions with a large solvent dependence is notoriously difficult, and we have not attempted to carry out extensive calculations on this system. Rudimentary modeling at the Hartree–Fock, DFT, or MP2 level provided similar transition states for the gas-phase concerted reaction of (*E*)-diiodoethene and iodide ion (see Figures S7 and S8 in the Supporting Information). We also evaluated an alternative stepwise mechanism, analogous to an E1cb mechanism, in which the iodide first attacks, removing one iodine from the substrate, leading to the formation of a carbanion. However, in these calcula-

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tions, the carbanion intermediate is not a stationary point, dissociating directly to acetylene and iodide ion (see Figure S9 in the Supporting Information).

Conclusions

Diiodoalkenes reacted with a variety of Lewis bases to eliminate iodine and form the corresponding alkyne. The reaction follows a concerted bimolecular mechanism, analogous to the E2 reaction, with nucleophilic attack on one iodine precipitating elimination of the other as iodide. Stronger nucleophiles, such as iodide, reacted faster than stronger bases, such as pyrrolidine, which indicates that the nucleophilicity of the Lewis base is a better predictor of reactivity than Brønsted basicity, and the choice of solvent strongly influenced the rate. The reaction is not catalytic because the nucleophile reacted with the byproduct I_2 to form an inactive species. These new insights suggest the complete carbonization of PIDA may be possible under mild conditions by using a simple halide salt in a polar aprotic solvent.

Experimental Section

General Procedures: Air was purged from the NMR tubes used for the kinetic experiments by displacement with argon gas prior to the addition of any reagents. All other experiments were conducted in closed small vials or NMR tubes under atmospheric conditions. Prior to insertion in the spectrometer, the reaction mixture was kept in the dark by wrapping aluminium foil around the NMR tube. The temperature of the NMR kinetic experiments was held constant at 25 °C by using a standard probe temperature controller. The temperature of the UV/Vis kinetic experiments was ambient. To determine the relative concentrations of starting material and product, peaks corresponding to alkene **1** and alkyne **2** were integrated; peak area overlap was not an issue. These integrals were compared and the fractions of **1** and **2** were calculated to determine the percentage conversion. All solvents and reagents were used without further purification. UV/Vis absorption spectra were collected with a Jasco V630 spectrophotometer. Kinetic NMR data were collected with a Bruker Avance 500 spectrometer equipped with CryoProbe Prodigy, and were analyzed using Mestrenova software.

For the kinetics studies, it was of the utmost importance to measure out the quantities of iodine and pyrrolidine carefully, given the small scale of the reactions reported here. All kinetic experiments were conducted by using solutions prepared in volumetric flasks to ensure the concentrations could be accurately determined. Small deviations in reagent concentrations were found to markedly affect conversion percentages.

(4*E*)-4,5-Diiodooct-4-ene (**1**) and dimethyl (2*E*)-2,3-diiodobut-2-enedioate (**8**) were prepared according to the procedure of Terentev et al.^[27] (*E*)-2,3-Diiodobut-2-ene-1,4-diol (**3**) was prepared according to the procedure of Hollins and Campos.^[28] All other starting materials were used as purchased. The spectral data for oct-4-yne (**2**), but-2-yne-1,4-diol (**4**), and dimethyl acetylenedicarboxylate (**10**), and *trans*-2,3-dibromobut-2-ene-1,4-diol (**11**) matched the corresponding spectra from the Spectral Database for Organic Compounds.^[29] The NMR spectra for (*E*)-4-chloro-5-iodooct-4-ene (**6**) matched the spectroscopic data reported by Organ et al.^[18]

Preparative-Scale Synthesis of (*E*)-4-Bromo-5-iodooct-4-ene (7**):** A 1 M IBr solution in CH_2Cl_2 (4.5 mL, 4.5 mmol) was added to an argon-flushed and aluminium-foil-wrapped round-bottomed flask equipped with a magnetic stirring bar. Compound **2** (0.60 mL, 0.4506 g, 4.09 mmol) was then added. After 1 d, CH_2Cl_2 (20 mL) was added to the solution. The organic layer was washed with 5% $Na_2S_2O_3$ (20 mL \times 2) and then deionized water (30 mL \times 2). The organic layer was then dried with anhydrous $MgSO_4$ and filtered before rotary evaporation. A short plug of silica, using 100% hexanes as the eluent, was used to separate alkyne **2** from the resulting clear pale-yellow liquid. The product was an inseparable mixture of *cis* and *trans* isomers of alkene **7**. 1H NMR (400 MHz, $CDCl_3$): δ = 2.73–2.65 (m, 4 H), 1.67–1.54 (m, 4 H), 1.00–0.90 (m, 6 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 122.7, 121.7, 102.0, 100.0, 60.3, 52.6, 47.5, 46.9, 42.5, 34.5, 21.6, 20.9, 13.0, 11.8 ppm. MS (EI): m/z = 316 $[M]^+$, 318. HRMS (EI): calcd. for $C_8H_{14}IBr$ $[M]^+$ 315.93238; found 315.93257. The NMR spectra are provided in the Supporting Information.

Testing for Triiodide-Induced Iodine Elimination: nBu_4NI (0.0510 g, 0.137 mmol) and iodine (0.0348 g, 0.137 mmol) were added to an aluminium-foil-wrapped vial. $[D_5]$ Nitrobenzene (1.0 mL) was added and the vial was shaken. The mixture was subjected to sonication for 15 s to ensure homogeneity. Compound **1** (20.1 μ L, 0.0502 g, 0.137 mmol) was then added and the vial was shaken. The contents of the vial were transferred to an NMR tube and an initial NMR spectrum was recorded. A 1H NMR spectrum was measured on a daily basis for 1 week, but showed no change from the initial spectrum of compound **1**.

Measuring Triiodide Concentration by UV/Vis Spectroscopy: The standard curve shown in Figure S10 in the Supporting Information was prepared as follows: A stock triiodide solution of 1.00×10^{-2} M was prepared by dissolving nBu_4NI (0.1847 g, 0.500 mmol) and I_2 (0.1269 g, 0.500 mmol) in acetonitrile to a volume of 50 mL in a 50-mL volumetric flask. Working solutions were prepared from the stock solution by serial dilution (1.00×10^{-4} , 2.00×10^{-4} , 3.00×10^{-4} , 4.00×10^{-4} , 5.00×10^{-4} , and 8.00×10^{-4} M).

nBu_4NI (0.1016 g, 0.275 mmol) was loaded into a 1-mL volumetric flask. Acetonitrile was introduced into the flask just below the mark to dissolve nBu_4NI , followed by compound **1** (0.1002 g, 0.275 mmol). The solution was quickly diluted to the mark, shaken, and an aliquot of 36.0 μ L was removed as an initial data point. The aliquot was diluted in a 25-mL volumetric flask with acetonitrile for UV/Vis analysis. The UV/Vis experiment was set-up as a double-beam experiment with an acetonitrile blank. Aliquots of 36.0 μ L were removed and diluted at the indicated intervals in Figure 3. Absolute concentrations were then calculated based on the measured standard curve.

Testing for Iodination by Triiodide: nBu_4NI (0.0510 g, 0.137 mmol) and iodine (0.0348 g, 0.137 mmol) were added to an aluminium-foil-wrapped vial. $[D_5]$ Nitrobenzene (1.0 mL) was added and the vial was shaken. The mixture was subjected to sonication for 15 s to ensure homogeneity and then allowed to stand for 24 h. Compound **2** (20.1 μ L, 0.0151 g, 0.137 mmol) was then added and the vial was shaken. The contents of the vial were transferred to an NMR tube and an initial NMR spectrum was recorded. A 1H NMR spectrum was recorded on a daily basis for 3 d, but showed no change from the initial spectrum of compound **2**.

Procedure for Dehalogenation by nBu_4NF : TBAF hydrate (0.0358 g, 0.137 mmol) was added to an aluminium-foil-wrapped vial. $[D_5]$ -Nitrobenzene (0.5 mL) was added, and the vial was shaken. The mixture was subjected to sonication for 15 s to ensure homogeneity. Compound **1** (0.0502 g, 0.137 mmol) was then added, and the vial

was shaken. The contents of the vial were transferred to a NMR tube, and an initial NMR spectrum was recorded. ^1H and ^{13}C NMR spectra were collected on a daily basis for 8 d. The reaction mixture was then left in the NMR tube wrapped in aluminium foil. The triplet corresponding to **2** at $\delta = 2.04$ ppm and the multiplet corresponding to **1** at 2.45–2.50 ppm were integrated. The conversion was calculated by using the integral of **2** expressed as a percentage of the total integral sum. A change in color from pale yellow to a deep reddish-brown was observed. The NMR spectra are given in the Supporting Information.

Procedure for Dehalogenation by $n\text{Bu}_4\text{NCl}$: TBACl (0.0381 g, 0.137 mmol) was added to an aluminium-foil-wrapped vial. $[\text{D}_5]$ -Nitrobenzene (0.5 mL) was added, and the vial was shaken. The mixture was subjected to sonication for 15 s to ensure homogeneity. Compound **1** (0.0502 g, 0.137 mmol) was then added, and the vial was shaken. The contents of the vial were transferred to an NMR tube, and an initial NMR spectrum was recorded. ^1H and ^{13}C NMR spectra were collected on a daily basis for 8 d. The reaction mixture was then left in the NMR tube, wrapped in aluminium foil. The triplet corresponding to **2** at $\delta = 2.04$ ppm and the multiplet at 2.45–2.58 ppm corresponding to **1** at the start of experiment and to **6** at the end of the experiment were integrated to determine the conversion. A change in color from pale yellow to a deep reddish-brown was observed. The NMR spectra are given in the Supporting Information.

Procedure for Dehalogenation by $n\text{Bu}_4\text{NBr}$: TBABr (0.0442 g, 0.137 mmol) was added to an aluminium-foil-wrapped vial. $[\text{D}_5]$ -Nitrobenzene (0.5 mL) was added, and the vial was shaken. The mixture was subjected to sonication for 15 s to ensure homogeneity. Compound **1** (0.0502 g, 0.137 mmol) was then added, and the vial was shaken. The contents of the vial were transferred to a NMR tube, and an initial NMR spectrum was recorded. ^1H and ^{13}C NMR spectra were collected on a daily basis for 8 d. The reaction mixture was then left in the NMR tube, wrapped in aluminium foil. The triplet corresponding to **2** at $\delta = 2.04$ ppm and the multiplet at 2.45–2.58 ppm corresponding initially to compound **1** and later to compound **7** were integrated to calculate the conversion. A change in color from pale yellow to a deep reddish-brown was observed. The NMR spectra are given in the Supporting Information.

Testing for KOH-Induced Iodine Elimination in $[\text{D}_4]\text{MeOD}$: Compound **1** (20.0 μL , 0.0501 g, 0.138 mmol) was added to MeOH (0.5 mL) in a round-bottomed flask equipped with a magnetic stirring bar. An aqueous solution of 0.5 M KOH (0.83 mL, 0.4 mmol) was then added to the flask. After 48 h, it was neutralized by the addition of an aq. 0.5 M HCl solution (0.83 mL). The solution was extracted with hexanes (1.0 mL \times 3). The organic phase was washed with brine (1.0 mL \times 3) and then dried with MgSO_4 . The solvent was removed in vacuo. The residue was dissolved in $[\text{D}_5]$ -nitrobenzene for NMR analysis. Only compound **1** was observed in the ^1H NMR spectrum.

Triethylamine-Induced Iodine Elimination: Triethylamine (0.0139 g, 0.137 mmol) was placed in an aluminium-foil-wrapped vial, $[\text{D}_5]$ -nitrobenzene (0.5 mL) was added, and the vial was shaken. Compound **1** (0.0502 g, 0.137 mmol) was then added and the contents of the vial were mixed by shaking. The contents of the vial were transferred to an NMR tube, and an initial NMR spectrum was recorded. A ^1H NMR spectrum was collected after 1 d, and only compound **2** was observed. A change in color from pale yellow to a deep reddish-brown was observed.

$n\text{Bu}_4\text{NI}$ -Induced Iodine Elimination from Diester **8:** $n\text{Bu}_4\text{NI}$ (0.0510 g, 0.137 mmol) and $[\text{D}_5]\text{PhNO}_2$ (0.5 mL) were added to an aluminium-foil-wrapped vial. The mixture was subjected to soni-

ation for 15 s to ensure homogeneity. Compound **8** (0.0546 g, 0.137 mmol) was then added, and the vial was shaken. After a few minutes, a white solid precipitated out. The vial was heated and kept at 45 $^\circ\text{C}$ to keep the white solid in solution. ^1H NMR analysis was conducted after 40 h, and showed compound **10** with a trace amount of **8**.

$n\text{Bu}_4\text{NI}$ -Induced Iodine Elimination from Diol **3:** Compound **3** (0.0469 g, 0.138 mmol), $[\text{D}_6]$ acetone (0.5 mL), and tetrabutylammonium iodide (0.0510 g, 0.138 mmol) were mixed together in an aluminium-foil-wrapped vial. The mixture was heated at reflux to dissolve all components. The reaction mixture was then cooled to room temperature and allowed to stand without stirring in the dark at room temperature for 48 h. ^1H and ^{13}C NMR analysis showed 96% conversion to compound **4**.^[29]

Reaction of $n\text{Bu}_4\text{NI}$ and Diol **11:** Compound **11** (0.339 g, 1.38 mmol) was added to acetonitrile (5 mL) in a round-bottomed flask equipped with a magnetic stirring bar. Tetrabutylammonium iodide (0.510 g, 1.38 mmol) was added to the solution, and the reaction mixture was heated to 80–85 $^\circ\text{C}$. After 1 d the solvent was removed in vacuo. The crude sample was dissolved in $[\text{D}_5]$ nitrobenzene and subjected to ^1H NMR analysis, which showed only compound **11**.^[29]

Testing for Iodopyrrolidinium-Induced Iodine Elimination: Iodine (0.140 g, 0.550 mmol) was mixed with pyrrolidine (45.2 μL , 0.0391 g, 0.550 mmol) and $[\text{D}_5]$ nitrobenzene in a 1-mL volumetric flask. This solution was allowed to stand at room temperature in the dark for 24 h to ensure complete reaction of iodine and pyrrolidine. An aliquot of 0.50 mL of this stock solution was placed in a clean 1-mL volumetric flask, followed by the addition of compound **1** (40.0 μL , 0.1000 g, 0.275 mmol). The solution was diluted with $[\text{D}_5]$ nitrobenzene, immediately transferred to an NMR tube, and an initial spectrum was collected after 15 min. The mixture was observed by ^1H and ^{13}C NMR for 3 d. Compound **1** was found to remain stable over the 3-day period.

Kinetic Investigation of the Reaction Between Iodine and Pyrrolidine: Iodine (0.1396 g, 0.550 mmol) was dissolved in $[\text{D}_5]$ nitrobenzene in a 2-mL volumetric flask. A 1.0-mL aliquot of the 0.275 M solution was transferred to an NMR tube. Pyrrolidine (22.6 μL , 0.0196 g, 0.275 mmol) was then added to the NMR tube, and the tube was shaken. The time elapsed between the addition of pyrrolidine and collection of the first ^1H NMR spectrum was 3 min. A total of 55 spectra were collected at 3.3 min intervals to obtain a kinetic profile (see Figure S6 in the Supporting Information). A change in color from pale yellow to a deep reddish-brown was observed.

Reaction of Compound **2 and Iodine:** $[\text{D}_5]$ Nitrobenzene (0.6 mL) and iodine (0.0350 g, 0.138 mmol) were added to an aluminium-foil-wrapped vial. The mixture was subjected to sonication for 30 min to ensure homogeneity. Compound **2** (0.0151 g, 0.137 mmol) was then added, and the vial was shaken. The contents of the vial were transferred to an NMR tube and an initial NMR spectrum was collected. The time elapsed between mixing of reagents and collection of the initial spectrum was 7 min. A ^1H NMR spectrum was recorded every 15 min for 12.5 h. At 12.5 h the reaction showed 95% conversion of compound **2** into compound **1**.

Representative Procedure for Experiments with Substoichiometric $n\text{Bu}_4\text{NI}$: $n\text{Bu}_4\text{NI}$ (0.0442 g, 0.137 mmol) was added to a 1-mL volumetric flask and diluted with $[\text{D}_5]$ nitrobenzene. The solution was thoroughly shaken and then subjected to sonication for 15 s to ensure homogeneity. An aliquot (0.5 mL) of this solution was then added to an NMR tube. The sample was inserted into the NMR instrument for locking and shimming, then ejected so that com-

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pound **1** (20.0 μ L, 0.0501 g, 0.137 mmol) could be added to the tube. ^1H NMR spectra were recorded initially and after 24 h. The triplets at $\delta = 2.53$ ppm corresponding to **1** and at 2.06 ppm corresponding to **2** were integrated to calculate the conversion. A change in color from pale yellow to a deep reddish-brown was observed.

Representative Procedure for Experiments with Substoichiometric Pyrrolidine: Pyrrolidine (22.6 μ L, 0.0196 g, 0.275 mmol) was added to a 1-mL volumetric flask and diluted with $[\text{D}_5]$ nitrobenzene. The solution was thoroughly shaken and then subjected to sonication for 15 s to ensure homogeneity. A 1-mL syringe was used to extract 0.50 mL of the solution, which was diluted in another 1-mL volumetric flask to make a stock solution with a concentration of 0.14 M. An aliquot of 0.50 mL was then extracted from the diluted solution and introduced into an NMR tube. Compound **1** (0.0501 g, 0.137 mmol) was then added by syringe into the NMR tube, and an initial ^1H NMR spectrum was recorded. A ^1H NMR spectrum was collected on a daily basis for 3 d. In between, the reaction mixture was kept in the NMR tube, covered with aluminium foil. The triplets at $\delta = 0.83$ ppm corresponding to alkene **1** and at 0.92 ppm corresponding to alkyne **2** were integrated to determine the percentage of compound **2**. A change in color from pale yellow to a deep reddish-brown was observed.

Representative Procedure for Iodine Elimination by Potassium Salts: KBr (0.0160 g, 0.137 mmol) and 18-crown-6 (36.1 mg, 0.137 mmol) were added to an aluminium-foil-wrapped vial. Toluene (1 mL) was added, and the vial was shaken. The mixture was subjected to sonication for 1 min to ensure homogeneity. Compound **1** (0.0501 g, 0.137 mmol) was then added, and the vial was shaken. The reaction was monitored by TLC (SiO_2 /hexanes) for 5 d, with no observed change (compound **1** has $R_f = 0.7$, whereas compound **2** has $R_f = 0$ under these conditions). In addition, there was no observed change in color.

Supporting Information (see footnote on the first page of this article): Kinetic NMR spectroscopic data, computational details, and additional NMR spectra.

Acknowledgments

The authors thank Dr. Vladimir Fainzilberg for helpful discussions. The authors thank the National Science Foundation (CHE-0911540) for support of this research.

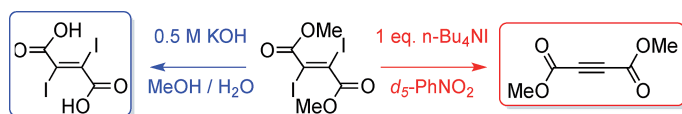
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Received: July 25, 2014

Published Online: ■

Dehalogenation of Diiodoalkenes



A diiodoalkene diester undergoes hydrolysis on treatment with KOH, but eliminates iodine on reaction with iodide salts. This orthogonal reactivity is just one example of

the interesting chemistry that arises from the reactions of diiodoalkenes with Lewis bases. The mechanism for this mild reaction has been studied experimentally.

D. Resch, C. H. Lee, S. Y. Tan, L. Luo,
N. S. Goroff* 1–9

Mechanism and Scope of the Base-Induced
Dehalogenation of (*E*)-Diiodoalkenes



Keywords: Reaction mechanisms / Lewis
bases / Iodine / Elimination