3742 J. Org. Chem. **1994**, *59*, 3742−3743

Triiodoethylene: A Product of the Thermal Decomposition of Diiodoacetylene

S. Edward Krikorian*,[1a] and William R. Moore[1b]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received January 25, 1994

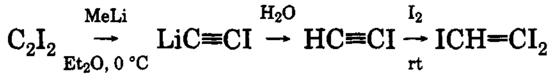
During a study of the thermal decomposition of diiodoacetylene (C_2I_2) in refluxing hydrocarbon solvents at 150 °C, a high-boiling reddish oil was isolated from each of the reaction mixtures, elemental and spectral analysis of which suggested it to be triiodoethylene. Previous reports of either the thermal decomposition[2,3] or photochemical degradation[4,5] of diiodoacetylene do not mention this compound as a product. Indeed, a search of the literature reveals that triiodoethylene, in fact, has not heretofore been reported or characterized as a discrete chemical entity at all. In the most recent literature to date, only its presence in a mixture along with tetraiodoethylene as a product of a reaction between acetylene and cupric halides has been described,[6] and certain of its thermodynamic properties have been estimated by calculation using group contribution methods.[7] This omission contrasts with the characterization of the other five iodoethylenes and the three other trihaloethylenes, all of which have previously been reported. We wish, therefore, to describe here the isolation, spectral characterization, and proof of structure by synthesis of triiodoethylene obtained as one of the products of the thermal decomposition of C_2I_2 in three different hydrocarbon solvents (cumene, cyclooctane, and *n*-nonane).

Results and Discussion

Refluxing of 1 mmol of C_2I_2 in each of the three solvents (bp 150 °C) for 6 h resulted in reddish-violet solutions. The rate of disappearance of C_2I_2 (monitored by GLC) followed first-order kinetics and was solvent-dependent, the half-life of C_2I_2 being ca. 10 min, 30 min, and 3 h in cumene, cyclooctane, and *n*-nonane, respectively.[8] Monoiodoacetylene (isolated by a gas-sweeping and -trapping train), tetraiodoethylene (isolated as solid crystals), I_2 (determined by titration), and HI (determined by titration and by precipitation as yellow AgI) were readily identified as products of the decomposition of C_2I_2.[8] This evidence plus the presence of solvent-derived products (e.g., α-methylstyrene and dicumyl from cumene and cyclooctyl iodide from cyclooctane) supports the operation of a free-radical reaction initiated by homolysis of a C−I bond of C_2I_2 and followed by attack of the subsequent free radicals produced on hydrogen atoms of the hydrocarbon solvents.

In all of the above reactions, an additional high-boiling product was always detectable using GLC. Clearly, then, this product could not be derived from the solvent. Its isolation by preparative GLC from all three reaction mixtures yielded a red-brown liquid whose IR, NMR, and mass spectra in each case were identical and were consistent with it being *triiodoethylene*. This was deduced by assigning IR absorption bands to =C−H stretching and bending and =C−I stretching modes, by observation of a singlet proton NMR absorption band at a chemical shift of δ 8.5 ppm, and by the appearance of a molecular ion at *m/z* 406 along with a fragmentation pattern in the mass spectrum consistent with this structural assignment (e.g., peaks representing $[M - I]^+$, I_2^+, $[M - I_2]^+$, and I^+). The position of the NMR singlet observed for the lone alkene proton of the isolated triiodoethylene compares with the chemical shift values of δ 7.13 ppm and 6.45 ppm reported for the proton of tribromo- and trichloroethylene, respectively,[9] and with the value 8.08 ppm calculated for triiodoethylene using a table of "additive shielding increments for olefins".[10]

As further proof of the structure of the isolated oil, triiodoethylene was synthesized by the addition of I_2 to monoiodoacetylene prepared by the reduction of diiodoacetylene via a lithium−halogen exchange reaction.



$$C_2I_2 \xrightarrow[\text{Et}_2\text{O, 0 °C}]{\text{MeLi}} \text{LiC}{\equiv}\text{CI} \xrightarrow{H_2O} \text{HC}{\equiv}\text{CI} \xrightarrow[\text{rt}]{I_2} \text{ICH}{=}\text{CI}_2$$

The successful generation of lithioiodoacetylide as an intermediate in this scheme was proven in a trial run by quenching the first reaction with D_2O to yield monoiodoacetylene-*d* and by trapping it with cyclohexanone to yield 1-(iodoethynyl)cyclohexanol.[8] The monoiodoacetylene was confirmed spectrometrically prior to its iodination.[8] The final product was isolated as a pale yellow oil, whose elemental analysis corroborated the molecular formula C_2HI_3 and whose GLC retention time and IR spectrum were identical to those for the product isolated from the thermal decomposition of C_2I_2 in the three solvents.

Triiodoethylene could be expected to arise during the thermal decomposition of C_2I_2 in the solvents employed via either addition of I_2 to monoiodoacetylene (vide supra) or addition of HI to diiodoacetylene. The low calculated dissociation energy of the C−I bond of C_2I_2 (ca. 30 kcal/mol)[8] suggests that homolysis of this bond could serve as the initial source of free radicals, whose subsequent reaction with solvent hydrogen atoms would lead to the reactants (HI, HC≡CI, and I_2) required for generating triiodoethylene. In fact, the feasibility of hydroiodinating C_2I_2 under our experimental conditions was demonstrated by conducting its thermal decomposition in refluxing *n*-nonane with concurrent passage of gaseous HI through the reaction mixture. Under these conditions, consumption of C_2I_2 was complete in 1 h with concomitant rapid production of triiodoethylene, compared to its incomplete consumption even after 6 h in refluxing pure *n*-nonane.

In conclusion, spectral characterization of this product of the thermal decomposition of diiodoacetylene, comparison with an independently synthesized sample thereof, and consideration of the most likely chemistry responsible

---

[1] Present address: (a) Department of Pharmaceutical Sciences, University of Maryland, School of Pharmacy, Baltimore, MD 21201. (b) Department of Chemistry, West Virginia University, Morgantown, WV 26506.

[2] Schenck, R.; Litzendorff, J. *Chem. Ber.* **1904**, *37*, 3453.

[3] Vaughn, T. H.; Nieuwland, J. A. *J. Am. Chem. Soc.* **1932**, *54*, 787.

[4] Emschwiller, G. *C. R. Hebd. Seances Acad. Sci.* **1934**, *198*, 1151.

[5] Tamblyn, J. W.; Forbes, G. S. *J. Am. Chem. Soc.* **1940**, *62*, 99.

[6] Uddeholms Aktiebolag, Neth. Patent 6 510 390, 1966; *Chem. Abstr.* **1966**, *65*, 3744.

[7] Beckwith, W. F.; Fahien, R. W. *Chem. Eng. Prog. Symp. Ser.* **1963**, *59*, 75.

[8] Krikorian, S. E. Ph.D. Thesis, Massachusetts Institute of Technology, Jan 1967.

[9] Tobey, S. W. *J. Org. Chem.* **1969**, *34*, 1281.

[10] Abraham, R. J.; Loftus, P. *Proton and Carbon-13 NMR Spectroscopy*; Heyden: London, 1978; p 18.

0022-3263/94/1959-3742$04.50/0

for the reaction serving as its source all are consistent with the subject compound's identification as triiodoethylene.

Experimental Section

General. Cumene (Eastman) and cyclooctane (Cities Service) were purified by washing with sulfuric acid;[11] *n*-nonane (Aldrich) and α-methylstyrene (Aldrich) were used as received. Methyllithium (0.5–1.0 M) was prepared from CH_3I via lithium–halogen exchange in ether solution[12] and was standardized using a double-titration method.[13] Diiodoacetylene was synthesized by the reaction of acetylene with NaOI,[14] dicumyl by peroxide-induced coupling of cumene,[15] and cyclooctyl iodide by reaction of cyclooctanol with HI.[16]

All reactions were carried out in a nitrogen atmosphere in a 50-mL, side arm, pear-shaped flask fitted with a reflux condenser and containing a glass-covered magnetic stirring bar. The side arm was closed with a silicone rubber no-air stopper through which reagents were added and reaction aliquots removed using a syringe fitted with a 20-gauge needle.

Analytical GLC was performed using a Wilkens Aerograph Model 600-B gas chromatograph equipped with a flame ionization detector (FID) and using a 2-ft × $^1/_8$-in. glass column packed with 1% Carbowax 20M on 80/100 mesh Chromosorb W and operated at 100 °C. Preparative GLC was performed using a $^1/_4$-in. version of this same column in an F & M Model 810 gas chromatograph equipped with an FID and a 10:1 effluent splitter. The desired eluates were condensed in capillary tubes cooled in a dry ice–acetone bath.

Infrared and ^1H NMR spectra were obtained in CCl_4 solution using a Perkin-Elmer Model 337 IR spectrometer and Varian Model A-60 NMR spectrometer, respectively. EI (70 eV) mass spectra were recorded on neat samples using a CEC Model 21-130 mass spectrometer. Elemental analysis was performed by S. M. Nagy and associates (MIT, Cambridge, MA).

Procedure for Conducting the Thermal Decomposition of Diiodoacetylene. A solution of 0.278 g (1.0 mmol) of C_2I_2 in 7 mL of the solvent (cumene, cyclooctane, or *n*-nonane) was heated at reflux (oil bath temp 165 °C) with stirring for 6 h. During this time, 0.1-mL aliquots of the reaction mixture were periodically withdrawn and analyzed by GLC for starting material and products. Both the consumption of C_2I_2 and production of a number of products, one of which was common to all three of the reaction systems, were discerned using this procedure.

Solvent-derived products were identified, after isolation by GLC, by comparison of their IR spectra and GLC retention times with those for authentic specimens obtained either commercially (α-methylstyrene) or by synthesis (dicumyl, cyclooctyl iodide). Because of the slow rate of decomposition of C_2I_2 in *n*-nonane and the resulting low product yields, no attempt was made to characterize products derived from this solvent.

In a typical reaction using cumene as the reaction medium, yields of the primary products from the decomposition of 1.0 mmol of C_2I_2 (fully consumed) were 0.2 mmol of $HC{\equiv}CI$ (by GLC), 0.2 mmol of $I_2C{=}CI_2$ (isolated), 0.3 mmol of α-methylstyrene (by GLC), 15 mg of the "common" compound (isolated) (0.04 mmol of $IHC{=}CI_2$), 0.06 mmol of I_2 (by titration), 0.06 mmol of HI (by titration), and 10 mg of a black amorphous solid (isolated). Thus, ca. 45% of the "C_2" content and ca. 65% of the iodine content of the original C_2I_2 are accounted for, not counting any contributions of "C_2" and iodine to the composition of the amorphous solid.

Isolation and Spectral Analysis of "Common" Compound from Thermal Decomposition of C_2I_2. Each of the above three reaction mixtures was concentrated by distillation through a Holtzmann spiral-wire column at the water pump (bp 34 °C/11 mm). The residual oil from each reaction still retained a GLC peak representing the "common" product, which was then collected by preparative GLC. The capillary tubes containing the reddish-brown oil were washed down with a few microliters of CCl_4, and after centrifugation the resulting solutions were transferred in turn to a small-volume 0.1-mm-pathlength NaCl IR cavity cell using a 10-μL syringe. The IR spectra of all three recovered oils proved to be identical: $\bar{\nu}$ 3050, 1190, 720, 605 cm^{-1}. The CCl_4 solution from the IR cell was then transferred directly to a spherical cavity NMR microcell using a long-needle microliter syringe. The ^1H NMR spectrum of the product from each of the three reactions yielded a single sharp absorption band at δ 8.5 ppm (external Me_4Si as reference). Finally, the CCl_4 solution was transferred from the NMR tube to a capillary tube, solvent was removed by warming in a water bath, and the mass spectrum of the residual oil was obtained using the direct-probe inlet system of the spectrometer: MS *m/z* (rel intensity) 127 (100, I^+), 152 (27, $[HC{\equiv}CI]^+$), 254 (22, I_2^+), 279 (20, $[ICH{=}CI]^+$), 406 (9, M^+).

Thermal Decomposition of C_2I_2 in the Presence of HI. The above reaction in *n*-nonane as solvent was repeated but with the following modification: the top of the reflux condenser was connected via rubber tubing to the stem of a glass funnel inverted over a beaker of water to serve as a gas trap. The no-air stopper in the side arm of the reaction flask was replaced by a one-hole rubber stopper containing a glass tube which reached to the bottom of the flask. The tube was in turn connected via silicone rubber tubing to an HI generator (a 200-mL, three-neck, round-bottom flask fitted with an addition funnel, reflux condenser, and nitrogen inlet tube for sweeping gaseous HI into the reaction flask). The generator was charged with 50 g of red phosphorus, and a solution of 100 g of I_2 in 50 g of 57% aqueous HI was added from the addition funnel at such a rate as to cause a steady stream of gaseous HI[17] to pass into the reaction flask containing the solution of C_2I_2 in *n*-nonane. The latter was then refluxed with stirring and continuous passage of HI for a total of 4 h. GLC analysis of reaction aliquots revealed that consumption of C_2I_2 was complete within 1 h, and a peak representing triiodoethylene (vide infra) reached maximum intensity within 30 min and then gradually diminished in intensity over the remainder of the reaction period. After 4 h, flow of HI was stopped by addition of water to the generator flask.

Triiodoethylene. To an ice-cold solution of 0.278 g (1.0 mmol) of C_2I_2 in 7 mL of dry ether was added dropwise with stirring 1.8 mL of a 0.55 M solution (1.0 mmol) of CH_3Li in ether over a period of 2 h. After the solution was warmed to room temperature, stirring was continued for an additional 30 min, and the reaction was then quenched by addition of 2 mL of water. The ether layer containing $HC{\equiv}CI$ (GLC) was dried over anhyd Na_2SO_4, and a solution of 0.258 g (1.0 mmol) of I_2 in 2 mL of ether was added. The mixture was stirred in the dark at room temperature for 72 h. The reaction was then stopped by adding 2 mL of 0.2 M $Na_2S_2O_3$ solution, and the ether layer was washed with water and dried over Na_2SO_4. GLC analysis of the solution revealed a peak having the same retention time as the "common" product isolated from the thermal decomposition of C_2I_2 in the three solvents. Evaporation of solvent at the water pump yielded a brownish oil, which was flash-distilled in a small Hickman still at 0.02 Torr using an air bath maintained at 40–60 °C to afford the product as a yellow oil (40 mg, 10%): IR (CCl_4) $\bar{\nu}$ 3050, 1190, 720, 605 cm^{-1}. Anal. Calcd for C_2HI_3: I, 93.83. Found: I, 94.17.

---

[11] Bartlett, P. D.; Benzing, E. P.; Pincock, R. E. *J. Am. Chem. Soc.* **1960**, *82*, 1762.

[12] King, B. J. Ph.D. Thesis, Massachusetts Institute of Technology, Aug 1965.

[13] Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* **1964**, *2*, 447.

[14] Dehn, W. H. *J. Am. Chem. Soc.* **1911**, *33*, 1598.

[15] Farmer, E. H.; Moore, C. G. *J. Chem. Soc.* **1951**, 131.

[16] Ruzicka, L.; Plattner, R. A.; Wild, H. *Helv. Chim. Acta* **1945**, *28*, 395.

[17] Vogel, A. I. *A Textbook of Practical Organic Chemistry*, 3rd ed.; Longmans, Green: London, 1956; p 182.