CHEMISTRY LETTERS, pp. 2245-2248, 1992.

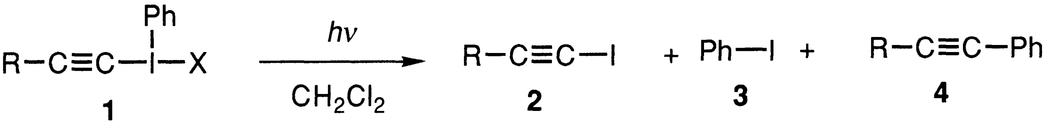
Photolysis of Alkynyl(phenyl)iodonium Salts. Remarkable Solvent Effect and Generation of Acids

Tsugio KITAMURA,* Toshimasa TANAKA, and Hiroshi TANIGUCHI*
Department of Chemical Science and Technology, Faculty of Engineering,
Kyushu University 36, Hakozaki, Fukuoka 812

Photolysis of alkynyl(phenyl)iodonium salts in CH_2Cl_2 resulted in major formation of iodobenzene, while the photolysis in EtOH, Et_2O, or THF gave iodoalkynes as the main product. In addition to the organic products, acids were generated almost quantitatively by the photolysis and initiated polymerization of styrene.

Alkynyl(phenyl)iodonium salts have recently become valuable reagents in organic synthesis, especially as alkynylating reagents.$^{1)}$ On the other hand, much attention has been paid to onium salts such as aryldiazonium, triarylsulfonium, and diaryliodonium salts because they act as photoinitiators for cationic polymerization$^{2)}$ and as photochemical acid generators for chemical amplication in imaging systems.$^{3)}$ Such developement of the chemistry of the onium salts allows us to study photochemical decomposition of alkynyl(phenyl)iodonium salts. To date, photolysis of diaryliodonium salts has been studied$^{4,5)}$ but there are no reports on photolysis of alkynyl(phenyl)iodonium salts as far as we know. Hence, we want to report on photochemical decomposition of alkynyl(phenyl)iodonium salts, which shows a remarkable solvent effect and acts as an acid generator.

A solution of alkynyl(phenyl)iodonium tosylates **1** (X = OTs) (0.2 mmol) in CH_2Cl_2 (10 ml) was irradiated at 15 ^{o}C for 10 min in a merry-go-round apparatus equipped with a Pyrex-filtered high-pressure Hg lamp (400 W). After the irradiation, the mixture was extracted with hexane and the hexane extract was analyzed by GC-MASS and by GC retention time compared with the authentic samples. The identified volatile products were 1-iodo-1-alkynes **2**, iodobenzene **3**, and 1-phenyl-1-alkynes **4**. The major product was iodobenzene **3** in all cases (entries 1-4). This result indicates that the fission of the alkynyl carbon-iodine bond is easy rather than that of the phenyl-iodine bond under photolytic conditions and the substituent R does not affect significantly on the product distribution.



$$\underset{\mathbf{1}}{R{-}C{\equiv}C{-}\overset{\overset{Ph}{|}}{I}{-}X} \xrightarrow[CH_2Cl_2]{h\nu} \underset{\mathbf{2}}{R{-}C{\equiv}C{-}I} + \underset{\mathbf{3}}{Ph{-}I} + \underset{\mathbf{4}}{R{-}C{\equiv}C{-}Ph}$$

a: R = *t*-Bu, **b**: R = *n*-Bu, **c**: R = *n*-Hex, **d**: R = Ph
X = OTs, OTf, ClO_4

Table 1. Products from Photolysis of Alkynyl(phenyl)iodonium Salts **1**

Entry		Iodonium salt **1**		Solvent	Proudct yield/%[a)]			Φ_{dis}[c)]
		R	X		**2**	**3**	**4**	
1	**1a**	*t*-Bu	OTs	CH_2Cl_2	12	51	8	0.58
2	**1b**	*n*-Bu	OTs	CH_2Cl_2	20	56	12	
3	**1c**	*n*-Hex	OTs	CH_2Cl_2	16	45	9	
4	**1d**	Ph	OTs	CH_2Cl_2	19	49	4	
5	**1a**	*t*-Bu	OTs	benzene[b)]	27	51	39	
6	**1a**	*t*-Bu	OTs	hexane[b)]	15	48	14	
7	**1a**	*t*-Bu	OTs	EtOH	52	10	trace	1.71
8	**1a**	*t*-Bu	OTs	Et_2O	69	20	trace	
9	**1a**	*t*-Bu	OTs	THF	62	9	trace	
10	**1a**	*t*-Bu	OTf	CH_2Cl_2	10	60	8	
11	**1a**	*t*-Bu	OTf	EtOH	59	4	1	
12	**1a**	*t*-Bu	ClO_4	CH_2Cl_2	19	65	trace	
13	**1a**	*t*-Bu	ClO_4	EtOH	55	2	2	

a) GC yields based on iodonium salts **1**. b) Solvent described (8 ml) and CH_2Cl_2 (2 ml). c) Quantum yields were measured by pottasium ferric trioxalate actinomer.

As it has been discussed on photolysis of diaryliodonium salts, there are two possible cleavages of the carbon-iodine(III) bond, that is, heterolysis[5)] and homolysis.[4)] If the major process is heterolysis of the carbon-iodine bond, alkynyl cations are generated because the fission of the alkynyl carbon-iodine bond preferentially takes place rather than that of the another bond. However, since alkynyl cations are much less stable than phenyl cation,[6)] the heterolytic cleavage should be minor. Accordingly, it is considered that the products **2** and **3** are directly derived from the iodine-containing part generated by the homolytic cleavage of the carbon-iodine bond. The major formation of PhI is consistent with the ease of the fission of the alkynyl carbon-iodine bond which is attributable to a high ionization potential of iodoacetylene.[7)]

A remarkable solvent effect on decomposition of *t*-butylethynyl(phenyl)iodonium tosylate **1a** (X = OTs) was observed (entries 5-9). A similar cleavage pattern of the carbon-iodine bonds was observed in the photolysis in benzene and hexane. However, in the cases of solvent such as EtOH, Et_2O, or THF the decomposition pattern was quite different and the major product was iodoalkyne **2**. This result suggests that the decomposition occurs in a different mechanism from that in the other solvents. Quantum yields of the decomposition were 0.58 in CH_2Cl_2 and 1.71 in EtOH (entries 1 and 7). This means that an electron transfer process is in part involved and produces a 9-I-2 σ-iodinanyl radical which causes the cleavage of the phenyl-iodine bond favorably,[8] as the electron transfer process has been discussed in the photolysis of diaryliodonium salts.[4,5] The involvement of the decomposition via an electron transfer process increases the yield of iodoacetylene and the quantum yield. Similarly, photolysis of *t*-butylethynyl(phenyl)iodonium triflate **1a** (X = OTf) or perchlorate **1a** (X = ClO_4) showed the solvent effect described above (entries 10-13).

Brϕnsted acids are generally generated by photolysis of diaryliodonium salts.[2-5] The yield of *p*-toluenesulfonic acid was determined by absorption spectroscopic method using sodium *p*-nitrophenoxide in the photolysis of *t*-butylethynyl(phenyl)iodonium tosylate **1a** (X = OTs). Formation of the acid by photolysis of **1a** (X = OTs) in CH_2Cl_2 or in EtOH is almost complete within 10 min-irradiation in CH_2Cl_2 or within 5 min-irradiation in EtOH, respectively. Then, cationic polymerization of styrene was examined by using a Brϕnsted acid generated by the photolysis. A solution of styrene monomer in CH_2Cl_2 containing a catalytic amount of a *t*-butylethynyl(phenyl)iodonium salt **1a** was irradiated similarly for 30 min. After the irradiation the mixture was poured into methanol and the precipitates were filtered and dried. The yield of the polymer is strongly dependent on the counter anion of the iodonium salts **1a**. A strong acid generated from the triflate or the perchlorate provides a good result as the polymerization (Table 2).

Table 2. Polymerization Initiated by Photolysis of **1a**[a]

Iodonium salt	Irradiation time/min	Yield/%	M_n
1a (X = OTs)	30	2	-
1b (X = OTf)	30	95	1120
1c (X = ClO_4)	30	96	2500

a) A solution of styrene (50.0 mmol) in CH_2Cl_2 (10 ml) containing **1a** (0.1 mmol) was irradiated for 30 min at 15 ℃ by using a Pyrex-filtered high-pressure Hg lamp (400 W).

In conclusion, alkynyl(phenyl)iodonium salts **1** decompose photochemically with a high efficiency. The resulting Brϕnsted acid causes polymerization of styrene. These results suggest a further utility as a photochemical acid generator as well as the known diaryliodonium salts.[2,3]

This work was supported by the Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency No. 03233101 from the Ministry of Education, Science and Culture, Japan.

References

1) M. D. Bachi, N. Bar-Ner, C. M. Crittel, P. J. Stang, and B. L. Williamson, *J. Org. Chem.*, **56**, 3912 (1991); T. Kitamura, I. Mihara, H. Taniguchi, and P. J. Stang, *J. Chem. Soc., Chem. Commun.*, **1990**,

614; J. S. Lodaya and G. F. Koser, *J. Org. Chem.*, **55**, 1513 (1990); P. J. Stang and C. M. Crittel, *Organometallics*, **9**, 3139 (1990); M. Ochiai, T. Ito, Y. Takaoka, Y. Masaki, M. Kunisima, S. Tani, and Y. Nagao, *J. Chem. Soc., Chem. Commun.*, **1990**, 118; P. J. Stang, T. Kitamura, M. Boehshar, and H. Wingert, *J. Am. Chem. Soc.*, **111**, 2225 (1989); P. J. Stang, M. Boehshar, H. Wingert, and T. Kitamura, *J. Am. Chem. Soc.*, **110**, 3272 (1989); P. J. Stang and T. Kitamura, *ibid.*, **109**, 7516 (1987); M. Ochiai, M. Kunishima, Y. Nagao, K. Fuji, and E. Fujita, *J. Chem. Soc., Chem. Commun.*, **1987**, 1708; P. J. Stang, B. W. Surber, Z. C. Chen, K. A. Roberts, and A. G. Anderson, *J. Am. Chem. Soc.*, **109**, 228 (1987); P. J. Stang and B. W. Surber, *ibid.*, **107**, 1452 (1985).

2) C. G. Willson and M. J. Bowden, *J. Chemtech*, **19**, 182 (1989); Y. Yagci and W. Schnabel, *Makromol. Chem., Macromol. Symp.* **13/14**, 161 (1988); S. P. Pappas, *Progr. Org. Coat.*, **13**, 35 (1985); J. V. Crivello, *Adv. Polym. Sci.*, **62**, 1 (1984).

3) H. Ito and M. Ueda, *J. Photopolym. Sci. Techn.*, **2**, 1 (1989).

4) R. J. Devoe, M. R. V. Sahyun, E. Schmidt, N. Serpone, and D. K. Sharma, *Can. J. Chem.*, **66**, 319 (1988); R. J. Devoe, M. R. V. Sahyun, N. Serpone, and D. K. Sharma, *Can. J. Chem.*, **65**, 2342 (1987); S. P. Pappas, B. C. Pappas, L. R. Gatechair, and W. Schnabel, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 69 (1984); J. V. Crivello and J. H. W. Laml, *Macromolecules*, **10**, 1307 (1977); J. V. Crivello and J. H. W. Lam. *J. Polym. Sci., Symp. No. 56*, **1976**, 383.

5) N. P. Hacker, D. V. Leff, and J. L. Dektar, *J. Org. Chem.*, **56**, 2280 (1991); J. L. Dektal and N. P. Hacker, *J. Org. Chem.*, **56**, 1838 (1991); J. L. Dektar and N. P. Hacker, *J. Org. Chem.*, **55**, 639 (1990).

6) $HC\equiv C^+$ is ca 540 kJ/mol less stabel than Ph^+. See, G. Angelini, M. Hanack, J. Vermehren, and M. Speranza, *J. Am. Chem. Soc.*, **110**, 1298 (1988); P. J. Stang, Z. Rappoport, M. Hanack, and L. R. Subramanian, "Vinyl Cations," Academic Press, New York (1979), Chap. 9.

7) Ionization potentials are 9.94 eV for $HC\equiv CI$ and 8.73 eV for PhI. See, "Kagakubinran Kisohen," Chemical Society of Japan, Maruzen, Tokyo (1984), Vol. II; K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, "Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules," Japan Scientific Societies Press, Tokyo (1981); J. W. Robinson, "Handbook of Spectroscopy," Chemical Rubber Co., Cleveland (1974), Vol. 1.

8) The heats of formation of radicals are 329 kJ/mol for $Ph^{\cdot}$ and 565 kJ/mol for $^{\cdot}C\equiv C$; See, F. McMillen and D. M. Golden, *Ann. Rev. Phys. Chem.*, **33**, 493 (1982).

(Received August 24, 1992)