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VINYLIODONIUM SALTS : THEIR STEREOSPECIFIC SYNTHESIS AND REACTIONS AS THE ACTIVATED VINYL HALIDES

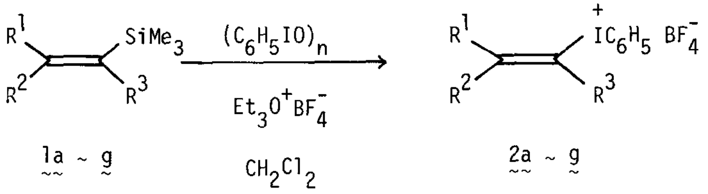
Masahito Ochiai, Kenzo Sumi, Yoshimitsu Nagao, and Eiichi Fujita*

Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, Japan

Summary: Vinyliodonium salts **2** were synthesized from vinylsilanes **1** by the reaction with iodosylbenzene and triethyloxonium tetrafluoroborate. The reaction occurs stereospecifically with retention of configuration. Vinyliodonium salts **2** are highly effective as the activated species of vinyl iodides. Thus, a variety of substituted olefins including α-cyano and α-nitro olefins, vinyl sulfides, vinyl halides, and α,β-unsaturated esters, were prepared from **2** under mild reaction conditions.

In spite of numerous studies on the chemistry of diaryliodonium salts,[1] the synthetic method and utility of the vinyliodonium salts are limited and often inefficient. A few β-chlorovinyliodonium salts have been prepared and they are mostly utilized as the source of acetylene itself.[2] Vinylaryliodonium compounds having no chlorine substituents in the vinyl moieties have been obtained by the reaction of vinylmercuric bromides or vinyl(trichloro)stannanes with (dichloroiodo)arenes.[3] We now wish to report a new, general,stereoselective synthesis of vinyliodonium salts from vinylsilanes utilizing a hypervalent organoiodine compound and their utility in organic synthesis, especially in a sense of the activated, reactive species of vinyl iodides.

Vinylsilanes react readily with a variety of electrophiles to give substitution or addition



1a ~ **g** **2a** ~ **g**

a $R^1=R^3=H$, $R^2=n\text{-}C_8H_{17}$
b $R^1=n\text{-}C_8H_{17}$, $R^2=R^3=H$
c $R^1=R^3=H$, $R^2=C_6H_5$
d $R^1=R^3=H$, $R^2=C_6H_5CH_2$
e $R^1=C_6H_5(CH_2)_2$, $R^2=Me$, $R^3=H$
f $R^1=Me$, $R^2=C_6H_5(CH_2)_2$, $R^3=H$
g $R^1=H$, R^2, $R^3=CH_2CH(t\text{-}Bu)(CH_2)_2$

Table 1. Synthesis of vinyliodonium salts from vinylsilanes[a]

Entry	Vinylsilane	Reaction Conditions	Product	Yield,[b] %	mp,°C	FABMS *m/z*[c]
1	**1a**	25°C, 4h	**2a**	72	30 - 30.5	343
2	**1b**[d]	25°C, 5h	**2b**	–[e]		
3	**1c**	25°C, 18h	**2c**	61	98.5 - 99	307
4	**1d**	25°C, 20h	**2d**	69	oil	321
5	**1e** + **1f** (90 : 10)	25°C, 3.5h	**2e** + **2f** (90 : 10)[f,g]	89		349
6	**1e** + **1f** (38 : 62)	25°C, 3h	**2e** + **2f** (35 : 65)[f,g]	71		
7	**1g**	0°C, 1h then 25°C, 2.5h	**2g**	74	82 - 82.5	341

a) Unless otherwise noted, reactions were performed as described in the text. b) Yields of pure isolated products. c) Peaks corresponding to $(\text{M-BF}_4)^+$. d) The reaction was carried out using 1.2 equiv of iodosylbenzene and 1 equiv of triethyloxonium fluoborate. e) 1-Decyne was obtained in 90% yield (GLC yield). f) The stereoisomeric ratios were determined by 'H NMR analysis. g) The stereochemistry of the products was determined by the measurement of the nuclear Overhauser effect.

products. Iodosylbenzene,[4] however, was not reactive enough towards the nucleophilic attack of vinylsilanes. Triethyloxonium tetrafluoroborate was found to be an effective reagent for the activation of iodosylbenzene. Vinyliodonium salts **2** were synthesized from vinylsilanes **1** by their reaction with iodosylbenzene in the presence of triethyloxonium tetrafluoroborate.

A solution of triethyloxonium tetrafluoroborate (2.5 mmol) in dichloromethane (5 ml) was added dropwise over 10 min to a suspension of a vinylsilane **1** (1 mmol) and iodosylbenzene (2.5 mmol) in dichloromethane (10 ml) under nitrogen. A pale yellow color of the suspension turned gradually to a bright yellow color. After being stirred under the conditions described in Table 1, the reaction mixture was quenched by the addition of distilled water,[5] and extracted with dichloromethane. The results are summarized in Table 1. Fast atom bombardment mass spectra (FABMS) showed relatively abundant fragments corresponding to the cationic portion of the salts **2**. IR spectra of **2** showed very large broad bands at 1100-1000 cm^{-1} characteristic of the BF_4^- anion.

The reaction proceeds in a highly stereospecific manner with retention of configuration.[6] *E*-1-(Trimethylsilyl)-1-decene (**1a**) gave the crystalline *E*-1-decenyl(phenyl)iodonium tetrafluoroborate (**2a**)[7] in 72% yield (Entry 1). On the other hand, the *Z*-vinylsilane **1b** did not produce the **2b** at all, while the dehydrosilylation of **1b** proceeded in good yield (Entry 2).

Careful NMR tube experiment, however, showed the transient formation of the unstable intermediate 2b[7,8] in 21% yield, after standing the reaction mixture for 4h at 25°C with occasional shaking. These results clearly indicate the reasonable rate of *anti*-β-elimination of hydrogen and $C_6H_5I^+$ group of 2b, in comparison with that of *syn*-β-elimination of 2a.

The versatility of the vinyliodine(III) compounds 2 in organic synthesis is noteworthy. It seems reasonable to assume that 2 may behave like the highly activated vinyl halides, because iodine(III) at the hypervalent state is known to be a good leaving group.[9] Actually, a variety of nucleophiles can be introduced to the double bond of 2 with concomitant loss of iodobenzene. The transformations shown for 4-t-butyl-1-cyclohexenyl(phenyl)iodonium tetrafluoroborate (2g) in Figure 1 are representative. The specific reagents and reaction conditions are as follows: (A) Me_2CuLi, THF, -78°C, 4h; n-Bu_2CuLi, Et_2O, -78°C, 3h; $(C_6H_5)_2CuLi$, THF, -30°C, 5h; (B) $KCu(CN)_2$, DMF, 25°C, 12h; (C) $CuSO_4$,$NaNO_2$, DMF-H_2O, 25°C, 28h; (D) C_6H_5SNa, dioxane, 25°C, 29 min; (E) CuI, KI, DMF, 25°C, 1h; (F) CuBr, KBr, DMF, 25°C, 12h; (G) CuCl, KCl, DMF, 25°C, 12h; (H) cat.

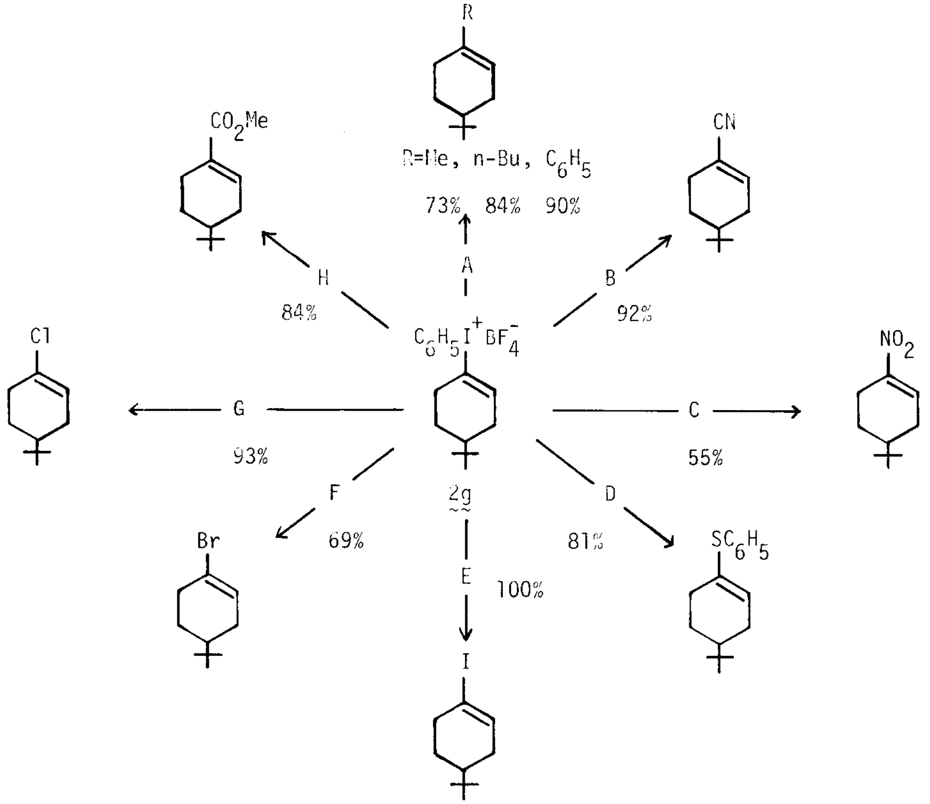


Figure 1. Substitution reaction of vinyliodonium salt 2g. Reagents and conditions are indicated in the text.

$Pd(OAc)_2$, CO, n-Bu_3N, MeOH, 25°C, 2h. In the reactions (A)-(G), no Michael type of addition products was obtained at all. Thus, synthetically important, substituted olefins, such as α-cyano and α-nitro olefins, vinyl sulfide, vinyl halide, and α,β-unsaturated ester were prepared in good yields. Especially noteworthy are their mild reaction conditions[10] required for the transformations.

Vinylsilanes usually act as vinyl cation equivalent species. Therefore, the reaction described above offers a new methodology for the umpolung of reactivity of vinylsilanes.

References and Notes

1. (a) F. M. Beringer, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Am. Chem. Soc.*, **75**, 2705 (1953); (b) F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner, and E. Sommer, *ibid.*, **81**, 342 (1959); (c) B. F. Koser and R. H. Wettach, *J.Org. Chem.*, **42** 1476 (1977); (d) S. Gronowitz and B. Holm, *Tetrahedron*, **33**, 557 (1977); (e) Y. Yamada and M. Okawara, *Bull. Chem. Soc. Japan*, **45**, 1860 (1972); (f) Y. Yamada, K. Kashima, and M. Okawara, *ibid.*, **47**, 3179 (1974).
2. (a) R. Kh. Freidlina, E. M. Brainina, and A. N. Nesmeyanov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **1945**, 647; (b) E. M. Brainina and R. Freidlina, *ibid.*, **1947**, 623; (c) F. M. Beringer and R. A. Nathan, *J. Org. Chem.*, **35**, 2095 (1970); (d) *idem, ibid.*, **34**, 685 (1969).
3. (a) A. N. Nesmeyanov, T. P. Tolstaya, N. F. Sokolova, V. N. Varfolomeeva, and A. V. Petrakov, *Dokl. Akad. Nauk SSSR*, **198**, 115 (1971); (b) A. N. Nesmeyanov, T. P. Tolstaya, and A. V. Petrakov, *ibid.*, **197**, 1337 (1971); (c) A. N. Nesmeyanov, T. P. Tolstaya, A. V. Petrakov, and A. N. Goltsev, *ibid.*, **235**, 591 (1977); (d) A. N. Nesmeyanov, T. P. Tolstaya, A. V. Petrakov, and I. F. Leshcheva, *ibid.*, **238**, 1109 (1978).
4. Iodosylbenzene was proposed to be a polymer: (a) H. Siebert and M. Handrich, *Anorg. Allg. Chem.*, **426**, 173 (1976); (b) R. Bell and K. J. Morgan, *J. Chem. Soc.*, **1960**, 1209.
5. On the usage of water containing nucleophiles like chloride ion, further reactions of the product **2**, that is, substitution and/or β-elimination, proceed.
6. In the protodesilylation or Friedel-Crafts acylation of vinylsilanes, retention of the configuration was usually observed: T. H. Chan and I. Fleming, *Synthesis*, **1979**, 761.
7. The vicinal coupling constants between vinylic protons of **2a** and **2b** in 'H NMR spectra were found to be 13.7 Hz and 6.0 Hz, respectively.
8. In the reaction, the presence of 1-decyne (36%) and 1b (43%) was also observed.
9. R. M. Moriarty and H. Hu, *Tetrahedron Lett.*, **22**, 2747 (1981).
10. (a) Elevated reaction temperature was required for the substitution reaction of vinyl iodides using copper(I) cyanide, phenylthiolate, and halides: A. Commercon, J. Normant, and J. Villieras, *J. Organometal. Chem.*, 93, 415 (1975); (b) Palladium-catalyzed carboalkoxylation of vinyl halides was usually carried out at 80°-100°C: A. Schoenberg, I. Bartoletti, and R. F. Heck, *J. Org. Chem.*, **39**, 3318 (1974).

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