

- T. H.; Fleming, I. *Synthesis* 1979, 761. (c) Ochiai, M.; Fujita, E. *Yuki Gosei Kagaku Kyokaiishi (J. Synth. Org. Chem., Jpn.)* 1982, 40, 508.
- (a) Ochiai, M.; Fujita, E. *Tetrahedron Lett.* 1983, 24, 777. (b) Muzart, J.; Pale, P.; Pete, J. P. *ibid.* 1982, 23, 3577. (c) Riahi, A.; Cossy, J.; Muzart, J.; Pete, J. P. *ibid.* 1985, 26, 839.
  - (a) Mizuno, K.; Nishiyama, T.; Terasaka, K.; Yasuda, M.; Shima, K.; Otsuji, Y. *Tetrahedron* 1992, 48, 9673. (b) Mitani, M.; Osakabe, Y. *J. Chem. Soc., Chem. Commun.* 1994, 1759 and references therein.
  - (a) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* 1973, 95, 8678. (b) Kira, M.; Taki, T.; Sakurai, H. *J. Org. Chem.* 1989, 54, 5647 and references therein.
  - (a) Seifert, D. *Organometallic Compounds Containing a Vinyl Group*; (Translated into Russian), Izd. Mir, Moscow, 1964. (b) Kliegman, J. M. *J. Organomet. Chem.* 1971, 29, 73. (c) Akhrem, I. S.; Chistovalova, N. M.; Vol'pin, M. E. *Russian Chem. Rev.* 1983, 52, 542 and references therein.
  - (a) Muzart, J.; Pale, P.; Pete, J. P. *J. Chem. Soc., Chem. Commun.* 1981, 668. (b) Muzart, J.; Pale, P.; Pete, J. P. *Tetrahedron Lett.* 1983, 24, 4567.
  - Muzart, J.; Riahi, A. *Organometallics* 1992, 11, 3478 and references therein.
  - Crozet, M.; Muzart, J.; Pale, P.; Tordo, P. *J. Organomet. Chem.* 1983, 244, 191.
  - Vermeersch, G.; Marko, J.; Muzart, J. *J. Chem. Soc., Perkin Trans. 2* 1986, 383.
  - (a) Farid, S. private communication. (b) Gould, I. R.; Ege, E.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* 1987, 109, 3794 footnote 5.
  - Arylallyltrimethylsilanes were prepared by the reported methods: Seyferth, D.; Wursthorn, K. R.; Lim, T. F. O. *J. Organometal. Chem.* 1979, 181, 293 and see ref. 1b, p. 778 (Preparation of Allylsilanes by Wittig Reaction). In this case, however, arylallylsilanes were only produced by reflux for 15 h at final step.  
**Spectral data of (E)-1-methyl-1-phenyl-3-(trimethylsilyl)-1-propene (1b)**; liquid at room temp.; IR (KBr) 3057, 3027, 2955, 1659, 1599, 1493, 1447, 1248, 855, 754, 696  $\text{cm}^{-1}$ ; UV (*n*-hexane)  $\lambda_{\text{max}}$  255, 295 nm;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 0.01 (9H, s,  $-\text{SiMe}_3$ ), 1.60 (2H, d,  $-\text{SiCH}_2$ ,  $J=ca.$  8 Hz), 2.00 (3H, s,  $-\text{Me}$ ), 5.90 (1H, t,  $=\text{CH}$ ,  $J=ca.$  8 Hz), 7.30 (5H, m, phenyl); MS (EI)  $m/e$  204 ( $\text{M}^+$ )  
**Spectral data of 1,1-diphenyl-3-(trimethylsilyl)-1-propene (1c)**; liquid at room temp.; IR (KBr) 3057, 3023, 2955, 1620, 1597, 1494, 1445, 1248, 851, 760, 700  $\text{cm}^{-1}$ ; UV (*n*-hexane)  $\lambda_{\text{max}}$  258, 298 nm;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 0.01 (9H, s,  $-\text{SiMe}_3$ ), 1.65 (2H, d,  $-\text{SiCH}_2$ ,  $J=ca.$  8 Hz), 6.20 (1H, t,  $=\text{CH}$ ,  $J=ca.$  8 Hz), 7.30 (10H, m, phenyl); MS (EI)  $m/e$  266 ( $\text{M}^+$ )  
**Spectral data of (E)-1-( $\alpha$ -naphthyl)-3-(trimethylsilyl)-1-propene (1d)**; liquid at room temp.; IR (KBr) 3057, 3029, 2955, 1630, 1599, 1504, 1383, 1248, 855, 754, 694  $\text{cm}^{-1}$ ; UV (*n*-hexane)  $\lambda_{\text{max}}$  228, 300 nm;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 0.11 (9H, s,  $-\text{SiMe}_3$ ), 1.80 (2H, d,  $-\text{SiCH}_2$ ,  $J=ca.$  8.5 Hz), 6.25 (1H, d of t,  $=\text{CH}$ ,  $J=ca.$  15 Hz and  $ca.$  8.5 Hz), 6.95 (1H, d,  $=\text{CH}$ -naphthyl,  $J=ca.$  15 Hz), 7.60 (7H, m, naphthyl); MS (EI)  $m/e$  240 ( $\text{M}^+$ )
  - HPLC conditions: column, Shodex SIL-5B column; detector, ERMA ERC-7210 UV detector at 280 nm; eluting solvents, *n*-hexane/diethyl ether (100 : 1, v/v); flow rate, 2 mL/min.
  - LPLC conditions: column, Yamazen Co. prepacked Si-25 column; detector, Yamazen Co. Prep. UV-10V detector at 280 nm; eluting solvents, *n*-hexane/diethyl ether (50 : 1, v/v); flow rate, 5 mL/min.
  - 7a** is bezaldehyde, **7b** is acetophenone, **7c** is benzophenone, **7d** is  $\alpha$ -naphthaldehyde, **8a** is cinnamaldehyde, and **8c** is  $\beta$ -phenylcinnamaldehyde.
  - Spectral data of (E)- $\beta$ -methylcinnamaldehyde (8b)**; liquid at room temp.; IR (KBr) 3030, 2950, 2850, 1670, 1150, 1020; 855, 750  $\text{cm}^{-1}$ ; UV (*n*-hexane)  $\lambda_{\text{max}}$  275, 283 nm;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 2.00 (3H, s,  $-\text{Me}$ ), 5.90 (1H, d,  $=\text{CH}$ ,  $J=12$  Hz), 7.30 (5H, m, phenyl), 9.60 (1H, d,  $-\text{CHO}$ ,  $J=12$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 195.2, 149.6, 138.3, 135.1, 129.9, 129.4, 128.6, 10.9; MS (EI)  $m/e$  146 ( $\text{M}^+$ ), 117 ( $\text{M}^+-\text{CHO}$ )  
**Spectral data of (E)-3-( $\alpha$ -naphthyl)-2-propenal (8d)**; liquid at room temp.;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 6.83 (1H, d of d,  $=\text{CH}-\text{CO}$ ,  $J=24$  Hz and 12 Hz), 7.40-8.20 (7H, m, naphthyl), 8.32 (1H, d,  $=\text{CH}$ -naphthyl,  $J=24$  Hz), 9.84 (1H, d,  $-\text{CHO}$ ,  $J=12$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 193.6, 149.3, 133.8, 131.6, 131.2, 130.9, 129.0, 127.3, 126.4, 125.7, 122.8; MS (EI)  $m/e$  182 ( $\text{M}^+$ ), 153 ( $\text{M}^+-\text{CHO}$ )
  - Kim, S. S.; Yoo, D. Y.; Kim, A. R.; Cho, I. H.; Shim, S. C. *Bull. Korean Chem. Soc.* 1989, 10, 66.
  - Braun, A. M.; Maurette, M. T.; Oliveros, E. In *Technologie Photochimique*; Presses polytechniques romandes: Lausanne, Switzerland, 1986; Chapter 11.
  - (a) Fleming, I.; Dunogues, J.; Smithers, R. In *Organic Reactions*; Wiley: New York, 1989; Vol. 37, p 57. (b) Dang, H. S.; Davies, A. G. *Tetrahedron Lett.* 1991, 32, 1745.

### Preparation of $\alpha$ -Nosyloxy Carbonyl Compounds Using [Hydroxy(nosyloxy)iodo]benzene







Jong Chan Lee\*, Yoon Seok Oh, and Sung Hye Cho

Department of Chemistry,  
Chung-Ang University,  
Seoul 156-756, Korea

Received July 26, 1996

In recent years, there has been a significant interest in the synthetic utilities of [*p*-nitrophenyl)sulfonyloxy]carbonyl compounds due to their much simpler reactivity than that of the analogous  $\alpha$ -halo ketones.<sup>1,2a</sup> Various kinds of densely functionalized carbon skeletons were prepared from these intermediates.<sup>2,3</sup> Preparation of synthetically useful  $\alpha$ -azido ketones by reaction of  $\alpha$ -(nosyloxy)ketones with sodium azide was reported recently.<sup>4</sup> Conventional methods for preparation of  $\alpha$ -(nosyloxy)ketones have been essentially based upon the conversion of enol acetates<sup>5</sup> and silyl enol ethers<sup>6</sup> by treatment with *p*-nitrobenzenesulfonyl peroxide (pNBSP).<sup>2a</sup>

**Table 1.** Direct  $\alpha$ -Nosyloxylation of Carbonyl Compounds

Entry <sup>a</sup>	Carbonyl compound	Temp. (°C)	Time (h)	Product <sup>b</sup>	Yield (%)
1 <sup>d</sup>	CH <sub>3</sub> COCH <sub>3</sub>	reflux	0.5	CH <sub>3</sub> COCH <sub>2</sub> ONs	90(86 <sup>e</sup> )
2 <sup>c</sup>	PhCOCH <sub>3</sub>	reflux	1	PhCOCH <sub>2</sub> ONs	81(90 <sup>e</sup> )
3 <sup>f</sup>	PhCOCH <sub>2</sub> CH <sub>3</sub>	reflux	2.5	PhCOCH(ONs)CH <sub>3</sub>	96(95 <sup>e</sup> )
4		r.t.	6		75(92 <sup>e</sup> )
5	CH <sub>3</sub> CH <sub>2</sub> COCH <sub>2</sub> CH <sub>3</sub>	reflux	1.5	CH <sub>3</sub> CH <sub>2</sub> COCH(ONs)CH <sub>3</sub>	93(69 <sup>e</sup> )
6 <sup>c</sup>	(CH <sub>3</sub> ) <sub>2</sub> CHCOCH(CH <sub>3</sub> ) <sub>2</sub>	reflux	3	(CH <sub>3</sub> ) <sub>2</sub> CHCOC(ONs)(CH <sub>3</sub> ) <sub>2</sub>	86(71 <sup>e</sup> )
7	CH <sub>3</sub> COCH <sub>2</sub> COCH <sub>3</sub>	r.t.	0.3	CH <sub>3</sub> COCH(ONs)COCH <sub>3</sub>	96(72 <sup>e</sup> )
8 <sup>c</sup>		reflux	1		95
9		reflux	2		91
10	EtO <sub>2</sub> CCH <sub>2</sub> CO <sub>2</sub> Et	reflux	3	EtO <sub>2</sub> CCH(ONs)CO <sub>2</sub> Et	65
11	CH <sub>3</sub> COCH <sub>2</sub> CO <sub>2</sub> Et	reflux	1	CH <sub>3</sub> COCH(ONs)CO <sub>2</sub> Et	90(57 <sup>e</sup> )
12	CH <sub>3</sub> COCH <sub>2</sub> CO <sub>2</sub> Bu	reflux	0.3	CH <sub>3</sub> COCH(ONs)CO <sub>2</sub> Bu	98(51 <sup>e</sup> )
13	PhCOCH <sub>2</sub> CO <sub>2</sub> Et	reflux	0.3	PhCOCH(ONs)CO <sub>2</sub> Et	91(65 <sup>e</sup> )
14 <sup>c</sup>	PhCOCH <sub>2</sub> CON(Et) <sub>2</sub>	r.t.	0.3	PhCOCH(ONs)CON(Et) <sub>2</sub>	97

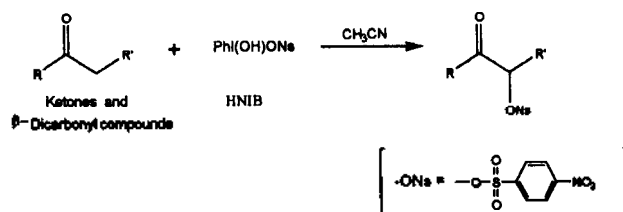
<sup>a</sup>Unless stated otherwise, the products were crystallized in *n*-hexane/EtOAc. <sup>b</sup>Products were isolated and identified by spectral data and comparison with the data reported in the literature. <sup>c</sup>Yields in parentheses are the highest one obtained from alternative routes reported in the references. <sup>d</sup>The products were purified by column chromatography (silica gel, *n*-hexane/EtOAc/acetone = 5/1/1). <sup>e</sup>The products were crystallized in MeOH. <sup>f</sup>The product was crystallized in acetone. <sup>g</sup>Reaction solvent: CH<sub>3</sub>CN/DMF = 5/2.

Regiospecific preparation of  $\alpha$ -(nosyloxy)ketones from the reaction of *tert*-butyl- $\beta$ -keto esters with pNBSP and subsequent decarboxylation was also reported.<sup>3</sup> In addition, the  $\alpha$ -(nosyloxy)- $\beta$ -keto esters were accessible by the reaction of  $\beta$ -keto esters with pNBSP.<sup>7</sup> Potential drawbacks to these syntheses are the unavoidable use of the highly unstable organic peroxide (pNBSP), or the needs for several reaction steps. We therefore decided to look for a more convenient alternative route to the preparation of  $\alpha$ -(nosyloxy)ketones and  $\alpha$ -(nosyloxy)- $\beta$ -keto esters involving the use of a stable [hydroxy(nosyloxy)iodo]benzene (HNIB). Structurally modified hypervalent iodine compounds<sup>8</sup> have been used for the introduction of tosyloxy,<sup>9</sup> mesyloxy,<sup>10</sup> camphorsulfonyloxy,<sup>11</sup> and trifluoromethanesulfonyloxy<sup>12</sup> groups into  $\alpha$ -position of carbonyl compounds.

To our knowledge, the use of HNIB in the oxidative attachment of nosyloxy group to the  $\alpha$ -position of carbonyl compounds has been previously unprecedented. We now wish to report a facile procedure for the preparation of  $\alpha$ -(nosyloxy)- $\beta$ -keto esters from the corresponding carbonyl compounds using HNIB in CH<sub>3</sub>CN.

The representative results summarized in Table 1 present the direct nosyloxylation of various ketones and  $\beta$ -dicarbonyl compounds.

In general, the nosyloxylation reaction proceeded smoothly in short reaction times at reflux in acetonitrile and gave good or excellent yields. In case of entry 6, use of CH<sub>3</sub>CN-DMF solvent mixture as a reaction medium was required for optimum yield. As can be expected, the carbonyl compounds with higher enol tautomer fractions afforded much better yields compared to the other carbonyl compounds with lower enol contents (entries 4 and 10). Accordingly, present protocol proved to be superior to the previous methods utilizing



pNBSP in the aspects of safety, convenience, and yield. The requisite HNIB was a stable solid compound and readily prepared in 93% yield by the reaction of iodobenzene diacetate (16.1 g, 50 mmol) with *p*-nitrobenzenesulfonic acid (20.3 g, 100 mmol) in acetonitrile (350 mL) as described previously.<sup>13</sup> The HNIB was easily handled and presented no stability problems during the experimental procedures. The general procedure is as follows. To a well-stirred solution of HNIB (5.5 mmol) in CH<sub>3</sub>CN (10 mL) was added a solution of the carbonyl compound (5.0 mmol) in CH<sub>3</sub>CN (10 mL). The mixture was magnetically stirred at the conditions given in the Table 1. When the reaction was completed, the reaction mixture was concentrated under reduced pressure to remove CH<sub>3</sub>CN. The crude product mixture was purified by crystallization or column chromatography to give desired product. All products showed spectral data consistent with their proposed structure.

In conclusion, we have shown that HNIB induced direct nosyloxylation is a practical and reliable route to a number of synthetically useful  $\alpha$ -nosyloxy carbonyl compounds. The application of the  $\alpha$ -nosyloxy carbonyl compounds thus obtained is now in progress.

**Acknowledgment.** This work was financially supported by 1996 Chung-Ang University Research Fund.

## References

- Hoffman, R. V.; Jankowski, B. C.; Carr, S. C.; Duesler, E. N. *J. Org. Chem.* **1986**, *51*, 130.
- (a) Hoffman, R. V. *Tetrahedron* **1991**, *47*, 1109. (b) Hoffman, R. V.; Kim, H.-O.; Wilson, A. L. *J. Org. Chem.* **1990**, *55*, 2820. (c) Hoffman, R. V.; Kim, H.-O. *J. Org. Chem.* **1991**, *56*, 6759.
- Hoffman, R. V.; Kim, H.-O.; Lee, J. C. *J. Org. Chem.* **1994**, *59*, 1933.
- Patonay, T.; Hoffman, R. V. *J. Org. Chem.* **1994**, *59*, 2902.
- Hoffman, R. V. *Synthesis* **1985**, 760.
- Hoffman, R. V.; Carr, C. S.; Jankowski, B. C. *J. Org. Chem.* **1985**, *50*, 5148.
- Hoffman, R. V.; Wilson, A. L.; Kim, H.-O. *J. Org. Chem.* **1990**, *55*, 1267.
- For a review see: Moriarty, R. M.; Vaid, R. K.; Koser, G. F. *Synlett* **1990**, 365.
- Koser, G. F.; Relenyi, A. G.; Kalos, A. N.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1982**, *47*, 2487.
- Lodaya, J. S.; Koser, G. F. *J. Org. Chem.* **1988**, *53*, 210.
- Hatzigrigoriou, E.; Varvoglis, A.; Bakola-Christianopoulou, M. *J. Org. Chem.* **1990**, *55*, 315.
- Moriarty, R. M.; Epa, W. R.; Penmasta, R.; Awasthi, A. K. *Tetrahedron Lett.* **1989**, *30*, 667.
- Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1977**, *42*, 1476.

### Development of Corona Excited Supersonic Jet System for the Vibronic Emission Spectra of Transient Molecules

Myoung Sun Han, Iek Soon Choi, and Sang Kuk Lee\*

*Department of Chemistry, College of  
Natural Sciences Pusan National University,  
Pusan 609-735, Korea*

*Received July 30, 1996*

One of the most interesting subjects in modern molecular spectroscopy is to observe the spectrum of transient molecules in the gas phase.<sup>1</sup> For this purpose, numerous experimental techniques have been developed so far. Among the techniques developed, the supersonic free jet expansion has been proven to be a powerful spectroscopic tool for obtaining the spectrum of gas phase molecular species since early work<sup>2</sup> on the NO<sub>2</sub>, allowing the study of rotationally resolved spectra of large molecules at low temperature. The spectral simplification and stabilization associated with the rare gas expansion usually cannot be obtained in any other way. The majority of these supersonic expansion applications have been carried out in the ultraviolet and visible frequency regions because of the sensitivity of fluorescence-based detection schemes.

Transient molecules are characterized as existing in low concentrations and in abnormal conditions, and thus their

observation requires that available instrumentation be pushed to its limit.<sup>1</sup> The supersonic expansion method has been applied to the fluorescence spectra of radicals,<sup>3</sup> ions,<sup>4,5</sup> and clusters<sup>6</sup> in free jets. In these cases, excitation occurs either before or after expansion. For example, in the Engelking-type corona discharge,<sup>7</sup> pyrolysis jet,<sup>8</sup> Hg-photosensitized reactions inside the throat of a Campargue-type free jet,<sup>9</sup> and laser metal vaporization cluster sources,<sup>10</sup> the gases are excited before expansion, whereas in cw<sup>4,5</sup> and pulsed electron beams,<sup>11</sup> as well as VUV and multiphoton ionization devices,<sup>12</sup> excitation occurs outside the expansion region. Very recently, Cossart and Cossart-Magos<sup>13</sup> have developed a new emission source which is effective for the molecular ions using Penning-type electric discharge in a supersonic free jet. Of the emission sources, the only one giving enough continuous photon intensity for high resolution studies of weak transitions in a jet was the Engelking-type corona discharge which has been widely used for the observation of the vibronic emission spectrum of transient molecules.<sup>14</sup> However, this device has suffered from destabilizing the discharge of messy precursor over a long period.

Recently, we have chosen<sup>15</sup> to develop in our laboratory an emission source for the vibronic spectra of transient molecules using a corona discharge in a jet and a long path length of monochromator. It would be useful for obtaining the vibronic emission spectra of transient molecules as well as stable molecules. This communication details the design of the instrumentation developed.

Figure 1 shows the schematic diagram of the corona excited supersonic jet system which is mainly divided into three parts; electric discharge, supersonic expansion and spectrometer. For the generation of transient molecules in a jet from the precursor molecules, we have employed a conventional corona discharge system which is similar to that developed by Engelking.<sup>7</sup> A conventional corona discharge<sup>16</sup> coupled with a supersonic expansion is consisted of a thin metal rod, terminated with a sharp point, mounted inside an insulating and inert tube. A small pinhole or slit is cut into the end of the tube, forming a supersonic nozzle. The metal tip is placed very close to the exit hole and a high positive voltage is applied to the rod. Thus, the nozzle body, in this work, was formed from a thick-walled quartz tube of 12 mm outer diameter, 2 mm thickness, and 250 mm length, narrowed by flame heating at one end to a capillary of the desired pinhole size. The nozzle was connected to threaded adaptor (Ace glass model 5027-05). A long and sharpened anode, made of a 1.6 mm diameter stainless steel rod was inserted through a rubber o-ring into the quartz nozzle for the generation and excitation of transient molecules. The o-ring was tightened by a teflon bushing with a hole in center through which the anode was connected to the high voltage electric dc power supply (Bertan model 210-05R).

The position of the metal tip used for the anode has been proven to be critical for the stability of the discharge over a long period. For example, in Engelking type corona discharge the metal tip is located inside the nozzle and the molecules are excited before expansion, which substantially reduces the stability of the discharge when organic compounds are used as precursors. The messy fragments generated by an electric discharge of the organic precursor easily block the narrow hole of the nozzle. Thus, in this design we put