**Boc-Ser$_1$($PO_3Ph_2$)-Ser$_2$($PO_3Ph_2$)-NHMe (4).** *N*-Methylmorpholine (0.59 g, 5.88 mmol) in THF (2 mL) and isobutyl chloroformate (0.745 g, 5.46 mmol) in THF (2 mL) were successively added to a solution of Boc-Ser($PO_3Ph_2$)-OH (2.57 g, 5.88 mmol) in THF (10 mL) at −20 °C. After an activation period of 3 min, a solution of peptide **3** (1.62 g, 4.20 mmol) and *N*-methylmorpholine (0.424 g, 4.20 mmol) in THF (5 mL) was added to the solution, and the resulting solution was stirred for 2 h at −20 °C prior to the addition of 5% $NaHCO_3$ (5 mL). After 30 min at 20 °C, dichloromethane (100 mL) was added and the organic phase washed with 5% $NaHCO_3$ (2 × 30 mL) and 1 M HCl (2 × 30 mL), dried ($Na_2SO_4$), and filtered. Evaporation of the solvent under reduced pressure gave peptide **4** as a white crystalline solid (3.09 g, 96 %), mp 107–108 °C: $[\alpha]^{23}_D$ +0.47° (*c* 1, $CHCl_3$); $^1H$ NMR ($CDCl_3$) δ 1.41 (s, 9 H, Boc $CH_3$), 2.65 (d, 3 H, $J_{NH-H}$ = 4.61 Hz, NHC$H_3$), 4.20–4.80 (m, 6 H, Ser$_{1,2}$ α-CH and β-$CH_2$), 5.73 (br d, 1 H, $J_{NH-H}$ = 5.71 Hz, Ser$_1$ NH), 6.93 (br q, 1 H, $J_{NH-H}$ = 5.49 Hz, NHCH$_3$), 7.10–7.80 (m, 20 H, Ar H), 7.60 (br d, 1 H, $J_{NH-H}$ = 5.71 Hz, Ser$_2$ NH); $^{13}C$ NMR ($CDCl_3$) δ 26.22, 28.07, 53.44 (d, 6.10 Hz), 55.31 (d, 7.33 Hz), 67.91 (d, 6.10 Hz), 68.15 (d, 6.10 Hz), 80.75, 119.94 (d, 4.89 Hz), 125.59, 129.83, 150.06 (d, 7.32 Hz), 155.66, 167.75, 168.62; $^{31}P$ NMR ($CDCl_3$) δ −11.23, −11.44; FAB mass spectrum (Ar, positive mode), *m/z* (rel intensity) 792 (0.1, M + $Na^+$), 770 (1, $MH^+$), 671 (5), 464 (6), 420 (3), 292 (18), 251 (65), 214 (54), 196 (22), 170 (100), 154 (16), 110 (18), 101 (18).

**Boc-Ser$_1$($PO_3Ph_2$)-Ser$_2$($PO_3Ph_2$)-Ser$_3$($PO_3Ph_2$)-NHMe (6).** *N*-Methylmorpholine (0.325 g, 3.22 mmol) in THF (2 mL) and isobutyl chloroformate (0.41 g, 3.00 mmol) in THF (2 mL) were successively added to a solution of Boc-Ser($PO_3Ph_2$)-OH (1.41 g, 3.22 mmol) in THF (10 mL) at −20 °C. After an activation period of 3 min, a solution of dipeptide **5** (1.62 g, 2.30 mmol) and *N*-methylmorpholine (0.232 g, 2.30 mmol) in THF (5 mL) was added to the solution, and the resulting solution was stirred for 2 h at −20 °C prior to the addition of 5% $NaHCO_3$ (3 mL). After 30 min at 20 °C, dichloromethane (100 mL) was added and the organic phase washed with 5% $NaHCO_3$ (2 × 30 mL) and 1 M HCl (2 × 30 mL), dried ($Na_2SO_4$), and filtered. Evaporation of the solvent under reduced pressure gave tripeptide **6** as a clear oil (2.46 g, 98%): $[\alpha]^{23}_D$ +0.71° (*c* 1, $CHCl_3$); $^1H$ NMR ($CDCl_3$) δ 1.43 (s, 9 H, Boc $CH_3$), 2.51 (d, 3 H, $J_{NH-H}$ = 4.61 Hz, NHC$H_3$), 4.10–5.00 (m, 9 H, Ser$_{1,2,3}$ α-CH and β-$CH_2$), 5.61 (br d, 1 H, $J_{NH-H}$ = 5.71 Hz, Ser$_1$ NH), 6.91 (br q, 1 H, $J_{NH-H}$ = 8.13 Hz, NHCH$_3$), 7.10–7.80 (m, 30 H, Ar H), 8.04 and 8.13 (each br d, 1 H, $J_{NH-H}$ = 7.44 and 8.57 Hz, Ser$_2$ and Ser$_3$ NH); $^{13}C$ NMR ($CDCl_3$) δ 25.90, 28.05, 53.86 (d, 7.69 Hz), 54.04 (d, 4.39 Hz), 54.62 (d, 6.59 Hz), 67.34 (d, 6.59 Hz), 67.97 (d, 6.59 Hz), 68.27 (d, 6.59 Hz), 119.83 (d, 5.49 Hz), 125.46, 129.66, 149.99 (d, 6.60 Hz), 154.96, 167.64, 167.74, 168.76; $^{31}P$ NMR ($CDCl_3$) δ −11.10, −11.25, −11.49; FAB mass spectrum (Ar, positive mode), *m/z* (rel intensity) 1111 (2, M + $Na^+$), 1089 (1, $MH^+$), 989 (5), 857 (2), 783 (2), 533 (8), 515 (5), 489 (24), 292 (38), 283 (73), 251 (100), 219 (41), 196 (12), 154 (38), 111 (35).

**Hydrogenolytic Deprotection. General Procedure.** A rapidly stirred solution of **2**, **4**, or **6** (0.4 mmol) in 50% TFA/AcOH containing 83% platinum oxide (1.1 mmol $PtO_2$ per mmol phenyl group) was charged with hydrogen at atmospheric pressure. On cessation of hydrogen uptake (~1–3 h), the platinum was removed by gravity filtration and the solvent removed by evaporation under reduced pressure. Repeated trituration of the residue with diethyl ether (3 × 30 mL) followed by high vacuum drying gave the *P*Ser peptide **7**, **8**, or **9** as light white flakes.

**$CF_3CO_2H$·H-*P*Ser-NHMe (7)** (0.120 g, 96%): $[\alpha]^{23}_D$ +0.36° (*c* 1, $H_2O$); $^{13}C$ NMR ($D_2O$) 25.98, 53.46 (d, 5.49 Hz), 63.14 (d, 4.40 Hz), 167.18; $^{31}P$ NMR ($D_2O$) −0.01; FAB mass spectrum (Ar, positive mode), *m/z* (rel intensity) 221 (25, M − H + $Na^+$), 199 (100, $M^+$), 167 (2), 140 (5), 110 (17), 101 (45, $M^+$ − 98).

**$CF_3CO_2H$·H-*P*Ser-*P*Ser-NHMe (8)** (0.184 g, 96%): $[\alpha]^{23}_D$ +0.04° (*c* 1, $H_2O$); $^{13}C$ NMR ($D_2O$) 26.3, 53.6 (d, 8.79 Hz), 54.9 (d, 5.12 Hz), 63.3 (d, 3.66 Hz), 64.3 (d, 3.66 Hz), 167.5, 170.9; $^{31}P$ NMR ($D_2O$) +0.15, −0.24; FAB mass spectrum (Ar, positive mode), *m/z* (rel intensity) 388 (2, M − H + $Na^+$), 366 (100, $M^+$), 268 (20, $M^+$ − 98), 170 (40, *m/z* 268 − 98), 140 (25).

**$CF_3CO_2H$·H-*P*Ser-*P*Ser-*P*Ser-NHMe (9)** (0.243 g, 94%): $[\alpha]^{23}_D$ −0.38° (*c* 1, $H_2O$); $^{13}C$ NMR ($D_2O$) δ 26.1, 53.5 (d, 7.69 Hz), 54.2 (d, 7.69 Hz), 54.7 (d, 7.69 Hz), 63.2 (d, 4.39 Hz), 64.1 (d, 4.39 Hz), 64.2 (d, 4.39 Hz), 167.1, 170.6 and 171.1; $^{31}P$ NMR ($D_2O$) δ +0.09, +0.09, and −0.15; FAB mass spectrum (Ar, positive mode), *m/z* (rel intensity) 555 (5, M − H + $Na^+$), 533 (7, $M^+$), 435 (3, $M^+$ − 98), 391 (2), 369 (2), 337 (5, *m/z* 435 − 98), 267 (6), 251 (10), 242 (12), 239 (10, *m/z* 337 − 98), 229 (7), 216 (10), 175 (32), 140 (20), 110 (100), 102 (88).

**Acknowledgment.** We acknowledge financial support from the Australian Wool Corporation and are grateful to Dr. A. L. Chaffee (CSIRO, Division of Energy Chemistry, N.S.W.) for obtaining the FAB mass spectra.

**Registry No.** **1**, 105751-07-3; **2**, 114790-95-3; **3**, 114790-97-5; **4**, 114819-63-5; **5**, 114819-65-7; **6**, 114790-98-6; **7**, 114791-00-3; **8**, 114791-02-5; **9**, 114791-04-7.

---

## Improved Synthesis of Alkynylphenyliodonium Arylsulfonates (RC≡CIPh•$OSO_2Ar$)

Tsugio Kitamura and Peter J. Stang*

*Chemistry Department, The University of Utah, Salt Lake City, Utah 84112*

*Received December 23, 1987*

Multicoordinate (hypervalent)iodine chemistry is undergoing a renaissance.[1] The latest member of the family of polyvalent iodine compounds, alkynylphenyliodonium arylsulfonates (**3**), has rapidly become a key reagent in numerous, novel transformations. Koser and co-workers[2] have employed **3** in the preparation of aryl(2-furyl)-iodonium tosylates that serve as microbicides.[3] We have used **3** as precursors to hitherto unknown, unique alkynyl sulfonate esters,[4] alkynyl phosphates,[5] and alkynyl carboxylates.[5,6] Moreover, **3** serves as a progenitor of a novel tricoordinate vinyliodinane species[7] and alkylidenecarbene–iodonium ylides.[7,8] Finally, the stereoselective formation of conjugated enynes via coupling of alkynyliodonium tosylates and vinylcopper reagents has been reported.[9]

To date the only known procedure for the preparation of these useful alkynylphenyliodonium arylsulfonates (**3**) involves the reaction of [hydroxy(tosyloxy)iodo]benzene[10] (**2**) with terminal acetylenes (**1**) as discovered by Koser[11] and elaborated by us,[4] as outlined in eq 1. However, this

(1) For reviews, see: (a) Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244. (b) Varvoglis, A. *Synthesis* **1984**, 709. (c) Koser, G. F. In *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; Chapter 25, pp 1265–1351. (d) Olah, G. A. *Halonium Ions*, Wiley: New York, 1975. (e) Banks, D. F. *Chem. Rev.* **1966**, *66*, 243.

(2) Margida, A. J.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 4703.

(3) Carman, C. S.; Koser, G. F. *J. Org. Chem.* **1983**, *48*, 2534 and references therein.

(4) (a) Stang, P. J.; Surber, B. W.; Chen, Z. C.; Roberts, K. A.; Anderson, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 228. (b) Stang, P. J.; Surber, B. W. *J. Am. Chem. Soc.* **1985**, *107*, 1452.

(5) Stang, P. J.; Boehshar, M.; Lin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7832.

(6) Stang, P. J.; Boehshar, M.; Wingert, H.; Kitamura, T. *J. Am. Chem. Soc.*, in press.

(7) Stang, P. J.; Wingert, H.; Arif, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 7235.

(8) Kitamura, T.; Stang, P. J. *Tetrahedron Lett.*, in press.

(9) Stang, P. J.; Kitamura, T. *J. Am. Chem. Soc.* **1987**, *109*, 7561.

(10) Neiland, O.; Karele, B. *J. Org. Chem. USSR (Engl. Transl.)* **1970**, *6*, 889. Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1977**, *42*, 1476.

(11) Rebrovic, L.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 4700. Koser, G. F., Rebrovic, L.; Wettach, R. H. *Ibid.* **1981**, *46*, 4324.

0022-3263/88/1953-4105$01.50/0 

$$\underset{1}{RC{\equiv}CH} + \underset{2}{PhIOH{\cdot}OTs} \rightarrow \underset{3}{RC{\equiv}CIPh{\cdot}OTs} + \underset{4}{R(TsO)C{=}CHIPh{\cdot}OTs} \quad (1)$$

procedure suffers from a number of serious shortcomings. Formation of **3** is generally accompanied by the related vinyl species **4** that both decreases the yields of **3** and causes purification problems. Moreover, the original Koser procedure[10] did not give any **3** when the R in **1** (or **3**) was a small primary group such as Me, *n*-Pr, or *n*-Bu. Although our modified procedure[4] afforded these particular compounds, the yields were very poor, with only 19% and 12% respectively for R = $CH_3$ and *n*-Bu. Finally, no $Me_3SiC{\equiv}CIPh{\cdot}OTs$ could be isolated from the reaction of $Me_3SiC{\equiv}CH$ and **2**.

Hence, we wish to report a simple, much improved procedure for the ready preparation of **3**. This procedure involves the reaction of readily available iodosobenzene (**5**) with 1-(trimethylsilyl)-1-alkynes (**6**) in chloroform in the presence of equimolar amounts of $BF_3{\cdot}OEt_2$ followed by sequential treatment with aqueous $NaOSO_2Ar$ as shown in eq 2. Physical and spectral data for representative

$$\underset{5}{PhIO} + RC{\equiv}CSiMe_3 \xrightarrow[\text{room temp}]{\text{(1) } BF_3{\cdot}OEt_2,\ CHCl_3} \xrightarrow{\text{(2) aq } NaOSO_2Ar} RC{\equiv}CIPh{\cdot}OSO_2C_6H_4X\text{-}p \quad (2)$$

**6a**, R = Me
**6b**, R = Et
**6c**, R = *n*-Pr
**6d**, R = *n*-Bu
**6e**, R = $Me_3Si$

**3a**, R = Me; X = Me
**3b**, R = Me; X = $NO_2$
**3c**, R = Et; X = Me
**3d**, R = *n*-Pr; X = Me
**3e**, R = *n*-Bu; X = Me
**3f**, R = $Me_3Si$; X = Me

reactions are summarized in the Experimental Section. The experimental procedure itself is similar to that of Fujita[12] reported for the preparation of the related alkynylphenyliodonium tetrafluoroborates ($RC{\equiv}CIPh{\cdot}BF_4$).

As the data indicate, good to excellent yields of a variety of alkynylphenyliodonium sulfonates (**3**) may be prepared by this procedure. All compounds are stable crystalline solids. Most gratifying is the observation that simple primary alkyl groups such as Me, Et, *n*-Pr, and *n*-Bu work very well. Moreover, $Me_3SiC{\equiv}CSiMe_3$ affords the hitherto unknown silyl-substituted iodonium salt in 70% isolated yield. The products were characterized by spectral means as summarized in the Experimental Section. The spectral data are all in accord with expectations for the individual compounds.

We believe that this improved, more general procedure will further increase the availability and uses of these relatively new and valuable alkynyliodonium species.

## Experimental Section

**General Procedure.** To a suspension of iodosobenzene (**5**) (PhIO, 5.0 mmol) and the appropriate 1-(trimethylsilyl)-1-alkyne (**6**) (5.0 mmol, prepared from 1-alkyne and $Me_3SiCl$ in nearly quantitative yield or a commercial sample) in 10 mL of $CHCl_3$ was slowly added 5.0 mmol of $BF_3{\cdot}OEt_2$ at 0 °C. After addition was complete the mixture was stirred at room temperature for 3–4 h. After the resulting yellow homogeneous solution was recooled to 0 °C, a solution of the appropriate sodium arylsulfonate (20 mmol) in water (20 mL) was added and the resulting mixture was vigorously stirred for a few minutes. The organic phase was separated and the aqueous phase extracted with additional $CHCl_3$. The combined organic phase was washed with water, dried over anhydrous $MgSO_4$, and concentrated. The residual oil solidified upon addition of ether. The solid was filtered, washed with ether, and air-dried. In no case was any **4** observed in these reactions. The respective yields and physical and spectral data are as follows. **3a**: yield 62%; mp 123–125 °C dec (lit.[4a] mp 123–127 °C); $^1H$ NMR ($CDCl_3$) $\delta$ 2.07 (s, Me), 2.30 (s, Me), 7.02–7.63 (m, ArH), 7.95–8.08 (m, ArH); IR (Nujol) 2185 (m, C≡C), 1220 (s), 1150 (vs), 1115 (s), 1025 (m), 993 (s), 982 (m), 820 (m), 735 (s), 680 (s) $cm^{-1}$; FABMS *m/e* 243 ($MeC{\equiv}CIPh^+$). **3b**: yield 69%; mp 135–138 °C dec; $^1H$ NMR ($CDCl_3$–DMSO-$d_6$) $\delta$ 2.17 (s, Me), 7.33–7.72 (m, ArH), 7.88–8.20 (m, ArH); IR (Nujol) 2185 (m, C≡C), 1522 (s), 1345 (s), 1235 (s), 1180 (s), 1160 (s), 1115 (s), 1020 (s), 998 (s), 983 (w), 850 (s), 734 (s), 628 (s) $cm^{-1}$; FABMS *m/e* 243 ($MeC{\equiv}CIPh^+$). **3c**: yield 81%; mp 108–110 °C dec; $^1H$ NMR ($CDCl_3$) $\delta$ 1.10 (t, *J* = 7.5 Hz, Me), 2.30 (s, Me), 2.40 (q, *J* = 7.5 Hz, $CH_2$), 7.00–7.60 (m, ArH), 7.93–8.04 (m, ArH); IR (Nujol) 2180 (m, C≡C), 1220 (s), 1160 (s), 1110 (m), 1024 (m), 1000 (s), 985 (w, sh), 810 (w), 738 (m), 675 (s) $cm^{-1}$; FABMS *m/e* 257 ($EtC{\equiv}CIPh^+$). **3d**: yield 89%; mp 93–95 °C dec; $^1H$ NMR ($CDCl_3$) $\delta$ 0.90 (t, *J* = 7.5 Hz, Me), 1.50 (sext, *J* = 7.5 Hz, $CH_2$), 2.30 (s, Me), 2.40 (t, *J* = 7.5 Hz, $CH_2$), 6.98–7.62 (m, ArH), 7.93–8.05 (m, ArH); IR (Nujol) 2185 (m, C≡C), 1229 (s), 1140 (s), 1110 (m), 1025 (w), 995 (s), 807 (w), 743 (m), 675 (s); FABMS *m/e* 271 (*n*-$PrC{\equiv}CIPh^+$). **3e**: yield 76%; mp 76–78 °C dec (lit.[4a] mp 81–83 °C); $^1H$ NMR ($CDCl_3$) $\delta$ 0.73–0.92 (m, Me), 1.12–1.58 (m, $CH_2CH_2$), 2.30 (s, Me), 2.30–2.50 (m, $CH_2$), 6.98–7.60 (m, ArH), 7.92–8.05 (m, ArH); IR (Nujol) 2185 (m, C≡C), 1225 (s), 1175 (m), 1145 (vs), 1115 (m), 1025 (m), 1000 (s), 985 (m, sh), 807 (m), 730 (m), 675 (s) $cm^{-1}$; FABMS *m/e* 285 (*n*-$BuC{\equiv}CIPh^+$). **3f**: yield 70%; mp 107–109 °C dec; $^1H$ NMR ($CDCl_3$) $\delta$ 0.15 (s, Me), 2.30 (s, Me), 7.00–7.61 (m, ArH), 7.97–8.07 (m, ArH); IR (Nujol) 1222 (s), 1145 (vs), 1112 (m), 1023 (m), 998 (s), 985 (w, sh), 850 (s), 835 (m, sh), 810 (w), 742 (w), 700 (m), 674 (s) $cm^{-1}$; FABMS *m/e* 301 ($Me_3SiC{\equiv}CIPh^+$). Acceptable combustion analytical data for C and H (±0.4%) were obtained for **3a**, **3c**, **3d**, and **3f**; compounds **3a** and **3b** are known compounds.[4a]

**Acknowledgment.** This research was supported by the NCI of NIH, Grant CA 16903-11.

**Registry No.** **3a**, 94957-41-2; **3b**, 114820-32-5; **3c**, 114820-34-7; **3d**, 114820-36-9; **3e**, 94957-42-3; **3f**, 114820-38-1; **5**, 536-80-1; **6a**, 6224-91-5; **6b**, 62108-37-6; **6c**, 18270-17-2; **6d**, 3844-94-8; **6e**, 14630-40-1; $NaOSO_2C_6H_4Me$-*p*, 657-84-1; $NaOSO_2C_6H_4NO_2$-*p*, 5134-88-3.

(12) Ochiai, M.; Kunishima, M.; Sumi, K.; Nagao, Y.; Fujita, E.; Arimoto, M.; Yamaguchi, H. *Tetrahedron Lett.* **1985**, *26*, 4501.

---

## Synthesis of Dihydrophosphorins by the Thermal Transformation of Phosphole–Dichlorocarbene Adducts

György Keglevich, Beáta Androsits, and László Tőke*

*Organical Chemical Technology Department, Technical University of Budapest, 1521 Budapest, Hungary*

*Received February 9, 1988*

Ring enlargement of unsaturated cyclic compounds through dichlorocarbene adducts is a useful synthetic method.[1-3] The addition of dichlorocarbene to the double

(1) (a) Bergman, E. *J. Org. Chem.* **1963**, *28*, 2210. (b) Sonnenberg, J.; Winstein, S. *J. Org. Chem.* **1962**, *27*, 748. (c) Lindsay, D. G.; Reese, C. B. *Tetrahedron* **1965**, *21*, 1673. (d) De Selms, R. C.; Combs, C. M. *J. Org. Chem.* **1963**, *28*, 2206. (e) Parham, W. E.; Reiff, H. E.; Swartzentruber, P. *J. Am. Chem. Soc.* **1956**, *78*, 1437. (f) Cromarty, A.; Haque, K. E.; Proctor, G. R. *J. Chem. Soc. C* **1971**, 3536.

(2) (a) Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 1. (b) Kraus, W.; Klein, G.; Sadlo, H.; Rothenwöhler, W. *Synthesis* **1972**, 485. (c) Jefford, C. W.; Sweeney, A.; Delay, F. *Helv. Chim. Acta* **1972**, *55*, 2214. (d) Jefford, C. W.; Heros, V.; Burger, U. *Tetrahedron Lett.* **1976**, 703. (e) Kwantes, P. M.; Klumpp, G. W. *Tetrahedron Lett.* **1976**, 707.

(3) Lantos, I.; Bhattacharjee, D.; Eggleston, D. S. *J. Org. Chem.* **1986**, *51*, 4147.

0022-3263/88/1953-4106$01.50/0 