SHORT PAPER

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Hypervalent iodine in synthesis 51: a facile novel synthetic access to Se-phenyl O,O-dialkyl phosphoroselenoates[†]

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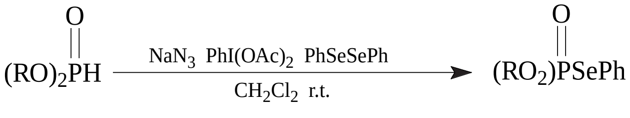
O,O-Dialkyl phosphorous acids react at room temperature with phenyliodine diacetate (PID), sodium azide and diphenyl diselenide, to afford Se-phenyl *O,O*-dialkyl phosphoroselenoates in good yields.

It has been established that phenyliodine diacetate PID and sodium azide act as efficient sources of various carbon centered radicals, through the action of the *in situ* generated $N_3^{\bullet}$ on organic molecules with weak C–H bonds or olefin groups. An example was provided by the generation of the propanoyl radical from propanal and $N_3^{\bullet}$. The resultant radical was trapped by protonated heteroaromatic bases.[1] Vicinal phenylseleno azides have been formed by trapping a carbon centered radical prepared from an olefin, with diphenyl diselenide.[2] Thus, the radical initiating property of the PID/NaN_3 combination enables some C–C and C–X (X=Se,N *etc.*) bonding process to be achieved through radical processes.

However, no attempt has been made to generate heteroatom centered radicals by the combination of PID/NaN_3. In the course of our studies on the applications of hypervalent iodine reagents in synthesis, we considered the possibility of extending this methodology to some heteroatom-heteroatom bonding reactions. In particular, the active P–H bonds in *O,O*-dialkyl phosphorous acids promoted such an idea.

As depicted in Scheme 1, our goal was the synthesis of Se-phenyl *O,O*-dialkyl phosphoroselenoates, which are of marked utility in organic chemistry[3,4] and biochemistry.[5] The literature preparation of these compounds include the Arbuzov-type reaction of trialkyl phosphites with benzeneselenenyl bromide[6] or chloride,[7] the benzeneselenation of mercury *O,O*-dialkyl phosphorates with benzeneselenenyl bromide,[6] or the action of lithium selenophenolate on *O,O*-dialkyl phosphoryl chlorides.[3] By comparison, the present reaction would provide a facile effective one-pot procedure for the synthesis of Se-phenyl *O,O*-dialkyl phosphoroselenoates from readily accessible starting materials.



$$(RO)_2\overset{O}{\overset{\|}{P}}H \xrightarrow[CH_2Cl_2\ \text{r.t.}]{NaN_3\ PhI(OAc)_2\ PhSeSePh} (RO_2)\overset{O}{\overset{\|}{P}}SePh$$

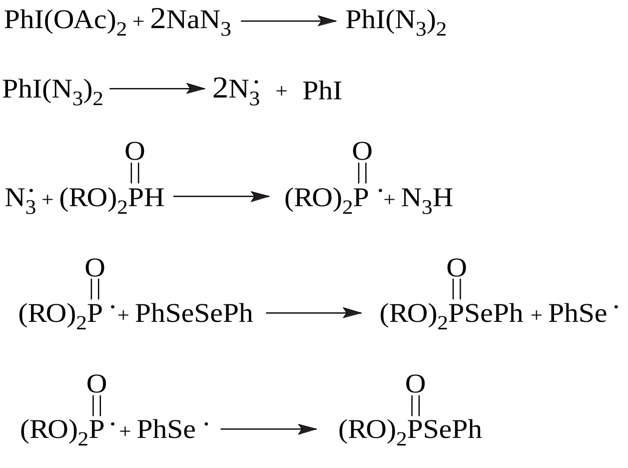
Scheme 1

In fact, simple stirring the mixture of *O,O*-dialkyl phosphorous acid,PID,sodium azide and diphenyl diselenide at room temperature under an N_2 atmosphere gave, after work up and isolation,the desired Se-phenyl *O,O*-dialkyl phosphoroselenoate. The reaction is clean and efficient. The variation of the alkyl groups in *O,O*-dialkyl phosphorous acids does not significantly alter the final yields.

Table 1 Synthesis of Se-phenyl *O,O*-dialkyl phosphoroselenoates

Entry	R	Time(h)	isolated yield(%)
1	Me	2	88
2	Et	2	91
3	Pr	2	83
4	*i*-Pr	2	86
5	Bu	2	82
6	*s*-Bu	2.5	78

As shown in Scheme 2, we propose a possible mechanism for the formation of Se-phenyl *O,O*-dialkyl phosphoroselenoates. The reactive species, phenyliodine bisazide is formed by the ligand exchange reaction, and affords the azido radical via a homolytic decompostion, as proposed by Kita and coworkers.[8] The phosphorus centered radicals are then generated by H-abstraction, and trapped by diphenyl diselenide to afford Se-phenyl *O,O*-dialkyl phosphoroselenoates. The products are also formed by coupling the resulting phenylseleno radical and the phosphorous centered one.



$$PhI(OAc)_2 + 2NaN_3 \longrightarrow PhI(N_3)_2$$

$$PhI(N_3)_2 \longrightarrow 2N_3^{\bullet} + PhI$$

$$N_3^{\bullet} + (RO)_2\overset{O}{\overset{\|}{P}}H \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}{}^{\bullet} + N_3H$$

$$(RO)_2\overset{O}{\overset{\|}{P}}{}^{\bullet} + PhSeSePh \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}SePh + PhSe^{\bullet}$$

$$(RO)_2\overset{O}{\overset{\|}{P}}{}^{\bullet} + PhSe^{\bullet} \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}SePh$$

Scheme 2

In conclusion, the novel phosphorus centered radicals prepared by the PID/NaN_3 combination can effect the facile synthesis of Se-phenyl *O,O*-dialkyl phosphoroselenoates.

Experimental

IR spectra were recorded on a PE-683 Spectrophotometer. ^1H-NMR spectra were recorded on a PMX-60 Spectrometer, using CCl_4 as the solvent with TMS as an internal standard.

General procedure for the synthesis of Se-phenyl O,O-dialkyl phosphoroselenoates: A mixture of *O,O*-dialkyl phosphorous acid (1 mmol), diphenyl diselenide (0.6 mmol), sodium azide (2.5 mmol) and

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

PID (1.5 mmol) in CH_2Cl_2 (10 ml) was stirred at room temperature under N_2 atmosphere. When the reaction was complete as detected by TLC, the mixture was washed with water, dried (anhydrous $MgSO_4$) and concentrated *in vacuo*. The residue was purified by preparative TLC using petroleum ether (30–60°C)—EtOAc (8:1) as eluent.

Entry 1: oil. b.p.$_{0.04}$ 110?(Lit.[6] b.p.$_{0.005}$91–92°C). IR (film): 1585, 1490, 1450, 1260, 1185, 1020, 785, 740cm^{-1}. ^{1}H-NMR: 7.83–7.17(m,5H), 3.67(d,6H,J 12Hz).

Entry 2: oil. b.p.$_{0.04}$121°C(Lit.[6] b.p.$_{0.005}$102°C). IR (film): 1585, 1490, 1440, 1255, 1165, 1020, 970, 790, 745cm^{-1}. ^{1}H-NMR: 7.80–7.17(m,5H), 4.50–3.80(m,4H), 1.28(t,6H,J 6Hz).

Entry 3: oil. b.p.$_{0.04}$ 129°C(Lit.[6] b.p.$_{0.005}$109°C). IR (film): 1590, 1490, 1453, 1400, 1255, 1000, 740cm^{-1}. ^{1}H-NMR: 7.75–7.12(m,5H), 4.20–3.71(4H), 1.92–1.35(m,4H), 0.95(t,6H,J 6Hz).

Entry 4: oil. b.p.$_{0.04}$ 120°C(Lit.[6] b.p.$_{0.005}$101°C). IR (film): 1580, 1490, 1445, 1390, 1380, 1252, 975, 740cm^{-1}. ^{1}H-NMR: 7.83–7.12(m,5H), 5.00–4.35(m,2H), 1.25(t,12H,J 6Hz).

Entry 5: oil. b.p.$_{0.04}$ 146°C(Lit.[6] b.p.$_{0.005}$123°C). IR (film): 1585, 1490, 1450, 1390, 1255, 1150, 1125, 1000, 740cm^{-1}. ^{1}H-NMR:7.70–7.06(m,5H), 4.26–3.65(m,4H), 1.90–0.60(m,14H).

Entry 6: oil. b.p.$_{0.04}$ 137°C(Lit.[6] b.p.$_{0.005}$115°C). IR (film): 1580, 1475, 1440, 1380, 1250, 1170, 1125, 1110, 1090, 1025, 975, 740cm^{-1}. ^{1}H-NMR: 7.80–7.05(m,5H), 4.75–4.11(m,2H), 1.90–0.65(m,16H).

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