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A convenient preparation of organyltellurophosphates using a polymer-supported hypervalent iodine(III) reagent

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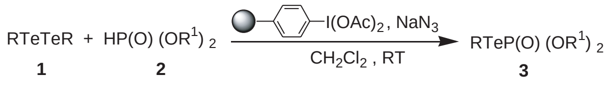
Organyltellurophosphates can be synthesised smoothly in moderate to good yields by the free radical reaction of diorganyl phosphites with diorganyl ditellurides using poly[styrene(iodosodiacetate)] and sodium azide; the polymer reagent can be regenerated and recycled with no loss of reactivity.

Keywords: organyltellurophosphate, free redical reaction, hypervalent iodine(III) reagent

Organic dichalcogenides are good free radical acceptors toward carbon radicals[1] in the order RSSR < RSeSeR < RTeTeR.[2] On the other hand, phosphonyl radicals can be generated from dialkyl phosphites in the presence of peroxides, azo compounds or ultraviolet light.[3] However, direct synthesis of arylchalcogenophosphates from organic dichalcogenides and dialkyl phosphites by a free radical procedure has seldom been discussed.[4] Our group has achieved the preparation of aryltellurophosphates by a free radical reaction initiated by azobisisobutyronitrile (AIBN),[4b] but the yields were low as the aryltellurophosphates are unstable compounds[5] and may decompose under the conditions. Azidyl radicals can be generated from sodium azide in the presence of (diacetoxyiodo)benzene and are widely used in organic synthesis.[6] Poly[styrene(iodosodiacetate)] has similar reactivity to (diacetoxyiodo)benzene and the by-product, poly(iodostyrene), can be regenerated[7]. Herein, we wish to report an efficient method for the preparation of organyltellurophosphates as shown in Scheme 1.



Scheme 1

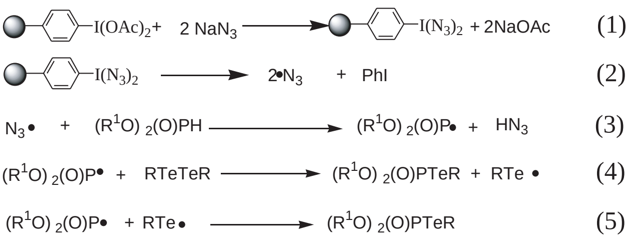
Diphenyl ditelluride **1a** was treated with dimethyl phosphite **2a** in the presence of poly[styrene(iodosodiacetate)] and sodium azide [**see Safety Note in Experimental Section**] in dry dichloromethane at room temperature for 48 h to produce the *O*,*O*-dimethyl *Te*-phenyl tellurophosphonate **3a** in moderate yield (59%). This result encouraged us to prepare other organyltellurophosphates and the results are shown in Table 1. The regenerated poly[styrene(iodosodiacetate)] has the same activity as the initial poly[styrene(iodosodiacetate)] (Table 1, Entry **11**).

A possible reaction pathway for the formation of the organyltellurophosphates is proposed as shown in Scheme 2. The initial step of the free radical reaction is the reaction of poly[styrene(iodosodiacetate)] with sodium azide to generate the azidyl radical and subsequently the phosphonyl radical. Organyltelluro group abstraction from the diorganyl ditelluride by the phosphonyl radical affords the product and an equivalent of the organyltelluryl radical. The organyltelluryl radical might then combine with the phosphonyl radical to form another molecule of the product.

Table 1 Preparation of organyltellurophosphates **3**

Entry	Product	Yield/%[a]
1	$C_6H_5TeP(O)(OCH_3)_2$, **3a**	59
2	$C_6H_5TeP(O)(OC_2H_5)_2$, **3b**	64
3	$C_6H_5TeP(O)[OCH(CH_3)_2]_2$, **3c**	51
4	$C_6H_5TeP(O)(O\ n\text{-}C_3H_7)_2$, **3d**	68
5	$C_6H_5TeP(O)(O\ n\text{-}C_4H_9)_2$, **3e**	64
6	$C_6H_5TeP(O)(OC_6H_5)_2$, **3f**	82
7	$n\text{-}C_4H_9TeP(O)(OCH_3)_2$, **3g**	63
8	$p\text{-}ClC_6H_4TeP(O)(OCH_3)_2$, **3h**	58
9	$p\text{-}ClC_6H_4TeP(O)(OC_2H_5)_2$, **3i**	61
10	$\alpha\text{-}C_{10}H_7TeP(O)(OCH_3)_2$, **3j**	65
11	$C_6H_5TeP(O)(OCH_3)_2$, **3a**	58[b]

[a]Isolated yields based on diorganyl ditellurides.
[b]Use of regenerated poly[styrene(iodosodiacetate)].



Scheme 2

In conclusion, poly[styrene(iodosodiacetate)]-initiated free radical reaction of dialkyl phosphites and diorganyl ditellurides provided a novel route to the versatile organyltellurophosphates. It has the advantages of easily available starting materials and simple operation and occurs under mild conditions. The polymer reagent can be regenerated and recycled with no loss of reactivity. The applications of the organyltellurophosphates are now being studied in our group.

Experimental

^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer in $CDCl_3$ with TMS as the internal standard. ^{13}C NMR spectra were recorded on a Bruker AC-400 (100 MHz) spectrometer in $CDCl_3$. IR spectra were recorded on a Shimadzu IR-408 spectrometer. EIMS were run on a HP 5989B mass spectrometer and HRMS were recorded on a Kratos Concept 1H Series Mass spectrometer. Diorganyl ditellurides,[8] diorganyl phosphites[9] and poly[styrene(iodosodiacetate)][10] were prepared according to literature procedures. The functional group of poly[styrene(iodosodiacetate)] is present at 2.80 mmol/g by iodometry.

CAUTION: Due precautions need to be taken in view of the hazardous nature of soduim azide and the HN_3 product.

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General procedure for the free radical reaction of diorganyl ditellurides and diorganyl phosphites: In a round bottomed flask, a suspension of diorganyl ditellurides (0.5 mmol), diorganyl phosphite (1.2 mmol), NaN_3 (2.5 mmol) and poly[styrene(iodosodiacetate)] (1.2 mmol) in CH_2Cl_2 (15 ml) was stirred at room temperature. The red mixture gradually turned to yellow or even colourless and the reaction was monitored by TLC. Then the mixture was washed with brine, extracted with CH_2Cl_2 (2×10 ml) and dried over $MgSO_4$. After evaporating the solvent, the residue was subjected to preparative TLC on silica gel to afford the organyltellurophosphates (Hexane/EtOAc, 3/1).

O,O-Dimethyl Te-phenyl tellurophosphonate **3a**: Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.32 (m, 3 H), 7.25–7.21 (m, 2 H), 3.69 (d, *J* = 13.6 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.4 (d, *J* = 4.9 Hz), 130.2 (d, *J* = 1.5 Hz), 129.5 (d, *J* = 2.4 Hz), 108.7 (d, *J* = 7.3 Hz), 64.1 (d, *J* = 4.4 Hz); MS (EI): *m/z* (rel. intensity) = 316 [$(M+2)^+$, 16.0], 155 (9.7), 109 (100), 93 (15.3), 79 (28.6), 77 (75.0), 51 (54.5), 47 (22.6); IR (film): ν_{max} = 2949, 2847, 2243, 2167, 1573, 1474, 1436, 1239, 1180, 1017, 909, 818, 779, 731, 690, 647 cm^{-1}; HRMS: calcd. for $(C_8H_{11}O_3PTe)^+$: 315.9508. Found: 315.9531.

O,O-Diethyl Te-phenyl tellurophosphonate **3b**: Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.82 (m, 2 H), 7.38–7.31 (m, 1 H), 7.28–7.23 (m, 2 H), 4.22–4.08 (m, 4 H), 1.33–1.28 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.3 (d, *J* =3.8 Hz), 130.1 (d, *J* = 1.9 Hz), 129.3 (d, *J* = 2.5 Hz), 109.2 (d, *J* = 8.4 Hz), 63.9 (d, *J* = 5.6 Hz), 16.1 (d, *J* = 7.0 Hz); MS (EI): *m/z* (rel. intensity) = 344 [$(M+2)^+$, 18.0], 342 (M^+, 17.4), 109 (100), 91 (37.8), 81 (63.2), 77 (88.1), 51 (58.6); IR (film): ν_{max} = 2983, 2936, 2902, 2239, 2162, 1573, 1474, 1436, 1390, 1240, 1161, 1096, 1015, 965, 783, 734, 691 cm^{-1}; HRMS: calcd. for $(C_{10}H_{15}O_3PTe)^+$: 343.9821. Found: 343.9801.

O,O-Di-iso-propyl Te-phenyl tellurophosphonate **3c**: Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.84 (m, 2 H), 7.37–7.33 (m, 1 H), 7.23–7.21 (m, 2 H), 4.80–4.73 (m, 2 H), 1.39–1.34 (m, 9 H), 1.25 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.9 (d, *J* = 5.9 Hz), 129.9 (d, *J* = 1.4 Hz), 129.1 (d, *J* = 2.3 Hz), 110.0 (d, *J* = 8.7 Hz), 73.1 (d, *J* = 4.9 Hz), 24.3 (d, *J* = 3.2 Hz), 23.8 (d, *J* = 6.7 Hz); MS (EI): *m/z* (rel. intensity) = 372 [$(M+2)^+$, 8.3], 370 (M^+, 7.1), 123 (12.1), 99 (17.1), 51 (15.5), 43 (100), 41 (51.5); IR (film): ν_{max} = 2981, 2935, 2158, 1723, 1574, 1468, 1436, 1386, 1243, 1178, 1142, 1104, 972, 764, 735, 691 cm^{-1}; HRMS: calcd. for $(C_{12}H_{19}O_3PTe)^+$: 372.0133. Found: 372.0116.

O,O-Dipropyl Te-phenyl tellurophosphonate **3d**: Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.79 (m, 2 H), 7.34–7.28 (m, 1 H), 7.23–7.19 (m, 2 H), 4.06–3.94 (m, 4 H), 1.70–1.62 (m, 4 H), 0.89–0.84 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.3 (d, *J* = 4.1 Hz), 130.0 (d, *J* = 2.0 Hz), 129.3 (d, *J* = 3.2 Hz), 109.2 (d, *J* = 8.0 Hz), 69.3 (d, *J* = 7.0 Hz), 23.7 (d, *J* = 6.7 Hz), 10.5; MS (EI): *m/z* (rel. intensity) = 372 [$(M+2)^+$, 5.2], 370 (M^+, 4.9), 123 (25.2), 77 (29.5), 51 (16.7), 43 (100), 41 (36.1); IR (film): ν_{max} = 2969, 2880, 2161, 1723, 1574, 1474, 1435, 1389, 1239, 1152, 989, 910, 828, 735, 690 cm^{-1}; HRMS: calcd. for $(C_{12}H_{19}O_3PTe)^+$: 372.0133. Found: 372.0120.

O,O-Di-n-butyl Te-phenyl tellurophosphonate **3e**: Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.82 (m, 2 H), 7.36–7.33 (m, 1 H), 7.28–7.22 (m, 2 H), 4.11–3.99 (m, 4 H), 1.66–1.59 (m, 4 H), 1.38–1.29 (m,4 H), 0.90–0.87 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.3 (d, *J* = 4.4 Hz), 130.0 (d, *J* = 2.7 Hz), 129.2 (d, *J* = 2.9 Hz), 109.2 (d, *J* = 8.3 Hz), 67.6 (d, *J* = 6.2 Hz), 32.3 (d, *J* = 6.8 Hz), 19.1, 14.0; MS (EI): *m/z* (rel. intensity) = 400 [$(M+2)^+$, 10.9], 398 (M^+, 10.5), 137 (29.4), 77 (46.0), 57 (100), 51 (23.6), 41 (77.0); IR (film): ν_{max} = 2961, 2874, 1574, 1473, 1435, 1382, 1267, 1149, 1024, 895, 793, 734, 691 cm^{-1}; HRMS: calcd. for $(C_{14}H_{23}O_3PTe)^+$: 400.0446. Found: 400.0428.

O,O-Diphenyl Te-phenyl tellurophosphonate **3f**: Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.33 (m, 6 H), 7.28–7.16 (m, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9 (d, *J* = 7.3 Hz), 141.1 (d, *J* = 4.4 Hz), 130.3 (d, *J* = 6.3 Hz), 129.7, 126.1, 121.5 (d, *J* = 4.9 Hz), 120.5 (d, *J* = 5.1 Hz), 116.9; MS (EI): *m/z* (rel. intensity) = 440 [$(M+2)^+$, 2.0], 438 (M^+, 1.8), 326 (41.9), 325 (28.0), 94 (27.3), 77 (100), 65 (62.9), 51 (54.8); IR (film): ν_{max} = 3072, 2249, 1730, 1590, 1489, 1456, 1297, 1226, 1188, 1162, 1071, 1025, 1010, 965, 909, 754, 733, 688 cm^{-1}; HRMS: calcd. for $(C_{18}H_{15}O_3PTe)^+$: 439.9820. Found: 439.9801.

O,O-Dimethyl Te- n-butyl tellurophosphonate **3g**: Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.67 (d, *J* = 11.6 Hz, 6 H), 2.87–2.77 (m, 2 H), 1.82–1.75 (m, 2 H), 1.40–1.31 (m, 2 H), 0.90–0.86 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.6 (d, *J* = 5.4 Hz), 34.7 (d, *J* = 2.7 Hz), 25.2, 13.6, 9.1 (d, *J* = 3.7 Hz); MS (EI): *m/z* (rel. intensity) = 297[$(M+3)^+$, 70.7], 296[$(M+2)^+$, 20.4], 295[$(M+1)^+$, 66.5], 294 (M^+, 17.3), 293[$(M-1)^+$, 41.3], 292[$(M-2)^+$, 24.2], 109 (100), 93 (46.5), 79 (48.3), 57 (72.5), 41 (92.0); IR (film): ν_{max} = 2958, 2874,2246, 1717, 1460, 1380, 1234, 1180, 1019, 909, 817, 780, 733, 649 cm^{-1}; HRMS: calcd. for $(C_6H_{15}O_3PTe)^+$: 295.9820. Found: 295.9836.

O,O-Dimethyl Te- p-chlorophenyl tellurophosphonate **3h**: Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.75 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2 H), 7.23 (d, *J* = 7.6 Hz , 2 H), 3.74 (d, *J* = 13.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =141.7 (d, *J* = 2.7 Hz), 136.3 (d, *J* = 3.6 Hz), 130.5 (d, *J* = 3.0 Hz), 106.2 (d, *J* = 8.2 Hz), 64.1 (d, *J* = 5.9 Hz); MS (EI): *m/z* (rel. intensity) = 350 [$(M+2)^+$, 13.1], 348 (M^+, 10.6), 109 (100), 79 (18.8), 75 (22.2), 50 (11.3) ; IR (film): ν_{max} = 2948, 2846, 2166, 1719, 1567, 1472, 1384, 1243, 1179, 1088, 1007, 812, 776, 754, 722 cm^{-1}; HRMS: calcd. for $(C_8H_{10}ClO_3PTe)^+$: 349.9117. Found: 349.9102.

O,O-Diethyl Te- p-chlorophenyl tellurophosphonate **3i**: Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78–7.76 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 2 H), 7.25–7.23 (dd, *J* = 6.0 Hz *J* = 2.0 Hz , 2 H), 4.20–4.12 (m, 4 H), 1.35 (m, 6 H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.6 (d, *J* = 4.7 Hz), 136.1 (d, *J* = 3.2 Hz), 130.4 (d, *J* = 2.6 Hz), 106.8 (d, *J* = 8.1 Hz), 64.0 (d, *J* = 5.6 Hz), 16.2 (d, *J* = 7.0 Hz); MS (EI): *m/z* (rel. intensity) = 378 [$(M+2)^+$, 10.5], 376 (M^+, 9.2), 137 (22.2), 109 (100), 91 (30.7), 81 (49.6), 75 (25.8), 43 (10.9); IR (film): ν_{max} = 2982, 2928, 2162, 1719, 1567, 1472, 1385, 1240, 1159, 1088, 1008, 965, 811 cm^{-1}; HRMS: calcd. for $(C_{10}H_{14}ClO_3PTe)^+$: 377.9430. Found: 377.9412.

O,O-Dimethyl Te-naphthyl tellurophosphonate **3j**: Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33–8.29 (m, 2 H), 7.92 (d, *J* = 8.4 Hz, 1 H), 7.81 (d, *J* = 8.0 Hz, 1 H), 7.62–7.53 (m, 2 H), 7.37–7.33 (m, 1 H), 3.67 (d, *J* = 13.6 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.3 (d, *J* = 4.1 Hz), 126.7 (d, *J* = 2.5 Hz), 124.0 (d, *J* = 1.9 Hz), 122.8, 121.1 (d, *J* = 2.6 Hz), 119.2, 117.6, 116.8 (d, *J* = 2.9 Hz), 102.2 (d, *J* = 8.5 Hz), 43.9 (d, *J* = 5.8 Hz); MS (EI): *m/z* (rel. intensity) = 366 [$(M+2)^+$, 13.3], 364 (M^+, 11.8), 236 (29.9), 127 (58.7), 109 (48.9), 79 (18.4), 60 (26.9), 43 (100); IR (film): ν_{max} = 2950, 2247, 1717, 1558, 1500, 1457, 1376, 1237, 1180, 1021, 909, 819, 796, 770, 733, 648 cm^{-1}; HRMS: calcd. for $(C_{12}H_{13}O_3PTe)^+$: 365.9663. Found: 365.9679.

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