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A New Facile Synthesis of Tertiary Dithioesters

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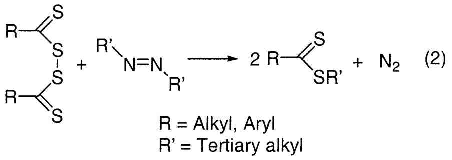
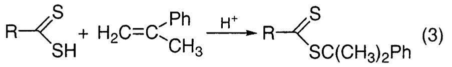
Abstract: Thermal decomposition of tertiary azo compounds in the presence of a triphenylmethyl dithioester results in the formation of the corresponding tertiary dithioesters. This procedure is especially useful for the synthesis of tertiary phosphoryldithioformates, but also represents an easy synthetic methodology of general applicability.

Dithioesters [RC(S)SR′] have been known for a long time and their preparation and reactivity have been widely investigated.[1] More recently these compounds attracted the attention of polymer chemists for their ability to control radical polymerization: indeed the RAFT (Reversible Addition Fragmentation chain Transfer) radical polymerization of such monomers as styrene and methacrylates is based on the use of these compounds as transfer agents.[2−4] In this respect, the behavior of dithioesters is reminiscent of that of xanthates and dithiocarbamates that also undergo radical addition−fragmentation[5] and have been used in controlled radical polymerization.[6] In order for the dithioesters to play such a role efficiently, the R′ residues present in their molecules must be amenable to undergoing easy radical displacement by the growing polymer radical, and therefore it must be an intrinsically resonance-stabilized radical (benzyl, allyl, ...), a tertiary radical (*tert*-butyl, 2-cyanopropyl, ...), or a combination of the two (cumyl, ...).[7] While primary and secondary dithioformates are readily obtained by reacting the appropriate sodium dithioester with the pertinent primary or secondary alkyl bromide (reaction 1), the preparation of the tertiary dithioformates is less straightforward.

Actually, two different routes leading to these derivatives have been reported recently: the first consists of the reaction of a bis(thiocarbonyl)disulfide [RC(S)SSC(S)R] with an azo compound R′N═NR′, where R′ is a tertiary alkyl group (reaction 2),[8,9] while the second involves the acid-catalyzed reaction of dithiocarboxylic acids with an appropriate olefin (reaction 3).[3]





In the past few years we have studied the reactivity of organic free radicals toward dithioformates bearing a dialkoxyphosphoryl group bound to the thiocarbonyl carbon,[10−14] and following the results on the reaction of benzyl diethoxyphosphoryl- and diethoxythiophosphoryldithioformates, we successfully exploited these two derivatives as RAFT agents in the radical polymerization of styrene.[4] The results prompted us to investigate the "RAFT efficiency" of other members of these families where benzyl is replaced by a tertiary group. The syntheses of these compounds through the easy and inexpensive one-pot process used for the benzyl derivatives (Scheme 1)[11] were not considered worth trying due to the inefficiency of nucleophilic substitution of tertiary halides.

On the other hand, the two synthetic routes outlined in reactions 2 and 3 also could not be used. In the former case this was due to the impossibility of synthesizing the necessary starting compounds. Indeed, while the required disulfides RC(S)SSC(S)R can be readily synthesized when

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(1) Duus, F. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Jones, D. N. Eds.; Pergamon Press: Oxford, UK, 1979.

(2) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559. Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Krstina, J.; Moad, G.; Postma, A.; Thang, S. H. *Macromolecules* **2000**, *33*, 243 and references therein.

(3) Barner-Kowollik, C.; Quinn, J. F.; Nguyen, T. L. U.; Heuts, J. P. A.; Davis, T. P. *Macromolecules* **2001**, *34*, 7849.

(4) Laus, M.; Sparnacci, K.; Alberti, A.; Benaglia, M.; Macciantelli, D. *Macromolecules* **2001**, *34*, 7629 and references therein.

(5) Zard, S. Z. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 672.

(6) Otsu, T.; Yoshida, M. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 127.

(7) Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Thang, S. H. *Macromol. Symp.* **1999**, *143*, 291. Mayadunne, R. T. A.; Goto, A.; Sato, K.; Tsujii, Y.; Fukuda, T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2001**, *34*, 402.

(8) Bouhadir, G.; Legrand, N.; Quiclet-Sire, B.; Zard, S. Z. *Tetrahedron Lett.* **1999**, 277.

(9) Thang, S. H.; Chong, Y. K.; Mayadunne, R. T. A.; Moad, G.; Rizzardo, E. *Tetrahedron Lett.* **1999**, 2435.

(10) Levillain, J.; Masson, S.; Hudson, A.; Alberti, A. *J. Am. Chem. Soc.* **1993**, *115*, 8444.

(11) Alberti, A.; Benaglia, M.; Della Bona, M. A.; Macciantelli, D.; Heuzé, B.; Masson, S.; Hudson, A. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1057.

(12) Alberti, A.; Benaglia, M.; Bonora, M.; Borzatta, V.; Hudson, A.; Macciantelli, D.; Masson, S. *Polym. Degrad. Stab.* **1998**, *62*, 559.

(13) Alberti, A.; Benaglia, M.; Hapiot, P.; Hudson, A.; Le Coustomer, G.; Macciantelli, D.; Masson, S. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1908.

(14) Alberti, A.; Benaglia, M.; Macciantelli, D.; Hudson, A.; Masson, S. *Magn. Reson. Chem.* **2002**, *40*, 387.

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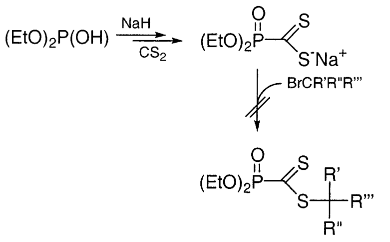
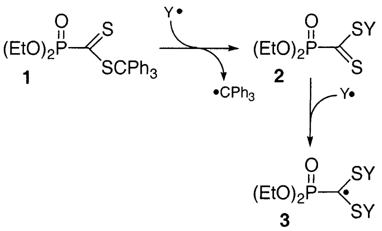
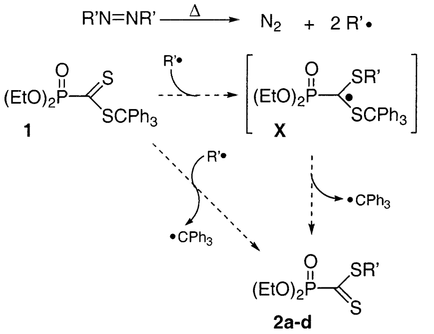
SCHEME 1



SCHEME 2



SCHEME 3

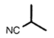
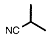
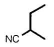
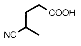
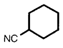
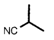


a, R′ = 2-Cyanoprop-2-yl
b, R′ = 4-Carboxy-2-cyanobut-2-yl
c, R′ = 2-Cyanobut-2-yl
d, R′ = 1-Cyanocyclohex-1-yl

R is an alkyl, an aryl, an amino, an alkoxy, or a thioalkyl residue, under no circumstances could we obtain the analogous derivatives where R is a phosphorus-centered group. The alternative route involving the reaction of dithiocarboxylic acids with an appropriate olefin[3] was also unfeasible, because it likewise proved impossible to prepare the starting dialkoxyphosphoryldithioformic acid.

In the course of our studies on the addition of free radicals to phosphoryl- and thiophosphoryldithioformates,[11] we found that the reaction of $Y^{\bullet}$ radicals with triphenylmethyl diethoxyphosphoryldithioformate **1** led to the EPR detection of the $Ph_3C^{\bullet}$ radical itself along with the Y-adduct **3**, implying the in situ formation of the corresponding Y-dithioformate **2** (see Scheme 2). Prompted by this finding we exploited this reaction as a synthetic strategy leading to tertiary phosphoryldithioformates. We report here that refluxing for 3 h a deaerated toluene solution of compound **1** and an excess of AIBN leads to the formation of 2-cyanoprop-2-yl diethoxyphosphoryldithioformate **2a** (yield 80% after chromatographic separation). In a similar fashion, the use of other azo compounds containing different tertiary alkyl residues also leads to the formation of the corresponding diethoxyphosphoryldithioformates **2b**−**d**, most likely through the process outlined in Scheme 3 and involving homolytic displacement of the triphenylmethyl moiety by other $^{\bullet}R'$ radicals.

TABLE 1. Products and Yields of the Thermal Reaction between Dithioesters RC(S)SR″ and Azocompounds R′N=NR′

R	R”	R’	Product	Yield (%)
$(EtO)_2(O)P$	CPh_3		**2a**	80[a]
$(EtO)_2(O)P$	Fluoren-9-yl		**2a**	54[a]
$(EtO)_2(O)P$	CPh_3		**2b**	70[a], 87[b]
$(EtO)_2(O)P$	CPh_3		**2c**	85[b]
$(EtO)_2(O)P$	CPh_3		**2d**	82[a]
Ph	CPh_3		**7**	70[b]

[a] Toluene, reflux, 3 h. [b] Ethyl acetate, reflux, 15 h.

We are not able to tell whether in the homolytic displacement the release of the triphenylmethyl fragment is synchronous to the addition of the tertiary $^{\bullet}R'$ radical or if a two-step process is involved where radical adduct **X** is initially formed, but we wish to emphasize that we have never been able to detect by EPR any adduct **X** either in the present study concerning tertiary radicals or in the previous study[9] involving the addition of other primary and secondary radicals to compound **1**. The driving force of this reaction stems from the stability of triphenylmethyl radical, which makes its homolytic displacement by the incoming $^{\bullet}R'$ very easy. On this basis, the reaction is expected to occur also when replacing the triphenylmethyl fragment with other readily displaceable R″ groups, although with a conversion related to the stability of the individual leaving radical $^{\bullet}R''$. The relative stability of alkyl radicals formed by the S−R″ bond dissociation can be related to differences in the bond dissociation energies BDE[R″-H], the key argument being that owing to the formation of $H^{\bullet}$ as a common product the energy required to break an individual bond reflects the relative stability of the alkyl radical formed in each case. Available BDE values for toluene (88 kcal mol^{-1}),[15] triphenylmethane (81.1 kcal mol^{-1}),[16] and fluorene (79.8 kcal mol^{-1})[16] indicate that the benzyl radical is significantly less stable than the triphenylmethyl radical, which in turn should be slightly less stable than the fluoren-9-yl radical. We thus reacted AIBN with 9-fluorenyl diethoxyphosphoryldithioformate **4** and with benzyl diethoxyphosphoryldithioformate **5**. In the former case the reaction resulted again in the formation of the dithioester **2a**, although in a lower conversion than in the case of **1** (see Table 1), while in the latter no displacement took place and the starting compound **5** was recovered unreacted.

This last result may be associated with the lower stability of the benzyl radical than the triphenylmethyl radical, yet the conversion yield of the reaction involving the fluoren-9-yl derivative **4** would be expected to be at

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[15] Zhang, X.-M.; Bruno, J. W.; Enyinnaya, E. *J. Org. Chem.* **1998**, *63*, 4671.

[16] Zhang, X.-M.; Bordwell, G. G. *J. Org. Chem.* **1992**, *57*, 4163.

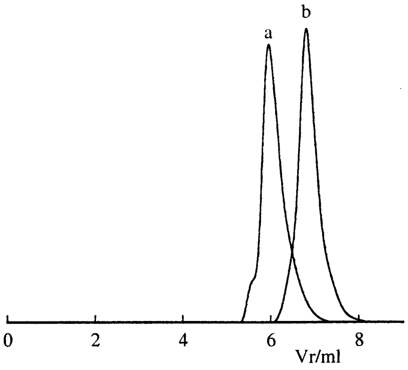

FIGURE 1. SEC curves of poly(methyl methacrylate) (a) and poly(styrene) (b) samples obtained using compound **2a** as RAFT agent.

least the same as that of the reaction of **1**. While the lower conversion observed with **4** seems to be in conflict with the BDE[R-H] values, it has been recently pointed out[17] that the utmost care should be exerted when relating radical stabilities to BDE[R-X] values, and that this particular method leads to erroneous results in those cases when X is not a hydrogen atom, unless additional parameters are considered, such as the electronegativity difference between the atoms or groups involved in the bond to be broken. This would appear to be the case in our reaction, that in fact involves cleavage of a carbon−sulfur bond, which might account for the lower than expected conversion observed for the reaction of AIBN with the fluoren-9-yl diethoxyphosphoryldithioformate.

We believe this reaction represents a unique synthetic route to tertiary α-phosphorus-substituted dithioesters. On the other hand, it also can be applied with success to the synthesis of tertiary dithiobenzoates and possibly of tertiary dithioesters in general, although in these cases other convenient routes to the reaction products are available.[3,8,9,18] As an example of this general applicability, we have synthesized compound **7** by refluxing triphenylmethyl dithiobenzoate **6** and AIBN in ethyl acetate (see Table 1).

We also believe that the synthetic process outlined in Scheme 3, although reminiscent of that described earlier,[8,9] is particularly relevant in that it provides an easy and possibly unique access to a variety of tertiary α-phosphorus-substituted dithioformates, which are valuable RAFT transfer agents in controlled radical polymerization processes. As an example, we have used 2-cyanoprop-2-yl diethoxyphosphoryldithioformate (**2a**) to control the AIBN-initiated polymerizations of styrene and methyl methacrylate. Figure 1 shows the SEC curves of the poly(styrene) and poly(methyl methacrylate) samples we obtained by heating at 60 °C for 8 h a mixture of monomer/**2a**/AIBN in a molar ratio of 935/1/0.185 for the former and 630/1/0.526 for the latter case.

The resulting poly(styrene) sample, obtained in 3.4% yield, had a number average molar mass $M_n = 9100$ with a polydispersity index $M_w/M_n = 1.33$, whereas the poly(methyl methacrylate) sample, obtained in 44.0% yield, showed $M_n = 38\,200$ with $M_w/M_n = 1.37$. Heating of the polymers at 60 °C after further addition of AIBN and the corresponding monomer led to their complete conversion with a molar mass distribution centered at higher molar mass values, thus substantiating their "living" nature.

In conclusion, we believe that the reaction described in Scheme 3 may represent a new useful tool in the hands of synthetic chemists for the preparation of tertiary dithioformates in general, and especially of tertiary α-phosphorus-substituted derivatives.

Experimental Section

All solvents were distilled and dried. Styrene (99%) and methyl methacrylate (99%) were also distilled under vacuum just before use. NMR spectra were recorded on either a 400-MHz or on a 200-MHz spectrometer while mass spectra were obtained by means of a high-resolution spectrometer.

Synthetic Procedures. (a) Triphenylmethyl diethoxyphosphoryldithioformate (1). A solution of diethyl phosphite (2.99 g, 21.7 mmol) in THF (5 mL) was added dropwise to a suspension of NaH (0.528 g, 22 mmol) in anhydrous THF (20 mL). After being refluxed for 5 min the solution was cooled to −78 °C and CS_2 (8.39 g, 110 mmol) was added. The solution was allowed to warm to room temperature and stirring was continued for 2 h. After the solution was cooled in an ice bath, Ph_3CBr (7.11 g, 22 mmol) was added and stirring was continued for 3 h at room temperature. After CH_2Cl_2 (100 mL) was added the solution was filtered, the solvent removed under reduced pressure, and the residue quickly chromatographed (SiO_2/ethyl ether). Compound **1** was obtained as blue-violet crystals, mp 82 °C (8.12 g, yield 81%). ^1H NMR (400 MHz) ($CDCl_3$) δ_{ppm} 1.315 (td, $J_{1,2} = 7.6$ Hz, $J_{HP} = 0.76$ Hz, 6H), 4.098−4.251 (m, 4H), 7.253 (s, 15H). ^{13}C NMR (100 MHz) ($CDCl_3$) δ_{ppm} 17.85 (d, $J_{CP} = 6.1$ Hz), 28.186 (s), 65.818 (d, $J_{CP} = 6.9$ Hz), 128.614 (s), 128.894 (s), 131.351 (s), 225.351 (d, $J_{CP} = 168.35$ Hz).^{31}P NMR (85 MHz) ($CDCl_3$) δ_{ppm} from $H_3PO_4-H_2O$ 30%, −5.759. MS, *m/z* M^+ absent, 243, 165.

(b) Fluoren-9-yl Diethoxyphosphoryldithioformate (4). A solution of diethyl phosphite (2.99 g, 21.7 mmol) in THF (5 mL) was added dropwise to a suspension of NaH (0.528 g, 22 mmol) in anhydrous THF (20 mL). After being refluxed for 5 min the solution was cooled to −78 °C and CS_2 (8.39 g, 110 mmol) was added. The solution was allowed to warm to room temperature and stirring continued for 2 h. 9-Bromofluorene (5.39 g, 22 mmol) was added and stirring was continued for another 3 h. The solvent was removed under reduced pressure, ethyl ether was added to the residue, the insoluble salts were filtered off, and the solution was flash chromatographed (eluent: ethyl ether). Red crystals, mp 35 °C (5.40 g, yield 65%); ^1H NMR (400 MHz) ($CDCl_3$) δ_{ppm} 1.412 (t, $J_{1,2} = 7.2$ Hz, 6H), 4.342 (m, 4H), 6.642 (s, 1H), 7.283 (dd, $J_{1,2} = J_{1,2} = 7.4$ Hz, 2H), 7.422 (dd, $J_{1,2} = J_{1,2} = 7.4$ Hz, 2H), 7.476 (d, $J_{1,2} = 7.4$ Hz, 2H), 7.743 (d, $J_{1,2} = 7.4$ Hz, 2H); ^{13}C NMR (100 MHz) ($CDCl_3$) δ_{ppm} 16.501 (d, $J_{C,P} = 5.9$ Hz), 51.178 (d, $J_{C,P} = 3.2$ Hz), 64.995 (d, $J_{C,P} = 7.3$ Hz), 120.103 (s), 125.015 (s), 127.581 (s), 128.784 (s), 141.067 (s), 141.317 (s), 228.392 (d, $J_{C,P} = 173.2$ Hz); ^{31}P NMR (85 MHz) ($CDCl_3$) δ_{ppm} from H_3PO_4/H_2O 30%, −4.256; MS, *m/z* 378 (M^+), 197, 182, 165; High-resolution MS calcd for $[C_{18}H_{19}O_3PS_2]^+$ 378.0513, found 378.0511.

(c) Benzyl Diethoxyphosphoryldithioformate (5). A solution of diethyl phosphite (1.25 mL, 9.7 mmol) in THF (5 mL) was added dropwise to a suspension of NaH (0.23 g, 9.7 mmol) in anhydrous THF (10 mL). After being refluxed for 5 min the solution was cooled to −78 °C and CS_2 (2.9 mL, 48.1 mmol) was added. The solution was allowed to warm to room temperature and stirring continued for 2 h. Benzyl bromide (1.3 mL, 10.7 mmol) was added. After an additional hour hexane (30 mL) was added, the solution filtered, the solvent evaporated, and the residue quickly chromatographed (SiO_2) using cyclohexane as the first eluent to remove the impurities, then ethyl ether. Compound **5** was obtained as a dark-red oil (2.3 g, 78% yield). ^1H NMR (400 MHz) ($CDCl_3$) δ_{ppm} 1.36 (t, $J_{1,2} = 7.6$ Hz, 6H), 4.26

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[17] Zavitsas, A. A. *J. Chem. Edu.* **2001**, *78*, 417.

[18] Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. PCT International Application WO 9801478 A1 980115, Jan 25, 1998.

(m, 4H), 4.46 (s, 2H), 7.30 (s, 5H); ^{13}C NMR (100 MHz) (CDCl$_3$) δ_{ppm} 16.20 (d, J_{CP} = 6.34), 40.63 (d, J_{CP} = 2.72), 64.70 (d, J_{CP} = 6.94), 128.00 (s), 128.77 (s), 129.26 (s), 133.53 (s), 228.16 (d, J_{CP} = 174.54); ^{31}P NMR (85 MHz) (CDCl$_3$) δ_{ppm} from H$_3$PO$_4$/H$_2$O 30%, −4.57; MS *m/z* 304 (M$^+$), 276, 248, 182, 121, 91.

(d) Triphenylmethyl Dithiobenzoate (6). A THF solution (20 mL) of bromobenzene (1.34 mL, 12.7 mmol) was added dropwise to a mixture of Mg (0.31 g, 12.8 mg atom) and a crystal of I$_2$ in THF (100 mL). After 3 h the reaction was cooled at 0 °C and CS$_2$ (0.988 g, 13 mmol) was added. When the addition was over, the solution was allowed to reach room temperature. Stirring was continued for ca. 2 h, then a solution of BrCPh$_3$ (4.10 g, 12.7 mmol) in THF (15 mL) was added dropwise. After another 3 h of stirring, CH$_2$Cl$_2$ (150 mL) was added, the solution filtered, the solvent removed under reduced pressure, and the residue quickly chromatographed (eluent hexane/CH$_2$Cl$_2$ 80/20). Compound **6** was obtained as a purple solid, mp 44 °C (5.02 g, yield 80%). ^{1}H NMR (400 MHz) (CDCl$_3$) δ_{ppm} 7.372 (m, 12H), 7.536 (d, $J_{1,2}$ = 8 Hz, 6H), 8.018 (d, $J_{1,2}$ = 8 Hz, 2H);^{13}C NMR (100 MHz) (CDCl$_3$) δ_{ppm} 74.979, 126.697, 127.021, 127.476, 127.937, 130.143, 131.546, 141.632, 145.779, 224.231; MS, *m/z* 396 (M$^+$, weak), 243, 165.

(e) 2-Cyanoprop-2-yl Diethoxyphosphoryldithioformate (2a). A carefully deaerated toluene (50 mL) solution of **1** (4.56 g, 10 mmol) and AIBN (3.52 g, 21.5 mmol) was refluxed for 3 h. The solvent was evaporated under reduced pressure and the residue quickly chromatographed (SiO$_2$) using as eluent CH$_2$Cl$_2$/ethyl ether/toluene (45/45/10). Compound **2a** was obtained as a deep red oil (2.25 g, yield 80%). Replacing compound **1** with compound **4** (3.78 g, 10 mmol) lowered the yield to 54%. ^{1}H NMR (400 MHz) (CDCl$_3$) δ_{ppm} 1.369 (t, $J_{1,2}$ = 7 Hz, 6H), 1.861 (s, 6H), 4.246 (m, 4H); ^{13}C NMR (100 MHz) (CDCl$_3$) δ_{ppm} 16.387 (d, $J_{C,P}$ = 5.9 Hz), 26.055 (s), 41.674 (d, $J_{C,P}$ = 5.5 Hz), 65.147 (d, $J_{C,P}$ = 6.9 Hz), 118.361 (s), 225.55 (d, $J_{C,P}$ = 170 Hz); ^{31}P NMR (85 MHz) (CDCl$_3$) δ_{ppm} from H$_3$PO$_4$/H$_2$O 30%, −6.791; MS, *m/z* 281 (M$^+$), 213, 109, 91; high-resolution MS calcd for [C$_9$H$_{16}$NO$_3$PS$_2$]$^+$ 281.030926, found 281.031074.

(f) 2-Cyanobut-2-yl Diethoxyphosphoryldithioformate (2b). A carefully deaerated ethyl acetate solution (10 mL) of **1** (0.2 g, 0.44 mmol) and azobis(2-cyanobutane) (0.1 g, 0.50 mmol) was refluxed for 15 h. The solvent was evaporated under reduced pressure and the residue quickly chromatographed (SiO$_2$) using ethyl ether as eluent. Compound **2b** was obtained as a deep red oil (0.112 g, yield 87%). ^{1}H NMR (400 MHz) (CDCl$_3$) δ_{ppm} 1.172 (t, $J_{1,2}$ = 7.2 Hz, 3H), 1.360 (t, $J_{1,2}$ = 6.8 Hz, 6H), 1.824 (s, 3H), 2.017 (m, 1H), 2.181 (m, 1H), 4.236 (m, 4H); ^{13}C NMR (100 MHz) (CDCl$_3$) δ_{ppm} 9.183 (s), 16.378 (d, $J_{C,P}$ = 5.9 Hz), 23.024 (s), 31.989 (s), 47.227 (d, $J_{C,P}$ = 5.9 Hz), 61.117 (d, $J_{C,P}$ = 7.1 Hz), 61.135 (d, $J_{C,P}$ = 7.1 Hz), 171.413 (s), 225.294 (d, $J_{C,P}$ = 170 Hz); ^{31}P NMR (85 MHz) (CDCl$_3$) δ_{ppm} from H$_3$PO$_4$/H$_2$O 30%, −6.786; MS, *m/z* 295 (M$^+$), 280, 138, 109, 91; high-resolution MS calcd for [C$_{10}$H$_{18}$NO$_3$PS$_2$]$^+$ 295.046576, found 295.046709.

(g) 4-Carboxy-2-cyanobut-2-yl Diethoxyphosphoryldithioformate (2c). A carefully deaerated ethyl acetate solution (30 mL) of **1** (0.5 g, 1.1 mmol) and 4,4′-azobis(4-cyanovaleric acid) (0.35 g, 1.26 mmol) was refluxed for 15 h. The solvent was evaporated under reduced pressure and the residue chromatographed on a reverse-phase RP18 using water/ACN (60/40) as eluent. Compound **2c** was obtained as a deep red oil (0.317 g, yield 85%). ^{1}H NMR (400 MHz) (CDCl$_3$) δ_{ppm} 1.325 (t, $J_{1,2}$ = 7.2 Hz, 6H), 1.827 (s, 3H), 2.25−2.78 (m, 4H), 4.237 (m, 4H), 7.43 (br s, 1H); ^{13}C NMR (100 MHz) (CDCl$_3$) δ_{ppm} 1.370 (d, $J_{C,P}$ = 5.9 Hz), 23.636 (s), 29.406 (s), 32.988 (s), 45.642 (d, $J_{C,P}$ = 5.9 Hz), 65.485 (d, $J_{C,P}$ = 6.9 Hz), 116.867 (s), 174.829 (s), 224.814 (d, $J_{C,P}$ = 172.3 Hz); ^{31}P NMR (85 MHz) (CDCl$_3$) δ_{ppm} from H$_3$PO$_4$/H$_2$O 30%, −7.233; MS, *m/z* 339 (M$^+$), 280, 125, 109; high-resolution MS calcd for [C$_{11}$H$_{18}$NO$_5$PS$_2$]$^+$ 339.036405, found 339.036785.

(h) 1-Cyano-1-cyclohexyl Diethoxyphosphoryldithioformate (2d). A carefully deaerated toluene solution (10 mL) of **1** (0.2 g, 0.44 mmol) and azobis(2-cyanobutane) (0.12 g, 0.51 mmol) was refluxed for 3 h. The solvent was evaporated under reduced pressure and the residue quickly chromatographed (SiO$_2$) using ethyl ether/toluene (30/70) as eluent. Compound **2d** was obtained as a purple-red oil (0.115 g, yield 82%). ^{1}H NMR (400 MHz) (CDCl$_3$) δ_{ppm} 1.362 (t, $J_{1,2}$ = 7.2 Hz, 6H), 1.7−1.9 (m, 8H), 2.48−2.54 (m, 2H), 4.237 (m, 4H); ^{13}C NMR (100 MHz) (CDCl$_3$) δ_{ppm} 16.387 (d, $J_{C,P}$ = 5.9 Hz), 22.719 (s), 25.906 (s), 34.372 (s), 48.373 (d, $J_{C,P}$ = 5.5 Hz), 65.096 (d, $J_{C,P}$ = 6.8 Hz), 117.065 (d, $J_{C,P}$ = 1.3 Hz), 224.823 (d, $J_{C,P}$ = 169.5 Hz); ^{31}P NMR (85 MHz) (CDCl$_3$) δ_{ppm} from H$_3$PO$_4$/H$_2$O 30%, −6.831; MS, *m/z* 321 (M$^+$), 245, 113, 138, 111; high-resolution MS calcd for [C$_{12}$H$_{20}$NO$_3$PS$_2$]$^+$ 321.062226, found 321.062369.

(i) 2-Cyanoprop-2-yl Dithiobenzoate (7). A carefully deaerated ethyl acetate solution (10 mL) of **6** (0.2 g, 0.51 mmol) and azobis(2-cyanobutane) (0.095 g, 0.58 mmol) was refluxed for 15 h. The solvent was evaporated under reduced pressure and the residue quickly chromatographed (SiO$_2$) using ethyl ether as eluent. Compound **6** was obtained as a purple oil (0.078 g, yield 70%). ^{1}H NMR (400 MHz) (CDCl$_3$) δ_{ppm} 1.923 (s, 6H), 7.31−7.64 (m, 3H), 7.87−7.98 (m, 2H); ^{13}C NMR (100 MHz) (CDCl$_3$) δ_{ppm} 26.234, 41.540, 119.785, 126.435, 128.365, 132.782, 144.267, 223.005; MS, *m/z* 221 (M$^+$), 153, 121,77.

Polymerization Studies. Polymerizations of styrene and methyl methacrylate in the presence of **2a** as transfer agent were carried out as described below. Average molar masses were determined by SEC of THF solutions by means of a chromatograph equipped with refractive index and ultraviolet detectors, using a PLgel MIXED-D column calibrated with polystyrene standard samples.

(a) RAFT Styrene Polymerization. A solution of styrene (5.0 mL, 43.3 mmol), AIBN (1.4 mg, 8.6 μmol), and **2a** (13.1 mg, 46.6 μmol) was placed in a polymerization ampule and degassed by freeze and thaw cycles. The ampule was then sealed under nitrogen. The polymerization was performed at 60 °C for 8 h. The reaction mixture was diluted with CH$_2$Cl$_2$ and precipitated into methanol, and the resulting polymer was washed with methanol, purified by precipitation from CH$_2$Cl$_2$ into methanol, then dried on silica gel in vacuo for several hours. Conversion of styrene was 3.4% (estimated by weighting the obtained polymer).

(b) RAFT Methyl Methacrylate Polymerization. A solution of methyl methacrylate (3.7 mL, 34.7 mmol), AIBN (5.0 mg, 30.4 μmol), and **2a** (15.6 mg, 55.6 μmol) in benzene (1.3 mL) was placed in a polymerization ampule and degassed by freeze and thaw cycles. The ampule was then sealed under nitrogen. The polymerization was performed at 60 °C for 8 h. The reaction mixture was diluted with CH$_2$Cl$_2$ and precipitated into methanol, and the resulting polymer was washed with methanol, purified by precipitation from CH$_2$Cl$_2$ into methanol, and dried on silica gel in vacuo for several hours. Conversion of methyl methacrylate was 44.0% (estimated by weighting the obtained polymer).

Supporting Information Available: ^{1}H, ^{13}C, and ^{31}P NMR spectra of compounds **1**, **2a**−**d**, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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