On the Mechanism of Reductive Degradation of Dithiocarbonates by Tributylstannane

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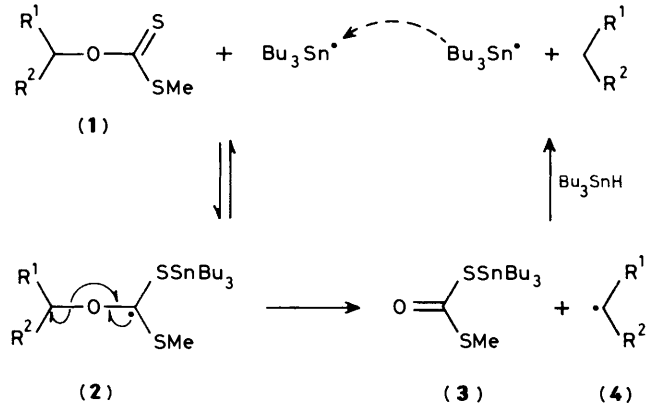
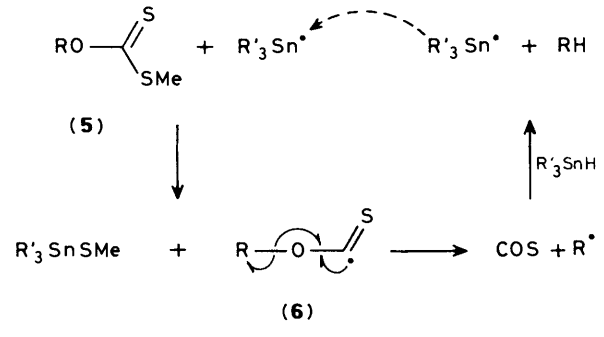
Product analysis of the reaction between *O*-isopropyl *S*-4-phenylbut-3-enyl dithiocarbonate and tributylstannane, initiated by azoisobutyronitrile in boiling benzene or toluene, indicates that the first step in the reductive degradation of dithiocarbonates by trialkylstannanes involves the homolytic attack of trialkyltin radical on the thioxo sulphur according to the Barton mechanism, rather than on the thio sulphur as displayed in a proposed alternative mechanism.

Several years ago, Barton and McCombie described a method for the deoxygenation of secondary alcohols to the corresponding hydrocarbons through the reductive degradation of *O*-alkyl *S*-methyl dithiocarbonates (**1**) by tributylstannane with free-radical initiation. The mechanism they originally proposed,[1,2] and recently slightly modified with respect to the reversibility of the first propagation step,[3] is outlined in Scheme 1. The tributylstannyl radical attacks, in a fast and reversible



Scheme 1.

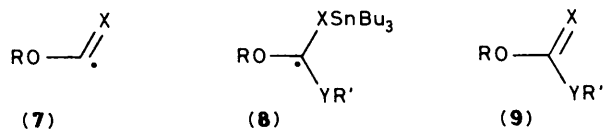
reaction, the thioxo sulphur forming a radical intermediate (**2**) which undergoes β-cleavage to the dithiocarbonate (**3**) and alkyl radical (**4**). Hydrogen transfer from tributylstannane affords the alkane $R^1CH_2R^2$ and tributylstannyl radical, which completes the cycle of the chain reaction. An alternative mechanism, proposed by Barker and Beckwith,[4] involving a direct S_H2 attack of the stannyl radical on the thio sulphur of the dithiocarbonate (**5**), is described in Scheme 2. The alk-



Scheme 2.

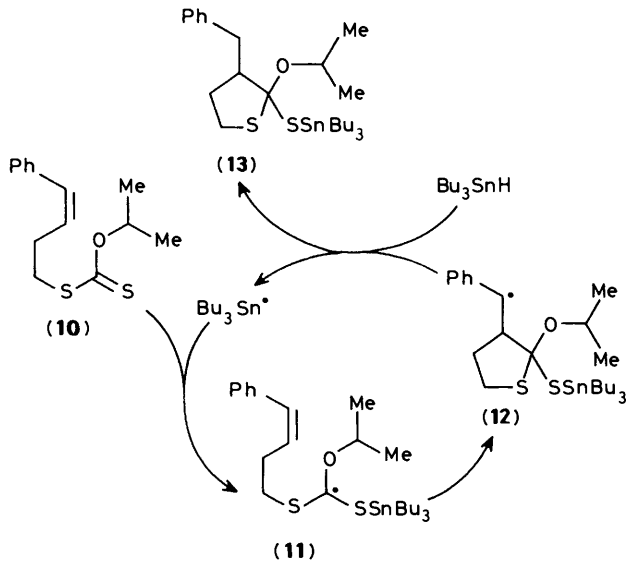
oxythiocarbonyl radical (**6**) so obtained, undergoes β-fission to carbonyl sulphide and alkyl radical. The latter abstracts a hydrogen atom from the trialkylstannane to give the alkane RH and trialkylstannyl radical.

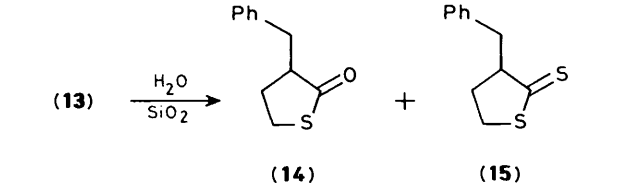
We recently investigated a method for the synthesis of α-alkylidene-γ-lactones based on the cyclization of acetylenic alkoxycarbonyl radicals.[5] In this study, we observed that tri-hetero substituted carbon centred free-radicals such as compounds (**7**; X = O) and (**8**; X = S, YR′ = imidazolyl), undergo practically quantitative intramolecular addition to a carbon–carbon multiple bond suitably positioned on the side-chain R linked to the oxygen. Radicals of type (**7**) can be readily generated from selenocarbonates (**9**; X = O, Y = Se, R′ = Ph) with tributylstannyl radicals, whereas radicals of type (**8**; X = S, YR′ = imidazolyl) can be similarly generated from thio-imidazolides (**9**; X = S, YR′ = imidazolyl). We now suggest that dithiocarbonates (**9**; X = Y = S) in which a suitably positioned and activated double bond is incorporated into the side-chain R′ linked to the sulphur, rather than into the side-chain R linked to the oxygen, may serve as diagnostic reagents to distinguish between the mechanism proposed by Barton *et al.* and that proposed by Barker and Beckwith for the reductive degradation of dithiocarbonates.[6]



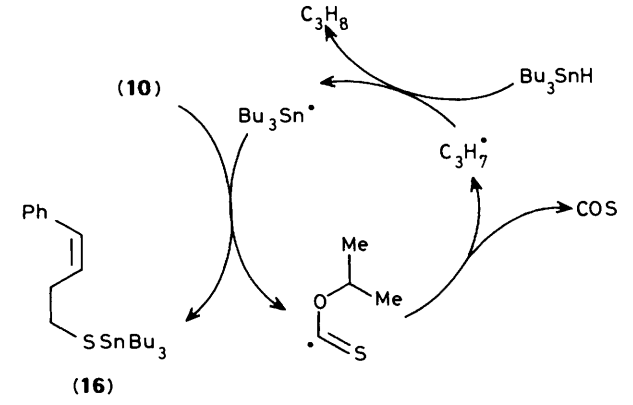
O-Isopropyl (*Z*)-*S*-4-phenylbut-3-enyl dithiocarbonate (**10**) was selected as the substrate for this mechanistic study. It was conveniently prepared by phase-transfer catalysed alkylation of potassium *O*-isopropyl dithiocarbonate with (*Z*)-4-phenylbut-3-enyl methanesulphonate. We reasoned that if the tributylstannyl radical attacks the thioxo sulphur of the dithiocarbonate (**10**), the resulting tri-hetero substituted free-radical (**11**) will propagate a chain reaction involving intramolecular addition to give the radical (**12**), and hydrogen abstraction, affording the dithio-ortholactone (**13**) as shown in Scheme 3. Hydrolysis of the ortho compound (**13**) would then give the thiolactone (**14**) and/or the dithiolactone (**15**). On the other hand, if the tributylstannyl radical attacks the thio sulphur of the dithiocarbonate (**10**) the chain reaction outlined in Scheme 4 will take place, resulting in the tin compound (**16**), carbonyl sulphide, and propane.

To reduce possible interference of competitive secondary reactions of tributylstannyl radicals with the product, a 4-fold excess of dithiocarbonate (**10**) *versus* tributylstannane was employed. In a typical experiment, tributylstannane (0.25 mol equiv) and azoisobutyronitrile (catalytic amount) were slowly





Scheme 3.



Scheme 4.

added to a boiling solution of the dithiocarbonate (**10**) in benzene. The crude reaction product was hydrolysed on silica gel to give the thiolactones (**14**) (71%) and (**15**) (2%). Reaction under higher conversion, *e.g.* using 1 mol equiv. of tributylstannane, resulted in a substantial decrease in yield due to secondary reactions of the product.

These results prove that the reduction of dithiocarbonate by tributylstannane in boiling benzene or toluene follows the mechanism proposed by Barton *et al.*[1–3] Our conclusions refer to reactions performed with tributylstannane at high temperatures and, therefore, are not in contradiction to Barker and Beckwith's observation of e.s.r. signals for alkoxythiocarbonyl radicals of type (**6**) in experiments performed with hexamethylditin at −30 °C.[4]

Experimental

Unless otherwise stated, dry solvents were used and the reactions were performed in flame-dried glassware under an atmosphere of argon. Work-up refers to separation of the reaction (1 mmol) between ethyl acetate (70 ml) and water (30 ml), washing the organic layer with cold dilute HCl (30 ml), saturated aqueous sodium hydrogen carbonate (30 ml), brine (30 ml), and water (30 ml), drying over magnesium sulphate, and evaporation of the solvent. Flash chromatographic separations were performed on silica gel (Merck, Kieselgel 60, 230—400 mesh). Products were distilled with a Buchi Kugelrohr apparatus and the temperatures refer to the oven temperature. Proton n.m.r. spectra were measured in deuteriated chloroform on a Bruker WH-270 n.m.r. spectrometer. I.r. spectra were measured on a Nicolet MX-100 Fourier transform spectrometer. High resolution mass spectra were determined on a Varian Mat 731 spectrometer. Mass spectra were performed on a Finnigan 4500 GC-MS spectrometer and are reported in mass units with the relative intensities in parentheses.

(Z)-4-*Phenylbut*-3-*en*-1-*ol*.—4-Phenylbut-3-yn-1-ol[7] (3.75 g, 25.6 mmol) was added to suspension of palladium (5% on barium sulphate) (70 mg) and quinoline (70 mg) in ethyl acetate (50 ml). The reaction mixture was stirred under hydrogen (1 atm) for 5.5 h. The suspension was filtered through Celite and the filtrate was washed with dilute acid (5 ml), water (5 ml), and brine (5 ml), dried, and evaporated. Bulb-to-bulb distillation of the residue (twice) at 65 °C/0.15 mmHg gave the *title compound* (3.33 g, 88%) as a clear oil; $\nu_{max.}(CCl_4)$ 3 370br s, and 1 601 cm^{-1}; δ 1.67 (1 H, s, OH), 2.62 (2 H, dq, *J* 1.7 and 6.7 Hz, CH_2CH_2O), 3.75 (2 H, t, *J* 6.5 Hz, CH_2O), 5.69 (1 H, td, *J* 7.3 and 11.7 Hz, PhCH=C*H*), 6.58 (1 H, d, *J* 11.7 Hz, PhCH), and 7.20—7.39 (5 H, m, ArH); *m/z* 148 (M^+, 24), 118 (23), 117 (100), 115 (51), and 91 (33).

(Z)-4-*Phenylbut*-3-*enyl Methanesulphonate*.—The title compound was prepared according to the procedure of Crossland and Servis[8] from (*Z*)-4-phenylbut-3-en-1-ol (1.33 g, 9 mmol), methanesulphonyl chloride (0.9 ml, 11.5 mmol), and triethylamine (1.87 ml, 13.5 mmol) in dichloromethane (60 ml). The crude product obtained after work-up was essentially clean and could be used without further purification. Flash chromatography with hexane–ethyl acetate (3:1) as eluant followed by bulb-to-bulb distillation at 80 °C/1 mmHg yielded the analytically pure *title compound* (1.91 g, 94%) as a pale orange oil; $\nu_{max.}(CCl_4)$ 1 601w, 1 368s, 1 349s, and 1 179s cm^{-1}; δ 2.78 (2 H, dq, *J* 1.7 and 6.9 Hz, $CHCH_2$), 2.98 (3 H, s, MeS), 4.30 (2 H, t, *J* 6.6 Hz, CH_2O), 5.66 (1 H, dt, ABX_2, J_{AB} 11.7 and J_{BX} 7.2 Hz, CH=C*H*CH_2), 6.62 (1 H, br d, *J* 11.7 Hz, PhC*H*=CH), and 7.23—7.37 (5 H, m, ArH) (Found: C, 58.5; H, 6.1; S, 14.2. $C_{11}H_{14}O_3S$ requires C, 58.4; H, 6.2; S, 14.2%); *m/z* 226 (M^+, 1%), 130 (M − $HOSO_2Me$, 100), 129 (50), 117 (33), 115 (56), and 91 (34).

O-*Isopropyl*(Z)-S-4-*Phenylbut*-3-*enyl Dithiocarbonate* (**10**).—Potassium *O*-isopropyl dithiocarbonate (1.5 g, 8.6 mmol) and (*Z*)-4-phenylbut-3-enyl methanesulphonate (1.71 g, 7.6 mmol) were treated with tetrabutylammonium chloride (326 mg, 1.1 mmol) as phase-transfer catalyst, in water (10 ml) at 70 °C for 5 h.[9] After work-up, bulb-to-bulb distillation at 100 °C/0.1 mmHg yielded the *dithiocarbonate* (**10**) (1.79 g, 89%) as a pale yellow oil; $\nu_{max.}$(film) 1 599, 1 385, 1 372, 1 233s, 1 091s, and 1 045s cm^{-1}; δ 1.35 (6 H, d, *J* 6.2 Hz, $CHMe_2$), 2.72 (2 H, dq, *J* 1.7 and 7.3 Hz, $CHCH_2CH_2$), 3.19 (2 H, t, *J* 7.4 Hz, CH_2S), 5.66 (1 H, dt, ABX_2, J_{AB} 11.5 and J_{BX} 7.2 Hz, CH=C*H*CH_2), 5.75 (1 H, quint, *J* 6.2 Hz, C*H*Me_2), 6.52 (1 H, br d, *J* 11.5 Hz, PhCH), and 7.18—7.40 (5 H, m, Ar*H*) (Found: C, 63.4; H, 6.9; S, 23.7. $C_{14}H_{18}OS_2$ requires C, 63.1; H, 6.8; S, 24.1%); *m/z* 130 (M − $HSC(S)OC_3H_7$, 100%), 129 (23), and 115 (19).

Reaction of O-*Isopropyl* (Z)-S-4-*Phenylbut*-3-*en*-1-*yl Dithiocarbonate* (**10**) *with Tributylstannane*.—Individual solutions of tributylstannane (0.2 ml, 0.75 mmol) and azoisobutyronitrile (11 mg, 0.07 mmol) in benzene (10 ml) were added, with stirring over 2.5 h, to a refluxing solution of the dithiocarbonate (**10**) (804 mg, 3.02 mmol) in benzene (150 ml). More initiator (6.5 mg) was added after 1 h and the reaction was continued for an additional 1 h and then cooled. The residue which remained after removal of the solvent at atmospheric pressure was dissolved in dichloromethane (10 ml) and silica gel (Merck, Kieselgel 60, 70—230 mesh; 4.5 g) was added. The slurry was shaken for 2 h and dichloromethane carefully removed. The impregnated silica was placed on top of a column packed with the same type of silica gel (46 g). Elution with hexane, followed by mixtures of hexane and ethyl acetate of increasing polarity, yielded partially clean dithiocarbonate (**10**) and the thiolactone (**14**). Flash chromatography of these portions yielded: (a) dithiocarbonate (**10**) (442 mg); (b) 3-*benzyl*-4,5-*dihydrothiophen*-2(3H)-*one* (**14**) (102.5 mg, 71% based on tributylstannane) as a clear oil; $\nu_{max.}(CCl_4)$ 1 707vs (C=O) and 1 605w cm^{-1}; δ 1.84—1.99 (1 H, m, 4-H), 2.25—2.36 (1 H, m, 4′-H), 2.60 (1 H, dd, *J* 9.7 and 13.5 Hz, PhC*H*H), 2.68—2.80 (1 H, dddd, *J* 9.7, 3.8, 10.5, and 6.6 Hz, 3-H), 3.20—3.24 (2 H, m, SCH_2), 3.25 (1 H, dd, *J* 3.8 and 13.5 Hz, PhCH*H*), and 7.19—7.37 (5 H, m, ArH) (Found: C, 68.7; H, 6.7. $C_{11}H_{12}OS$ requires C, 68.75; H, 6.25) [Found: 192.0622 (M^+, 52%). $C_{11}H_{12}OS$ requires 192.0608]; *m*/*z* 192 (M^+, 23%), 164 (20), 117 (51), 91 (100), and 65 (27); and (c) 3-*benzyl*-4,5-*dihydrothiophene*-2(3H)-*thione* (**15**) (2%, based on tributylstannane) as an orange oil, identified by comparing its physical data with an authentic sample prepared as described below.

3-*Benzyl*-4,5-*dihydrothiophene*-2(3H)-*thione* (**15**).—Phosphorus pentasulphide (3.5 g, 7.9 mmol) was added to a solution of 3-benzyltetrahydrofuran-2-one (659 mg, 3.7 mmol) in xylene (25 ml). The suspension was boiled under reflux for 5 h. The reaction mixture was diluted with hexane (75 ml) and filtered through a short column of silica gel. The solvent was evaporated and the residue subjected to flash chromatography with hexane as eluant to give the *thione* (**15**) (587 mg, 75%) as an orange oil which was distilled at 110 °C/0.05 mmHg; $\nu_{max.}(CCl_4)$ 1 604, 1 177s, and 1 153m cm^{-1}; δ 2.01—2.15 (1 H, m, 4-H), 2.41—2.52 (1 H, m, 4′-H), 2.57 (1 H, dd, *J* 13.8 and 10.2 Hz, PhC*H*H), 2.97—3.08 (1 H, dddd, *J* 10.2, 4.0, 6.6, and 8.9 Hz, 3-H), 3.31—3.41 (2 H, m, SCH_2), 3.56 (1 H, dd, *J* 4.0 and 13.7 Hz, PhCH*H*), and 7.19—7.34 (5 H, m, ArH) (Found: C, 63.2; H, 5.9; S, 30.2. $C_{11}H_{12}S_2$ requires C, 63.45; H, 5.8; S, 30.7%) [Found: 208.0381 (M^+, 100%). $C_{11}H_{12}S_2$ requires 208.0380]; *m*/*z* 208 (M^+, 33%), 175 (11), 91 (100), 65 (26), and 51 (13).

Acknowledgements

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References

1 D. H. R. Barton and S. W. McCombie, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1574.
2 D. H. R. Barton, D. Crich, A. Löbberding, and S. Z. Zard, *J. Chem. Soc., Chem. Commun.*, 1985, 646.
3 D. H. R. Barton, D. Crich, A. Löbberding, and S. Z. Zard, *Tetrahedron*, 1986, **42**, 2329.
4 P. J. Barker and A. L. J. Beckwith, *J. Chem. Soc., Chem. Commun.*, 1984, 683.
5 M. D. Bachi and E. Bosch, *Tetrahedron Lett.*, 1986, **27**, 641.
6 A preliminary communication was presented at the Nato Advanced Workshop on Substituent Effects in Radical Chemistry, Louvain-La-Neuve, Belgium, 1986; 'Substituent Effects in Radical Chemistry,' H. G. Viehe, Z. Janousek, R. Merenéyi, eds. D. Reidel Publishing Co. 1986, p. 387.
7 Prepared according to the general procedure described by M. Yamaguchi and I. Hirao, *Tetrahedron Lett.*, 1983, **24**, 391.
8 R. K. Crossland and K. L. Servis, *J. Org. Chem.*, 1970, **35**, 3195.
9 I. Degani and R. Fochi, *Synthesis*, 1978, 366.

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