Thermal Degradation of Polyalkylene Sulphides

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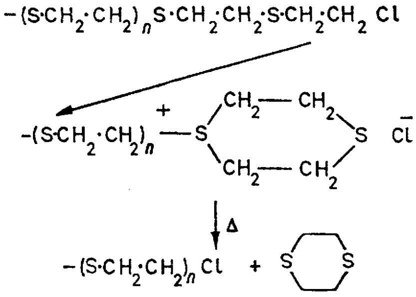
The thermal stabilities of polyethylene sulphide and suitable model compounds have been examined. At temperatures greater than 200° the polymers rapidly decompose to afford, in the main, heterocyclic products together with linear sulphur compounds, hydrogen sulphide, and olefins. Based on the analysis of products formed from the thermal breakdown of model compounds two mechanisms by which massive decomposition could occur have been suggested.

THE thermal degradation of polyethylene sulphide was studied[1] briefly in 1927 by Bell, Bennett, and Hock who showed that *p*-dithian was formed in high yield from polymers bearing a terminal halogen atom. They also found that in the absence of halogen atoms the yield of *p*-dithian was negligible. This was attributed to sulphonium ion formation accompanied by a cyclodepolymerisation process, a view which was in broad agreement with the results of studies on model compounds. Apart from these early studies little else has appeared. By the process outlined above, analogous reactions should occur with polypropylene sulphide although nothing has been reported.



In the case of polyethylene sulphide, the ease with which thermal degradation occurs varies considerably, depending on the initiator used to prepare it.[2] (In the presence of suitable stabilisers, certain polyethylene sulphides are efficienctly protected against thermal degradation up to 250°.) When metal thiolates are used as initiators the polymers of ethylene and propylene sulphide both degrade rapidly in the range 200—220°[2] and it has been established that, in part, this is due to the presence of polysulphidic links in the polymer backbone.[3] We have now shown from studies of the degradation of model compounds that significant decomposition also occurs at the metal–sulphur bonds of the initiating site.

RESULTS AND DISCUSSION

Propylene sulphide is polymerised to high molecular weight only by catalysts containing metal atoms, *e.g.*, metal alkyls, metal thiolates, *etc.* Thus the polymers

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[1] E. V. Bell, G. M. Bennett, and A. L. Hock, *J. Chem. Soc.*, 1927, 1803.

[2] R. T. Wragg, D. R. Morgan, and G. T. Williams, *European Polymer J.*, in the press.

[3] D. R. Morgan and W. Cooper, *European Polymer J.*, in the press.

chosen for degradation studies were those in which the polymerisation was initiated by soluble zinc or cadmium thiolates, *e.g.*, $Zn(S{\cdot}CH_2{\cdot}CH_2{\cdot}SBu)_2$, $Cd(SCH_2CH{=}CH_2)_2$, *etc.*

Table 1

	Component (%) Degradation temperature		
Peak	220°	250°	Identification
A (multiplet)	17	40	Mainly Pr^nSH and Pr^iSH (also H_2S, C_3H_6)
B	2	4	
C	9	14	
D	4	4	
E	23	17	2,2,4-Trimethyl-1,3-dithiolan
F	23	7	2-Ethyl-4-methyl-1,3-dithiolan
G	13	9	2,6-Dimethyl-1,4-dithian
H	7	4	
I	2		

When samples of these polymers (*M*, 2—3 × 10^5) were heated *in vacuo* to a temperature of 220° for 1—2 hr. very rapid decomposition occurred and large quantities of highly coloured distillate could be collected in traps cooled in liquid nitrogen. The residue, about 10% (w/w) of the original polymer, was a black resin which liberated hydrogen sulphide on treatment with dilute acid. The degradation products were subjected to g.l.c. and the major components identified by comparison of retention times and i.r. spectra with those of authentic samples. The component identities from degradation carried out at 220 and 250° are shown in Table 1. The analysis was carried out on a 5 ft. ethylene glycol adipate column at 150°, with a Gow-Mac detector and hydrogen flow rate of 50 ml./min. Even at 220° extensive decomposition occurs to give very low molecular weight products (peak *A*) and at higher temperatures the formation of these components is increased considerably. The nature and distribution of the products appears to be independent of the nature of the metal atom in the initiator molecule. In the case of polyethylene sulphide prepared by use of the initiators mentioned earlier, rapid degradation occurred at *ca.* 220° and within 1—2 hr. about 85% of the polymer had decomposed to distillable products. Identification of these by g.l.c. under the conditions outlined in Table 1 showed that at 220° the main degradation products were 2-methyl-1,3-dithiolan (60—65%) and 1,4-dithian (8—10%). Also produced were diethyl disulphide (6%), diethyl sulphide, ethylene sulphide, ethanethiol, hydrogen sulphide, ethylene, and a number of unidentified fragments.

Melt viscosity measurements on polypropylene and polyethylene sulphides as determined in a Davenport polyethylene grader[2] or even by simple test-tube experiments, suggest that at above 200° random splitting of polymer chains occurs. The drop in viscosity with time is too great to be attributed solely to an unzipping process initiated at a chain end, but would be consistent with the presence of polysulphide groups in the polymer backbone.[3] 5,8,11,14-Tetrathiaoctadecane, prepared by the reaction of butyl 2-mercaptoethyl sulphide with 1,2-dibromoethane, showed no tendency to decompose even on prolonged heating at 250—260°. This model compound represents the ideal polyethylene sulphide molecule and indicates the inherent stability of such a structure.

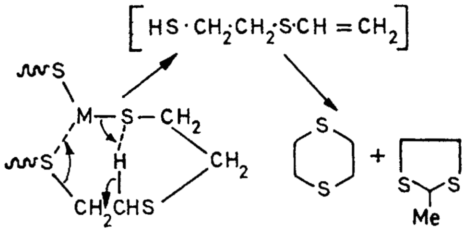
In order to check the thermal stability of metal–sulphur bonds in the polymer matrix the zinc and cadmium thiolates of butyl 2-mercaptoethyl sulphide were prepared. These compounds represent the products formed from the insertion of ethylene sulphide into the metal–sulphur bond of the corresponding butyl thiolate and therefore resemble closely the environment of the metal atoms in the polymer. When heated *in vacuo* at 180—190° these model compounds began to decompose and at 220° distillate was collected rapidly in a cold trap and after prolonged heating, the residue was found to consist mainly (95—97%) of the metal sulphide. G.l.c. of the distillates yielded very similar results and the major peaks and retention times are indicated in Table 2.

Table 2

			Yield (%) from	
Component	Retention time (min.)	Identification	$Zn(S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}Bu)_2$	$Cd(S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}Bu)_2$
A	0—1	C_2H_4, H_2S, C_2H_4S, *etc.*	Low	Low
B	1·5	Bu^nSH	5·0	5·0
C	2·0		0·2	0·3
D	9·0	Bu_2S	5·5	3·6
E	14·0		1·0	2·2
F	15·5	$BuS{\cdot}SBu$	20·4	16·9
G	17·5	$BuS{\cdot}CH_2{\cdot}CH_2{\cdot}SH$		2·9
H	20·0		2·0	1·5
I	21·5		0·2	0·8
J	23·0		2·0	2·3
K	24·5	$BuS{\cdot}CH_2{\cdot}CH_2{\cdot}SBu$	24·0	25·8
L	26·0		0·5	0·6
M	30·0		2·0	2·6
N	33·0		0·2	0·5
O	37·0		2·5	3·6
P	40·0	$BuS{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}SBu$	34·5	29·2

Degradation temp. 220°. G.l.c. on a 6 ft. polyethylene glycol adipate column programmed from 40° to 200° at 5°/min. Injection temperature 195° and flow rate 30 ml./min. N_2.

Mechanistic Implications.—The fact that 5,8,11,14-tetrathiaoctadecane does not degrade under conditions in which the initiators and polymers undergo extensive decomposition indicates the inherent stability of the polyethylene sulphide chain. A lack of suitable model compounds prevents this conclusion being extended to polypropylene sulphide but there is no reason to suppose that any great differences would exist. It is safe to assume, therefore that degradation is initiated by (i) random chain scission of S_x bonds or (ii) unzipping reactions from catalyst sites. These suggestions lead to mechanistic complications since massive decomposition could occur simultaneously by radical, ionic, or co-ordinated processes and the overall distinction of one from another is impossible. The ratio of 2-methyl-1,3-dithiolan to 1,4-dithian in the degradation products from polyethylene sulphide suggests that these compounds are not formed by recombination of small fragments, which would be expected to be quite random, but rather by a more selective process. In accordance with this a co-ordination-assisted zipping mechanism occurring at a metal site could account for the observed products as shown in Scheme 1. The co-ordination of sulphur atoms to the metal atom could result in the transient formation of 2-mercaptoethyl vinyl sulphide, the rapid cyclisation of which would give the 5- or 6-membered ring. Indeed, the reactivity of vinyl sulphides towards thiol addition [4] and the catalysis of such reactions by zinc and cadmium salts has been reported.[5] The thermal degradation of zinc and cadmium 5,8-dithiadecane-10-thiolates, model compounds which reasonably represent the environment of the metal atom in the polymer, under conditions identical with those used for polymers, yielded the 5- and 6-membered heterocycles in 1 and 3% yields respectively. This suggests that although the model molecule should afford the respective heterocycles according to Scheme 1, the yields are far less than expected. It appears, therefore, that a further and more important process of formation, in the case of polymers, is operative.



SCHEME 1

The thermal degradation of the initiators zinc and cadmium 5-thiaheptane-7-thiolates yielded the products listed in Table 2. On the basis of mass balance the products were formed with good reproducibility in the molar quantities shown in Table 3. It is significant that reactions involving recombination are very important. Also, the amount of hydrogen sulphide formed is approximately half that of the ethylene. Consistent with the above observations the mechanism of Scheme 2 is suggested. Hydrogen sulphide and butanethiol could arise by hydrogen-abstraction reactions of sulphur and thiol radicals. By this mechanism it is possible to obtain two molecules of ethylene for every atom of sulphur liberated, in agreement with the observations. The reaction of butanethiol with cadmium thiolates, present in the reaction mixture, would product cadmium bis(butylthiolate) by a process of transfer (8).[6] We have

$$R^1S{\cdot}Cd{\cdot}SR^1 + R^2SH \rightleftharpoons R^1S{\cdot}Cd{\cdot}SR^2 + R^1SH \qquad (8)$$

shown that the thermal decomposition of zinc and cadmium butylthiolates affords dibutyl sulphide in >90% yield [reaction (7)]. It would be expected, therefore that a mechanism of this type could also be operative within a polyalkylene sulphide molecule but would still have to reconcile the formation of large amounts of heterocycles by a rather specific radical process. In the case of polyethylene sulphide Scheme 3 is tentatively suggested. Apart from recombination of the radicals, species (I) can undergo hydrogen-abstraction

TABLE 3

Product (%)	Moles/mole $Cd(SCH_2{\cdot}CH_2{\cdot}SBu)_2$
Bu^nSH (5·0)	0·14
Bu_2S (2·6)	0·06
$Bu{\cdot}S{\cdot}S{\cdot}Bu$ (16·9)	0·24
$BuS{\cdot}CH_2{\cdot}CH_2{\cdot}SH$ (2·9)	0·04
$BuS{\cdot}CH_2{\cdot}CH_2{\cdot}SBu$ (25·8)	0·30
$BuS{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}SBu$ (29·2)	0·27
$CH_2{=}CH_2$	0·36 *
H_2S	0·16 *

* Determined in separate experiments.

$$BuS{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}Cd{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}SBu \longrightarrow BuS{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot} + CdS + BuS{\cdot}CH_2{\cdot}CH_2{\cdot} \qquad (1)$$

$$BuS{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot} + {\cdot}CH_2{\cdot}CH_2{\cdot}SBu \longrightarrow BuS{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}SBu \qquad (2)$$

$$BuS{\cdot}CH_2{\cdot}CH_2S{\cdot} \longrightarrow BuS{\cdot} + \text{cyclo-}C_2H_4S \qquad (3)$$

$$\text{cyclo-}C_2H_4S \longrightarrow S + C_2H_4 \qquad (4)$$

$$2BuS{\cdot} \longrightarrow BuS{\cdot}SBu \qquad (5)$$

$$BuS{\cdot}CH_2{\cdot}CH_2{\cdot} \longrightarrow BuS{\cdot} + C_2H_4 \qquad (6)$$

$$BuS{\cdot}Cd{\cdot}SBu \longrightarrow Bu_2S + CdS \qquad (7)$$

SCHEME 2

$$\begin{array}{c}
\sim\!\sim SCH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}Cd{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}\text{-} \\
CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S\sim\!\sim \\
\Big\downarrow \Delta \\
\underset{(I)}{\sim\!\sim S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}} + CdS + \\
\underset{(II)}{{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S\sim\!\sim}
\end{array}$$

SCHEME 3

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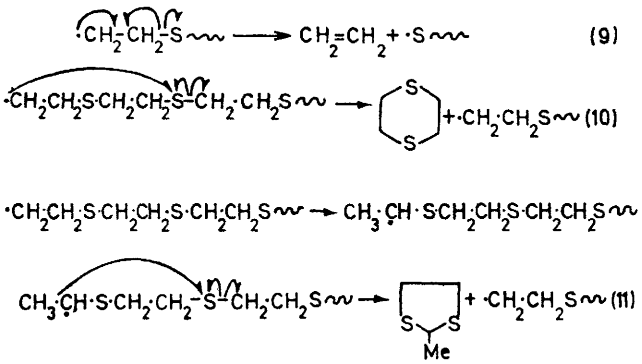
[4] E. E. Reid, 'Organic Chemistry of Bivalent Sulphur,' Chemical Publishing Co., New York, 1960, vol. II, p. 44.

[5] W. Reppe, *Annalen*, 1956, **601**, 111.

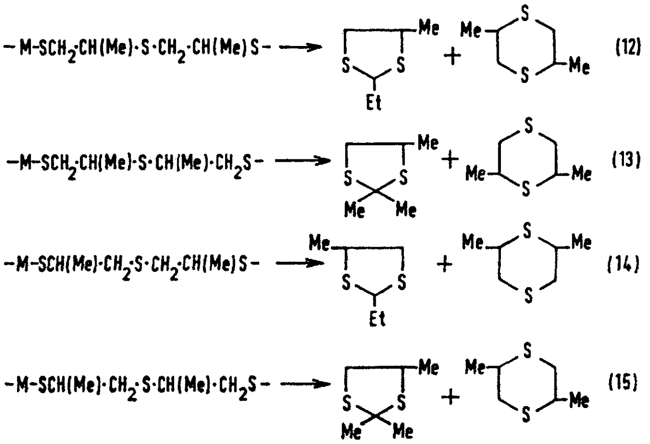
[6] W. Cooper, D. Morgan, and R. T. Wragg, *European Polymer J.*, 1969, **5**, 71.

reactions, elimination of ethylene sulphide or dithian, disulphide formation, *etc*. Addition to ethylene would form a type (II) moiety also produced possibly by a concerted elimination of sulphur from (I) without the intermediacy of ethylene sulphide. Type (II) species would probably undergo, in part, ethylene elimination (9), dithian formation (10), or rearrangement followed by elimination (11) of 2-methyl-1,3-dithiolan. The rearrangement of the primary radical in reaction (11) is not unreasonable by virtue of the formation of a secondary radical, α to a sulphur atom and stabilised by the sulphur *d* orbitals. Such a degradation mechanism would also be applicable to reactions occurring as a result of homolysis of polysulphidic links, known to be present in the polymer chain.[3] The rate of degradation as indicated by viscosity measurements would be expected to increase with time owing to the participation of other highly active species, *e.g.*, S produced in the reactions outlined above and this is found to be so.[2]



The formation of negligible amounts of 5- and 6-membered heterocycles from the metal thiolates of 5,8-dithiadecane-10-thiolates is understandable on the basis of the above arguments since such radical reactions would involve the cleavage of the Bu–S bond and there is no evidence, from product analysis, for such a reaction. In this case, therefore, it is possible that the heterocycles are formed *via* a co-ordinated process of the type outlined earlier.

The major degradation products from polypropylene sulphide, *viz.*, 2-ethyl-4-methyl-1,3-dithiolan, 2,2,4-trimethyl-1,3-dithiolan, and 2,5-dimethyl-1,4-dithiane can be considered as being formed by a co-ordinated process or by a radical process from the structures shown in equations (12)—(15) according to the preceeding arguments. The formation of the two different dithiolans in comparable amounts is indicative of a blocky structure in the original polymers. The amount of carbon–carbon bond cleavage is insignificant since 4-methyl-1,3-dithiolan and 2,4-dimethyl-1,3-dithiolan, the formation of which would have been indicative of the cleavage of –C–C– bonds, were completely absent from the products. Finally, the formation of dithiolans by a ring-contraction process from 1,4-dithians can be discounted since separate experiments conducted in the temperature range 200—350° showed that no 2-methyl-1,3-dithian was formed from 1,4-dithian.



EXPERIMENTAL

Polymer Samples.—Samples of purified ethylene and propylene sulphide were polymerised in bulk to theoretical molecular weights of 2—3 × 10^5 with the zinc or cadmium sulphides of $BuS{\cdot}CH_2{\cdot}CH_2SH$ as initiators.

Thermal Degradation Experiments.—Weighed samples of polymers or model compounds were placed in a Pyrex bulb to which was connected a pair of traps cooled in liquid nitrogen. After evacuation to 1×10^{-2} mm. and sealing, the bulb was heated to 220° until distillation of products appeared complete. The system was then opened and the products analysed by g.l.c. The ethylene and hydrogen sulphide formed were estimated by allowing the volatile materials to expand into a large evacuated bulb of known volume, immersed in liquid nitrogen, and the pressure of which could be measured on a mercury manometer. After bringing the bulb to atmospheric pressure with nitrogen, samples were withdrawn and the constituents determined by g.l.c.

Preparation of Model Compounds.—Zinc and cadmium thiolates of butyl 2-mercaptoethyl sulphide. These compounds were prepared by the reaction of the thiol with the metal acetate in alcoholic ammonia[7] and were purified by continuous extraction with ether.

5,8,11,14-*Tetrathiaoctadecane.* To a solution of sodium (4·6 g.) in ethanol (200 ml.) was slowly added butyl 2-mercaptoethyl sulphide (15·0 g.) under nitrogen. The mixture was heated to reflux and 1,2-dibromoethane (18·8 g.) was added dropwise. After 30 min. the mixture was cooled and poured into water (*ca.* 2 l.). The precipitate was filtered off, washed with water, and recrystallised from ethanol to afford the *tetrathiaoctadecane* (91%), m.p. 62° (Found: C, 51·4; H, 9·2; S, 39·4. $C_{14}H_{30}S_4$ requires C, 51·5; H, 9·2; S, 39·3%).

2,2,4-*Trimethyl*-1,3-*dithiolan.* Propane-1,2-dithiol (21·8 g.), acetone (13·0 g.), acetic acid (5·0 ml.), and boron trifluoride ether complex (3 drops) were heated on a water-bath for 4 hr. The mixture was distilled under reduced pressure to afford the dithiolane (95%), b.p. 45—46°/4·0 mm. (Found: C, 48·7; H, 8·0; S, 43·3. Calc. for $C_6H_{12}S_2$: C, 48·7; H, 8·1; S, 43·2%).

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[7] R. T. Wragg, *J. Chem. Soc.* (*C*), 1969, 2087.

2-*Ethyl*-4-*methyl*-1,3-*dithiolan*. Propane-1,2-dithiol (21·8 g.), propionaldehyde (redistilled, 13·0 g.), acetic acid (5·0 ml.), and boron trifluoride ether complex (3 drops) were heated to reflux for 16 hr. After being cooled the product was poured into water and the organic layer was extracted with ether. After being washed (dilute $NaHCO_3$) and dried ($MgSO_4$) the extracts were distilled under reduced pressure to afford the dithiolan (93%), b.p. 72°/4·1 mm., n_D^{22} 1·5308 (Found: C, 48·6; H, 8·1; S, 43·4. Calc. for $C_6H_{12}S_2$: C, 48·7; H, 8·1; S, 43·2%). Similarly prepared were 2-methyl-1,3-dithiolan (90%, from ethanedithiol and acetaldehyde), b.p. 76—78°/13·5 mm., and 2,4 dimethyl-1,3-dithiolan.[8]

5,8-*Dithiadecane*-10-*thiol*. To a solution of cadmium (5-thiaheptane)-7-thiolate (0·25 g.) in 5-thiaheptane-7-thiol (60·5 g., 0·4 mole) was added ethylene sulphide (5·2 g., 0·08 mole). The mixture was shaken for 4—5 days until no ethylene sulphide could be detected by g.l.c. Fractional distillation of the clear product afforded unchanged 5-thiaheptane-7-thiol, b.p. 58°/0·3 mm., and 5,8-*dithiadecane*-10-*thiol* (11·0 g., 64%), b.p. 95°/0·05 mm. (Found: C, 45·4; H, 8·6; S, 45·7. $C_8H_{18}S_3$ requires C, 45·8; H, 8·6; S, 45·8%).

Cadmium (5,8-*dithiadecane*)-10-*thiolate*. To a refluxing solution of cadmium acetate dihydrate (2·81 g.) in deoxygenated ethanol (200 ml.) was added the thiol (4·43 g.) under an inert atmosphere. After 15 min. a solution of sodium hydroxide (0·84 g.) in ethanol (10 ml.) was added. After cooling, the precipitate was filtered off, washed thoroughly with distilled water, and dried *in vacuo*, to afford the thiolate (96%) (Found: C, 35·9; H, 6·0; Cd, 19·9; S, 33·8. $C_{16}H_{16}CdS_6$ requires C, 36·2; H, 6·4; Cd, 20·9; S, 36·0%).

Zinc (5,8-*dithiadecane*)-10-*thiolate*. As in the preceding example zinc chloride (1·63 g.), the thiol (5·03 g.) and sodium hydroxide (0·96 g.) were allowed to react to form the *zinc thiolate* (93%) as a noncrystalline product readily soluble in ethanol, benzene, and light petroleum (Found: C, 38·5; H, 6·8; S, 38·0; Zn, 13·6. $C_{16}H_{16}S_6Zn$ requires C, 38·7; H, 7·1; S, 38·7; Zn, 13·5%).

5,8-*Dithiadecyl disulphide*. To 5,8-dithiadecane-10-thiol (1·90 g.) in an excess of aqueous NaOH (15%) was slowly added a solution of iodine (1·15 g.) in a small amount of aqueous KI. After each addition the mixture was shaken thoroughly until decolourised. When the total addition was complete, the organic layer was extracted with benzene and dried ($MgSO_4$). Removal of the solvent afforded the *disulphide* (86%) which was crystallised from methanol as leaflets, m.p. 57—58° (Found: C, 45·6; H, 8·0; S, 45·3. $C_{16}H_{34}S_6$ requires C, 45·9; H, 8·1; S, 45·9%).

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[8] B. E. Leggetter and R. K. Brown, *Canad. J. Chem.*, 1963, **41**, 2671.