The Invention of New Radical Chain Reactions. Part 9. Further Radical Chemistry of Thiohydroxamic Esters; Formation of Carbon–Carbon Bonds

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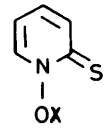
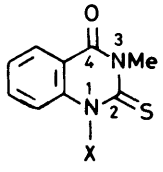
Carbon radicals derived from the esters of several types of thiohydroxamic acids have been trapped in a number of different ways. Particular attention has been paid to carbon–carbon bond formation by addition to suitably activated ethylenic linkages. Carboxylic acids can be conveniently converted into homo- and bishomo-acids by free radical chemistry based on thiohydroxamic esters. In a coda the tautomerism of the thiohydroxamic acids have been examined by physical methods. It is confirmed that the esters used are derivatives of the thione tautomer.

In Part 8 of this series[1] we described novel radical chemistry based on the esters of the thiohydroxamic acid *N*-hydroxypyridine-2-thione (**1**), readily prepared from the commercially available salt (**2**). The radical chain chemistry of the esters of this compound has been analysed in terms of three driving forces: (i) the change thiocarbonyl→carbonyl, (ii) the increased aromaticity in passing from the esters of (**1**) to a pyridine system, and (iii) an increase in entropy. It is clear that the first and last of these forces would be present in simple thiohydroxamic esters. We decided therefore to investigate several other systems of the thiohydroxamic type.[2]

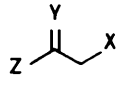
The known cyclic thiohydroxamic acid (**4**) was synthesized in 44% overall yield according to a literature procedure.[3] Zinc and ammonium chloride reduction of ethyl 2-nitrobenzoate, addition of the resulting hydroxylamine to methyl isothiocyanate, and subsequent base mediated cyclisation afforded (**4**). This was then converted into its *O*-palmitoyl ester (**5**) (96%) by *p*-dimethylaminopyridine (DMAP) catalysed treatment with palmitoyl chloride and pyridine in benzene at reflux.



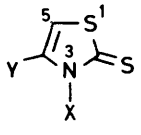
(**1**) X = H
(**2**) X = Na
(**3**) X = $CO(CH_2)_{14}CH_3$



(**4**) X = OH
(**5**) X = $OCOC_{15}H_{31}$
(**6**) X = H

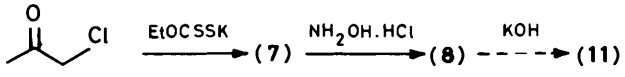


(**7**) X = EtOCSS, Y = O, Z = Me
(**8**) X = EtOCSS, Y = NOH, Z = Me
(**9**) X = Br, Y = NOH, Z = Ph
(**10**) X = EtOCSS, Y = NOH, Z = Ph



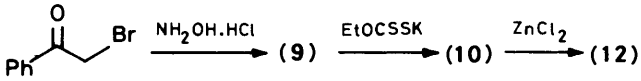
(**11**) X = OH, Y = Me
(**12**) X = OH, Y = Ph
(**13**) X = $OCOC_{15}H_{31}$, Y = Me
(**14**) X = $OCOC_{15}H_{31}$, Y = Ph
(**15**) X = H, Y = Me

The *N*-hydroxythiazolinthione (**11**) was prepared by a three-step procedure (53% overall yield) from chloroacetone as outlined in Scheme 1.



Scheme 1.

Esterification of (**11**) with palmitoyl chloride in ether–pyridine afforded the colourless crystalline ester (**13**) (94%). The 5-phenyl-*N*-hydroxythiazolinthione (**12**) was prepared from phenacyl bromide by treatment of its derived oxime (**9**) with potassium *O*-ethylxanthate followed by cyclisation with anhydrous zinc chloride in ether (overall yield 32%; Scheme 2). We



Scheme 2.

were unable to effect the cyclisation of (**10**) to (**12**) with either triethylamine or HCl gas in ether.

Treatment of (**12**) with palmitoyl chloride and pyridine in ether gave the colourless crystalline *O*-ester (**14**) (92%).

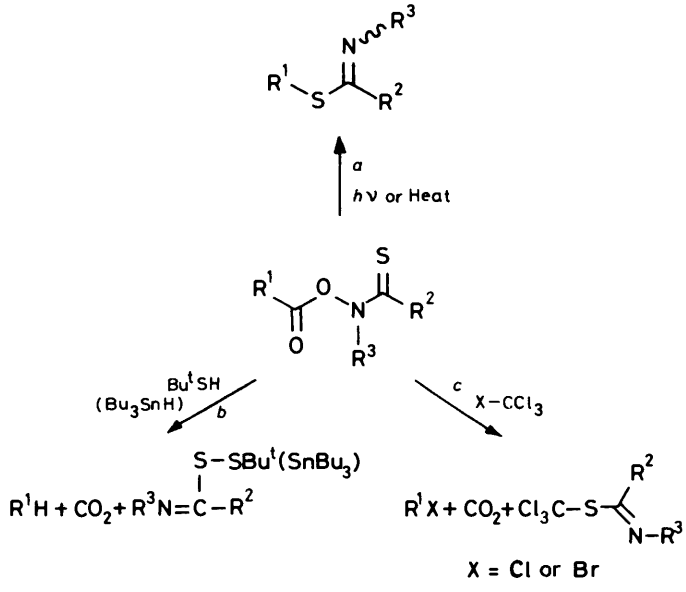
The open chain thiohydroxamic acid (**16**) was prepared according to a literature procedure[4] in low yield (16%) by sequential treatment of phenylmagnesium bromide with carbon disulphide and *N*-methylhydroxylamine. Acylation with palmitoyl chloride and pyridine in ether gave the ester (**17**) as a yellow solid (99%). Having thus obtained the palmitoyl esters of a series of four thiohydroxamic acids we proceeded to study the importance of aromatisation as a thermodynamic driving force in their free radical chemistry.

We first turned our attention to the decarboxylative rearrangement of the above esters to nor-alkyl sulphides (Scheme 3, path *a*), a reaction which proceeds either *via* a radical chain or a (leaky) radical cage mechanism. The thiobenzoyl hydroxamate (**17**) underwent rearrangement with reluctance. When heated in a melting point apparatus, decomposition (gas evolution) began at *ca.* 130 °C. On a preparative scale (Table 1, entry 1) the ester (**17**) was heated to 170 °C under a nitrogen atmosphere for 3 h to give the expected imino sulphide (**19**) (60%). *N*-Methylthiobenzamide (**18**) was also isolated from this reaction (21% yield). The thermal stability of the ester (**5**) was roughly comparable to that of the ester (**17**). Thus, when heated to 160 °C for 3 h in the absence of solvent (**5**) gave the sulphide (**22**) (56%) and the thiouracil derivative (**6**) (20%) (Table 1, entry 2). After being heated to reflux in toluene for 3 h (**5**) was recovered (91%; Table 1, entry 3); when heated for a prolonged (40 h) period under reflux in xylene however, (**5**) underwent de-

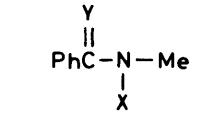
Table 1. Rearrangements

Entry	Ester	Solvent	Temp. (°C)	Time (h)	Products (% Yield)
1	(**17**)	None	170	3	(**19**) (60) + (**18**) (21)
2	(**5**)	None	160	3	(**6**) (20) + (**22**) (56)
3	(**5**)	Toluene	110	3	(**5**) (91)
4	(**5**)	Xylene	140	40	(**22**) (54) + (**6**) (23) + (**30**) (16)
5	(**13**)[a]	Toluene	110	0.75	(**24**) (84)
6	(**13**)	Benzene	80	1.5	(**24**) (50) + (**13**) (46)
7	(**14**)	Benzene	80	2	(**25**) (82)
8	(**13**)	Toluene	20 (300W W)	1	—
9	(**13**)	Toluene	20 (100W Hg)	0.5	(**24**) (70)
10	(**14**)	Benzene	20 (300W W)	8	(**25**) (*ca.* 50)
11	(**74**)	Ether	20 (100W Hg)	0.75	(**76**) (82)

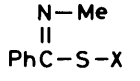
[a] *in situ* Generation of the ester.



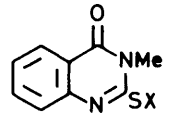
Scheme 3.



(**16**) X = OH, Y = S
(**17**) X = $OCOC_{15}H_{31}$, Y = S
(**18**) X = H, Y = S



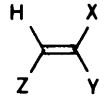
(**19**) X = $(CH_2)_{14}CH_3$
(**20**) X = Bu^t
(**21**) X = SBu^t



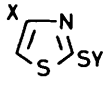
(**22**) X = $(CH_2)_{14}CH_3$
(**23**) X = SBu^t

$CH_3(CH_2)_{14}$–X

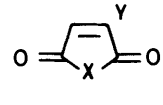
(**30**) X = H
(**31**) X = Br
(**32**) X = Cl



(**33**) X = CN, Y = Z = H
(**34**) X = CO_2Me, Y = Z = H
(**35**) X = NO_2, Y = Z = H
(**36**) X = Ac, Y = Z = H
(**37**) X = CN, Y = Cl, Z = H
(**38**) X = CN, Y = H, Z = CN



(**24**) X = Me, Y = $(CH_2)_{14}CH_3$
(**25**) X = Ph, Y = $(CH_2)_{14}CH_3$
(**26**) X = Me, Y = SBu^t
(**27**) X = Ph, Y = SBu^t
(**28**) X = Me, Y = CCl_3
(**29**) X = Ph, Y = CCl_3



(**39**) X = $C(CH_3)_2$, Y = H
(**40**) X = $C(CH_3)_2$, Y = $C_{15}H_{31}$
(**41**) X = O, Y = H
(**42**) X = O, Y = $C_{15}H_{31}$
(**43**) X = NMe, Y = H

composition to give the rearrangement product (**22**) (54%), the thiouracil (**6**) (23%), and the reduction product (**30**). The last named presumably arises by hydrogen abstraction by the pentadecyl radical from the solvent (16% yield; Table 1, entry 4). The methylthiazolinethione derivative (**13**) rearranged slowly in benzene at reflux (Table 1, entry 6) to the aryl sulphide (**24**). However, this same ester underwent rapid rearrangement to (**24**) (84%) when heated to reflux in toluene (Table 1, entry 5). The phenylthiazolethione ester (**14**) readily gave (**25**) (84%) when heated in refluxing benzene for 2 h (Table 1, entry 7). Having established that the esters (**13**) and (**14**) suffer thermal decarboxylative rearrangement at a similar rate to the pyridinethione derivative (**3**) we turned our attention to their photochemically induced rearrangement. The bright yellow ester (**3**) has the distinct advantage of being activated by normal white light as provided by a tungsten lamp. Unfortunately, but not unexpectedly, the colourless ester (**13**) is inert towards irradiation with a tungsten lamp at room temperature (Table 1, entry 8). However on irradiation with a medium pressure mercury lamp for 30 min at room temperature it underwent rearrangement to (**24**) (70%, Table 1, entry 9). The phenylthiazolinethione ester (**14**), with its extended conjugation was rearranged, albeit slowly (Table 1, entry 10), to the sulphide (**25**) (50%) on irradiation with a tungsten lamp.

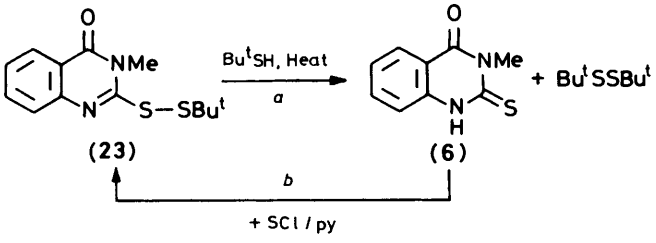
Subsequently we investigated the decarboxylative reduction (Scheme 3, path *b*) brought about by treatment of the esters with either tributylstannane or better with 1,1-dimethylethanethiol. As was the case with the rearrangement, the ester (**5**) was completely unchanged in benzene at reflux, but on treatment with tributylstannane in toluene at reflux it gave pentadecane (**30**) (57%; Table 2, entries 2 and 3). Increasing the temperature

Table 2. Reductions

Entry	Ester	Solvent	Temp. (°C)	Time (h)	Reductant	Products (% Yield)
1	(5)	Xylene	142	48	Bu^{t}SH	(5) (9) + (6) (75) + (22) (5) + (30) (74)
2	(5)	Benzene	78	3	Bu^{t}SH	(5) (97)
3	(5)	Toluene	110	1	Bu^{t}SnH	(30) (57) + (6) (82)
4	[a](17)[a]	Benzene	78	0.5	Bu^{t}SH	(18) (82) + (39) (83)
5	(17)	Toluene	110	1	Bu^{t}SH	(30) (85) + (20) (34) + (18) (48)
6	[a](13)[a]	Benzene	78	2	Bu^{t}SH	(30) (90) + (26) (92)
7	(14)	Benzene	20 (300 W)	0.33	Bu^{t}SH	(30) (97) + (27) (98)

[a] *in situ* Generation of the ester.

to 142 °C (xylene) provided (**30**) (74%), the rearrangement product (**22**) (5%), and the thiouracil (**6**) (75%; Table 2, entry 1). In the reduction of the ester (**5**) with 1,1-dimethylethanethiol none of the expected [1] disulphide by-product (**23**) was observed. We considered that (**23**) underwent reaction *in situ* with an excess of the thiol present to give the thiouracil (**6**), the observed by-product, and di-t-butyl disulphide (Scheme 4, path *a*). In order to verify this hypothesis we synthesized the disulphide (**23**) (63%) by treatment of (**6**) with t-butylsulphenyl chloride and pyridine (Scheme 4, path *b*) and treated it with an excess of 1,1-dimethylethanethiol under typical reaction conditions (toluene at reflux for 1.5 h). As expected we were able to isolate (**6**) (81%) and di-t-butyl disulphide (56%).

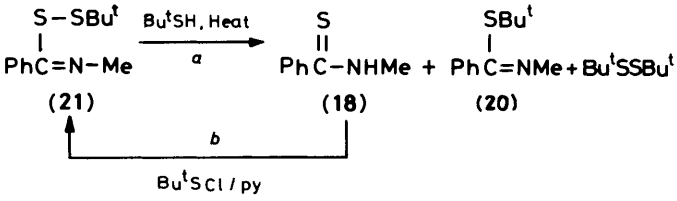


Scheme 4.

In direct contrast to its rather difficult rearrangement reaction, the thiobenzoylhydroxamate (**17**) was readily reduced with 1,1-dimethylethanethiol in benzene at reflux (Table 2, entry 4) to give pentadecane (**30**) (83%); *N*-methylthiobenzamide (**18**) was produced (82%) as a by-product in this reaction. In toluene at reflux (Table 2, entry 5) the yield of pentadecane (**30**) was almost unchanged but less (48%) *N*-methylthiobenzamide (**18**) was formed. The iminosulphide (**20**) was also isolated in this experiment. We assumed (**18**) and (**20**) to be the products arising from the reaction of the imino disulphide (**21**), which is necessarily produced in the reduction reaction, with the excess of reductant in a manner analogous to that outlined above for formation of the uracil (**6**). Thus we synthesized the imino disulphide (**21**) by treatment of (**18**) with t-butylsulphenyl chloride (Scheme 5, path *b*). On reaction with 1,1-dimethylethanethiol under typical reaction conditions (Scheme 5, path *a*), (**21**) indeed provided (**18**) (64%), (**20**) (27%), and di-t-butyl disulphide (47%).

As expected, when heated to reflux in benzene with 1,1-dimethylethanethiol the ester (**13**) gave pentadecane (**30**) in excellent yield (Table 2, entry 6) together with the disulphide (**26**). The ester (**14**) reacted with 1,1-dimethylethanethiol at room temperature on irradiation with a tungsten lamp (Table 2, entry 7) to give pentadecane (**30**) (97%) and the expected disulphide (**27**) (98%).

For a final comparison we chose to study the decomposition



Scheme 5.

of the esters (**5**), (**13**), (**14**), and (**17**) in the presence of bromotrichloromethane or carbon tetrachloride which in the case of esters of thiohydroxamic acid (**1**) provide an excellent alternative to the classical Hunsdiecker reaction and its many variants (Scheme 3, path *c*). When heated to reflux in a mixture of bromotrichloromethane and toluene for 4 h the ester (**5**) was unchanged; furthermore, irradiation of the refluxing solution with a 300 W tungsten lamp for 1 h failed to initiate any reaction (Table 3, entry 1). The ester (**17**) gave pentadecyl bromide (**31**) (77%) when heated to reflux in bromotrichloromethane–toluene for 45 min (Table 3, entry 2). *N*-Methylbenzamide, which probably arises from hydrolysis on work-up of the iminotrichloromethyl sulphide necessarily formed in the reaction, was also isolated (83%). The ester (**17**) also underwent decarboxylative chlorination in carbon tetrachloride–toluene at reflux relatively easily (Table 3, entry 3). As expected, the ester (**13**) readily suffered decarboxylative halogenation when heated at reflux in either bromotrichloromethane or carbon tetrachloride (Table 3, entries 4 and 5). In both cases the trichloromethyl sulphide (**28**) was formed in high yield in accordance with the proposed radical chain mechanism. Small quantities of the rearrangement product (**24**) could also be isolated in both cases. Finally, irradiation with a 300 W tungsten lamp of a solution of the ester (**14**) in a mixture of bromotrichloromethane and benzene at room temperature provided pentadecyl bromide (**31**) and the trichloromethyl sulphide (**29**) in excellent yield (Table 3, entry 6).

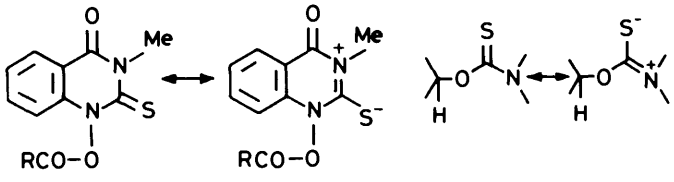
It is evident from the above results that the decarboxylative rearrangement of *O*-esters of thiohydroxamic acids (Scheme 3, path *a*) is assisted by the additional driving force provided by the aromatisation of either the thiazole nucleus [esters (**13**) and (**14**)] or of the pyridine nucleus [1] [*e.g.* ester (**3**)]. Each of the esters (**13**), (**14**), and (**3**) undergoes facile decarboxylative rearrangement to aryl alkyl sulphides. On the other hand, the esters (**5**) and (**17**), which do not suffer aromatisation on rearrangement, only rearrange under much more forcing conditions. The importance of aromatisation as a driving force is, however, somewhat diminished for the decarboxylative reductions and halogenations (Scheme 3, paths *b* and *c*), reactions which both proceed *via* efficient radical chain reactions. As expected, the thiazolinethione derivatives (**13**) and (**14**) react smoothly and efficiently under mild conditions. The

Table 3. Halogenations

Entry	Ester	Solvent	Time (h)	Products (% Yields)
1	(**5**)	$BrCCl_3$–toluene	4 + 1 (300W)	
2	(**17**)	$BrCCl_3$–toluene	0.45	(**31**) (77) + (*N*-methylbenzamide) (83)
3	(**17**)[a]	CCl_4–toluene	15	(**32**) (35) + (**18**) (16) + (*N*-methylbenzamide) (42)
4	(**13**)[a]	$BrCCl_3$–benzene	1	(**31**) (92) + (**28**) (93) + (**24**) (6)
5	(**13**)[a]	CCl_4	2	(**32**) (82) + (**28**) (74) + (**24**) (13)
6	(**14**)	$BrCCl_3$–benzene (300 W)	2	(**31**) (96) + (**29**) (92)
7	(**74**)	$BrCCl_3$–ether (100W; Hg)	0.5	(**75**) (58) + (**28**) (58)

[a] *in situ* Generation of the ester.

real difference between the rearrangement and reduction and halogenation reactions is seen in the behaviour of the ester (**17**), which is reduced and halogenated at much lower temperatures than that at which it rearranges. The ester (**5**) which rearranges under forcing conditions is reduced with difficulty by thiol even in xylene at reflux (although this probably reflects the low boiling point of the thiol and hence its low concentration in xylene at reflux) but seemingly relatively easily with tributylstannane in toluene at reflux. Nor did the ester (**5**) give the decarboxylative halogenation reaction. The relative ease with which the ester (**17**) undergoes reduction and halogenation as compared to rearrangement can probably be attributed to the greater chain propagating merits of the 1,1-dimethylethylthiyl and trichloromethyl radicals as compared to the pentadecyl radical. A second plausible explanation is that unlike the reduction and halogenation reactions the rearrangement reaction proceeds *via* a (leaky) radical cage and requires aromatisation to stabilise the intermediate thiyl radical. This possibility is currently under investigation in our laboratories. Finally the ester (**5**) undergoes neither rearrangement, reduction, nor halogenation with particular ease. This observation possibly reflects the diminished thiocarbonyl nature of the ester owing to the importance of other canonical forms (Scheme 6). A similar explanation can be put forward for

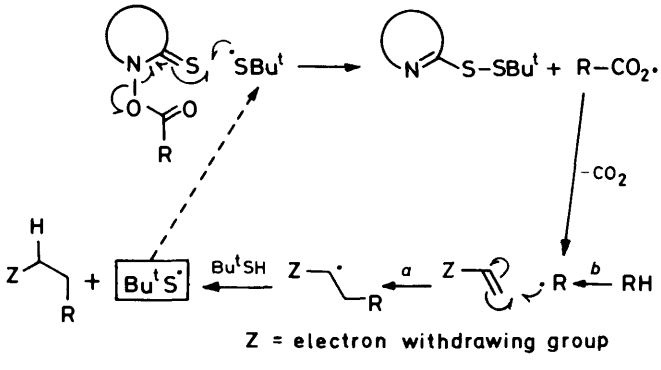


Scheme 6.

the lack of reactivity of *N,N*-dialkylthiocarbamates towards tributylstannane as compared to other thiocarbonyl esters[5] (Scheme 6).

It is evident that the thiohydroxamic acids (**11**) and (**12**) are both excellent alternatives to *N*-hydroxypyridine-2-thione (**1**) and that, furthermore, they have the advantage of forming stable isolable and usually crystalline esters. Bearing this in mind we have synthesized the acid (**11**) on a several hundred gram scale and it is now in everyday use in our laboratories.

In recent years much progress has been made in the design of selective free radical reactions and their application to the modification and synthesis of complex natural products. The functionalisation of steroidal angular methyl groups by radical reactions is well known.[6] The use of template effects leading to selective remote functionalisation by free radicals has been well demonstrated by Breslow.[7] Parts 1—8[8] of this series deal with mild and neutral radical methods for functional group modification. The formation of new carbon–carbon bonds by the addition of radicals to olefins and acetylenes represents a significant challenge to the synthetic radical chemist. The theory of such addition reactions has been the subject of several excellent review articles[9] and continues to attract the attention of theoretical chemists.[10] From a practical standpoint the discovery and application by Giese *et al.*[11] and others[12] of the addition of radicals, generated by the actions of borohydride on alkylmercury derivatives, to activated olefins represented a significant advance in this field. Further progress was represented by the addition by the Giese[13] and subsequently Baldwin[14] groups of radicals derived from halides and pseudohalides (by reaction with tin hydride reagents) to activated olefins. Free radical allylation[15] represents a slightly different but nontheless interesting concept. Following Julia's pioneering studies[16] on free radical cyclisation, Stork[17], Hart,[18], and others[19] have designed and completed syntheses involving the cyclisation of carbon radicals. Each of the above methods represents the overall addition of a carbon and then a hydrogen radical to a double bond. Relatively few methods allow for the trapping of the adduct radical by anything other than a hydrogen donor. The addition of radicals to captodative olefins followed by dimerisation of the adduct radical described by Viehe and coworkers[20] is one such example. Other elegant examples are provided by the work of Stork[21] and Kraus and Landgrebe.[22] The evident topicality of this subject prompted us to search for a new synthetic method, involving the addition of radicals generated by our decarboxylation process,[1] to activated olefins. To the best of our knowledge[23] there are few examples of decarboxylation with addition to olefins in the literature. From the outset we envisaged two possible radical chain reactions. One (Scheme 7) in which the adduct radical would be trapped



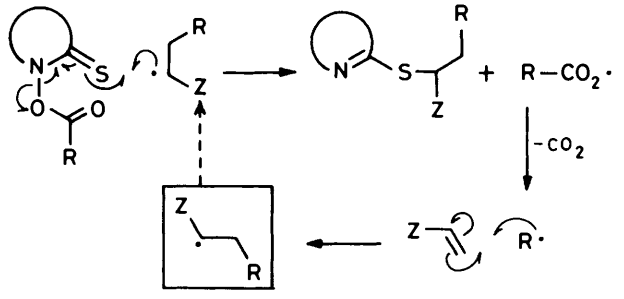
Scheme 7.

by 1,1-dimethylethanethiol thus providing the 1,1-dimethylethylthiyl radical as chain carrier and a second (Scheme 8) in which the adduct radical itself would propagate the chain by attacking the thiocarbonyl group of the thiohydroxamic acid-*O*-

Table 4. Addition to olefins

Entry	Ester	Olefin (equiv.)	Method*	Temp. (°C)	Time (min.)	Products (% Yield)
1	(3)	(33) (30)	A	20	15	(54) (47) + (53) (19)
2	(3)	(33) (15)	A	20	15	(54) (51) + (53) (12)
3	(3)	(33) (10)	A	20	20	(54) (49) + (53) (15)
4	(3)	(33) (5)	A	20	20	(54) (57) + (53) (10)
5	(3)	(33) (2)	A	20	15	(54) (40) + (53) (15)
6	(3)	(33) (15)	A	0	30	(54) (45) + (53) (14)
7	(3)	(34) (2)	A	20	15	(55) (83)
8	(3)	(34) (5)	A	20	15	(55) (63)
9	(3)	(35) (1.1)	A	20	60	(56) (53)
10	(3)	(37) (1.1)	A	20	30	(57) (40)
11	(3)	(38) (1.2)	B	110	60	(58) (60)
12	(3)	(38) (1.2)	C	110	60	(58) (45)
13	(64)	(34) (2)	A	20	15	(59) (35)
14	(65)	(35) (1.2)	A	20	15	(60) (52)
15	(65)	(38) (1.2)	B	80	10	(61) (57)
16	(66)	(35) (1.2)	A	20	60	(62) (45)
17	(66)	(38) (1.2)	B	110	60	(63) (56)
18	(13)	(36) (5)	B	110	60	(67) (43) + (24) (6)
19	(13)	(39) (1.5)	D	20	90	(40) (70) + (24) (*ca.* 15)
20	(13)	(41) (1.5)	D	20	45	(42) (69) + (68) (92)
21	(13)	(43) (1.5)	D	20	60	(69) (93) + (24) (2)
22	(13)	(44) (2)	C	110	60	(70) (30) + (24) (58)
23	(13)	(45) (2)	C	110	90	(46) (26) + (24) (28)
24	(13)	(47) (5)	C	110	90	(48) (27)
25	(13)	(51) (5)	B	110	60	(71) (38) + (24) (33)
26	(13)	(52) (2.5)	B	110	60	(72) (50)
27	(14)	(36) (5)	A	110	180	(68) (40) + (25) (4)
28	(13)	(49) (1)	C	110	60	(50) (*ca.* 30) + (24) (*ca.* 31)

* A: 300W; W. B: reflux, rapid addition. C: reflux dropwise addition. D: 100W; Hg.



Scheme 8.

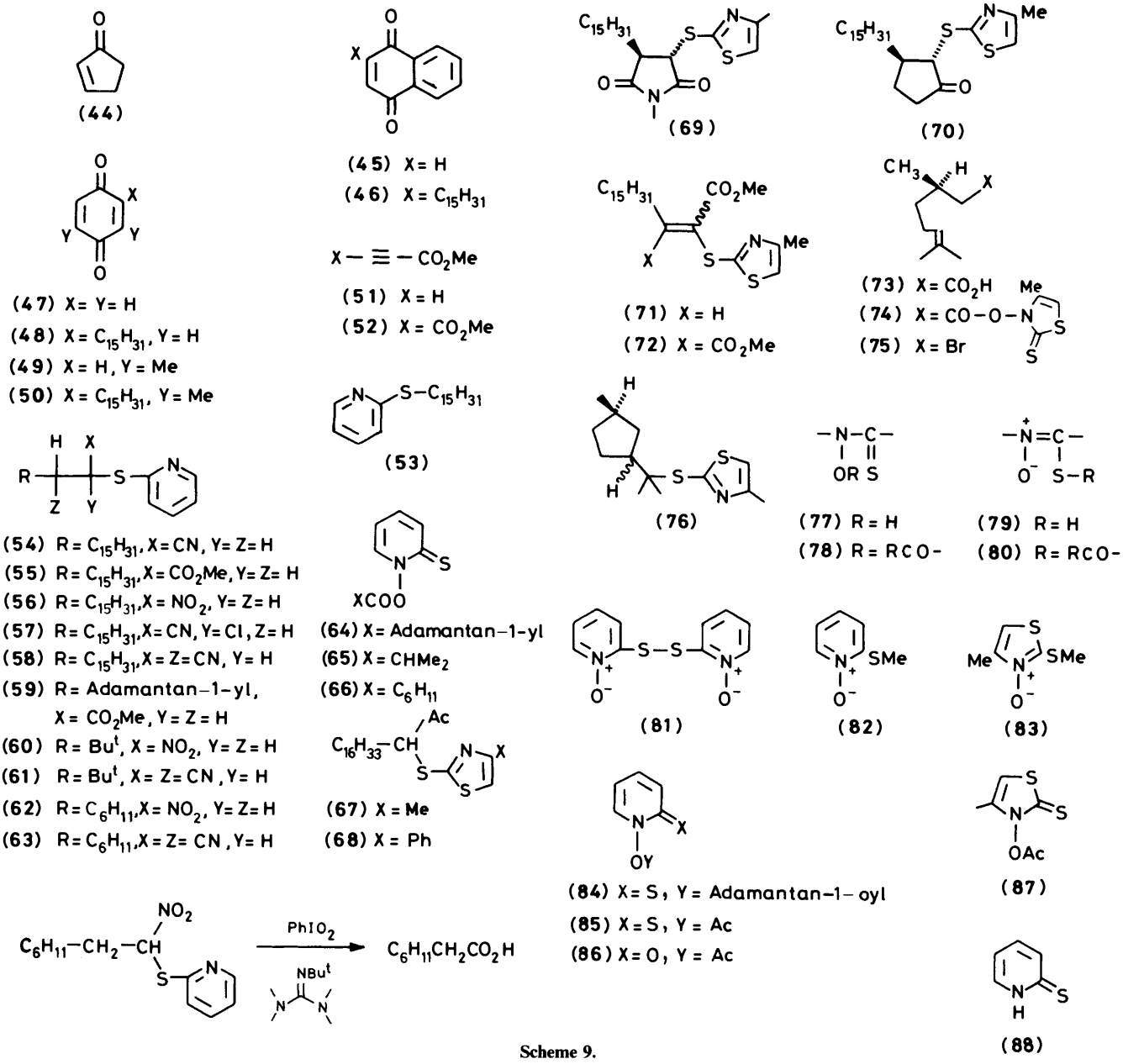
ester. We examined both possibilities with esters derived from the two readily available thiohydroxamic acids (**1**) and (**11**).

We were unable to coax the first (Scheme 7) of these two reactions into being as we were unable to suppress reduction of the radical to the nor alkane (Scheme 3, path *b*).

We met with more success with the second case. As can be seen from Table 4 we were able to add primary, secondary, and tertiary radicals derived from *O*-esters of the thiohydroxamic acid (**1**) to a variety of terminal olefins. In each case the yields are isolated and optimised. We encountered two mutually opposed problems. The use of insufficiently activated, or internal olefins, even in large excess, did not suppress the rearrangement (Scheme 3, path *a*) of the esters. With standard Michael acceptors such as acrylonitrile or methyl acrylate the reaction outlined in Scheme 8 did indeed take place, although significant amounts of rearrangement product were often found. Attempts to limit the formation of rearrangement product by augmenting the olefin concentration usually resulted in significant amounts of polymerisation and thus diminished yields. The results therefore represent a compromise between rearrangement and polymerisation. It was therefore necessary to determine the optimum amount of olefin required for each different reaction and each different radical. The addition of radicals to either α-chloroacrylonitrile (**37**) or nitroethylene[24] (**35**) is particularly interesting in so far as the products are readily transformable into carboxylic acids, thus providing a useful alternative to the classical Arndt-Eistert reaction[25] [treatment of diazo esters with silver(I) oxide]. We demonstrated this possibility by applying our novel oxidative version of the Nef reaction[26] to the adduct (**62**). Thus treatment of (**62**) in dichloromethane at room temperature with an excess of iodoxybenzene and t-butyltetramethylguanidine gave cyclohexylacetic acid (45%; Scheme 9).

The use of *m*-iodoxybenzoic acid, which is usually preferred over iodoxybenzene, led to complications in isolating the product.

The addition of radicals to internal olefins proved to be possible in the case of cyclopent-2-enone (**44**) (Table 4, entry 22), a reaction which is probably assisted by the relief of ring strain on addition. Otherwise we were only able to add radicals to the doubly activated internal double bonds (**33**), (**39**),[27] (**41**), and (**43**) (Table 4, entries 11, 12, 15, 17, 19, 20, and 21). We were also able to add primary radicals to the quinones (**45**), (**47**), and (**49**) (Table 4, entries 23, 24, and 28). As expected addition to the quinone (**49**) took place at the less substituted end of the double bond. In the case of each of the quinones and two of the doubly activated olefins (**39**) and (**41**) the 2-thiazolinethione derived moiety was eliminated during work-up providing the substituted olefins and quinones. Addition to the highly activated and non-polymerisable cyclic five-membered olefins (**39**), (**41**), and (**43**) gave especially pleasing yields (Table 4, entries 19, 20, and 21). Addition to activated acetylenes was also possible (Table 4, entries 25 and 26); predictably the doubly activated dimethyl acetylenedicarboxylate (**52**) gave the higher



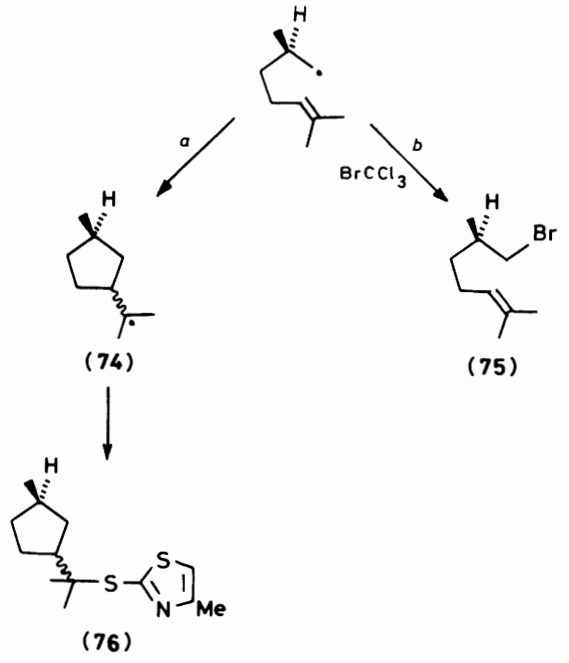
Scheme 9.

yield. With esters derived from the thiohydroxamic acid (**1**) reactions could be carried out either thermally or photochemically with a tungsten lamp. As noted above, the photoinitiated reactions of the ester (**13**) necessitated the use of a medium pressure mercury lamp. However, the ester (**14**) derived from the phenylthiazolinethione (**12**) could be added to methyl vinyl ketone on irradiation with a tungsten lamp (Table 4, entry 27).

As a conclusion to our studies on the addition of radicals to double bonds we attempted a radical cyclisation reaction. Thus ester (**74**) was prepared in 98% yield *via* the acid chloride from optically pure (*R*)-(+)-citronellic acid (**73**) which itself was obtained by a literature procedure[28] from (*R*)-(+)-pulegone. Cyclisation of the radical obtained on decarboxylation of (**74**) is a highly favoured[29] 5-*exo-trig* process and ought normally to present no problem (Scheme 10, path *a*).

Indeed when the ester (**74**) was irradiated in ether with a mercury lamp for 45 min, cyclisation did occur to give the product (**76**) (82%), as a mixture of diastereoisomers (Table 1, entry 11). No simple non-cyclised rearrangement product was observed. However when we attempted cyclisation by irradiation of a solution of (**74**) in bromotrichloromethane (Table 3, entry 7) no cyclisation was observed and the only substrate derived product isolated was the Hunsdiecker product (**75**) (58%; Scheme 10, path *b*). The trapping of a primary alkyl radical by $BrCCl_3$ is, therefore, faster than the cyclisation of this particular hex-5-enyl radical.

Coda.—Thiohydroxamic acids can, in principle, be represented as thione (**77**) or thiol (**79**) tautomers, with the corresponding esters being as in (**78**) or (**80**). We are, of course, aware that the term ester is convenient, but perhaps misleading, for compounds which are formed from the elimination of water from two acidic hydroxy groups. The name anhydride, or mixed anhydride would be more correct. However, we consider it better to regard thiohydroxamic acids as misnamed, and to



Scheme 10.

retain the term ester for the compounds we have now used extensively in radical chemistry.

All the esters that we have used have been in the thione form (**78**) as shown by their i.r. carbonyl maxima. Thiohydroxamic esters contain one single carbonyl group regardless of which structure [(**78**) or (**80**)] they adopt. This carbonyl group has an i.r. maximum typically between 1 790 and 1 810 cm^{-1}. Normal thiol esters have carbonyl maxima in the 1 690—1 710 cm^{-1} region.[30] Furthermore *O*-esters of hydroxamic acids can also exist in two forms [(**78**) and (**80**) S=O]. If such esters were to exist in form [(**80**) S=O] they would only have one carbonyl absorption; however they are found[31] to have two carbonyl absorptions and therefore exist as [(**78**) S=O] (1 780 and 1 670 cm^{-1}). If the 1 670 cm^{-1} is attributed to the pyridone carbonyl then the 1 780 cm^{-1} must be attributed to the ester, in good correlation with our value of 1 790 to 1 810 cm^{-1}. The position of the tautomerism of the parent thiohydroxamic acids is less clear and we undertook to cast some light onto this matter. Katritzky and Jones have concluded on the basis of i.r.[32] and u.v. studies in aqueous media over a range of pH values[33] that the thiohydroxamic acid (**1**) exists in the form (**77**). Therefore we first looked at the u.v. spectra of (**1**) and some of its derivatives in various organic solvents (Table 5). The disulphide bis-*N*-oxide (**81**), prepared according to a literature procedure,[34] provides an example of (**1**) in the form (**79**) whilst the ester (**84**) is an example of the form (**77**). Compounds (**81**) and (**84**) are undoubtedly monomeric. The bathochromic effect observed in the spectra of (**81**) on passing from ethanol solution (Table 5, entry 4) to acetonitrile solution (Table 5, entry 5) can probably be assigned to H-bonding with the solvent. Comparison of the spectra of (**81**) and (**84**) leads to the conclusion that *N*-hydroxypyridine-2-thiones (**77**) have their two maxima at $\lambda_{max.}$ 286 and 364 nm whilst 2-mercaptopyridine *N*-oxides (**79**) have their maxima at $\lambda_{max.}$ *ca.* 245, 270, and 280 nm. It is then immediately obvious that at low concentration in cyclohexane (Table 5, entry 3) and acetonitrile (Table 5, entry 2) the thiohydroxamic acid (**1**) exists, uniquely as such, *i.e.* in the form (**77**). The situation in ethanol (Table 5, entry 1) is entirely different and compound (**1**) obviously exists as an equilibrium mixture of (**77**) and (**79**).

We were more concerned about the position of the equilibrium (**77**) $\rightleftharpoons$ (**79**) in more concentrated solutions. Thus we undertook a ^1H and ^{13}C n.m.r. study of both (**1**) and (**11**). The ^1H and ^{13}C n.m.r. spectra of (**1**) were compared with those of various model compounds. Structure (**82**) represents the tautomer (**79**) whilst (**85**) and (**88**) are representative of the tautomeric form (**77**). Consideration of all the ^1H chemical shifts in Table 6 suggests that (**1**) exists in the form (**77**); that is, as *N*-hydroxypyridine-2-thione. More definite proof was looked for in the ^{13}C spectra. The ester (**85**) has one carbonyl group and one thiocarbonyl and these were attributed the signals at δ 175.8 and 165.9 p.p.m., respectively (Table 6). These assignments were corroborated by the fact that pyridine-2-thione (**88**)[35,36] has its thiocarbonyl carbon at 176.4 p.p.m. and also by the fact that *N*-acetoxypyridin-2-one (**86**)[37] has two carbonyl absorptions, δ 166.4 and δ 156.9 p.p.m. If the latter is attributed to the amide group then the former must be the ester group and is in excellent agreement with the assignment of δ 165.9 p.p.m. to the ester in (**85**). The C-2 signal in (**82**) was assigned to the 152.4 p.p.m. absorption. The C-2 signal of (**1**) is found at 167.5 p.p.m., close to the thiocarbonyls of (**85**) and (**88**), which renders an unequivocal decision between the tautomers (**77**) and (**79**) difficult. As with the ^1H n.m.r. spectra, consideration of all the ^{13}C values and especially those for the C=S signals favours form (**77**).

If the picture for (**1**) remains a little obscure, that of (**11**) is perfectly clear. Compound (**83**) represents form (**79**) and ester

Table 5. U.v. spectra.

Entry	Compd.	Solvent	$\lambda_{max.}$/nm (ε)
1	(**1**)	EtOH	251 (9 700), 295 (5 200), 362 (1 900)
2	(**1**)	MeCN	282 (13 500), 352 (3 900)
3	(**1**)	c-C_6H_{12}	292 (17 100), 370 (3 800)
4	(**81**)	EtOH	243 (38 000), 270 (15 000)
5	(**81**)	MeCN	247 (34 500), 281 (11 700)
6	(**84**)	EtOH	286 (14 00), 364 (4 400)

Table 6. ^1H and ^{13}C N.m.r.[a] spectra of derivatives of (**1**)

							δ					
Entry	Compd.	δ 3-H	δ 4-H	δ 5-H	δ 6-H	Others (assign.)	C-2	C-3	C-4	C-5	C-6	Others (assign.)
1	(**1**)	7.7	7.3	6.8	8.1		167.5	131.4[b]	132.4[b]	113.9	132.5	
2	(**82**)	7.1	7.1	7.1	8.2	2.43 (CH_3S)	152.4	120.1[b]	125.2	119.6[b]	137.6	13.2(SCH_3)
3	(**85**)	7.7	7.3	6.8	7.95	2.50 (CH_3COO)	175.8	133.7	137.2[b]	112.7	137.7[b]	18.4 (CH_3CO), 165.9 (CO)
4	(**88**)[35,36]	7.5	7.4	6.8	7.7		176.4	133.6	138.1	114.2	137.0	
5	(**86**)						156.9	122.6	135.3	105.0	135.3	17.8 (CG_3CO), 166.4 (CO)

[a] All spectra in $CDCl_3$. [b] These assignments are interchangeable.

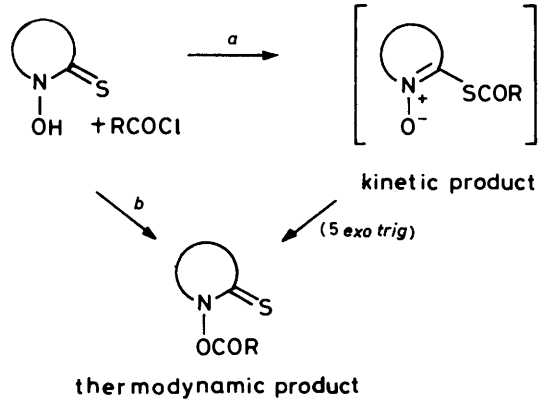
Table 7. ^{1}H and ^{13}C N.m.r.[a] spectra of derivatives of (**11**)

Entry	Compd.	δ 4-H	δ 6-H	Others (assign.)	δ C-2	δ C-4	δ C-6	Others (assign.)
1	(**11**)	6.25	2.35		171.8	102.5	135.7	13.3 (Ar–CH_3)
2	(**83**)	6.93	2.30	2.50 (SCH_3)	145.7[b]	110.7	142.6[b]	14.7 (S–CH_3), 15.5 (Ar–CH_3)
3	(**87**)	6.20	2.0	2.25 (CH_3CO)	180.7	102.5	136.9	13.2 (ArCH_3), 17.9 (CH_3CO), 165.7 (CH_3CO)

[a] All spectra in $CDCl_3$. [b] These assignments are interchangeable.

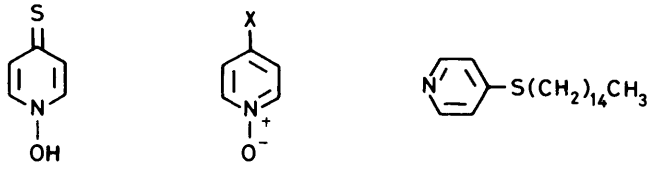
(**87**) the tautomer (**77**). It is immediately evident from the chemical shifts of the 4-H signals in (**11**), (**83**), and (**87**) (Table 7) that (**11**) exists in the thiocarbonyl form. This is corroborated by the ^{13}C n.m.r. spectra of the same compounds. Compounds (**11**) and (**87**) have thiocarbonyl absorptions at 171.8 and 180.7 p.p.m. whilst the lowest field signal in (**83**) is the aromatic signal at 145.7 p.p.m. (Table 7). We are, therefore, of the opinion that, in potentially aromatic aprotic solvents, thiohydroxamic acids capable of the tautomerism (**77**) ⇌ (**79**) exist as (**77**) and not as mercapto *N*-oxides (**79**).

Finally it is interesting to speculate on the mechanism of acylation of thiohydroxamic acids. There are two possibilities. The first (Scheme 11, path *a*) implies acylation at thiocarbonyl sulphur giving a kinetic product which immediately rearranges to the observed thermodynamic product, a highly favoured 5-*exo-trig* transposition.[29] The second (Scheme 11, path *b*) is



Scheme 11.

direct acylation at oxygen. Comparison with acylation of pyridine-2-thiones[38] suggests that both are real possibilities. There is reasonable precendent[37] for the 5-*exo-trig* rearrangement required by path *a*. Interestingly, alkylation with methyl iodide of (**1**) and (**11**) leads to the formation of the methylthio *N*-oxides (**82**) and (**83**), respectively, as the only observable products. This is predictable by HSAB theory. The rearrangement of the kinetic products (**82**) and (**83**) to the corresponding thiohydroxamic acid *O*-methyl esters would be highly disfavoured,[29] and does not take place.[39] Significantly acylation of the vinylogous thiohydroxamic acid *N*-hydroxypyridine-4-thione[33] (**89**) gives one main product, the 4-acylthioxypyridine-*N*-oxide (**91**),[40] the intramolecular rearrangement (Scheme 11, path *a*) to the *O*-ester being impossible. On the whole it would seem then that although thiohydroxamic acids exist in the tautomeric form (**77**), they undergo acylation and alkylation *via* the tautomer (**79**) and that when possible the so formed kinetic product rearranges to give esters of the thione form.



(**89**) (**90**) X= S–C(=NH)NH_2.HCl. (**92**)
(**91**) X= $SCO(CH_2)_{14}CH_3$

Experimental

N.m.r. spectra were recorded at 60 MHz unless otherwise stated with either a Varian T60 or EM360 L spectrometer for solutions in deuteriochloroform. Chemical shifts are in p.p.m. downfield from $SiMe_4$ as internal standard. 200 MHz N.m.r. spectra were measured with a Brucker WM 200 spectrometer. I.r. spectra were measured with a Perkin-Elmer 297 spectrophotometer and u.v. spectra with a Jobin Yvon Duospac 203 spectrophotometer. 70 eV E.i. mass spectra were recorded on either an AEI MS-9 or an AEI MS-50 apparatus. Melting points were taken on a Reichert hot stage apparatus and are uncorrected. All solvents were dried and distilled by standard procedures. Ether refers to diethyl ether.

O-Ethyl S-(2-Oximinopropyl) Dithiocarbonate (**8**).—Dry pyridine was added dropwise over 15 min to a stirred suspension of (**7**)[41] (46.7 g, 0.26 mol) and hydroxylamine hydrochloride (20.0 g, 0.29 mmol) in dry methanol (100 ml) at 0 °C. After 16 h at room temperature the resulting homogeneous solution was evaporated to dryness and the residue taken up in ether. The ethereal solution was washed with dilute hydrochloric acid and water, dried ($MgSO_4$), filtered, and evaporated to dryness to give a viscous oil which recrystallised from pentane to give the *oxime* (**8**), (42.9 g, 85%), m.p. 59—60 °C; δ 1.40 (3 H, t, *J* 7 Hz), 1.95 (3 H, s), 3.90 and 4.05 (2 H, 2 s, ratio 3:1), 4.65 (2 H, q, *J* 7 Hz), and 8.45 (1 H, br); *m/z* 193 (M^+) and 176 (M^+ − OH); $\nu_{max.}$(Nujol) 3 400br, 1 230, 1 040, and 720 cm^{-1} (Found: C, 37.4; H, 5.65; N, 7.0; S, 33.15. $C_6H_{11}NO_2S_2$ requires C, 37.28; H, 5.69; N, 7.25; S, 33.15%).

3-Hydroxy-4-methylthiazole-2(3H)-thione (**11**).—The oxime (**8**) (42.8 g, 0.22 mol) in CH_2Cl_2 (80 ml) was added with ice cooling over 10 min to vigorously stirred aqueous (100 ml) potassium hydroxide (50.0 g, 0.89 mol). After 30 min the reaction was diluted with water (100 ml) and the organic phase decanted off and the aqueous phase washed with pentane (150 ml). The aqeuous phase was carefully acidified with ice cooling to pH 3 with concentrated hydrochloric acid and extracted with dichloromethane (5 × 150 ml). The extract was dried ($MgSO_4$) and evaporated to dryness and the residue was recrystallised from methanol to yield the cyclic *thiohydroxamic acid* (**11**) (25.8 g, 79%) as colourless needles, m.p. 93—94 °C; δ (80 MHz), 2.35 (3 H, weak allylic coupling), 6.25 (1 H, weak allylic coupling),

and 9.20 (1 H, br); *m/z* 147 (M^+), 131 ($M^+ - O$), 130 ($M^+ - OH$), and 115 ($M^+ - S$); $\nu_{max.}$(Nujol), 2 650br, 1 580, 1 330, 1 170, 1 000, and 980 cm^{-1}; $\lambda_{max.}$(EtOH) 296 nm (ε 13 500) (Found: C, 32.4; H, 3.55; N, 9.25; S, 43.7. $C_4H_5NOS_2$ requires C, 32.63; H, 3.42; N, 9.51; S, 43.56%).

O-Ethyl S-(2-*Oximino*-2-*phenylethyl*) *Dithiocarbonate* (**10**).—A solution of phenacyl bromide oxime (**9**)[42] (22.0 g, 0.10 mol) in acetone was added dropwise to a stirred solution of potassium *O*-ethyl dithiocarbonate (18 g, 0.11 mol) in acetone (150 ml) and the reaction mixture stirred for a further 4 h at room temperature. It was then filtered, evaporated to dryness, and the residue taken up in ether. The resulting solution was washed with water (3 × 50 ml) dried ($MgSO_4$), and evaporated to dryness, to give pure (n.m.r., t.l.c.) (**10**) as a bright yellow viscous oil (26.0 g, 100%). Further purification was effected by filtration over silica gel (eluant: ether–pentane 1:1) to give the *dithiocarbonate* (**10**) (23.5 g, 90%); δ (200 MHz), 1.30 (3 H, t, *J* 7 Hz), 4.28 (s, SCH_2 *anti* oxime main isomer), 4.48 (s, SCH_2 *syn* oxime), 4.58 (2 H, q, *J* 7 Hz), 7.00—7.90 (5 H), and 8.4 (1 H, br); *m/z* 156 ($M^+ + 1$) and 1.8 ($M^+ - OH$); $\nu_{max.}$(film): 3 230br cm^{-1} (Found: C, 51.7; H, 5.2; N, 5.25; S, 24.9. $C_{11}H_{13}NO_2S_2$ requires C, 51.74; H, 5.13; N, 5.48; S, 25.11%).

3-*Hydroxy*-4-*phenylthiazole*-2(3H)-*thione* (**12**).—The dithiocarbonate (**10**) (29.9 g, 0.12 mol) in dry ether (100 ml) was added over 15 min to a vigorously stirred, ice cooled suspension of powdered, anhydrous zinc chloride (17.7 g, 0.13 mol) in dry ether (200 ml) and the stirring was continued for a further 12 h at room temperature. After decantation of the solvent the residue was thoroughly washed with ether [evaporation to dryness of the combined organic phases gave a small amount of (**12**) (0.55 g) and the crude recovered *syn* isomer of (**10**) as a brown yellow oil (15.0 g, 50%)]. The solid residue was vigorously stirred overnight in a two phase system comprising 6M-hydrochloric acid (200 ml) and dichloromethane (100 ml). Rapid filtration gave the crude product (10.5 g) as a colourless powder which was recrystallised from chloroform–ethanol to afford (**12**) as colourless needles (9.4 g). The organic phase contained an additional portion (1.2 g) of (**12**) which was isolated by extraction into aqueous sodium hydroxide, acidification, and extraction into chloroform. The combined yield of the *thiohydroxamic acid* (**12**) was 11.15 g (46%), m.p. 150—151 °C; δ[$CDCl_3$–$(CD_3)_2SO$, 1:1], 6.75 (1 H, s), 7.30—8.00 (5 H), and 11.8 (1 H, br); *m/z* 209 (M^+), 193 ($M^+ - O$), and 134 ($M^+ - HONCS$); $\nu_{max.}$(Nujol) 2 650br, 1 340, 1 160, 1 050, 970, 960, and 850 cm^{-1}; $\lambda_{max.}$(EtOH) 229 nm (ε 9 160), 264 nm (ε 12 800), and 307 nm (ε 7 980) (Found: C, 51.4; H, 3.45; N, 6.85; S, 30.7%. $C_9H_7NOS_2$ requires C, 51.65; H, 3.37; N, 6.69; S, 30.64%).

3-*Methyl*-1-*palmitoyloxy*-2-*thioxo*-1,2-*dihydroquinazoline*-4-(3H)-*one* (**5**).—A mixture of (**4**)[3] (687 mg, 3.3 mmol), DMAP (37 mg, 0.3 mmol), pyridine (0.5 ml, 6.3 mmol), and palmitoyl chloride (825 mg, 3.0 mmol) was heated to reflux in benzene (40 ml) under nitrogen for 2 h. The mixture was then evaporated to dryness, the residue taken up in dichloromethane, and the solution quickly washed with dilute aqueous sodium hydrogen carbonate (5 ml) and dilute hydrochloric acid (5 ml); it was then dried ($MgSO_4$), filtered, and evaporated to dryness. The residue was recrystallised from light petroleum–CCl_4 to yield the *ester* (**5**) (1.28 g, 96%), m.p. 104 °C; δ 0.40—2.10 (29 H), 2.73 (2 H, t, *J* 7 Hz), 3.80 (3 H, s), and 6.85—8.30 (4 H, m); *m/z* 446 (M^+), 402 ($M^+ - CO_2$), 369, 355, 239, 208, and 192; $\nu_{max.}$(Nujol) 1 790 and 1 695 cm^{-1} (Found: C, 67.3; H, 8.4; N, 6.35; S, 7.1. $C_{25}H_{28}N_2O_3S$ requires C, 67.23; H, 8.58; N, 6.27; S, 7.17%).

4-*Methyl*-3-*palmitoyloxythiazol*-2(3H)-*thione* (**13**).—A mixture of thiohydroxamic acid (**11**) (1.50 g, 10.2 mmol), pyridine (1 ml), DMAP (37 mg, 0.3 mmol), and palmitoyl chloride (2.75 g, 10.0 mmol) was stirred at room temperature for 20 min in dry ether (50 ml). The precipitated pyridinium hydrochloride was filtered off and the ether removed under reduced pressure to give a viscous oil which was recrystallised from pentane (20 ml) to yield the ester (**13**) as a colourless powder (3.65 g, 94%), m.p. 54 °C; δ 0.65—2.00 (29 H, m), 2.15 (3 H, weak allylic coupling), 2.66 (2 H, t, *J* 7 Hz), and 6.17 (1 H, weak allylic coupling); *m/z* 385 (M^+) and 341 ($M^+ - CO_2$); $\nu_{max.}$(Nujol) 1 800 cm^{-1}.

3-*Palmitoyloxy*-4-*phenylthiazolin*-2-(3H)-*thione* (**14**).—This compound, prepared in 92% yield from (**12**) and palmitoyl chloride in an analogous manner to the ester (**13**), was colourless and crystalline, m.p. 61—62 °C; δ 0.50—1.90 (29 H, m), 2.50 (2 H, m), 6.60 (1 H, s), and 7.60 (5 H); *m/z* 443 ($M^+ - CO_2$) and 193; $\nu_{max.}$(Nujol) 1 800 cm^{-1}; $\lambda_{max.}$(CH_2Cl_2) 242 nm (ε 7 600) and 324 nm (ε 10 900) (Found: C, 67.05; H, 8.3; N, 3.35; S, 14.2. $C_{25}H_{37}NO_2S_2$ requires C, 67.07; H. 8.33; N, 3.13; S, 14.32%).

N-*Methyl*-N-*palmitoyloxythiobenzamide* (**17**).—Palmitoyl chloride (2.61 g, 9.5 mmol) was added at room temperature to a stirred solution of the thiohydroxamic acid (**16**)[4] (1.67 g, 10.0 mmol) and pyridine (1 ml) in dry ether (30 ml). After 30 min the filtered solution was quickly washed with dilute aqueous sodium hydrogen carbonate (5 ml) and dilute hydrochloric acid (5 ml) dried, filtered, and evaporated to dryness. The resultant yellow *ester* (**17**) (3.82 g, 99%) was analytically pure and had m.p. 36—38 °C; δ 0.60—1.80 (29 H, m), 2.17 (2 H, t, *J* 6 Hz), 3.77 (3 H, s), and 7.33 (5 H, m); *m/z* 405 (M^+), 361 ($M^+ - CO_2$), 360, 239, 151, 119, and 118; $\nu_{max.}$(film) 1 790 cm^{-1} (Found: C, 71.25; H, 9.65; N, 3.25; S, 7.7. $C_{24}H_{39}NO_2S$ requires C, 71.06; H, 9.69; N, 3.45; S, 7.90%).

Thermolysis of the Ester (**17**) *at* 170 °C.—A sample of the ester (**17**) (1.0 g, 2.46 mmol) was heated to 170 °C for 3 h. Chromatography of the resultant mixture gave two products: *N*-methylthiobenzamide (**18**) (80 mg, 21%) (eluant: CH_2Cl_2), m.p. 77—78 °C (ether–CCl_4) [lit.,[43] 80.5—81 °C (water)] followed by the *rearrangement product* (**19**) (0.54 g, 60%) (eluant: ethyl acetate–CH_2Cl_2), which was a light yellow solid, m.p. 28—31 °C; δ 0.61—1.90 (29 H), 3.45 and 3.15 (3 H, 2 × s, *E*/*Z* isomers ratio *ca.* 1.8:1), 2.60 and 3.03 (2 H, 2 × t), and 7.15—7.65 (5 H, m); *m/z* 361 (M^+), 314, 211, 165, 151, 119, and 118; $\nu_{max.}$(film) 2 900, 2 830, 1 610, 1 450, 1 440, 1 200, 990, 760, and 700 cm^{-1} (Found: C, 76.5; H, 10.5; N, 3.7; S, 8.7. $C_{23}H_{39}NS$ requires C, 76.39; H, 10.87; N, 3.87; S, 8.86%).

Thermolysis of the Ester (**5**) *at* 160 °C.—The ester (**5**) (1.34 g, 3.0 mmol) was heated to 160 °C for 3 h. After which it was cooled to room temperature. The residue was extracted several times with hot pentane and the insoluble residue recrystallised from ethanol–toluene to give 3-methyl-2-thiono-1,2-dihydroquinazolin-4(3*H*)-one (**6**) (120 mg, 20%) as needles, m.p. 269—270 °C, (lit.,[44] 267 °C). From the pentane extracts the *rearrangement product* (**22**) was obtained as a colourless powder (0.68 g, 56%), m.p. 61—62 °C (pentane); δ 0.65—2.20 (29 H), 3.23 (2 H, t, *J* 7 Hz), 3.55 (3 H, s), and 7.10—8.30 (4 H, m); *m/z* 401 (M^+), 387, 369, 355, 193, and 192; $\nu_{max.}$(Nujol) 1 660 and 1 550 cm^{-1} (Found: C, 71.6; H, 9.5; N, 7.1; S, 8.15. $C_{24}H_{38}N_2OS$ requires C, 71.59; H, 9.51; N, 6.96; S, 7.69%).

Thermolysis of the Ester (**5**) *in Xylene at Reflux*.—The ester (**5**) (4.47 g, 10.0 mmol) was heated to reflux in xylene (50 ml) under nitrogen until all the starting material had been consumed (40 h). The solvent was removed under reduced pressure and the residue subject to filtration through silica.

Elution with pentane gave a mixture of pentadecane (**30**) and the rearrangement product (**22**). This mixture was subjected to Kugelrohr distillation (bath temp. 170 °C/13 mmHg) to give pure pentadecane (**30**) (350 mg, 16%). The distillation residues were crystallised from pentane to give the sulphide (**22**) (2.20 g, 54%), m.p. 60—62 °C, identical with the above described compound. Further elution with ethyl acetate gave the quinazolinone (**6**) (0.45 g, 23%) identical with the sample described above.

Thermolysis of the Ester (**13**).—This ester was stable below 100 °C, gas evolution begining at *ca.* 100 °C on a melting point apparatus.

(i) *Decomposition in toluene*: in situ *generation of the ester*. Palmitoyl chloride (825 mg, 3.0 mmol) was added to a stirred, dried solution of the thiohydroxamic acid (**11**) (486 mg, 3.30 mmol), pyridine (0.4 ml, 5.0 mmol), and DMAP (37 mg, 0.3 mmol) at reflux under nitrogen in toluene (20 ml). After 45 min at reflux the solvent was removed under reduced pressure and the residue taken up in dichloromethane (20 ml). The solution was washed with saturated aqueous sodium hydrogen carbonate (5 ml) and 2M hydrochloric acid (5 ml), dried ($MgSO_4$), filtered, and evaporated to dryness; the residue was subjected to chromatography on silica gel. Elution with pentane–ethyl acetate (70:30) gave the *sulphide* (**24**) (0.86 g, 84%), as a light yellow solid, m.p. 27—30 °C; δ 0.60—2.00 (29 H, m), 2.36 (3 H), 3.13 (2 H, t, *J* 7 Hz), and 6.62 (1 H, s); *m/z* 341 (M^+), 308, 294, 214, 200, 186, 173, 158, 145, and 131; $\nu_{max.}$(film) 3 070, 2 900, 2 825, 1 520, 1 460, 1 430, 1 400, 1 360, 1 290, and 1 020 cm^{-1}; $\lambda_{max.}$(EtOH) 283 nm (ε 4 600) (Found: C, 66.6; H, 10.25; N, 4.1; S, 18.55. $C_{19}H_{35}NS_2$ requires C, 66.80; H, 10.33; N, 4.10; S, 18.77%).

(ii) *Decomposition in benzene*. This was carried out in a similar manner to the decomposition in toluene, the products being isolated by chromatography over silica gel.

Photolysis of the Ester (**13**).—Irradiation of the ester (**13**) in toluene under nitrogen at room temperature with a 300 W tungsten lamp for 1 h caused no reaction.

Irradiation of the ester (**13**) (1 mmol) in toluene under nitrogen at room temperature with a 100 W medium pressure mercury lamp for 30 min caused complete reaction. After evaporation of the solvent the residue was filtered through silica (eluant: ether-pentane) to give the pure sulphide (**24**) (240 mg, 70%) identical with the product obtained by thermolysis.

Thermolysis of the Ester (**14**).—The ester (**14**) (896 mg, 2.0 mmol) was heated to reflux in benzene (10 ml) under nitrogen for 2 h. The mixture was then evaporated to dryness and the residue filtered through silica gel to give the *sulphide* (**25**) (665 mg, 82%), m.p. 53 °C (pentane); δ 0.65—2.30 (29 H, m), 3.28 (2 H, t, *J* 7.0 Hz), and 7.10—8.20 (6 H, m); *m/z* 403 (M^+), 356 and 193; $\nu_{max.}$(Nujol) 1 065, 1 035, 915, 840, 770, 725, 715, and 690 cm^{-1}; $\lambda_{max.}$(EtOH) 228 nm (ε 9 870), 246 nm (ε 14 130), and 273 nm (ε 8 970) (Found: C, 71.65; H, 9.15; N, 3.65; S, 15.7. $C_{24}H_{37}NS_2$ requires C, 71.40; H, 9.24; N, 3.47; S, 15.88%).

Irradiation of the ester (**14**) in benzene at room temperature with a 300 W tungsten lamp for 2 h gave a 1:1 mixture of the ester (**14**) and the sulphide (**25**).

Reduction of the Ester (**5**) *with* 1,1-*Dimethylethanethiol*.—(i) *In benzene*. When refluxed under nitrogen in benzene for 3 h with an excess of 1,1-dimethylethanethiol the ester was recovered unchanged in 97% yield.

(ii) *In xylene*. A solution of the ester (**5**) (2.23 g, 5.0 mmol) and 4,4-dimethylethanethiol (7.0 ml, 62 mmol) in xylene (40 ml) were heated to reflux under nitrogen for 48 h, with an efficient double surface condenser, further thiol (5 ml) being added after 26 h. At the end of the reaction most of the solvent was removed under reduced pressure and on cooling the quinazolinone (**6**) crystallised out as colourless needles (0.72 g, 75%), m.p. 265—267 °C, identical with a sample isolated as above. The mother liquors were evaporated to dryness and the residual oil subjected to Kugelrohr distillation (150—170 °C/13 mm) to yield pentadecane (**30**) (0.78 g, 74%) as a colourless oil. Crystallisation of the residue from light petroleum gave the unchanged ester (**5**) (200 mg, 9%) and, subsequently, the rearrangement product (**22**) (110 mg, 5%).

Reduction of the Ester (**5**) *with Tributylstannane*.—A toluene solution (25 ml) of the ester (**5**) (1.07 g, 2.39 mmol), tributylstannane (1.5 ml, 5.5 mmol), and AIBN (20 mg, 0.12 mmol) was heated to reflux under nitrogen for 1 h. After removal of the solvent under reduced pressure, the oily residue was chromatographed on silica. Elution with pentane gave an oily product which was treated with an ethereal solution of iodine until the brown colour persisted. The solution was then diluted with further ether (20 ml) and added to an aqueous solution of potassium fluoride (10 ml, 10%) and the two-phase system vigorously stirred overnight. The organic phase was decanted off, dried ($MgSO_4$), evaporated to dryness, and the residue distilled (170 °C/13 mm) in a Kugelrohr apparatus to give pentadecane (**30**) as a colourless oil (0.29 g, 57%). The quinazolinone (**6**) (0.38 g, 82%), m.p. 269—270 °C was eluted from the the column with ethyl acetate.

Synthesis of Disulphide (**23**).—Sulphuryl chloride (1.30 ml, 16.0 mmol) in dry ether (5 ml) was added dropwise over 5 min to an ice cold, stirred solution of di-t-butyl disulphide (2.67 g, 15.0 mmol) in dry ether (5 ml). This solution was maintained at 0 °C for 2 h and was then added dropwise at room temperature to a stirred suspension of (**6**) (0.99 g, 5.15 mmol) in dichloromethane (30 ml) and pyridine (5 ml). The reaction mixture was stirred for 2 h and then washed with aqueous sodium hydroxide (10%; 5 ml) and 2M-hydrochloric acid (10 ml), dried (Na_2SO_4), filtered, and evaporated to dryness. The residue was filtered through silica (eluant: ether) and finally recrystallised from pentane to give the disulphide (**23**) as colourless prisms (0.91 g, 63%), m.p. 83 °C; δ 1.40 (9 H, s), 3.61 (3 H, s), and 6.95—8.05 (4 H, m); *m/z* 280 (M^+), 224, 192, and 191; $\nu_{max.}$(Nujol) 1 680 cm^{-1}.

Reduction of the Disulphide (**23**) *with* 1,1-*Dimethylethanethiol*.—A solution of the disulphide (**23**) (466 mg, 1.66 mmol) in toluene (5 ml) was refluxed for 2 h during which time no reaction occurred (t.l.c.). 1,1-Dimethylethanethiol (2.0 ml, 17 mmol) was then added and the mixture refluxed for 1.5 h. On cooling, the quinazolineone (**6**) separated as colourless needles (0.26 g, 81%), m.p. 265—266 °C. The mother liquors were concentrated under reduced pressure and the residue filtered through silica (eluant: pentane) to give di-t-butyl disulphide (165 mg, 56%) after Kugelrohr distillation (100 °C/13 mmHg).

Reduction of the Ester (**17**) *with* 1,1-*Dimethylethanethiol*.—(i) *In benzene*. Palmitoyl chloride (1.38 g, 5.0 mmol) was added to a stirred solution of the thiohydroxamic acid (**16**) (0.92 g, 5.5 mmol) and pyridine (0.79 g, 10.0 mmol) in benzene (10 ml) at reflux under nitrogen. After 20 min at reflux 1,1-dimethylethanethiol (5.0 ml, 44 mmol) was added rapidly and heating continued for 30 min. After cooling and evaporation of the solvent the crude reaction mixture was thoroughly extracted with pentane (3 × 15 ml) and the residue chromatographed on silica. Elution with pentane–ether 1:1 gave *N*-methylthiobenzamide (**18**) (0.62 g, 82%) identical with the product isolated above. The pentane extracts were concentrated and submitted to fractional distillation in a Kugelrohr apparatus, to yield di-t-butyl disulphide (150 mg) (100—110 °C/13 mmHg)

and the pentadecane (**30**) (0.88 g, 83%) (150—170 °C/13 mmHg) both as colourless oils which were identical with authentic samples.

(ii) *In toluene.* The ester (**17**) (1.62 g, 4.0 mmol) was added to a solution of 1,1-dimethylethanethiol (5.0 ml, 44 mmol) in toluene (25 ml) at reflux under nitrogen. After 1 h the solvent was removed under reduced pressure and the residue chromatographed on neutral alumina. Elution with pentane and subsequent Kugelrohr distillation gave pentadecane (0.72 g, 85%). Elution with pentane–ether 9:1, followed by Kugelrohr distillation at 110 °C/0.1 mmHg gave compound (**20**) as a colourless oil (288 mg, 34%). This known compound was a 66:34 mixture of *E* and *Z* isomers (n.m.r.); δ 1.22 (*E*), 1.55 (*Z*) (9 H, 2s), 3.60 (*E*), 3.10 (*Z*) (3 H, 2s), and 7.15—7.90 (5 H, m); $\nu_{max.}$(film) 1 620 cm^{-1}. Small signals at δ 1.17, 1.29, 3.19, and 3.63 were indicative of the presence of the disulphide (**21**) as an impurity. Further elution with ether gave (**18**) (0.29 g, 48%) identical with an authentic sample.

Preparation of the Disulphide (**21**).—A solution of 1,1-dimethylethanesulphenyl chloride (30 mmol) in ether (10 ml) (prepared from the disulphide and SO_2Cl_2 as above) was added dropwise to a solution of *N*-methylthiobenzamide (**18**) (0.82 g, 5.43 mmol) in dry ether (3 ml). Overnight a viscous oil separated from the reaction. After being washed with pentane and dried *in vacuo* this oil was taken up in dichloromethane (3 ml) and pyridine (0.60 g, 7.6 mmol). After 5 min at room temperature the reaction was diluted with ether (25 ml), filtered, and evaporated. Chromatography of the residue on neutral alumina using pentane–ether (9:1) as solvent gave the *E*/*Z* disulphide mixture (**21**) as a colourless oil (0.75 g, 57%); δ 1.18 and 1.30 (9 H, 2 s, ratio 3:1), 3.63 and 3.20 (3 H, 2 s), and 7.15—7.70 (5 H, m); $\nu_{max.}$(film) 3 040, 3 000, 2 950, 1 610, 1 440, 1 385, 1 360, 1 270, 1 220, 1 160, 990, 900, 760, and 690 cm^{-1} (Found: C, 59.95; H, 7.1; N, 5.85; S, 26.75. Calc. for $C_{12}H_{17}NS_2$: C, 60.21; H, 7.16; N, 5.85; S, 26.78%).

Reduction of the Disulphide (**21**) *with* 1,1-*Dimethylethanethiol.*—The disulphide (**21**) (0.37 g, 1.54 mmol) was heated to reflux in toluene (3 ml) for 3 h with no observable change in composition. 1,1-Dimethylethanethiol (2.0 ml, 17 mmol) was then added and the reaction maintained at reflux for 1.5 h. After concentration the reaction was chromatographed on silica. Elution with pentane and subsequent Kugelrohr distillation (100 °C/13 mmHg) gave di-t-butyl disulphide (130 mg, 47%). Elution with ether followed by Kugelrohr distillation (110 °C/0.1 mmHg) gave the sulphide (**20**) (87 mg, 27%), identical with the sample isolated above; finally, elution with ethyl acetate gave *N*-methylthiobenzamide (**18**) (150 mg, 64%).

Reduction of the Ester (**13**) *with* 1,1-*Dimethylethanethiol.*—Palmitoyl chloride (825 mg, 3.0 mmol) was added in one portion to a stirred solution of thiohydroxamic acid (**11**) (486 mg, 3.30 mmol), DMAP (37 mg, 0.3 mmol), 1,1-dimethylethanethiol (1.0 ml, 8.8 mmol), and pyridine (0.5 ml, 6.3 mmol) in benzene (35 ml) at reflux under nitrogen. After a further 2 h at reflux the solvent was removed under reduced pressure and the residue filtered through silica gel. Elution with pentane and Kugelrohr distillation (150—170 °C/13 mmHg) gave pentadecane (**30**) as a colourless oil (572 mg, 90%). Further elution with ethyl acetate and Kugelrohr distillation (130 °C/0.1 mmHg) gave the *mixed disulphide* (**26**) as a colourless oil (0.61 g, 92%); δ 1.40 (9 H, s), 2.33 (3 H, weak allylic coupling), and 6.73 (1 H, weak allylic coupling); *m*/*z* 219 (M^+), 165, 164, 163, 132, 131, and 130; $\nu_{max.}$(film): 3 070, 2 950, 2 900, 2 840, 1 520, 1 440, 1 405, 1 360, 1 290, 1 215, 1 160, 1 040, and 720 cm^{-1} (Found: C, 44.1; H, 6.0; N, 6.6; S, 43.8. $C_8H_{13}NS_3$ requires C, 43.80; H, 5.97; N, 6.38; S, 43.79%).

Irradiated Reduction of the Ester (**14**) with 1,1-*Dimethylethanethiol.*—The ester (**14**) (830 mg, 1.85 mmol) and 1,1-dimethylethanethiol (1.0 ml) were dissolved in benzene (15 ml) and irradiated at room temperature and under nitrogen with a 300 W tungsten lamp for 20 min. The benzene was evaporated off and the colourless residue chromatographed through silica gel. Elution with pentane and Kugelrohr distillation (150—170 °C/13 mmHg) gave pentadecane (**30**) (381 mg, 97%). Further elution with ether gave the *disulphide* (**27**) as a crystalline solid (514 mg, 98%), m.p. 79 °C (pentane); δ 1.47 (9 H, s) and 7.34—8.16 (6 H, m); *m*/*z* 281 (M^+), 225, and 193; $\nu_{max.}$(Nujol) 1 360, 1 150, 1 065, 1 035, 910, 830, 770, 725, 715, 685, and 660 cm^{-1} (Found: C, 55.45; H, 5.4; N, 5.1; S, 33.95. $C_{13}H_{15}NS_3$ requires C, 55.47; H, 5.37; N, 4.98; S, 34.17%).

Reaction of the Ester (**17**) *with Bromotrichloromethane.*—The ester (**17**) (1.23 g, 3.03 mmol) was added to bromotrichloromethane (7.9 g, 40.0 mmol) in toluene (20 ml) at reflux under nitrogen. After 45 min at reflux the solution was concentrated and directly chromatographed on silica. Elution with pentane gave an oil which was Kugelrohr distilled (150 °C/0.2 mmHg) to yield 1-bromopentadecane (**31**) (0.68 g, 77%); δ 0.45—2.00 (29 H) and 3.37 (2 H, t, *J* 7.7 Hz); *m*/*z* 292, 290 (M^+), 211 (M^+ − Br), 151, 149, 137, and 135, identical with an authentic sample. Further elution with ethyl acetate and recrystallisation from tetrachloromethane gave *N*-methylbenzamide (0.34 g, 83%), m.p. 80 °C (lit.,[45] 80—81 °C).

Reaction of the Ester (**17**) *with Tetrachloromethane.*—Palmitoyl chloride (825 mg, 3.00 mmol) was added with stirring at room temperature to a solution of thiohydroxamic acid (**14**) (0.55 g, 3.29 mmol) and pyridine (0.5 ml) in tetrachloromethane (30 ml) and toluene (30 ml) under nitrogen. After 10 min the reaction was brought to 120 °C (bath temp.) and heated for 15 h; it was then cooled, washed with dilute hydrochloric acid (2 × 5 ml), dried, filtered and evaporated. 1-Chloropentane (**32**) (260 mg, 35%), eluted with pentane and Kugelrohr distilled (180 °C/13 mmHg), was identical with a previously isolated sample. Elution with 30% ethyl acetate in pentane gave *N*-methylthiobenzamide (**18**) (75 mg, 16%), m.p. 76—79 °C, and finally *N*-methylbenzamide (170 mg, 42%) was eluted with pure ethyl acetate.

Reaction of the Ester (**13**) *with Bromotrichloromethane.*—Palmitoyl chloride (825 mg, 3.00 mmol) was added under nitrogen, with stirring, to a dried solution of thiohydroxamic acid (**11**) (486 mg, 3.30 mmol), DMAP (37 mg, 0.3 mmol) and pyridine (0.5 ml) in bromotrichloromethane (8.90 g, 45 mmol) and benzene (30 ml). After 1 h under reflux the reaction mixture was evaporated and the residue taken up in toluene. This solution was washed with saturated aqueous sodium hydrogen carbonate (5 ml) and 2M hydrochloric acid (5 ml), dried, filtered, evaporated, and chromatographed on silica gel. Elution with pentane gave 1-bromopentadecane (**31**) as a colourless oil (0.81 g, 92%). Further elution with 30% ethyl acetate in pentane and subsequent Kugelrohr distillation (140 °C/0.1 mm) gave 5-methyl-2-trichloromethylthiothiazole (**28**) (0.70 g, 93%) as a colourless oil; δ 2.55 (3 H, weak allylic coupling) and 7.23 (1 H, weak allylic coupling); *m*/*z* 253, 251, 249, 247 (M^+), 216, 214, 212 (M^+ − Cl), and 130 (M − CCl_3); $\nu_{max.}$(film) 3 075, 2 950, 2 900, 2 840, 1 500, 1 430, 1 380, 1 350, 1 285, 1 030, and 860 cm^{-1} (Found: C, 24.2; H, 1.7; N, 5.9; S, 25.65. $C_5H_4Cl_3NS_2$ requires C, 24.16; H, 1.62; N, 5.63; S, 25.79%). The distillation residue (70 mg, 6%) was shown by t.l.c. and n.m.r. to consist mainly of the sulphide (**24**).

Reaction of Ester (**13**) *with Tetrachloromethane.*—The ester (**11**) (3.00 mmol) was prepared *in situ* as described immediately

above in tetrachloromethane (40 ml) as solvent. After 2 h at reflux the reaction mixture was worked up as above to give, by chromatography and Kugelrohr distillation, also according to the procedure described above, 1-chloropentadecane (**32**) (0.61 g, 82%), 5-methyl-2-trichloromethylthiothiazole (**28**) (0.55 g, 74%), and the crude sulphide (**24**) (130 mg, 13%).

Reaction of the Ester (**14**) *with Bromotrichloromethane.*—A solution of the ester (**14**) (672 mg, 1.50 mmol) in benzene (5 ml) and bromotrichloromethane (5 ml) was irradiated under nitrogen at room temperature for 2 h with a 300 W tungsten lamp. The solvents were then removed under reduced pressure and the residue chromatographed on silica gel. Elution with pentane gave 1-bromopentadecane (**31**) (420 mg, 96%), identical with a sample prepared above. Elution with ether and subsequent recrystallisation gave *5-phenyl-2-trichloromethylthiothiazole* (**29**) (430 mg, 92%) as bright yellow needles, m.p. 95 °C (hexane); δ 7.27—8.27 (5 H, m) and 7.90 (1 H, s); *m/z* 315, 313, 311, 309 (M^+), 278, 276, 274 (M − Cl), 192 (M − CCl_3), and 134 (M − CCl_3 − NCS); $\nu_{max.}$(Nujol) 1 030, 840, 780, 750, and 730 cm^{-1} (Found: C, 38.7; H, 2.2; N, 4.3; S, 20.8. $C_{10}H_6Cl_3NS_2$ requires C, 38.66; H, 1.95; N, 4.51; S, 20.64%).

Addition to Olefins.—Method A. The appropriate acid chloride (1 mmol) in benzene (1 ml) was added to a stirred solution of (**1**) (140 mg, 1.1 mmol) and pyridine (0.25 ml) in benzene (10 ml) at room temperature under nitrogen. The mixture was stirred for 30 min after which the white precipitate was filtered off and the olefin added to the filtrate. The solution so obtained was then irradiated at room temperature (water bath) with stirring under nitrogen with a 300 W tungsten lamp. At the end of the reaction (t.l.c.) the solvent was removed under reduced pressure and the products isolated by chromatography on silica gel.

Method B. A solution of the ester (1 mmol) [either prepared *in situ* from the acid chloride and (**1**) as above or a purified sample as in the case of esters (**13**) and (**17**)] was added as quickly as possible to a solution of the olefin in the appropriate solvent (10 ml) at reflux under nitrogen. After completion, the solvent was evaporated off and the products isolated by chromatography.

Method C. Method C was a variant of Method B in which the ester was added dropwise to the refluxing solution of the olefin.

Method D. Method D consisted of irradiation with a 100 W medium pressure mercury lamp of the mixture of ester and olefin in benzene under nitrogen at room temperature. Work-up involved evaporation of the solvent and chromatography.

1-(2-*Pyridylthio*)*octadecanonitrile* (**53**) *and Pentadecyl 2'-Pyridyl Sulphide* (**53**).—Careful chromatography on silica gel (eluting solvent: CH_2Cl_2–pentane 3:1) enabled the separation of (**54**) and (**53**). The sulphide (**53**) was eluted first and was identical with an authentic sample. The addition *product* (**54**) was a colourless oil; δ 0.82 (3 H, t, *J* 7 Hz), 1.30 (28 H, m), 1.90 (2 H, m), 4.80 (1 H, t, *J* 7 Hz), 6.8—7.7 (3 H, m), and 8.45 (1 H, d, *J* 5 Hz): *m/z* 374 (M^+); $\nu_{max.}$(film) 2 920, 2 850, 2 220 (w), 1 580, 1 450, and 1 120 cm^{-1} (Found: C, 73.8; H, 10.2. $C_{23}H_{38}N_2S$ requires C, 73.74; H, 10.21%).

Methyl 1-(2-*Pyridylthio*)*octadecanoate* (**55**).—This ester was obtained as a white crystalline *substance*, m.p. 38—39 °C (pentane), b.p. 240 °C/0.2 mmHg (Kugelrohr) which was eluted with 100% CH_2Cl_2; δ 0.90 (3 H, t), 1.40 (30 H, m), 3.80 (3 H, s), 4.60 (1 H, t, *J* 8 Hz), 6.9—7.7 (3 H, m) and 8.45 (1 H, d, *J* 5 Hz); *m/z* 407 (M^+); $\nu_{max.}$(film melt) 2 920, 2 850, 1 730, 1 580, 1 450, 1 150, 1 120, 955, and 910 cm^{-1} (Found: C, 70.8; H, 10.15; N, 3.7; S, 7.7. $C_{24}H_{41}NO_2S$ requires C, 70.71; H, 10.14; N, 3.44; S, 7.87%).

1-*Nitro*-1-(2-*pyridylthio*)*heptadecane* (**56**).—This unstable oil was eluted with 100% dichloromethane. It had δ 0.88 (3 H, t), 1.30 (28 H, m), 2.30 (2 H, m), 6.50 (1 H, t, *J* 8 Hz), 6.9—7.7 (3 H, m), and 8.40 (1 H, d, *J* 5 Hz); *m/z* 362 (M^+ − 32) and 348 (M^+ − NO_2).

1-*Chloro*-1-(2-*pyridylthio*)*octadecanonitrile* (**57**).—This crystalline *compound*, m.p. 38—39 °C (pentane) was eluted with 100% dichloromethane. It had δ 0.90 (3 H, t), 1.35 (28 H, m), 2.45 (2 H, m), 7.20—7.70 (3 H, m), and 8.65 (1 H, d, *J* 5 Hz); *m/z* 373 (M^+ − HCl); $\nu_{max.}$(CH_2Cl_2) 2 900, 2 850, 1 570, 1 560, 1 420, 1 120, 990, 900, and 890 cm^{-1} (Found: C, 67.75; H, 9.2; Cl, 8.4; N, 6.75; S, 7.65. $C_{24}H_{37}N_2ClS$ requires C, 67.53; H, 9.11; Cl, 8.67; N, 6.85; S, 7.84%).

3-*Cyano*-1-(2-*pyridylthio*)*octadecanonitrile* (**58**).—After evaporation of the solvent, excess of unchanged olefin was removed by sublimation in a Kugelrohr apparatus (80 °C/water pump) and the resulting residue purified by chromatography on silica gel. Elution with pentane–CH_2Cl_2 1:1 gave (**58**) as a mixture of two diastereoisomers which were not separated. The mixture had m.p. 37—38 °C (pentane); δ 0.90 (3 H, t), 1.40 (26 H, m), 1.80 (2 H, m), 3.30 (1 H, m), 5.35 (0.5 H, d, *J* 1.6 Hz) and 5.40 (0.5 H, d, *J* 2 Hz), 7.0—7.7 (3 H), and 8.40 (1 H, m); *m/z* 400 (M^+ − 1), 399 (M^+), 3.98 (M^+ − 1), and 188 [2-pyridylthio-CH(CN)–CHN^+]; $\nu_{max.}$(CH_2Cl_2) 2 900, 2 850, 2 220, 1 570, 1 560, 1 115, 980, and 900 cm^{-1} (Found: C, 72.15; H, 9.45; N, 10.6; S, 7.95%. Calc. for $C_{24}H_{37}N_3S$: C, 72.13; H, 9.33; N, 10.51; S, 8.02%).

Methyl 3-*Adamantan*-1-*yl*-2-(2-*pyridylthio*)*propionate* (**59**).—This *colourless oil* had b.p. 230—250 °C/0.1 mm (Kugelrohr); δ 1.66 (11 H, m), 2.00 (6 H, m), 3.70 (3 H, s), 4.65 (1 H, dd, J_1, J_2 8 Hz), 6.8—7.6 (3 H, m), and 8.55 (1 H, d, *J* 5 Hz); *m/z* 331 (M^+), 196 [2-pyridylthio-CH(CO_2CH_3)–CH_2^+], and 135 ($C_{10}H_{15}^+$); $\nu_{max.}$(CH_2Cl_2) 2 900, 2 850, 1 720, 1 570, 1 560, 1 080, 990, and 900 cm^{-1} (Found: C, 68.7; H, 7.5; N, 3.95; S, 9.35. $C_{19}H_{25}NO_2S$ requires C, 68.85; H, 7.60; N, 4.23; S, 9.67%).

3,3-*Dimethyl*-1-(2-*pyridylthio*)-1-*nitropropane* (**60**).—This *colourless oil* had b.p. 200 °C/0.2 mmHg (Kugelrohr); δ 1.10 (9 H, s), 1.95 (1 H, dd, J_1 14 Hz, J_2 6 Hz), 2.36 (1 H, dd, J_1 14 Hz, J_3 6 Hz), 6.50 (1 H, dd, J_2, J_3 6 Hz), 6.80—7.20 (2 H, m), 7.40 (1 H, dd, J_4 8 Hz, J_5 2 Hz), and 8.30 (1 H, dd, J_5 2 Hz, J_6 5 Hz); *m/z* 241 (M^+ + 1) and 194 (M^+ − NO_2); $\nu_{max.}$(CH_2Cl_2) 1 570, 1 550, 1 350, 1 115, and 900 cm^{-1} (Found: C, 55.25; H, 6.75; N, 11.65; S, 13.4. $C_{11}H_{16}N_2O_2S$ requires C, 54.98; H, 6.71; N, 11.66; S, 13.34%).

3-*Cyano*-4,4-*dimethyl*-2-(2-*pyridylthio*)*valeronitrile* (**61**).—After evaporation of the solvent the excess of olefin was sublimed off in a Kugelrohr apparatus (80 °C/water pump) and the residue then subjected to column chromatography. Elution with 100% CH_2Cl_2 gave (**61**) as a 3:1 mixture of two diastereoisomers; δ 1.30 (9 H, s), 2.95 (0.7 H, d, J_1 3 Hz) and 3.35 (0.3 H, d, J_2 6 Hz), 5.4 (0.7 H, d, J_1 3 Hz) and 6.3 (0.3 H, d, J_2 6 Hz), 7.00—7.20 (2 H, m), 7.60 (1 H, m), and 8.35 (1 H, m); *m/z* 245 (M^+) and 188 (M^+ − C_4H_9); $\nu_{max.}$(CH_2Cl_2) 2 900, 2 850, 2 230, 1 580, 1 560, 1 120, and 900 cm^{-1} (Found: C, 63.75; H, 6.25; N, 16.95; S, 12.85. $C_{13}H_{15}N_3S$ requires C, 63.64; H, 6.16; N, 17.12; S, 13.07%).

1-*Cyclohexyl*-2-(2-*pyridylthio*)-2-*nitroethane* (**62**).—This *colourless oil* was eluted with CH_2Cl_2–pentane 1:1, and had b.p. 180 °C/0.2 mmHg (Kugelrohr); δ 1.00—2.5 (13 H), 6.65 (1 H, t, *J* 8 Hz), 7.00—7.30 (2 H, m), 7.65 (1 H, dd, J_1 7 Hz, J_2 2 Hz), and 8.55 (1 H, dd, J_2 2 Hz, J_3 5 Hz); *m/z* 220 (M^+ − NO_2); $\nu_{max.}$(CH_2Cl_2) 2 900, 2 850, 1 570, 1 560, and 1 120 cm^{-1}

(Found: C, 58.7; H, 6.75; N, 10.75; S, 12.1. $C_{13}H_{18}N_2O_2S$ requires C, 58.62; H, 6.81; N, 10.52; S, 12.04%).

3-*Cyano*-2-*cyclohexyl*-3-(2-*pyridylthio*)*propionitrile* (**63**).—After removal of the solvent the excess of olefin was sublimed off in a Kugelrohr apparatus (80 °C/water pump) and the residue chromatographed (100% CH_2Cl_2) on silica to give (**63**) as a colourless oil which was a mixture of two diastereoisomers and had b.p. 220 °C/0.2 mmHg (Kugelrohr); δ 1.00—2.20 (11 H), 3.00 (0.5 H, m) and 3.25 (0.5 H, m), 5.20 (0.5 H, d, *J* 9 Hz) and 5.35 (0.5 H, d, *J* 5 Hz), 7.0—7.30 (2 H, m), 7.60 (1 H, m), and 8.40 (1 H, m); *m/z* 272 (M^+) and 188 (2 pyridylthio − CHCN − $CHCN^+$); $\nu_{max.}$(CH_2Cl_2) 2 900, 2 850, 2 225, 1 575, 1 560, 1 400, 1 120, 990, and 910 cm^{-1} (Found: C, 66.65; H, 6.35; N, 15.25; S, 11.65. Calc. for $C_{15}H_{17}N_3S$: C, 66.39; H, 6.31; N, 15.48; S, 11.81%).

3-(5-*Methylthiazol*-2-*ylthio*)*nonadecan*-2-*one* (**67**).—Chromatography on silica gel of the crude product (eluant: pentane–ether, 9:1) gave first the sulphide (**24**), (6%), identical with an authentic sample, and then the *addition product* (**67**) (43%), as a colourless solid, m.p. 35—37 °C (pentane); δ 0.60—2.20 (33 H), 2.33 (3 H, s), 2.40 (3 H, d, *J* 1 Hz), 4.23 (1 H, t, *J* 7 Hz), and 6.77 (1 H, m); *m/z* 411 (M^+), 386 (M^+ − CH_3CO), and 131 (M^+ − methylthiazolylthio); $\nu_{max.}$(film) 3 075, 1 705, 1 510, 1 450, 1 405, 1 345, 1 285, 1 150, 1 025, and 720 cm^{-1} (Found: C, 66.85; H, 10.05; N, 3.65; S, 15.35. $C_{23}H_{41}NOS_2$ requires C, 67.09; H, 10.04; N, 3.40; S, 15.57%).

2,2-*Dimethyl*-4-*pentadecylcyclopent*-4-*ene*-1,3-*dione* (**40**).—The ester (772 mg, 2.00 mmol) in benzene (10 ml) was added dropwise over 10 min to an irradiated (100 W Hg) solution of the olefin (**39**)[27] (372 mg, 3.00 mmol) in benzene (20 ml) under nitrogen. After 1.5 h the benzene was evaporated and the residue chromatographed on silica gel. Elution with pentane–ether 95:5 gave a mixture (560 mg) of rearrangement product (**24**) (*ca.* 15%) and of the addition product (**40**). Fractional crystallisation from pentane gave pure (**40**) (470 mg, 70%) as a bright yellow *solid*, m.p. 34—36 °C; δ 0.70—2.10 (35 H, $C_{14}H_{29}$ + 2 Me groups), 2.45 (2 H, t, *J* 7 Hz), 6.72 (1 H, t, *J* 1 Hz); 334 (M^+), 319 (M − CH_3), 306 (M − CO), 263, and 138 [M − $C_{14}H_{28}$ (Maclafferty)]; $\nu_{max.}$(film) 1 700 and 1 605 cm^{-1} (Found: C, 78.65; H, 11.45. $C_{23}H_{38}O_2$ requires C, 79.98; H, 11.45%).

Pentadecylmaleic Anhydride (**42**).—The ester (**11**) (1.00 g, 2.59 mmol) in benzene (15 ml) was added dropwise to an irradiated (100 W Hg) solution of freshly recrystallised maleic anhydride (400 mg, 4.00 mmol) in benzene (20 ml) under nitrogen at room temperature. After irradiation for a further 40 min the solvent was removed and the residue subjected to fractional distillation in a Kugelrohr apparatus. Maleic anhydride (100 mg) sublimed at 50 °C/0.1 mmHg. This was followed by a mixture of two products (890 mg) (170—240 °C/0.1 mmHg). Extraction of this mixture with pentane left a solid yellow residue (315 mg, 92%), m.p. 86—87 °C which was the thiazolethione (**15**), (lit.,[46] 88—89 °C); δ 2.22 (3 H, d, *J* ⩽ 1 Hz) and 6.13 (1 H, m); *m/z* 131 (M^+). The pentane solution was then evaporated to dryness and repeated Kugelrohr distillation (180 °C/0.1 mmHg) of the residue gave *pentadecylmaleic anhydride* (**42**) (550 mg, 69%) as a colourless solid, m.p. 42—44 °C (pentane). An analytically pure sample was obtained on distillation from P_2O_5; δ 0.60—2.00 (29 H, m), 2.57 (2 H, allylic coupling), and 6.66 (1 H, t, *J ca.* 0.8 Hz); *m/z* 308 (M^+), 290 (M^+ − H_2O), 280 (M^+ − CO), and 112 [M − $C_{14}H_{28}$ (Maclafferty)]; $\nu_{max.}$(melt) 1 840 and 1 770 cm^{-1} (Found: C, 74.25; H, 10.5. $C_{19}H_{32}O_2$ requires C, 73.98; H, 10.46%).

1-*Methyl*-3-(5-*methylthiazol*-2-*ylthio*)-2-*pentadecylpyrrolidine*-2,5-*dione* (**69**).—Chromatography (pentane–ether 9:1) on silica gel of the crude reaction mixture gave first the sulphide (**24**) (2%) and then the *addition product* (**69**) (93%) as a solid, m.p. 55—56 °C (MeOH–H_2O); δ 0.65—2.20 (31 H, m), 2.30 (3 H, m), 2.77—3.33 (1 H, m), 3.03 (3 H, s), 3.85 (1 H, d, *J* 3.0 Hz, *trans* coupled 3-H), and 6.79 (1 H, m); *m/z* 452 (M^+), 419, 321 (M^+ − 5-methylthiazolethione), 2.41 (M^+ − $C_{15}H_{31}$), 209, 202, 201, and 131 (5-methylthiazolethione$^+$); $\nu_{max.}$(Nujol) 1 770 and 1 690 cm^{-1} (Found: C, 63.95; H, 8.7; N, 6.2; S, 14.2. $C_{24}H_{40}N_2O_2S_2$ requires C, 63.67; H, 8.90; N, 6.19; S, 14.16%).

2-(5-*Methylthiazol*-2-*ylthio*)-3-*pentadecylcyclopentanone* (**70**).—Chromatography on silica gel of the crude reaction mixture gave first the rearrangement product (**24**) (58%) on elution with pentane–CH_2Cl_2 (1:1) which was identical with an authentic sample. Further elution with pure ether gave the addition product (**70**) as a bright yellow viscous *oil* (30%); δ 0.63—1.76 (31 H, m), 1.76—2.76 (8 H, m, thiazole CH_3 + $CHCH_2CH_2CO$), 3.43 (1 H, d, *J* 9.0 Hz), and 6.73 (1 H, s); *m/z* 423 (M^+), 293 (M^+ − 5-methylthiazolethione$^+$), 212 (M^+ − $C_{15}H_{31}$), 132, and 131; $\nu_{max.}$(film) 1 740 cm^{-1} (Found: C, 67.85; H, 9.65; N, 3.4; S, 15.35. $C_{24}H_{41}NOS_2$ requires C, 68.03; H, 9.75; N, 3.30; S, 15.13%).

2-*Pentadecyl*-1,4-*naphthoquinone* (**4b**).—The crude reaction mixture was chromatographed on silica. Elution with hexane–ether 9:1 gave a yellow oil which was taken up in pentane and cooled to obtain 2-pentadecyl-*p*-benzoquinone (**46**) (26%) as yellow needles, m.p. 71—72 °C (lit.,[23c] 71—72 °C). The mother liquors contained the rearrangement product (**24**) (28%).

2-*Pentadecyl*-p-*benzoquinone* (**48**).—The crude black mixture obtained on evaporation of the solvent was subject to chromatography on silica gel. Elution with pentane–ether gave an orange–yellow mixture of the *addition product* (**48**) and the rearrangement product (**24**). Fractional crystallisation from pentane gave the *p*-benzoquinone (**48**) (27%) as orange–yellow needles, m.p. 71—72 °C; δ 0.60—2.00 (29 H, m), 2.40 (2 H, m), 6.50 (1 H, t, *J* ⩽ 0.5 Hz), and 6.65 (2 H, m); *m/z* 318 (M^+), 320 (M^+ + 2 H), 294, 131, and 123; $\nu_{max.}$(Nujol) 1 650 cm^{-1} (Found: C, 78.95; H, 10.6. $C_{21}H_{34}O_2$ requires C, 79.19; H, 10.76%).

(E/Z)-*Methyl* 2-(5-*Methylthiazol*-2-*ylthio*)*octadec*-2-*enoate* (**71**).—Chromatography on silica of the crude reaction mixture gave, on elution with pentane–ether (95 : 5), the rearrangement product (**24**) (33%) and then the addition product, which was a virtually colourless oil, as an *E*/*Z* mixture (38%); δ (main isomer italicized) 0.73—1.73 (29 H, m), *2.38* and 2.41 (*ca.* 60:40) (3 H, 2 × d, *J* 1 Hz), 2.45—2.73 (2 H, m, allylic CH_2), 3.74 and *3.75* (3 H, 2 × s, CO_2CH_3), 6.73 (1 H, m), 6.83 (t, *J* 8 Hz) and *7.56* (t, *J* 7.5 Hz) (total 6.83 and 7.56 = 1 H); *m/z* 425 (M^+), 294 (M^+ − OCH_3), 293, 292, 246, 214, 156, and 131; $\nu_{max.}$(film) 1 720 cm^{-1} (Found: C, 65.15; H, 9.25; N, 3.2; S, 14.85. Calc. for $C_{23}H_{39}NO_2S_2$: C, 64.89; H, 9.23; N, 3.29; S, 15.06%).

(E/Z)-*Methyl* 2-(5-*Methylthiazol*-2-*ylthio*)-3-*methoxycarbonyloctadec*-2-*enoate* (**72**).—The crude reaction mixture was chromatographed on silica gel. Elution with ethyl acetate afforded an *E*/*Z* mixture of the addition product (**72**) as an almost colourless oil (50%); δ (major isomer italicized) 0.65—2.00 (29 H, m), 2.43 (3 H, m), 2.70 (2 H, t, *J* 7.0 Hz), *3.67* and 3.80 (*ca.* 3:1) (3 H, 2s) and *3.62* and 3.84 (*ca.* 3:1) (3 H, 2 s), and 6.90 (1 H, m); *m/z* 483 (M^+), 452 (M^+ − OCH_3), 451, 450, 426, 425, and 424 (M − CH_3CO_2); $\nu_{max.}$(film) 1 725 and 1 595 cm^{-1} (Found: C, 61.95; H, 8.5; N, 3.2; S, 13.5. Calc. for $C_{25}H_{41}NO_4S_2$: C, 62.07; H, 8.54; N, 2.89; S, 13.25%).

3-(5-*Phenylthiazol*-2-*ylthio*)*nonadecan*-2-*one* (**68**).—Chromatography (pentane–ether 95:5) of the crude reaction mixture gave first the rearrangement product (**25**) (4%) and then the addition product (**68**) (40%) as a colourless *solid*, m.p. 51—52 °C (pentane–MeOH); δ 0.50—2.20 (33 H, m), 2.35 (3 H, s), 4.40 (1 H, t, *J* 7 Hz), and 7.25—8.05 (6 H, m); *m/z* 473 (M^+), 430 ($M - CH_3CO$), 384, 194, and 193 (5-phenylthiazolethione$^+$); $\nu_{max.}$(melt) 3 080, 1 700, 1 470, 1 465, 1 440, 1 420, 1 350, 1 050, and 1 025 cm^{-1} (Found: C, 70.7; H, 9.05; N, 3.05; S, 13.5. $C_{28}H_{43}NOS_2$ requires C, 70.98; H, 9.15; N, 2.95; S, 13.53%).

2,6-*Dimethyl*-3-*pentadecyl*-p-*benzoquinone* (**50**).—The crude reaction mixture was chromatographed on silica. Elution with pentane–ether gave a *ca.* 1:1 mixture (as estimated by n.m.r.) of the addition product (**50**) and the rearrangement product (**24**). The two compounds were inseparable by normal chromatography, crystallisation, and distillation. A pure sample of (**50**) was obtained by normal phase h.p.l.c. on silica, using 5% EtOAc in hexane as eluant, as a bright yellow solid, m.p. 45—46 °C; δ (200 MHz) 0.63—1.96 (29 H, m), 2.33—2.80 (2 H, m), 2.07 (6 H, s), and 6.53 (1 H, s); *m/z* 346 (M^+) and 150 ($M^+ - C_{14}H_{28}$). The more polar fraction from the original column was unchanged 2,6-dimethyl-*p*-benzoquinone (69%).

Synthesis of the Ester (**74**).—Enantiomerically pure ($[\alpha]_D^{25} = +10.3°$ in $CHCl_3$) (*R*)-(+)-citronellic acid[28] (1.70 g, 10.0 mmol) was dissolved in benzene (20 ml) and treated with oxalyl chloride (4.0 g, 30 mmol) and DMF (1 drop). The mixture was stirred for 40 min at room temperature and then evaporated to dryness and the residue taken up in ether (10 ml); the latter was then added to a solution of thiohydroxamic acid (**11**) (1.50 g, 10.2 mmol) in ether (40 ml) and pyridine. The mixture was stirred for 10 min at room temperature after which it was filtered, concentrated, and filtered through silica gel using ether–pentane as eluant to yield the analytically pure *ester* (**74**) as a bright yellow *oil* (2.94 g, 98%); δ 1.10 (3 H, d, *J* 7.0 Hz, $CHCH_3$), 1.25—1.45 (5 H, m), 1.65 (3 H, s), 1.72 (3 H, s), 2.23 (3 H, d, $J \leqslant 1$ Hz, thiazole Me), 2.45—2.85 (2 H, m, CH_2CO), 5.20 (1 H, t, *J* 7.0 Hz), and 6.33 (1 H, m, thiazole H); *m/z* 299 (M^+), 260, 255 ($M - CO_2$), 153, 152, 149, 148, 147, 131, 130, and 109; $\nu_{max.}$(film) 3 080, 1 810, and 1 600 cm^{-1} (Found: C, 55.95; H, 7.05; N, 4.8; S, 21.25. $C_{14}H_{21}NO_2S_2$ requires C, 56.15; H, 7.07; N, 4.67; S, 21.41%).

Photolysis of the Ester (**74**).—A solution of the ester (**74**) (1.55 g, 5.18 mmol) in ether (20 ml) was irradiated under nitrogen at room temperature with a 100 W medium pressure mercury lamp for 45 min. The solvent was then evaporated and the residue chromatographed on silica with pentane–ether (95:5) to give the cyclisation product (**76**) as a 1:1 mixture of diastereoisomers. The mixture so obtained was a colourless, analytically pure oil (1.08 g, 82%), with δ 1.02 and 1.00 (3 H, 2 d, *ca.* 1:1, *J* 7.0 Hz), 1.40 (6 H, s), 1.20—2.40 (8 H, m), 2.55 (3 H, m, thiazole Me), and 7.05 (1 H, m); *m/z* 255 (M^+), 132, and 131; $\nu_{max.}$(film) 3 070, 1 510, 1 445, 1 365, 1 295, 1 140, and 1 020 cm^{-1} (Found: C, 61.1; H, 8.3; N, 5.65; S, 24.95. Calc. for $C_{13}H_{21}NS_2$: C, 61.42; H, 8.28; N, 5.48; S, 25.10%).

Irradiation of the Ester (**74**) *in the Presence of Bromotrichloromethane*.—The ester (**74**) (562 mg, 1.876 mmol) dissolved in ether (30 ml) and bromotrichloromethane (5 ml) was irradiated at room temperature under nitrogen with a 100 W medium pressure mercury lamp for 30 min. The solvent was removed under reduced pressure and the residue chromatographed on silica gel. Pentane–ether (95:5) eluted a colourless liquid which on fractional Kugelrohr distillation (100 °C/13 mmHg) yielded the bromide (**75**) as a colourless liquid (222 mg, 58%); δ 1.03 (3 H, d, *J* 7.0 Hz), 1.2—2.3 (5 H, m), 1.67 (3 H, s), 1.74 (3 H, s), 3.45 (2 H, d, *J* 6.0 Hz) and 5.20 (1 H, t, *J* 7.0 Hz); *m/z* 206 (205), 204 (203) (M^+), 125 (M − Br), and 69 (); $\nu_{max.}$(film) 2 950, 2 900, 2 850, 1 430, 1 380, and 1 230 cm^{-1}. The distillation residue was a pure (n.m.r.) sample of the sulphide (**28**) (400 mg, 86%) which was identical with the above isolated sample.

Treatment of the Adduct (**62**) *with Iodoxybenzene–t–Butyltetramethylguanidine*.—t-Butyltetramethylguanidine[47] (0.3 ml) was added at room temperature to a stirred suspension of iodoxybenzene[48] (250 mg) and of (**62**) (105 mg) in dichloromethane (5 ml) at room temperature. The reaction which was complete (t.l.c.) within 2 h at room temperature, was filtered through a glass wool plug and extracted into dilute aqueous sodium hydrogen carbonate (20 ml). The extracts were washed with dichloromethane (10 ml), acidified with 6M HCl, and finally re-extracted into dichloromethane (20 ml). The extracts were dried ($MgSO_4$), filtered, and evaporated to dryness to give cyclohexylacetic acid (25 mg, 45%) which was recrystallised from formic acid, m.p. 33 °C (lit.,[49] m.p. 33 °C).

1-*Acetyloxypyridine*-2-(1H)-*thione* (**85**).—Acetyl chloride (2 ml) was added at room temperature to a stirred suspension of 1-hydroxypyridine-2-(1*H*)-thione (590 mg) and DMAP (10 mg) in benzene (10 ml). The yellow solution was stirred overnight in the dark, filtered, and evaporated to dryness to give a yellow-green semisolid which was t.l.c. and n.m.r. pure. The compound was dried *in vacuo* at room temperature for 6 h to give an analytically pure sample of the *ester* (**85**) (403 mg, 71%); $\nu_{max.}$(Nujol) 1 800, 1 610, 1 530, 1 420, 1 290, 1 230, 1 200, 1 150, 860, and 750 cm^{-1}; *m/z* 169 (M^+), 127 ($M^+ - 42$), 110, and 79 (Found: C, 49.75; H, 4.25; N, 8.5; S, 19.15. $C_7H_7NO_2S$ requires C, 49.69; H, 4.17; N, 8.28; S, 18.95%).

1-*Acetoxy*-5-*methylthiazoline*-2-(1H)-*thione* (**87**).—(This experiment was in collaboration with Miss. B. G. Lacher.) Acetyl chloride (3.66 g) was added to a solution of 1-hydroxy-5-methylthiazoline-(1*H*)-2-thione (7.6 g) and pyridine (4.11 g) in ether at room temperature. The precipitated pyridinium hydrochloride was filtered off and washed with a little ether. The organic phases were then evaporated to dryness and the residue recrystallised from ether to give the white crystalline *ester* (**87**) (39%) m.p. 97—98 °C; $\nu_{max.}$(Nujol) 1 810 cm^{-1}; *m/z* 189 (M^+) and 147 (M − 42) (Found: C, 38.25; H, 3.6; N, 7.55; S, 34.0. $C_6H_7NO_2S_2$ requires C, 38.08; H, 3.73; N, 7.40; S, 33.88%).

2-*Methylthiopyridine* N-*Oxide* (**82**).—1-Hydroxypyridine-2-thione (2 g) was dissolved in methyl iodide (10 ml) and the solution set aside at room temperature for 18 h. The yellowish crystals that formed were filtered off and washed with a little pentane and then dissolved in saturated aqueous sodium hydrogen carbonate (50 ml). The resulting solution was extracted with chloroform (3 × 50 ml), the combined extracts dried ($MgSO_4$), filtered, and evaporated to dryness to give the crude product (1.5 g); this was recrystallised from EtOAc–hexane to give the pure *title compound* (**82**) (1.3 g, 59%) as needles, m.p. 81 °C (Found: C, 51.1; H, 4.95; N, 9.9; S, 22.65. C_6H_7NOS requires C, 51.04; H, 4.99; N, 9.92; S, 22.71%).

5-*Methyl*-2-*methylthiothiazole* N-*Oxide* (**83**).—This compound (54%), prepared in a manner exactly analogous to that for its pyridine analogue, was a white crystalline substance, m.p. 42—43 °C (EtOAc–hexane), *m/z* 161 (M^+) and 144 ($M - 17^+$).

Isothiuronium Salt (**90**).—4-Chloropyridine *N*-oxide (2.12 g) and thiourea (124 g) were heated to reflux for 2 h in absolute ethanol (20 ml). As the mixture cooled the isothiuronium salt

(**90**) crystallised out as needles (2.82 g, 84%), m.p. 160 °C (decomp.) (lit.,[33] 169—170 °C).

1-*Hydroxypyridine*-4-(1H)-thione (**89**).—The isothiuronium salt (**90**) (4 g) was added to a solution of sodium carbonate (2.1 g) and sodium sulphide (150 mg) in water (16 ml) and the resulting solution stirred at room temperature for 3 h. Acidification with 18% hydrochloric acid (3 ml) caused precipitation of (**89**), which was filtered off and recrystallised from aqueous ethanol to give the pure title compound (**89**) (1.07 g, 43%), m.p. 140 °C (decomp.) (lit.,[33] 140 °C); δ(D_2O) 7.55 (2 H, d, *J* 8 Hz) and 7.94 (2 H, d, *J* 8 Hz); *m/z* 127 (M^+) (Found: C, 47.3; H, 3.8; N, 11.15; S, 25.3. Calc. for C_5H_5NOS: C, 47.22; H, 3.90; N, 11.01; S, 25.16%).

Ester (**91**) *and Sulphide* (**92**).—1-Hydroxypyridine-4-(1*H*)-thione (**89**) (120 mg) in THF (4 ml) and pyridine (1 ml) was added dropwise under nitrogen at room temperature to a solution of palmitoyl chloride (236 mg) in toluene (5 ml). The solution was stirred for 1 h at room temperature after which the i.r. spectrum of an aliquot showed two carbonyl bonds (1 710 and 1 818 cm^{-1}) in the ratio of 10:1 indicative of the *S* and *O* esters of (**89**). The solution was then heated to reflux for 2 h before it was evaporated and the residue chromatographed on silica gel. Elution with dichloromethane–pentane (1:1) gave the sulphide (**92**) as an oil (10 mg, 5%); δ(CCl_4) 0.9—1.6 (29 H, m), 3.0 (2 H, t, *J* 8 Hz), 7.27 (2 H, d, *J* 7 Hz), and 8.62 (2 H, d, *J* 7 Hz); $\nu_{max.}$(CCl_4) 2 910, 2 850, 1 460, and 1 405 cm^{-1}; *m/z* 321 (M^+). Further elution with dichloromethane–ethyl acetate–ethanol (20:1:1) gave the ester (**91**) (250 mg, 80%) and some palmitic acid. The ester had δ(CCl_4) 0.9—1.6 (29 H, m), 2.33 (2 H, t, *J* 7 Hz), 7.4 (2 H, d, *J* 8 Hz), and 8.3 (2 H, d, *J* 8 Hz); $\nu_{max.}$(CCl_4) 2 920, 2 850, 1 715, 1 460, 1 275, and 1 165 cm^{-1}.

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