Studies of Heterocyclic Compounds. Part XVI.[1] Mechanism of Electrophilic Substitution of 6a-Thiathiophthens and Related Compounds: Nitrosation with Rearrangement

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Nitrosation of 6a-thiathiophthens and related compounds occurs with rearrangement. 6a-Thiathiophthens, 1-oxa-6,6a-dithiapentalenes, and 1,6a-dithia-6-azapentalenes rearrange into 1-oxa-6,6a-dithia-2-azapentalenes, and 1,6-dioxa-6a-thiapentalenes into 1,6-dioxa-6a-thia-2-azapentalenes. 6a-Thiathiophthens react with nitrous acid with difficulty unless activated by strongly electron-releasing substituents. 2-t-Butyl-6a-thiathiophthen reacted at position 4 to give 3-formyl-5-t-butyl-1-oxa-6,6a-dithia-2-azapentalene in low yield. 2-Methylthio-5-t-butyl- and 2-dimethylamino-5-t-butyl-6a-thiathiophthen reacted readily at position 3 to give the methyl 3-dithiocarboxylate and the 3-*NN*-dimethylthiocarboxamide of 5-t-butyl-1-oxa-6,6a-dithia-2-azapentalene, respectively, selective desulphurisation of which afforded the corresponding *S*-methyl thioester and *NN*-dimethylcarboxamide. 5-Phenyl-, 5-t-butyl-, and 2,5-dimethyl-1-oxa-6,6a-dithiapentalene reacted smoothly at position 3 to give the corresponding 3-formyl(acetyl)-1-oxa-6,6a-dithia-2-azapentalenes. 6-Methyl-2-phenyl- and 6-methyl-2-t-butyl-1,6a-dithia-6-azapentalene also gave 3-formyl-1-oxa-6,6a-dithia-2-azapentalenes by hydrolysis *in situ* of the intermediate 3-methyliminomethyl-1-oxa-6,6a-dithia-2-azapentalenes. 1-Oxa-6,6a-dithiapentalenes and 1,6a-dithia-6-azapentalenes in which the reactive position 3(4) is blocked, reacted at position 3(4) with elimination of the formyl or methyliminomethyl group to yield 1-oxa-6,6a-dithia-2-azapentalenes. Nitrosation of 1,6-dioxa-6a-thiapentalene with nitrosyl hexafluorophosphate gave 3-formyl-1,6-dioxa-6a-thia-2-azapentalene, the first reported derivative of the 1,6-dioxa-6a-thia-2-azapentalene system. A mechanism is proposed to account for the various features of the electrophilic substitution of 6a-thiathiophthens and related hypervalent heterocyclic systems. It is proposed that reaction proceeds by way of stable 6π-electron *monocyclic* cations, such as 1,2-dithiolium and 1,2-oxathiolium.

ELECTROPHILIC bromination [2] and Vilsmeier formylation [3] of 6a-thiathiophthens proceed normally to give 3-bromo- and 3-formyl-6a-thiathiophthens, respectively. However, nitrosation of 2,5-diphenyl-6a-thiathiophthen (1) gives the oxadithia-azapentalene (12), rearrangement and partial desulphurisation accompanying the introduction of the nitroso-group.[2] The structure of the product (12) was indicated by its i.r. spectrum ($\nu_{C=O}$ 1640 cm^{-1}) and was confirmed by a crystallographic structure determination.[4] Rearrangement without loss of sulphur occurred during the nitrosation of the 2,5-disubstituted 6a-thiathiophthens (2)—(4). The products were assigned the rearrangement structures (13)—(15), respectively, on the basis of the similarity of their u.v. spectra to that of the benzoyl derivative (12). Rearrangement has also been encountered [5] in the attempted nitration of 2-phenyl-6a-thiathiophthen (6) with tetranitromethane, which resulted in *nitrosation*. Two products (16) (major) [$\nu_{C=O}$(KBr) 1677 cm^{-1}] and (17) were obtained. 2-t-Butyl-6a-thiathiophthen (7) likewise gave mainly compound (18) [$\nu_{C=O}$(KBr) 1669 cm^{-1}] together with the deformylation product (19). An analogous rearrangement of 6a-thiathiophthens and related compounds into 1,6a-dithia-5,6-diazapentalenes

[1] Part XV, A. S. Ingram, D. H. Reid, and J. D. Symon, *J.C.S. Perkin I*, 1974, 242.

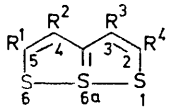
[2] R. J. S. Beer, D. Cartwright, R. J. Gait, and D. Harris, *J. Chem. Soc.* (*C*), 1971, 963, and preliminary communications referred to therein.

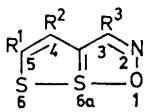
[3] (*a*) J. G. Dingwall, D. H. Reid, and K. O. Wade, *J. Chem. Soc.* (*C*), 1969, 913; (*b*) G. Duguay, D. H. Reid, K. O. Wade, and R. G. Webster, *ibid.*, 1971, 2829; (*c*) J. Bignebat and H. Quiniou, *Compt. rend.*, 1968, **267** C, 180; 1969, **269** C, 1129.

[4] P. L. Johnson, K. I. G. Reid, and I. C. Paul, *J. Chem. Soc.* (*B*), 1971, 946.

[5] J. G. Dingwall, A. R. Dunn, D. H. Reid, and K. O. Wade, *J.C.S. Perkin I*, 1972, 1360.

during substitution reactions with arenediazonium fluoroborates has been discovered recently.[6] However, neither the mechanism of the normal electrophilic substitution reactions of 6a-thiathiophthens and related





	R^1	R^2	R^3	R^4
(1)	Ph	H	H	Ph
(2)	Ph	H	H	MeS
(3)	Ph	H	H	Me_2N
(4)	MeS	H	H	MeS
(5)	H	H	H	H
(6)	Ph	H	H	H
(7)	Bu^t	H	H	H
(8)	Bu^t	H	H	MeS
(9)	Bu^t	H	H	Me_2N
(10)	Bu^t	H	Bu^tCO	MeS
(11)	H	Me	Me	H

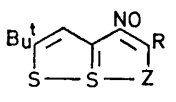
	R^1	R^2	R^3
(12)	Ph	H	Bz
(13)	Ph	H	CS_2Me
(14)	Ph	H	$CS{\cdot}NMe_2$
(15)	MeS	H	CS_2Me
(16)	Ph	H	CHO
(17)	Ph	H	H
(18)	Bu^t	H	CHO
(19)	Bu^t	H	H
(20)	Bu^t	H	CS_2Me
(21)	Bu^t	H	$CS{\cdot}NMe_2$
(22)	Bu^t	H	$CO{\cdot}SMe$
(23)	Bu^t	H	$CO{\cdot}NMe_2$
(24)	Me	H	CO·Me
(25)	H	Me	Me
(26)	H	- $[CH_2]_3$ -	
(27)	Ph	H	Me
(28)	Ph	H	CH:NMe
(29)	Bu^t	H	CH:NMe

compounds nor that of those reactions which proceed with rearrangement has been investigated. In this paper we describe the results of further nitrosation studies and propose a general mechanism which accounts for the various features of the electrophilic substitution of 6a-thiathiophthens and related hypervalent heterocyclic systems.

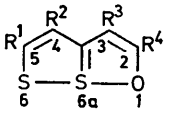
Nitrosation Reactions.—6a-*Thiathiophthens.* 6a-Thiathiophthens reacted with nitrous acid with difficulty, unless activated by strongly electron-releasing substituents. 6a-Thiathiophthen (5) and the 2-phenyl derivative (6) gave several products in trace amounts none of which was identified. 2-t-Butyl-6a-thiathiophthen (7) afforded the aldehyde (18) in low yield (9%) by partial desulphurisation and rearrangement [*cf.* (1) ⟶ (12) [2]], whereas nitrosation of 2-methylthio-5-t-butyl- (8) and 2-dimethylamino-5-t-butyl- (9) 6a-thiathiophthen took place smoothly, giving the dithioester (20) (40%) and the thioamide (21) (97%). Selective desulphurisation of compounds (20) and (21) with mercury(II) acetate in chloroform afforded the thioester (22) and the amide (23), whose strong i.r. carbonyl absorption [$\nu_{C=O}$(KBr) for (22), 1650; for (23), 1625 cm^{-1}] confirms that they are 1-oxa-6,6a-dithia-2-azapentalenes rather than the isomeric nitroso-compounds (30) and (31). The u.v. spectra of the dithioester (20) and the thioester (22) were similar, as were those of the thioamide (21) and the amide (23), which shows that the pairs of compounds (20) and (22), and (21) and (23) have similar structures. The combined spectral data indicate, therefore, that the nitrosation products have the rearrangement structures (20) and (21) rather than the 3-nitroso-structures (32) and (33), respectively.

1-*Oxa*-6,6a-*dithiapentalenes.* The 2,5-diphenyl derivative (34) gives the same product (12) as is obtained from the corresponding 6a-thiathiophthen (1).[2] We have studied the nitrosation of the six derivatives (35)—(40). All were nitrosated smoothly in high yield. Compounds (35)—(37) gave the 3-acyl-1-oxa-6,6a-dithia-2-azapentalenes (16), (18), and (24), respectively, by nitrosation and rearrangement. The aldehyde (18) was accompanied by a trace of second product whose mass spectrum suggests that it is the nitro-compound (41). I.r. spectral evidence has already been adduced [5] in favour of the 3-formyl-1-oxa-6,6a-dithia-2-azapentalene structures (16) and (18), and the 3-acetyl structure (24) is also confirmed by the presence of strong i.r. carbonyl absorption at 1673 cm^{-1} (KBr). The oxadithiapentalenes (38)—(40), in which the reactive position 3 is blocked, gave the oxadithia-azapentalenes (25)—(27) by nitrosodeformylation and rearrangement. Small quantities of the nitromethylenedithioles (42) (1%) and (43) (6%) were isolated in addition to the main products (25) and (26). The minor products doubtless arise by direct nitration of the oxadithiapentalenes (38) and (39), rather than by subsequent oxidation of the major products (25) and (26), since compounds (25) and (26), when subjected to the nitrosation reaction conditions, gave no trace of the nitromethylenedithioles and were recovered almost quantitatively.

1,6a-*Dithia*-6-*azapentalenes.* The products from the dithia-azapentalenes (44)—(46) were identical with those from the corresponding oxadithiapentalenes (35),



	R	Z
(30)	MeS	O
(31)	Me_2N	O
(32)	MeS	S
(33)	Me_2N	S



	R^1	R^2	R^3	R^4
(34)	Ph	H	H	Ph
(35)	Ph	H	H	H
(36)	Bu^t	H	H	H
(37)	Me	H	H	Me
(38)	H	Me	Me	H
(39)	H	- $[CH_2]_3$ -		H
(40)	Ph	H	Me	H
(41)	Bu^t	H	NO_2	H

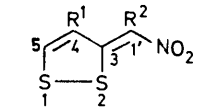
(36), and (40), namely, the oxadithia-azapentalenes (16), (18), and (27). The primary nitrosation products from compounds (44) and (45) are doubtless the imines (28) and (29), which are formed by rearrangement and undergo acid-catalysed hydrolysis. The blocked dithia-azapentalene (46) lost the *N*-methyliminomethyl group and gave the oxadithia-azapentalene (27). Yields were good in the case of the dithia-azapentalenes (44)

[6] R. M. Christie, A. S. Ingram, D. H. Reid, and R. G. Webster, *J.C.S. Chem. Comm.*, 1973, 92.

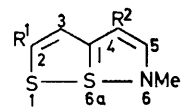
[⟶ (16) (70%)] and (45) [⟶ (18) (74%)] but poor in the case of the blocked substrate (46) [⟶ (27) (8%)].

1,6-*Dioxa*-6a-*thiapentalene*. 1,6-Dioxa-6a-thiapentalene (47) is sensitive to acid and was destroyed by nitrous acid in acetic acid. We resorted to the use of nitrosyl hexafluorophosphate in dichloromethane, with calcium carbonate present in excess to remove acid. The aldehyde (48) [$\nu_{C=O}(CCl_4)$ 1715 cm^{-1}] was obtained in excellent yield. It is the first reported derivative of the 1,6-dioxa-6a-thia-2-azapentalene system.

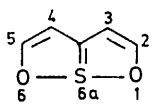
Mechanism and Discussion.—A theoretical study [7] of the reactivity of 6a-thiathiophthens by the CNDO/2 SCFMO procedure predicted, correctly, that position 3 should be more reactive than position 2 towards electrophiles. Conventional Wheland intermediates of the type (49) [attack at C(3)] and (50) (attack at sulphur) were employed in calculations of electrophilic localisation energies. However, this approach stops short of explaining the rearrangement process in nitrosation and diazo-coupling reactions. We propose here a mechanism which accounts for the various features of the electrophilic substitution of 6a-thiathiophthens and related hypervalent heterocyclic systems.



	R^1	R^2
(42)	Me	Me
(43)	$-[CH_2]_3-$	



	R^1	R^2
(44)	Ph	H
(45)	Bu^t	H
(46)	Ph	Me



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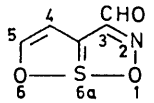

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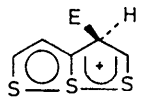

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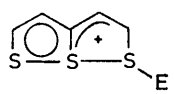
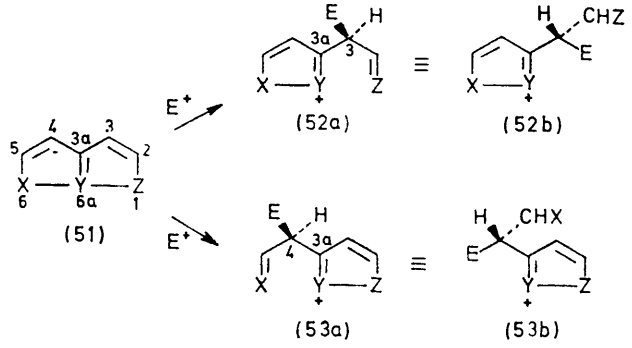


(50)

The essential step (Scheme 1) is the addition of the electrophile E^+ at position 3 or 4 * of the substrate (51; X, Y, and Z are heteroatoms of Groups V and VI and Y is a second- or lower-row element) with accompanying *breaking of the Y–Z or Y–X bond* and formation of a stable 6 π-electron *monocyclic* intermediate (52) or (53). Free rotation about the C(3a)–C(3) or C(3a)–C(4) bond allows the group E to come into proximity to Y [conformations (52b) and (53b)]. In the case where E is an atom (*e.g.* Br) or group (*e.g.* $CH=\overset{+}{N}Me_2$) which cannot interact with Y to complete a stable three-centre hetero-atom sequence, loss of a proton from the intermediate



(51) (52a) (52b) (53a) (53b)

SCHEME 1

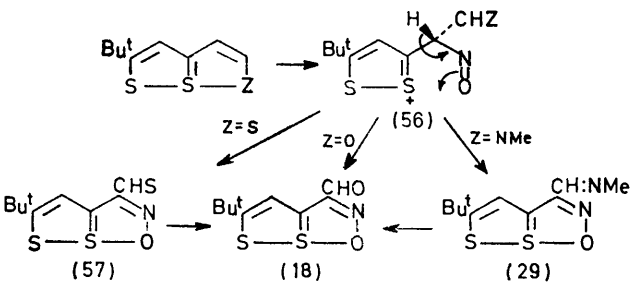
[conformation (52a) or (53a)] gives the normal substitution product [*e.g.* (54) ⟶ (55)]. However, if E is a

(54) (55)

R = Me or Ph, E = Br (ref. 2)

R = H or Ph, E = $CH=\overset{+}{N}Me_2$ (ref. 3)

group (*e.g.* N=O) containing a heteroatom (O) which is able to bond to Y, two routes are open to each intermediate (52) and (53), depending on the relative strengths of the original (X–Y–Z) and the new [(52), X–Y–O; (53), Z–Y–O] interaction. If the original interaction is stronger the product is again a 3(4)-E-substituted derivative of (51). This course of reaction has not yet been encountered in nitrosation reactions. Alternatively, if the new interaction is stronger, a rearrangement product is formed *via* conformation (52b) or (53b). This route is followed in nitrosation and diazo-coupling reactions. For example, 2-t-butyl-6a-thiathiophthen (7) and its oxygen (36) and nitrogen (45) analogues give (Scheme 2) the primary reaction products (57), (18), and (29) *via* the



(57) (18) (29)

SCHEME 2

intermediate (56). Subsequent oxidation and/or hydrolysis of the thioaldehyde (57) and hydrolysis of the imine (29) give compound (18) as the final product from all three reactions. An alternative route from the non-activated 2-t-butyl-6a-thiathiophthen (7) to the product (18), not excluded at present, would involve initial

* Attack at sulphur [S(1), S(6)] may also occur as a competing reaction, leading, for example, to oxidative and/or hydrolytic desulphurisation or to further decomposition. The primary intermediates in these processes may be formulated as 3-E-thiovinyl-1,2-dithiolium or 5-E-thiovinylisothiazolium cations.

[7] D. T. Clark and D. Kilcast, *Tetrahedron*, 1971, 4367.

oxidative desulphurisation by nitrous acid or oxides of nitrogen to give the corresponding oxadithiapentalene (36), subsequent nitrosation of which would afford the aldehyde (18). Substitution of the activated 2-methylthio-derivatives (2), (4), and (8) and the 2-dimethylamino-derivatives (3) and (9) occurs much more rapidly [intermediate (58)], and the greater stability of the CS_2Me and $CS{\cdot}NMe_2$ groups compared with the CHS group ensures the survival of the primary nitrosation products (59). The imines (28) and (29) are doubtless the primary reaction products from the nitrosation of the dithia-azapentalenes (44) and (45), since recent work [8] has shown that 1,6a-dithia-6-azapentalenes are protonated reversibly in acid, without detectable hydrolysis at room temperature to 1-oxa-6,6a-dithiapentalenes.

In the case of blocked derivatives of 6a-thiathiophthens and related compounds, elimination of the CHZ group (Z = S, O, or NMe) is thought to result from nucleophilic attack by water on intermediates of the type (60). Evidence is being gathered in support of this mechanism.

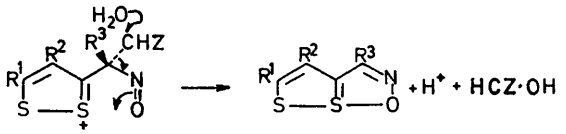
The proposed intermediate (61) in the electrophilic substitution of 1,6-dioxa-6a-thiapentalene (47) is noteworthy in being a derivative of the unknown 1,2-oxathiolium cation. Substitution of 1-oxa-6,6a-dithiapentalenes at position 4, which has not yet been observed, would also proceed *via* 1,2-oxathiolium intermediates. This suggests that the 1,2-oxathiolium system may be less stable than the 1,2-dithiolium system. Experiments to direct the electrophilic substitution of 1-oxa-6,6a-dithiapentalenes into position 4, and of 1,6a-dithia-6-azapentalenes into position 3, are in progress.

For the synthesis of the hitherto unknown 6a-thiathiophthens (8) and (9) the dithioester (62) was prepared by the method of Thuillier and Vialle [9] and converted into the thione (63). *S*-Methylation of the thione gave the methosulphate (64a) and thence the perchlorate (64b), which was condensed with the dithioester (62) according to a modification of the procedure of Beer.[2]

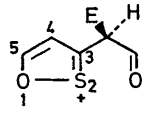
(58) (59)

$R^1 = Bu^t$, R^2 = MeS or Me_2N
$R^1 = Ph$, R^2 = MeS or Me_2N (ref. 2)
$R^1 = R^2$ = MeS (ref. 2)

Protodeacylation of the resulting pivaloyl derivative (10) gave 2-methylthio-5-t-butyl-6a-thiathiophthen (8) which, with ethanolic dimethylamine, afforded 2-dimethylamino-5-t-butyl-6a-thiathiophthen (9). The oxadithiapentalenes (36) and (38) have previously been synthesised [10] on a small scale from 2-t-butyl- and 3,5-dimethyl-4*H*-thiopyran-4-thione, respectively. Compound (36) is obtained in quantity more conveniently by treatment of the Vilsmeier salt (65) with sodium hydroxide.[11] The yield of the oxadithiapentalene (38) from the Vilsmeier salt (66) is satisfactory (62%) in small-scale (2 mmol) preparations but falls inexplicably



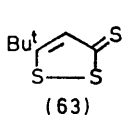
(60) Z = S, O, or NMe



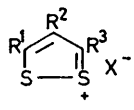
(61)

$Bu^tCO{\cdot}CH_2{\cdot}CS_2Me$

(62)



(63)



	R^1	R^2	R^3	X
(64a)	Bu^t	H	MeS	$MeSO_4$
(64b)	Bu^t	H	MeS	ClO_4
(65)	Bu^t	H	$Me_2N{\cdot}CH{:}CH$	ClO_4
(66)	H	Me	$Me_2N{\cdot}CH{:}CMe$	ClO_4
(67)	Ph	H	Et	ClO_4

to *ca.* 25% in larger-scale (10—40 mmol) reactions, in which substantial quantities (*ca.* 25%) of the corresponding 6a-thiathiophthen (11) are produced concomitantly. The oxadithiapentalene (38)[12] is prepared in quantity best by partial desulphurisation of the readily available 6a-thiathiophthen (11).[8] Nitrosation of the dithiolium salt (67) by established procedures [5] gave the oxadithia-azapentalene (27) by an unambiguous route.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. U.v. spectra were measured with a Unicam SP 800 spectrophotometer. Light absorption data refer to solutions in cyclohexane, unless otherwise stated. I.r. spectra were recorded with a Perkin-Elmer 621 spectrometer. ^1H N.m.r. spectra were determined at 100 MHz with a Varian HA100 spectrometer. Solutions were 0·4M in deuteriochloroform, unless otherwise stated. Chemical shifts (δ) are given in p.p.m. downfield from tetramethylsilane as internal reference. *J* Values were measured on the 100 Hz scale. Multiplicity refers to the appearance of spectra on the 100 Hz scale. Unless otherwise stated values refer to singlet absorptions. Solutions were dried over sodium sulphate and evaporated at reduced pressure. Column chromatography was carried out with Spence grade H alumina, unless otherwise indicated. Solvent mixtures are described in ratios by volume. Criteria used in the identification of products included m.p.s, t.l.c. behaviour, and n.m.r. and mass spectra. Perchloric acid refers to 70—72% (w/w)

[8] J. G. Dingwall, A. S. Ingram, D. H. Reid, and J. D. Symon, *J.C.S. Perkin I*, 1973, 2351.
[9] A. Thuillier and J. Vialle, *Bull. Soc. chim. France*, 1962, 2182.
[10] J. G. Dingwall, D. H. Reid, and J. D. Symon, *J. Chem. Soc.* (*C*), 1970, 2412.
[11] J. G. Dingwall, S. McKenzie, and D. H. Reid, *J. Chem. Soc.* (*C*), 1968, 2543.
[12] E. Klingsberg, *J. Amer. Chem. Soc.*, 1963, **85**, 3244.

perchloric acid. Light petroleum was of boiling range 40—60°.

Synthesis of 2-*Methylthio*-5-*t*-*butyl*-6a-*thiathiophthen* (8) *and* 2-*Dimethylamino*-5-*t*-*butyl*-6a-*thiathiophthen* (9) (with M. Touche).—A mixture of sodium (46 g, 2 g atom), 2-methylbutan-2-ol (176 g, 220 ml, 2 mol), and benzene (1 l) was refluxed overnight, then the solution was decanted while still hot from unchanged sodium. Pinacolone (100 g, 125 ml, 1 mol) and then carbon disulphide (76 g, 60 ml, 1 mol) were added to the stirred solution cooled to 5—10°, and the resulting mixture was left for 4 h at room temperature. Methyl iodide (142 g, 62·5 ml, 1 mol) was added dropwise to the stirred mixture which was then set aside overnight before being extracted with water (2 × 500 ml). The extracts were acidified with 5M-hydrochloric acid (250 ml) and the resulting mixture was extracted with ether. Distillation of the residue from the washed, dried, and evaporated extracts gave *methyl pivaloyldithioacetate* (62) (80·7 g, 43%) as a yellow oil, b.p. 92—94° at 2 mmHg (Found: C, 50·8; H, 7·4. $C_8H_{14}OS_2$ requires C, 50·5; H, 7·4%); δ (keto form, *ca.* 10%) 1·21 (9H, Bu^t), 2·64 (3H, SMe), and 4·31 (2H, CH_2); δ (enol form, *ca.* 90%) 1·21 (9H, Bu^t), 2·58 (3H, SMe), 6·39 (1H, olefinic H), and 13·69 (1H, OH).

The dithioester (62) (47·6 g, 250 mmol) in xylene (250 ml) was added during 20 min to a stirred suspension of phosphorus pentasulphide (166·5 g, 750 mmol) in xylene (750 ml) at room temperature. The mixture was boiled for 30 min, cooled, and filtered. The solid was treated with water and the resulting mixture was extracted with ether. The combined ethereal extracts and xylene filtrate were washed with water, dried, and evaporated. Chromatography (alumina; 30 × 5·8 cm) of the dark oil, initially with light petroleum–benzene (3 : 1) to remove residual xylene, and then with benzene, gave orange-yellow eluates. Evaporation, and crystallisation of the residual solid from hexane, gave 5-t-butyl-1,2-dithiole-3-thione (63) in two crops (33·14 g) as orange-yellow needles, m.p. 69—69·5° (lit.,[13] 70°; lit.,[14] 70°) (Found: C, 44·2; H, 5·4. Calc. for $C_7H_{10}S_3$: C, 44·2; H, 5·3%); $\lambda_{max.}$ 412 (log ε 3·94), 330br (3·79), 259sh (3·98), 251 (4·02), and 232 nm (3·94); δ 1·42 (9H, Bu^t) and 7·11 (1H, 4-H). Rechromatography (alumina; 50 × 3·8 cm) of the residue from the mother liquors with light petroleum–benzene (3 : 1) brought through red eluates which were discarded. Continued elution with benzene gave yellow eluates which yielded a further quantity (5·05 g) of the thione (total yield 38·19 g, 80%).

A mixture of the thione (63) (19 g, 100 mmol) and dimethyl sulphate (12·2 ml, 130 mmol) was heated at 130° for 20 min. The resulting oil was dissolved in ethanol (20 ml). Addition of ether precipitated the methosulphate (64a) as a pink oil which slowly solidified. The ether layer was decanted and the methosulphate was redissolved in ethanol (30 ml). Addition of perchloric acid (20·2 ml, 240 mmol) and subsequent gradual addition of much ether precipitated 3-*methylthio*-5-*t*-*butyl*-1,2-*dithiolium perchlorate* (64b) (29·15 g, 96%), colourless spars (from ethanol containing 1% perchloric acid), m.p. 143·5—144·5° (Found: C, 31·5; H, 4·3. $C_8H_{13}ClO_4S_3$ requires C, 31·5; H, 4·6%); $\lambda_{max.}$ (EtOH–1% $HClO_4$) 359 (log ε 4·28), 278 (3·77), and 216 nm (3·76); δ ($CF_3{\cdot}CO_2H$) 1·64 (9H, Bu^t), 3·05 (3H, SMe), and 8·01 (1H, 4-H).

A mixture of the perchlorate (64b) (18·3 g, 60 mmol), the dithioester (62) (12·35 g, 65 mmol), pyridine (7 ml), and acetic acid (500 ml) was boiled for 4 h, cooled, diluted with much water, and extracted with benzene. The extracts were washed successively with water (× 2), aqueous 0·2M-sodium hydroxide, and water, dried, and evaporated. Crystallisation of the solid from hexane gave 2-*methylthio*-3-*pivaloyl*-5-*t*-*butyl*-6a-*thiathiophthen* (10) (5·60 g), orange-red spars, m.p. 113—113·5° (Found: C, 52·0; H, 6·5. $C_{15}H_{22}OS_4$ requires C, 52·0; H, 6·4%); $\lambda_{max.}$ 485 (log ε 4·09), 339br (3·80), 252 (4·63), and 194 nm (4·36); $\nu_{max.}$ ($CHCl_3$) 1680 (C=O) cm^{-1}; δ 1·35 (9H, 5-Bu^t or COBu^t), 1·39 (9H, COBu^t or 5-Bu^t), 2·65 (3H, SMe), and 7·11 (1H, 4-H). Chromatography (alumina; 50 × 3·8 cm) of the residue from the hexane mother liquors with light petroleum–benzene (3 : 1) gave orange eluates from which the 6a-thiathiophthen (8) (279 mg, 1·8%) was isolated. Continued elution with light petroleum–benzene (1 : 1) brought through orange-red eluates from which more (5·28 g) of the ketone (10) was obtained (total yield 10·88 g, 52%).

A solution of the ketone (10) (10·38 g, 30 mmol) and 49% (w/w) aqueous hydrogen bromide (5 ml) in acetic acid (500 ml) was boiled for 45 min, cooled, poured into water, and extracted with ether (× 4). The extracts were washed successively with water (× 2), aqueous 2M-sodium hydroxide (× 2), and water, dried, and evaporated. Chromatography (alumina; 40 × 3·8 cm) of the residual solid with light petroleum–benzene (4 : 1) gave pale yellow eluates which were discarded, and subsequently orange eluates which afforded 2-*methylthio*-5-*t*-*butyl*-6a-*thiathiophthen* (8) (5·888 g, 75%), orange-red spars from methanol, m.p. 85·5—86° (Found: C, 46·0; H, 5·7. $C_{10}H_{14}S_4$ requires C, 45·8; H, 5·4%); $\lambda_{max.}$ 482 (log ε 4·12), 340br (3·81), 257 (4·63), and 237 nm (4·47); δ 1·38 (9H, Bu^t), 2·60 (3H, SMe), 7·28 (1H, 4-H), and 7·63 (1H, 3-H).

The 6a-thiathiophthen (8) (2·62 g, 10 mmol) in 33% (w/w) ethanolic dimethylamine (400 ml) was boiled under an ice condenser for 5 h, cooled, and diluted with water. The mixture was extracted with ether and the extracts were washed with water, dried, and evaporated. Chromatography (silica; 30 × 2·8 cm) of the residual solid with light petroleum–benzene (1 : 1) gave an orange fraction from which starting material (105 mg, 4%) was recovered. Continued elution with benzene–ether (4 : 1) brought through yellow eluates which yielded 2-*dimethylamino*-5-*t*-*butyl*-6a-*thiathiophthen* (9) (2·46 g, 95%), yellow needles from hexane, m.p. 114—115° (Found: C, 50·7; H, 6·4; N, 5·3. $C_{11}H_{17}NS_3$ requires C, 50·9; H, 6·6; N, 5·4%); $\lambda_{max.}$ 456 (log ε 4·06), 336br (3·79), 254 (4·59), and 232 nm (4·50); δ 1·34 (9H, Bu^t), 3·25 (6H, NMe_2), 6·88 (1H, 4-H), and 6·99 (1H, 3-H).

5-*t*-*Butyl*-1-*oxa*-6,6a-*dithiapentalene* (36) (with K. O. Wade).—Aqueous 2M-sodium hydroxide (50 ml) was added to a solution of the Vilsmeier salt (65) [3a] (3·28 g, 10 mmol) in dimethylformamide (50 ml). The mixture was diluted with water and extracted with benzene, and the extracts were washed with water (× 3), dried, and evaporated. Chromatography (alumina; 30 × 2·8 cm) of the residue with light petroleum–benzene (3 : 2) gave pale blue eluates which were discarded. Subsequent elution with benzene brought through yellow eluates which afforded 5-t-butyl-1-oxa-6,6a-dithiapentalene (1787 mg, 89%), yellow rods from hexane, m.p. 74—75° (lit.,[10] 73—74°).

3,4-*Dimethyl*-1-*oxa*-6,6a-*dithiapentalene* (38) (with J. D. Symon).—*By partial desulphurisation of* 3,4-*dimethyl*-6a-

[13] A. Thuillier and J. Vialle, *Bull. Soc. chim. France*, 1962, 2187.

[14] P. Yates and T. R. Lynch, *Canad. J. Chem.*, 1971, **49**, 1477.

thiathiophthen (11). A suspension of mercury(II) acetate (7·98 g, 25 mmol) in acetic acid (10 ml) was added to a solution of 3,4-dimethyl-6a-thiathiophthen (11) [8] (4·70 g, 25 mmol) in chloroform (80 ml), and the resulting mixture was stirred at room temperature for 18 h. More mercury(II) acetate (3·99 g, 12·5 mmol) and acetic acid (2 ml) were added, whereupon the colour of the 6a-thiathiophthen was discharged. The mixture was filtered, the solid was washed with chloroform, and the combined filtrates were washed with water (× 2), saturated sodium hydrogen carbonate solution, and water, dried, and evaporated. Chromatography (alumina; 50 × 3·7 cm) of the residue with benzene–ether (3 : 1) brought through yellow eluates which yielded 3,4-dimethyl-1-oxa-6,6a-dithiapentalene (3·80 g, 88%), yellow plates from cyclohexane, m.p. 122—123° (lit.,[10] 122—123°), $\lambda_{max.}$ 450sh (log ε 3·98), 432 (4·04), 279 (3·73), 273 (3·73), and 231 nm (4·19).

From 3-(2-*dimethylamino*-1-*methylvinyl*)-4-*methyl*-1,2-*dithiolium perchlorate* (66). (*a*) Aqueous 2M-sodium hydroxide (10 ml) was added to a solution of the Vilsmeier salt (66) [8] (600 mg, 2 mmol) in methanol (12 ml) and acetonitrile (12 ml). The resulting solution was diluted with water and extracted with ether. The residue from the washed, dried, and evaporated extracts was chromatographed (alumina; 30 × 2·0 cm) with benzene. The initial red eluates gave 3,4-dimethyl-6a-thiathiophthen (8 mg, 2%) and the succeeding yellow eluates afforded 3,4-dimethyl-1-oxa-6,6a-dithiapentalene (214 mg, 62%).

(*b*) The procedure was identical with that of the preceding experiment (*a*). Treatment of the salt (66) (3·0 g, 10 mmol) in methanol (60 ml) and acetonitrile (60 ml) with aqueous 2M-sodium hydroxide (50 ml) and chromatography (alumina; 50 × 2·6 cm) of the product gave 3,4-dimethyl-6a-thiathiophthen (460 mg, 25%) and 3,4-dimethyl-1-oxa-6,6a-dithiapentalene (510 mg, 30%).

Nitrosation of 3-*Ethyl*-5-*phenyl*-1,2-*dithiolium Perchlorate* (67).—Sodium nitrite (690 mg, 10 mmol) was added to a stirred solution of the salt (67) [11] (1533 mg, 5 mmol) in acetonitrile (50 ml) and acetic acid (50 ml) at room temperature. Stirring was continued for 20 min before the mixture was poured into water and extracted with benzene. The extracts were washed with water (× 2), saturated sodium hydrogen carbonate solution (× 2), and water, dried, and evaporated. Chromatography (alumina; 20 × 2·7 cm) of the residue with benzene–ether (9 : 1) afforded 3-*methyl*-5-*phenyl*-1-*oxa*-6,6a-*dithia*-2-*azapentalene* (27) (994 mg, 84%), red needles from cyclohexane, m.p. 121—122° (Found: C, 56·0; H, 4·0; N, 5·8. $C_{11}H_9NOS_2$ requires C, 56·1; H, 3·9; N, 6·0%); $\lambda_{max.}$ 418 (log ε 3·94), 318 (3·91), 229 (4·45), and 208 nm (4·39); δ 2·73 (3H, 3-Me), 7·4—7·5 (3H, m, 2 *m*- + *p*-protons of 5-Ph), 7·79—7·90 (2H, m, 2 *o*-protons of 5-Ph), and 8·19 (1H, 4-H).

Nitrosation of 6a-*Thiathiophthens*, 1-*Oxa*-6,6a-*dithiapentalenes, and* 1,6a-*Dithia*-6-*azapentalenes*.—The following general procedure was used (deviations are given in individual cases). Sodium nitrite (690 mg, 10 mmol) was added to a stirred solution of the substrate (5 mmol) in acetonitrile (50 ml) and acetic acid (50 ml) at room temperature. The mixture was stirred for 10 min, a second portion of sodium nitrite (345 mg, 5 mmol) was added, and the mixture was stirred for a further 10 min before being diluted with water and extracted with benzene. The extracts were washed with water (× 2), saturated sodium hydrogen carbonate solution, and water, dried, and evaporated. In several cases a modified general procedure was used in which a smaller second portion (173 mg, 2·5 mmol) of sodium nitrite was added. Subsequent work-up varied and is described for each reaction.

6a-*Thiathiophthen* (5) *and* 2-*phenyl*-6a-*thiathiophthen* (6). The crude products from the substrates (5) [11] and (6) [11] contained several coloured components (t.l.c.), none in sufficient quantity to be isolated. The product from 2-phenyl-6a-thiathiophthen did not contain the aldehyde (16) (*cf.* the next experiment).

2-*t*-*Butyl*-6a-*thiathiophthen* (7).[3b] Chromatography (alumina; 55 × 2·8 cm) with light petroleum–benzene (1 : 1) gave successively a red fraction from which starting material (20 mg) was recovered, and traces of two other compounds which were discarded. Continued elution with benzene–ether (9 : 1) brought through a two-component yellow fraction. Evaporation, and rechromatography of the residue gave yellow eluates which yielded 3-formyl-5-t-butyl-1-oxa-6,6a-dithia-2-azapentalene (18) [5] (100 mg, 9%), red needles from light petroleum, m.p. 139—140°, $\lambda_{max.}$ 400 (log ε 4·12), 293 (4·21), 255 (4·46), 215sh (4·49), and 208 nm (4·50). The second, orange component, present in small quantity, was not isolated.

2-*Methylthio*-5-*t*-*butyl*-6a-*thiathiophthen* (8). Chromatography (alumina; 30 × 2·7 cm) with benzene gave a pale yellow fraction which was discarded, and subsequent red eluates which yielded *methyl* 5-*t*-*butyl*-1-*oxa*-6,6a-*dithia*-2-*azapentalene*-3-*dithiocarboxylate* (20) (580 mg, 40%), red prisms from light petroleum, m.p. 124·5—125° (Found: C, 40·9; H, 4·4; N, 4·8. $C_{10}H_{13}NOS_4$ requires C, 41·2; H, 4·5; N, 4·8%); $\lambda_{max.}$ 400 (log ε 3·85), 335 (4·12), 262sh (3·96), and 218br nm (4·24); δ 1·47 (9H, Bu^t), 2·79 (3H, SMe), and 9·38 (1H, 4-H).

2-*Dimethylamino*-5-*t*-*butyl*-6a-*thiathiophthen* (9). Chromatography (alumina; 20 × 2·6 cm) with benzene gave NN-*dimethyl* 5-*t*-*butyl*-1-*oxa*-6,6a-*dithia*-2-*azapentalene*-3-*thiocarboxamide* (21) (1·40 g, 97%), yellow needles from cyclohexane m.p. 125—125·5° (Found: C, 45·7; H, 5·6; N, 9·5. $C_{11}H_{16}N_2OS_3$ requires C, 45·8; H, 5·6; N, 9·7%); $\lambda_{max.}$ 405 (log ε 3·73), 283 (4·11), 230sh (4·21), and 206 nm (4·34); δ 1·47 (9H, Bu^t), 3·30 (3H, NMe), 3·68 (3H, NMe), and 8·38 (1H, 4-H).

5-*Phenyl*-1-*oxa*-6,6a-*dithiapentalene* (35).[11] The modified general procedure was used. Chromatography (silica; 45 × 2·7 cm) with benzene gave yellow eluates which afforded 3-formyl-5-phenyl-1-oxa-6,6a-dithia-2-azapentalene (16) [5] (744 mg, 60%), red needles from cyclohexane, m.p. 174—175°, $\lambda_{max.}$ 415 (log ε 4·00), 330 (4·04), 297 (3·96), 238 (4·35), and 220 nm (4·43). Continued elution with ether gave an unidentified yellow compound (10 mg).

5-*t*-*Butyl*-1-*oxa*-6,6a-*dithiapentalene* (36). The modified general procedure was used. Chromatography (alumina; 25 × 2·0 cm) with ether afforded 3-formyl-5-t-butyl-1-oxa-6,6a-dithia-2-azapentalene (18) [5] (820 mg, 72%). Continued elution with ether gave a trace of a yellow compound whose mass spectrum (M^+ 245) suggested that it is compound (41).

2,5-*Dimethyl*-1-*oxa*-6,6a-*dithiapentalene* (37).[15] Chromatography (alumina; 20 × 2·0 cm) with benzene gave 3-*acetyl*-5-*methyl*-1-*oxa*-6,6a-*dithia*-2-*azapentalene* (24) (860 mg, 86%), orange plates from cyclohexane, m.p. 106° (Found: C, 41·8; H, 3·6; N, 7·0. $C_7H_7NO_2S_2$ requires C, 41·8; H, 3·5; N, 7·0%); $\lambda_{max.}$ 395 (log ε 3·78), 286 (3·87), 245 (4·16), and 218 nm (4·13); $\nu_{max.}$ (KBr) 1673 (C=O) cm^{-1};

[15] F. Arndt, E. Aron, C. Martius, and R. Schwarz, *Rev. Fac. Sci. Univ. Istanbul*, 1948, *A*13, 57.

δ 2·80 (3H, COMe), 2·89 (3H, d, $J_{5\text{-Me},4}$ 0·7 Hz, 5-Me), and 9·15br (1H, 4-H).

3,4-*Dimethyl*-1-*oxa*-6,6a-*dithiapentalene* (38). The modified general procedure was used. Chromatography (alumina; 25 × 2·0 cm) with benzene–ether (9 : 1) gave successively 3,4-dimethyl-1-oxa-6,6a-dithia-2-azapentalene (25) [5] (520 mg, 60%), red needles from cyclohexane, m.p. 127—128°, δ 2·90 (6H, 3- + 4-Me) and 9·06 (1H, 5-H); and 4-methyl-3-(1-nitroethylidene)-3*H*-1,2-dithiole (42) [5] (8 mg, 1%), orange needles from benzene, m.p. 191—192°, M^+, 189. When a solution of the oxadithia-azapentalene (25) (346 mg, 2 mmol) in acetonitrile (25 ml) and acetic acid (25 ml) was treated with successive portions (2 mmol + 2 mmol) of sodium nitrite under the conditions of the foregoing experiment, no trace of the nitromethylenedithiole (42) was detected, and starting material (339 mg, 98%) was recovered.

4,5-*Dihydro*-3H-*benzo*[cd]-1-*oxa*-6,6a-*dithiapentalene* (39).[5] The modified general procedure was used. Chromatography (alumina; 25 × 2·7 cm) with benzene–ether (9 : 1) gave yellow eluates which afforded 4,5-dihydro-3*H*-benzo[*cd*]-1-oxa-6,6a-dithia-2-azapentalene (26) [5] (756 mg, 82%), thick red needles from cyclohexane, m.p. 95—96°, δ 2·15 (2H, quint, 4-H_2), 3·14 (2H, t, 5- or 3-H_2), 3·20 (2H, t, 3- or 5-H_2), and 9·05 (1H, 6-H). Continued elution with benzene–ether (1 : 1) brought through a second yellow band which yielded 5,6-dihydro-7-nitro-4*H*-benzo[*c*][1,2]dithiole (43) [5] (63 mg, 6%), orange needles from benzene–cyclohexane, m.p. 213·5—214·5°, δ 1·97 (2H, quint, 5-H_2), 2·84 (2H, m, 4-H_2), 2·90 (2H, t, 6-H_2), and 7·83 (1H, t, $J_{3,4\text{-}H_2}$ 1·1 Hz, 3-H). When a solution of the oxadithia-azapentalene (26) (370 mg, 2 mmol) in acetonitrile (25 ml) and acetic acid (25 ml) was treated with sodium nitrite (2 mmol + 2 mmol) under the conditions of the preceding experiment, no trace of the nitromethylenedithiole (43) was detected, and compound (26) (361 mg, 98%) was recovered.

3-*Methyl*-5-*phenyl*-1-*oxa*-6,6a-*dithiapentalene* (40).[11] The modified general procedure was used. Crystallisation of the product from cyclohexane gave 3-methyl-5-phenyl-1-oxa-6,6a-dithia-2-azapentalene (27) (840 mg). Recrystallisation of the residue from the mother liquors from hexane gave a further quantity (64 mg) of product (total yield 904 mg, 77%).

6-*Methyl*-2-*phenyl*-1,6a-*dithia*-6-*azapentalene* (44).[8] Chromatography (alumina; 30 × 2·0 cm) with benzene–ether (1 : 1) gave, successively, yellow eluates from which a compound (40 mg) of unknown structure was isolated, and a second yellow band which yielded 3-formyl-5-phenyl-1-oxa-6,6a-dithia-2-azapentalene (16) [5] (872 mg, 70%).

6-*Methyl*-2-*t*-*butyl*-1,6a-*dithia*-6-*azapentalene* (45).[8] Chromatography (alumina; 20 × 2·0 cm) with benzene–ether (1 : 1) gave yellow eluates which yielded 3-formyl-5-t-butyl-1-oxa-6,6a-dithia-2-azapentalene (18) [5] (846 mg, 74%).

4,6-*Dimethyl*-2-*phenyl*-1,6a-*dithia*-6-*azapentalene* (46).[8] Chromatography (alumina; 30 × 2·0 cm) with benzene gave 3-methyl-5-phenyl-1-oxa-6,6a-dithia-2-azapentalene (27) (100 mg, 8%).

Nitrosation of 1,6-*Dioxa*-6a-*thiapentalene* (47).—Nitrosyl hexafluorophosphate (2·64 g, 15 mmol) was added to a stirred solution of 1,6-dioxa-6a-thiapentalene [16] (641 mg, 5 mmol) in dichloromethane (100 ml) containing powdered calcium carbonate (10 g) in suspension. The mixture was stirred for 30 min at room temperature, diluted with water, and extracted with ether. The extracts were washed with water, aqueous sodium carbonate and water, dried, and evaporated. Sublimation of the residue at 100—105° and 15 mmHg afforded 3-*formyl*-1,6-*dioxa*-6a-*thia*-2-*azapentalene* (48) (724 mg, 92%), volatile pale yellow crystals, m.p. 43—46° (Found: C, 38·4; H, 1·9; N, 9·2. $C_5H_3NO_3S$ requires C, 38·2; H, 2·0; N, 8·9%); M^+, 156·983113; $\lambda_{max.}$ 345 (log ε 3·73), 279 (3·54), 213 (3·90), and 198 nm (3·77); $\nu_{max.}$ (CCl_4) 1715 (C=O) cm^{-1}; δ 8·01 (1H, d, $J_{4,5}$ 2·2 Hz, 4-H), 9·26 (1H, d, $J_{5,4}$ 2·2 Hz, 5-H), and 10·40 (1H, CHO).

Selective Desulphurisations with Mercury(II) *Acetate*.—*Methyl* 5-*t*-*butyl*-1-*oxa*-6,6a-*dithia*-2-*azapentalene*-3-*dithiocarboxylate* (20). Mercury(II) acetate (636 mg, 2 mmol) was added to a solution of the dithioester (291 mg, 1 mmol) in chloroform (40 ml), and the mixture was stirred at room temperature for 15 min. More mercury(II) acetate (636 mg, 2 mmol) was added, and stirring was continued for a further 15 min before the mixture was filtered. The filtrate was diluted with benzene, and the resulting solution was washed with water, dried, and evaporated. Chromatography (alumina; 20 × 2·2 cm) of the residue with benzene–ether (4 : 1) brought through yellow eluates which afforded S-*methyl* 5-*t*-*butyl*-1-*oxa*-6,6a-*dithia*-2-*azapentalene*-3-*thiocarboxylate* (22) (58 mg, 21%), red spars from light petroleum, m.p. 99—101° (Found: C, 43·5; H, 4·8; N, 5·1. $C_{10}H_{13}NO_2S_3$ requires C. 43·6; H, 4·8; N, 5·1%); $\lambda_{max.}$ 401 (log ε 3·89), 301 (4·02), 246 (4·22), and 212 nm (4·27); $\nu_{max.}$ (KBr) 1650 (C=O) cm^{-1}; δ 1·53 (9H, Bu^t), 2·48 (3H, SMe), and 9·14 (1H, 4-H).

NN-*Dimethyl* 5-*t*-*butyl*-1-*oxa*-6,6a-*dithia*-2-*azapentalene*-3-*thiocarboxamide* (21). The procedure was identical with that of the preceding experiment, with the thioamide (21) (288 mg, 1 mmol) in place of the dithioester. NN-*Dimethyl* 5-*t*-*butyl*-1-*oxa*-6,6a-*dithia*-2-*azapentalene*-3-*carboxamide* (23) (252 mg, 93%) was obtained as orange needles from methanol, m.p. 85—86° (Found: C, 48·7; H, 6·0; N, N, 10·0. $C_{11}H_{16}N_2O_2S_3$ requires C, 48·5; H, 5·9; N, 10·3%); $\lambda_{max.}$ 397 (log ε 3·77), 276sh (3·71), 236 (4·22), and 204 nm (4·18); $\nu_{max.}$ (KBr) 1625 (C=O) cm^{-1}; δ 1·50 (9H, Bu^t), 3·23 (6H, NMe_2), and 8·46 (1H, 4-H).

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[16] D. H. Reid and R. G. Webster, *J.C.S. Chem. Comm.*, 1972, 1283.