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PREPARATION AND PROPERTIES OF SOME THIOURONIUM FLUORENYLIDES AND CYCLOPENTADIENYLIDES AND THE ATTEMPTED PREPARATION OF SELENOURONIUM AND GUANIDINIUM FLUORENYLIDES

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Abstract—Some stable thiouronium fluorenylides and cyclopentadienylides, prepared by treatment of the corresponding thiouronium salts with non-aqueous base, exist as tautomeric mixtures of the fluorenylide and fluorenyl*iso*thiourea, but undergo reactions typical of ylides, e.g. Wittig reactions with aldehydes or nitrosobenzene; a 2,3,4-triphenylcyclopentadienylide gave anomalous products. The ylides also react with acids, alkali, benzyl bromide, and dimethylacetylene dicarboxylate. *N,N'*-Diphenyl-selenouronium and -guanidinium analogues appear to exist entirely as the non-ylidic tautomers.

Thiouronium salts are very commonly used as derivatives, but thiouronium ylides, which might be obtained from these salts by the action of bases, have received almost no attention. Three thiouronium ylides, all stabilised by α-carbonyl groups in the ylide moiety, have been obtained via thiouronium salts, from 2-bromotetronic acid,[1,2] 2-bromodimedone,[3] and 3-bromo-4-hydroxycoumarin.[4] The dimedone derivative was also prepared by the action of thiourea on the corresponding phenyliodonium ylide.[5] In addition, thiouronium dicyanomethylide and its *N,N'*-ethylene and *N,N,N',N'*-tetramethyl-derivatives have been prepared by the action of thiourea or its *N*-substituted derivatives on 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene oxide,[6] and of thioureas on tetracyanoethylene oxide.[7] The unsubstituted thiouronium ylides were stable at room temperature but the tetramethylthiouronium example[6] decomposed in a few hours. Other than some examination of the effect of acid or base,[2,4] no study has been made of their chemistry. In the work presently described a number of thiouronium fluorenylides and cyclopentadienylides have been prepared and their properties investigated.

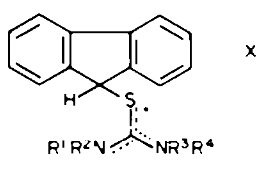
Fluorenylides and cyclopentadienylides were prepared by the action of base on thiouronium salts; fluorenylphosphonium,[8] -arsonium,[9,10] -sulphonium[11,12] and -pyridinium[13] salts had given ylides on treatment with aqueous base, but when the thiouronium salt **1a** was treated with aqueous sodium hydroxide or with ethanolic sodium ethoxide the thiol(**2**) resulted. By the use of non-aqueous bases the fluorenylides **3a–3f** were obtained as crystalline solids. The ylide **3g** decomposed too rapidly to be isolated but its formation was inferred from reactions carried out *in situ*. Phenyl lithium as base provided all these ylides from the salts; the aryl-substituted ylides **3d–f**, but not the others, could also be obtained in high yield using triethylamine as base.

Similarly the cyclopentadienylides **4a**, **4b** and **5** were obtained in solution from the corresponding thiouronium salts by the action of phenyl lithium in tetrahydrofuran or triethylamine in methanol, but were not isolable.

An analogous attempt to prepare the cyclopentadienylide **4c** gave instead a compound which could not be reconverted into a thiouronium salt by acid, possibly the mercaptofulvene **6a**, which could have been formed as shown via 1,4-cyclisation. Formation of this product from the ylide must be very rapid because it is formed in the presence of *p*-nitrobenzaldehyde rather than the product from the Wittig reaction. A similar product **6b** was also obtained from a similar attempted preparation of the ylide **4d**. Reaction of 2,3,4-triphenylcyclopentadienylthiouronium bromide with either aqueous hydroxide or with t-butoxide gave the hitherto unreported 2,3,4-triphenylcyclopentadienylthiol.

A variety of ylides has been made by the decomposition of diazo-compounds in the presence of suitable carbene acceptors.[14] When 9-diazofluorene was decomposed in the presence of *N*-phenyl-, *N,N'*-diphenyl- or *N*-methyl-*N'*-phenyl-thiourea with copper bronze present as catalyst, only *N,N'*-diphenylthiourea provided a trace of the desired ylide, the major products being bifluorenyl and/or bifluorenylidene. Bifluorenylidene is known to arise from thermal decomposition of 9-diazofluorene alone,[15] while diazocyclopentadienes are known to react with acids whose conjugate bases are of low nucleophilicity to give dihydrofulvalenes.[14] Traces of fluorenone ketazine were also formed; this compound has been shown to be formed in related reactions of 9-diazofluorene, by reaction of ylide which is formed initially with unreacted diazofluorene.[14]

The products hitherto described as thiouronium ylides, if they are not tetra-substituted on nitrogen, might also exist in a tautomeric form, e.g. 7. However their chemical reactions, and especially those with aldehydes and nitrosobenzene, require an ylide structure, but the ylide



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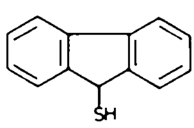
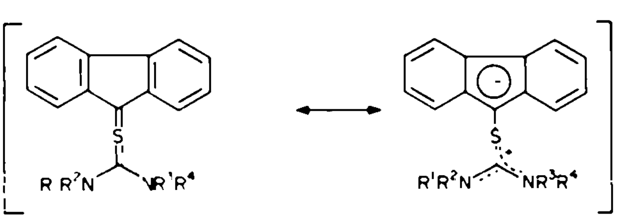


2

In 1 and 3:
(a) $R^1 = R^2 = R^3 = R^4 = H$
(b) $R^1 = R^3 = Me$; $R^2 = R^4 = H$
(c) R^1 and $R^3 = CH_2CH_2$; $R^2 = R^4 = H$
(d) $R^1 = R^3 = Ph$; $R^2 = R^4 = H$
(e) $R^1 = Ph$; $R^2 = R^3 = R^4 = H$
(f) $R^1 = Ph$; $R^3 = Me$; $R^2 = R^4 = H$
(g) $R^1 = R^2 = R^3 = R^4 = Me$



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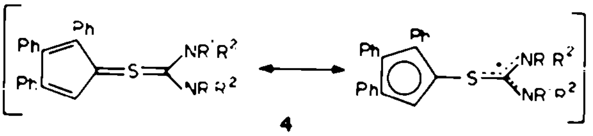
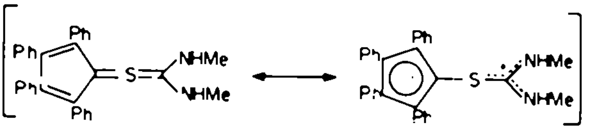


4

In 4:
(a) $R^1 = Me$; $R^2 = H$
(b) R^1-$R^1 = -CH_2CH_2-$, $R^2 = H$
(c) $R^1 = R^2 = Me$
(d) $R^1 = R^2 = H$



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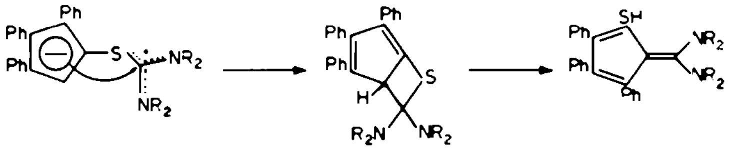


(a) – Me
(b) – H

4c, 4d 6

and fluorenyl (or cyclopentadienyl) isothiourea forms might coexist in tautomeric equilibrium. A similar situation obtains for guanidinium fluorenylides.[16]

Spectroscopic evidence is not conclusive but would seem to support the presence of such a tautomeric mixture. The electronic spectra of the ylides closely resemble those of the related salts 1 but with an additional peak at 300–310 nm (see Table 1), which could arise from a small contribution of the ylide form.

The PMR spectra of the ylides are apparently odd in that they show two separate NH signals (see Table 2). This could be due to restricted rotation in the thiouronium group but this is unlikely because the methyl signals of 3b appear as a singlet; it has also been shown that multiplication of signals due to restricted rotation is not characteristic of simple thiouronium salts.[17] If however the fluorenyl structure 7 is a major contributor to the mixture of tautomeric forms then separate one-proton signals will be expected, one due to the 9-fluorenyl proton and the other due to an NH-proton. Because the MeHN–C=NMe moiety is an amidine system the two nitrogen atoms will be in effect identical and both substituent groups will be represented by one signal. Furthermore, the chemical shifts of one of the one-proton signals for each ylide resemble those for the 9-H in the corresponding salts, with the latter being somewhat downfield in each case due to the neighbouring positive charge in the salt.

Table 1. Electronic spectra of fluorenylides and related salts

Compound	λ_{max}(nm)(log ε)(in methanol)
Salt (1; $R^1, R^2, R^3, R^4 = H$)	258 (4.12), 270 (4.15), 282 sh
Ylide (3; $R^1, R^2, R^3, R^4 = H$)	258 (4.06), 270 (4.11), 283 sh, 296 sh, 306 (3.17)
Salt (1; $R^1, R^3 = Me$; $R^2, R^4 = H$)	256 (4.09), 270 (4.10), 282 sh
Ylide (3; $R^1, R^3 = Me$; $R^2, R^4 = H$)	258 (4.16), 269 (4.15), 283 sh, 296 sh, 306 (3.23)
Salt (1; $R^1, R^3 = Ph$; $R^2, R^4 = H$)	257 sh, 269 (4.39), 282 sh, 305 sh
Ylide (3; $R^1, R^3 = Ph$; $R^2, R^4 = H$)	248 sh, 258 (4.42), 273 (4.39), 304 sh, 312 sh
Salt (1; $R^1, R^2, R^3, R^4 = Me$)	234 (4.35), 267 (4.34), 284 sh
Ylide (3; $R^1, R^2, R^3, R^4 = Me$)	244, 257 sh, 281, 392*

*log ε values not obtainable; ylide generated *in situ*.

Table 2. ^{1}H NMR spectra of fluorenylides and related salts

Compound	τ
Ylide (1; R^1, R^2, R^3, R^4 = H)^a	2.41 (m, 8H), 3.59 (br. s., 4H)
Ylide (1; R^1, R^3 = Me; R^2, R^4 = H)^b	2.5 (m, 8H), 4.60 (br.s., 1H), 6.15 (br. s., 1H), 7.10 (br. s., 6H)
Ylide (1; R^1, R^3 = Ph; R^2, R^4 = H)^b	2.8 (m)
Ylide (1; R^1 = Me; R^3 = Ph; R^2, R^4 = H)^b	2.68 (m, 13H), 4.62 (br. s., 1H), 5.68 (v. br. s., 1H), 7.31 (s, 3H)
Ylide (1; R^1-R^3 = $(CH_2)_2$; R^2, R^4 = H)^b	2.48 (m, 8H), 3.97 (s, 1H), 5.65 (br. s., 1H), 6.29 (s, 4H)
Salt (3; R^1, R^2, R^3, R^4 = H)^c	0.30 (br. s., 5H), 2.44 (m, 8H)
Salt (3; R^1, R^3 = Me; R^2, R^4 = H)^b	1.88 (br. s., 2H), 2.55 (m, 8H), 4.00 (s, 1H), 7.04, (br. d., 6H)
Salt (3; R^1, R^3 = Ph; R^2, R^4 = H)^b	2.65 (m, 18H), 4.27 (br. s., 1H)
Salt (3; R^1-R^3 = $CH_2{\cdot}CH_2$; R^2, R^4 = H)^a	2.36 (m, 8H), 3.55 (s, 1H), 5.92 (s, 4H)

Solvents: ^{a}[$^2H_6$]DMSO; ^{b}C^{2}HCl$_3$; ^{c}[$^2H_5$]pyridine.

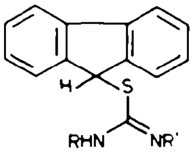
It is perhaps noteworthy that the one ylide **3g** which cannot tautomerise is different from the others in properties in that it is markedly less stable (for this reason its PMR spectrum was not obtained), and when it is formed from the salt there is in this case a real difference in the electronic spectra. In accord with the present results the previous workers who investigated thiouronium dicyanomethylides also found their *N,N,N',N'*-tetramethyl derivative to be strikingly less stable than the unsubstituted or *N,N'*-disubstituted analogues.[6]

The dipole moments of thiouronium fluorenylides, which will be discussed more fully in a subsequent paper, also conform with this interpretation, for they are markedly smaller than the dipole moments of other heteronium fluorenylides (see Table 3). This is explicable if the ylide is in equilibrium with the tautomeric fluorenyl form.

Table 3. Dipole moments of fluorenylides

	μ(D)
Dimethylsulphonium[19]	6.2
Triphenylphosphonium[20]	7.09
Tri-n-butylphosphonium[21]	7.39
Triphenylarsonium[22]	7.80
Thiouronium	2.15 ± 0.1 (in dioxan, 30°)†
N,N'-Diphenylthiouronium	2.35 (in benzene, 30°)†

†Kindly recorded by Prof. H. Lumbroso and Mrs Ch. Liégeois, Université Pierre-et-Marie Curie, Paris, France.



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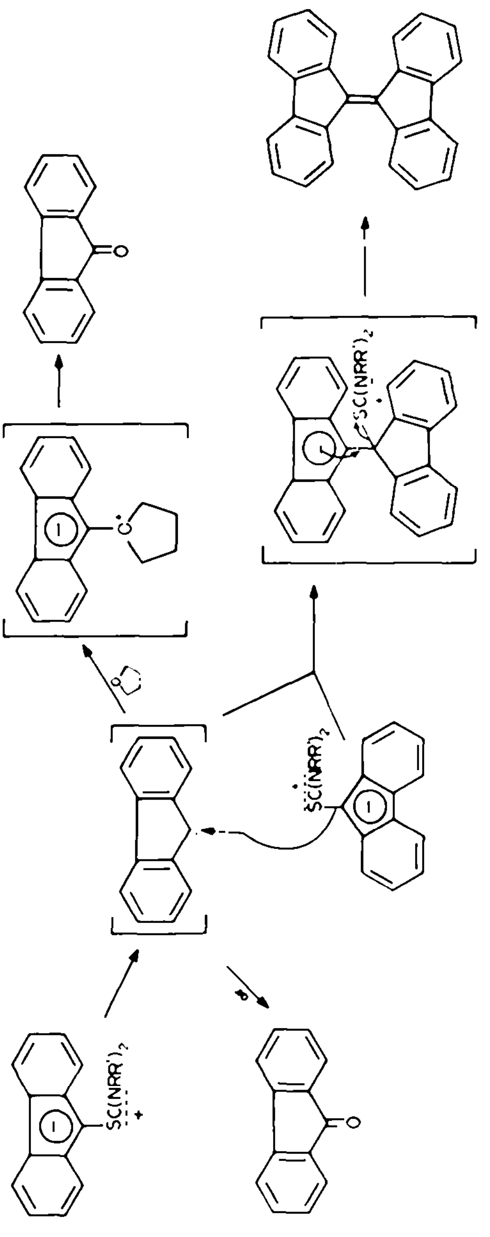
Thus all this evidence accords with the idea that these compounds exist as tautomeric mixtures, to which non-ylide forms 7 are the major contributors, but their chemical reactions, described below, are those of the ylide form, which must therefore contribute to the overall equilibrium. The situation thus closely resembles that in the only recorded guanidinium fluorenylide,[16] but is different in the case of selenouronium derivatives, also mentioned below. In the subsequent discussion the term ylide is used to refer to the tautomeric mixture of ylide and non-ylide.

The mass spectra of the fluorenylides normally showed fairly small molecular ion peaks but large peaks due to fluorenyl fragments and also moderate peaks due to S-fluorenyl.

Thermal decomposition. *N*-Alkyl substituted thiouronium fluorenylides appear to have decreased thermal stability as the number of *N*-substituents increases. Thus whereas the unsubstituted ylide **3a** could be kept indefinitely at room temperature, the *N,N'*-disubstituted ylides **3b**, **3c** could only be kept for a few days before extensive decomposition was evident, and the tetrasubstituted ylide **3g** was too unstable to allow its isolation from solution, even at low temperatures. A similar trend is found with thiouronium dicyanomethylides.[6] The difference must be connected at least in part with the tautomeric equilibrium discussed above, although steric crowding may also contribute. In air fluorenone is formed but in the absence of air in an inert solvent bifluorenylidene is the main product, presumably formed as shown in Scheme 1, by a method which has been proposed in the case of some other thermally unstable fluorenylides. If the solvent is tetrahydrofuran, fluorenone is formed even in the absence of air; a possible mechanism is proposed in Scheme 1, which involves transitory formation of an unstable oxonium ylide which in turn decomposes to give fluorenone. The *N*-aryl ylides **3d**–**3f** are stable indefinitely at room temperature, but decompose rapidly above their melting points. In air a high yield of fluorenone is obtained and carbene formation is again probably involved.

It may be noted that the present thiouronium fluorenylides show no tendency to undergo intramolecular ring closure to form thiirans or their breakdown products fulvenes, reactions which have been mentioned as characteristic properties of unstabilised thiouronium ylides.[6,7]

Hydrolysis. When the non-aryl substituted ylides **3a**–**3c** were treated with excess methanolic sodium hydroxide fluorenone was formed rapidly and in high yield. It seems likely that the hydroxide ion attacks the thiouronium carbon atom to give the corresponding urea and fluorenethione, which is then rapidly converted into fluorenone. The effect of the substituents on the rate of hydrolysis was noted by monitoring the growth of the peak at 256 nm in the electronic spectrum due to fluorenone. The resultant spectra show good isosbestic points and the rates were in the order **3a** > **3c** > **3b**; the



Scheme 1.

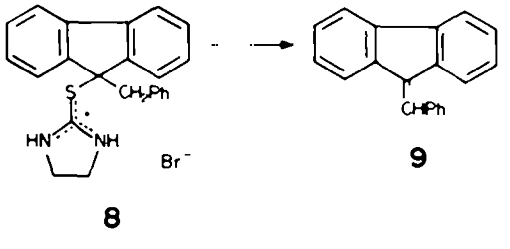
differences may be due to steric ease of approach of the hydroxide ion to the carbon atom.

Reaction with electrophiles

(i) *Protonation and basicity.* All the ylides **3** are protonated in strong acid to form the corresponding fluorenyl *iso*thiouronium salts **1**. The *N*-aryl ylides **3d–3f** are less basic than the other ylides. This is shown by the fact that the salts **1d–1f** may be converted into ylides by triethylamine, which is not basic enough to convert the other salts **1** into ylides.

The pK_a for the equilibrium **1** ⇄ **3** for the *N*-alkyl ylides must thus exceed 13 (Et_3N, $pK_a \sim 13$). These ylides are hence appreciably more basic than dimethylsulphonium fluorenylide (pK_a of conjugate acid in aq. dioxan = 7.3[12]). It has been suggested that the effectiveness of *d*-orbital overlap of a sulphonium ylide, which in turn causes reduced basicity of the ylide, is related to the degree of positive charge on the sulphur atom.[21] In the thiouronium ylides positive charge is delocalised from the sulphur atom onto the carbon and nitrogen atoms, which infers that they should be more basic than corresponding dialkylsulphonium ylides wherein comparable delocalization of the positive charge is not possible.

(ii) *Reaction with benzyl bromide.* When an ethereal solution of the ylide **3c** and benzyl bromide was kept at room temperature an almost colourless precipitate separated out. Attempts to characterise the product by converting it into a perchlorate or picrate failed since decomposition took place, but its mass spectrum suggested that it was the benzylfluorenyl salt **8**, since there was an intense fragment peak at *m/e* 254.110, corresponding to the fulvene **9** ($C_{20}H_{14}$ requires *m/e* 254.110), whose formation can be best rationalised from **8**. An analogous reaction has been reported with trimethylammonium fluorenylide; in this case the fulvene **9** was isolated by heating the initial reaction product.[24]



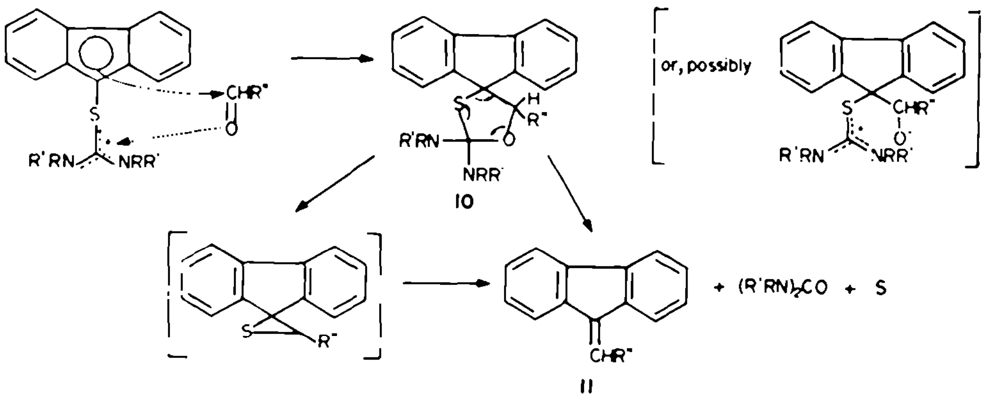
(iii) *Reactions with aldehydes.* The fluorenylides **3** reacted readily with *p*-nitrobenzaldehyde to give a fulvene (**11**, $R'' = C_6H_4NO_2(p)$) and the appropriate urea (see Table 4). The *N*-alkyl ylides are much more reactive than the *N,N'*-diphenyl ylide; this may be due to steric hindrance. The former are quite reactive ylides in that reaction takes place, albeit more slowly, with a less reactive aldehyde such as *p*-anisaldehyde, as well as with *p*-nitrobenzaldehyde, but no product was obtained from the reactive ketones *p*-nitroacetophenone or cyclohexanone. These ylides are thus of roughly comparable reactivity to triphenylphosphonium fluorenylide,[20] more reactive than dimethylsulphonium fluorenylide[12,23] and less reactive than tributylphosphonium[9] or triphenylarsonium[10] fluorenylides.

They differ from other sulphonium ylides, however, by forming alkenes rather than epoxides. The other product, isolated in effectively quantitative yield is a urea; elemental sulphur is also formed. It is possible that

Table 4. Reactions of fluorenylides with aldehydes

Ylide	N-substituents	Carbonyl compound	Reaction time	Reaction temp.§	Yield (%)
3a	—	p-$NO_2C_6H_4CHO$	16 hr	r.t.	90
3b	N,N'-dimethyl	p-$NO_2C_6H_4CHO$	20 hr	r.t.	85
3b	N,N'-dimethyl†	p-$NO_2C_6H_4CHO$	1 hr	r.t.	40
3c	N,N'-ethylene	p-$NO_2C_6H_4CHO$	20 hr	r.t.	89
3d	N,N'-diphenyl	p-$NO_2C_6H_4CHO$	72 hr	61°	1.5
3e	tetramethyl†	p-$NO_2C_6H_4CHO$	1 hr	r.t.	40
3c	N,N'-ethylene	p-$MeOC_6H_4CHO$	19 days	r.t.	30
3c	N,N'-ethylene	p-$NO_2C_6H_4COMe$	28 days	r.t.	0‡
3b	N,N'-dimethyl†	PhCH:CHCHO	48 hr	r.t.	28
3b	N,N'-dimethyl†	cyclohexanone	13 days	r.t.	0

†Ylide not isolated; reaction *in situ*.
‡Gave bifluorenylidene (22%).
§r.t. – room temperature.



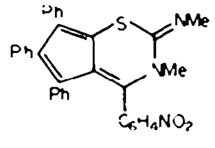
reaction proceeds by a homo-Wittig mechanism with a five atom, instead of the usual four atom, transition stage **10**. This intermediate stage could either collapse directly to the alkene and urea, or via a thiiran which then extrudes sulphur. The driving force could be the formation of the very stable ureas.

N,N'-Dimethylthiouronium tetraphenylcyclopentadienylide **5** also reacted with p-nitrobenzaldehyde to give a very small yield of a fulvene but the triphenylcyclopentadienylides **4a**, **4b** gave only small amounts of the expected fulvenes together with other coloured products which are tentatively assigned the pseudoazulenoid structures **12** and **13**, both of which can also have canonical structures with ten peripheral π-electrons. p-Anisaldehyde reacted in the same way with **4b** to give an anisyl analogue of **13**.

Formation of such products involves attack by the aldehyde on the free 5-position of the cyclopentadienide ring rather than at the 1-position as in a normal Wittig reaction, with concomitant attack at one of the thioureido nitrogen atoms. The oxidation level of the product could be achieved by a hydride transfer to a further aldehyde molecule and this would be consistent with the observation that the highest yield obtainable appeared to be 32%, because half the aldehyde present is required for this oxidation process, being itself reduced to benzyl alcohol.

The structures **12** and **13** are assigned on the basis of molecular formulae and PMR spectra, and by the fact that **13** can be dehydrogenated to a purple product which has the molecular formula and spectrum consistent with structure **14**, which has a peripheral 14 π-electron system. Dehydrogenation could be brought about by o-chloranil or dichlorodicyanobenzoquinone but not by benzoquinone.

Also in accord with the proposed structure, compound **14** is extraordinarily stable. It does not decompose in air at its melting point (~300°) and its mass spectrum shows a single peak at m/e 253 (M^+), with the absence of any significant breakdown. On addition of bromine to **14** in methylene chloride an intensely purple coloured solution resulted but work-up procedures provided only unreacted starting material. When this purple solution was examined by TLC using chloroform–methanol as eluant, initially a purple spot was seen which lagged behind a spot of **14** on a comparative run, but once development of the plate was complete, the purple colour had disappeared and the resultant spot and the spot of authentic **14** had the same R_f values. This compound thus appears to form a molecular



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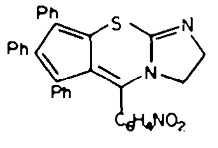

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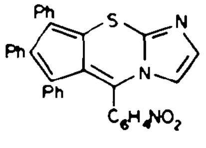

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complex with bromine instead of undergoing electrophilic substitution, which is characteristic of very stable heterocyclic systems.

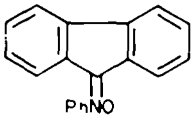
(iv) *Reactions with nitrosobenzene.* The fluorenylides react with nitrosobenzene, but instead of giving fluorenone anil, as might be expected by analogy with their reactions with aldehydes, they give the anil oxide **15** and a thiourea. The formation of anil oxides in reactions of ylides with nitrosobenzene is thought to derive from spontaneous ring-opening of an oxaziran, formed analogously to an epoxide in the reaction of an ylide with a carbonyl compound.[26] The reason for the different mode of reaction of these fluorenylides with aldehydes and with nitrosobenzene is not obvious, but it is possible that a five atom transition stage comparable to **10** is again involved but that this then fragments in a different way to give an oxaziran and a thiourea. As with aldehydes the *N,N'*-dialkyl ylides reacted faster than the *N,N'*-diphenyl ylide. The tetraphenylcyclopentadienylide **5** provided both fluorenone anil and anil oxide, while the triphenylcyclopentadienylide **6b** again provided an unexpected product, which was dark blue and had a moleculear weight and formula corresponding to a dimer of triphenylcyclopentadienone anil less two hydrogen atoms. Its NMR spectrum showed only phenyl resonances and the structure is unknown.

Dipolar addition reactions. If the reactions of thiouronium fluorenylides with aldehydes or nitrosobenzene proceed as suggested via a 5-membered ring transition stage then it seemed likely that these ylides might also undergo other 1,3-dipolar cycloaddition reactions. When the ylide **3c** was heated with dimethyl acetylenedicarboxylate in chloroform a product was isolated whose molecular formula and PMR spectrum corresponded with those expected for the cycloadduct **16**.

Attempted preparation of an unsubstituted cyclopentadienylide. Cyclopentadienylides unsubstituted in the 5-membered ring **17** have been prepared by the action of base on cyclopentene–bisheteronium salts **18**.[27] Treatment of the salt **19** with triethylamine provided the bis*iso*thioureido compound **20** instead of a cyclopentadienylide. No trace of ylide could be found although the mass spectrum of the product showed an intense peak at *m/e* 166 corresponding to the molecular formula of the ylide or a tautomer, presumably formed by elimination of a thiourea moiety.

Attempted preparation of a selenouronium ylide. 9-Bromofluorene reacted readily with *N,N'*-diphenylselenourea to give the selenouronium salt **21**, and when this salt was treated with triethylamine a free base was liberated. Like the corresponding thiourea derivatives this might have either an ylide structure **22** or a fluorenylselenourea structure **23** or exist as an equilibrium mixture of the two species. All the available evidence suggests that only structure **23** contributes.

The failure of this compound to react with nitrosobenzene indicates the absence of an ylide form, for the sulphur analogue **3d** reacts readily with this reagent, yet selenonium ylides are normally more reactive towards aldehydes than are sulphonium ylides.[28] Treatment of the salt **21** with base provides no change in the electronic spectrum and there is no additional peak at longer wavelength as appears when fluorenylthiouronium salts are treated with base. In the PMR spectrum, in addition to signals due to aryl protons, two signals each due to one proton appear, again consistent with structure **23**.



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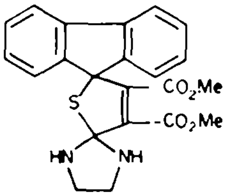

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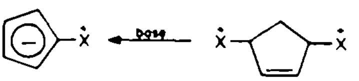
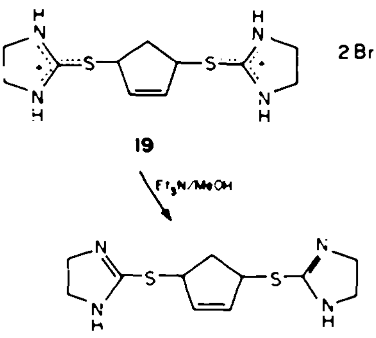


17 **18**

X = pyridine, PPh_3, SMe_2, $AsPh_3$



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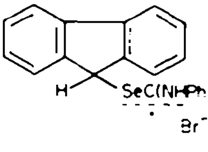

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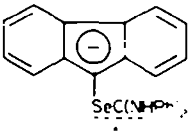

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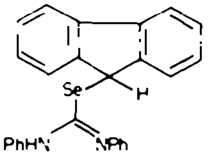


23

Attempted preparation of guanidinium ylides. Treatment of *N,N'*-ethylene-*N''*-(9-fluorenyl)guanidinium iodide with base gave a product which, from its molecular formula and properties, appeared to be a tautomeric mixture of fluorenylguanidine and guanidinium fluorenylide [**24**, $RR = -(CH_2)_2-$].[16] The guanidinium salt was prepared by the reaction between 9-aminofluorene and *S*-methyl-*N,N'*-ethylene*iso*thiouronium iodide but similar attempted reactions using either *N,N',S*-trimethyl- or *S*-methyl-*N,N'*-diphenyl*iso*thiouronium salts gave none of the desired products.

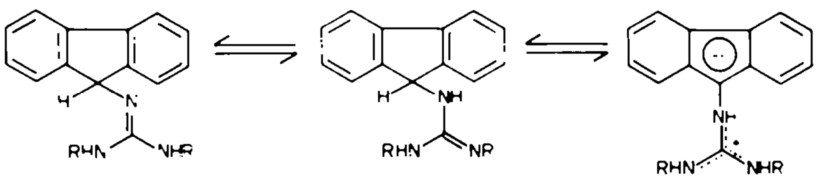
An alternative approach to guanidinium fluorenylides was therefore investigated involving thermal decomposition of 9-diazofluorene in the presence of a guanidine. When diazofluorene and *N,N'*-diphenylguanidine were melted together a high yield of fluorenone ketazine was obtained but if copper bronze was added to the mixture a product (**25**; see later) was obtained in low yield (22%) whose composition corresponded with that of the ylide or fluorenyl compound (**24**, R = Ph), together with some fluorenone ketazine and bifluorenylidene. Fluorenone ketazine is known[14] to be formed by reaction of 9-diazofluorene with some fluorenylides so it seems likely that in the absence of catalyst, as soon as any ylide is formed it reacts further with undecomposed diazofluorene. In accord with this suggestion, if product **25** was kept with diazofluorene at room temperature for several weeks, fluorenone ketazine was formed.

Because of the low yield of **25** an alternative mode of preparation, by the reaction of 9-aminofluorene with *N,N'*-diphenylcarbodiimide, generated *in situ* by reaction of *S*-methyl-*N,N'*-diphenyl*iso*thiourea with silver nitrate,[29] was investigated. This gave a good yield of a product which also analysed correctly for (**24**, R = Ph) but which was different from product **25**. Its mode of formation made it likely that it indeed had a structure **24**, which in turn suggests that the product got from diazofluorene had the isomeric structure **25**. Evidence to support this comes from the mass spectra of the two compounds, for **25** shows a fragment peak corresponding to *N*-phenyl-9-aminoguanidine, while no such peak occurs in the spectrum of **24**. It is surprising that reaction should take place at the more hindered and less nucleophilic nitrogen atom to give **25** but attack on such a nitrogen atom is evidently feasible since 9-diazofluorene reacts similarly with *sym*-triphenylguanidine.

When diazofluorene is heated with guanidine in the presence of copper bronze fluorenone ketazine alone was isolated, probably formed via the ylide; in the absence of catalyst reaction proceeded explosively.

With *N,N,N',N'*-tetramethylguanidine in the presence of copper bronze reaction took place even at −20°. Fluorenone ketazine was again formed, in almost quantitative yield at −20°, and accompanied by increasing quantities of bifluorenylidene as the reaction temperature was raised. The very low temperature at which reaction ensues suggests that at any rate in this instance, carbenic decomposition of the diazo-compound is not the first step. Diazofluorene reacts with triphenylphosphine at room temperature to give a phosphinazine,[30] and it seems possible that it reacts similarly with the tetramethylguanidine to give an unstable azine **26** which decomposes to give nitrogen plus the ylide which in turn either reacts with more diazo-compound to form the ketazine, or decomposes to give bifluorenylidene, with the latter reaction contributing more with increased temperature. Phosphinazines decompose when heated and in some cases phosphonium ylides have been isolated.[30,31]

Compound (**24**, R = Ph) showed no ylide-like properties, for example it was decomposed by acid and did not undergo a Wittig-type reaction with nitrosobenzene. Unlike (**24**, $RR = -(CH_2)_2-$),[16] and the diphenylthiouronium analogue **3d** but like the selenium analogue **23**, this aryl derivative (**24**, R = Ph) thus apparently effectively exists entirely in the non-ylide tautomeric form.



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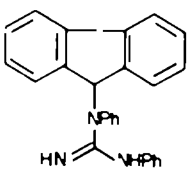


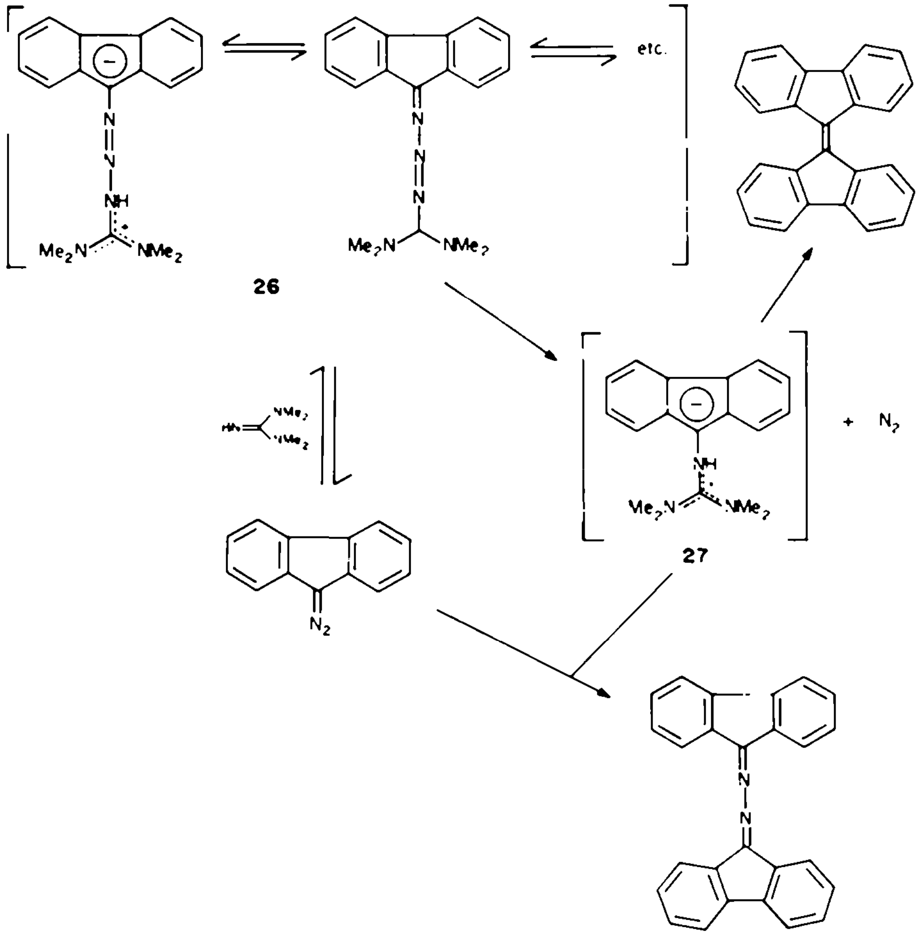
25

Again the totally different properties of the *N,N,N',N'*-tetramethyl derivative **27**, which must perforce have an ylide structure, may be noted; this difference is in complete accord with the previously mentioned difference between tetra-*N*-substituted and *N,N'*-disubstituted thiouronium ylides.

EXPERIMENTAL

Light petroleum refers to alkane fraction b.p. 60–80° unless otherwise stated. Column chromatography was carried out on either activated alumina, type H (100/200 mesh) or on silica gel, grade M60. Thin-layer chromatograms (TLC) were run on silica coated plates, MN Kieselgel G. Samples analysed by means of molecular weight determinations were pure (TLC, spectra) unless otherwise indicated. Electronic spectra were recorded in methanolic solution unless stated otherwise. All m.ps are uncorrected. Tetrahydrofuran was distilled from $LiAlH_4$.

S-(9-*Fluorenyl*)iso*thiouronium salts*. Equimolar amounts of 9-bromofluorene and the appropriate thiourea in ethanol (*ca.* 15 ml solvent/0.01 mol of reactants) were heated under reflux for the times indicated below. If the thiouronium salt did not precipitate on cooling the solution was concentrated *in vacuo*. The precipitated bromide was filtered off, washed well with ether, and recrystallised from methanol or ethanol. Perchlorates were prepared by adding an equimolar amount of perchloric acid (70%) to a slurry of the bromide in methanol. The mixture was then warmed until the solid had dissolved. If the perchlorate did not separate out when the mixture was cooled a small amount of water was added to assist its precipitation. Perchlorates were recrystallised from methanol. By this means the following fluorenyl*iso*thiouronium salts were prepared: N-*unsubstituted bromide* **1a** (15 min) m.p. 216–219° (90%) (Found: C, 52.3; H, 4.0; N, 8.7. $C_{14}H_{13}BrN_2S$ requires: C, 52.3; H, 4.0; N, 8.7%); N-*unsubstituted perchlorate*, m.p. 144–147° (47%) (Found: C, 49.0;



H, 3.9; N, 8.2. $C_{14}H_{13}ClN_2O_4S$ requires: C, 49.3; H, 3.8; N, 8.2%); N,N'-*dimethyl bromide* **1b** (1 h), m.p. 95–108° (86%); N,N'-*dimethyl perchlorate*, m.p. 65–72° (56%) (Found: C, 51.6; H, 4.8; N, 7.5. $C_{16}H_{17}ClN_2O_4S$ requires: C, 52.1; H, 4.6; N, 7.6%); N,N'-*ethylene bromide* **1c** (15 min), m.p. 232–238° (96%); N,N'-*ethylene perchlorate*, m.p. 202–204° (86%) (ylide analysed); N,N'-*diphenyl bromide* **1d** (30 min; precipitated by excess ether), m.p. 167–169° (89%) (Found: C, 65.5; H, 4.7; N, 5.7. $C_{26}H_{21}BrN_2S$ requires: C, 65.9; H, 4.4; N, 5.9%); N-*phenyl bromide* **1e** (30 min), m.p. 164–168° (79%) (ylide analysed); N-*methyl*-N'-*phenyl bromide* **1f** (30 min), m.p. 197–200° (95%) (Found: C, 61.2; H, 4.9; N, 6.9. $C_{21}H_{19}BrN_2S$ requires: C 61.3; H, 4.7; N, 6.8%); N,N,N',N'-*tetramethyl bromide* **1g** (90 min), converted *in situ* into *perchlorate*, m.p. 167–169° (64%) (Found: C, 54.3; H, 5.4; N, 7.2. $C_{18}H_{21}ClN_2O_4S$ requires: C, 54.5; H, 5.3; N, 7.1%). Spectra are listed in Tables 1 and 2. Yields for perchlorates are overall yields from bromofluorene.

S-(2,3,4-*Triphenylcyclopentadienyl*)iso*thiouronium salts*. Equimolar quantities of 5-chloro- (or 5-bromo-) 2,3,4-triphenylcyclopentadiene[14a] and the thiourea in ethanol (60–70 ml solvent/0.01 mol of reactants) were heated under reflux for the times specified. The hot solution was filtered and cooled. If the thiouronium salt did not precipitate the solution was concentrated *in vacuo*, ether was added and the mixture was stirred to precipitate the salt. When necessary the halide salts were purified by reprecipitation from ethanolic solution by ether. Picrates were prepared by addition of an equimolar quantity of a saturated methanolic solution of picric acid to a hot saturated solution of the chloride in methanol. When the solutions cooled the picrates separated and were recrystallised from methanol. A perchlorate was prepared similarly using perchloric acid (70%). The following salts were prepared in this way: N-*unsubstituted chloride* (6 days), m.p. 155° (decomp) (74%); N-*unsubstituted bromide* (30 min), m.p. 170–185° (71%) (Found: C, 63.7; H, 4.8; N, 6.1. $C_{24}H_{21}BrN_2S$ requires: C, 64.1; H, 4.7; N, 6.2%); N-*unsubstituted picrate*, m.p. 198–201°, λ_{max} 235, 341, 410 (sh) nm (log ϵ = 4.48, 4.53, –), $\tau([^2H_6]DMSO)$ 0.92 (s, 2H), 2.82 (m, 15H), 5.93 (m, 1H), 6.48 (m, 1H) (Found: C, 59.9; H, 3.7; N, 11.5. $C_{30}H_{21}N_5O_7S$ requires: C, 60.3; H, 3.8; N, 11.7%); N,N'-*dimethyl chloride* (6 days), m.p. 204–207° (70%) τ ($[^2H_6]DMSO$) 2.80 (m, 16H), 5.92 (s, 1H), 6.61 (s, 2H), 7.05 (m, 6H); N,N'-*dimethyl picrate*, m.p. 155–158°, λ_{max} 235 sh, 347, 410 (sh) nm (log ϵ = –, 4.32, –), $\tau(C^2HCl_3)$ 1.24 (s, 2H), 2.90 (m, 16H), 6.05 (s, 1H), 6.56 (s, 2H), 6.91 (m, 6H), light sensitive, (Found: N, 10.7. $C_{32}H_{27}N_5O_7S$ requires: N, 11.2%); N,N'-*ethylene chloride* (3 days), m.p. 218–224° (96%) $\tau([^2H_6]DMSO)$ 2.80 (m, 16H), 5.89 (s, 2H), 6.13 (s, 4H); N,N'-*ethylene picrate*, m.p. 182–184°, λ_{max} 232 sh, 344 nm (log ϵ = –, 4.37), (Found: C, 61.3; H, 4.0; N, 10.9. $C_{32}H_{25}N_5O_7S$ requires: C, 61.6; H, 4.0; N, 11.2%); N,N,N',N'-*tetramethyl chloride* (5 days), m.p. 163–169° (64%); N,N,N',N'-*tetramethyl perchlorate*, m.p. 220–223° (54% overall) λ_{max} 245, 262 sh, 340 nm log ϵ = 4.32, –, 3.92), $\tau(C^2HCl_3)$ 2.83 (m, 15H), 6.14 (s, 2H), 6.81 (s, 12H) (Found: C, 63.8; H, 5.6; N, 5.2. $C_{28}H_{29}ClN_2O_4S$ requires: C, 64.1; H, 5.5; N, 5.3%).

N,N' - *Dimethyl* - S - (2,3,4,5 - *tetraphenylcyclopentadienyl*)iso*thiouronium bromide*. Prepared as the triphenylcyclopentadienyl salts this pale yellow *bromide* (93%) had m.p. 157–170° (from methanol–ether), λ_{max} (ether) 247, 335 nm, $\tau(C^2HCl_3)$ 2.82 (m, 20H), 3.89 (s, 1H), 7.2 (m, 6H).

*Reactions of S-fluorenyl*iso*thiouronium salts with phenyl lithium*. (For spectra of products see Tables 1 and 2).

(a) *S*-Fluorenyl*iso*thiouronium perchlorate (8.18 g, 24 mmol) was dissolved in dry tetrahydrofuran (80 ml). A freshly prepared ethereal solution of phenyl lithium (0.90M, 26.6 ml, 24 mmol) was added with stirring and under a stream of nitrogen. The solution was stirred for a further 20 min. Solvent was then removed *in* *vacuo* and the residue was extracted with methylene chloride (100 ml). The extract was washed with water (5 × 100 ml), dried ($MgSO_4$) and evaporated *in vacuo*. Needles (1.16 g) which precipitated were filtered off and washed with ether. Further removal of solvent and trituration of the residue with ether provided a further crop (1.12 g) which was filtered off and washed with light petrol (b.p. 40–60°) and then ether-light petrol (b.p. 40–60°). Total yield of *thiouronium fluorenylide* **3a** was 40%, m.p. 120–122° (Found: C, 69.8; H, 4.9; N, 11.8. $C_{14}H_{12}N_2S$ requires: C, 70.0; H, 5.0; N, 11.7%).

(b) N,N'-*Dimethylthiouronium fluorenylide* **3b** (83%), m.p. 111–112° [from methylene chloride-light petrol (b.p. 40–60°)] was prepared in the same way from the *N,N'*-dimethylthiouronium perchlorate (Found: C, 71.5; H, 6.1; N, 10.4. $C_{16}H_{16}N_2S$ requires: C, 71.6, H, 6.0; N, 10.4%). It was stored at −40°.

(c) N,N'-*Ethylenethiouronium fluorenylide* **3c** (68%), m.p. 101–104° was prepared similarly from the *N,N'*-ethylenethiouronium perchlorate. (Found: C, 71.5; H, 5.0; N, 10.9. $C_{16}H_{14}N_2S$ requires: C, 72.1; H, 5.2; N, 10.5%). It was stored at −40°.

(d) N,N'-*Diphenylthiouronium fluorenylide* **3d** (83%) prepared similarly from the *N,N'*-diphenylthiouronium bromide had m.p. 125–128° (Found: C, 79.3; H, 5.0; N, 7.3. $C_{26}H_{20}N_2S$ requires: C, 79.6; H, 5.1; N, 7.1%).

Reactions of S-fluorenylisothiouronium salts with triethylamine. (For spectra of products see Tables 1 and 2).

(a) Triethylamine (0.3 ml, 2.2 mmol) was added to a solution of *S*-fluorenyl-*N,N'*-diphenylthiouronium bromide (950 mg, 2 mmol) in methanol (7 ml). The precipated solid was filtered off immediately and washed with methanol (730 mg, 94%). It had m.p. 128–130° and was identical to the ylide **3d** prepared by the use of phenyl lithium.

(b) Triethylamine (1.5 ml, *ca.* 11 mmol) was added to a slurry of *S*-fluorenyl-*N*-phenyl*iso*thiouronium bromide (3.97 g, 10 mmol) in methanol (10 ml). A transient clear solution resulted but N-*phenylthiouronium fluorenylide* **3e** soon precipitated and was filtered off and washed with a small amount of methanol (2.9 g, 92%), m.p. 120–124° (from methanol) (Found: C, 75.8; H, 5.3; N, 9.0. $C_{20}H_{16}N_2S$ requires: C, 76.0; H, 5.1; N, 9.0%).

(c) Triethylamine (1.5 ml, *ca.* 11 mmol) was added to a warm solution of *S*-fluorenyl-*N*-methyl-*N'*-phenylthiouronium bromide (4.11 g, 10 mmol) in warm methanol (30 ml). When the solution cooled needles of N-*methyl*-N'-*phenylthiouronium fluorenylide* **3f** formed and were filtered off and washed with methanol (2.8 g, 85%), m.p. 145–147° (Found: C, 76.4; H, 5.7; N, 8.4. $C_{21}H_{18}N_2S$ requires: C, 76.3; H, 5.5; N, 8.5%).

Cyclopentadienylides. The ylides **4a**, **4b** and **5** were prepared by addition of an ethereal solution of phenyl lithium (*ca.* 1–1.3*M*, 2.2 mmol) to a suspension of the appropriate thiouronium salt (2 mmol) in dry tetrahydrofuran and the solutions were used immediately.

2,3,4-*Triphenylcyclopentadienylthiol.* *S*-(2,3,4-Triphenylcyclopentadienyl)thiouronium bromide (400 mg, 1 mmol) was dissolved in t-butanol (70 ml) and a solution of potassium t-butoxide (0.5 g potassium in 1 ml t-butanol) was added. The *thiol* separated as a yellow solid (90 mg, 28%), m.p. 193–196° [from benzene-light petroleum (1:1)]. A less pure product (44%) was obtained when aqueous sodium hydroxide was used as base. (Found: C, 83.5; H, 5.4; N, 0.0. $C_{23}H_{18}S$ requires: C, 84.6; H, 5.5; N, 0.0%).

Attempted preparations of ylides **4c**, **4d**. (a) *S*-(2,3,4-Triphenylcyclopentadienyl)-*N,N,N',N'*-tetramethylthiouronium perchlorate (1.05 g, 2 mmol) was treated with an ethereal solution of phenyl lithium (1.06 M, 2.05 ml, 2.2 mmol). A red solid was obtained on trituration with ether. It was washed with ether and reprecipitated from methylene chloride by ether to give a product possibly **6a**, (220 mg, 26%) m.p. 146–155° (decomp.), τ (C^2HCl_3) 2.93 (m, 16H), 7.16 (m, 12H) (Found: M 422.181. $C_{28}H_{26}N_2S$ requires: 422.182).

(b) Ethereal phenyl lithium (0.84M, 4.5 ml, 3.85 mmol) was added to a suspension of *S*-(2,3,4-triphenylcyclopentadienyl)thiouronium chloride (1.40 g, 3.5 mmol) in dry tetrahydrofuran. The solution was stirred for 20 min and solvent was then removed *in vacuo*. The residue was dissolved in methylene chloride and dried ($MgSO_4$). Removal of the solvent left a residue which, on trituration with ether-light petroleum (b.p. 40–60°) (1:6) (80 ml) gave a pale yellow solid, possibly **6b** (950 mg, 71%), m.p. 153–163° (decomp.), τ (C^2HCl_3) 2.88 (m), 6.3 (br. s). (Found: M 366.118. $C_{24}H_{18}N_2S$ requires: 366.119).

Reaction of ylide **3c** *with benzyl bromide.* Benzyl bromide (1.13 g, 6.6 mmol) was added to a solution of the ylide **3c** (1.60 g, 6 mmol) in ether (50 ml) and the mixture was kept at room temperature for 16 days. A solid was filtered off (400 mg, 14%) m.p. 150° (decomp) whose mass spectrum suggested it was the *S*-(9-benzylfluorenyl)thiouronium salt **8** [intense fragment peak at *m/e* 254.110; fulvene **9** requires M 254.110]. τ ($^2H_6$-DMSO) 2.05 (m, 5H), 2.42 (m, 8H), 6.00 (s, 4H), 6.16 (d, 2H).

Reactions of fluorenylides with aldehydes or ketones. In general a solution of equimolar quantities of the ylide and aldehyde or ketone in methylene chloride were kept at room temperature for the times listed in Table 4, wherein yields are also given. A typical example (a) is given.

(a) Ylide **3c** and *p*-nitrobenzaldehyde. After 20 h the solution was washed thrice with water and dried ($MgSO_4$). The aqueous washings were evaporated *in vacuo* to give *N,N'*-ethyleneurea (84%). Removal of methylene chloride *in vacuo* gave yellow crystals of *p*-nitrobenzylidenefluorene (89%), m.p. (from ethanol) and mixed m.p. 166–168°. An insoluble pale yellow residue from the recrystallisation was washed well with ethanol to give sulphur (8%) (M 255.781. S requires 255.777; correct breakdown pattern). Other reactions listed in Table 4 were conducted similarly but sometimes, in the cases listed below, modified work-up procedures were required.

(b) Ylide **3d** and *p*-nitrobenzaldehyde. A solution of the ylide (980 mg, 2.5 mmol) and *p*-nitrobenzaldehyde (378 mg, 2.5 mmol) in carbon tetrachloride (25 ml) was heated under reflux for 3 days. The solution was filtered and solvent was evaporated *in vacuo*. The yellow residue was dissolved in benzene (3 ml) and applied to an alumina column prepared with benzene–light petroleum (1:1). Elution with this solvent gave an orange band of bifluorenylidene (8 mg, *ca.* 1%) followed by a yellow band, which after removal of solvent and trituration with ethanol gave yellow crystals of *p*-nitrobenzylidenefluorene (m.p. and m.m.p. 160–166°).

(c) Ylide **4c** and *p*-anisaldehyde. The crude product was chromatographed on alumina with benzene as solvent and eluant to provide *p*-methoxybenzylidenefluorene, m.p. 125–128° (from acetic acid) (lit. 128–129°).[12]

Reaction of tetraphenylcyclopentadienylide **5** *with p-nitrobenzaldehyde.* A soln of the ylide (3 mmol) in tetrahydrofuran was freshly prepared. *p*-Nitrobenzaldehyde (453 mg, 3 mmol) was added to the stirred solution. Stirring was continued for a further 2 h and the solution was then kept for 16 h. Solvent was removed *in vacuo* and the residue was dissolved in methylene chloride. The solution was washed four times with water, dried ($MgSO_4$) and evaporated *in vacuo*. This residue was chromatographed on silica gel with benzene-light petroleum (1:1) as eluant to give 6-*p*-nitrobenzylidene-1,2,3,4-tetraphenylfulvene (5 mg, 0.3%), identical (m.p., m.m.p.) with an authentic sample (M 503.189. Calc. for $C_{36}H_{25}NO_2$ 503.188).

Reactions of triphenylcyclopentadienylides **4a**, **4b** *with aldehydes.* (a) A solution of the ylide **4a** in tetrahydrofuran was prepared from its hydrochloride (3.02 g, 7 mmol) and an ethereal solution of phenyl lithium (1.20 M, 7.0 ml, 8.4 mmol). *p*-Nitrobenzaldehyde (1.06 g, 7 mmol) was added, with stirring. Stirring was continued for 2 hr and the solution was kept overnight. Solvent was evaporated *in vacuo* and a solution of the residue in methylene chloride (50 ml) was washed with water (4 × 75 ml) and dried ($MgSO_4$). Solvent was removed and a solution of the residue in the minimum quantity of benzene was applied to an alumina column. Elution with benzene–light petroleum (1:2) brought off an unidentified green product (50 mg) insoluble in common solvents but soluble in trifluoroacetic acid giving a purple solution, followed by a brown product which was triturated with methanol to give 6-*p*-nitrophenyl-2,3,4-triphenylfulvene (20 mg, 0.7%) m.p. and m.m.p. with an authentic sample, 145–151°. Benzene–light petroleum (3:1) then brought off an orange product (140 mg, 3.7%) believed to be the *pseudoazulene* **12**, m.p. 263–264° (from benzene then nitromethane), λ_{max} ($CHCl_3$)

394 nm (log ϵ = 4.06), τ (TFA) 2.82 (m, 19H), 6.82 (s, 3H), 6.87 (s, 3H) (Found: N, 7.9%; M 527.166. $C_{33}H_{25}N_3O_2S$ requires: N, 8.0%; M 527.167).

(b) The ylide **4b** (2 mmol) was prepared and reacted with *p*-nitrobenzaldehyde (2 mmol) as in (a). Chromatography of the product (alumina/methylene chloride) provided red-brown crystals (135 mg, 13%) believed to be the *heterocycle* **13**, m.p. 279–286°, ν_{max} (Nujol) 1515, 1345 cm^{-1}, τ (TFA) 2.78 (m, 19H), 5.79 (s, 4H) (Found: M 525.150. $C_{33}H_{23}N_3O_2S$ requires: M 525.151), followed by 6-*p*-nitrophenyl-2,3,4-triphenylfulvene (20 mg, 2.5%), m.p. and m.m.p. 165–172°. When the reaction mixture was kept for 3 days, the yield of **13** rose to 32% and it could be isolated merely by evaporating the methylene chloride solution and triturating the residue with acetone.

(c) A solution of the ylide **4b** (7.5 mmol) and *p*-anisaldehyde (7.5 mmol) in tetrahydrofuran was kept for 5 weeks. Chromatography on alumina with benzene-light petroleum (1:2) provided 6-*p*-anisyl-2,3,4-triphenylfulvene (10 mg, 0.3%), m.p. 136–150° (Found: M 412.182. $C_{31}H_{24}O$ requires: M 412.183), and with benzene-ether (95:5) a red product presumed to be the analogue of **13** (140 mg, 3.7%), m.p. 259–265° (Found: M 510.176. $C_{34}H_{26}N_2OS$ requires: M 510.176).

Dehydrogenation of product **13**. A solution of **13** (790 mg, 1.5 mmol) and chloranil (738 mg, 3 mmol) in toluene (25 ml) was heated under reflux for 16 hr. The solution was filtered hot and the residue was washed with benzene until the washings were colourless. The combined filtrate and washings were evaporated *in vacuo* and the residue was chromatographed on alumina. Methylene chloride brought off the *heteroannulene* **14** (120 mg, 15%) m.p. 299–301° (from nitromethane), λ_{max} ($CHCl_3$) 289, 376, 520 nm (log ϵ = 4.49, 4.15, 2.91), ν_{max} (Nujol) 1520, 1350 cm^{-1}, τ (C^2HCl_3) 2.85 (m), (TFA) 2.70 (m) (Found: N, 8.0%; M 523.136. $C_{33}H_{21}N_3O_2S$ requires: N, 8.0%; M 523.135).

Reactions of fluorenylides with nitrosobenzene. (a) A soln of nitrosobenzene (320 mg, 3 mmol) in ether–benzene (1:1) (25 ml) was added to a solution of ylide **3c** (800 mg, 3 mmol) in ether (30 ml). After 10 min the solvent was removed *in vacuo* and the residue was dissolved in methylene chloride (50 ml). This solution was washed with water (2 × 30 ml), dried ($MgSO_4$) and evaporated *in vacuo*. The residue crystallised when cooled and was the anil oxide **15** (580 mg, 72%), m.p. 193–195° (from ethanol) (lit. m.p. 189–191°[28]). When a similar reaction was carried out in benzene, after 3 weeks crystals of *N,N'*-ethylenethiourea (130 mg, 61%) separated out, and the anil oxide (78%) was also obtained.

(b) A solution of the ylide **3d** (980 mg, 2.5 mmol) and nitrosobenzene (270 mg, 2.5 mmol) in methylene chloride (20 ml) was kept at room temperature for 24 hr, then concentrated *in vacuo* and chromatographed (alumina/methylene chloride). In turn this provided unreacted ylide (30 mg, 3%), the anil oxide **15** (460 mg, 69%) and *N,N'*-diphenylthiourea (260 mg, 44%).

Reaction of tetraphenylcyclopentadienylide **5** *with nitrosobenzene*. Nitrosobenzene (55 mg, 0.5 mmol) was added to a freshly prepared soln of the ylide (0.5 mmol) in chloroform. Chromatography of the reaction mixture on alumina with benzene-light petroleum as eluant provided (i) *N*-phenyl-2,3,4,5-tetraphenylcyclopentadienone anil (15 mg, 6.5%), m.p. (from methanol) and mixed m.p. 223–227°, (ii) 2,3,4,5-tetraphenylcyclopentadienone (30 mg, 16%), m.p. (from methanol) and mixed m.p. 215–219°, and with benzene as eluant provided *N*-phenyl-2,3,4,5-tetraphenylcyclopentadienone ketoxime (30 mg, 12.5%), m.p. (from 1-propanol) and mixed m.p. 219–221°.

Reaction of triphenylcyclopentadienylide **4b** *with nitrosobenzene*. Nitrosobenzene (110 mg, 1 mmol) was added to a freshly prepared solution of the ylide (1 mmol) in chloroform. Examination of the resultant solution by TLC showed that no trace of 2,3,4-triphenylcyclopentadienone anil or anil oxide was present. After 75 min the solution was chromatographed on alumina and methylene chloride brought off a deep blue product (55 mg, 14.5%), τ (C^2HCl_3) 2.9 (m), which, after trituration with methanol had m.p. 132–147° and had M corresponding to a dimer of the anil less 2 hydrogen atoms (Found: M 764.317. $C_{58}H_{40}N_2$ requires: M 764.319).

Reaction of ylide **3e** *with dimethyl acetylenedicarboxylate*. A soln of the ylide (800 mg, 3 mmol) and the acetylenic ester (470 mg, 3.3 mmol) in chloroform (15 ml) was heated under reflux for 14 hr. After evaporation of the solvent *in vacuo* the residue was dissolved in the minimum quantity of benzene and applied to an alumina column. Elution with benzene-light petroleum (1:1) provided an unidentified orange solid (35 mg), m.p. 97–100°, and tetrahydrofuran brought off the buff *cycloadduct* **16** (80 mg, 6%) m.p. 110° (decomp), τ (C^2HCl_3) 2.50 (m, 8H), 6.15 (m, 10H) (M 408.114. $C_{22}H_{20}N_2O_4$ requires: M 408.114).

Cyclopentene-3,5-*bis*(N,N'-*ethylene*iso*thiouronium*)*dibromide* **19**. A solution of 3,5-dibromocyclopentene (0.1 mol) in chloroform 21 ml), prepared from cyclopentadiene and bromine in chloroform, was added to a suspension of *N,N'*-ethylenethiourea (20.4 g, 0.2 mol) in methanol (200 ml). The mixture was heated under reflux for 1 hr. Removal of solvent *in vacuo* left a residue which was dissolved in cold water (250 ml). The solution was washed with methylene chloride (2 × 150 ml). Solvent was removed *in vacuo* and the viscous residue was stirred with acetone. Crystallisation was completed in 1 hr. The crystals were filtered off, dissolved in the minimum amount of methanol and reprecipitated by excess ether. The precipitate was filtered off and washed with ether to give the *dibromide* (18.0 g, 42%), m.p. 197–199° (from methanol), λ_{max} 222 nm (log ϵ = 4.25), τ ([$^2H_6$]DMSO) 3.72 (s, 2H), 4.95 (d, 2H, *J* = 8Hz), 6.08 (s, 8H), 6.60 (s, 2H) (Found: C, 30.6; H, 4.2; N, 12.9. $C_{11}H_{18}Br_2N_4S_2$ requires: C, 30.7; H, 4.2; N, 13.0%).

Reaction of the dibromide **19** with triethylamine. Triethylamine (1.1 ml, 8 mmol) was added dropwise to a solution of the dibromide (1.92 g, 4 mmol) in warm methanol (10 ml). The soln was cooled wnd the precipitate was filtered off and washed with methanol and ether to give 3,5-*bis*-(N,N'-*ethylene*)iso*thioureidocyclopentene* **20** (710 mg, 66%), m.p. 154–155° (decomp.) (from much ethanol), virtually insoluble in all common solvents. (Found: C, 48.9; H, 6.3; N, 20.7%; M 166.056. $C_{11}H_{16}N_4S_2$ requires: C, 49.2; H, 6.0; N, 20.9%; M 166.056).

N-*Fluorenyl*-N',N''-*diphenylselenourea* **23**. A solution of *N,N'*-diphenylselenourea (825 mg, 3 mmol) and 9-bromofluorene (735 mg, 3 mmol) in ethanol (10 ml) was heated under reflux for 15 min and then filtered and evaporated *in vacuo*. Ether (15 ml) was added to the residual glass which crystallised overnight to give the slightly hygroscopic pale yellow *selenouronium bromide* **21** (1.05 g, 68%), m.p. 135–140° (from ethanol). Addition of ethanolic picric acid to a soln of this bromide in ethanol, followed by ether, precipitated the *picrate*, m.p. 144–147°, which on attempted recrystallisation from acetonitrile decomposed to give the selenourea **23**. Treatment of a solution of the bromide **21** (*ca.* 700 mg) in a minimal quantity of ethanol with triethylamine (1 ml) precipitated the selenourea **23** (230 mg, 40%), m.p. 130–132° (from ethanol), λ_{max} 227, 275 sh, 310 sh (log ϵ = 4.56, –, –), τ (C^2HCl_3) 2.72 (m, 18H), 4.3 (br. s. 1H), 4.74 and 4.92 (s, 1H) (Found: C, 70.8; H, 4.8; N, 6.4. $C_{26}H_{20}N_2Se$ requires: C, 71.1; H, 4.6; N, 6.4%). When a solution of this selenourea (*ca.* 30 mg) and nitrosobenzene (*ca.* 30 mg) in chloroform (2 ml) was kept at room temperature for 4 weeks, TLC showed that extensive decomposition had taken place, but no anil oxide or anil had been formed.

N,N'-*Ethylene*-N''-*fluorenylguanidinium salts*. A soln of *N,N'*-ethylene-*S*-methyl*iso*thiouronium iodide (4.88 g, 20 mmol) and 9-aminofluorene (5.43 g, 30 mmol) in ethanol (100 ml) was heated under reflux for 30 h. The soln was then evaporated *in vacuo* to *ca.* 50 ml. Ether (250 ml) was added to the cooled soln and a sticky solid was deposited on the walls of the flask. The ether was poured off and trituration of the deposit with acetone (10 ml) afforded crystals of N,N'-*ethylene*-N''-*fluorenylguanidinium iodide* (1.25 g, 17%), m.p. 258–265° (from methanol). The iodide (377 mg, 1 mmol) was dissolved in the minimum amount of hot methanol and a soln of picric acid (230 mg, 1 mmol) dissolved in the minimum amount of hot methanol was added. Crystals of the *picrate* separated, m.p. 204–207° (from methanol), λ_{max} 225, 233, 256, 262 nm (log ϵ = 4.50, 4.50, 4.25, 4.76), τ ($^2H_6$-DMSO) 1.44 (s, 2H), 2.46 (m, 8H), 4.26 (s, 1H), 6.25 (s, 4H) (Found: C, 55.0; H, 3.8; N, 17.7. $C_{22}H_{18}N_6O_7$ requires: C, 55.2; H, 3.8; N, 17.5%).

N,N'-*Ethylene*-N''-*fluorenylguanidine* **24**; RR = –$(CH_2)_2$–. *N,N'*-Ethylene-N''-fluorenylguanidinium iodide (12.8 g, 34 mmol) was suspended in dry tetrahydrofuran (200 ml) and a freshly prepared ethereal soln of phenyl lithium (1.10M, 31 ml, 34 mmol) was added.

with stirring. After 10 min solvent was evaporated *in vacuo*, and the residue was dissolved in chloroform (250 ml). This soln was washed with water (4 × 250 ml) and dried ($MgSO_4$). Removal of solvent *in vacuo* left a solid which was washed with ether to give the *base* **24**, RR = $-(CH_2)_2-$ (4.35 g, 53%), m.p. 225–230° (decomp) (sealed tube), τ (C^2HCl_3) 2.44 (m, 8H), 4.45 (br. s, 3H), 6.84 (s, 4H) (M 249.126. $C_{16}H_{15}N_3$ requires M 249.126). This compound decomposed fairly quickly when stored *in vacuo* at room temperature, but could be kept for a longer time at −40°. With an equimolar amount of picric acid in methanol it gave a picrate, m.p. 195–199°, identical with an authentic sample.

Reactions of 9-diazofluorene with guanidines. The guanidine (6 mmol), 9-diazofluorene (3 mmol) and copper bronze (250 mg) were ground together and then put into a flask which was flushed with oxygen-free nitrogen and plunged into an oil bath at the temperature mentioned and heated for the stated time. The residue was dissolved in chloroform (25 ml), filtered and then evaporated *in vacuo*. Ether (5 ml) was added to the residue causing fluorenone ketazine (A) to be precipitated; it was filtered off. Crystals of unreacted arylguanidines separated from the filtrate. The residual solution was evaporated *in vacuo* and on addition of methanol bifluorenylidene (B) separated. Removal of methanol from the filtrate and trituration with ether–light petroleum (b.p. 40–60°) afforded the fluorenylguanidine. Bath temperatures, times and products were as follows: (a) from *N*,*N'*-diphenylguanidine, 142°, 10 min, A 19%, B22%, N-*fluorenyl*-N,N'-*diphenylguanidine* **25** (29%), m.p. 139–141° (from methanol), λ_{max} 231, 263, 296, 308 nm (log ϵ − 4.2, 4.33, 3.61, 3.43), τ (C^2HCl_3) 2.75 (m, 18H), 3.65 (br. s, 1H), 4.2 (br. s, 1H), 5.6 (br. s, 1H) (Found: C, 82.9; H, 5.3; N, 11.0. $C_{26}H_{21}N_3$ requires: C, 83.1; H, 5.6; N, 11.2%); (b) from *N*-methyl-*N'*,*N''*-diphenylguanidine, 138–140°, 5 min, A 10%, B 13%; (c) from *sym*. triphenylguanidine, 140–142°, 4 min, B 2%, N-*fluorenyl*-N,N',N''-*triphenylguanidine* (2%), m.p. 118–135° (M 451.205. $C_{32}H_{25}N_3$ requires: 451.205); (d) from guanidine, 115–122°, 10 min, A 24%; (e) from *N*,*N*,*N'*,*N'*-tetramethylguanidine, 60–70°, 45 min, A 33%, B 30%; 0°, 150 min, A 58%, B 2%; −20°, 24 hr, A 77%, B 0%.

N-*Fluorenyl*-N',N''-*diphenylguanidine*. (**24**; R = Ph) 9-Aminofluorene (5.44 g, 25 mmol) was added to a soln of diphenylcarbodi-imide (25 mmol) in dimethylformamide,[29] and when all the amine had been dissolved by shaking the mixture, it was kept at 50–55° for 16 hr. It was then poured into water (300 ml), made strongly basic (pH > 12) with aqueous sodium hydroxide (40%, *ca*. 30 ml), and kept overnight. N-*Fluorenyl*-N',N''-*diphenylguanidine* (4.2 g, 45%) was filtered off, washed with hot methanol and dried, and had m.p. 165–166° (from benzene), λ_{max} 229, 263, 295 sh, 306 nm (log ϵ = 4.45, 4.41, –, 3.60), τ (C^2HCl_3) 2.70 (m, 18H), 3.53 (s, 1H), 5.6 (br. s, 1H) (Found: C, 82.1; H, 5.5; N, 11.0. $C_{26}H_{21}N_3$ requires: C, 83.1; H, 5.6; N, 11.2%).

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