

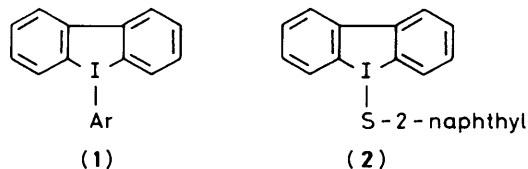
Dialkylcarbamoyl(diaryl)iodanes

Elvira Kotali and Anastassios Varvoglis*

Laboratory of Organic Chemistry, University of Thessaloniki, Thessaloniki 540 06, Greece

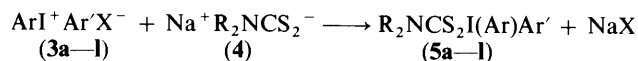
A series of the title compounds (**5**) have been prepared. Their physical properties suggest covalent character for the iodine-sulphur bond, and the most interesting chemical property of these compounds is the decomposition to aryl dithiocarbamates (**6**). One iodane shows considerable antimicrobial activity.

Diaryliodonium salts are useful arylating agents for a great variety of nucleophiles, especially carbanions but also various O, S, N, and P nucleophiles.¹ Several mechanisms have been shown to be operative in these arylations, which take place under widely differing experimental conditions² and these include: (a) electron transfer pathways, (b) nucleophilic aromatic substitution, and (c) nucleophilic attack at iodine with the formation of transient or stable trico-ordinated iodine species, the iodanes. Two types of stable iodanes are presently known, either with three carbon-iodine bonds,³ e.g. (**1**) or with two carbon-iodine bonds and one sulphur-iodine bond,⁴ e.g. (**2**). It is of interest to note that the presence of iodine in a five-membered ring confers enhanced stability on these iodanes. It has been assumed that in these compounds the iodine bonds have no ionic character; their most prominent features are the yellow colour and the ready thermal or photochemical homolytic decomposition.



Our interest generally in the chemistry of hypervalent iodine has led us to a search for other iodanes with an S-I bond. Because of the strong biocidal properties of iodonium salts,⁵ we thought it would be interesting to combine them with a sulphur nucleophile of a similar biological action, in the hope that the resulting product might be more potent than either individual component. For this purpose we chose the dialkyldithiocarbamate ion and we report that this combination indeed leads to fairly stable iodanes (**5**), one, at least, of which exhibits remarkable biological activity. Furthermore, these iodanes decompose easily to aryl dithiocarbamates in good yields. The characteristics of this decomposition are also briefly examined.

Simple stirring of diaryliodonium halides (**3**) with sodium *N,N*-diethyldithiocarbamate (**4**) in acetonitrile or water at 0–20 °C in the dark results in the formation of dialkylcarbamoyl-(diaryl)iodanes (**5**):



- a; Ar = Ar' = phenyl
- b; Ar = Ar' = *p*-chlorophenyl
- c; Ar = Ar' = *p*-tolyl
- d; Ar = Ar' = *p*-methoxyphenyl
- e; Ar = Ar' = mesityl
- f; Ar = Ar' = *m*-nitrophenyl
- g; Ar-Ar' = 2,2'-biphenylylene
- h; Ar = phenyl, Ar' = mesityl
- i; Ar = phenyl, Ar' = *p*-chlorophenyl
- j; Ar = phenyl, Ar' = *m*-nitrophenyl
- k; Ar = phenyl, Ar' = *p*-methoxyphenyl
- l; Ar-Ar' = 2,2'-biphenylylene.

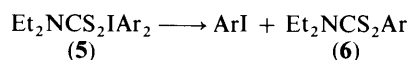
For all compounds R = Et, except for (**5l**), where R₂ = -(CH₂)₄-.

All iodanes are yellow or orange compounds, which apart from the aromatic absorption at 235–267 nm show also a well-defined inflection or a normal band in the region between 320 and 326 nm (Table 3). They are low melting crystalline compounds, some of which are fairly soluble in several organic solvents, including chloroform and acetonitrile. With the exception of (**5g**) and (**5l**) they decompose on attempted recrystallisation; (**5l**) was recrystallised from chloroform-hexane and its X-ray structure analysis has been reported.⁶ Its stability is further demonstrated from its mass spectrum, in which the molecular ion is present, and which has a different fragmentation pattern from its isomeric decomposition product, the biphenylic ester (**7b**). A comparison of the main fragments in the mass spectra of these compounds is shown below, with relative intensities (%).

(5l) <i>m/z</i>	(7b) <i>m/z</i>
425 (<i>M</i> ⁺ , 7)	425 (<i>M</i> ⁺ , 2)
298 (<i>M</i> ⁺ - I, 8)	298 (<i>M</i> ⁺ - I, 78)
279 [<i>M</i> ⁺ - S ₂ CN(CH ₂) ₄ , 11]	
184 [298 - SCN(CH ₂) ₄ , 37]	184 [298 - SCN(CH ₂) ₄ , 77]
152 (184 - S, 100)	152 (184 - S, 19)

All these properties indicate covalent character for the iodine-sulphur bond, except that the shortest bond distance has been found⁶ to be 3.053 Å, whereas the sum of covalent radii for these elements is 2.37 Å (if hypervalent iodine is assumed to be similar with univalent iodine) and the sum of the van der Waals radii is 4.00 Å. In order to clarify the nature of this bond the conductivity of (**5l**) was measured in DMF and found to be 7.1 × 10⁻⁶ S cm⁻¹, a value considerably lower than the conductivity of 2,2'-biphenylylenyliodonium chloride, which is 4.5 × 10⁻⁵ S cm⁻¹, also in DMF. We conclude that despite the rather long I-S distance of (**5l**) it is more appropriate to consider compounds (**5**) as iodanes rather than iodonium salts. It is noted that other organoiodine(III) compounds generally accepted as salts actually possess hypervalent character and the principle of hypercovalency requires an elongated σ-bond for the axial iodine-ligand bond, where the most electronegative ligand is the axial one.⁵ It may be relevant here to mention that iodine and sulphur have the same electronegativity in the Pauling scale (2.5) and triaryl sulphonium iodides, Ar₃S⁺I⁻, also have more covalent than ionic character.⁷

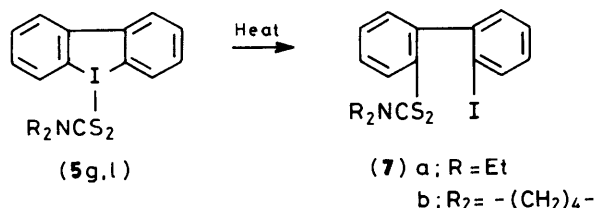
The iodanes (**5**) are stable in the dark but when allowed to stand in diffuse daylight for a few days they liquefy, decomposing to a mixture of aryl iodides and aryl diethyldithiocarbamates (**6**), most of which are new compounds. The



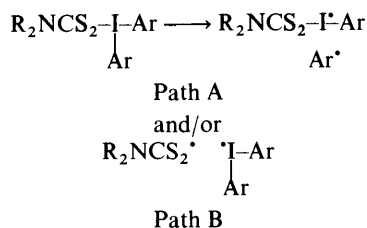
spectroscopic data of these esters are collected in Table 4. The yields of compound (**6**) from 'symmetrical' (**5**) are in the range

53–82%—better yields for the known esters (**6a** and **c**) than those reported from the reaction between sodium diethyldithiocarbamate and aryldiazonium salts.⁸ The decomposition of (**5a**) was also carried out in solution, using various solvents: pyridine was found to be the best, since it accelerated the decomposition with a slight increase in the yield of the ester. Thus the reaction at room temperature was again completed in 24 h (instead of several days) and the yield of (**6a**) rose to 77% [from (71%)]. Other solvents used included cyclohexane, cyclopentene, and ethanol. These were used in experiments with and without u.v. irradiation in the hope of obtaining products arising from solvent participation, as with compound (**2**).⁴ In all cases no such products could be detected and the ester was always the sole product, along with aryl iodide. By-products were in most cases diphenyl disulphide in trace amounts and in some reactions diphenyliodonium iodide [the latter in up to 12% yield from the photochemical reaction of (**5a**) in MeCN–cyclopentene]. These compounds were isolated and their properties (m.p., i.r., and mass spectra) were identical with those of authentic samples. No arenes or biaryls were found.

The iodanes (**5g–l**) did not decompose at an appreciable rate under the above conditions. Their conversion into the biphenylic esters (**7**) was effected after reflux in *p*-xylene in low yields.



The mild conditions leading to the decomposition of iodanes mean that nucleophilic aromatic substitution, as suggested for the pyrolysis of diaryliodonium halides^{9,10} is unlikely. Instead, light-promoted, homolytic pathways are likely to operate. The generation of free radicals is evident in (**5a**) and (**5h**), whose ¹H n.m.r. spectra could not be recorded, owing to the immediate flattening of all proton resonances. The free radicals produced must be paired, since they do not react with the solvent, and they do not combine with or abstract H[•]. The initial homolysis may proceed *via* two paths:

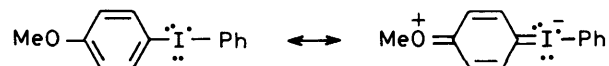


Path B seems to be favoured, because the I–S bond is weak, but path A cannot be rejected, since the free radical R₂NCS₂–I[•]–Ar is likely to be stabilised.

The ‘unsymmetrical’ iodanes (**5h–k**) were allowed to decompose neat in order to obtain more information about the preferred pathway. Mixtures of the esters (**6**) were obtained, as follows:

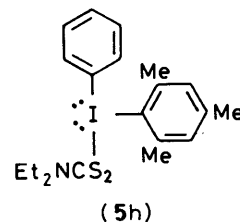
Iodane	Aryl esters Et ₂ NCS ₂ Ar (relative %)
(5h)	Phenyl (9) + Mesityl (91)
(5i)	Phenyl (56) + <i>p</i> -Chlorophenyl (44)
(5j)	Phenyl (57) + <i>m</i> -Nitrophenyl (43)
(5k)	Phenyl (84) + <i>p</i> -Methoxyphenyl (16)

The relative quantities of the esters were measured by gas chromatography and checked by simultaneous measuring of the aryl iodides obtained after the decomposition. Pure esters and iodides were used as standards. In all cases the amounts of the two esters were complementary to the amounts of the two iodides, *e.g.* (**5i**) gave phenyl iodide and *p*-chlorophenyl iodide in relative proportions 45:55. Electron-withdrawing groups in one of the phenyl rings (NO₂, Cl) do not significantly influence the ratio of the two esters, which are produced almost in the same relative amounts. The electron-donating methoxy group however has a pronounced effect, as the phenyl ester predominates over the *p*-methoxyphenyl ester. If we consider all three likely free radicals, *i.e.* phenyl and *p*-methoxyphenyl for



path A and *p*-methoxyphenyl(phenyl)iodanyl, for path B, we note that the *p*-methoxyphenyl free radical should be better stabilised than the phenyl radical, so that one would expect mainly the *p*-methoxyphenyl ester, if path A were followed. On the other hand, the *p*-methoxyphenyl(phenyl)iodanyl free radical, a (9-I-2) species,¹¹ can also be stabilised mesomerically to become a (11-I-2) species, in which the rupture of the *p*-methoxyphenyl C–I bond is not favoured and *p*-methoxyphenyl iodide is the main product. Therefore path B seems more likely to be operative.

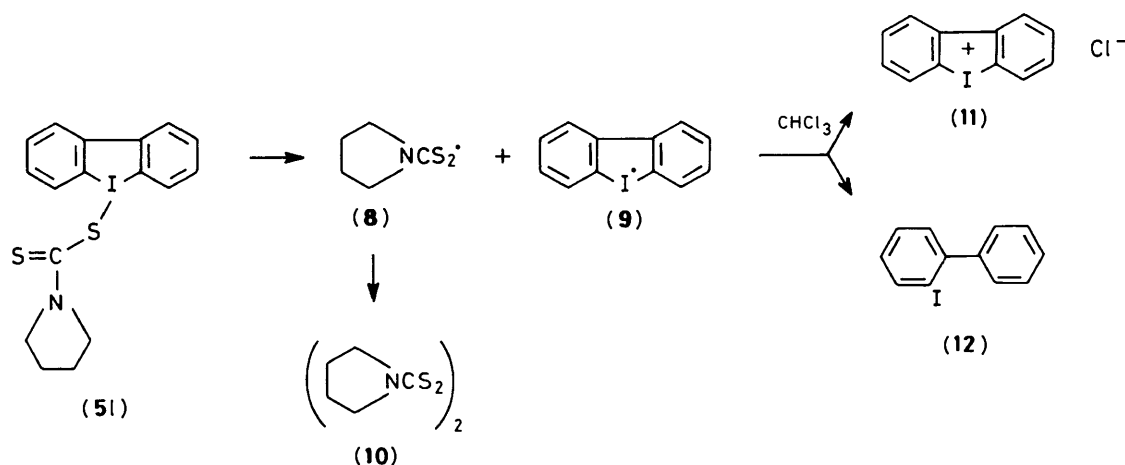
The case of compound (**5h**) where the mesityl ester greatly predominates must be considered separately. We attribute this spectacular change in product composition to steric reasons, assuming that (**5h**) has a configuration with the bulky mesityl group occupying the less crowded equatorial position. It is then



expected that the dithiocarbamate group will interact with the equatorial mesityl group rather than the axial phenyl group, which is too far away. Similar explanations have been suggested for the pyrolysis of various unsymmetrical diaryliodonium halides.^{9,10}

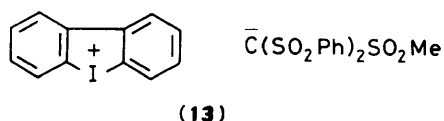
The formation of diaryl disulphides in some cases indicates that some arylthiyl free radicals, ArS[•], may be formed during the decomposition of (**5**). The present data cannot offer an explanation about their formation but it is relevant to mention that independent photolysis or thermolysis of the esters (**6**) did not produce any disulphide. Also, disulphide fragments were present in the mass spectra of all of the iodanes (**5**) but not in the mass spectra of (**6**). Therefore the disulphides do not come from the esters (**6**).

Most of the iodanes usually gave the esters (**6**) in mixtures of chloroform–cyclopentene without being heated but the cyclic (**5l**) gave no ester at all, its main product being the disulphide derivative (**10**) along with 2,2'-biphenylyliodonium chloride (**11**) and 2-iodobiphenyl (**12**). Apparently here I–S bond homolysis takes place and the iodine radical (**9**) abstracts either H[•] or Cl[•] (from CHCl₃) to give (**11**) and (**12**), whereas the radical (**8**) is dimerised. This change in reactivity could not be accounted for.



The tendency of iodanes to decompose homolytically did not permit metathesis reactions with various nucleophiles, either carbanions or neutral-anionic S, P, and N compounds. However, in one case the reaction between the trisulphone ($\text{PhSO}_2)_2\text{CHSO}_2\text{Me}$ and the cyclic iodane (**5g**) in DMF has led to the formation of the iodonium salt (**13**). The use of other solvents such as water, MeCN, and CH_2Cl_2 left the reactants unchanged.

The highly acidic character of the trisulphone in addition to



the steric congestion about the tertiary carbon makes it unlikely that compound (**13**) has covalent character; the lack of the usual yellow colour of triaryliodonanes, its stability and its high melting point point to an ionic rather than a covalent structure. Therefore (**13**) must be a true iodonium salt whose counter ion for the first time is a carbanion.

The idea that the iodanes (**5**) may be biologically more active than either of their individual components has been fully substantiated for (**5i**). This compound has been found¹² to cause potent inhibition (ca. 80%) of both *Escherichia coli* HB 101 and *Staphylococcus aureus*, two micro-organisms representative for gram-negative and gram-positive bacteria, respectively, at concentrations in the range of 10^{-6} – 10^{-7}M , i.e. 100–1 000 fold lower than its components. The ester (**7b**) exerted negligible biological activity against these bacteria.

Experimental

I.r. spectra were recorded with a Perkin-Elmer 257 spectrometer. U.v. and visible spectra were recorded with a Shimadzu 214-A spectrophotometer. ^1H N.m.r. spectra were recorded on a Varian A-60A spectrometer. Mass spectra were obtained from a Hitachi-Perkin-Elmer RMU-6L single focussing spectrometer at 70 eV. Conductivity measurements were performed with a Beckman PC-18A conductivity bridge operating at $3\,000\text{ Hz s}^{-1}$ and at $25 \pm 0.002\text{ }^\circ\text{C}$; a Jones-type cell (constant 0.077 cm^{-1}) was used. G.l.c. was carried out using a 5830A Hewlett-Packard gas chromatograph, equipped with a F.I.D. detector and a 6 ft SE-30 Chromosorb column, operating at 70 – $220\text{ }^\circ\text{C}$.

The iodonium halides were prepared by standard methods,² in the form of chlorides, bromides, or iodides. The use of the

more ionic¹³ chlorides appears to give somewhat better yields. Light petroleum refers to the fraction boiling in the range 40 – $60\text{ }^\circ\text{C}$.

N,N-Dialkyldithiocarbamoyl(diaryl)iodanes (5): General Procedure.—A solution or suspension of the appropriate iodonium halide (2 mmol) in acetonitrile (20 ml) or water [20 ml; for (**5a**) and (**5f**)] was treated with sodium dialkyldithiocarbamate (2 mmol) at room temperature with protection from daylight. After a suitable period of stirring [from 15 min for (**5i**) to 24 h for (**5l**)] the yellow precipitate was collected by filtration and washed with water and then with diethyl ether or light petroleum. Compound (**5d**) was soluble in acetonitrile and was obtained by direct crystallisation at $-15\text{ }^\circ\text{C}$. For the asymmetric iodanes (**5h**, **i**, **j**, and **k**), best results were obtained when the reaction was carried out at $0\text{ }^\circ\text{C}$ for 30 min in a smaller amount of solvent [acetonitrile (5 ml)]. The iodanes were dried over phosphorus pentoxide. Melting points, yields, and analytical and spectroscopic data appear in Tables 1 and 3.

Table 1. Melting points, yields and analytical data for the iodanes (**5**)

Compound (Formula)	M.p. ($^\circ\text{C}$)	Yield (%)	Found (%) (Required)		
			C	H	N
(5a) ($\text{C}_{17}\text{H}_{20}\text{INS}_2$)	78–80	91	47.5 (47.55)	4.5 (4.66)	3.0 (3.26)
(5b) ($\text{C}_{17}\text{H}_{18}\text{Cl}_2\text{INS}_2$)	99–100	82	40.7 (40.97)	3.6 (3.64)	2.9 (2.81)
(5c) ($\text{C}_{19}\text{H}_{24}\text{INS}_2$)	97–98	66	49.5 (49.88)	5.25 (5.29)	3.4 (3.06)
(5d) ($\text{C}_{19}\text{H}_{24}\text{INO}_2\text{S}_2$)	109–110	41	46.7 (46.62)	4.8 (4.94)	2.8 (2.86)
(5e) ($\text{C}_{23}\text{H}_{32}\text{INS}_2$)	97–99	75	53.6 (53.79)	6.1 (6.28)	2.7 (2.73)
(5f) ($\text{C}_{17}\text{H}_{18}\text{IN}_3\text{O}_4\text{S}_2$)	83–84	82	39.5 (39.31)	3.4 (3.49)	7.8 (8.09)
(5g) ($\text{C}_{17}\text{H}_{18}\text{INS}_2$)	137	48	47.9 (47.73)	4.3 (4.25)	3.3 (3.28)
(5h) ($\text{C}_{20}\text{H}_{26}\text{INS}_2$)	78–79	74	51.2 (50.95)	5.4 (5.56)	3.0 (2.97)
(5i) ($\text{C}_{17}\text{H}_{19}\text{ClINS}_2$)	83	84	44.2 (44.02)	4.1 (4.13)	3.1 (3.02)
(5j) ($\text{C}_{17}\text{H}_{19}\text{IN}_2\text{O}_2\text{S}_2$)	74–75	74	43.0 (43.03)	4.1 (4.04)	5.8 (5.90)
(5k) ($\text{C}_{18}\text{H}_{22}\text{INOS}_2$)	89–90	81	46.9 (47.05)	4.7 (4.83)	3.0 (3.05)
(5l) ($\text{C}_{17}\text{H}_{16}\text{INS}_2$)	141–142	61	48.1 (48.00)	3.8 (3.79)	3.0 (3.29)

Aryl Dialkyldithiocarbamate Esters (6) and (7): General Procedure.—A quantity of the iodane (5) was allowed to stand for several days at room temperature in daylight; alternatively, a solution (in several solvents) was also allowed to stand for a shorter period of time; compounds (5g) and (5i) were refluxed in *p*-xylene for 7 h. When the decomposition was complete the solvents were removed and the residue was chromatographed

on a silica gel column, using light petroleum–chloroform as the eluant. The aryl iodides eluted first, and then the esters. Melting points [after recrystallisation from light petroleum for (6a and c) or ethanol for the rest], yields, and analytical and spectroscopic data appear in Tables 2 and 4.

Phenyl diethyldithiocarbamate (6a). A suspension of (5a) (1.86 mmol, 800 mg) in pyridine (4 ml) was stirred at room temperature for 24 h. After the solvent had been removed along with some phenyl iodide, the residue was column chromatographed (silica gel; eluant light petroleum–CHCl₃ mixtures) and gave first phenyl iodide (228 mg, 60%), then diphenyl disulphide (15 mg), and finally (6a) (323 mg, 77%).

Table 2. Melting points, yields, and analytical data for the esters (6) and (7)

Compound (Formula)	M.p. °C (lit. m.p.)	Yield (%) ^a (lit. yield)	Found (%) (Required)		
			C	H	N
(6a)	44–46 (46) ⁸	71 (17) ⁸			
(6b)	88–89 (88) ¹³	53			
(6c)	75–77 (77–78) ⁸	75 (30) ⁸			
(6d)	75–76	79	56.4	6.6	5.2
(C ₁₂ H ₁₇ NOS ₂)			(56.43	6.71	5.48)
(6e)	103–105	78	62.85	8.0	5.0
(C ₁₄ H ₂₁ NS ₂)			(62.87	7.91	5.24)
(6f)	91–92	82	48.7	5.2	10.2
(C ₁₁ H ₁₄ N ₂ O ₂ S ₂)			(48.82	5.22	10.35)
(7a)	104–105	18	47.6	4.15	3.2
(C ₁₇ H ₁₈ INS ₂)			(47.73	4.25	3.28)
(7b)	180–181	14	48.0	3.95	3.0
(C ₁₇ H ₁₆ INS ₂)			(48.00	3.79	3.29)

^a The yields refer to decomposition without solvent.

2,2'-Biphenylenyliodonium Methylsulphonylbis(phenylsulphonyl)methanide (13).—An equimolecular mixture (1 mmol each) of (5g) (427 mg) and 1,1-bis(phenylsulphonyl)methyl methyl sulphone¹⁴ (374 mg) was stirred in DMF (10 ml) for 80 h. The solvent was removed from the reaction mixture under reduced pressure, ethanol (5 ml) was added to the residue, and the resulting solution was allowed to stand at 10 °C for 24 days, after which time the salt (13) (250 mg, 38%) crystallised, m.p. 192–196 °C (from ethanol); ν_{\max} (Nujol) 3 100, 3 040, 1 280, and 1 110 cm⁻¹; δ (Me₂SO) 2.87 (3 H, s) and 7.15–8.62 (18 H, m) (Found: C, 47.85; H, 3.2. C₂₆H₂₁IO₆S₃ requires C, 48.04; H, 3.21%).

Decomposition of the Iodane (5i) in Cyclopentene.—A suspension of (5i) (522 mg, 1.23 mmol) in cyclopentene (3 ml) and chloroform (10 ml) was stirred at room temperature for 6 days. A new precipitate was formed (140 mg) which was identified as 2,2'-biphenylenyliodonium chloride. This was

Table 3. Spectroscopic data for the iodanes (5)

Compound	U.v. ^a nm/(log ε)	I.r. (Nujol) cm ⁻¹	δ_{H} (CDCl ₃)
(5a)	320sh (3.72)	1 405, 1 260, 1 205	<i>b</i>
(5b)	321 (4.13)	1 410, 1 260, 1 205	<i>d</i>
(5c)	<i>c</i>	1 405, 1 260, 1 205	1.23 (6 H, t, <i>J</i> 7 Hz), 2.33 (6 H, s), 4.03 (4 H, q, <i>J</i> 7 Hz), 7.13 (4 H, d, <i>J</i> 8 Hz), 7.78 (4 H, d, <i>J</i> 8 Hz)
(5d)	320sh (4.12)	1 575, 1 555, 1 400, 1 250, 1 200	1.23 (6 H, t, <i>J</i> 7 Hz), 3.71 (6 H, s), 3.98 (4 H, q, <i>J</i> 5 Hz), 6.73 (4 H, d, <i>J</i> 9 Hz), 7.64 (4 H, d, <i>J</i> 9 Hz)
(5e)	319sh (3.93)	1 600, 1 410, 1 255, 1 205	1.23 (6 H, t, <i>J</i> 7 Hz), 2.16–2.63 (18 H, m), 4.02 (4 H, q, 7 Hz), 6.83 (4 H, s)
(5f)	<i>c</i>	1 520, 1 410, 1 340, 1 260, 1 205	<i>d</i>
(5g)	325 (4.11)	1 580, 1 395, 1 250, 1 205	1.30 (6 H, t, <i>J</i> 7 Hz), 4.10 (4 H, q, <i>J</i> 7 Hz), 7.28–8.15 (8 H, m)
(5h)	320sh (3.82)	1 400, 1 260, 1 205	<i>b</i>
(5i)	323 (3.87)	1 400, 1 255, 1 205	1.23 (6 H, t, <i>J</i> 7 Hz), 4.02 (4 H, q, <i>J</i> 7 Hz), 7.08–8.10 (9 H, m)
(5j)	320sh (3.93)	1 515, 1 400, 1 340, 1 255, 1 200	1.27 (6 H, t, <i>J</i> 7 Hz), 4.05 (4 H, q, <i>J</i> 7 Hz), 7.27–8.03 (9 H, m)
(5k)	318sh (3.72)	1 580, 1 570, 1 400, 1 295, 1 250, 1 205	1.27 (6 H, t, <i>J</i> 7 Hz), 3.81 (3 H, s), 4.05 (4 H, q, <i>J</i> 7 Hz), 6.88 (2 H, d, <i>J</i> 7 Hz), 7.32 (3 H, m), 7.73 (4 H, m)
(5l)	326 (4.08)	1 400, 1 160	1.75–2.18 (4 H, m), 3.58–4.12 (4 H, m), 7.17–8.23 (8 H, m)

^a Absorptions at λ_{\max} > 300 nm are recorded only, in MeCN. ^b Decomposition occurred during the recording of the spectrum. ^c Only an end-absorption above 300 nm. ^d Insoluble in several solvents.

Table 4. Spectroscopic data for compounds (6) and (7)

Compound	I.r. (Nujol)/cm ⁻¹	δ_{H} (CDCl ₃) ^a
(6a)	1 480, 1 410, 1 350, 1 265, 1 200	1.28 (6 H, t), 3.87 (4 H, q), 7.42 (5 H, s)
(6b)	1 570, 1 480, 1 415, 1 265, 1 200	1.31 (6 H, t), 3.91 (4 H, q), 7.43 (4 H, s)
(6c)	1 480, 1 410, 1 260, 1 200	1.34 (6 H, t), 2.42 (3 H, s), 3.98 (4 H, q), 7.35 (2 H, d, <i>J</i> 8 Hz), 7.40 (2 H, d, <i>J</i> 8 Hz)
(6d)	1 480, 1 410, 1 260, 1 200	1.27 (6 H, t), 3.41–4.38 (7 H, m), 7.00 (2 H, d, <i>J</i> 9 Hz), 7.48 (2 H, d, <i>J</i> 9 Hz)
(6e)	1 600, 1 480, 1 410, 1 265, 1 205	1.30 (6 H, t), 2.32 (9 H, br s), 3.89 (4 H, q), 6.88 (2 H, s)
(6f)	1 510, 1 490, 1 420, 1 345, 1 265, 1 200	1.34 (6 H, t), 3.87 (4 H, q), 7.73 (2 H, m), 8.36 (2 H, m)
(7a)	1 480, 1 415, 1 265, 1 200	1.10 (6 H, t), 3.75 (4 H, q), 6.90–8.20 (8 H, m)
(7b)	1 430, 1 335, 1 250, 1 160	1.67–2.30 (4 H, m), 3.47–4.16 (4 H, m), 7.17–8.23 (8 H, m)

^a CCl₄ for (6a). *J* values are not given for ethyl protons, because their resonances were unresolved.

filtered off and the filtrate was evaporated. The residue was chromatographed on a silica gel column, using light petroleum–chloroform as the eluant to give 2-iodobiphenyl (65 mg) and the bis(tetramethylenethiocarbamoyl) disulphide (**10**) (95 mg, 53%), m.p. 137–139 °C (from ethanol), v_{\max} (Nujol) 1 320, 1 240, and 1 140 cm^{-1} ; $\delta(\text{CDCl}_3)$ 2.03 (8 H, m) and 3.93 (8 H, m); m/z 292 (M^+) (Found: C, 40.9; H, 5.4; N, 9.4. $\text{C}_{10}\text{H}_{16}\text{N}_2\text{S}_4$ requires C, 41.05; H, 5.51; N, 9.58%).

Photochemical Reaction of the Iodane (5a).—A solution of (**5a**) (2 mmol, 858 mg) in MeCN (5 ml) and cyclopentene (2 ml) was irradiated with a 400 W low-pressure mercury lamp for 100 min. A white precipitate formed, m.p. 181–182 °C, which was identified as diphenyliodonium iodide (48 mg, 12%). The residue after removal of volatiles was chromatographed (silica gel, eluting with light petroleum– CHCl_3) to give phenyl iodide (163 mg, 40%), a trace of diphenyl disulphide, and phenyl *N,N*-diethyldithiocarbamate (144 mg, 32%).

Acknowledgements

We wish to thank Dr. G. Ritzoulis, from the Laboratory of Physical Chemistry, Thessaloniki University, for the conductivity measurements.

References

- 1 A. Varvoglis, *Synthesis*, 1984, 709.
- 2 G. A. Olah, 'Halonium Ions,' Wiley-Interscience, New York and London, 1975.
- 3 (a) F. M. Beringer and L. L. Chang, *J. Org. Chem.*, 1971, **36**, 4055; (b) H. J. Reich and C. S. Cooperman, *J. Am. Chem. Soc.*, 1973, **95**, 5077.
- 4 J. W. Greidanus, W. J. Rebel, and R. B. Sandin, *J. Am. Chem. Soc.*, 1962, **84**, 1504.
- 5 G. F. Koser, 'Halonium Ions,' in 'The Chemistry of Functional Groups,' Suppl. D, Wiley, 1983, ch. 25, pp. 1314–1316.
- 6 (a) E. Kotali, A. Varvoglis, A. Bozopoulos, and P. Rentzeperis, *J. Chem. Soc., Chem. Commun.*, 1985, 1819; (b) A. P. Bozopoulos and P. J. Rentzeperis, *Acta Crystallogr., Sect. C*, 1986, **42**, 1014.
- 7 J. W. Knapczyk and W. E. McEwen, *J. Am. Chem. Soc.*, 1969, **91**, 145.
- 8 A. M. Clifford and J. G. Lichty, *J. Am. Chem. Soc.*, 1932, **54**, 1163.
- 9 (a) Y. Yamada and M. Okawara, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1860 and 2515; (b) Y. Yamada, K. Kashima, and M. Okawara, *ibid.*, 1974, **47**, 3179.
- 10 K. M. Lancer and G. H. Wiegand, *J. Org. Chem.*, 1976, **41**, 3360.
- 11 J. C. Martin, *Science*, 1983, **221**, 509.
- 12 A. Tsiftoglou and D. Genimata, University of Thessaloniki, unpublished results.
- 13 V. S. Petrosyan and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, 1967, **175**, 613.
- 14 H. Böhme and R. Marx, *Chem. Ber.*, 1941, **74**, 1667.

Received 3rd November 1986; Paper 6/2122