Competition between Oxazolium and Sulphonium Salt Formation in the Acid-induced Interaction of 2-Diazoacetophenones with Diaryl Sulphides in Acetonitrile

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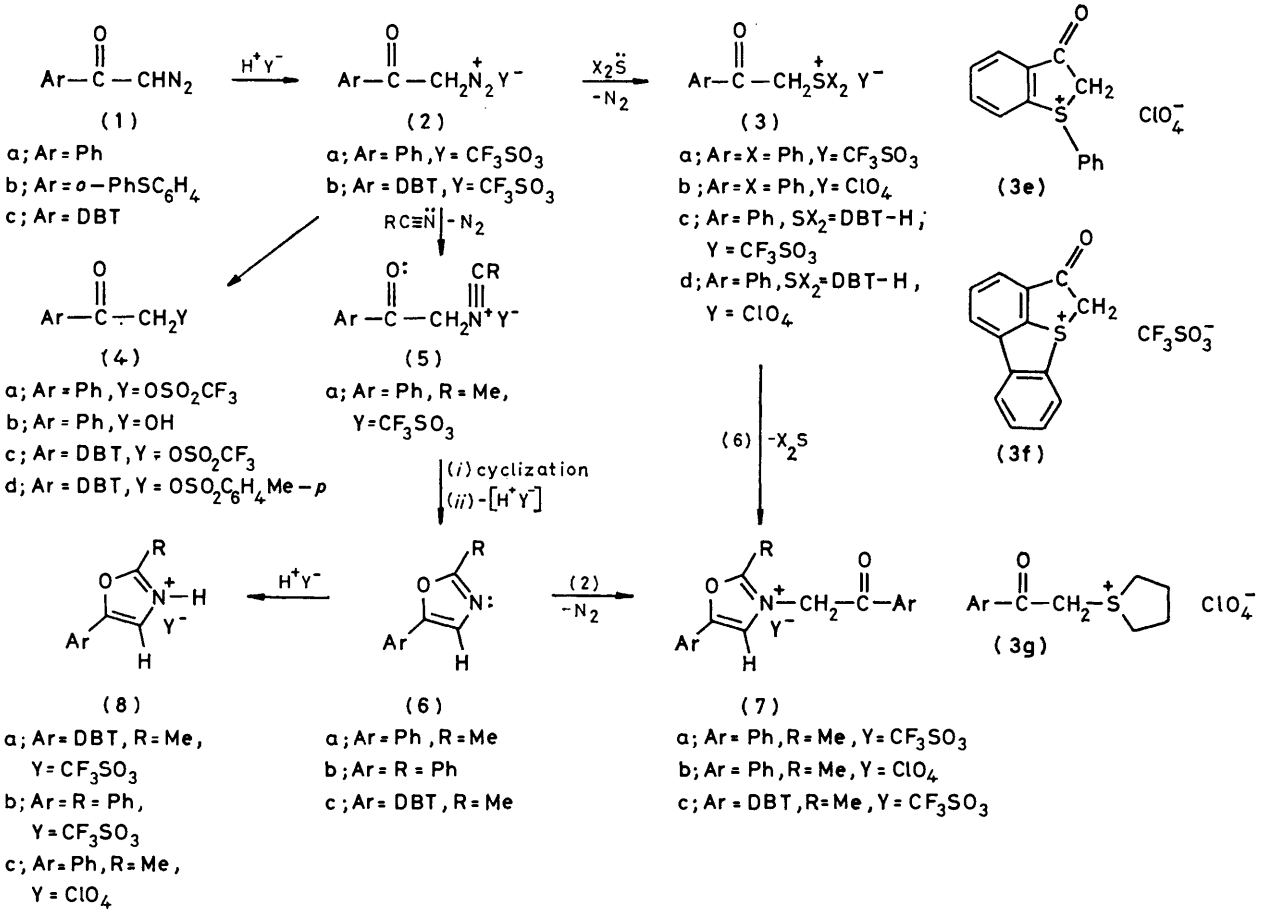
Diphenyl sulphide and dibenzothiophen react with 2-diazoacetophenone (1a) and trifluoromethanesulphonic acid in dichloromethane to provide the corresponding phenacylsulphonium salts (3a) and (3c), respectively. Under similar conditions, 4-(diazoacetyl)dibenzothiophen (1c) gives the trifluoromethanesulphonate ester (4c) and not the cyclic sulphonium salt (3f). Interaction of diazoacetophenone (1a) and trifluoromethanesulphonic acid in acetonitrile yields 2-methyl-3-phenacyl-5-phenyloxazolium trifluoromethanesulphonate (7a) by phenacylation of the initially formed 2-methyl-5-phenyloxazole (6a); 4-(diazoacetyl)dibenzothiophen (1c) behaves analogously. 2-Diazoacetophenone (1a), trifluoromethanesulphonic acid, and benzonitrile afford 2,5-diphenyloxazole (6b) which does not undergo phenacylation. Both phenacyl-diphenylsulphonium (3a) and -dibenzothiophenium (3d) salts readily transfer their phenacyl groups to the nitrogen of 2-methyl-5-phenyloxazole (6a).

RECENTLY we have shown [1] that dialkyl and alkyl aryl sulphides react with 2-diazoacetophenones (1) in the presence of perchloric acid in acetonitrile (Scheme) to provide phenacylsulphonium salts (3) [*e.g.* equation (1)]. The reaction also proceeds intramolecularly with 2-diazo-2'-(phenylthio)acetophenone [(1b) ⟶ (3e)], but fails with diphenyl sulphide,[1] giving a mixture containing nitrogen which can only have come from the solvent.

We now report on the results of reactions carried out in inert solvents and on the intervention of nitriles in such reactions. When chloroform was used as solvent for the reaction of diazoacetophenone (1a), diphenyl



SCHEME

sulphide, and perchloric acid, the desired phenacyldiphenylsulphonium perchlorate (3b) was obtained in low yield; however, a near-quantitative yield of the

$$PhCO{\cdot}CHN_2 + MeSR + HClO_4 \longrightarrow PhCO{\cdot}CH_2{\cdot}\overset{+}{S}RMe\ ClO_4^- + N_2 \quad (1)$$
$$R = Me \text{ or } Ph$$

phenacylsulphonium salt (3a) was obtained when trifluoromethanesulphonic acid [2] in dry dichloromethane was employed.

While this work was in progress, a variety of α-diazocarbonyl compounds were reported [3] to react with trifluoromethanesulphonic acid in liquid sulphur dioxide at −78 °C to afford the corresponding sulphonate esters [equation (2)] which were effective alkylation reagents

$$RCO{\cdot}CHN_2 + HOSO_2CF_3 \longrightarrow RCO{\cdot}CH_2{\cdot}OSO_2CF_3 + N_2 \quad (2)$$

for sulphides: in particular, phenacyl trifluoromethanesulphonate (4a) with diphenyl sulphide in acetonitrile gave the expected sulphonium salt (3a) in unspecified yield. In our 'one-pot' procedure [(1a) ⟶ (3a)] it would appear that the sulphonate ester (4a) is not an intermediate, as reaction of the latter with diphenyl sulphide is reported to be slow, whereas our reaction is almost instantaneous.

RESULTS AND DISCUSSION

The addition of diazoacetophenone (1a) to dibenzothiophen and trifluoromethanesulphonic acid in dichloromethane gave the expected sulphonium salt (3c) in 35% yield and the balance of the dibenzothiophen was recovered. This low yield presumably reflects the lower nucleophilicity of the sulphur atom in dibenzothiophen relative to that in diphenyl sulphide.[4] The remainder of the diazoketone was apparently converted into phenacyl trifluoromethanesulphonate (4a) since, following aqueous work-up, the major components of the reaction mixture were its hydrolysis products, trifluoromethanesulphonic acid and the ketol (4b). Intramolecular attack of an acyldiazonium ion (2) onto sulphur normally proceeds more readily than its intermolecular counterpart.[1] When, however, 4-(diazoacetyl)dibenzothiophen (1c) was added to trifluoromethanesulphonic acid in dichloromethane, the sole product was the acyclic sulphonate ester (4c); no bridgehead sulphonium salt (3f) could be isolated presumably on account of its unfavourable stereochemistry.

To investigate the participation of acetonitrile in reactions such as those described above, diazoacetophenone (1a) was added to acetonitrile containing trifluoromethanesulphonic acid when there resulted the *N*-phenacyloxazolium salt (7a) in 42% yield. Similar results were obtained with perchloric acid although in lower yield. It thus appears that interaction of the phenacyldiazonium ion (2a) and a molecule of acetonitrile provides the nitrilium salt (5a), cyclisation [5] of which affords 2-methyl-5-phenyloxazole (6a); *N*-alkylation of (6a) with a second molecule of diazonium ion (2a) then provides the observed product (7a) (Scheme) as has been verified in a separate experiment. Interestingly, when benzonitrile was used in place of acetonitrile as solvent, the reaction stops at the oxazole (6b) stage in accord with the observation [6] that the presence of a methyl group in the 2-position of an oxazole brings about an unexpectedly high increase in nucleophilicity at nitrogen. Indeed, as separate experiments showed, 2,5-diphenyloxazole (6b) failed to undergo phenacylation under those conditions where excellent yields were obtained with 2-methyl-5-phenyloxazole (6a).

On the basis of the above mechanism, formation of the oxazole (6) is catalytic in H^+. To reduce competition between nitrile and trifluoromethanesulphonate anion for the phenacyldiazonium ion (2a), it appeared reasonable to reverse the above order of addition, since gradual addition of the acid to the diazoketone (1a) would then provide the requisite H^+ whilst limiting the amount of competing counter-anion. When this was done, the yield of the *N*-phenacyloxazolium salt (7a) was raised to 66% in accord with equation (3). Avoidance of phenacyl trifluoromethanesulphonate (4a) formation is clearly important since, under the conditions used, such a reagent does not phenacylate acetonitrile; [3] at ambient temperature only phenacyldiazonium ion (2a) can perform this function.

$$2\ PhCO{\cdot}CHN_2 + MeCN + HOSO_2CF_3 \longrightarrow \text{Me, O, N}^+\text{—CH}_2\text{COPh, Ph, H, } CF_3SO_3^- + 2N_2 \quad (3)$$

The above results, taken with our previous findings,[1] make it apparent that the phenacylsulphonium salt (3) may be prepared from the interaction of protonated 2-diazoacetophenone (1) and dialkyl or alkyl aryl sulphides using acetonitrile as solvent. When, however, less nucleophilic sulphides such as diphenyl sulphide and dibenzothiophen are employed, sulphonium salt formation becomes more difficult and competing oxazole formation sets in. Furthermore, the accumulating oxazole (6a) may serve to remove the phenacyl group from the sulphonium salt that has been formed. This is clearly illustrated by the observation that both phenacyldibenzothiophenium (3d) and -diphenylsulphonium (3a) salts quantitatively transfer their phenacyl residues to the nitrogen of 2-methyl-5-phenyloxazole (6a). It is hardly surprising, therefore, that interaction of diazoacetophenone (1a), dibenzothiophen, and perchloric acid in acetonitrile gave exclusively the *N*-phenacyloxazolium salt (7b) and no sulphonium salt (3d). The latter may, however, be obtained, albeit in low yield,

when this reaction is carried out in chloroform. Again, as discussed above, the diazonium ion (2b) from 4-(diazoacetyl)dibenzothiophen (1c) does not cyclize to the sulphonium salt (3f) in dichloromethane solution. When, however, acetonitrile is used as solvent, the corresponding *N*-phenacyloxazolium salt (7c) is obtained in high yield.

The formation of oxazoles from nitriles and phenacyl halides in the presence of Lewis acids is well known,[6] although yields are poor except when there is an aryl group α to the nitrilium centre.[7] Very recently,[8,9] diazoketones in combination with Lewis acids and nitriles have been shown to afford oxazoles which, however, are apparently not phenacylated under the conditions employed. *N*-alkyloxazolium salts are, of course, well known but few of the corresponding *N*-phenacyl-analogues appear to have been described except for those of some 2-amino-oxazoles.[6]

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 397 spectrophotometer, ^{1}H n.m.r. spectra on a Perkin-Elmer R32A spectrometer, and mass spectra on A.E.I. MS45 and MS902 spectrometers. Light petroleum refers to the fraction with b.p. 60—80 °C. In all reactions with protonic acids, diazoketones evolved the theoretical quantity of nitrogen, after gas volumes had been reduced to S.T.P. All the known compounds gave satisfactory analytical and spectroscopic data. Physical data for phenacylsulphonium and *N*-phenacyloxazolium salts are given in the Table. For products marked with an asterisk, further spectral data are given in Supplementary Publication No. SUP 22465 (4 pp.).†

Diazoketones.—These were prepared from diazomethane and the appropriate carboxylic acid chloride by standard procedures.[10] 4-(Diazoacetyl)dibenzothiophen [11,*] (1c) (87%), m.p. 158.5—160.0 °C (from acetonitrile) [lit.,[11] m.p. 161—162 °C (from ethanol)], $\nu_{max.}$ 2 138m and 2 090s (N=N) cm^{-1}; τ($CDCl_3$) 1.5—2.8 (7 H, m, Ar-H) and 3.88 (1 H, s, CO·CHN_2); it was characterized as its triphenylphosphine adduct [12] and as its decomposition product with toluene-*p*-sulphonic acid monohydrate.[13] N-[2-(4-*Dibenzothienyl*)-2-*oxoethylidene*]-PPP-*triphenylphosphadiazene* * (36%) (Found: N, 5.1; P, 5.6. $C_{32}H_{23}N_2OPS$ requires N, 5.4; P, 6.0%) had m.p. 125—129 °C (decomp.) (from diethyl ether); $\nu_{max.}$ 1 612s (C=O) cm^{-1}; τ($CDCl_3$)

† For details of Supplementary Publications, see *J.C.S. Perkin I*, 1978, Index issue.

Physical data for phenacylsulphonium and *N*-phenacyl oxazolium salts

Compound	M.p. (°C) (solvent)	$\nu_{max.}$/cm^{-1} [a,b]	τ (CH_3CN)	Formula	Found (required) (%) C	H	Cl	F	N	S
(3a)	171.0—172.5 EtOH	1 677s (C=O)	1.9—2.1 (6 H, m, Ar-H, *ortho* to COR and S$^+$), 2.2—2.5 (9 H, m, Ar-H), and 3.99 (2 H, s, CH_2)	$C_{21}H_{17}F_3O_4S_2$	55.2 (55.5)	3.9 (3.8)		12.3 (12.5)		13.7 (14.1)
(3b)	183.5—184.5 EtOH	1 682s (C=O)	1.9—2.1 (6 H, m, Ar-H *ortho* to COR and S$^+$), 2.2—2.5 (9 H, m, Ar-H), and 4.00 (2 H, s, CH_2)	$C_{20}H_{17}ClO_5S$	59.3 (59.3)	4.3 (4.2)	9.0 (8.8)			7.8 (7.9)
(3c)	120.0—121.5 MeCN–Et_2O	1 678s (C=O)	1.6—1.8 (4. H m, Ar-H *ortho* to COR and S$^+$), 1.9—2.5 (9 H, m, Ar-H), and 4.43 (2 H, s, CH_2)	$C_{21}H_{15}F_3O_4S_2$	55.7 (55.7)	3.3 (3.3)		12.4 (12.6)		14.1 (14.2)
(3d)	152.0—153.5 MeCN	1 668s (C=O)	1.7—1.9 (4 H, m, Ar-H *ortho* to COR and S$^+$), 2.0—2.6 (9 H, m, Ar-H), and 4.48 (2 H, s, CH_2)	$C_{20}H_{15}ClO_5S$	59.3 (59.6)	3.8 (3.8)	9.1 (8.8)			7.5 (8.0)
(3g)	177.0—179.5 EtOH	1 680s (C=O)	1.9—2.1 (2 H, Ar-H *ortho* to COR, J_{ortho} 8.0, J_{meta} 2.0 Hz), 4.73 (2 H, s, CH_2COR), 6.46 (4 H, m, CH_2, α to S$^+$), and 7.77 (4 H, m, CH_2 β to S$^+$) [c]	$C_{12}H_{15}ClO_5S$	46.9 (47.0)	5.0 (4.9)	11.8 (11.6)			10.3 (10.4)
(7a)	122.5—123.5 [d]	3 108m (=CH, α to N$^+$) 1 702s (C=O) 1 642m (C=N$^+$)	1.64 (1 H, s, Ar-H *ortho* to N$^+$), 1.94 (2 H, Ar-H *ortho* to COR), 2.2—2.6 (8 H, m, Ar-H), 3.67 (2 H, s, CH_2) and 7.03 (3 H, s, Me) [e]	$C_{19}H_{16}F_3NO_5S$	53.1 (53.4)	4.1 (3.8)		13.4 (13.3)	3.5 (3.3)	7.4 (7.5)
(7b)	195.5—197.5 EtOH	3 143m (=CH, α to N$^+$) 3 133m (=CH, α to N$^+$) 1 703s (C=O) 1 646m (C=N$^+$)	1.55 (1 H, s, Ar-H *ortho* to N$^+$), 1.91 (2 H, Ar-H *ortho* to COR, J_{ortho} 7.5, J_{meta} 2.0 Hz), 2.1—2.5 (8 H, m, Ar-H), 3.80 (2 H, s, CH_2) and 7.00 (3 H, s, Me) [e]	$C_{18}H_{16}ClNO_6$	57.0 (57.2)	4.3 (4.3)	9.4 (9.4)		3.7 (3.7)	
(7c)	266—270 [f] (decomp.)	3 145m (=CH, α to N$^+$) 1 680s (C=O) 1 640m (C=N$^+$)	1.2—2.5 (15 H, m, Ar-H), 3.50 (2 H, s, CH_2), and 6.84 (3 H, s, Me) [e]	$C_{31}H_{20}F_3NO_5S_3$	57.9 (58.2)	3.0 (3.2)		9.0 (8.9)	2.2 (2.2)	14.8 (15.0)

[a] All perchlorate salts showed a characteristic absorption at 1 083s,br cm^{-1} (ClO_4^-), and trifluoromethanesulphonates at 1 280—1 245s,br, 1 160—1 150s, and 1 030s cm^{-1} ($CF_3SO_3^-$). [b] For Nujol or hexachlorobutadiene mulls. [c] In $(CD_3)_2SO$: (3a—d) decompose in this solvent. [d] From EtOH–light petroleum. [e] In $CDCl_3$. [f] Washed with $CHCl_3$.

1.55 (1 H, CO·CH=N–N=P, J_{HP} 2.3 Hz) and 1.7—3.1 (22 H, m, Ar-H). 2-(4-*Dibenzothienyl*)-2-*oxoethyl toluene*-p-*sulphonate* * (4d) (97%) (Found: C, 63.8; H, 3.8; S, 16.2. $C_{21}H_{16}O_4S_2$ requires C, 63.6; H, 4.1; S, 16.2%) had m.p. 138.5—141.5 °C (from acetonitrile–methanol); $\nu_{max.}$ 1 687s (C=O), 1 367s (SO_2), and 1 178s (SO_2) cm^{-1}; τ($CDCl_3$) 1.6—2.7 (11 H, m, Ar-H), 4.57 (2 H, s, CH_2), and 7.62 (3 H, s, Me); *m/e* 396 (13.1%, M^+).

2-*Methyl*-5-*phenyloxazole* (6a).—Prepared from acetic anhydride and 2-aminoacetophenone hydrochloride as described by Wolfheim,[14] this had m.p. 57.5—58.5 °C (from (from light petroleum) (lit.,[8,14] m.p. 58—60 °C).

Phenacylsulphonium Salts.—(*a*) When 2-diazoacetophenone (1a) (1.46 g, 0.01 mol) in dry dichloromethane (15 ml) was added with stirring during 20 min to trifluoromethane sulphonic acid (3.00 g, 0.02 mol) and diphenyl sulphide (3.73 g, 0.02 mol) in the same solvent (35 ml), nitrogen (224 ml, 100%) was evolved briskly. After 30 min the solvent was removed under reduced pressure, ice–water (100 ml) was added and the mixture shaken for 5 min before decanting off the aqueous layer. Trituration of the residual oily solid with light petroleum (4 × 50 ml) afforded the crude product (4.17 g, 92%), which was separated and recrystallized from ethanol to provide phenacyldiphenylsulphonium trifluoromethanesulphonate * (3a) as colourless plates, m.p. 171.0—172.5 °C (lit.,[3] m.p. 168—169.5 °C) (see Table). The use of 72% w/w perchloric acid (2.79 g, 0.02 mol) and chloroform as solvent in place of the trifluoromethanesulphonic acid and dichloromethane gave, in the same way, *phenacyldiphenylsulphonium perchlorate* * (3b) (27%).

(*b*) When, in both of the above experiments, the diphenyl sulphide was replaced by dibenzothiophen [15] (3.69 g, 0.02 mol), there resulted 5-*phenacyldibenzothiophenium trifluoromethanesulphonate* * (3c) (35%) and *perchlorate* * (3d) (14%), respectively. Here, the crude water-washed products were triturated with diethyl ether (4 × 50 ml) to remove unchanged dibenzothiophen, and then recrystallized from acetonitrile–ether.

(*c*) To trifluoromethanesulphonic acid (1.55 g, 10.3 mmol) in dry dichloromethane (30 ml) was added, as in (*a*) above, 4-(diazoacetyl)dibenzothiophen (1c) (1.30 g, 5.15 mmol) in the same solvent (15 ml). The solvent was removed under reduced pressure and, after stirring the residual solid in dry ether (50 ml) for 30 min, the crude product (1.61 g, 83.5%) was separated and recrystallized from acetonitrile (charcoal) at 0 °C to provide 2-(4-*dibenzothienyl*)-2-*oxoethyl trifluoromethanesulphonate* * (4c) (Found: C, 47.9; H, 2.3; F, 15.0; S, 16.8. $C_{15}H_9F_3O_4S_2$ requires C, 48.1; H, 2.4; F, 15.2; S, 17.1%), m.p. 153—158 °C (decomp.); $\nu_{max.}$ 1 685s (C=O) cm^{-1}; τ($CDCl_3$) 1.4—2.6 (7 H, m, Ar-H) and 4.13 (2 H, s, CH_2); *m/e* 374 (38.9%, M^+). When, in this experiment, the trifluoromethanesulphonic acid was replaced by 72% w/w perchloric acid (2 mol equiv.), a complex mixture resulted, in contrast to the high yield (⩾ 85%) of the cyclic sulphonium perchlorate (3e) obtained in the same way from 2-diazo-2′-(phenylthio)acetophenone [1] (1b) in either acetonitrile [1] or chloroform as solvent. The salt (3e) had m.p. 185.0—185.5 °C (from acetonitrile–ether) (lit.,[1] m.p. 177—180 °C from ethanol); τ(MeCN) 1.7—2.0 (4 H, m, Ar-H *ortho* to COR and S^+), 2.2—2.4 (5 H, m, Ar-H), and 5.27 (2 H, AB quartet, $J_{AB} = J_{gem} = 18$ Hz, CH_2).

Acid-induced Interaction of Diazoketones and Nitriles.—(*a*) To 2-diazoacetophenone (1.46 g, 0.01 mol) in dry acetonitrile (15 ml) was added with stirring during 20 min trifluoromethanesulphonic acid (3.00 g, 0.02 mol) in the same solvent (35 ml). When the evolution of nitrogen had ceased (after *ca.* one-third of the addition), the solvent was removed under reduced pressure, ice–water (100 ml) was added and the suspension set aside at 0 °C overnight. The solid was separated and washed with water to remove acid, and then with ether until it was colourless. Recrystallization of the crude product (1.42 g, 66%) from ethanol–light petroleum provided 2-*methyl*-3-*phenacyl*-5-*phenyloxazolium trifluoromethanesulphonate* * (7a). In the same way, 72% w/w perchloric acid gave 2-*methyl*-3-*phenacyl*-5-*phenyloxazolium perchlorate* * (7b) (29%). When the addition of acid to diazoketone (1a) was reversed, yields of the oxazolium salts [(7a) and (7b)] were reduced to 42% and 14% respectively.

(*b*) When 2-diazoacetophenone (1.46 g, 0.01 mol) in acetonitrile (15 ml) was added with stirring during 20 min to 72% w/w perchloric acid (2.79 g, 0.02 mol) and dibenzothiophen (3.68 g, 0.02 mol) in acetonitrile (50 ml), work-up as above provided the oxazolium perchlorate (7b) (0.93 g, 49%), identical (mixed m.p. and spectra) with that obtained above. In the same way, when the dibenzothiophen was replaced by tetrahydrothiophen (1.76 g, 0.02 mol) there resulted 1-*phenacyl-tetrahydrothiophenium perchlorate* * (3g) (2.45 g. 80%).

(*c*) To 4-(diazoacetyl)dibenzothiophen (1c) (2.13 g, 8.44 mmol) in dry acetonitrile (15 ml) was added, as in (*a*) above, trifluoromethanesulphonic acid (1.50 g, 10.0 mmol) in acetonitrile (15 ml). Work up, in the same way, afforded the crude product which was washed with a little chloroform to provide 5-(4-*dibenzothienyl*)-3-[2-(4-*dibenzothienyl*)-2-*oxoethyl*]-2-*methyloxazolium trifluoromethanesulphonate* * (7c) (1.92 g, 71%); this material proved tedious to recrystallize.

When the diazoketone (1c) (1.56 g, 6.18 mmol) was added portion wise with stirring during 20 min to trifluoromethanesulphonic acid (1.86 g, 12.4 mmol) in dry acetonitrile (50 ml), the crude product obtained as in (*c*) above was freed from the sulphonate ester (4c) (0.70 g, 30%) by washing repeatedly with dry ether (5 × 200 ml). The residual solid, as indicated by its i.r. spectrum, proved to be the protonated oxazolium salt * (8a) contaminated with a smaller amount of the *N*-phenacyl derivative (7c). In order to deprotonate (8a), the mixture was stirred in water (100 ml) for 2 h, and after drying, was extracted with toluene (4 × 25 ml) to afford the insoluble oxazolium salt (7c) (0.53 g, 27%). Concentration of the combined toluene extracts to low bulk gave a solid (0.61 g, 37%), recrystallization of which from ethanol–light petroleum (charcoal) provided 5-(4-*dibenzothienyl*)-2-*methyloxazole* * (6c) (Found: C, 72.1; H, 3.9; N, 5.3; S, 11.8. $C_{16}H_{11}NOS$ requires C, 72.4; H, 4.2; N, 5.3; S, 12.1%), m.p. 113.0—115.0 °C; τ($CDCl_3$) 1.7—2.6 (8 H, m, Ar-H) and 7.35 (3 H, s, Me); *m/e* 265 (100%, M^+).

(*d*) 2-Diazoacetophenone (1.30 g, 8.90 mmol) in benzonitrile (5 ml) was added, as in (*b*) above, to trifluoromethanesulphonic acid (2.77 g, 18.5 mmol) in benzonitrile (10 ml). When nitrogen evolution was complete, dry ether (200 ml) was added and, after 6 h at 0 °C, the solid was separated and washed with dry ether (2 × 25 ml) to provide pale green prisms of 2,5-*diphenyloxazolium trifluoromethanesulphonate* * (8b) (1.21 g, 37%) (Found: C, 51.4; H, 3.9; F, 15.4; N, 3.8; S, 8.7; $C_{16}H_{12}F_3NO_4S$ requires C, 51.7; H, 3.3; F, 15.4; N, 3.8; S, 8.6%), m.p. 186—191 °C; $\nu_{max.}$ 3 110m (=CH α to N^+), 3 000—2 500m vbr (max. *ca.* 2 688) ($=N^+H-$), and 1 640m ($C=N^+$) cm^{-1}. The salt (507

mg, 1.37 mmol), after stirring in water (30 ml) for 2 h, afforded 2,5-diphenyloxazole (6b) (298 mg, 98%), m.p. 71.0—72.5 °C (from light petroleum) (lit.,[16] m.p. 73 °C).

N-*Phenacylation of 2-Methyl-5-phenyloxazole* (6a).—(*a*) To trifluoromethanesulphonic acid (3.00 g, 0.02 mol) and the oxazole (6a) (3.18 g, 0.0.2 mol) in dry dichloromethane (35 ml) was added, as in (*b*) above, 2-diazoacetophenone (1.46 g, 0.01 mol) in dry dichloromethane (15 ml). Work-up as in (*a*) above gave the oxazolium salt (7a) (3.68 g, 86%). When, in this experiment, the trifluoromethanesulphonic acid was replaced by 72% w/w perchloric acid (2.79 g, 0.02 mol), no nitrogen was evolved due to the precipitation of 2-methyl-5-phenyloxazolium perchlorate[17] (8c). On addition of an equal volume of acetonitrile, however, reaction proceeded overnight to provide, in the same way, the oxazolium salt (7b) (2.97 g. 79%).

(*b*) The sulphonium perchlorate (3d) (927 mg, 2.30 mmol) and the oxazole (6a) (367 mg, 2.31 mmol) were set aside overnight in acetonitrile (30 ml). The solvent was removed under reduced pressure and, on stirring the residue in ether (50 ml) for 30 min, there separated the oxazolium salt (7b) (867 mg) in quantitative yield. In the same way, equimolar proportions of the sulphonium trifluoromethanesulphonate (3a) and the oxazole (6a) gave the oxazolium salt (7a) (97%).

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