# STUDIES OF ACYL AND THIOACYL ISOCYANATES – XII<sup>1</sup>

## THE REACTIONS OF BENZOYL AND THIOBENZOYL ISOCYANATES WITH SULFONIUM YLIDES AND WITH DIAZOALKANES

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Abstract – Benzoyl isocyanates react with ethyl (dimethylsulfuranilidene) acetate, dimethyl sulfonium phenacylide and dimethyloxosulfonium methylide to give the corresponding stable benzoylcarbamoylsulfonium ylides which on pyrolysis, are converted into oxazoles. However, with dimethylsulfonium phenacylide, thioacyl isocyanate affords the thiazole derivative. In connection with the formation of oxazoles, the reaction of benzoyl isocyanates with some diazoalkanes was also investigated: the products are not 1,2,3-triazolones as reported by Neidlein, but instead benzoylcarbamoyldiazo compounds which were thermally decomposed to oxazoles.

Recently the chemistry of ylides has been the subject of considerable interest.<sup>2</sup> It is known<sup>3.4</sup> that alkyl and aryl isocyanates react with sulfonium ylides to afford the corresponding stable carbamoylsulfonium ylides. nium ylides. We wish now to report our findings on the reactions of benzoyl (1) and thiobenzoyl isocyanates (12) with sulfonium ylides. In this context, the formation of oxazoles from the reaction of 1 with diazoalkanes is also reported.



On the other hand, Agawa *et al.*<sup>5</sup> reported that the reaction of benzoyl isocyanate with phosphonium ylides gave products of different types, whose structures depend on the nature of ylides used as shown in Scheme 1.

However, little attention has been paid to the reaction of acyl or thioacyl isocyanate with sulfo-

### **RESULTS AND DISCUSSION**

Reaction of benzoyl isocyanates with sulfonium ylides. Benzoyl isocyanates (1n-1c) reacted with carbonyl-stabilized sulfonium ylides such as ethyl (dimethylsulfuranilidene) acetate (2a) and dimethylsulfonium phenacylide (2b) to give the corresponding 1:1 adducts 3a-3f in good yields. The

f:  $\mathbf{R} = \mathbf{NO}_2$ ,  $\mathbf{R}' = \mathbf{Ph}$ 



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SCHEME 1

Table 1.	Benzo	ylcarbamoy	ylsulf	fonium <sup>·</sup>	ylides	3
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	3		X7 11	1 14 45			IR (K	(Br), cn	Microanalysis Found (Calc.), %				
_	R	R'	Yield %	M.p. °C dec.	Appearance	ν <sub>NH</sub>		$\nu_{i}$	0		С	Н	N
8	н	OEt	81	81 176	colourless needles	3180	1710	1660	1620	1540	56-95 (56-94)	5.68 (5.80)	4·90 (4·74)
b	C1	OEt	86	178	colourless needles	3180	1710	1660	1625	1530	50·79 (50·98)	4·79 (4·86)	4·21 (4·25)
c	NO2	OEt	78	192	pale yellow needles	not definite	1720	1680	1620	1550	49·54 (49·41)	4·64 (4·74)	8·40 (8·23)
d	н	Ph	81	186	colourless prisms	not definite	1705	1660	1535		66-24 (66-05)	5·24 (5·24)	4-19 (4-28)
e	Cl	Ph	90	202-203	colourless prisms	3080	1710	1660	1550		59-58 (59-75)	4·40 (43·3)	3∙86 (3∙87)
f	NO2	Ph	75	207208	pale yellow needles	3070	1720	1670	1555		57-92 (58-06)	4·52 (4·33)	7·39 (7·52)

NMR (CDCl<sub>3</sub>)  $\delta$  ppm: 3b 1·31 (3H, t, -CH<sub>2</sub>CH<sub>3</sub>), 3·07 (6H, s,  $-\dot{S}(CH_3)_2$ ), 4·24 (2H, q, -<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 7·2, 8·06 (each 2H, m, aromatic protons), 12·56 (1H, broad, NH, exchanged with D<sub>2</sub>O). 3e 3·1 (6H, s,  $-\dot{S}(CH_3)_2$ ), 7·3-8·2 (9H, m, aromatic protons), 13·7 (1H, broad, NH, exchanged with D<sub>2</sub>O).

yields, physical properties and results of microanalyses of 3 are summarized in Table 1.

The adducts 3 were deduced to be the corresponding benzoylcarbamoylsulfonium ylides on the basis of their spectral data.

The reaction of 1a with dimethyloxosulfonium methylide (4) gave dimethyloxosulfonium benzoylcarbamoylmethylide (5) and dibenzoylcarbamoylmethylide (6) in 41 and 29% yields respectively. The structures were confirmed by their spectral data and microanalyses.



Thus, the behavior of benzoyl isocyanates toward sulfonium ylides is very similar to that of ordinary isocyanates. Pyrolyses of benzoylcarbamoylsulfonium ylides. When sulfonium ylide 3b was heated in refluxing decalin for 2 hr, two crystalline compounds, 7b and 8b, were obtained in 50 and 8% yields respectively.

Microanalysis and molecular ion  $(M^+ m/e 267)$ and 269 (rel. intensity 3:1)) of 7b agreed with the molecular formula of the compound derived by the elimination of dimethylsulfide from ylide 3b. Its IR spectrum showed the bands which were ascribed to a H-bonded OH group and to  $\nu_{C=0}$ , and in the NMR spectrum a singlet exchangeable with D<sub>2</sub>O appeared at  $\delta$  5.32 ppm. Furthermore, a colour test with ferric chloride indicated the presence of an OH group in 7b.

These observations suggested that 7b is 2p-chlorobenzoyl-5-ethoxycarbonyl-4-hydroxyoxazole and indeed, it was identical with an authentic sample prepared from 1b and ethyl diazoacetate, as described below.

On the other hand, the results of microanalysis and mass spectrum of the minor product 8b agreed with the molecular formula of chlorobenzoyl derivative of 7b. Its IR spectrum did not show any bands assignable to  $\nu_{OH}$ , but displayed bands of  $\nu_{C=0}$  and  $\nu_{C=N}$ . Furthermore, 8b was identical with the product obtained from 7b and p-chlorobenzoyl chloride. On the basis of these observations, it is clear that 8b is 4-p-chlorobenzoyloxy-2-p-chlorophenyl-5-ethoxycarbonyloxazole. The NMR spectrum supports the proposed structure. Similarly, pyrolysis of ylides 3a and 3c afforded the corresponding oxazole derivatives 7a, 7c and 8c. In the case of 3a, however, the isolation of benzoyloxy derivative 8a was unsuccessful. The yields, physical properties and results of microanalyses of oxazoles 7 and 8 are given in Table 2.

Ylide 3e was thermally decomposed to afford two products, 9b and 10b, in 51 and 9% yields respectively, in addition a small amount of bis(*p*-chlorobenzoyl)urea was formed. The major product 9b was confirmed, by spectral data as well as by the microanalysis, to be 5-benzoyl-2-*p*-chlorophenyl-4-hydroxyoxazole of the same type as 7, and it was identical with an authentic sample prepared from 1b and diazoacetophenone.

On the other hand, the minor product was established to be 5-benzoyl-2-*p*-chlorophenyl-4-phenacyloxyoxazole (10b) by the following evidence. Its IR spectrum did not show any bands ascribable to  $\nu_{OH}$ , and the NMR spectrum exhibited a singlet (2H) assignable to methylene protons at  $\delta$  5.77 ppm, besides aromatic protons (14H). Furthermore, 10b was obtained by the reaction of 9b with ylide 2b.

It is of interest to note that the compound of type 8, 4-benzoyloxy derivative, was not formed but 4-phenacyloxy oxazole 10b was obtained in the pyrolysis.

Although no pure product could be isolated in a similar pyrolysis of 3d, the corresponding 4-hydroxyoxazole 9c was obtained from 3f.



a:  $\mathbf{R} = \mathbf{H}$ , b:  $\mathbf{R} = \mathbf{Cl}$ , c:  $\mathbf{R} = \mathbf{NO}_2$ 

Table 2. Oxazoles 7 and	8
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		Viald	i M.p. ℃	Appearance	IR (KBr), cm <sup>-1</sup>				NMR,	Microanalysis Found (Calc.), %			
	R				ν <sub>OH</sub>	ν	:0	VC=N	он	с	Н	N	М+ <i>m e</i>
78	н	47	117	colourless grains	2760 2600	17	20	1640	5·34(s)	61·65 (61·80)	4·57 (4·75)	6·06 (6-01)	233
7b	Cl	50	137	pale yellow prisms	2760 2500	17	20	1640	5·32(s)	53-80 (53-83)	3·74 (3·74)	4-99 (5-23)	267, 269
7c	NO2	50	189	yellow needles	2760 2600	17	20	1640	5-10(s)	51-90 (51-80)	3·87 (3·62)	9•96 (10•07)	278
8b	Cl	8	145-146	colouriess needles	none	1760	1725	1605	none	56-02 (56-10)	3·25 (3·20)	3·54 (3·44)	405
8c	NO2	8	214-215	pale yellow needles	none	1780	1 <b>740</b>	1608	none	53·43 (53·40)	2·97 (3·07)	9·61 (9·83)	427



b:  $\mathbf{R} = \mathbf{Cl}$ , c:  $\mathbf{R} = \mathbf{NO}_2$ 

Pyrolysis of benzoylcarbamoylmethylide 5 at 140° for 5 min gave a product 11 ( $C_9H_7NO_2$ , M<sup>+</sup> m/e 161) in 72% yield. On the basis of its spectral data, two isomers, 2-phenyl-4-oxazolone (11-1) and -5-oxazolone (11-2), are possible for the structure of 11. However, the structure of 11 was confirmed to be 11-1, as shown by a comparison with an authentic sample prepared from isocyanate 1a and diazomethane.<sup>6</sup> Similarly, pyrolysis of dibenzoyl-carbamoylmethylide 6 gave oxazolone 11-1.



Reaction of thiobenzoyl isocyanate with sulfonium ylides. Although no pure products could be isolated in the reaction of thiobenzoyl isocyanate (12) with ethyl (dimethylsulfuranilidene) acetate (2a), 12 reacted with dimethylsulfonium phenacylide (2b) at room temperature to give directly 5-benzoyl-4-hydroxy-2-phenylthiazole (13) in 43% yield. Structure 13 was confirmed on the basis of spectral data, microanalysis and colour test with ferric chloride. In this case, the thiobenzoylcarbamoyl ylide intermediate was not isolated.



Pyrolytic pathway of benzoylcarbamoylsulfonium ylides. Although exact pyrolytic pathways for the formation of oxazoles from benzoylcarbamoylsulfonium ylides are not clear, we proposed the following routes (Scheme 2).

It is conceivable that ylide 3 exists in equilibrium

with tautomers such as 3-1 and 3-2 under the reaction conditions. The formation of 4-hydroxyoxazoles 7 and 9 could then be easily understood in terms of cyclization with the elimination of dimethylsulfide from 3-1 as shown in Scheme 2.

As mentioned above, the pyrolysis of 3e (Ar=p- $ClC_6H_4$ , R=Ph) gave small amounts of bis(pchlorobenzoyl)urea which arose from p-chlorobenzoyl isocyanate. Oxazole 10b (Ar=p-ClC<sub>6</sub>H<sub>4</sub>) corresponds to an insertion product of benzoylmethylene to 4-OH group of 9b (Ar=p-ClC<sub>6</sub>H<sub>4</sub>). These facts indicate that a part of ylide 3 would dissociate, via tautomer 3-2, into the corresponding acyl isocyanate 1 and sulfonium ylide 2 on pyrolysis. Since the reaction of 4-hydroxyoxazole 7b with isocyanate 1b in refluxing decalin afforded pchlorobenzoyloxyoxazole 8b, it might be deduced that 8 would be formed from the urethane of 7 with the elimination of HNCO.\* However, the reaction of 4-hydroxyoxazole 9b with isocyanate 1b under similar conditions did not afford the corresponding benzoyloxyoxazole derivative.

On the other hand, phenacyloxyoxazole 10 may be viewed as being formed from the reaction of 4-hydroxyoxazole 9 with ylide 2b (or benzoylmethylene). In fact, oxazole 9b reacted with ylide 2b in refluxing decalin to afford phenacyloxyoxazole 10b, together with tribenzoylcyclopropane. The reaction of oxazoles 7b and 9b with ylide 2a afforded the corresponding 4-methoxyoxazole 14a and 14b, respectively. Although the exact pathway for the formation of 14 is not clear, it might be viewed to arise from the initial formation of 4-ethoxycarbonylmethyloxyoxazole, followed by hydrolysis and subsequent decarboxylation as shown in Scheme 3. However, attempts to separate 4-methoxyoxazole 14a from the pyrolysis of benzoylcarbamoylmethylide 3b were unsuccessful.

Similarly, the formation of oxazolone 11 from the pyrolysis of benzoylcarbamoylmethylide 5 could be explained in terms of cyclization, with concurrent elimination of dimethylsulfoxide from 5.

Reactions of benzoyl isocyanates with diazoalkanes. As mentioned above, with diazomethane benzoyl isocyanate (1a) gave 2-phenyloxazol-4-one (11-1).<sup>6</sup> In contrast with the case of diazomethane, Neidlein<sup>7</sup> reported that the reaction of 1a with ethyl diazoacetate afforded 1-benzoyl-4-ethoxycarbonyl-1,2,3-triazol-5(4H)-one, m.p. 116-117°. It is possible that oxazole 7a would be formed from the corresponding 1,2,3-triazolone.

<sup>\*</sup>When benzoyl isocyanate was heated with phenol in refluxing decalin, phenyl benzoate was formed together with other products (see experimental section).





In order to identify the structures of products formed by pyrolysis of ylides 3, we investigated the reactions of benzoyl isocyanates (1) with ethyl diazoacetate (15) and diazoacetophenone (16).

When 1a was reacted with 15 under conditions identical to those reported by Neidlein, a 1:1 adduct 17a, m.p. 121°, was obtained in 59% yield. On the basis of spectral data, 17a was deduced to be ethyl benzoylcarbamoyldiazoacetate and *not* the 1,2,3-triazolone as reported by Neidlein. Similar reactions of isocyanates 1b and 1c with 15 gave the corresponding benzoylcarbamoyldiazoacetates 17b and 17c, together with small amounts of oxazoles 7b and 7c. The yields, physical properties and results of microanalyses of 17 are given in Table 3. Isocyanate 1c reacted with 16 to give the corresponding benzoylcarbamoyldiazoacetophenone 18c in refluxing benzene, although 1a and 1b did not react with 16 under similar conditions. However, the reaction of 1a and 1b with 16 at 110° without solvent afforded the corresponding benzoylcarbamoyldiazoacetophenone 18; a small amount of oxazole 9c was also formed in the reaction with 1b. The yields, physical properties and results of microanalyses of 18 are also summarized in Table 3.

Pyrolysis of 17 and 18 gave the corresponding oxazoles 7 and 9 which were also formed on pyrolysis of ylides 3 (Table 4).

$$17 \text{ or } 18 \xrightarrow{a} 7 \text{ or } 9$$

 $1 + N_2 CHCOR' \longrightarrow R - CONHCOC COR' and/or 7 or 9$  15: R' = OEt 16: R' = Ph 17: R' = OEt 18: R' = Ph

			N/:-14			IR (KBr), cm <sup>-1a</sup>				Found (Calc.), %			
	R	R'	r leid ∞	м.р. °С	Appearance	ν <sub>NH</sub>	$\nu_{\rm N=N}$	ν	C0	С	Н	N	m/e
17a	Н	OEt	59	121 <sup>ø</sup>	pale yellow needles	3280	2195	1740	1670	55·14 (55·17)	4·49 (4·24)	15·82 (16·09)	261
17b°	Cl	OEt	45	113	pale yellow needles	3280	2200	1740	1670	48∙88 (48∙80)	3∙53 (3∙38)	13·94 (14·20)	not detected
17¢°	NO2	OEt	24	117	yellow needles	3280	2200	1750	1680	46-98 (47•06)	3·55 (3·29)	18·09 (18·30)	306
1 <b>8</b> a	Н	Ph	25	150151 dec	colourless needles	~ 3220	2190	1740	1680	65·40 (65·52)	3-58 (3-78)	14·08 (14·33)	293
18b°	Cl	Ph	72	136-137 dec	colourless needles	~ 3220	2180	1740	1690	58·74 (58·74)	2∙81 (3∙06)	12·55 (12·82)	not detected
18c	NO2	Ph	38	149~150 dec	yellow grains	3400	2190	1740	1690	56·78 (56·81)	3·24 (2·98)	16·28 (16·56)	338

Table 3. Benzoylcarbamoyldiazoacetates 17 and -diazoacetophenones 18

"Neidlein did not report the spectral data of 7a.

<sup>o</sup>M.p. reported by Neidlein: 116-117°.

In these cases, oxazoles 7b, 7c, and 9b were obtained in 2, 16, and 6% yields, respectively.

### EXPERIMENTAL

All m.ps are uncorrected. IR spectra were measured as KBr pellets on a Nippon Bunko IR-S spectrophotometer and mass spectra were obtained on a Hitachi RMS-4 mass spectrometer with a direct inlet (ionization energy 70 eV). NMR spectra were determined at 60 MHz with a Hitachi R-20 NMR spectrometer with TMS as an internal reference and microanalyses were performed by Miss M. Akita of our laboratory.

Benzoyl isocyanates (1a-1c) and thiobenzoyl isocyanate (12) were prepared by the methods of Speziale<sup>8</sup> and Goerdeler<sup>9</sup> respectively. Dimethylethoxycarbonylmethylsulfonium bromide,<sup>10</sup> dimethylphenacylsulfonium bromide,<sup>10</sup> trimethyloxosulfonium chloride,<sup>11</sup> diazomethane,<sup>12</sup> ethyl diazoacetate (15),<sup>13</sup> and diazoacetophenone (16)<sup>14</sup> were prepared by the methods described in the literatures.

Reaction of benzoyl isocyanates (1) with carbonylstabilized sulfonium ylide (2). The procedure used is illustrated with the reaction of 1a with 2a.

A solution of 2a was prepared by the following procedure. To a stirred suspension of dimethylethoxycarbonylmethylsulfonium bromide  $(3 \cdot 0 g)$  in 60 ml of THF, NaH (0.8 g) was added as a 50% mineral oil dispersion in one portion. After the mixture was then stirred at room temp for 15 hr, it was filtered to remove the NaBr, thus giving a yellow solution of 2a.

After 1a (2.0 g) was added to the soln of 2a. the mixture was stirred at room temp for 12 hr, during which time crystals were formed. Filtration gave colourless crystals, which on recrystallization from benzene afforded 3a, m.p. 176° dec, as colourless needles, yield, 2.6 g (81%).

Reaction of 1a with dimethyloxosulfoniummethylide (4). A suspension of trimethyloxosulfonium chloride (1-2g) and NaH (0-7g) in 50 ml THF was refluxed for 5 hr, and then it was filtered to remove the NaCl, thus giving a soln of 4. To this soln 1a (0-8g) was added and the mixture stirred at room temp for 12 hr, during which time crystals were formed. Filtration and recrystallization from CHCl<sub>3</sub>-light petroleum (b.p. 35-45°) mixture afforded 6 (0-61 g, 29%), m.p. 184-185° dec, as colourless needles. (Found: C, 58-96; H, 4-90; N, 7-12. Calc. for C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>S: C, 59-06; H, 4-70; N, 7-25%); IR cm<sup>-1</sup>:  $\nu_{NH}$  3310,  $\nu_{C-0}$ 1720, 1650, 1640; NMR (in DMSO-d<sub>3</sub>)  $\delta$  ppm: 3-89 (6H, s, S(CH<sub>3</sub>)<sub>2</sub>), 7-4-8-0 (10H, m, aromatic protons), 11-8 (2H, broad s, NH, exchanged with D<sub>2</sub>O).

The THF filtrate was evaporated in vacuo to leave a residue, which on recrystallization from EtOH afforded 5 (0.53 g; 41%), m.p. 141° dec, as colourless prisms. (Found: C, 55·45; H, 5·57; N, 5·74. Calc. for  $C_{11}H_{13}NO_3S$ : C, 55·23; H, 5·48; N, 5·86%); IR cm<sup>-1</sup>:  $\nu_{NH}$  3240,  $\nu_{C=0}$  1680, 1605, 1595; NMR (in DMSO-de)  $\delta$  ppm: 3·51 (6H, s, S(CH<sub>3</sub>)<sub>2</sub>), 7·4–8·05 (5H, m, aromatic protons), 10·0 (1H, s, NH, exchanged with D<sub>2</sub>O).

Pyrolysis of dimethylsulfoniumethoxycarbonyl-p-chlorobenzoylcarbamoylmethylide (3b). A soln of 3b (1.0 g) in 10 ml decalin was refluxed for 2 hr, during which time insoluble resinous material was separated. The resinous material was isolated by decantation from the warm mixture. After cooling of the soln, crystals were collected by

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filtration. Recrystallization from decalin gave 7b (0.4 g; 50%), m.p. 137°, as colourless grains.

Several recrystallizations of the resinous material from EtOH afforded 8b (0.1 g; 8%), m.p. 145-146°, as colourless needles.

Similarly, pyrolysis of 3a and 3c was carried out: the results are given in Table 2.

Benzoylation of 7b. A soln of 7b (15 mg) in 2 ml pyridine was refluxed with a small excess of p-chlorobenzoyl chloride for 2 hr, and then it was cooled. After water was added to the mixture, filtration gave crystals, which on several recrystallizations from EtOH afforded p-chlorobenzoylated product (7 mg; 31%), m.p.  $145-146^\circ$ , as colourless needles. This compound was identical with the product 8b from pyrolysis of 3b.

Pyrolysis of dimethylsulfonium-p-chlorobenzoylcarbamoylphenacylide (3e). After a soln of 3e (1.2 g) in 10 ml decalin was heated under reflux for 2 hr, the mixture was cooled and then crystals were collected by filtration. The crystals were washed with CH2Cl2 to leave a trace amount of bis(p-chlorobenzoyl)urea. The washings was evaporated in vacuo to leave a crystalline compound, which on recrystallization from light petroleum (b.p. 35-45°) afforded 9b (0.6g; 51%), m.p. 211-212°, as pale yellow prisms. (Found: C, 63-99; H, 3-18; N, 4-73. Calc. for C10H10NO3Cl: C, 64·10; H, 3·34; N, 4·67%); IR cm<sup>-1</sup>: 3240-3150 (H-bonded OH), vc-o 1620; NMR (in CDCl<sub>a</sub>)  $\delta$  ppm: 6.43 (1H, s, OH, exchanged with D<sub>2</sub>O), 7.5-8.45 (9H, m, aromatic protons); mass m/e: 299, 301 (rel. intensity 3:1) (M<sup>+</sup>); 271, 273 (3:1) (M<sup>+</sup>--CO); 243, 245 (3:1) (271<sup>+</sup> and 273<sup>+</sup>--CO); 138, 140 (3:1) (Cl-()-C≡NH); 134  $(271^+ \text{ and } 273^+ - Cl - CN); 111, 113 (3:1)$ (CIC<sub>6</sub>H<sup>+</sup>).

To the decalin filtrate was added light petroleum to precipitate crystals, which on recrystallization from EtOH gave 10b (0·1 g; 9%), m.p. 188°, as colourless needles. (Found: C, 69·07; H, 3·71; N, 3·49. Calc. for C<sub>24</sub>H<sub>16</sub>NO<sub>4</sub>Cl: C, 68·98; H, 3·83; N, 3·35%); IR cm<sup>-1</sup>:  $\nu_{C=0}$  1710, 1635; NMR (in CDCl<sub>3</sub>)  $\delta$  ppm: 5·77 (2H, s, CH<sub>2</sub>), 7·3-8·2 (14H, m, aromatic protons); mass *m*/*e*: 417 (M<sup>+</sup>).

No pure product could be isolated in a similar pyrolysis of 3d, but 3f gave 28% of the corresponding 9c, m.p. 251° dec, as yellow prisms (from benzene). (Found: C, 61·74; H, 3·00; N, 8·98. Calc. for  $C_{18}H_{10}N_2O_5$ : C, 61·94; H, 3·25; N, 9·03%); IR cm<sup>-1</sup>:  $\nu_{0H}$  3200,  $\nu_{C-0}$  1625. 4-Acetoxy derivative of 9c, m.p. 161°. (Found: C, 61·64; H, 3·58; N, 8·11. Calc. for  $C_{18}H_{12}N_2O_6$ : C, 61·36; H, 3·43; N, 7·95%); IR cm<sup>-1</sup>:  $\nu_{C=0}$  1790, 1642.

Reaction of oxazole 7b with isocyanate 1b. A soln of 7b (0.3 g) and 1b (1.0 g) in 10 ml decalin was refluxed for 2 hr. After the mixture was allowed to stand overnight, pale brown crystals were collected by filtration. The crystals were washed with MeOH to leave 0.15 g bis(*p*-chlorobenzoyl)urea. To the MeOH washing was added water to give 0.2 g *p*-chlorobenzonitrile. The decalin filtrate was subjected to steam distillation to leave pale yellow crystals. Recrystalization from EtOH afforded 50 mg (11%) of 8b, m.p. 145-146°, as colourless needles.

However, the reaction of oxazole 9b with 1b did not give the corresponding benzoyloxyoxazole.\*

Reaction of phenol with isocyanate 1a. A soln of phenol (4.5 g) and 1a (7.0 g) in 30 ml decalin was refluxed for 2 hr. After cooling, filtration gave a small amount of dibenzoylurea. The decalin soln was analyzed by gas chromatography: benzonitrile 0.61 g, phenol 3.6 g, phenyl benzoate 0.9 g (10.5%).

Reaction of oxazole 9b with ylide 2b. After a soln of 9b

<sup>\*</sup>A mixture of oxazole 9b (0.15 g) and 1b (0.1 g) in decalin (5 ml) was refluxed for 2 hr. After cooling, crystals were filtered. The crystals were washed with acctone to leave 70 mg of bis(*p*-chlorobenzoyl)urea. The acctone filtrate was evaporated to give 0.1 g of unreacted oxazole 9b.

 $(0.1 \text{ g in 5 ml decalin was refluxed with an excess of 2b for 2 hr, crystals were collected by filtration. Fractional recrystallization from EtOH gave 63 mg (45%) of 10b, m.p. 188°, as colourless needles, and tribenzoylcyclopropane<sup>15</sup> resulting from 2b.$ 

Reaction of oxazole 7b with ylide 2a. A soln of 7b (0·1 g) in 5 ml decalin was added to a soln of 2a prepared from 0·3 g of the corresponding sulfonium bromide and 65 mg of NaH in 20 ml of THF. After the THF was distilled off, the mixture was refluxed for 2 hr. To the mixture was added light petroleum and the soln was chromatographed on alumina. From the elution with benzene, 14a, m.p. 86°, was obtained as colourless needles, yield, 50 mg. (Found C, 55·43; H, 4·19; N, 4·86. Calc. for C<sub>13</sub>H<sub>12</sub>NO<sub>4</sub>Cl: C, 55·43; H, 4·29; N, 4·98%); IR cm<sup>-1</sup>:  $\nu_{C=0}$  1730; NMR (in CCL<sub>1</sub>)  $\delta$  ppm: 1·38 (3H, t, CH<sub>2</sub>CH<sub>3</sub>), 4·09 (3H, s, OCH<sub>3</sub>), 4·31 (2H, q, CH<sub>2</sub>CH<sub>3</sub>), 7·4, 8·06 (each 2H, d, aromatic protons).

Similarly, 9b (0.3 g) reacted with 2a to give 14b (0.12 g), m.p. 137-139°, as yellow grains. (Found: C, 64.88; H, 3.61; N, 4.53. Calc. for  $C_{17}H_{12}NO_3Cl$ : C, 65.07; H, 3.85; N, 4.47%); IR cm<sup>-1</sup>:  $\nu_{C=0}$  1630; NMR (in CCl<sub>4</sub>)  $\delta$  ppm: 4.06 (3H, s, OCH<sub>3</sub>), 7.3-8.15 (9H, m, aromatic protons).

Reaction of benzoyl isocyanate (1a) with ethyl diazoacetate (15). A soln of 1a  $(2 \cdot 2 \text{ g})$  and 14  $(1 \cdot 95 \text{ g})$  in 20 ml xylene was refluxed for 1 hr. After cooling, 20 ml light petroleum was added to the mixture and then resulting soln was allowed to stand in a refrigerator, giving crystals. Recrystallization from light petroleum (b.p.  $60-65^\circ$ ) afforded  $2 \cdot 3 \text{ g} (50\%)$  of 17a. Similarly, the reaction of 1b or 1c with 15 afforded the corresponding 17b or 17c, together with small amounts of oxazoles 7b or 7c. The results, physical properties and microanalyses of 17 are given in Table 3.

Reaction of 1a with diazoacetophenone (16). A mixture of 1a (0.5 g) and 16 (0.5 g) was stirred at 110° for 15 min. After cooling, several recrystallization of the mixture from benzene afforded 18a (0.25 g; 25%). Similarly, the reaction of 1b or 1c with 16 gave the corresponding 18b or 18c. The results, physical properties and microanalyses of 18 are also given in Table 3.

Pyrolysis of benzoylcarbamoyldiazoacetate 17c. Compound 17c (40 mg) was heated at 120° for 2 hr; during which time the evolution of  $N_2$  was observed. After cool-

1 able 4										
	Temp. ℃	Time, hr	Product	Yield, %						
17a	130	2	7a	44						
17b	120	2	7ъ	33						
17c	120	2	7c	42						
18a	150	0.2	9a	55						
18b	150	0.5	9b	61						
18c	150	0.5	9c	32						

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ing, recrystallization from benzene afforded 7c (16 mg; 42%). Similar pyrolyses of 17a, 17b, 18a, 18b and 18c gave the corresponding oxazoles 7 and 9, respectively. The conditions and yields of oxazoles are given in Table 4.

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