Aust. J. Chem., 1995, **48**, 997–1007

The Anomalous Reactions of Some Fluoronitrobenzenes with Some *N*,*N*-Dialkylamines

Douglas J. Gale, Judi Rosevear and John F. K. Wilshire

Division of Biomolecular Engineering, CSIRO, Parkville, Vic. 3052.

Abstract

The reactions of 1-fluoro-2,4- and -2,6-dinitrobenzene with certain *N*,*N*-dialkylamines in dimethyl sulfoxide solution in the presence of potassium carbonate give the corresponding dinitrophenyl *N*,*N*-dialkylcarbamates as well as the corresponding *N*,*N*-dialkyldinitroanilines. The extent of carbamate formation is governed by steric factors. The corresponding reactions of 1-fluoro-4-nitrobenzene with diisopropylamine and di-s-butylamine give poor yields of the corresponding 4-nitrophenyl *N*,*N*-dialkylcarbamates but none of the corresponding *N*,*N*-dialkyl-4-nitroanilines; in these reactions, the major product is 4,4′-dinitrodiphenyl ether. The ^{1}H and ^{13}C n.m.r. spectra of the 2,4- and 2,6-dinitrophenyl *N*,*N*-dialkylcarbamates reveal that their aliphatic protons and carbon atoms are magnetically non-equivalent.

Introduction

In connection with another investigation, we required samples of the *N*-2,4-dinitrophenyl and *N*-2,6-dinitrophenyl derivatives of the sterically hindered amines diisopropylamine and di-s-butylamine. Apart from (2,4-dinitrophenyl)-diisopropylamine (1a), which has been obtained by the reaction of 1-chloro-2,4-dinitrobenzene with diisopropylamine in the absence of solvent (no yield given),[1] and in benzene solution (2% yield),[2] these derivatives appear to be unknown. Interestingly, the major products formed in the latter solvent were *N*-(2,4-dinitrophenyl)isopropylamine (mainly) and *N*-(2,4-dinitrophenyl)propylamine (i.e., dealkylation and rearrangement had occurred). The difficulty encountered in preparing the 2,4-dinitrophenyl derivative of diisopropylamine is not surprising because it has been reported[1] that this hindered amine reacts 30000 times more slowly with chlorodinitrobenzene (in ethanol) than does dimethylamine. In the present communication, we describe the reactions of 1-fluoro-2,4- and -2,6-dinitrobenzene with diisopropylamine and di-s-butylamine, and with several related *N*,*N*-dialkylamines, in dimethyl sulfoxide solution.

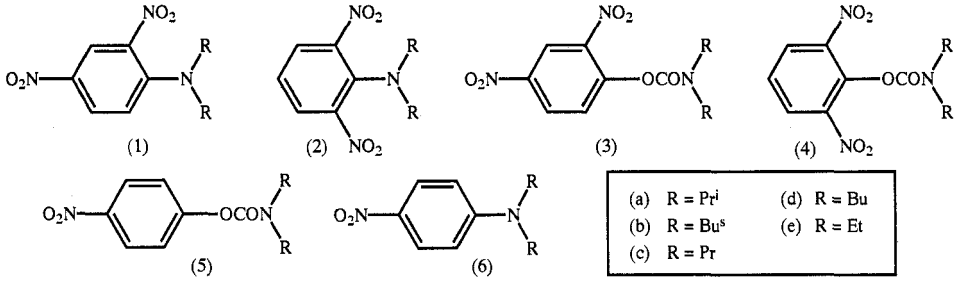
Results and Discussion

Dimethyl sulfoxide was chosen as the reaction solvent because reactions in ethanol [the solvent often employed in reaction studies (cf.[1])] may cause ethanolysis

[1] Brady, O. L., and Cropper, F. R., *J. Chem. Soc.*, 1950, 507.
[2] Nudelmann, N. S., and Socolovsky, S. E., *Tetrahedron Lett.*, 1980, **21**, 3331.

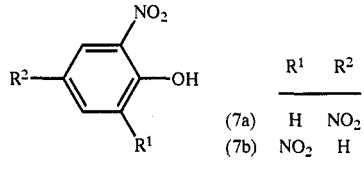
Manuscript received 8 November 1994 0004-9425/95/050997$05.00

of the fluoro nitro aromatic compound. Indeed, compounds described[3] as (2,4-dinitrophenyl)diisopropylamine and (2,4-dinitrophenyl)propylamine are probably 1-ethoxy-2,4-dinitrobenzene. In the present work, we were able to prepare (2,4-dinitrophenyl)diisopropylamine (1a), albeit in low (14%) yield, by the reaction of 1-fluoro-2,4-dinitrobenzene with diisopropylamine in dimethyl sulfoxide solution in the presence of triethylamine as supporting base. A similar reaction with 1-fluoro-2,6-dinitrobenzene, however, failed to give (2,6-dinitrophenyl)diisopropylamine (2a).

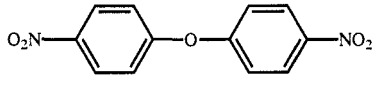


These disappointing results prompted us to examine the use of potassium carbonate as supporting base (cf. other base-catalysed reactions[4] involving reactive aromatic fluoro compounds). To our surprise, we found that the reactions of 1-fluoro-2,4- and -2,6-dinitrobenzene with diisopropylamine in the presence of potassium carbonate gave, in moderate yield, 2,4-dinitrophenyl *N*,*N*-diisopropylcarbamate (3a) and its 2,6-dinitrophenyl analogue (4a) respectively. Similar reactions of 1-fluoro-2,4- and -2,6-dinitrobenzene with di-s-butylamine gave 2,4- and 2,6-dinitrophenyl *N*,*N*-di-s-butylcarbamates [(3b) and (4b), respectively]. In only one reaction, namely that of 1-fluoro-2,4-dinitrobenzene with diisopropylamine, was the desired 2,4-dinitrophenyl derivative (1a) also obtained [but in very poor (2%) yield]. In many reactions, the corresponding dinitrophenols (7a,b) were significant by-products. A control experiment showed that 1-fluoro-2,4-dinitrobenzene in dimethyl sulfoxide solution reacted with potassium carbonate in the absence of the secondary amine to give 2,4-dinitrophenol (7a) in excellent yield. It is concluded, therefore, that, when reactions involving 1-fluoro-2,4- and -2,6-dinitrobenzene with secondary amines are very slow, alkaline hydrolysis of the reagent is likely to intervene to give the corresponding dinitrophenol.

The corresponding reactions of 1-fluoro-2,4-dinitrobenzene with the less sterically hindered secondary amines, dipropylamine, dibutylamine and diethylamine gave the corresponding 2,4-dinitrophenyl derivatives (1c–e) in excellent yield, but none of the corresponding 2,4-dinitrophenyl *N*,*N*-dialkylcarbamates. Reactions of 1-fluoro-2,6-dinitrobenzene with all three amines gave, however, mixtures of



	R^1	R^2
(7a)	H	NO_2
(7b)	NO_2	H



[3] Zemanova, E., and Zeman, S., *J. Chromatogr.*, 1978, **154**, 33.
[4] Rosevear, J., and Wilshire, J. F. K., *Aust. J. Chem.*, 1991, **44**, 1097.

the corresponding 2,6-dinitrophenyl derivatives (2c–e) and the corresponding 2,6-dinitrophenyl *N*,*N*-dialkylcarbamates (4c–e) in approximately equal amounts. This result indicates that reaction with 1-fluoro-2,6-dinitrobenzene is more sterically hindered than with 1-fluoro-2,4-dinitrobenzene; accordingly, carbamate formation is facilitated.

The reactions of 1-fluoro-4-nitrobenzene with diisopropylamine and with di-s-butylamine were also investigated and found, as expected, to be much slower (a large proportion of the reagent was recovered unchanged). Nevertheless, small conversions into the corresponding 4-nitrophenyl *N*,*N*-dialkylcarbamates (5a,b) occurred; the corresponding *N*,*N*-dialkyl-4-nitroanilines (6a,b) were not obtained. In both reactions, a considerable amount of 4,4′-dinitrodiphenyl ether (8) was formed as a by-product. A control experiment showed that 1-fluoro-4-nitrobenzene in dimethyl sulfoxide solution reacted with potassium carbonate alone to give this by-product (8) in moderate yield, presumably from reaction of the reagent with 4-nitrophenol (formed by base-catalysed hydrolysis of the reagent). Indeed, 4,4′-dinitrodiphenyl ether (8) was obtained, but in much higher yield, by the corresponding reaction of 1-fluoro-4-nitrobenzene with 4-nitrophenol (see Experimental).

The structures of the 2,4- and 2,6-dinitrophenyl, and of the 4-nitrophenyl *N*,*N*-dialkylcarbamates were established on the basis of (i) their microanalytical data,

Table 1. *N*,*N*-Dialkylanilines and aryl *N*,*N*-dialkylcarbamates: melting points and analytical data [general formulae (1)–(5)]

Compound	R	M.p. (°C)	Empirical formula	Found (%) C	H	N	Required (%) C	H	N
N,*N*-Dialkylanilines [general formulae (1) and (2)]									
2,4-Dinitrophenyl series									
(1a)	Pr^i	127–129[A]	$C_{12}H_{17}N_3O_4$	53·9	6·6	15·9	53·9	6·4	15·7
(1c)	Pr	39–40[A]	$C_{12}H_{17}N_3O_4$						
(1d)	Bu	oil[A]	$C_{14}H_{21}N_3O_4$						
(1e)	Et	68–70[A]	$C_{10}H_{13}N_3O_4$						
2,6-Dinitrophenyl series									
(2c)	Pr	53–55[A]	$C_{12}H_{17}N_3O_4$	54·2	6·7	15·7	53·8	6·4	15·7
(2d)	Bu	oil	$C_{14}H_{21}N_3O_4$	57·1	7·2	14·2	56·9	7·2	14·2
(2e)	Et	46–48[A]	$C_{10}H_{13}N_3O_4$						
Aryl *N*,*N*-dialkylcarbamates [general formulae (3)–(5)]									
2,4-Dinitrophenyl series									
(3a)	Pr^i	99–101[A]	$C_{13}H_{17}N_3O_6$	50·2	5·5	13·5	50·2	5·6	13·5
(3b)	Bu^s	oil	$C_{15}H_{21}N_3O_6$	53·4	6·4	12·6	53·1	6·2	12·4
(3e)	Et	68–70	$C_{11}H_{13}N_3O_6$	46·5	4·6	15·2	46·6	4·6	14·8
2,6-Dinitrophenyl series									
(4a)	Pr^i	98–100	$C_{13}H_{17}N_3O_6$	50·8	5·5	13·6	50·2	5·6	13·5
(4b)	Bu^s	50–52	$C_{15}H_{21}N_3O_6$	53·3	6·4	12·4	53·1	6·2	12·4
(4c)	Pr	74–76	$C_{13}H_{17}N_3O_6$	50·2	5·5	13·4	50·2	5·5	13·5
(4d)	Bu	oil	$C_{15}H_{21}N_3O_6$	53·1	6·5	12·5	53·1	6·2	12·4
(4e)	Et	86–88	$C_{11}H_{13}N_3O_6$	46·7	4·6	15·2	46·6	4·6	14·8
4-Nitrophenyl series									
(5a)	Pr^i	57–58[A]	$C_{13}H_{18}N_2O_4$	58·7	6·7	10·5	58·6	6·8	10·5
(5b)	Bu^s	oil	$C_{15}H_{22}N_2O_4$	61·0	7·6	9·8	61·2	7·5	9·5

[A] Known compound (see Experimental section).

and (ii) their infrared spectra (strong carbonyl absorption at 1720–1740 cm^{-1}). In addition, alkaline hydrolysis of the *N*,*N*-diisopropylcarbamates (3a) and (4a) gave 2,4- or 2,6-dinitrophenol (7a) and (7b) respectively. Unequivocal proof of structure in the case of the *N*,*N*-diisopropylcarbamates (3a), (4a) and (5a) was obtained by an independent route, namely the reaction in pyridine solution of *N*,*N*-diisopropylcarbamoyl chloride [$(Pr^i)_2NCOCl$] with 2,4- and 2,6-dinitrophenol, and with 4-nitrophenol respectively (see Experimental). Similar reactions of *N*,*N*-diethylcarbamoyl chloride gave 2,4- and 2,6-dinitrophenyl *N*,*N*-diethylcarbamate (3e) and (4e) respectively. Melting points and analytical data for the carbamates obtained in this investigation, and for several related dinitrophenyl derivatives are presented in Table 1.

The outcome of the reactions with diisopropylamine and with di-s-butylamine suggests strongly that *N*,*N*-diisopropylcarbamic acid [$(Pr^i)_2NCOOH$] and *N*,*N*-di-s-butylcarbamic acid [$(Bu^s)_2NCOOH$] (presumably as their potassium salts), respectively, had participated in the reactions. The following simple equation

$$R_2NH + CO_3^{2-} \rightarrow R_2NCOO^- + OH^-$$

shows the formation of both the carbamate and hydroxide anions; the latter species is considered to be responsible for the by-products formed, although its formation could also arise from the very small amount (0·05%) of water present in the solvent. On one occasion, during the reaction of 1-fluoro-2,4-dinitrobenzene with diisopropylamine, a colourless crystalline solid collected in the neck of the flask (see Experimental); the ^1H n.m.r. spectrum of this solid revealed the presence of a diisopropyl group, and its empirical formula ($C_7H_{17}NO_3$) (derived from its microanalytical data) suggested that it was diisopropylamine bicarbonate [$(Pr^i)_2NH^+ HCO_3^-$] formed by the reaction of diisopropylamine with the carbon dioxide liberated during the reaction. Interestingly, a reported attempt[5] to obtain *N*,*N*-diisopropylcarbamic acid and *N*,*N*-dipropylcarbamic acid in aqueous solution failed; the present work suggests that these presumably unstable compounds, and their diethyl, dibutyl and di-s-butyl analogues, are moderately stable (presumably as their potassium salts), either in solution or in suspension, in the presence of dimethyl sulfoxide.

All the dinitrophenyl *N*,*N*-dialkylcarbamates obtained in this investigation exhibited marked magnetic non-equivalence in the *N*,*N*-dialkyl regions of their ^1H and ^{13}C n.m.r. spectra (see Tables 2 and 3 respectively) at 35° due to hindered rotation about their N–CO bonds, a phenomenon which has already been observed[6] (^1H n.m.r. spectrum) in the case of 4-nitrophenyl *N*,*N*-dimethylcarbamate (5; R = Me), where the coalescence temperature of the methyl signals was found to be 39°.[6] The occurrence of magnetic non-equivalence in carbamates of the general formulae (3) and (4) is enhanced by the presence of two nitro groups since similar (^1H n.m.r.) non-equivalence was absent in the case of the 4-nitrophenyl *N*,*N*-diisopropyl- and *N*,*N*-di-s-butyl-carbamates (5a) and (5b) respectively, the NCH signals of which were broadened somewhat at 35°. On the other hand, the ^{13}C n.m.r. spectra of 4-nitrophenyl *N*,*N*-diisopropylcarbamate (5a) and its di-s-butyl analogue (5b) did show evidence of hindered rotation about their

[5] Jensen, A., Jensen, M. H., and Fuarholt, C., *Acta Chem. Scand.*, 1954, **8**, 1129.
[6] Lustig, E., Benson, W. R., and Duy, N., *J. Org. Chem.*, 1967, **32**, 851.

Table 2. ***N*,*N*-Dialkylanilines and aryl *N*,*N*-dialkylcarbamates [general formulae (1)–(5)]: ^{1}H n.m.r. data**

Cpd	R	H3	H4	H5	H6	NCH	NCH_2	CH_2[A]	CH_2[A]	$CHCH_3$	CH_2CH_3[B]
						N,*N*-Dialkylanilines [general formulae (1) and (2)]					
						2,4-Dinitrophenyl series					
(1a)	Pr^i	8·49		8·14	7·33	3·66spt				1·30d[C]	
(1c)	Pr	8·62		8·18	7·11		3·27t	1·66			0·90
(1d)	Bu	8·62		8·19	7·11		3·30t	1·31	1·31		0·91
(1e)	Et	8·60		8·18	7·08		3·34q				1·25
						2,6-Dinitrophenyl series					
(2c)	Pr	7·80	7·15	7·80			2·93t	1·54			0·87
(2d)	Bu	7·80	7·15	7·80			2·99t	1·37	1·37		0·87
(2e)	Et	7·80	7·18	7·80			3·07q				1·10
						Aryl *N*,*N*-dialkylcarbamates [general formulae (3)–(5)]					
						2,4-Dinitrophenyl series					
(3a)	Pr^i	8·91		8·47	7·50	4·23spt				1·34d[C]	
						3·89spt				1·33d[C]	
(3b)	Bu^s	8·91		8·47	7·48	3·81m		1·68		1·34m[D]	1·01
						3·48m					0·93
(3e)	Et	8·89		8·48	7·55		3·50q				1·31
							3·40q				1·23
						2,6-Dinitrophenyl series					
(4a)[E]	Pr^i	8·22	7·46	8·22		4·21spt				1·30d[C]	
						3·80spt				1·29d[C]	
(4b)[E]	Bu^s	8·22	7·48	8·22		3·87m		1·71		1·32d	0·98
						3·42m				1·31d	0·91
(4c)[E]	Pr	8·25	7·51	8·25			3·39t	1·69			0·94
							3·31t				0·91
(4d)[E]	Bu	8·24	7·50	8·24			3·40t	1·47	1·47		0·92
							3·31t				0·90
(4e)	Et	8·25	7·50	8·25			3·52q				1·30
							3·32q				1·23
						4-Nitrophenyl series					
(5a)	Pr^i	8·25		8·25	7·30[F]	4·03spt				1·33d[C]	
(5b)	Bu^s	8·24		8·24	7·28[F]	3·81m		1·71		1·31d	0·96

[A] Multiplet. [B] Triplet. [C] $CH(CH_3)_2$. [D] Six signals observed. [E] Data obtained at 300 MHz. [F] H 2 and 6.

N–CO bonds; the spectrum of the diisopropylcarbamate (5a) revealed significant broadening of the singlets of the CH (aliphatic) and CH_3 carbons, whereas that of the di-s-butylcarbamate (5b) showed broadening of the CH (aliphatic) carbon, two signals each for the CH**Me** and the CH_2 carbons, and a singlet for the CH_2**Me** carbons (see Table 3). Curiously, the ^{13}C n.m.r. spectrum of 2,6-dinitrophenyl *N*,*N*-di-s-butylcarbamate (4b) contained *three* or *four* signals for each aliphatic carbon; this phenomenon was observable but to a much lesser extent with the corresponding 2,4-dinitrophenyl derivative (3b). We suggest that hindered rotation about the N–CO bond of carbamate (4b) causes such severe overcrowding in the aliphatic region that the individual s-butyl [CH(Me)Et] groups are conformationally different from one another.

Interestingly, a comparison of the ^1H n.m.r. spectrum of (2,4-dinitrophenyl)diisopropylamine (1a) with the spectra of the less sterically hindered 2,4-dinitrophenyl derivatives (1c–e) of dipropylamine, dibutylamine and diethylamine reveals

Table 3. Aryl *N*,*N*-dialkylcarbamates [general formulae (3)–(5)]: ^{13}C chemical shifts (aliphatic carbons)

Cpd	R	NCH	NCH_2	CH_2	$\mathbf{C}H_2CH_3$	$CH(\mathbf{C}H_3)_2$	$CH\mathbf{C}H_3$	$CH_2\mathbf{C}H_3$
				2,4-Dinitrophenyl series[A]				
(3a)	Pr^i	47·24				20·31		
		47·89				21·02		
(3b)	Bu^s	53·76			27·31		17·95	11·67
		54·14			28·24		18·87	
		54·46						
(3e)	Et		42·42					13·11
			42·91					13·92
				2,6-Dinitrophenyl series[A]				
(4a)	Pr^i [B]	47·40				20·28		
		48·27				20·89		
(4b)	Bu^s [B]	54·92			27·31		17·97	11·51
		54·65			27·40		18·03	11·61
		53·93			28·05		18·78	11·68
		53·67					18·88	
(4c)	Pr [B]		49·71		20·90			10·96
			50·22		21·62			11·16
(4d)	Bu [B]		47·62	29·60	19·63			12·48
			48·14	30·31	19·83			
(4e)	Et		42·47					13·06
			43·07					13·76
				4-Nitrophenyl series[A]				
(5a)	Pr^i	46·96[C]				20·74		
						21·29		
(5b)	Bu^s	53·48[D]			27·48		18·00	11·72
					28·40		19·30	

[A] Data (mean values) for aromatic and carbonyl carbons (tentative assignments for tertiary and carbonyl carbons). (i) 2,4-Dinitrophenyl series: δ 121·41 (C6); 126·47 (C1); 128·53 (C5); 142·10 (C3); 144·22 (C2); 149·58 (C4); 150·86 (C=O). (ii) 2,6-Dinitrophenyl series: δ 125·65 (C1); 129·59 (C4); 139·55 (C3/C5); 144·35 (C2/C6); 150·60 (C=O). (iii) 4-Nitrophenyl series: δ 122·23 (C2/C6); 124·99 (C3/C5); 144·57 (C1); 152·51 (C4); 156·41 (C=O).
[B] Data obtained at 75 MHz.
[C] Broad.
[D] Broad triplet.

significant differences (see Table 2) in the aromatic region. Thus, the H3 doublet (J *c.* 2 Hz) of (2,4-dinitrophenyl)diisopropylamine (1a) is shielded, and its H6 doublet (J *c.* 9 Hz) deshielded, relative to the corresponding doublets of the other three 2,4-dinitrophenyl derivatives. This phenomenon, which is presumably due to the effect of steric overcrowding (between the N,N-diisopropyl and 2-nitro groups) on the adjacent H3 and H6 protons, will be discussed elsewhere (as will the parallel differences observed in the ultraviolet spectra of all four 2,4-dinitrophenyl derivatives).

Experimental

(*a*) General

All melting points are uncorrected. The elementary analyses were carried out by either the Australian Microanalytical Service, Melbourne, or the Analytical Unit, Research School of Chemistry, Australian National University. Infrared spectra (KBr disks or Nujol) were recorded on a Perkin–Elmer 257 instrument. ^{1}H n.m.r. spectra were obtained in $CDCl_3$ solution either on a Varian A60D spectrometer or on a Jeol FX90 spectrometer. ^{13}C n.m.r. spectra were recorded on the latter instrument and on a Bruker 300 MHz instrument. 1-Fluoro-4-nitrobenzene and 1-fluoro-2,4-dinitrobenzene were Fluka grade. 1-Fluoro-2,6-dinitrobenzene, prepared from the corresponding chloro compound (Aldrich grade), was available from our previous work.[7] Diisopropylamine and di-s-butylamine were Fluka and Aldrich reagent grades respectively; dipropylamine and dibutylamine were Light grades. Unless otherwise indicated, either Merck silica gel 60 or alumina 90 was used for the column chromatography. Light petroleum refers to 40–60° grade. Powdered anhydrous potassium carbonate was kept in an oven at 110–120°.

N,N-Diisopropylcarbamoyl chloride was prepared by the following method (cf.[8]). A solution of diisopropylamine (22·2 g, 0·22 mol) and pyridine (17·5 g, 0·22 mol) in a mixture of benzene (80 ml) and toluene (40 ml) was added dropwise over a period of 2 h to a cooled (0°) stirred solution of phosgene (29 g, 0·30 mol) in toluene (200 ml). After standing overnight, the reaction mixture was purged with nitrogen to remove excess phosgene, and then filtered. The filtrate was washed four times with saturated salt solution before being dried over anhydrous sodium sulfate. Removal of the solvents followed by fractional distillation in a vacuum gave an oil (10·7 g, 30% yield), b.p. 78°/4 mm, which solidified to give a colourless solid, m.p. 57–59° [lit.[9] reports the isolation of a sublimable solid (no m.p. quoted), b.p. 90°/10 mm]. ^{1}H n.m.r. δ 1·30, d (J *c.* 7 Hz), CH_3; 3·68, vbr, CH. Diethylcarbamoyl chloride was an Aldrich product.

(*b*) Reactions of 1-Fluoro-2,4-dinitrobenzene

(i) *With Dipropylamine, Dibutylamine and Diethylamine*

The following procedure is typical. Thus: to a solution of dipropylamine (2·02 g, 20 mmol) and 1-fluoro-2,4-dinitrobenzene (3·72 g, 20 mmol) in dimethyl sulfoxide (30 ml) was added anhydrous potassium carbonate (3·04 g, 22 mmol). This mixture was then stirred on a steam bath for 3 h, and cooled before being poured onto ice/water. The resultant oil was isolated by an ether extraction, and the product chromatographed on neutral alumina (activity I; 40 g). Elution with light petroleum/methylene chloride (3:1) gave (2,4-dinitrophenyl)dipropylamine (1c) as a low-melting orange solid (4·82 g, 90% yield), m.p. 39–40° (lit.[10] 41–42°) [from pentane/methylene chloride (dry ice)]. Similarly, dibutyl(2,4-dinitrophenyl)amine (1d) was obtained as an orange oil (lit.[11] oil) in 91% yield. Because of the low boiling point (56°) of diethylamine, reaction to give (2,4-dinitrophenyl)diethylamine (1e) was carried out at 50°. This derivative (obtained in 92% yield), which had m.p. 68–70° [lit.[12] gives melting

[7] Wilshire, J. F. K., *Aust. J. Chem.*, 1967, **20**, 2809.
[8] Rivett, D. E., and Wilshire, J. F. K., *Org. Prep. Proced.*, 1969, **1**, 263.
[9] Gold-Aubert, P., and Gysin, E., *Helv. Chim. Acta*, 1961, **44**, 105.
[10] Bottini, A. T., and Olsen, R. E., *J. Am. Chem. Soc.*, 1962, **84**, 195.
[11] Ross, S. D., and Finkelstein, M., *J. Am. Chem. Soc.*, 1957, **79**, 6547.
[12] Blanksma, J. J., and Schreinemachers, H. H., *Recl Trav. Chim. Pay-Bas*, 1933, **52**, 428.

points 69 and 80° (dimorphous compound)], was not chromatographed but was crystallized from hexane/methylene chloride directly. Before chromatography or crystallization, the crude products were examined (by ^{1}H n.m.r. spectroscopy); the corresponding 2,4-dinitrophenyl *N*,*N*-dialkylcarbamates were not detected. No alkaline-soluble by-product was obtained by acidification (1 M hydrochloric acid) of the alkaline layer remaining after the ether extraction.

(ii) *With Diisopropylamine*

(A) Reaction (20 mmol scale) gave an oily solid (2·53 g), which was isolated by an ether extraction and chromatographed on a column of silica gel (65 g). Elution with methylene chloride/light petroleum (1:1) gave (2,4-dinitrophenyl)diisopropylamine (1a) (0·13 g, 1·6% yield), m.p. 127–129° (from hexane), identical (mixed m.p.) with the compound described in section (*f*)(i). Elution with methylene chloride/light petroleum (2:1), and mixtures containing increasing amounts of methylene chloride gave 2,4-dinitrophenyl *N*,*N*-diisopropylcarbamate (3a) (2·12 g, 34% yield), m.p. 99–101° (lit.[13] 100°) (from hexane/methylene chloride), identical (mixed m.p., and i.r. and ^{1}H n.m.r. spectra) with an authentic sample [see section (*e*) below]. Acidification (1 M hydrochloric acid) of the lower alkaline layer remaining after the ether extraction gave 2,4-dinitrophenol (7a) (1·36 g, 37% yield), m.p. 112–113°, which was identical (mixed m.p. and ^{1}H n.m.r. spectrum) with an authentic sample.

(B) In a similar experiment (10 mmol scale; 4 h) but with the use of a larger volume (100 ml) of dimethyl sulfoxide, a colourless crystalline precipitate (0·85 g) accumulated in the neck of the reaction flask. This solid was stirred with light petroleum in order to remove some oily material, and the resultant solid [diisopropylamine bicarbonate(?)], m.p. 125–130° (dec.), analysed (Found: C, 51·3; H, 9·8; N, 8·4. $C_7H_{17}NO_3$ requires C, 51·5; H, 10·5; N, 8·6%). ^{1}H n.m.r. (deuterium oxide) δ 1·30, d (*J* *c.* 6·5 Hz), CH_3; 3·50, septet (*J* *c.* 6·5 Hz), CH. The remainder of the reaction mixture was poured onto ice/water, and the oily product isolated by an ether extraction. Chromatography on alumina (100 g), and elution with benzene/light petroleum (1:1) gave (2,4-dinitrophenyl)diisopropylamine (1a) (0·17 g, 3% yield). Elution with methylene chloride alone gave the carbamate (3a) (0·31 g, 5% yield).

(iii) *With Di-s-butylamine*

Reaction (30 mmol scale) followed by the same workup as described in section (*b*)(ii)(A) gave 2,4-dinitrophenol (7a) (2·30 g, 42% yield) from the alkaline layer, and an ether-soluble oil which was chromatographed on silica gel (65 g). Elution with methylene chloride/light petroleum (1:1) gave *2,4-dinitrophenyl* N,N-*di-s-butylcarbamate* (3b) as a yellow oil (2·90 g, 28% yield) which crystallized partially on standing for several months.

(iv) *In the Absence of* N,N-*Dialkylamine*

A solution of 1-fluoro-2,4-dinitrobenzene (1·86 g, 10 mmol) in dimethyl sulfoxide (15 ml) was stirred with potassium carbonate (1·52 g, 11 mmol) on a steam bath for 3 h. On cooling, the reaction mixture was poured onto ice/water, salt added, and the mixture extracted with ether. The lower alkaline extract was acidified (1 M hydrochloric acid) to give 2,4-dinitrophenol (7a) (1·46 g, 79% yield), m.p. and mixed m.p. 113–115°.

(*c*) Reactions of 1-Fluoro-2,6-dinitrobenzene

(i) *With Dipropylamine, Dibutylamine and Diethylamine*

Reaction (5 mmol scale; 1·1 equiv. of anhydrous potassium carbonate; 3 h; steam bath) with dipropylamine was followed by ether extraction of the products and then by silica gel (35 g) column chromatography. Elution with light petroleum/methylene chloride (4:1) gave (2,6-dinitrophenyl)dipropylamine (2c) (0·40 g, 30% yield), m.p. 53–55° (lit.[14] 50–52°) (from hexane/methylene chloride). Elution with light petroleum/methylene chloride (1:3) gave *2,6-dinitrophenyl* N,N-*dipropylcarbamate* (4c) (0·51 g, 33% yield). A similar reaction

[13] Lambrech, J. A., U.S. Pat. No. 2,933,383 (April 19, 1960) (to Union Carbide) (*Chem. Abstr.*, 1960, **54**, 15820a).
[14] Hall, R. C., and Giam, C. S., *J. Agric. Food Chem.*, 1974, **20**, 546.

(5 mmol scale) with dibutylamine followed by silica gel chromatography of the reaction product gave *dibutyl(2,6-dinitrophenyl)amine* (2d) (0·44 g, 30% yield) followed by *2,6-dinitrophenyl* N,N-*dibutylcarbamate* (4d) (0·54 g, 32% yield). Both products were obtained as orange oils; samples for microanalysis were taken from the mid-zones obtained from a second silica gel chromatography of each compound. Because of the low boiling point (56°) of diethylamine, its reaction (5 mmol scale) with 1-fluoro-2,6-dinitrobenzene was conducted at 50°. Silica gel chromatography of the product gave (2,6-dinitrophenyl)diethylamine (2e) (0·52 g; 43% yield). m.p. 46–48° (from pentane) (lit.[3] 49°), followed by *2,6-dinitrophenyl* N,N-*diethylcarbamate* (4e) (0·50 g, 35% yield), m.p. 84–86°, identical (mixed m.p., and i.r. and ^{1}H n.m.r. spectra) with the authentic compound [see section (*e*) below]. In none of these reactions, did acidification of the lower alkaline layer (obtained by initial ether extraction of the products) yield 2,6-dinitrophenol (7b).

(ii) *With Diisopropylamine*

Reaction (10 mmol scale) for 3 h, and silica gel chromatography of the product gave, after elution with methylene chloride/light petroleum (2 : 1), *2,6-dinitrophenyl* N,N-*diisopropylcarbamate* (4a) (1·17 g, 42% yield), m.p. 98–100°, identical (mixed m.p., and ^{1}H n.m.r. spectrum) with the authentic compound [see section (*e*) below]. Acidification of the alkaline layer (remaining after the initial ether extraction of the products) gave crude 2,6-dinitrophenol (7b) (identified by its ^{1}H n.m.r. spectrum) as a dark solid (0·54 g, 29% yield) (isolated by an ether extraction).

(iii) *With Di-s-butylamine*

Reaction (12 mmol scale) gave *2,6-dinitrophenyl* N,N-*di-s-butylcarbamate* (4b) in 48% yield (1·69 g), m.p. 50–52° (from pentane). Acidification of the alkaline layer (remaining after the initial ether extraction of the products) gave 2,6-dinitrophenol (7b), m.p. 62–63° (from pentane), as a dark yellow solid (1·00 g, 45% yield) (isolated by an ether extraction), identical (mixed m.p., and ^{1}H n.m.r. spectrum) with an authentic sample.

(*d*) Reactions of 1-Fluoro-4-nitrobenzene

(i) *With Diisopropylamine and with Di-s-butylamine*

A mixture of 1-fluoro-4-nitrobenzene (5·64 g, 40 mmol), diisopropylamine (4·04 g, 40 mmol) and anhydrous potassium carbonate (6·07 g, 44 mmol) in dimethyl sulfoxide solution (60 ml) was stirred on a steam bath for 12 h. On cooling, the reaction mixture was poured onto ice/water to give an oil (isolated by an ether extraction) which was chromatographed on silica gel (65 g). Elution with light petroleum and light petroleum/methylene chloride (2 : 1) gave unreacted fluoro compound (3·35 g); elution with light petroleum/methylene chloride (1 : 1 and 2 : 3) gave 4,4′-dinitrodiphenyl ether (8) (0·76 g, 36% yield based on consumed reagent), m.p. 144–146°, identical (mixed m.p., and ^{1}H n.m.r. spectrum) with an authentic sample [see section (*f*)(iii)]; elution with methylene chloride/ethyl acetate (1 : 9 and 3 : 7) gave 4-nitrophenyl *N,N*-diisopropylcarbamate (5a) as a low-melting solid (0·61 g, 14% yield based on consumed reagent), m.p. 57–58° [from pentane (dry ice)], identified on the basis of its ^{1}H n.m.r. spectrum and on a mixed m.p. with an authentic sample [see section (*e*) below].

Reaction [same scale (16 h) and workup] with di-s-butylamine gave an oily product which was chromatographed on Florisil (65 g). Elution with light petroleum/methylene chloride (4 : 1 and 2 : 1) gave unreacted fluoro compound (2·79 g); elution with light petroleum/methylene chloride (1 : 2 and 1 : 4) gave 4,4′-dinitrodiphenyl ether (8) (1·11 g, 42% based on consumed reagent); elution with methylene chloride alone and methylene chloride/ethyl acetate (9 : 1) gave *4-nitrophenyl* N,N-*di-s-butylcarbamate* (5b) (0·48 g, 7% yield based on consumed reagent) as a yellow oil. The analytical sample was taken from the mid-zone of a second chromatography (silica gel); it was eluted with light petroleum/methylene chloride (1 : 3).

(ii) *In the Absence of* N,N-*Dialkylamine*

A solution of 1-fluoro-4-nitrobenzene (4·23 g, 30 mmol) in dimethyl sulfoxide (50 ml) was stirred with potassium carbonate (4·56 g, 33 mmol) on a steam bath for 12 h. Isolation of the

product by an ether extraction gave a yellow oily solid (3·39 g), which was extracted with boiling hexane. The insoluble residue (1·93 g, 49% yield), 4,4′-dinitrodiphenyl ether (8), m.p. 139–143°, was identical (mixed m.p., and ^{1}H n.m.r. spectrum) with the authentic material obtained as described below. The hexane extract contained unreacted fluoro compound and was not examined further.

(*e*) Preparation of Some Nitrophenyl *N*,*N*-Dialkylcarbamates

The preparation of 2,4-dinitrophenyl *N*,*N*-diisopropylcarbamate (3a) is typical. A solution of *N*,*N*-diisopropylcarbamoyl chloride (0·675 g, 4 mmol) and 2,4-dinitrophenol (0·736 g, 4 mmol) in pyridine (5 ml) was heated on a steam bath for 2 h. On cooling, the mixture was poured onto ice/water, and the product extracted with ether. The ether extract was successively washed with 1 M hydrochloric acid, water, 5% aqueous sodium bicarbonate solution, and again with water before being dried over anhydrous sodium sulfate. Removal of the ether gave 2,4-dinitrophenyl *N*,*N*-diisopropylcarbamate (3a), m.p. 99–101° (from hexane/methylene chloride), in 87% yield (1·08 g). A similar reaction with 2,6-dinitrophenol gave 2,6-dinitrophenyl *N*,*N*-diisopropylcarbamate (4a), m.p. 98–100°, in 50% yield. Reaction with 4-nitrophenol required a longer time (3 h), and a chromatographic purification [alumina (I); eluent: benzene/light petroleum (1:1)] was needed in order to separate 4-nitrophenyl *N*,*N*-diisopropylcarbamate (5a) (37% yield), m.p. 57–58° (from light petroleum) (lit.[15] m.p. not reported), from unreacted 4-nitrophenol, which remained at the top of the column.

The *N*,*N*-diethylcarbamates (3e) and (4e) were prepared in a similar fashion by the reaction of *N*,*N*-diethylcarbamoyl chloride with the appropriate dinitrophenol. *2,4-Dinitrophenyl* N,N-*diethylcarbamate* (3e), m.p. 68–70°, and *2,6-dinitrophenyl* N,N-*diethylcarbamate* (4e), m.p. 86–88°, were obtained in 78 and 76% yields respectively.

(*f*) Miscellaneous Experiments

(i) *Preparation of (2,4-Dinitrophenyl)diisopropylamine*

A solution of 1-fluoro-2,4-dinitrobenzene (1·86 g, 10 mmol) and diisopropylamine (1·01 g, 10 mmol) in dimethyl sulfoxide (50 ml) containing triethylamine (2·8 ml, 2 equiv.) was heated on a steam bath for 6 h. The mixture was cooled, poured onto ice/water, and the resultant oily product isolated by an ether extraction. Chromatography of this product on alumina (30 g), and elution with benzene/light petroleum (1:1), gave (2,4-dinitrophenyl)diisopropylamine (1a) as an orange solid (374 mg, 14% yield), m.p. 127–129° (from hexane) (lit.[2] 129–129·5°).

(ii) *Hydrolysis of Dinitrophenyl* N,N-*Dialkylcarbamates*

A solution of 2,4-dinitrophenyl *N*,*N*-diisopropylcarbamate (3a) (1·27 g) in a mixture of ethanol (15 ml) and 1 M sodium hydroxide (15 ml) was boiled under reflux for 2 h. On cooling, the mixture was poured into water, and extracted with ether. The lower alkaline layer was removed and acidified (1 M hydrochloric acid) to give 2,4-dinitrophenol (7a) (0·44 g, 59% yield), m.p. and mixed m.p. 113–115°. Similar hydrolysis of the corresponding di-s-butylcarbamate (3b) (1·37 g) gave 2,4-dinitrophenol (7a) in 69% yield, and of 2,6-dinitrophenyl *N*,*N*-diisopropylcarbamate (4a) gave 2,6-dinitrophenol (7b) in 43% yield.

(iii) *Preparation of 4,4′-Dinitrodiphenyl Ether (8) (Cf.*[16]*)*

A solution of 4-nitrophenol (2·78 g, 20 mmol) and 1-fluoro-4-nitrobenzene (2·82 g, 20 mmol) in dimethyl sulfoxide (40 ml) was stirred with anhydrous potassium carbonate (5·52 g, 40 mmol) on a steam bath for 5 h. The reaction mixture was cooled and poured onto water to give a pale yellow solid (4·69 g, 90% yield), m.p. 144–145° (from ethanol/methylene chloride) (lit.[17] 141–143°). ^{1}H n.m.r. δ 7·13, d (*J* *c.* 9 Hz), H2/H6; 8·30, d (*J* *c.* 9 Hz), H3/H5.

[15] Casida, J. E., Augustinsson, K. B., and Jonsson, G., *J. Econ. Entomol.*, 1960, **53**, 205 (*Chem. Abstr.*, 1961, **55**, 26081e).
[16] Wilshire, J. F. K., *Aust. J. Chem.*, 1988, **41**, 995.
[17] Lange, N. A., and Reed, W. R., *J. Am. Chem. Soc.*, 1926, **48**, 1071.

Acknowledgments

The authors are grateful to Mr B. M. Duggan, College of Pharmacy, Monash University, Parkville, Victoria, for recording the ^{1}H and ^{13}C n.m.r. spectra of several of the compounds described in this work, and to Dr N. S. Nudelmann, Chemistry Department, University of Buenos Aires, Argentina, for helpful correspondence.