1346. *Isomerisation of 2-Butyl-4,6-dinitrophenyl Thiocarbamates*

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Depending on the nature of the alkyl group, (dialkyl)thiocarbamoyl chloride and potassium 2-butyl-4,6-dinitrophenoxide give, on heating in acetone, a thionocarbamate, an *ON*-dialkyliminothiolocarbonate, or an *S*-phenyl thiolocarbamate. The thionocarbamates and the iminothiolocarbonates readily rearrange to the thiolocarbamates on heating. A mechanism is suggested for the rearrangements. The thionocarbamates and the iminothiolocarbonates are partly hydrolysed to the phenols, whereas the thiolocarbamates are stable when heated in ethanol–hydrochloric acid solution. All the compounds are attacked by potassium methoxide and yield the corresponding anisoles.

WHEN 2-s-butyl- and 2-t-butyl-4,6-dinitrophenols reacted with thiolo- and thiono-chloroformates, the expected thiolo- or thiono-carbonates were obtained.[1] On heating with nitric acid, the thiolocarbonates gave a negative test, whereas the thionocarbonates gave a positive test for the sulphate ion, indicative of a C=S bond.[2] When potassium 2-t-butyl-4,6-dinitrophenoxide (I; $R' = Bu^t$, $R'' = H$) was treated at room temperature with (diethyl)thiocarbamoyl chloride (II; $R = Et$), the iminothiolocarbonate (VII; $R = Et$, $R' = Bu^t$, $R'' = H$) was obtained and, on heating, was isomerised to the thiolocarbamate (IX; $R = Et$, $R' = Bu^t$, $R'' = H$).

The effect of the alkyl groups of (dialkyl)thiocarbamoyl chlorides on the structure of their condensation products with potassium 2-t-butyl-, 2-t-butyl-5-methyl-, and 2-s-butyl-4,6-dinitrophenoxides is shown in Table 1.

On heating in ethanol–hydrochloric acid for 19 hr. or on heating at 180—200° for 1·5 hr., the thionocarbamates (III) and the iminothiolocarbonates (VII; $R = Et$ or Pr^n, $R' = Bu^t$, $R'' = H$) were isomerised to the thiolocarbamates (IX). The iminothiolocarbonate (VII; $R = Et$, $R' = Bu^t$, $R'' = Me$) was hydrolysed to the parent phenol on heating in ethanol–hydrochloric acid, and isomerised to the thiolocarbamate (IX; $R = Et$, $R' = Bu^t$, $R'' = Me$) on heating at 180—200°. The structures of the thiolocarbamates (IX) were confirmed by negative tests for a C=S bond (Table 2). The iminothiolocarbonates were partly hydrolysed when heated under acid conditions, giving the phenols. The resulting *ON*-dialkyliminothiolo-ion would be expected to rearrange to the thionocarbamate form

$$\bar{S}\cdot C(OR){:}NR \longrightarrow \bar{O}\cdot CS\cdot NR_2$$

to give a positive C=S test. The thionocarbamates, as expected of amides, also underwent partial acid hydrolysis to the phenols. However, the thiolocarbamates (IX; $R = Me$ or Et, $R' = Bu^s$ or Bu^t, $R'' = H$) suffered little change after a long period of heating (16 hr.) in ethanol–hydrochloric acid, possibly owing to stabilisation through resonance structures such as (X).

Isomerisation of –O·C(S)– to –S·C(O)– is well known.[3] Electron-withdrawing groups in the *ortho*- and *para*-positions promoted the Schönberg rearrangement of diaryl thionocarbonates to diaryl thiolocarbonates;[4] the rearrangement was a first-order reaction[5] and was considered to involve a four-membered cyclic transition state.[4,5] Electron-withdrawing groups promoted also the Chapman rearrangement of aryl imido-esters into

[1] M. Pianka, *J. Sci. Food Agric.*, 1966, in the press.

[2] G. Hilgetag and R. Philippson, *Monatsber. Deut. Akad. Wiss. Berlin*, 1964, **6** (8), 585.

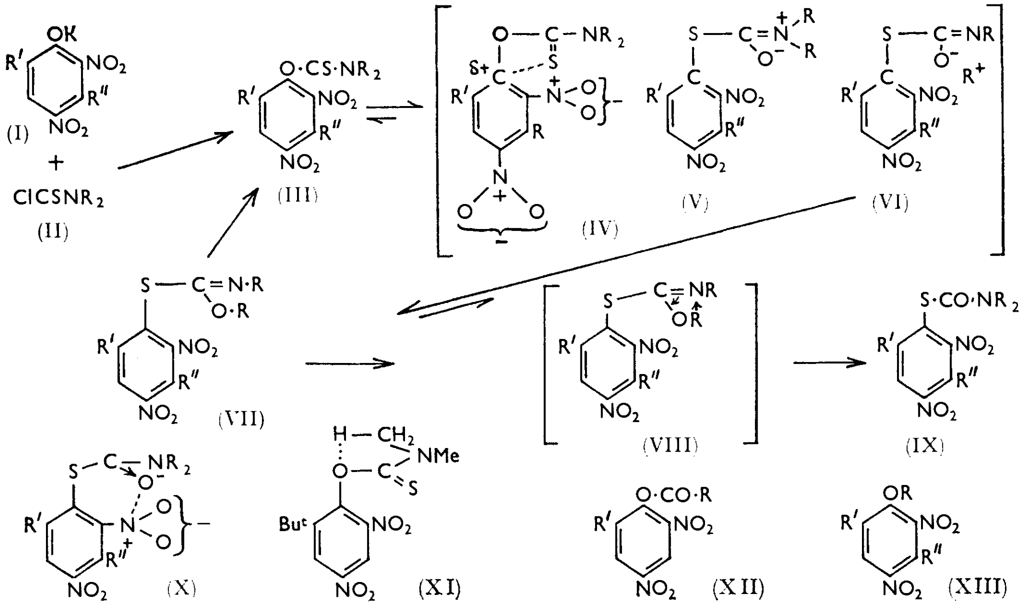
[3] H. L. Wheeler and B. Barnes, *Amer. Chem. J.*, 1899, **22**, 141; A. Schönberg and L. Vargha, *Ber.*, 1930, **63**, 178; A. Schönberg, L. Vargha, and W. Paul, *Annalen*, 1930, **483**, 107; S. A. Karjala and S. M. McElvain, *J. Amer. Chem. Soc.*, 1933, **55**, 2966; R. C. Elderfield and F. W. Short, *J. Org. Chem.*, 1953, **18**, 1092; J. R. Marshall, *J.*, 1965, 938.

[4] H. R. Al-Kazimi, D. S. Tarbell, and D. Plant, *J. Amer. Chem. Soc.*, 1955, **77**, 2479.

[5] D. H. Powers and D. S. Tarbell, *J. Amer. Chem. Soc.*, 1956, **78**, 70.

amides;[6] the rearrangement was found to be intramolecular[6,7] and was also regarded as involving a four-membered transition state.[7] An example of a Chapman rearrangement involving migration of an ethyl group (instead of an aryl) was also described.[8,*]

The ready isomerisation of our compounds may proceed *via* forms (IV)—(VI), in which the electron-withdrawing nitro-groups facilitate bonding between the nucleophilic sulphur[9] and the electron-deficient phenolic carbon, rupture of the Ph–O bond and rearrangement to the iminothiolocarbonate (VII)† through migration of the alkyl group, possibly as an alkyl cation R^+ (VI).‡ Hydrogen-bonding, as illustrated in structure (XI), may stabilise the thionocarbamate (III; R = Me, R′ = Bu^t, R″ = H) and steric hindrance due to the bulky n-butyl group the thionocarbamate (III; R = Bu^n, R′ = Bu^t, R″ = H). These thionocarbamates were isomerised to the thiolocarbamates (IX) only under the influence of heat. The steric effect due to the n-propyl group may inhibit also the formation of (VII; R = Pr^n, R′ = Bu^t, R″ = H) and was reflected in a lower yield (55·3% compared with 83% for the *ON*-diethyl homologue).



The formation of thiolocarbamates (IX) from potassium 2-s-butyl-4,6-dinitrophenoxide and (*a*) (dimethyl)- and (*b*) (diethyl)-thiocarbamoyl chlorides under conditions in which the

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[*] In a review on the Chapman rearrangement (*Org. Reactions*, 1965, **14**, 1.), which appeared after this manuscript was prepared, Schulenberg and Archer pointed out that the thermal rearrangement of alkyl imidates was, in contrast to the Chapman rearrangement, intermolecular[8a] and may be a free-radical process.[7] Since our iminothiolocarbonates (VII) rearranged readily (even on heating in aqueous ethanol) and in excellent yields to the thiolocarbamates (IX) we believe the rearrangement to be similar to that of Chapman.

[†] Grigat and Pütter[10] prepared the previously unknown ArOC(:NH)SR′, which readily decomposed to ArOH and R′SCN.

[‡] Hilgetag and Philippson[2] suggested ionisation of aryl methylthionocarbonates into the aryl thionocarbonate anion and methyl cation as the preliminary step in the isomerisation to aryl methylthiolocarbonates.

[6] O. Mumm, H. Hesse, and H. Volquartz, *Ber.*, 1915, **48**, 379; A. W. Chapman, *J.*, 1925, 1992; 1927, 1743; 1930, 2458.

[7] K. B. Wiberg and B. I. Rowland, *J. Amer. Chem. Soc.*, 1955, **77**, 2205.

[8] R. F. Meyer, *J. Org. Chem.*, 1963, **28**, 2902.

[8a] K. B. Wiberg, T. M. Shryne, and R. R. Kintner, *J. Amer. Chem. Soc.*, 1957, **79**, 3160.

[9] O. R. Quale and E. E. Royals, *J. Amer. Chem. Soc.*, 1942, **64**, 226; P. B. D. de la Mare and C. A. Vernon, *J.*, 1952, 3331.

[10] E. Grigat and R. Pütter, *Chem. Ber.*, 1964, **97**, 3022.

2-t-butyl derivative gave (*a*) the thionocarbamate (III) and (*b*) a mixture of the iminothiolocarbonate (VII) and thiolocarbamate (IX) may be explained on grounds of readier participation of forms (IV)—(VI) in s-butyl than in the t-butyl derivatives. The readier bonding in the s-butyl compounds of the nucleophilic sulphur and the electron-deficient phenolic carbon may be due to (*a*) a smaller $+I$ effect of the s-butyl group or (*b*) its lesser steric hindrance or both.

In order to identify the products resulting from the isomerisation of diaryl thiono- to diaryl thiolo-carbonates Schönberg *et al.*[3] treated the thiolocarbonates with alkali and obtained the arylthiols. On heating with potassium methoxide in methanol our thionocarbamates (III), thiolocarbamates (IX), and iminothiolocarbonates (VII) yielded the corresponding anisoles and parent phenols (Table 3). The nucleophilic attack of the methoxy-ion on the phenolic carbon is facilitated by the electron-withdrawing properties of the nitro-groups.[11] The production of the phenols from the intermediate iminothiolocarbonates (VII) may be due to some back-isomerisation to the thionocarbamates (III), which as amides would be expected to be hydrolysed under acid or alkaline conditions to yield the parent phenols.

In the thiolocarbamate (IX; R = Et, R′ = Bu^t, R″ = Me) the methyl group would have the effect of reducing the positive charge on the nitrogen of the nitro-group and thus of reducing the participation of structure (X). This would result in greater back-isomerisation of the iminothiolocarbonate to the thionocarbamate (III; R = Et, R′ = Bu^t, R″ = Me) and the expected acid hydrolysis to the phenol. The lower reactivity of this iminothiolocarbonate towards potassium methoxide may also be due to the reduction of the positive charge on the phenolic carbon by the methyl group.

Runti [12] could not prepare *S*-4-ethoxyphenyl thiolocarbamate from *S*-4-ethoxyphenyl ethyl thiolocarbonate and ammonium hydroxide. We could not prepare the thiolocarbamate (IX; R = Me or Et, R′ = Bu^t, R″ = H) from dialkylcarbamoyl chlorides and 2-t-butyl-4,6-dinitrothiophenol, using its salts or a hydrogen chloride acceptor; we could not prepare the thiolocarbamate from the thiophenoxide, phosgene, and dialkylamine. Nor could we obtain the thiophenol from the thiolocarbamate by heating the latter with potassium t-butoxide, hydrobromic acid in acetic acid, or aluminium chloride.

EXPERIMENTAL

Preparation of Thionocarbamates, Thiolocarbamates, and Iminothiolocarbonates (Table 1).—2-Alkyl-4,6-dinitrophenol (0·02 mole) and potassium carbonate (0·0206 mole), in acetone (~50 ml.), were heated under reflux until complete solution resulted (~0·5 hr.). To the solution of the potassium phenoxide (dialkyl)thiocarbamoyl chloride (0·02 mole) was added and the solution heated under reflux for 3 hr. The mixture was then worked up as follows.

Method 1. After filtration from the precipitated potassium chloride the acetone was distilled off *in vacuo*. The residue was shaken with benzene and 2N-sodium carbonate. The benzene solution was separated, washed with water, dried (Na_2SO_4), the benzene distilled off *in vacuo*, and the residue crystallised. *Method* 2. After filtration from the precipitated potassium chloride the acetone was distilled off *in vacuo*. The residue was extracted with di-isopropyl ether (*a*) or light petroleum (*b*). The extract was filtered, the solvent distilled off *in vacuo* and the residue crystallised.

Test for the C=S *Group*.—The sample (~10 mg.) was heated for 2 min. with fuming nitric acid (~0·4 ml.) (water-bath), the mixture was cooled, diluted with water (~3 ml.), and extracted with benzene (~5 ml.). The aqueous layer was tested for presence of sulphate ion using 5N-hydrochloric acid (~0·01 ml.) and 10% barium chloride (~0·2 ml.).

S-2-*t-Butyl*-4,6-*dinitrophenyl* ON-*Diethyliminothiolocarbonate* (VII; R = Et, R′ = Bu^t, R″ = H).—Potassium 2-t-butyl-4,6-dinitrophenoxide (0·02 mole) and (diethyl)thiocarbamoyl chloride (0·02 mole), in acetone (25 ml.), were set aside at room temperature for 16·5 hr. The mixture was then worked up by method 1. The *compound* (no. 1) (5·91 g., 83·2%) was obtained

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[11] N. Kharash and R. Swindler, *J. Org. Chem.*, 1954, **19**, 1704; S. S. Gitis and A. I. Glaz, *Zhur. obshchei Khim.*, 1958, **28**, 1334; S. S. Gitis, M. S. Malinovskii, and A. I. Glaz, *ibid.*, p. 2262.

[12] C. Runti, *Ann. Chim.* (*Italy*), 1956, **46**, 417.

TABLE 1

Compounds obtained by heating (dialkyl)thiocarbamoyl chlorides (II) with potassium phenoxides (I) in acetone under reflux for 3 hr.

No.	Compound	R	R′	R″	Method	M. p.	Yield (%)	Appearance	Test for C=S bond *
3	(III)	Me	$\mathrm{Bu^t}$	H	1	124—126° †	80·5	Yellow prisms ‡	+
5	(VII)	$\mathrm{Pr^n}$	$\mathrm{Bu^t}$	H	2(*a*)	106—107 §	55·3	Yellow prisms ‡	+
7	(III)	$\mathrm{Bu^n}$	$\mathrm{Bu^t}$	H	2(*b*)	74—75 ¶	63·1	Pale brown prisms ‡	+
9	(VII)	Et	$\mathrm{Bu^t}$	Me ‖		116—117 ¶	76·9	Yellow prisms ‡	+
11	(IX)	Me	$\mathrm{Bu^s}$	H	2(*a*)	120—121 ¶	84·7	Yellow needles	Negative
12	(IX)	Et	$\mathrm{Bu^s}$	H **	1	51—53 †	50·7	Brown prisms	Negative

Analyses

No.	Found (%)				Formula	Required (%)			
	C	H	N	S		C	H	H	S
3	47·9	5·2	12·6	9·8	$C_{13}H_{17}N_3O_5S$	47·7	5·2	12·8	9·8
5	53·1	6·3	10·8	8·6	$C_{17}H_{25}N_3O_5S$	53·3	6·5	11·0	8·4
7	55·6	7·1	10·1	8·0	$C_{19}H_{29}N_3O_5S$	55·5	7·1	10·2	7·8
9	52·2	6·3	11·4	8·7	$C_{16}H_{23}N_3O_5S$	52·0	6·2	11·4	8·7
11			8·7 ††		$C_{13}H_{17}N_3O_5S$			8·6	
12			7·6 ††		$C_{15}H_{21}N_3O_5S$			7·9	

* + indicates presence of sulphate ion after oxidation with nitric acid. † From methanol. ‡ Turned green on exposure to sunlight. § From light petroleum (b. p. 60—80°)–ethanol. ¶ From ethanol. ‖ Refluxed for 6 hr. ** Refluxed for 1¼ hr. †† Determined as aromatic nitro-groups by reduction with titanous chloride.

as pale yellow prisms, m. p. 109—110° (Found: C, 51·1; H, 6·1; N, 11·9; S, 9·2. $C_{15}H_{21}N_3O_5S$ requires C, 50·7; H, 5·9; N, 11·8; S, 9·0%). It gave a positive test for C=S and turned green on exposure to sunlight.

When potassium 2-t-butyl-4,6-dinitrophenoxide and (diethyl)thiocarbamoyl chloride, in acetone, were heated under reflux for 3 hr., worked up by method 1, and the residue crystallised from methanol, a mixture of crystals, m. p. 87—89°, was obtained (86·5%) from which compounds no. 1 and 2 could be separated by hand.

Hydrolysis of the Iminothiolocarbonate (VII; R = Et, R′ = $\mathrm{Bu^t}$, R″ = H).—The carbonate (3·55 g., 0·01 mole) was heated under reflux for 10 min. in a solution of potassium (0·78 g., 0·02 g.-atom) in methanol (10 ml.). An excess of 3N-sodium hydroxide was then added, and the mixture heated for 1 hr. The alkaline vapours evolved were condensed and then saturated with dry hydrogen chloride. The condensate was evaporated down to leave a solid which was triturated with dry ether, filtered off, and dried *in vacuo* (P_2O_5). It melted at 218—219° (diethylamine hydrochloride has m. p. 223·5°).

Heating of Iminothiolocarbonates and of Thionocarbamates in Ethanol–Hydrochloric Acid (Table 2).—The carbonate or carbamate (0·01 mole), dissolved in a mixture of ethanol (60 ml.)

TABLE 2

Compounds (IX) obtained by heating compounds 1, 3, 5, and 7 for 19 hr. under reflux in 0·118M-solution in ethanol–hydrochloric acid

No.	Compound R	R′	R″	From cpd.	M. p.	Yield (%)	Appearance	Recovery of phenol (%)	Test for C=S bond
2	Et	$\mathrm{Bu^t}$	H	1 *	99—100° †‡	50	Bright yellow prisms	33·0	Negative
4	Me	$\mathrm{Bu^t}$	H	3 *	122—123 ‡§	64·6	Pale yellow needles	26·3	Negative
6	$\mathrm{Pr^n}$	$\mathrm{Bu^t}$	H	5	83—84 †	74·0	Pale yellow plates	28·5	Negative
8	$\mathrm{Bu^n}$	$\mathrm{Bu^t}$	H	7	65—66 ¶	63·3	Bright yellow plates	34·0	Negative

Analyses

No.	Found (%)				Formula	Required (%)			
	C	H	N	S		C	H	N	S
2	50·7	5·9	11·9	8·8	$C_{15}H_{21}N_3O_5S$	50·7	5·9	11·8	9·0
4	47·4	5·2	13·0	9·6	$C_{13}H_{17}N_3O_5S$	47·7	5·2	12·8	9·8
6	53·3	6·6	11·4	8·5	$C_{17}H_{25}N_3O_5S$	53·3	6·5	11·0	8·4
8	55·3	7·0	10·0	7·9	$C_{19}H_{29}N_3O_5S$	55·5	7·1	10·2	7·8

* On heating for 100 min. at 180—200° compound 1 isomerised in 75% yield to compound 2, and compound 3 to compound 4. On heating for 19 hr. under reflux in aqueous ethanol compound 1 gave compound 2 (63·5%) and the parent phenol (10%). † From propan-2-ol. ‡ Depressed by parent compound. § From ethanol. ¶ From light petroleum (b. p. 40—60°).

and concentrated hydrochloric acid (25 ml.; ~9% w/v concentration of hydrogen chloride), was heated under reflux for 19 hr. Some hydrogen sulphide was evolved. The solution was concentrated by distillation. The concentrate was extracted with benzene and the benzene extract washed with 2N-sodium carbonate. The red sodium 2-t-butyl-4,6-dinitrophenoxide which precipitated was filtered off, acidified, and the phenol filtered off. The benzene solution was washed with water, dried (Na_2SO_4), the benzene distilled *in vacuo*, and the residue crystallised.

When the iminothiolocarbonate (VII; $R = Et$, $R' = Bu^t$, $R'' = Me$) was heated under reflux in ethanol–hydrochloric acid for 19 hr., then worked up as above, only the parent phenol (82·2%) and, from the benzene solution, the unchanged carbonate (1·5%) were obtained.

S-2-*t-Butyl*-4,6-*dinitro*-5-*methylphenyl* NN-*Diethylthiolocarbamate* (IX; $R = Et$, $R' = Bu^t$, $R'' = Me$).—The carbonate (VII; $R = Et$, $R' = Bu^t$, $R'' = Me$) was heated at 180—200° for 2 hr. The *compound* (no. 10) was obtained as off-white needles, m. p. 107° (from propan-2-ol) (Found: C, 52·3; H, 6·0. $C_{16}H_{23}N_3O_5S$ requires C, 52·0; H, 6·2%). It gave a negative test for C=S.

2-*t-Butyl*-4,6-*dinitrophenyl* NN-*Diethylcarbamate* (XII; $R = NEt_2$, $R' = Bu^t$).—Potassium 2-t-butyl-4,6-dinitrophenoxide and diethylcarbamoyl chloride, in cyclohexanone, were heated for 3 hr. and worked up by method 1. The *compound* (no. 13) (35%) was obtained as pale brown prisms, m. p. 89—91° [from methanol, then light petroleum (b. p. 40—60°)] [Found: N (as aromatic nitro-groups by titanous chloride reduction), 8·4. $C_{15}H_{21}N_3O_6$ requires N, 8·3%].

Heating of Carbamates in Ethanol–Hydrochloric Acid.—The carbamates (0·01 mole), in a mixture of ethanol (60 ml.) and concentrated hydrochloric acid (25 ml.), were heated under reflux for 16 hr., and the solution was poured into excess of water and filtered. The recovery of unchanged carbamates was as follows: compound 2, 92%; compound 4, 94%; compound 11, 88%; compound 13, 78% (on extracting the resulting oil with benzene).

Reaction of Carbonates and Carbamates with Potassium Methoxide.—The carbonates or carbamates (0·01 mole) were heated under reflux in a solution of potassium (0·78 g., 0·02 g.-atom) in methanol (25 ml.) for 25 min. The reaction mixture was then poured into water and the precipitated oil extracted with benzene. From the benzene layer the dinitroanisoles were obtained by concentrating the liquors and from the aqueous layers the phenols were recovered on acidification (when 2-t-butyl-4,6-dinitrophenol was treated with potassium methoxide as above no anisole was obtained).

Because of different experimental conditions the treatments of the carbonate (VII; $R = Et$, $R' = Bu^t$, $R'' = Me$) and carbamate (IX; $R = Me$, $R' = Bu^s$, $R'' = H$) with potassium methoxide in methanol are described separately; the results obtained are included in Table 3 for completeness.

TABLE 3

Reactions of 2-alkyl-4,6-dinitrophenyl *NN*-dialkylthiono- and -thiolo-carbamates, of *ON*-dialkyliminothiolocarbonates, and of 2-t-butyl-4,6-dinitrophenyl *NN*-diethylcarbamate with potassium methoxide

Compound	Anisole (%)	Phenol (%)	Compound	Anisole (%)	Phenol (%)
1	62·5 [13] (in 3 crops)	12·5	7	2·3	42·0
2	32 *	7·3	9	Present [13] †‡	15·2
3	53·8	31·2	11	Present [1] §	25·0
4	13·4	—	13	90·9	6·1
5	9·5	45·1			

* Detected by i.r. and p.m.r. (cf. compound 14 in Table 4), but was not isolated. † Unchanged carbonate (17%) was recovered. ‡ Detected by i.r. and p.m.r. (cf. compound 16 in Table 4), but was not isolated. § Detected by i.r. and p.m.r. (cf. compound 15 in Table 4) but was not isolated.

Reaction of Carbonate (VII; $R = Et$, $R' = Bu^t$, $R'' = Me$) *with Potassium Methoxide.*—The carbonate (3·69 g., 0·01 mole) was heated under reflux with a solution of potassium (0·78 g., 0·02 g.-atom) in methanol (25 ml.). After 5·5 hr. the reaction was not complete since, on cooling, a high proportion of the original carbonate precipitated out. The solution was therefore heated for a further 8 hr., poured into water (200 ml.), and extracted with benzene. The benzene extract was washed with water and dried (Na_2SO_4). On removing the benzene a black tarry residue remained from which, on addition of propan-2-ol, the original carbonate crystallised out (17%). No anisole could be separated from the tarry residue, but i.r. and p.m.r. examinations indicated its presence. From the aqueous layer the parent phenol (15·2%) was recovered.

[13] O. A. Zeide and B. M. Dubinin, *J. Gen. Chem., U.S.S.R.*, 1932, **2**, 455.

Reaction of Carbamate (IX; R = Me, R′ = Bu^s, R″ = H) *with Potassium Methoxide.*—The carbamate (3·27 g.) was heated under reflux with a solution of potassium (0·78 g.) in methanol (20 ml.) for 1·5 hr., then poured into water. The mixture was extracted with ether. The ether extract was washed with dilute hydrochloric acid, 2N-sodium carbonate, water, and dried (Na_2SO_4). The ether was evaporated off and the residue extracted with light petroleum (b. p. 40—60°). On evaporating the light petroleum a residue was obtained, n_D^{22} 1·5500 (0·4 g.). An examination of i.r. and p.m.r. spectra of the residue and of those of 2-s-butyl-4,6-dinitroanisole [14] (compound 14 in Table 4) showed that the residue contained the anisole. From the aqueous layer, on acidification and extraction with light petroleum, 2-s-butyl-4,6-dinitrophenol (25%) was recovered.

TABLE 4

Infrared absorption bands (cm.$^{-1}$) for CS_2 solutions and p.m.r. bands (τ values) for CCl_4 solutions (coupling constants in c./sec. in parentheses)

	Infrared bands			P.m.r. peaks			
Compound	C=O	NO_2	C–O–C	R	R′	Aromatic H	R″
1	—	1350	1085	8·70t (7·5) 6·27q (7·5) 8·57t (7·5) 6·03q (7·5)	8·52	1·30d (2·5) 1·47d (2·5)	—
2	1685	1348	—	8·77t (7·5) 6·58q (7·5)	8·40	1·45d (2·5) 1·68d (2·5)	—
3	—	1346	1094	6·54 6·49	8·53	1·28d (2·5) 1·47d (2·5)	—
4	1692	1350	—	6·92	8·41	1·48d (2·5) 1·68d (2·5)	—
5	—	1344	1095	9·03t (7) 8·17m 8·97t (7) 6·28m	8·54	1·32d (2·5) 1·48d (2·5)	—
6	1682	1345	—	9·06t (7) 8·42m 6·70t (7)	8·42	1·45d (2·5) 1·68d (2·5)	—
7	—	1346	1242	9·00t (6) 8·40m 6·25m	8·53	1·32d (2·5) 1·50d (2·5)	—
8	1682	1346	—	9·00t (6) 8·5m 6·67t (6·5)	8·38	1·45d (2·5) 1·67d (2·5)	—
9	—	1348	1086	8·74t (7) 6·33q (7) 8·68t (7) 6·22q (7)	8·58	1·90	7·54
10	1678 *	1340,* 1542 *	—	n.e.	n.e.	n.e.	n.e.
11	1692	1345	—	6·91	9·11t (7) 8·71d (7) 8·32m 6·53m	1·62d (2·5) 1·72d (2·5)	—
12	1680	1345	—	8·76t (7) 6·58q (7)	9·10t (7) 8·70d (7) 8·32m 6·53m	1·62d (2·5) 1·72d (2·5)	—
13	1742	1348	1218	8·81t (7) 6·64q (7) 8·65t (7) 6·42q (7)	8·52	1·30d (2·5) 1·51d (2·5)	—
14	—	1345	1255	6·06	8·52	1·55d (2·5) 1·63d (2·5)	—
15	—	1345	1265	6·03	9·08t (7) 8·68d (7) 8·30m 6·75m	1·55d (2·5) 1·78d (2·5)	
16 †	—	1345	1252	6·10	8·58	2·02	7·59

* $CHBr_3$ solution. † Impure specimen.

d, Doublet; t, triplet; q, quadruplet; m, multiplet; n.e., not examined.

2-*t-Butyl*-4,6-*dinitrothiophenol*.—This compound was prepared using Willgerodt's method.[15] 2-t-Butyl-4,6-dinitrophenyl chloride [16] (prepared by Kubota's method [17] from 2-t-butyl-4,6-dinitrophenol and toluene-*p*-sulphonyl chloride) was treated at room temperature with an excess of an ethanol solution of potassium hydrogen sulphide. On pouring the reaction solution into excess of water and acidifying, the compound precipitated. It was filtered off and purified by dissolving in ethanolic sodium hydroxide and reprecipitating with acid. The *compound* was obtained as orange plates, m. p. 178° (decomp.) [Found: C, 47·2; H, 5·7; N, 11·4; S, 13·1%; *M* (Rast), 265. $C_{10}H_{12}N_2O_4S$ requires C, 46·9; H, 4·7; N, 11·0; S, 12·5%; *M*, 256].

I. *Attempted preparation of* S-2-*t-Butyl*-4,6-*dinitrophenyl* NN-*Diethylthiolocarbamate*.—(*a*) Potassium 2-t-butyl-4,6-dinitrothiophenoxide was prepared by treating the thiophenol with

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[14] M. S. Carpenter and W. M. Easter, U.S.P. 2,476,815.

[15] C. Willgerodt, *Ber.*, 1884, **17**, 352.

[16] J. Cortier, M. Gilon, and A. Halleux, *Bull. Soc. chim. belges*, 1955, **64**, 667.

[17] T. Kubota, *J. Chem. Soc., Japan*, 1932, **53**, 404.

potassium methoxide in methanol and removing the solvent *in vacuo* (the unchanged thiophenol could be recovered from this salt on acidification). The potassium thiophenoxide was gently heated with excess of diethylcarbamoyl chloride until complete solution resulted. The residue obtained on concentrating the filtrate was worked up by method 1, diluted with propan-2-ol, and refrigerated. The desired carbamate could not be isolated from the reaction mixture.

(*b*) Well-ground potassium 2-t-butyl-4,6-dinitrothiophenoxide (prepared from 2·56 g. of the thiophenol) was added to a stirred, refrigerated solution of phosgene (5·5 g.) in dry ether (35 ml.) (Cardice–acetone bath). The mixture was allowed to warm up to 10° and then kept at 10° for 1 hr. Diethylamine (20·6 ml.) was added at −30 to −50°, the mixture was allowed to warm up to room temperature, and poured into water. From the ether solution an oil was obtained from which the desired carbamate could not be isolated.

(*c*) The brown solution of 2-t-butyl-4,6-dinitrothiophenol (2·50 g.) and diethylaniline (1·5 g.), in acetone (40 ml.), was added to phosgene (3·8 g.), in acetone (15 ml.), at −30 to −60°. The resulting yellow reaction mixture was kept for 30 min. at −40° and to it diethylamine (16·6 ml.) was added dropwise, with stirring. The reaction mixture was kept for 15 min. at room temperature and then poured into water (250 ml.). The oil and solid that precipitated were extracted with benzene, washed with 2N-sodium carbonate, then with water, and dried (Na_2SO_4). The residue that remained after the removal of the benzene was triturated with light petroleum (b. p. 40—60°), then crystallised from propan-2-ol to give a solid (1·25 g.), m. p. 164—166° [Found: N, 9·0; S, 10·4%; *M* (Rast), 208]. It gave no amine on treatment with alkali. Surprisingly, the same solid (0·95 g.) was obtained on acidification of the aqueous washings and could not be dissolved in aqueous alkali.

II. *Attempted Preparation of* S-2-*t-Butyl*-4,6-*dinitrophenyl* NN-*Dimethylthiolocarbamate*.—(*a*) The potassium thiophenoxide and dimethylcarbamoyl chloride were dissolved in dimethylformamide and kept for 1·5 hr., the solvent was removed *in vacuo* and the residue worked up by method 1. A gum was obtained which could not be crystallised.

(*b*) Dimethylcarbamoyl chloride (0·215 g.), 2-t-butyl-4,6-dinitrothiophenol (0·512 g.), and pyridine (0·16 g.), in benzene (10 ml.), were heated under reflux for 13·5 hr. (steam-bath). A little solid that separated was filtered off and the filtrate concentrated *in vacuo*. From the residue the solid (0·34 g.), m. p. 164—166°, identical with that under I(*c*), was recovered.

Reaction of 2-*t-Butyl*-4,6-*dinitrothiophenol with Iodine*.—The thiophenol (0·25 g.), in acetone, was added to iodine (0·13 g.), in ethanol (15 ml.), and the mixture was kept at room temperature until the solution was decolourised (3 days). On removing the solvents *in vacuo* a reddish brown solid, m. p. 155—160°, remained. The solid was purified by extracting its solution in ether with aqueous sodium carbonate, then water. Its m. p., 164—166°, was not depressed by the solid obtained under I(*c*) and II(*b*).

Attempted Hydrolysis of S-2-*t-Butyl*-4,6-*dinitrophenyl* NN-*Diethylthiolocarbamate*.—(*a*) The carbamate was warmed with an equivalent of potassium t-butoxide, in t-butyl alcohol, for 10 min. Alkaline vapours were evolved. After 20 hr. at room temperature the mixture was poured into an excess of water, extracted with ether, and acidified. No thiophenol was obtained.

(*b*) The carbamate was heated under reflux in a solution of glacial acetic acid and hydrobromic acid (47%) for 26 hr. On working up the reaction mixture, a solid, m. p. >350°, and some unchanged carbamate were recovered.

(*c*) The carbamate was boiled for 0·5 min. in a solution of aluminium chloride in nitrobenzene. The mixture was acidified with hydrochloric acid and the nitrobenzene layer extracted with sodium hydroxide solution. No thiophenol was obtained on acidification.

Attempted Reaction of S-2-*t-Butyl*-4,6-*dinitrophenyl* NN-*Diethyliminothiolocarbonate and Pyrrolidine*.—To a solution of compound No. 1 (3·6 g., 0·01 mole), in absolute ether, pyrrolidine (1·7 ml.) was added dropwise. The solution was heated for 1 hr. under reflux, then evaporated (water-bath). The thiolocarbonate was recovered unchanged.

Spectroscopic Measurements.—The infrared [18] and p.m.r.[19] measurements were conducted as described previously. They are listed in Table 4.

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[18] J. E. Page and S. E. Staniforth, *J.*, 1962, 1292.

[19] G. F. H. Green, J. E. Page, and S. E. Staniforth, *J.*, 1964, 144.