Structures and Pesticidal Activities of Derivatives of Dinitrophenols. Part V.† Reactions of Certain Dinitro-aryl Thiocarbamates with Potassium Hydroxide in Methanol and with Various Nucleophiles

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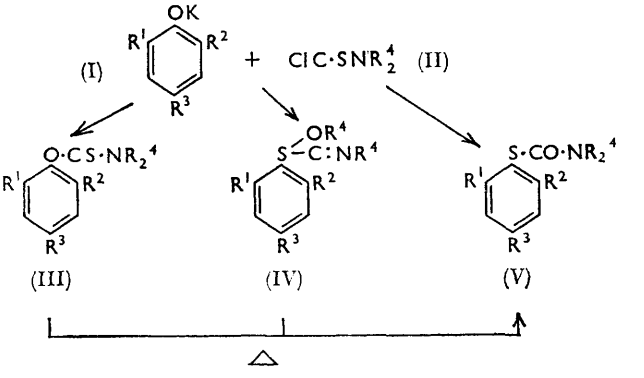
NN-Dialkylthiocarbamoyl chloride and potassium 2,4-dinitrophenoxide, 2-chloro- or 2-methyl-4,6-dinitrophenoxide, or 2,4-dinitro-1-naphthoxide, on heating in acetone, give *S*-aryl thiocarbamates, whereas potassium nitrophenoxide gives an *O*-aryl thiocarbamate. On treatment with potassium hydroxide in methanol at room temperature the 6-substituted-2,4-dinitrophenyl and 2,4-dinitro-1-naphthyl thiocarbamates and iminothiocarbonates yield highly coloured *p*-quinonoid potassium 1,1-*gem*-dimethoxy-*aci*-nitro-salts of different stabilities, in which the two methoxy-groups are equivalent. The *aci*-salts decompose in solution to the methyl ethers or potassium phenoxides, or both, depending on conditions. 2,4-Dinitrophenyl thiocarbamate does not yield the *aci*-salt, but hydrolyses with potassium hydroxide in methanol to the benzenethiolate. However, it produces an intense violet colour with acetone in the presence of alkali. Thiocarbamates, carbamates, and iminothiocarbonates give intense colours in the presence of alkali with various nucleophiles capable of producing the ion $RCHX^-$ where X is an electron-withdrawing group; carbonates, thio-, or dithio-carbonates do not give colours.

In Part II [1] we showed that when potassium 2,4-dinitro-6-s-butylphenoxide (I; $R^1 = Bu^s$, $R^2 = R^3 = NO_2$) and *NN*-dialkylthiocarbamoyl chloride (II; $R^4 =$ Me or Et), in acetone, were heated under reflux, thiocarbamate (V; $R^1 = Bu^s$, $R^2 = R^3 = NO_2$, $R^4 =$ Me or Et) resulted. Potassium 2,4-dinitro-6-t-butylphenoxide (I; $R^1 = Bu^t$, $R^2 = R^3 = NO_2$) and *NN*-dimethyl- or *NN*-dibutyl-thiocarbamoyl chloride (II; $R^4 =$ Me or Bu^n), under the same conditions, yielded thiocarbamate (III; $R^1 = Bu^t$, $R^2 = R^3 = NO_2$, $R^4 =$ Me or Bu^n), *NN*-dipropylthiocarbamoyl chloride gave iminothiocarbonate (IV; $R^1 = Bu^t$, $R^2 = R^3 = NO_2$, $R^4 = Pr^n$), and *NN*-diethylthiocarbamoyl chloride a mixture of iminothiocarbonate (IV; $R^1 = Bu^t$, $R^2 = R^3 = NO_2$, $R^4 =$ Et) and thiocarbamate (V; $R^1 = Bu^t$, $R^2 = R^3 = NO_2$, $R^4 =$ Et). The thiocarbamates (III) and iminothiocarbonates (IV) isomerised to thiocarbamates (V) on heating.

We now report that when potassium 2,4-dinitrophenoxide (I; $R^1 = H$, $R^2 = R^3 = NO_2$), 2-chloro- (I; $R^1 = Cl$, $R^2 = R^3 = NO_2$), 2-methyl-4,6-dinitrophenoxide (I; $R^1 = Me$, $R^2 = R^3 = NO_2$), or 2,4-dinitro-1-naphthoxide and *NN*-dimethyl-, -diethyl-, -dipropyl-, or -dibutyl-thiocarbamoyl chloride (II), in



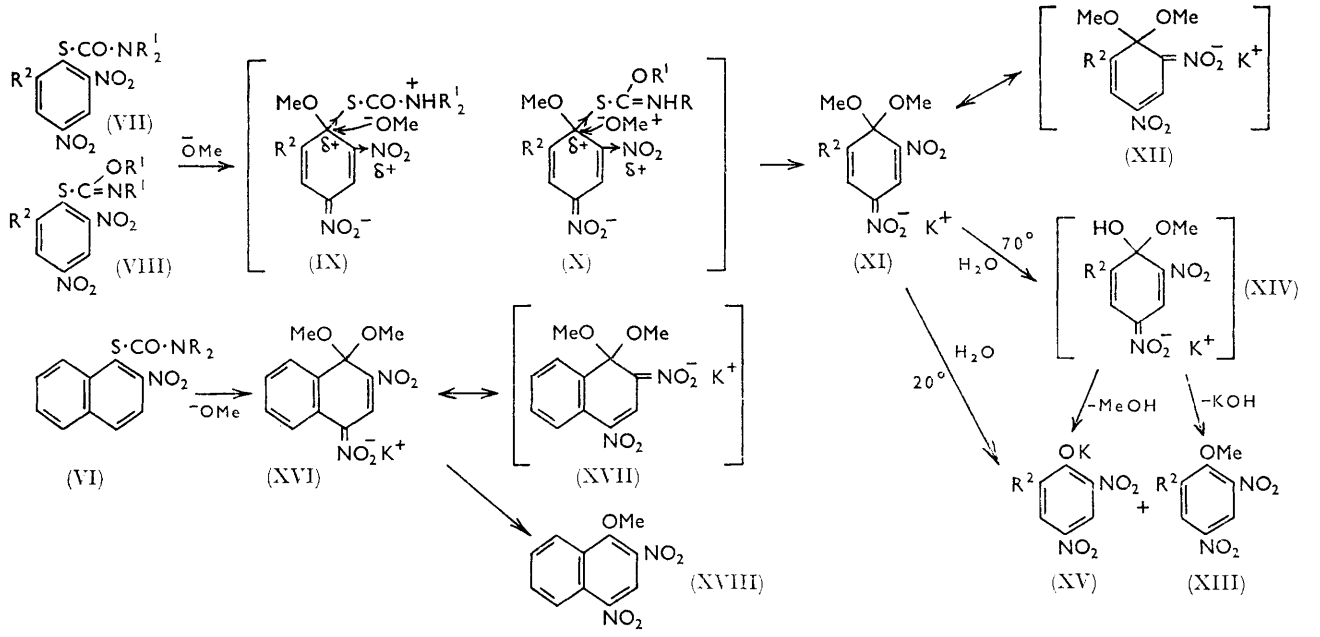
acetone, were heated under reflux, thiocarbamates (V) and (VI) were obtained. Potassium 2,6-dinitro-4-t-butylphenoxide (I; $R^1 = R^2 = NO_2$, $R^3 = Bu^t$) and

† Part IV, M. Pianka and J. D. Edwards, preceding Paper.

[1] J. D. Edwards and M. Pianka, *J. Chem. Soc.*, 1965, 7338.

NN-diethylthiocarbamoyl chloride yielded under the same conditions thiocarbamate (V; $R^1 = R^2 = NO_2$, $R^3 = Bu^t$, $R^4 = Et$), and potassium 4-nitrophenoxide and *NN*-dimethylthiocarbamoyl chloride gave thiocarbamate (III; $R^1 = R^2 = H$, $R^3 = NO_2$, $R^4 = Me$).*

In Part II [1] we postulated that isomerisation of thiocarbamates (III) to thiocarbamates (V) proceeds *via* iminothiocarbonates (IV). The isomerisation involves bonding between the nucleophilic sulphur and the phenolic carbon facilitated by electron-withdrawing groups, and rupture of the Ph–O bond. With *o*- or *p*-nitrophenyl thiocarbamates (III) isomerisation to thiocarbamates (V) occurs on heating at 170—180°.[2] With 2,4-dinitrophenyl compounds, not substituted in the 6-position with a highly efficient electron-donating group such as t-butyl, thiocarbamates (V) are readily produced.



Schönberg *et al.*[3] treated thiocarbonates, and Kwarts and Evans [4] and Newman and Karnes [2] treated thiocarbamates with alkali and obtained the arylthiols. Thiocarbamate (VII; $R^1 = Et$, $R^2 = Bu^t$) and iminothiocarbonate (VIII; $R^1 = Et$, $R^2 = Bu^t$) yielded, on heating with potassium methoxide in methanol, anisole (XIII; $R^2 = Bu^t$) and the phenoxide (XV; $R^2 = Bu^t$).[1] On treatment with potassium hydroxide in methanol at room temperature the thiocarbamates (VI) and (VII) and the iminothiocarbonates (VIII) yielded highly coloured potassium *aci*-salts (XVI) and (XI; $R^2 = Cl$, Me, or Bu^t). The formation of *aci*-salts from aliphatic 2,4,6-trinitro-aryl ethers and alkoxide ions was observed in the early part of this century [5] and studied more recently.[6] Gitis and his co-workers isolated *aci*-salts from 2,4-dinitro-1-naphthyl methyl ether and alkoxide ions [7] and from 2,4-dinitro-anisole and alkoxide ions.[8]

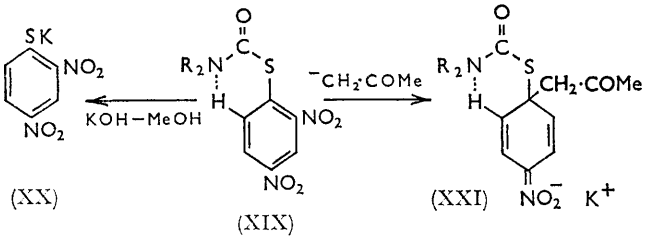
The two methoxy-groups in *aci*-salts (XI) and (XVI) were equivalent with n.m.r. peaks in dimethyl sulphoxide at τ 7·05—7·23. 2,4-Dinitro-anisoles showed peaks at τ 6·03—6·10 (nos. 14—16 in Part II [1]). This shift cannot be due to steric effects as molecular models of *aci*-salts (XI) and (XVI) show no steric hindrance of the methoxy-groups; it may be due to electronic effects. The equivalence of the *gem*-methoxy-groups supports the suggested *p*-quinonoid structures (XI) and (XVI) rather than the alternative *o*-quinonoid structures (XII) and (XVII) as molecular models show that in the latter the methoxy-groups are non-equivalent. Though thiocarbamate (V; $R^1 = R^2 = NO_2$, $R^3 = Bu^t$, $R^4 = Et$) and potassium hydroxide, in methanol, gave the characteristic mauve colour of the *aci*-salt, the *aci*-salt could not be isolated probably because of the lower stability of the *o*-quinonoid forms such as (XII).

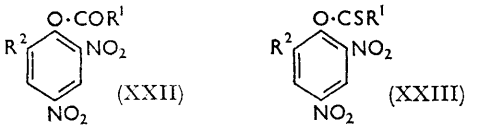
Gitis and Glaz [7] found that for transetherification of anisoles at least two electron-withdrawing substituents are required, of which one must be a nitro-group. No colour characteristic of the *aci*-salts was produced with

* Newman and Karnes,[2] whose Paper appeared after the completion of this work, prepared this compound from the phenol, the thiocarbamoyl chloride, and an organic base.

[2] M. S. Newman and H. A. Karnes, *J. Org. Chem.*, 1966, **31**, 3980.
[3] A. Schönberg and L. Vargha, *Ber.*, 1930, **63**, 178.
[4] H. Kwart and E. R. Evans, *J. Org. Chem.*, 1966, **31**, 410.
[5] C. L. Jackson and W. F. Boos, *Amer. Chem. J.*, 1898, **20**, 444; C. L. Jackson and F. H. Gazzolo, *ibid.*, 1900, **23**, 376; C. L. Jackson and R. B. Earle, *ibid.*, 1903, **29**, 89; J. Meisenheimer, *Annalen*, 1902, **323**, 205.
[6] R. Foster and D. L. Hammick, *J. Chem. Soc.*, 1954, 2153; J. B. Ainscough and E. F. Caldin, *ibid.*, 1956, 2528; R. Foster and R. K. Mackie, *ibid.*, 1963, 3796; V. Gold and C. H. Rochester, *ibid.*, 1964, 1687.
[7] S. S. Gitis and A. I. Glaz, *J. Gen. Chem.* (*U.S.S.R.*), 1963, **33**, 902.
[8] S. S. Gitis, A. I. Glaz, and A. Ya. Kaminskii, *J. Gen. Chem.* (*U.S.S.R.*), 1963, **33**, 3301.

2- or 4-nitroanisole and methoxide ion. Carbamate (XXII; $R^1 = NEt_2$, $R^2 = Bu^t$), thiocarbamate (III; $R^1 = Bu^t$, $R^2 = R^3 = NO_2$, $R^4 = Me$), iminothiocarbonate (VIII; $R^1 = Et$, $R^2 = Bu^t$) and thiocarbamates (VII; $R^1 = Me$ or Et, $R^2 = Cl$, Me, or Bu^t) and (VI; R = Et) and methoxide ion gave the characteristic colour of the *aci*-salts, whereas carbonate (XXII; $R^1 = EtO$, $R^2 = Bu^t$), thiocarbonate (XXII; $R^1 = SEt$, $R^2 = Bu^s$) or dithiocarbonate (XXIII; $R^1 = SMe$, $R^2 = Bu^t$) did not. The amido- or the imino-group may facilitate the formation of the *aci*-salt through quaternisation of the nitrogen atom, followed by polarisation of the Ph–S bond (or Ph–O bond in the case of carbamates), addition of the methoxide ion [(IX) and (X)], and elimination of thiocarbamate (or carbamate) ion with the formation of *aci*-salt (XI). Thiocarbamates (VII; $R^2 = H$) may be stabilised by hydrogen bonding (XIX). Quaternation of the amido-nitrogen is thus prevented, the electron-





deficiency of the phenolic carbon is reduced, and the thiocarbamate hydrolysed with potassium hydroxide, in methanol, to the benzenethiolate (XX). *aci*-Salt (XI; $R^2 = H$) was prepared by the action of methoxide ion on 2,4-dinitroanisole.[9]

aci-Salts (XI) and (XVI) were unstable in solution in methanol or water and decomposed to the colourless methyl ethers (XIII) and (XVIII). On heating with water *aci*-salts (XI) yielded mainly the potassium phenoxide (XV) and some anisole (XIII), whereas *aci*-salt (XVI) yielded a higher proportion of methyl ether (XVIII) than of potassium 2,4-dinitro-1-naphthoxide. The formation of the potassium phenoxide (and naphthoxide) may be due to a nucleophilic attack of hydroxide ions on the *aci*-salt with the formation of the intermediate (XIV) which is converted to phenoxide (XV) or anisole (XIII). The smaller proportion of the naphthoxide may be due to the greater stability of *aci*-salt (XVI).

Gitis and his co-workers [10,11] studied the nature of the coloured complex produced in the Yanovsky reaction [12] between acetone and polynitro-aromatic compounds in the presence of alcoholic alkali. They deduced from chemical degradation studies [11] that in the Yanovsky reaction the ketonic ion $CH_3COCH_2^-$ adds on to polynitro-aromatic compounds.

Carbamates, thio-carbamates, and iminothiocarbonates with two nitro-groups gave an intense mauve, violet, or red colour with potassium hydroxide in acetone. That thiocarbamate (XIX) also gave the characteristic intense colour with the ion $CH_3COCH_2^-$, but not with potassium hydroxide in methanol when the thiophenol was produced, may be due to the formation of *aci*-salt (XXI). Certain compounds capable of producing the ion $RCHX^-$ where X is an electron-withdrawing group (carbonyl, nitro, or cyano) also produced colour with thiocarbamates (V). Dehydroacetic acid [13] and acetylacetone [14] are enolised and hydrogen bonded and gave less intense colour. Sterically unhindered alkoxide ions produced colour, but the isopropoxide, t-butoxide, or phenoxide ion did not.

None of the carbamates, thiocarbonates, and iminothiocarbonates described earlier [1] and in this Paper possessed practically useful pesticidal activity.

EXPERIMENTAL

Preparation of Thiocarbamates (Table 1).—The method used was as described by Edwards and Pianka.[1] The 2,4-dinitro-phenol or -1-naphthol (0·04 mole) and potassium carbonate (0·044 mole), in acetone (40—100 ml.), were heated under reflux until complete solution resulted (0·5—1 hr.). To the solution of the potassium phenoxide or naphthoxide *NN*-dialkylthiocarbamoyl chloride (0·04 mole), neat or in acetone (15—25 ml.), was added and the solution heated under reflux for 3 hr. After filtration from the precipitated potassium chloride the acetone was distilled off *in vacuo*. The residue was extracted with benzene. The benzene solution was washed with 2N-sodium carbonate (where the sodium phenoxide or naphthoxide precipitated it was filtered off), sodium chloride solution, dried (Na_2SO_4), the benzene distilled off *in vacuo*, and the residue crystallised where appropriate.

Reaction of Thiocarbamates with Potassium Hydroxide in Methanol at Room Temperature.—The carbamates were dissolved at room temperature by shaking in solutions of potassium hydroxide pellets in methanol (7—22·5% w/v). The red solids that separated were filtered off after 2—16 hr., washed with methanol, then benzene, and dried *in vacuo* at 55°. The details of preparation and physical data of the *aci*-salts (XI) and (XVI) are summarised in Table 2.

From iminothiocarbonate (IV; $R^1 = Bu^t$, $R^2 = R^3 = NO_2$, $R^4 = Et$) (no. 23) [1] and potassium hydroxide in methanol at room temperature, compound no. 21, m. p. 160° (decomp.), was obtained (75%).

Under the same experimental conditions compound no. 2

[9] S. S. Gitis and A. I. Glaz, *J. Gen. Chem.* (*U.S.S.R.*), 1957, **27**, 1897.
[10] S. S. Gitis, *J. Gen. Chem.* (*U.S.S.R.*), 1957, **27**, 1894; S. S. Gitis, G. M. Oksengendler, and A. Ya. Kaminskii, *ibid.*, 1959, **29**, 2983; S. S. Gitis and A. Ya. Kaminskii, *ibid.*, 1960, **30**, 3810; S. S. Gitis and A. Ya. Kaminskii, *ibid.*, 1963, **33**, 3297.
[11] A. Ya. Kaminskii and S. S. Gitis, *J. Gen. Chem.* (*U.S.S.R.*), 1964, **34**, 3743.
[12] J. V. Yanovsky and L. Erb, *Ber.*, 1886, **19**, 2155; F. Reizenstein and G. Stamm, *J. prakt. Chem.*, 1910, **81**, 167.
[13] J. D. Edwards, J. E. Page, and M. Pianka, *J. Chem. Soc.*, 1964, 5200.
[14] G. Schwarzenbach and Ch. Wittwer, *Helv. Chim. Acta*, 1947, **30**, 659.

TABLE 1

Compounds obtained by heating *NN*-dialkylthiocarbamoyl chlorides (II) with potassium phenoxides (I) (or naphthoxide) in acetone under reflux for 3 hr.

No.	Compound R¹	R²	R³	R⁴	M. p. (n_D^{20})	Appearance	Yield (%)	Found: N (%) [a]	Formula	Reqd: N (%)
1 (III)	H	H	NO_2	Me	146—147° [b,c]	Pale yellow prisms	80			
2 (V)	H	NO_2	NO_2	Me	139—140 [b,g]	Yellow needles	77	10·3	$C_9H_9N_3O_5S$	10·3
3 (V)	H	NO_2	NO_2	Et	75—76 [b]	Yellow prisms	93	9·4	$C_{11}H_{13}N_3O_5S$	9·4
4 (V)	H	NO_2	NO_2	Pr^n	77—81 [c]	Yellow needles	77	8·5	$C_{13}H_{17}N_3O_5S$	8·6
5 (V)	H	NO_2	NO_2	Bu^n	—	Dark brown oil	67	7·9	$C_{15}H_{21}N_3O_5S$	7·9
6 (V)	Cl	NO_2	NO_2	Me	156—157 [c]	Pale brown needles	80	9·0	$C_9H_8ClN_3O_5S$	9·2
7 (V)	Cl	NO_2	NO_2	Et	74—75 [c]	Brown prisms	55	8·4	$C_{11}H_{12}ClN_3O_5S$	8·4
8 (V)	Cl	NO_2	NO_2	Pr^n	(1·5827)	Reddish-brown oil	90	7·6	$C_{13}H_{16}ClN_3O_5S$	7·7
9 (V)	Cl	NO_2	NO_2	Bu^n	—	Reddish-brown oil	78	7·0	$C_{15}H_{20}ClN_3O_5S$	7·2
10 (V)	Me	NO_2	NO_2	Me	157—159 [c]	Pale brown needles	66	9·8	$C_{10}H_{11}N_3O_5S$	9·8
11 (V)	Me	NO_2	NO_2	Et	79—81 [c]	Pale yellow prisms	61	9·0	$C_{12}H_{15}N_3O_5S$	9·0
12 (V)	Me	NO_2	NO_2	Pr^n	48—50 [c]	Yellow needles	34	8·2	$C_{14}H_{19}N_3O_5S$	8·2
13 (V)	Me	NO_2	NO_2	Bu^n	—	Black oil	73	7·4	$C_{16}H_{23}N_3O_5S$	7·6
14 (V)	NO_2	NO_2	Bu^t	Et	88—89 [c]	Light brown prisms	46	8·0	$C_{15}H_{21}N_3O_5S$	8·0
15 (VI)	R = Et				172—173 [d]	Yellow prisms	78	8·0	$C_{15}H_{15}N_3O_5S$	8·0
16 (VI)	R = Pr^n				137—139 [b,c]	Yellow needles	61	7·4	$C_{17}H_{19}N_3O_5S$	7·4
17 (VI)	R = Bu^n				83—84 [b]	Yellow needles	62	7·0	$C_{19}H_{23}N_3O_5S$	6·9

[a] Determined as aromatic nitro-groups by reduction with titanous chloride. [b] From ethanol. [c] From propan-2-ol. [d] From acetone. [e] From di-isopropyl ether. [f] Lit.,[2] m. p. 150—153°. [g] Some compound coprecipitated with the potassium chloride and was removed by washing with water.

TABLE 2

aci-Salts obtained from the reaction of 2,4-dinitro-phenyl- and -1-naphthyl-thiocarbamates with potassium hydroxide in methanol

Compound No.		R²	From cpd.	Concentration of KOH in MeOH w/v (%)	M. p.	Yield (%)	Found (%) C	H	Cl	N	Formula	Required (%) C	H	Cl	N
19	(XI)	Cl	7	10	186° [a]	77			11·2	8·8	$C_8H_8ClKN_2O_6,H_2O$			11·0	8·8
20	(XI)	Me	11	22·5	169 [b]	88	37·1	4·1		9·7	$C_9H_{11}KN_2O_6,\frac{1}{2}H_2O$	37·5	4·1		9·6
21	(XI)	Bu^t	18 [c]	20 [e]	160 [e]	40	43·5	5·3		8·8	$C_{12}H_{17}KN_2O_6$	44·5	5·3		8·7
22	(XVI)		15	7 [e]	180 [a,d]	76	43·2	4·4		8·9	$C_{12}H_{11}KN_2O_6$	43·2	3·6		9·0

[a] Decomposed. [b] Exploded. [c] 2,4-Dinitro-6-t-butylphenyl-*NN*-diethylthiocarbamate (compound no. 18) was prepared as in ref. 7. [d] Lit.,[7] m. p. 178° (decomp.). [e] The *aci*-salt separated on cooling the methanolic solution at 0°.

gave potassium 2,4-dinitrobenzenethiolate (XX) (no. 27) (62%). The filtrate, acidified with dilute hydrochloric acid, yielded a further 20% of 2,4-dinitrobenzenethiol, m. p. and mixed m. p. 126—128°.

TABLE 3

Reactions of carbamates with acetone in the presence of potassium hydroxide

No.	Compound R¹	R²	R³	R⁴	Colour	Yanovsky reaction
1 (III)	H	H	NO_2	Me	Yellow	Negative
24* (V)	H	H	NO_2	Me	Pale brown	Negative
2 (V)	H	NO_2	NO_2	Me	Intense violet	Positive
6 (V)	Cl	NO_2	NO_2	Me	Intense mauve	Positive
7 (V)	Cl	NO_2	NO_2	Et	Intense violet	Positive
11 (V)	Me	NO_2	NO_2	Et	Intense mauve	Positive
23 (IV)	Bu^t	NO_2	NO_2	Et	Intense red	Positive
18 (V)	Bu^t	NO_2	NO_2	Et	Intense mauve	Positive
25 (III)	Bu^t	NO_2	NO_2	Me	Intense red	Positive
26 (XXII)	NEt_2	Bu^t			Intense violet	Positive
15 (VI)	R = Et				Intense mauve	Positive
27 (XX)					Pale brown	Negative

* Prepared as in ref. 2.

Compound no. 14 gave a brilliant mauve fluorescent solution, from which the *aci*-salt could not be isolated. On dilution with methanol followed by water, the colour changed

TABLE 4

Reactions of thiocarbamates with nucleophilic reagents in the presence of potassium hydroxide

Compound	Reagent	Colour	Reaction
6	Methanol	Intense fluorescent red	Positive
11	Methanol	Deep red	Positive
6	Ethanol	Fluorescent red	Positive
6	Propan-2-ol	Pale yellow	Negative
6	t-Butanol	Pale yellow	Negative
6	Phenol	Yellow	Negative
6	Acetone	Intense mauve	Positive
11	Acetone	Intense mauve	Positive
11	Ethyl methyl ketone	Mauve	Positive
11	Isobutyl methyl ketone	Violet	Positive
11	Cyclohexanone	Violet	Positive
11	Acetophenone	Violet	Positive
6	Dibenzyl ketone	Violet	Positive
11	Benzophenone	Pale yellow	Negative
6	Dehydroacetic acid	Red	Positive
11	Ethyl acetate	Pale yellow	Negative
6	Acetylacetone	Red	Positive
11	Acetonylacetone	Intense violet	Positive
6	Ethyl acetoacetate	Intense mauve	Positive
11	Mesityl oxide	Violet	Positive
11	Isophorone	Violet	Positive
6	Nitromethane	Intense mauve	Positive
11	Malononitrile	Red	Positive
11	Formaldehyde	Pale yellow	Negative
11	Chloral	Pale yellow	Negative
11	Butyraldehyde	Intense mauve	Positive

TABLE 5

Infrared absorption bands (cm.$^{-1}$) for CS_2 solutions and n.m.r. bands (τ values) for $CDCl_3$ solutions (coupling constants in c./sec. in parentheses)

	Infrared bands			N.m.r. peaks		
Compound	C=O	NO_2	C–O–C	*N*-substituent	ring substituent	aromatic H
1	—	1340	1210, 1115	6·54		1·74d (d)
				6·64		2·78d (9)
2	1690	1350	—	6·90		1·20d (2)
						1·62dd (8,2)
						2·03d (8)
3	1684	1350	—	8·73t (7) [b] 7·53q (7) [b]		1·26d (2) [b]
						1·64dd (2, 8·5) [b]
						2·11d (8·5) [b]
4	1682	1350	—	9·02t (7) [b] 8·33m [b] 6·67t (7) [b]		1·28d (2) [b]
						1·65dd (2, 8·5) [b]
						2·13d (8·5) [b]
5	1678	1340	—	9·03t (7) 8·50m 6·60t (7)		1·19d (2)
						1·60dd (2, 8·5)
						2·05d (8·5)
6	1690	1340	—	6·88		1·41d (2)
						1·48d (2)
7	1685	1340	—	8·66t (7) 6·55q (7)		1·38d (2)
						1·47d (2)
8	1684	1338	—	9·05t (7) 8·35m 6·64t (7)		1·42d (2)
						1·47d (2)
9	1686	1340	—	9·02t (7) 8·50m 6·62t (7)		1·42d (2)
						1·49d (2)
10	1688	1340	—	6·90	7·37	1·53d (2)
						1·67d (2)
11	1676	1340	—	8·73t (7) 6·54q (7)	7·35	1·50d (2)
						1·64d (2)
12	1678	1340	—	9·03t (7) 8·33m 6·63t (7)	7·36	1·50d (2)
						1·64d (2)
13	1680	1340	—	9·03t (7) 8·50m 6·62t (7)	7·37	1·53d (2)
						1·67d (2)
14	1678	1345	—	8·78t (7) [b] 6·60q (7) [b]	(R^3, 8·58) [l]	1·99 [b]
15	1680	1338	—	8·72t (7) 6·50q (7)		1·15—1·6m
						2·0—2·3m
16	1685	1340	—	8·90m 8·30m 6·60m		1·1—1·4m
						1·40
						2·0—2·5m
17	1682	1336	—	9·0m 8·4m 6·58m		1·1—1·5m
						1·45
						2·0—2·5m
24	1675	1336	—	6·94		1·80d (9)
						2·36d (9)
				Methoxy-groups		
19 [c]	—	1370 [a] 1532 [a]	1052 [a] 1154 [a] 1178 [a] 1210 [a]	7·05 [d]		1·31d (2·5) [d]
						2·55d (2·5) [d]
20 [c]	—	1366 [a] 1534 [a]	1052 [a] 1135 [a] 1155 [a] 1206 [a]	7·17 [d]	8·25d (1) [d]	1·33d (2·5) [d]
						2·92dd (1, 2·5) [d]
21	—	1360 [a] 1540 [a]	1040 [a] 1115 [a] 1168 [a] 1212 [a]	7·14 [d]	8·73 [d]	1·37d (2) [d]
						2·67 (2) [d]
22	—	1355 [a] 1545 [a]	1052 [a] 1132 [a] 1183 [a] 1210 [a]	7·23 [d]		0·73 [d]
						1·25m [d]
						2·2—2·9m [d]
27	—	1330 [a] 1560 [a]	—	—		1·92d (2) [d]
						2·37dd (2, 8·5) [d]
						2·65d (8·5) [d]

[a] Nujol mull. [b] CCl_4 solution. [c] Infrared absorption band for Nujol mull at 3550 cm.$^{-1}$ and n.m.r. peak for Me_2SO solution at τ 6·6 due to moisture. [d] Me_2SO solution (cf. ref. 25).

to greenish-yellow and from the mixture 2,6-dinitro-4-t-butylanisole [15] separated (7·25%). On acidification of the filtrate 2,6-dinitro-4-t-butylphenol [16] separated (58%).

Thiocarbamate (VI; R = Et) was briefly warmed with potassium hydroxide in methanol (6·7% w/v) to give a deep red solution. After 5 min. the red solid started crystallising out and after 18 hr. at room temperature was filtered off. The filtrate, on acidification with hydrochloric acid, yielded ether (XVIII) [17] (10·4%), and the solid, on dissolving in methanol and acidification with hydrochloric acid, also yielded ether (XVIII) [17] (81%).

Reactions of aci-*Salts*.—Water was added at room temperature to a solution of the *aci*-salt in methanol. The mixture slowly lost its red colour. Where a solid precipitated it was filtered off and recrystallised from a suitable solvent, otherwise the mixture was extracted with ether, the ether evaporated, and the residue crystallised from a suitable solvent. Compound no. 19 yielded anisole (XIII; R^2 = Cl).[18] Compound no. 20 yielded anisole (XIII;

[15] A. Baur, *Ber.*, 1894, **27**, 1614.
[16] A. Studer, *Ber.*, 1881, **14**, 1472.
[17] F. Ullmann and W. Bruck, *Ber.*, 1908, **41**, 3932.
[18] A. F. Holleman, *Rec. Trav. chim.*, 1920, **39**, 462.

R^2 = Me).[19] Compound no. 21 gave anisole (XIII; R^3 = Bu^t) [20] and compound no. 22 gave ether (XVIII).[17]

Treatment of Products of Reactions of Thiocarbamates and Potassium Hydroxide in Methanol with Water at 70°.—Compound no. 6 was dissolved in potassium hydroxide–methanol (20% w/v). After one day at room temperature the mixture of dark red crystals and deep red liquid was poured into water at ~70° to yield a clear solution. On cooling, needles separated out. The mixture was acidified (hydrogen sulphide evolved) and filtered. 2-Chloro-4,6-dinitrophenol [21] (85%) was obtained.

(*b*) Compound no. 11 was dissolved in potassium hydroxide–methanol (4·2% w/v). After one day at room temperature the mixture of dark red crystals and deep red liquid was poured into water at ~70°. The solid that crystallised on cooling was filtered off, and found to be 2-methyl-4,6-dinitroanisole [19] (26·5%). The filtrate yielded on acidification 2-methyl-4,6-dinitrophenol [22] (42%).

Heating of Thiocarbamate (VI; R = Et) *with Potassium Hydroxide in Methanol.*—Compound no. 15, in potassium hydroxide–methanol (6·7% w/v), was heated under reflux for 1·5 hr. After 16 hr. at room temperature the mixture of dark red crystals and intensely red liquid was poured into water and extracted with benzene. The insoluble red solid was filtered off and, from it, on acidification, 2,4-dinitro-1-naphthol was obtained (23·3%). From the benzene extract ether (XVIII) [17] was obtained (47%).

Colour Reactions of Carbamates with Potassium Hydroxide in Methanol.—Thiocarbamate (III; R^1 = Bu^t, R^2 = R^3 = NO_2, R^4 = Me) (no. 25) [1] and carbamate (XXII; R^1 = NEt_2, R^2 = Bu^t) (no. 26) [1] were treated at room temperature with potassium hydroxide in methanol. The deep red colour characteristic of the *aci*-salt resulted. When drops of the solutions were placed on filter paper the deep crimson colour persisted for several days, slowly changing to pale yellow.

The carbonates (XXIII; R^1 = SMe, R^2 = Bu^t), (XXII; R^1 = SEt, R^2 = Bu^s), and (XXII; R^1 = OEt, R^2 = Bu^t), thiocarbamate (no. 1), thiocarbamate (V; R^1 = R^2 = H, R^3 = NO_2, R^4 = Me) [2] and 2-nitro- [23] and 4-nitro-anisoles [24] gave yellow or orange solutions on treatment with potassium hydroxide in methanol, not characteristic of the *aci*-salts.

Colour Reactions of Carbamates with Certain Reagents.—Aqueous potassium hydroxide (10%) was added to a solution of the carbamate in the reagent or in a mixture of the reagent and propan-2-ol. The colour that developed in the organic phase was observed. The colour was checked against the blank containing no reagent. Table 3 summarises reactions with acetone. Table 4 summarises reactions with other nucleophiles.

Spectroscopic Measurements.—The i.r.[26] and n.m.r.[27] measurements were conducted as described previously. They are listed in Table 5.[25]

We thank Dr. J. E. Page for the i.r. and n.m.r. spectra.

[7/352 *Received, March 22nd,* 1967]

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