Persulphate Oxidations. Part 12.[1] Generation and Reactions of *N*-Methoxy-benzamidyls and -benzsulphonamidyls

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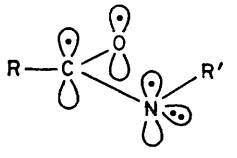
Several *N*-methoxybiphenyl-2-carboxamidyls and one *N*-methoxybiphenyl-2-sulphonamidyl have been generated by oxidation of the corresponding *N*-methoxy-amides with potassium persulphate, lead tetra-acetate, or t-butoxyl radicals (from irradiated di-t-butyl peroxide), and their e.s.r. spectral parameters evaluated. The methoxyamidyls cyclise onto the adjacent aryl ring to give *N*-methoxyphenanthridones and/or dimerise to hydrazines which fragment spontaneously, with evolution of nitrogen, to the methyl esters of the corresponding carboxylic acids.

EVIDENCE derived from both e.s.r.[2] and CIDNP[3] measurements strongly favours a π-ground state (1a) for amidyl radicals but molecular-orbital calculations[4] have been less consistent in their predictions. For example, recent *ab initio* calculations[5] could not distinguish between the π (1a), ε_N (1b), and ε_O (1c) energies of formamidyl. π-Amidyls should be capable of reacting on both oxygen and nitrogen but examples of reaction on oxygen are scarce.[6] A similar set of structures can be drawn for *N*-alkoxyamidyls (2) but of these the π-structure (2) should be energetically more favourable than (1a) because of the additional interaction of the unpaired electron with the lone pair on the alkoxy oxygen [(2a)↔(2b)]. This interaction is reinforced by the electron-withdrawing effect of the carbonyl oxygen as represented in structure (2c). Molecular-orbital calculations and e.s.r. measurements support this view;[7,8] *N*-alkoxyamidyls have smaller a_N values (a_N *ca.* 10.5 G) and larger *g*-values (2.005 9) than *N*-alkylamidyls. They are also more easily generated and survive longer than *N*-alkylamidyls, indeed long enough to dimerise to unstable dialkoxydiacylhydrazines[9] (see below).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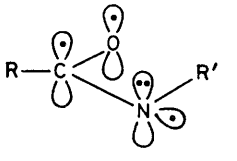
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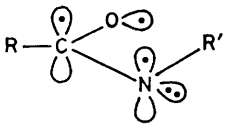
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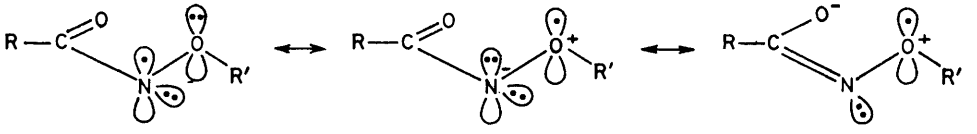
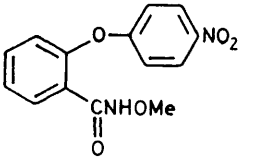

(2a) (2b) (2c)

In an earlier paper[6] we described how *o*-arylbenzamidyls, generated from the corresponding amides by reaction with persulphate, cyclised to give mainly phenanthridones. This work provided one of the rare examples of amidyls reacting on oxygen since significant amounts of lactone were also produced. The probability of reaction occurring on acyl oxygen should be higher for *N*-alkoxyamidyls than for *N*-alkylamidyls since the π-state of the former is energetically the more favourable. Hence a short series of *N*-alkoxy-*o*-phenylbenzenecarboxamidyls (7) and one *N*-methoxy-*o*-phenylbenzenesulphonamidyl (18) have been generated by oxidation of the corresponding *N*-methoxyamides with (*a*) persulphate in hot aqueous solution, and (*b*) lead tetra-acetate in benzene, and their reactions compared with those of the corresponding *N*-alkylamidyls.

RESULTS

Oxidation of Carboxamides.—The *N*-methoxyamides were prepared by reaction of the appropriate acid chlorides with methoxyamine. However, with *o*-(*p*-nitrophenoxy)benzoyl chloride and methoxyamine the Smiles rearrangement[10]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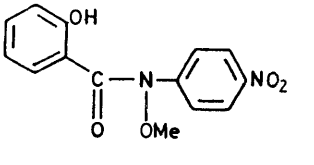
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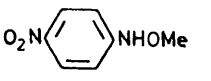
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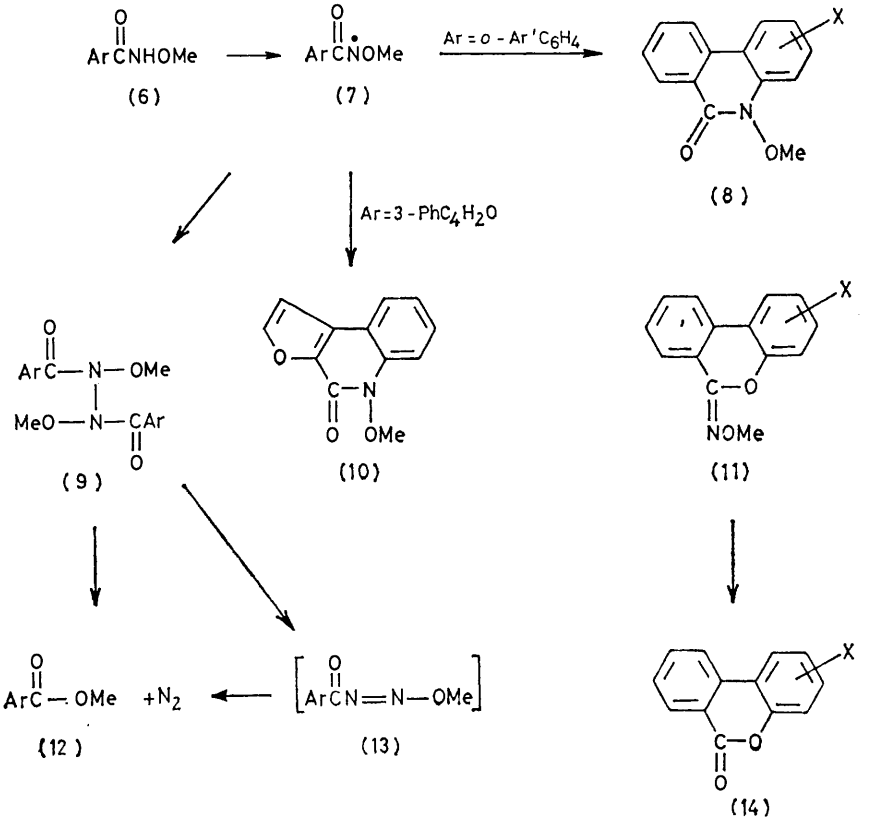
product (4), accompanied by smaller amounts of 4,4′-dinitroazobenzene, was produced. The latter presumably

arises by aerial oxidation of the *O*-methylhydroxylamine (5) which is a hydrolysis product of the phenol (4) (*cf.* ref. 11). The remarkable feature of this rearrangement [(3)→(4)] is the ease with which it is accomplished [shaking a solution of the alkoxyamide (3) briefly with cold alkali].

Persulphate Oxidations.—The main products were the cyclic *N*-methoxyamides (8) and (10), the methyl esters (12) of the parent carboxylic acids, and the diacylhydrazines (9). Lactones (14) were produced from two of the methoxyamides [6; Ar = *o*-PhC_6H_4 and *o*-(4-$NO_2C_6H_4$)C_6H_4] but only in very low yield. The structure of the cyclic amide (8; X = H) was confirmed by an independent synthesis. The diacyldimethoxyhydrazines (9) partly decomposed during work-up to the corresponding methyl ester (12) and nitrogen, and hence their yields were estimated from the n.m.r. spectra of the crude reaction mixtures. Only (9; Ar = *o*-PhC_6H_4) was isolated.

Lead Tetra-acetate (LTA) Oxidations.—At room temperature in benzene the *N*-methoxyamides (6) with LTA (0.7 mol. equiv.) gave the diacyldimethoxyhydrazines (9) in almost quantitative yield. Significant decomposition of these products occurred on attempted crystallisation even at low temperature. Crystalline samples of only two [9; Ar = *o*-PhC_6H_4 and *o*-(4-$NO_2C_6H_4$)C_6H_4] were obtained and satisfactory elemental analyses are reported for only one of these. The mass spectra of these hydrazines showed no molecular-ion peak and only low intensity peaks corresponding to ions of $m/e > M^+/2$. Their i.r. spectra showed no N–H absorptions, and carbonyl bands at much higher frequency (1 710—1 720 cm^{-1}) than those of the methoxyamides from which they were derived.

With LTA in boiling benzene the *N*-methoxyamides gave complex mixtures which were not separated. The yields of the components were evaluated from the relative intensities of their methoxyl resonances in the n.m.r. spectra of the crude reaction mixtures (Table 1). Significantly, cyclic amides were formed from only two of the four methoxyamides [6; Ar = *o*-PhC_6H_4 and *o*-(4-$NO_2C_6H_4$)-C_6H_4] oxidised, the yields being lower than those obtained from the persulphate oxidations.



DISCUSSION

Formation of the diacyldialkoxyhydrazines (9), and detection of the e.s.r. spectra of the *N*-methoxyamidyls (7) on treatment of the *N*-methoxyamides with LTA in the cavity strongly supports a free-radical mechanism for these oxidations. Mosher and his co-workers [9] reached a similar conclusion in a related study of simpler *N*-alkoxyamides but had little e.s.r. evidence, and were unable to obtain additional chemical evidence for the mediation of *N*-alkoxyamidyls. For example, neither intramolecular addition of the *N*-alkoxyamidyl to a vinyl group in the alkoxy-chain (with formation of a five-membered ring) nor intramolecular H-abstraction from the alkoxy-chain (*via* a six-membered transition-state) occurred.

The esters (12) could arise by a two-step (9)→(13)→(12) of a multi-centre fragmentation of the hydrazines (9), heterolytic or homolytic fission being possible for both routes. We have no direct evidence (i.r., n.m.r.) which supports the mediation of (13) in these decompositions. Further, when the hydrazine (9; Ar = *o*-PhC_6H_4) was decomposed (by heat or u.v. light) in the e.s.r. cavity

radicals were not detected, and when decomposed in the n.m.r. cavity no CIDNP effect was observed. Positive evidence for the polar nature of these fragmentations was adduced from the ease of fragmentation of the hydrazine (9; Ar = *o*-PhC_6H_4) in boiling chloroform, there is a *p*-nitro-substituent in the *o*-aryl ring (Table 1), and the rate of reaction of the sulphate radical-anion with arenes is known to be adversely affected by the presence of electron-withdrawing substituents.[14] Secondly, solvolysis of the radical-cation in the boiling aqueous

TABLE 1

Products (%) from oxidation of *N*-methoxyamides

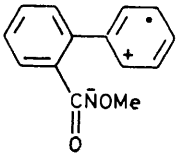
N-Methoxyamide	Method *	Lactam (8) or (10)	Ester (12)	Diacylhydrazine (9)	Other products
(6; Ar = *o*-PhC_6H_4)	(a)	20	20	18	2 (14; X = H)
	(b)			100	
	(c)	16	53	31	
[6; Ar = *o*-(2-$NO_2C_6H_4$)C_6H_4]	(a)	8	56	10	
	(b)			100	
	(c)		18	82	
[6; Ar = *o*-(4-$NO_2C_6H_4$)C_6H_4]	(a)	42	15	16	2 (14; X = 4-NO_2)
	(b)			100	
	(c)	2	26	72	
[6; Ar = 2(3-Ph)C_4H_2O]	(a)	8	35		
	(b)			100	
(17)	(a)		9		3 (22)
					8 (23)
(17)	(b)		32		
(17)	(c)		*ca.* 16		40 (21)

* (a) Oxidation with persulphate in boiling aqueous solution, (b) oxidation with lead tetra-acetate in benzene at room temperature, (c) oxidation with lead tetra-acetate in boiling benzene.

pyridine, and benzene. Decomposition occurred more rapidly in chloroform than in benzene despite its lower boiling point. Hence, we favour the multi-centre heterolytic fragmentation of the hydrazines with no accompanying N–N bond homolysis.[12]

The stability of the crystalline bis-(*o*-arylbenzoyl)-hydrazines [9; Ar = *o*-PhC_6H_4 and *o*-(4-$NO_2C_6H_4$)C_6H_4] was unexpected in view of the previously reported instability of their dibenzoyl analogues.[9] A study of the factors governing this stability was not an objective of this work but we surmise that non-bonding interactions between the *o*-aryl and methoxy-groups in [9; Ar = *o*-PhC_6H_4 and *o*-(4-$NO_2C_6H_4$)C_6H_4] prevent the molecule acquiring the conformation required for the concerted fragmentation to proceed. The destabilising effect of the 2′-nitro group in [9; Ar = *o*-(2-$NO_2C_6H_4$)C_6H_4], which causes the *o*-aryl ring to be twisted further out of the plane of the aryl ring, is consistent with this view.

We consider that the persulphate oxidations also proceed *via* *N*-methoxyamidyls (7) formed by electron transfer from the methoxyamide anion to the sulphate radical-ion. These amidyls then either dimerise to diacylhydrazines (9) or cyclise onto the adjacent aryl ring to give cyclohexadienyl radicals which are aromatised to give (8) by reaction with persulphate ion ($[S_2O_8]^{2-}$). No attempt was made to detect the intermediate methoxyamidyls (7) by e.s.r. in these persulphate oxidations but the similarity of the products to those formed with LTA in hot benzene strongly suggests that the same intermediates are involved in both oxidations. We discount the possibility that the cyclic methoxyamides (8) are formed by electron transfer from the *o*-aryl ring to the sulphate radical-anion, followed by capture of the methoxyamido-anion by the aryl radical-cation (15) so formed,[13] for the following reasons. First, the yield of cyclic methoxyamide (11) is higher when solution would be expected to compete with intramolecular capture of the methoxyamide anion and there is no



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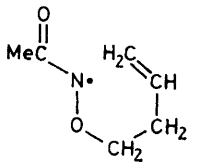

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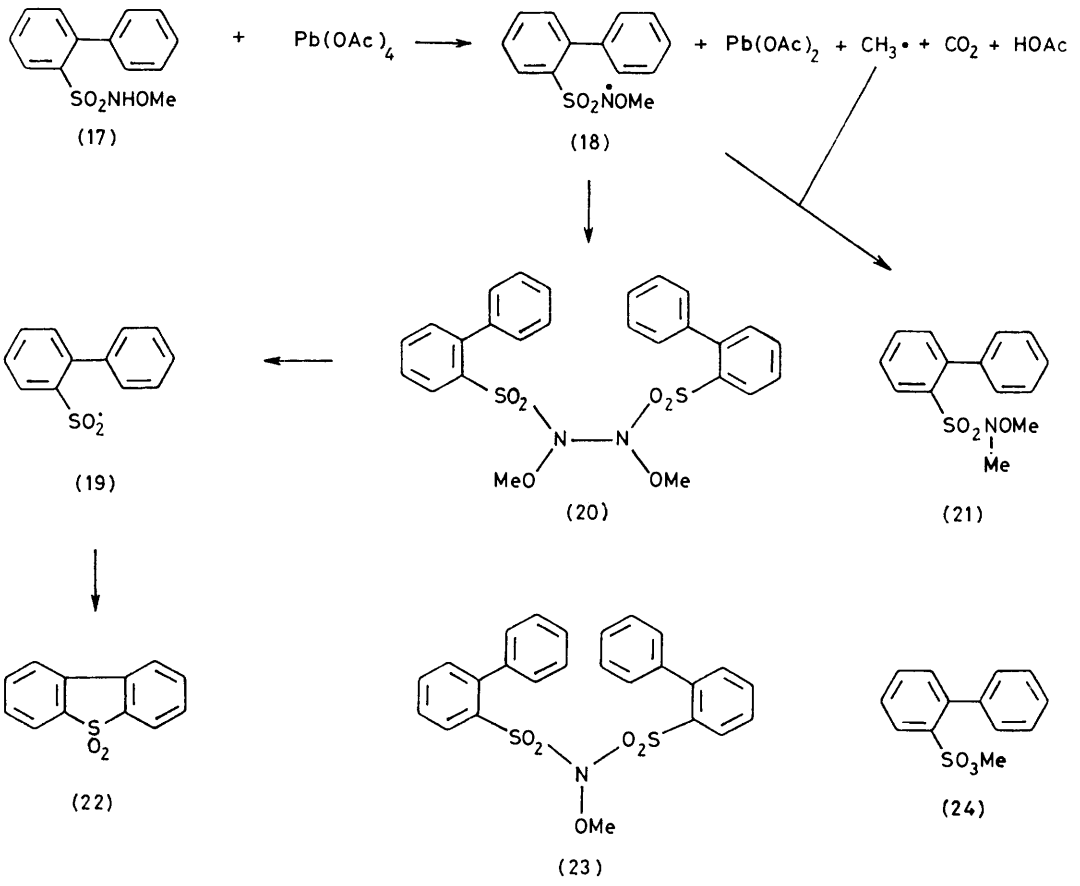
evidence, from product analysis, that solvolysis occurs.

The geometrical rigidity of the *N*-methoxy-*o*-arylbenzamidyls (7) which ensures the relative proximity of the 2′- and 6′-positions of the *o*-aryl ring to the nitrogen favours ring closure to *N*-alkoxyphenanthridones (8). In contrast, Mosher and his co-workers [9] found that the more flexible *N*-but-3-enyloxyacetamidyl (16) did not cyclise, giving only products derived from the hydrazine dimer. The 2′-nitro group in [7; Ar = *o*-(2-$NO_2C_6H_4$)-C_6H_4] causes the *o*-aryl ring to be twisted so that the 6′-carbon is, on average, more remote from the nitrogen than in (7; Ar = *o*-PhC_6H_4) and a lower yield of cyclic product ensues. Inspection of Dreiding models of the *N*-methoxyfuramidyl (7; Ar = 3-PhC_4H_2O) showed that the low yield of cyclic product in this case may be similarly explained. Interestingly, the nucleophilic character of the *N*-methoxyamidyls is revealed by the relatively high yield of *N*-methoxyphenanthridone formed from the nitro-*N*-methoxyamide [7; Ar = *o*-(4-$NO_2C_6H_4$)C_6H_4].

Dibenzo[*b*,*d*]pyrans were obtained from only two amides with persulphate and then only in very low yield. Hence, there is little evidence to support our initial proposition that the *N*-methoxyamidyls would react to a greater extent on oxygen than the *N*-alkylamidyls. Indeed, the yields of benzopyrans are so low

that they could have been formed by minor hydrolysis of the methoxyamides in the boiling aqueous persulphate solution followed by oxidative cyclisation of the acids so formed.

Oxidation of N-*Methoxybiphenyl-2-sulphonamide.*—The methoxysulphonamide (17) gave no cyclic sulphonamide on oxidation with persulphate or LTA. With persulphate the ester (24) and dibenzothiophen 5,5-dioxide (22) were obtained in low yield accompanied by a product, $C_{25}H_{21}NO_5S_2$, which showed no N–H absorption

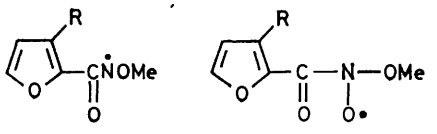


in the i.r. region, a methyl singlet at δ 2.84, and a ratio of aliphatic to aromatic proton signals of 1 : 6 in its n.m.r. spectrum. Since the same product was obtained in low yield by reaction of the *N*-methoxysulphonamide (17) with biphenyl-2-sulphonyl chloride we assign to it structure (23). The chemical shift of the methoxy protons (δ 2.84), in (23) is at unusually high field, but is similar to that of the model *NN*-di-*p*-tosyl-*O*-methylhydroxylamine (δ 2.98) which was synthesised for comparison. With LTA as oxidant, at room temperature, only the ester (24) was formed and at 80 °C a mixture (1 : 2) of the ester (24) and the *N*-methoxy-*N*-methylsulphonamide (21) (δ_{OMe} 3.42, δ_{NMe} 2.69).

Formation of the methyl ester (24) and detection (e.s.r.) of the intermediate sulphonamidyl (18) in the LTA reactions indicates that these oxidations follow a similar course to that of the *N*-methoxycarboxamides. However, one important difference is that the intermediate diacylhydrazine (20) was never detected (n.m.r.) and hence must fragment more easily than the diacylhydrazines (9). Formation of the *N*-methoxy-*N*-methylsulphonamide (21) on LTA oxidation probably arises as indicated in the Scheme. No analogous product was obtained from the *N*-methoxycarboxamides, from which we infer that there was a higher steady-state concentration of the sulphonamidyl (18) than there was of the carboxamidyl (7). With persulphate, formation of the dibenzothiophen dioxide (22) and the disulphonylhydroxylamine (23) indicates that free biphenyl-2-sulphonyl radicals are produced, presumably by fragmentation of the transient hydrazine (20) [by one-step or two-step fragmentation as discussed previously for (7) (*cf.* ref. 12)]. Cyclisation to dibenzothiophen 9,9-dioxide is an example of an intramolecular reaction with no intermolecular counterpart since normally arylsulphonyl radicals only react with polynuclear arenes.[15] Formation of the disulphonylhydroxylamine (23) again implies a high steady-state concentration of (18).

E.S.R. Spectra.—The *N*-alkoxyamidyls whose spectral parameters are listed in Table 2 were generated from the corresponding alkoxyamides (*a*) in benzene with LTA at 70—80 °C; and/or (*b*) in di-t-butyl peroxide by photolysis at or below room temperature. The spectral parameters are generally similar to those reported

previously by Koenig [7] and by Danen [8] for simpler alkoxyamidyls. However, the alkoxyfuramidyls (25; R = H and Ph) did show some additional unexpected splittings with one and two protons, respectively. In the spectrum of (25; R = H) one of the splittings must



(25) (26)

be due to H-3 of the furan ring and we tentatively assign the other to H-5. The spectrum of the methoxyfuramidyl (25; R = H) appeared relatively slowly when the corresponding *N*-methoxyamide was irradiated in di-t-butyl peroxide. Initially, another spectrum was detected which faded as that of the amidyl intensified. This initial spectrum had *g* 2.005 7, a_N 11.1 and splittings of 1.5 G (3 H) and 0.4 G (2 H). The splittings due to the methyl (1.5 G) and furan (0.4 G) protons are too small for the nitrogen to be attached directly to either. Hence, we attribute this initial spectrum to the acyl alkoxynitroxide (26) formed by reaction to the methoxyamidyl with small amounts of adventitious oxygen or hydroperoxide. Once these have been consumed the nitroxide spectrum fades and that of the alkoxyamidyl emerges. Acyl alkoxy nitroxides have not been reported previously.

The methoxysulphonamidyl (18) is the first alkoxysulphonamidyl to be reported.* It was identified from the general similarity of its spectrum to those of the *N*-methoxycarboxamidyls although the a_N value is larger and the *g*-value is lower. In Table 3 are listed typical a_N and *g*-values for the series of radicals, sulphonyl nitroxide,[16,17] sulphonamidyl,[18] and alkoxysulphonamidyl. The trend in a_N and *g*-values is similar to that exhibited by the corresponding series of carbonylamino-radicals [7,8,19] also listed in Table 3, but the sensitivity of a_N to changes in the groups attached to nitrogen is much lower. These differences can be rationalised if it is accepted that (*a*) spin delocalisation from nitrogen onto a sulphonyl group is negligible or at most much less efficient than it is onto carbonyl [20] and (*b*) the sulphonyl group, by distorting the ' planarity ' of the nitrogen (*cf.* de Boer *et al.*[17]) renders less efficient spin delocalisation from nitrogen onto an adjacent oxygen. Distortion of the ' planarity ' of the nitrogen by the sulphonyl group should result in consistently higher a_N values for the three sulphonylamino-radicals compared with those for the corresponding carbonylamino-radicals. However, the observed values of the carboxamidyls (RCONR) are *higher* than those of the sulphonamidyls ($RSO_2\dot{N}R$). The reasons for this apparent anomaly should become more obvious when a much wider range of sulphonamidyls and carboxamidyls has been examined.

TABLE 2

E.s.r. parameters of sulphonylamino- and acylamino-radicals

$RSO_2\dot{N}R$	13.0	2.0045	RCONR	15.0	2.0053
$RSO_2\dot{N}(O)R$	10.0	2.0060	$RCO\dot{N}(O)R$	7.0	2.0066
$RSO_2\dot{N}OR$	12.0	2.0049	RCONOR	10.5	2.0058

TABLE 3

E.s.r. spectra of amidyls

Amidyl	g [a]	a_N [b] (G)	a_{Me-H} (G)	$a_{other-H}$	Temperature (°C)	Generation
(7; Ar = *o*-PhC_6H_4)	2.0060	10.7	4.65		70—80 and r.t. [c]	LTA
	2.0058	10.5	4.8		r.t.	t-Bu_2O_2
[7; Ar = *o*-(2-$NO_2C_6H_4$)C_6H_4]	2.0061	10.3	4.8		70—80	LTA
[7; Ar = *o*-(4-$NO_2C_6H_4$)C_6H_4]	2.0060	10.4	4.7		70—80	LTA
(25; R = Ph)	2.0059	10.6	4.7	a_{5-H} 1.3	70—80	LTA
(25; R = H)	2.0058	10.4	4.8	$a_{3,5-H}$ 1.5	r.t.	t-Bu_2O_2
(25; R = Ph)	2.0058	10.4	4.8	$a_{3,5-H}$ 1.5	70—80	LTA
PhCONOMe	2.0059	10.0	5.0		+20 to −20	t-Bu_2O_2
PhCONOEt	2.0058	10.3	4.2 ($a_H^{CH_2}$)		r.t.	t-Bu_2O_2
(18)	2.0049	11.9	4.5		r.t.	t-Bu_2O_2
(18)	2.0049	11.9	4.5		70—80	LTA

[a] *g*-Values accurate to ±0.0001. [b] *a*-Values accurate to 0.1 G. [c] r.t. = room temperature.

EXPERIMENTAL

I.r. spectra were measured as KBr discs and n.m.r. spectra in deuteriochloroform unless stated otherwise. Petrol refers to light petroleum, b.p. 60—80 °C. Merck silica gel GF_{254} or HF_{254} was used for chromatographic separations

Preparation of N-*Alkoxyamides*.—The crude acid chloride (10 mmol) in tetrahydrofuran (14 ml) was added dropwise to a stirred suspension of methoxyamine hydrochloride (11 mmol) in pyridine (7.5 ml) under nitrogen at 0—10 °C. The reaction mixture was allowed to warm to room temperature before 2M sulphuric acid was added. The mixture was then extracted with ether, and the ethereal layer was extracted with saturated sodium bicarbonate solution and 2M sodium hydroxide. Acidification of the sodium hydroxide extracts gave the *N*-methoxyamide which was either collected, or extracted into ether and subsequently recovered by evaporation of the ether *in vacuo*. The following are new. N-*Methoxybiphenyl*-2-*carboxamide* (61%), m.p. 103—105 °C (from chloroform–petrol) (Found: C, 73.9; H, 6.0; N, 6.3%; M^+, 227.094 2. $C_{14}H_{13}NO_2$

* Since this paper was submitted J. B. F. N. Engberts and H. Teeninga, *Rec. Trav. chim.*, 1978, **97**, 59, have published data for other *N*-alkoxysulphonamidyls.

requires C, 74.0; H, 5.8; N, 6.2%; *M*, 227.094 6); $\nu_{max.}$ 3 200 and 1 640 cm^{-1}; δ_H 3.50 (3 H, s, Me), 7.3—7.7 (9 H, m, ArH), and 7.99 (1 H, s, NH); δ_C 63.8 (OMe) and 167.6 (NCO). *N-Methoxy-2′-nitrobiphenyl-2-carboxamide* (75%), needles, m.p. 143—146 °C (from petrol–chloroform) (Found: C, 61.7; H, 4.6; N, 10.1. $C_{14}H_{12}N_2O_4$ requires C, 61.8; H, 4.4; N, 10.3%); $\nu_{max.}$ 3240, 1645, 1530, and 1355 cm^{-1}; δ 3.46 (3 H, s, Me), 7.10—7.22 (1 H, m, Ar-H), 7.30—7.70 (6 H, m, Ar-H), 7.70—7.80 (1 H, m, Ar-H), and 8.69 (1 H, s, NH). *N-Methoxy-4′-nitrobiphenyl-2-carboxamide* (91%), m.p. 149—150 °C (from ethanol) (Found: C, 61.8; H, 4.4; N, 10.2. $C_{14}H_{12}N_2O_4$ requires C, 61.8; H, 4.4; N, 10.3%); $\nu_{max.}$ 3 200, 1 655, 1 520, and 1 355 cm^{-1}; δ(DMSO) 3.53 (3 H, s, OMe), 7.4—7.7 (6 H, m, Ar-H), 8.22—8.32 (2 H, m, Ar-H), and 11.4 (1 H, br s, NH). *N-Methoxy-3-phenylfuran-2-carboxamide* (65%), m.p. 74—75 °C (from chloroform–petrol) (Found: C, 66.3; H, 5.0; N, 6.3. $C_{12}H_{11}NO_3$ requires C, 66.3; H, 5.1; N, 6.5%); $\nu_{max.}$ 3 270 and 1 660 cm^{-1}; δ 3.80 (3 H, s, OMe), 6.60—6.62 (1 H, m, Ar-H), 7.3—7.5 (4 H, m, Ar-H), 7.6—7.75 (2 H, m, Ar-H), and 8.86 (1 H, s, NH). *N-Methoxyfuran-2-carboxamide*, a viscous oil (after short-path distillation) (Found: C, 51.1; H, 5.2; N, 10.0%; *M*$^+$, 141.042 2. $C_6H_7NO_3$ requires C, 51.1; H, 5.0; N, 9.9%; *M*, 141.042 5); $\nu_{max.}$ 3 200 and 1 635 cm^{-1}; δ 3.85 (3 H, s, OMe), 6.50 (1 H, m, 4-H), 7.18 (1 H, m, 3-H), 7.42 (1 H, m, 5-H), and 9.35 (1 H, br s, NH). *N-Methoxybiphenyl-2-sulphonamide* (94%) (from biphenyl-2-sulphonyl chloride),[21] m.p. 63 °C (from methanol–water) (Found: C, 59.3; H, 5.1; N, 5.3; S, 12.3. $C_{13}H_{13}NO_3S$ requires C, 59.3; H, 5.0; N, 5.3; S, 12.2%); $\nu_{max.}$ 3 240, 1 340, and 1 165 cm^{-1}; δ 3.63 (3 H, s, OMe), 6.30 (1 H, s, NH), 7.25—7.70 (8 H, m, Ar-H), and 8.15—8.25 (1 H, m, Ar-H); *m/e* 263 (*M*$^+$) (2%), 217 (100), 168 (4), 154 (7), 153 (71), 152 (45), and 151 (5).

Oxidation of N-*Methoxyamides with Persulphate.—General procedure*. The *N*-methoxyamide (0.002 mol) was dissolved in boiling 0.1M sodium hydroxide (20 ml) and a solution of potassium persulphate (0.002 2 mol) in water (10 ml) was added, dropwise, during 10 min. The reaction mixture was heated under reflux for a further 10 min, cooled, and then extracted with ether. The ethereal layer was extracted successively with saturated sodium bicarbonate solution, 2M sodium hydroxide, and water, and then dried ($MgSO_4$). Evaporation of the solvent gave an oily residue which was chromatographed (p.l.c.) with chloroform–petrol (2 : 1) as eluant.

N-Methoxybiphenyl-2-carboxamide. This (0.475 g) gave (*i*) 5-methoxyphenanthridone (94 mg, 20%); $\nu_{max.}$ 1 660 cm^{-1}; δ 4.13 (3 H, s, OMe), identical (i.r., n.m.r., mass spectrum, and t.l.c.) with synthetic material prepared by reduction of 2′-nitrobiphenyl-2-carboxylic acid with zinc,[11] followed by methylation of the resulting cyclic hydroxamic acid with dimethyl sulphate;[22] (*ii*) *NN′-dimethoxy-NN′-bis(biphenyl-2-ylcarbonyl)hydrazine* (85 mg, 18%), m.p. 133 °C (decomp.) (from chloroform–petrol) (Found: C, 74.4; H, 5.4; N, 6.2. $C_{28}H_{24}N_2O_4$ requires C, 74.3; H, 5.35; N, 6.2%); $\nu_{max.}$ 1 710 cm^{-1}; δ 3.12 (6 H, s, 2Me) and 7.2—7.6 (18 H, m, Ar-H); *m/e* (17 eV) 422 (*M*$^+$ − 30) (0.3%), 388 (0.6), 373 (2), 212 (4.5), 182 (6), 181 (100), 153 (7), and 152 (6); (*iii*) methyl biphenyl-2-carboxylate (89 mg, 20%), b.p. 140—142 °C at 0.5 mmHg; δ 3.60 (3 H, s, Me), identical with synthetic material; and (*iv*) dibenzo[*b,d*]pyran-6-one[6] (8 mg, 2%), $\nu_{max.}$ 1 720 cm^{-1}, identical with an authentic sample.

N-Methoxy-2′-nitrobiphenyl-2-carboxamide. This (500 mg) gave (*i*) *5-methoxy-1-nitrophenanthridone* (41 mg, 8%), pale yellow needles, m.p. 239—240 °C (from ethanol) (Found: C, 62.3; H, 3.8; N, 10.3. $C_{14}H_{10}N_2O_4$ requires C, 62.2; H, 3.7; N, 10.4%); $\nu_{max.}$ 1 670, 1 515, and 1 340 cm^{-1}; δ 4.20 (3 H, s, OMe) and 7.6—8.6 (7 H, m, Ar-H); *m/e* 270 (*M*$^+$) (71%), 240 (100), 194 (40), 182 (20), 166 (25), and 151 (14); (*ii*) methyl 2′-nitrobiphenyl-2-carboxylate, m.p. 58—60 °C (lit.,[23] 54—56 °C) identical with an authentic sample; and (*iii*) starting material (82 mg, 16%). The n.m.r. spectrum of the reaction mixture showed the presence of *NN′*-dimethoxy-*NN′*-bis-(2′-nitrobiphenyl-2-ylcarbonyl)-hydrazine (10%); δ 3.40 and 3.44 (each 3 H, s, 2 OMe) but fragmentation to methyl 2′-nitrobiphenyl-2-carboxylate occurred during chromatography.

N-Methoxy-4′-nitrobiphenyl-2-carboxamide. This (1 g) gave (*i*) *5-methoxy-3-nitrophenanthridone* (417 mg, 42%), pale yellow needles, m.p. 241—242 °C (from ethanol) (Found: C, 62.2; H, 4.0; N, 10.4. $C_{14}H_{10}N_2O_4$ requires C, 62.2; H, 3.7; N, 10.4%); $\nu_{max.}$ 1 670, 1 515, and 1 335 cm^{-1}; δ 4.21 (3 H, s, OMe) and 7.6—7.95 (2 H, m, Ar-H); *m/e* 270 (*M*$^+$) (71%), 241 (18), 240 (100), 226 (40), 194 (45), 182 (32), 166 (25), 151 (32), and 139 (28); (*ii*) methyl 4′-nitrobiphenyl-2-carboxylate[24] (146 mg, 15%); δ 3.67 (OMe), identical with an authentic sample; and (*iii*) 3-nitrodibenzo[*b,d*]pyran-6-one[6] (21 mg, 2%); $\nu_{max.}$ 1 740 cm^{-1}, identical with an authentic sample. *NN′*-Dimethoxy-*NN′*-bis-(4′-nitrobiphenyl-2-ylcarbonyl)hydrazine (16%), δ 3.35 (6 H, s, 2 OMe), was shown by n.m.r. to be present in the reaction mixture but decomposition occurred during the chromatographic work-up.

N-Methoxy-3-phenylfuran-2-carboxamide. This (500 mg) gave (*i*) *N-methoxyfuro*[2,3-c]*quinol-4*(5H)*-one* (38 mg, 8%), m.p. 151—153 °C (from chloroform–petrol) (Found: *M*$^+$, 215.058 1. $C_{12}H_9NO_3$ requires *M*, 215.058 2); $\nu_{max.}$ 1 670 cm^{-1}; δ 4.18 (3 H, s, OMe) and 7.08—7.94 (6 H, m, Ar-H); *m/e* 215 (*M*$^+$) (13%), 186 (40), 171 (100), and 115 (22); (*ii*) methyl 3-phenyl-2-furoate (116 mg, 35%); $\nu_{max.}$ 1 730 cm^{-1}; δ 3.83 (3 H, s, OMe), identical with an authentic sample; and (*iii*) starting material (105 mg, 21%). The n.m.r. spectrum of the reaction mixture showed that *NN′*-dimethoxy-*NN′*-bis-(3-phenyl-2-furoyl)hydrazine was not present.

N-Methoxybiphenyl-2-sulphonamide. This (900 mg) gave (*i*) methyl biphenyl-2-sulphonate (76 mg, 9%), m.p. 81—83 °C (lit.,[25] 83.5—85 °C) (Found: *M*$^+$, 248.050 6. Calc. for $C_{13}H_{12}O_3S$: *M*, 248.050 6); δ 3.54 (OMe); (*ii*) dibenzothiophen 5,5-dioxide[26] (22 mg, 3%) identical with an authentic sample; and (*iii*) *O-methyl-NN-bis(biphenyl-2-sulphonyl)hydroxylamine* (63 mg, 8%), m.p. 173—174 °C (from ether) [Found: C, 62.6; H, 4.4; N, 3.0; S, 13.4%. *M*$^+$, 479.086 2 and (*M*$^+$ − 216), 263.061 5. $C_{25}H_{21}NO_5S_2$ requires C, 62.6; H, 4.4; N, 2.9; S, 13.5%; *M*, 479.086 0 and (*M* − 216), 263.061 5]; $\nu_{max.}$ 1 370 and 1 170 cm^{-1} (SO_2); δ 2.84 (3 H, s, MeO), 7.25—7.75 (16 H, m, Ar-H), and 8.0—8.15 (2 H, m, ArH). This hydroxylamine was identical with the product obtained by reaction of biphenyl-2-sulphonyl chloride (138 mg, 0.548 mmol) in THF with *N*-methoxybiphenyl-2-sulphonamide (131 mg, 0.498 mmol) in pyridine at 70 °C overnight.

Oxidation of N-*Methoxyamides with Lead*(IV) *Acetate at Room Temperature.—General procedure*. Lead(IV) acetate (0.756 mmol) was added to a solution or suspension of the *N*-methoxyamide (1.08 mmol) in benzene (6.5 ml) and the reaction mixture was stirred for 45 min. Ether was then added and the resulting solution extracted with sodium

bicarbonate solution and water, and then dried. Evaporation of solvent *in vacuo* at 0 °C gave the product.

N-*Methoxybiphenyl-2-carboxamide*. This (1.0 g) gave *NN'*-dimethoxy-*NN'*-bis(biphenyl-2-ylcarbonyl)hydrazine (851 mg, 85%), m.p. 133 °C (from chloroform–petrol) identical with the product obtained from the persulphate oxidation. The n.m.r. spectrum of the product before crystallisation showed the presence of 5-methoxyphenanthridone (2%), δ 4.13 (OMe).

N-*Methoxy-2'-nitrobiphenyl-2-carboxamide*. This (1.0 g) gave NN'-*dimethoxy*-NN'-*bis*-(2'-*nitrobiphenyl-2-ylcarbonyl*)-*hydrazine* (quantitatively) as an oil; $\nu_{max.}$ 1 720, 1 525, and 1 350 cm^{-1}; δ [$(CD_3)_2SO$] 3.40 and 3.44 (6 H, br s, 2 Me); *m/e* (17 eV) 272 (M^+ − 270) (0.3%), 257 (4), 226 (5), 212 (5), 211 (100), 196 (9), 180 (9), and 168 (3.5). Attempted crystallisation of this product from chloroform–petrol gave methyl 2'-nitrobiphenyl-2-carboxylate.

N-*Methoxy-4'-nitrobiphenyl-2-carboxamide*. This (140 mg) gave NN'-*dimethoxy*-NN'-*bis*-(4'-*nitrobiphenyl-2-ylcarbonyl*)*hydrazine* (quantitatively), m.p. 77—82 °C (from chloroform–petrol); $\nu_{max.}$ 1 720, 1 515, and 1 345 cm^{-1}; δ 3.35 (6 H, s, 2 MeO), 7.30—7.60 (6 H, m, Ar-H), and 8.10—8.25 (2 H, m, Ar-H); *m/e* (17 eV) 481 (M^+ − 61) (<0.3%), 465 (0.3), 451 (0.3), 257 (63), 226 (100), 180 (63), 152 (22), and 149 (11).

N-*Methoxy-3-phenylfuran-2-carboxamide*. This (235 mg) gave *NN'*-dimethoxy-*NN'*-bis-(3-phenyl-2-furoyl)hydrazine (quantitatively) as an oil; $\nu_{max.}$ (film) 1 720 cm^{-1}; δ 3.87 (6 H, s, 2MeO), 6.60—6.65 (1 H, m, Ar-H), and 7.25—7.60 (6 H, m, Ar-H); *m/e* (17 eV) 217 (M^+ − 215) (0.3%), 202 (89), 171 (100), 115 (35), and 85 (94). Attempted crystallisation of this product gave methyl 3-phenyl-2-furoate.

N-*Methoxybiphenyl-2-sulphonamide*. This (35 mg) gave methyl biphenyl-2-sulphonate (32%) and starting material (68%) estimated by measurement of the relative intensities of their methoxy resonances at δ 3.54 and 3.63, respectively.

Oxidation of N-*Methoxyamides with Lead*(IV) *Acetate at* 80 °C.—*General procedure*. The *N*-methoxyamide (1.10 mmol) dissolved or suspended in benzene (5 ml) was added dropwise during 30 min to a solution of lead(IV) acetate (0.72 mmol) in refluxing benzene (60 ml). The reaction mixture was heated under reflux for a further 30 min before it was concentrated to half-volume and ether added. The ethereal solution was extracted with sodium bicarbonate solution, washed with water, and dried ($MgSO_4$). Evaporation of solvent gave a crude product mixture whose composition was determined by n.m.r. comparison of the relative intensities of the methoxy resonances of the components present.

See Table 1 for oxidations of *N*-methoxybiphenyl-2-carboxamide, *N*-methoxy-4'-nitrobiphenyl-2-carboxamide, and *N*-methoxy-2'-nitrobiphenyl-2-carboxamide.

N-*Methoxybiphenyl-2-sulphonamide*. This (83 mg, 0.32 mmol) gave (*i*) methyl biphenyl-2-sulphonate (δ 3.54) (20%); (*ii*) *N*-methoxy-*N*-methylbiphenyl-2-sulphonamide (δ 3.42) (40%); and (*iii*) starting material (δ 3.63) (5%). The first two of these products could not be separated chromatographically. The presence of *N*-methoxy-*N*-methylsulphonamide was established by comparison of the mass spectrum of the mixture with that of methyl biphenyl-2-sulphonate (Found: M^+, 277.077 2. $C_{14}H_{15}NO_3S$ requires *M*, 277.077 2); δ 2.69 (3 H, s, NMe) and 3.42 (3 H, s, OMe); *m/e* 277 (M^+) (0.7%), 248 (18), 217 (32), and 153 (100).

O-*Methyl*-NN'-*bis*-(p-*tolylsulphonyl*)*hydroxylamine*.— A solution of *NN'*-bis-(*p*-tolylsulphonyl)hydroxylamine[27] (77 mg, 0.235 mmol), methyl iodide (334 mg, 2.35 mmol), and potassium carbonate (36 mg, 0.259 mmol) in acetone (5 ml) was stirred at room temperature for one week. Chromatography (t.l.c.) of the reaction mixture with chloroform–petrol (1 : 1) as eluant gave O-*methyl*-NN-*bis*-(p-*tolylsulphonyl*)*hydroxylamine* (8 mg) as a solid (Found: M^+, 355.054 8. $C_{15}H_{17}NO_5S_2$ requires *M*, 355.054 7); δ 2.45 (6 H, br s, 2 Ar-*Me*), 2.98 (3 H, s, OMe), and 7.24—7.90 (8 H, m, Ar-H); *m/e* 355 (M^+) (0.3%), 310 (0.9), 211 (0.6), 200 (0.9), 185 (0.8), 172 (0.8), 168 (1.5), 157 (0.8), 155 (100), and 139 (13).

Thermolysis of NN'-*Dimethoxy*-NN'-*bis*(*biphenyl-2-ylcarbonyl*)*hydrazine*.—In separate experiments a solution of the hydrazine (100 mg) in (*a*) chloroform (1 ml), (*b*) benzene (1 ml), and (*c*) pyridine (1 ml) was heated under reflux for 1 h. Analyses of the product mixtures by n.m.r. and t.l.c. showed the presence of methylbiphenyl-2-carboxylate and starting material in the ratios (*a*) 80 : 20, (*b*) 33 : 67, and (*c*) 100 : 0.

E.S.R. Measurements.—These were made on a Varian E3 spectrometer; *g*-values were measured by comparison with the ' quartz signal '. The *N*-alkoxyamidyls were generated in the cavity by two different methods,

(*i*) *With lead*(IV) *acetate*. A solution of the *N*-alkoxyamide (10—20 mg) in benzene (0.5 ml) was deoxygenated in a stream of nitrogen and poured into an e.s.r. tube containing 3—5 crystals of lead(IV) acetate (free from acetic acid). The reaction mixture was mixed briefly by passage of a stream of nitrogen and then placed in the cavity which had been previously heated to 70—80 °C. The spectra were recorded immediately.

(*ii*) *By photolysis in di-t-butyl peroxide*. The *N*-alkoxyamide (10—30 mg) was dissolved in di-t-butyl peroxide (0.5 ml) or di-t-butyl peroxide containing sufficient t-butanol and/or benzene to ensure dissolution. The solution was degassed in a silica tube by several freeze-evacuate-thaw cycles and then irradiated in the cavity at room temperature with a 1 kW mercury-vapour lamp.

Smiles Rearrangement of N-*Methoxy*-o-(p-*nitrophenoxy*)-*benzamide*.—A solution of *o*-(*p*-nitrophenoxy)benzoyl chloride [from the corresponding acid (8.0 g, 31 mmol) and thionyl chloride] in THF (50 ml) was added dropwise to a stirred suspension of methoxyamine hydrochloride (34 mmol) in pyridine (25 ml) under nitrogen at 0—10 °C. The reaction mixture was allowed to warm to room temperature during 1 h before 2M sulphuric acid (50 ml) was added, and the resulting mixture was extracted with ether. The ethereal layer was extracted successively with saturated sodium bicarbonate solution and 2M sodium hydroxide. Acidification of the dark red sodium hydroxide extracts gave an oil which was extracted into chloroform. The chloroform extracts were washed with water, dried, and evaporated to give a mixture of two products in the approximate ratio 1 : 10. Fractional crystallisation of the mixture from chloroform–petrol gave 4,4'-dinitroazobenzene, m.p. 228—229 °C (lit.,[28] 221—222 °C) (Found: M^+, 272.054 5. Calc. for $C_{12}H_8N_4O_4$: *M*, 272.054 5) as the minor product, and as the major product N-*methoxy*-N-(p-*nitrophenyl*)*salicylamide*, m.p. 160—162 °C (Found: C, 58.5; H, 4.2; N, 9.9. $C_{14}H_{12}N_2O_5$ requires C, 58.3; H, 4.2; N, 9.7%); $\nu_{max.}$ 3 140 and 1 640 cm^{-1}; δ 3.75 (3 H, s, Me), 6.75—7.1 (2 H, m, Ar-H), 7.3—7.5 (1 H, m, Ar-H), 7.7—7.85 (3 H, m, Ar-H), and 8.2—8.35 (2 H, m, Ar-H).

Benzoylation of this product with benzoyl chloride in acetonitrile gave O-*benzoyl*-N-*methoxy*-N-(p-*nitrophenyl*)-*salicylamide*, m.p. 129—131 °C (from chloroform–petrol) (Found: C, 64.2; H, 4.1; N, 7.2. $C_{21}H_{16}N_2O_6$ requires C, 64.3; H, 4.1; N, 7.1%); $\nu_{max.}$ 1 740 (OCOPh) and 1 675 [CON(OMe)Ar] cm^{-1}; δ 3.52 (3 H, s, Me), 7.3—7.7 (9 H, m, Ar-H), and 8.0—8.2 (4 H, m, Ar-H).

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