Iminyls. Part 8.[1] Intramolecular Addition to Nitrile Groups

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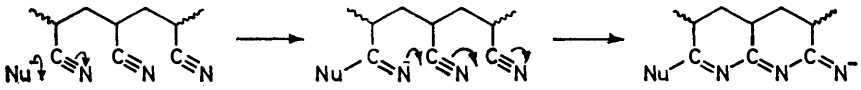
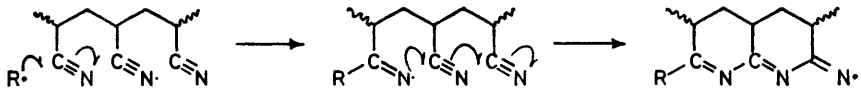
Evidence for the radical polymerisation of nitrile groups in polyacrylonitrile has been sought using model compounds. No evidence for the cycloaddition of iminyls to nitrile groups has been obtained but nucleophilic addition occurred easily. Thus, 1,8-dicyanonaphthalene reacted with hydroxylamine to give naphthalimide dioxime and with butyl-lithium to give azaphenalene derivatives but adamantyl radicals did not attack the nitrile functions.

3-Benzoyl-1,5-dimethylpimelonitrile and hydroxylamine yielded a piperidine and two decahydro-1,8-naphthyridine derivatives instead of the expected oxime. Reaction of the piperidine with bromoacetic acid gave an oxyacetic acid which was converted by persulphate oxidation into a *cis–trans* mixture of azopyridines. The structure of one of the decanaphthyridines has been established by *X*-ray crystallographic analysis.

COLOURATION of polyacrylonitrile on heating is generally attributed to the production of a polyimine by cyclisation of adjacent nitrile groups.[2-4] Both anionic [equation (1)] and radical [equation (2)] mechanisms have been



(1)



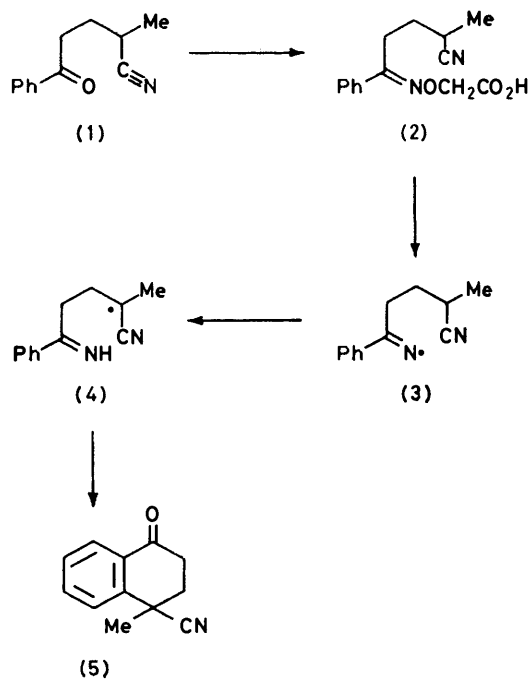
(2)

suggested for this cyclisation. The former is thought to operate at low temperatures and is initiated by structural defects in the polymer and/or by external nucleophiles. The latter proceeds at high temperatures and is considered to involve iminyl radical addition to nitrile. Experimental evidence for the nucleophilic process is convincing but the radical process has not been established although it may occur during thermolytic conversion of polyacrylonitrile into carbon fibre.

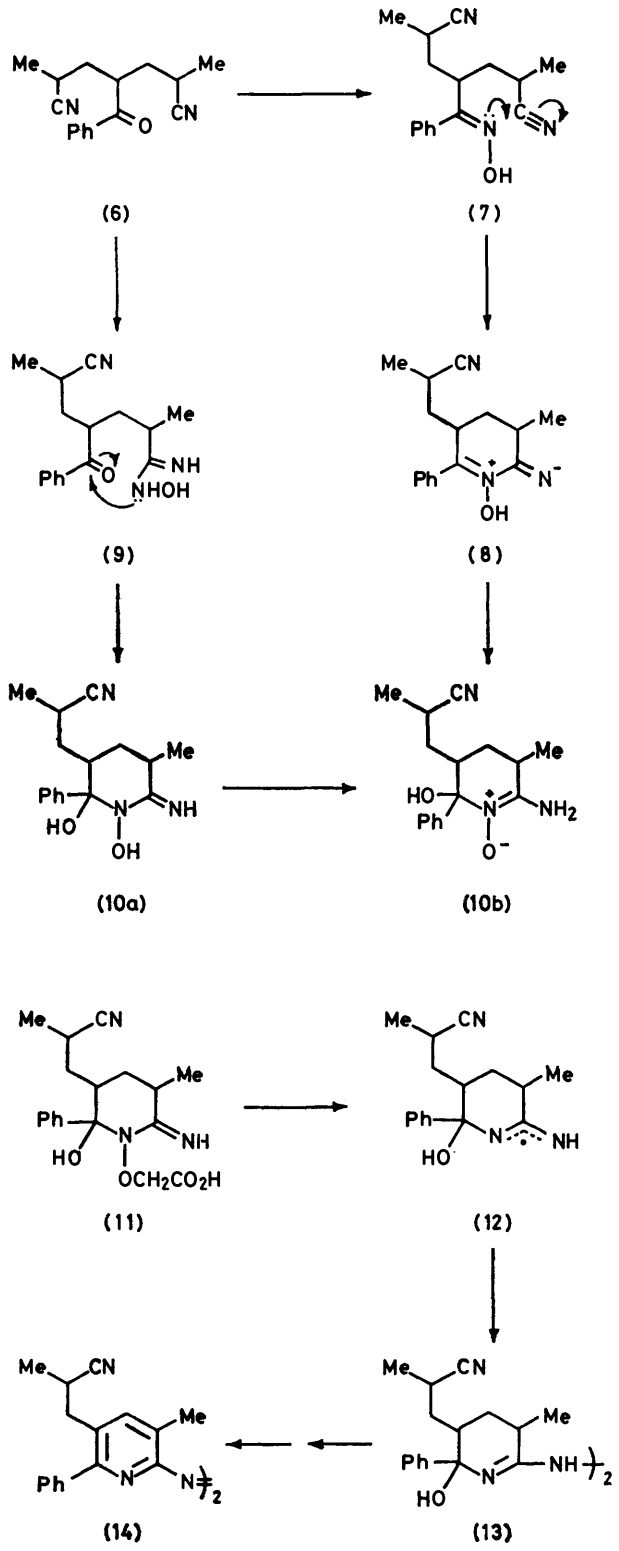
Intramolecular addition of alkyl radicals to aliphatic nitriles,[5] and of iminyl radicals to arenes [6] and alkenes [7] has previously been established. The possible radical addition of iminyls to nitriles has now been investigated by generating iminyls bearing γ-nitrile groups, *e.g.* (3). These models for the proposed sequential cyclisation of nitriles in polyacrylonitrile [equation (2)] were of two types. In one (Type 1) the nitrile group is attached to an alkyl chain and in the other (Type 2) to an aryl ring.

Type 1 *Models.*—The keto-nitrile [8] (1) was easily converted into the iminyl precursor (2) but subsequent persulphate oxidation did not lead to cyclisation of the ensuing iminyl (3) onto the nitrile group. Instead, intramolecular abstraction of the γ-hydrogen occurred to produce (4) and hence (5). We have studied related tetralone syntheses in some detail.[1,9]

During the preparation of the keto-nitrile (1) the keto-dinitrile (6) was also produced and this in some ways was more suitable than (1) for our purposes since it bears two γ-nitrile groups. Successive treatment of (6) with hydroxylamine and chloroacetic acid (without isolation of the intermediate oxime) gave an imino-oxyacetic acid which on oxidation with persulphate gave a mixture of products including benzamide and two stereoisomeric red compounds of molecular formula $C_{32}H_{30}N_6$. These we regard as the *cis*- and *trans*-azopyridines (14), $\lambda_{max.}$ 238,

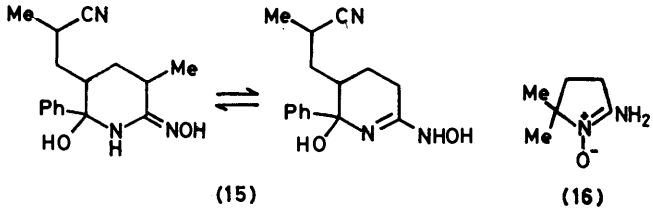


342, and 468 nm (*cf.* 216, 306, and 466 nm for *trans*-2,2-azopyridine and 228, 266, and 448 nm for the *cis*-isomer [10]). In addition to the secondary methyl groups the azo-compounds (14) contain two aromatic methyls (δ 2.64), two aromatic protons (δ 7.67), and the methylene groups are benzylic (δ 3.0). The red compounds were rapidly decolourised by dithionite and reoxidised to starting material by air. This *cis*, *trans*-mixture of isomers could be separated by p.l.c. but during removal from the plate and rechromatography equilibration occurred and two red compounds were present in each fraction. Two-dimensional chromatography gave a similar result. In all cases one isomer (presumably the *trans*) predominated.



Since the azopyridines (14) could arise by cyclisation of the iminyl derived from (6) onto the adjacent nitrile function we re-examined the initial product of reaction of the ketone (6) with hydroxylamine. The reaction was indeed more complex than initially envisaged and three compounds (A, B, and C) were isolated, none of which was a simple oxime.

Compound A, $C_{16}H_{21}N_3O_2$. This contained a nitrile function ($\nu_{max.}$ 2 240 cm^{-1}), an OH/NH group (3 620, 3 430, and 3 250br cm^{-1}), and one double-bond equivalent less than the starting ketone ($C_{16}H_{18}N_2O$). The n.m.r. and mass spectra provided evidence for Ph, tertiary OH, MeCH, and Me(CN)$CHCH_2$ groups and the combined data were consistent with structures (10) and (15) both of



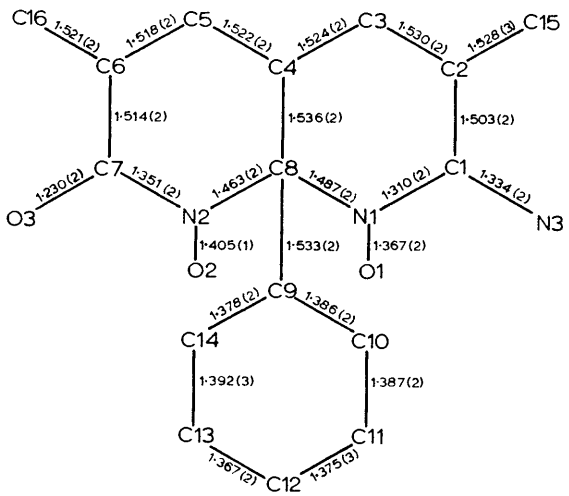
which have several tautomeric and stereochemical forms. The ^{15}N n.m.r. spectrum was not helpful since only two nitrogen signals were detected which we attributed [11] to C≡N (δ 236 relative to ammonia) and C=N (δ 264). No signal attributable to an sp^3 nitrogen (δ 50—100) was detected although the related amino-pyrroline 1-oxide [12] (16) showed NH_2 and $C=\overset{+}{N}(\bar{O})$ resonances at δ 60 and 210, respectively. It is possible that the =NH signal had failed to appear because the gated decoupling had removed the nuclear Overhauser effect.*

Analogy with compound B (*vide infra*), which can also be obtained by further reaction of compound A with hydroxylamine, leads us to favour the tautomeric structure (10a) ⇌ (10b) for compound A. Mechanistically formation of A (10) can be interpreted, as shown, either as initial attack by hydroxylamine on the nitrile group followed by cyclisation [(6) → (9) → (10)] or initial oxime formation followed by cyclisation and reaction with water [(6) → (7) → (8) → (10)]. Reaction of compound A with chloroacetic acid in alkaline solution yields the oxyacetic acid (11). The close agreement between the ^{13}C n.m.r. spectra of (10) and (11) shows that no rearrangement occurs during formation of the acid (11). Oxidative decarboxylation of the acid

* Personal communication from M. Cooper, P.C.M.U. Harwell.

(11) followed by fragmentation of the ensuing oxyalkyl radical with loss of formaldehyde leads to an amidinyl (12) which dimerises to the azine (13). Dehydration (the persulphate solution becomes acidic) and oxidation of the dihydropyridine rings by air or persulphate completes the conversion into the azopyridines (14). The low yield is not surprising since several other reactions are possible, in particular the amidinyl (12) could readily fragment (benzamide formation?). This reaction sequence provides a further example of the dehydroxylation process N–OH ⟶ N· which is a general route [13] to nitrogen-centred radicals.

Compound B. This was the major product of the reaction of the keto-dinitrile (6) with hydroxylamine, and was subsequently obtained by treatment of compound A in the same way. Compound B, $C_{16}H_{21}N_3O_3$, contains two secondary methyl groups and one obviously exchangeable hydrogen. It does not possess a nitrile function but has the same number of double-bond equivalents as A. Therefore it contains a third ring which is derived from the second nitrile group by reaction with hydroxylamine. There are several possible ways in which this third ring could arise and it was not possible to distinguish between these on the spectroscopic evidence. The problem was solved by *X*-ray crystallographic analysis. Compound B was shown to have structure (20) (see Figure) in which the two heterocyclic rings are *cis*-fused and the methyl substituents are equatorial. Its formation from (6) is rationalised by the

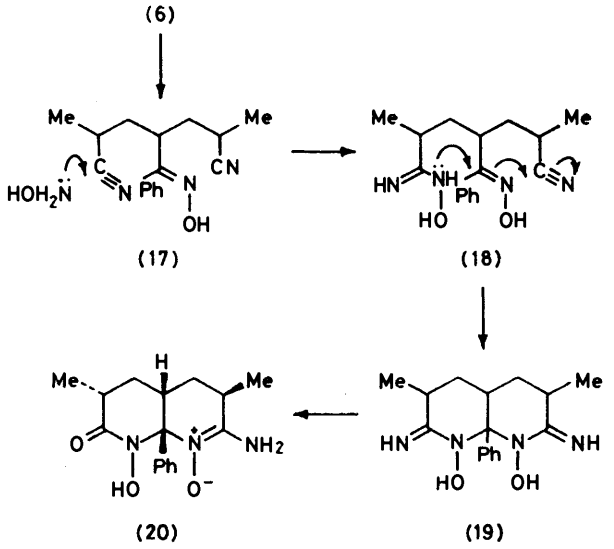


Crystallographic numbering and bond lengths for compound B (20)

sequence (6) ⟶ (17) ⟶ (18) ⟶ (19) ⟶ (20). The route from compound A presumably must involve ring-chain tautomerism (10a) ⟶ (9) and subsequent reaction of (9) with hydroxylamine.

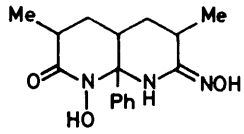
Compound C. This compound, isomeric with B, was isolated in trace amounts along with A and B. Its spectra were consistent with structure (21) or a tautomer.

As we were unable to convert the keto-dinitrile (6) into its oxime we overcame this problem by condensation with amino-oxyacetic acid in a sealed tube which gave the *O*-carboxymethyloxime (oximinoacetic acid) (22). However, on oxidation with persulphate it behaved like



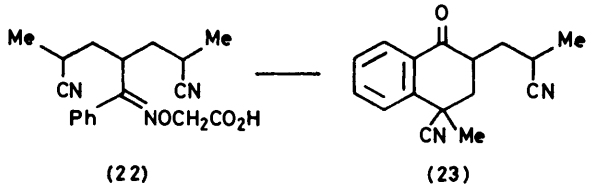
the acid (2), the iminyl so-formed effecting abstraction of a γ-hydrogen (there are two available) followed by cyclisation and hydrolysis to give the tetralone (23).

From the foregoing results it is clear that the absence



of a γ-hydrogen atom is essential if addition of iminyl to nitrile is to proceed. Hence the keto-nitrile (24) was prepared and transformed into the *O*-carboxymethyloxime (25) in the usual way. Oxidation of this acid with persulphate gave no cyclised products. Instead the iminyl (26) dimerised and abstracted hydrogen giving the azine (27) and the starting ketone (24) (after hydrolysis), respectively. Failure to observe cyclisation of iminyl onto nitrile with Type 1 models could be due to the flexibility of the alkyl chain, the radical centre reacting in other ways before it can adopt the geometrical and conformational arrangement necessary for intramolecular addition to occur. Thus, some degree of molecular rigidity (almost certainly a feature of polyacrylonitrile) may be necessary for the desired reaction to occur. Accordingly we turned our attention to a different model (Type 2) in which the iminyl and nitrile were in the *peri*-positions of the naphthalene nucleus.

Type 2 Models.—Synthesis of the naphthalene keto-nitrile (31) was achieved by adapting a preparation of aliphatic keto-nitriles [14] and is shown below (28) ⟶ (29) ⟶ (30). However, treatment of the keto-nitrile (31) with hydroxylamine–sodium acetate did not give the corresponding oxime. Instead, the cyclic imino-



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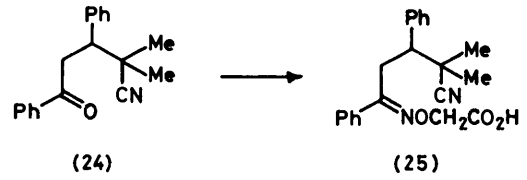
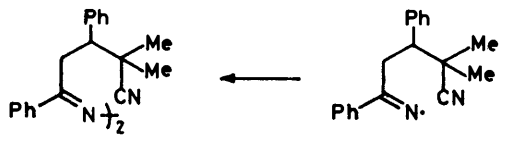


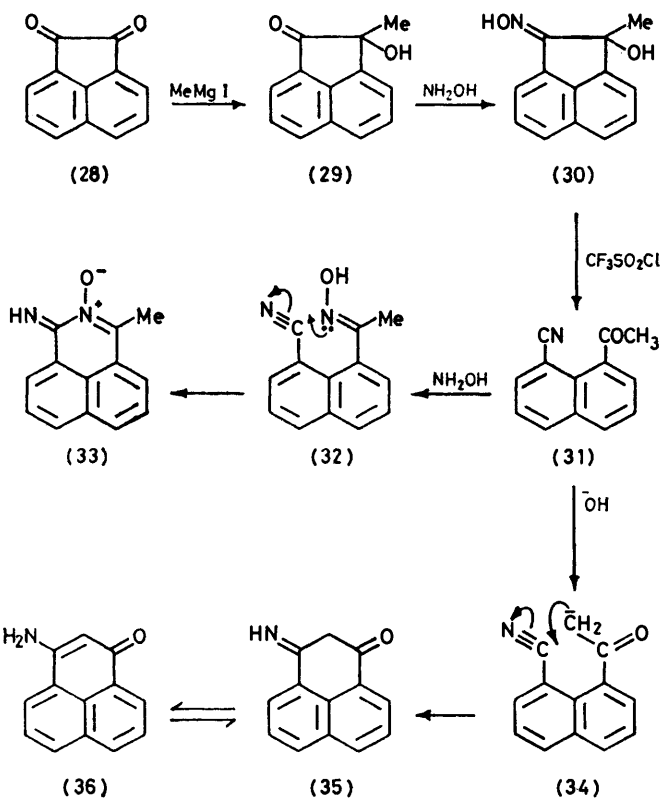
(24) (25)



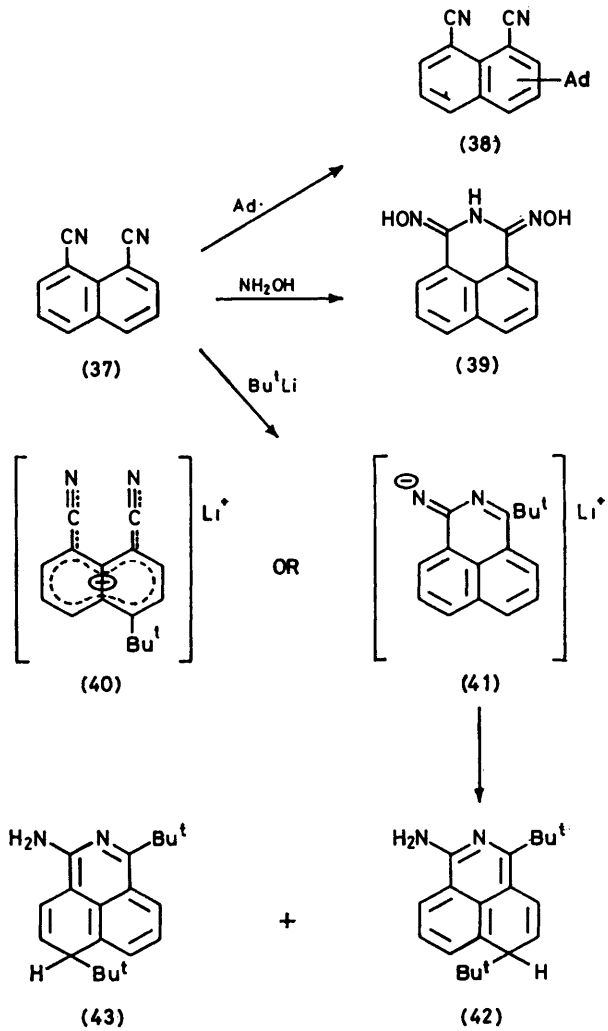
(27) (26)

nitrone (33) ($\nu_{max.}$ 3 170 cm^{-1}; no $\nu_{C\equiv N}$) was formed, a product easily derived from the intermediate oxime (32) by intramolecular nucleophilic addition to nitrile. Further attempts to produce the oxime (32) in alkaline solution yielded the amino-ketone (36) [$\nu_{max.}$ 3 350, 3 250, 1 635, and 1 510 cm^{-1} no $\nu_{C\equiv N}$; δ 5.95 (CH=)]. In this case intramolecular nucleophilic addition of the enolate anion to nitrile [(34) ⟶ (35)] again seems the likely course. In acid solution no reaction occurred. Formation of the *O*-carboxymethyloxime directly from the keto-nitrile (31) by reaction with amino-oxyacetic acid was also unsuccessful.

To overcome these difficulties we attempted to generate an iminyl *in situ* from the dinitrile (37) by intermolecular reaction with alkyl and aryl radicals but little reaction occurred. Decomposition of (a) acetyl peroxide, (b) t-butyl adamantanepercarboxylate, and (c) benzoyl peroxide in solutions of the dinitrile (37) in benzene all failed to give iminyl-derived products. In only one case (b) were easily separated products formed and these were partially identified as adamantyldicyanonaphthalenes (38). 2-Cyanonaphthalene behaved similarly. It appears that the naphthalene nucleus is more reactive towards alkyl and aryl radicals than is the nitrile group. This conclusion is supported by the ' methyl affinities ' [15] of benzonitrile and naphthalene which are 12.2 and 2.2, respectively (relative to benzene = 1). The relatively large ' methyl affinity ' of benzonitrile suggests that



(28) (29) (30) (33) (32) (31) (36) (35) (34)



(38) (37) (39) (40) (41) (43) (42)

radicals react at the nitrile group but there is little evidence of this from product studies.[16,17] Aliphatic nitriles (and cyanogen [18]) appear to be more reactive than arenonitriles in this respect and there are reports that adamantyl [19] and phenyl [20] radicals will add to acetonitrile. Nevertheless the reverse process, fragmentation [21] of iminyls, is by far the more common.

By comparison, nucleophilic addition to nitrile occurred with ease. Thus hydroxylamine gave the cyclic amidoxime (39) in good yield. With t-butyl-lithium a yellow oil ($C_{20}H_{26}N_2$) was obtained showing i.r. absorption due to NH_2 and C=N but not C≡N. The ^1H n.m.r. spectrum shows an ABX pattern arising from allylic and vinylic protons (CH–CH=CH), signals from three aromatic protons, one of which is a low-field multiplet (ArH *peri* to NH_2), and signals from two t-butyl groups one of which is a doublet (δ 0.80 and 0.87) indicating the presence of two closely related isomers (ratio 2 : 1). The oil readily formed an acetyl derivative which was also a 2 : 1 mixture of isomers (two Me, Bu^t, C*H*–CH=CH signals). On this evidence a mixture of stereoisomers or tautomers is discounted in favour of structural isomers (42) and (43). We detected a precursor of the cyclic amidines (42) and (43) when lower ratios of t-butyl-lithium to dicyanonaphthalene were used. This could not be completely separated from the amidines (42) and (43) and so was not fully identified. However, it did show nitrile absorption in the i.r. region and hence cannot be the hydrolysis product of the anion (41). Accordingly we prefer the reaction sequence (37) ⟶ (40) ⟶ (42) and likewise for (43).

In view of our failure to effect intramolecularly addition of iminyl radicals to nitriles with the two model systems we turned our attention to reactions of polyacrylonitrile and polymethacrylonitrile. Copolymers of acrylonitrile (AN) and methacrylontrile (MAN) with methyl vinyl ketone (MVK) were prepared and iminyl precursor groups introduced by reaction with aminooxyacetic acid. Oxidation of these modified polymers with persulphate gave yellow–brown products whose i.r. spectra were examined for evidence of nitrile group polymerisation. If oxidation of the copolymers leads to polymerisation of the nitrile group then the relative intensities of the i.r. bands due to carbonyl and nitrile should both decrease, the latter to a much greater extent than the former if oxidation is incomplete. Comparison of the intensities of the bands at 2 240 (C≡N), 1 740 (C=O), and 1 460 (CH_2) showed little differences in the ratio ν(CH_2)/ν(C≡N) before and after oxidation although ν(C=O) did decrease. Hence if any of the iminyl radicals in the copolymer added to the nitrile groups then the reaction only occurred at isolated parts of the polymer chain without major consumption of nitrile groups.

We conclude that under our conditions iminyls do not cyclise onto γ-nitrile groups. Although our evidence does not exclude such a reaction occurring at high temperature (*ca.* 1 000 °C) in the solid state such a route would not be followed in less energetic circumstances. Significantly intramolecular nucleophilic addition to nitrile occurred with several of our models and seems a more likely process for ring formation in polyacrylonitrile under mild conditions.

EXPERIMENTAL

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

4-Benzoyl-2-methylbutyronitrile (1).—To a stirred mixture of acetophenone (120 g, 1 mol) and potassium methoxide [from potassium (1.17 g) and methanol (25 ml)] methacrylonitrile (67.0 g, 1 mol) in dry benzene (100 ml) containing quinol (100 mg) was added dropwise with stirring. The reaction mixture was heated for 30 min and then left at room temperature overnight. Hydrochloric acid was added and the neutralised solution was extracted with ether. The ethereal extracts were evaporated and the residual oil distilled to give acetophenone (44 g, 33%), b.p. 40—48 °C/0.35 mmHg, and a yellow oil (85 g), b.p. 176—184 °C/0.35 mmHg. The latter was redistilled to give two fractions 160—167 °C/0.25 mmHg (8.5 g) and 167—180 °C/0.25 mmHg (72 g). The lower-boiling fraction was chromatographed (column) on silica using petroleum–chloroform as irrigant to give (a) *4-benzoyl-2-methylbutyronitrile* (2.5 g, 1.3%), m.p. 48 °C (from chloroform–benzene) (Found: C, 77.3; H, 7.2; N, 7.7. $C_{12}H_{13}NO$ requires C, 77.0; H, 7.0; N, 7.5%), $\nu_{max.}$ 2 240 and 1 685 cm^{-1}; δ ($CDCl_3$) 1.39 (3 H, d, *J* 7.0 Hz, CH_2CH_3), 1.89—2.21 (2 H, m, CH_2), 2.56—3.02 (1 H, m, CH), 3.22 (2 H, t, *J* 8.0 Hz, $CHCH_3$), 7.48—7.59 (3 H, m, ArH), and 7.92—8.10 (2 H, m, ArH), and (b) an oil from which *4-benzoyl-2,6-dimethylpimelonitrile* (6) crystallised, m.p. 69—70 °C (from ether) (Found: C, 75.4; H, 7.0; N, 11.1%; M^+, 254.1420. $C_{16}H_{18}N_2O$ requires C, 75.6; H, 7.1; N, 11.0%; *M*, 254.1419), $\nu_{max.}$ 2 230 (C≡N) and 1 677 cm^{-1}; δ ($CDCl_3$) 1.32 (3 H, d, *J* 7.0 Hz, Me), 1.35 (3 H, d, *J* 7.0 Hz, Me), 1.20—2.50 (6 H, m, $2CH_2CH$), 3.8—4.18 (1 H, m, CH), 7.40—7.70 (3 H, m, ArH), 7.9—8.1 (2 H, m, ArH); δ_{13C} 17.73(Me), 17.93(Me), 23.02[CH(Me)CN], 34.35(CH_2), 35.56(CH_2), 41.74(CHCO), 122.65(CN), 128.11(Ar), 128.98(Ar), 133.71(Ar), 135.77(Ar), and 200.84(CO).

4-Benzoyl-2,2-dimethyl-3-phenylbutyronitrile (24).—n-Butyl-lithium (0.032 mol, 35.34 ml) in hexane was added to a stirred solution of isobutyronitrile (2.42 g, 0.035 mol) in tetrahydrofuran (12 ml) at −74 °C under nitrogen. The temperature was allowed to rise to 0 °C and then recooled to −74 °C before 2-benzoylstyrene (6.24 g, 0.03 mol) in THF (12 ml) was added and the temperature allowed to rise to room temperature. The reaction mixture was poured into water and the oil which separated was chromatographed on silica (column) using petroleum–chloroform (1 : 1) as irrigant to give the starting ketone (1.8 g, 29%) and *4-benzoyl-2,2-dimethyl-3-phenylbutyronitrile* (950 mg, 17%), m.p. 109—110 °C (from petroleum–chloroform) (Found: C, 82.5; H, 6.9; N, 5.0. $C_{19}H_{19}NO$ requires C, 82.3; H, 6.9; N, 5.1%), $\nu_{max.}$ 2 251 and 1 688 cm^{-1}; δ 1.19 (3 H, s, Me), 1.46 (3 H, s, Me), 3.4—3.7 (3 H, m, $CHCH_2$), 7.31—7.50 (8 H, m, ArH), and 7.83—8.00 (2 H, m, ArH).

Reaction of 4-Benzoyl-2,6-dimethylpimelonitrile with Hydroxylamine.—A solution of the keto-dinitrile (5.08 g, 0.02 mol), hydroxylamine hydrochloride (1.74 g, 0.025 mol), and sodium acetate (2.14 g, 0.026 mol) in ethanol–water (1 : 1) (60 ml) was refluxed for 2 h. The ethanol was

removed under reduced pressure and the aqueous residue was extracted with ether. The ethereal extracts were washed with aqueous sodium hydrogen carbonate and brine and then dried ($MgSO_4$). The residue obtained on removal of solvent was chromatographed (column) on silica with chloroform–methanol to give *5-(2-cyanopropyl)-1,6-dihydroxy-2-imino-3-methyl-6-phenylpiperidine* (10) (compound A) (247 mg, 4.3%), m.p. 124—125 °C (from benzene–petroleum) (Found: C, 67.0; H, 7.7; N, 14.9. $C_{16}H_{21}N_3O_2$ requires C, 66.9; H, 7.4; N, 14.6%); $\nu_{max.}$ (KBr) 3 440, 3 240, 3 160, 2 240, and 1 668 cm^{-1}; (CCl_4) 3 620, 3 420, 3 250br, 2 240, and 1 660 cm^{-1}; δ 1.18 (3 H, d, *J* 7 Hz, Me), 1.25 (3 H, d, *J* 7 Hz, Me), 2.0—2.9 (7 H, m, CH_2CH), 6.73 (1 H, bs, NH or OH), and *ca.* 7.37 (5 H, m, ArH); δ(^{13}C) 17.01(Me), 17.78(Me), 24.62(CH), 29.73(CH), 32.77(CH_2), 36.50(CH_2), 105.03(6-C), 122.74(C≡N), 128.75(Ar), 129.14(Ar), 134.16(Ar), 135.75(Ar), and 151.49(C=N).

The above aqueous residue after extraction with ether was evaporated to dryness and the residue was extracted with hot chloroform. The chloroform extracts were dried and evaporated. Fractional crystallisation of the residue from methanol–ether gave (a) *7-amino-1-hydroxy-3,6-dimethyl-2-oxo-8a-phenyldecahydronaphthyridine 8-oxide* (20) (787 mg, 13%), as crystals, (compound B), m.p. 218—219 °C (Found: C, 63.6; H, 7.0; N, 13.6. $C_{16}H_{21}N_3O_3$ requires C, 63.4; H, 7.0; N, 13.9%), $\nu_{max.}$ (KBr) 3 400, 3 220, 3 130, and 1 630 cm^{-1}; δ [$(CD_3)_2SO$] 1.14 (3 H, d, *J* 7 Hz, Me), 1.18 (3 H, d, *J* 7 Hz, Me), 1.4—2.8 (7 H, m, CH_2, CH), and 7.3 (6 H, m, ArH and NH or OH); $\delta_{^{13}C}$ 16.32(Me), 18.48(Me), 25.87, 28.64, 30.51, 35.81, 85.55(C), 126.51(Ar), 127.98(Ar), 140.37(ArC), 151.69(C=O), and 168.45(CO).

(b) A second tautomer (21?) (compound C), m.p. 228—229 °C (from methanol) (Found: C, 63.5; H, 7.0; N, 13.8%; M^+, 303.1583. $C_{16}H_{21}N_3O_3$ requires C, 63.4, H, 7.0; N, 13.9%; *M*, 303.1582); $\nu_{max.}$ (KBr) 3 380, 3 200, and 1 630 cm^{-1}; δ 1.02 (3 H, d, *J* 7 Hz, Me), 1.17 (3 H, d, *J* 7 Hz, Me), 1.4—3.0 and 3.1—3.2 (7 H, m, CH_2, CH), 6.43 (1 H, bs, exchangeable, NH or OH), 7.34 (5 H, m, ArH), 9.27 (1 H, bs, exchangeable, NH or OH), and 9.72 (1 H, bs, exchangeable, NH or OH).

Preparation of O-*Carboxymethyloximes.*—*4-Benzoyl-2-methylbutyronitrile* O-*carboxymethyloxime* (2). A solution of 4-benzoyl-2-methylbutyronitrile (374 mg, 0.002 mol), hydroxylamine hydrochloride (160 mg, 0.0024 mol), and sodium acetate (200 mg) in aqueous alcohol was heated under reflux for 30 min. The product mixture was separated by chromatography to give the *oxime* (240 mg, 59%) as a viscous oil (Found: C, 71.6; H, 7.1; N, 13.7%; M^+, 202.1102. $C_{12}H_{14}N_2O$ requires C, 71.3; H, 6.9; N, 13.9%; *M*, 202.1106), $\nu_{max.}$ 3 370 and 2 220 cm^{-1}.

The oxime (404 mg), bromoacetic acid (556 mg), and sodium hydroxide (300 mg) in aqueous ethanol was heated, under reflux for 1 h. Work-up gave *4-benzoyl-2-methylbutyronitrile* O-*carboxymethyloxime* (400 mg, 77%) as an oil (Found: C, 64.4; H, 6.2; N, 10.7. $C_{14}H_{16}N_2O_3$ requires C, 64.6; H, 6.2; N, 10.8%), $\nu_{max.}$ 3 450—3 150, 2 220, and 1 760—1 720 cm^{-1}; δ ($CDCl_3$) 1.33 (3 H, d, *J* 7.0 Hz, Me), 1.72—2.08 (2 H, m, CH_2CH), 2.56—3.16 (3 H, m, CH and CH_2), 4.78 (2 H, s, OCH_2), 7.28—7.76 (5 H, m, ArH), and 9.18 (1 H, s, OH).

4-Benzoyl-2,2-dimethyl-3-phenylbutyronitrile O-*Carboxymethyloxime* was similarly prepared as a viscous oil (Found: M^+, 350.1628. $C_{21}H_{22}N_2O_3$ requires *M*, 350.1630), $\nu_{max.}$ 3 200, 2 237, and 1 730 cm^{-1}; δ ($CDCl_3$) 1.16 (3 H, s, Me), 1.50 (3 H, s, Me), 2.98—3.00 (3 H, m, CH_2CH), 4.70 (2 H, s, OCH_2), 7.16—7.38 (10 H, m, ArH), and 8.26 (1 H, s, OH).

5-(2-Cyanopropyl)-6-hydroxy-2-imino-3-methyl-6-phenylpiperidin-1-yloxyacetic acid (11). A solution of the piperidine (475 mg, 1.66 mmol), bromoacetic acid (339 mg, 2.44 mmol), and sodium hydroxide (195 mg, 4.88 mmol) in ethanol–water (10 ml) was left at room temperature overnight and then heated under reflux for 10 min. Work-up of the acidic product gave the *oxyacetic acid* (500 mg, 88%), as a viscous oil (Found: M^+, 327.1580. $C_{18}H_{23}N_3O_4$ requires *M*, 327.1592); $\nu_{max.}$ (film) 1 640, 1 740, 2 240, and 3 430 cm^{-1}; δ 1.19 (3 H, d, *J* 7 Hz, Me), 1.28 (3 H, d, *J* 7 Hz, Me), 2.0—2.9 (7 H, m, CH_2, CH), 4.49 (2 H, s, OCH_2), 6.72 (1 H, bs, exchangeable, NH or OH), 7.37 (5 H, s, ArH), and 8.96 (1 H, bs, exchangeable, NH or OH); $\delta_{^{13}C}$ 17.23(Me), 17.81(Me), 24.61(CH), 29.54(CH), 32.29(CH_2), 36.42(CH_2), 69.72(OCH_2), 106.13(6-C), 122.57(CN), 128.88(ArH), 129.14(ArH), 133.69(ArH), 135.36(ArH), 153.36(C=N), and 173.88(C=O).

4-Cyano-2-(2-cyanopropyl)valerophenone O-*Carboxymethyloxime* (22). A solution of the ketone (1.02 g, 4 mmol), amino-oxyacetic acid hemihydrochloride (1.09 g, 10 mmol), and sodium acetate (1.64 g, 20 mmol) in ethanol–water (2 : 1) (12 ml) was heated in a sealed tube at 127—130 °C for 19 h. Work-up gave the starting ketone (31%) and the O-*carboxymethyloxime* (426 mg, 32%). After crystallisation from isopropyl ether or benzene it gave needles, m.p. 121—122 °C (Found: C, 66.1; H, 6.5; N, 12.8%. $C_{18}H_{21}N_3O_3$ requires C, 66.0; H, 6.5; N, 12.8%); $\nu_{max.}$ (KBr) 2 240 and 1 725 cm^{-1}; δ 1.27 (3 H, d, *J* 7 Hz, Me), 1.30 (3 H, d, *J* 7 Hz, Me), 1.6—2.9 (6 H, m, $2CH_2CH$), 3.4—3.8 (1 H, m, 2-H), 4.79 (2 H, s, OCH_2), 7.3—7.7 (5 H, m, ArH), and 9.14 (1 H, m, CO_2H); $\delta_{^{13}C}$ (two isomers) 17.72(Me), 18.08(Me), 18.60(Me), 22.33(CH), 23.61(CH), 23.78(CH), 24.40(CH), 36.22(CH_2), 36.69(CH_2), 37.50(CH_2), 41.52(CH), 70.17(OCH_2), 70.66(OCH_2), 122.46(CN), 122.74(CN), 127.27, 127.86, 128.66, 128.94, 129.64, 130.04, 132.39, and 134.85 (all Ar), 158.48(C=N), 159.17(C=N), 175.32(CO), and 175.61(CO).

Oxidations with Persulphate.—*4-Cyano-2-(2-cyanopropyl)valerophenone* O-*carboxymethyloxime*. To a solution of the acid (336 mg, 1.03 mmol) in 0.1M-sodium hydroxide solution (10.3 ml) under reflux a solution of potassium persulphate (500 mg, 1.85 mmol) in water (25 ml) was added dropwise during 5 min. Heating was continued for 5 min before the mixture was cooled and extracted with ether. The ethereal extracts were shaken successively with dilute hydrochloric acid, aqueous sodium hydroxide and brine, and then dried ($MgSO_4$). The residue, when chromatographed on silica (t.l.c.) with methanol–benzene (1 : 9), gave two products of very similar R_F value. After successive crystallisations from ether and benzene–petroleum that with the lower R_F value gave *4-cyano-2-(2-cyanopropyl)-4-methyltetralone* (23) (40 mg, 15%) as needles, m.p. 138—140 °C (Found: C, 76.5; H, 6.6; N, 11.2%; M^+, 252. $C_{16}H_{16}N_2O$ requires C, 76.2; H, 6.4; N, 11.1%; *M*, 252); $\nu_{max.}$ 2 230 and 1 699 cm^{-1}; δ 1.41 (3 H, d, *J* 7 Hz, 2′-Me), 1.89 (3 H, s, 4-Me), *ca.* 1.2—3.3 (6 H, m, $2CH_2$, 2CH), 7.3—7.8 (3 H, m, ArH), and 8.05 (1 H, d, *J* 7 Hz, 8-ArH).

The second product was an oil whose i.r. and mass spectra were very similar to that of the first (M^+, 252.1262. $C_{16}H_{16}N_2O$ requires *M*, 252.1262).

5-(2-Cyanopropyl)-6-hydroxy-2-imino-3-methyl-6-phenylpiperidin-1-yloxyacetic acid. To a solution of the oxyacetic acid (500 mg, 1.45 mmol) in 0.2M-sodium hydroxide (7.2 ml) under reflux a solution of potassium persulphate (430 mg,

1.6 mmol) in water (5 ml) was added in one portion. The reaction mixture was heated under reflux for 5 min, cooled, and then extracted with ether. The ethereal extracts were shaken successively with dilute hydrochloric acid, aqueous sodium hydroxide, and water, and then dried ($MgSO_4$). The residue obtained after removal of solvent was crystallised from benzene–petroleum to give *5,5′-bis-(2-cyanopropyl)-3,3′-dimethyl-6,6′-diphenyl-2,2′-azopyridine* (14) (43 mg, 12%), m.p. 185—187 °C (Found: C, 76.9; H, 6.1; N, 17.2. $C_{32}H_{30}N_6$ requires C, 77.1; H, 6.1; N, 16.9%); $\nu_{max.}$ ($CHCl_3$) 2 240 cm^{-1}; $\lambda_{max.}$ (EtOH) 238, 342, and 468 nm (log ε 4.4, 4.1, and 3.1); δ 1.15 (3 H, d, *J* 7 Hz, Me), 2.64 (3 H, s, Me), *ca.* 2.6 (1 H, m, 2′-H), 3.0 (2 H, d, *J* 8 Hz, 1″-CH_2), 7.40 (5 H, m, ArH), and 7.67 (1 H, s, PyH); $\delta_{^{13}C}$ 17.10(Me), 17.80(Me), 26.37(CH), 36.51(CH_2), 122.04(CN), 128.54, 129.04, 129.64, 132.10, 139.28, 142.14, 156.50 (2- or 6-C), and 159.94 (2- or 6-C).

4-Benzoyl-2-methylbutyronitrile O-carboxymethyloxime. On similar oxidation with persulphate this compound gave *4-cyano-4-methyltetralone* (5) (145 mg, 66%), m.p. 63 °C (Found: C, 77.5; H, 5.9; N, 7.4. $C_{12}H_4NO$ requires C, 77.8; H, 5.9; N, 7.6%); $\nu_{max.}$ 2 219 and 1 690 cm^{-1}; δ ($CDCl_3$) 1.85 (3 H, s, Me), 2.28—2.60 (2 H, m, CH_2), 2.78—2.99 (2 H, m, CH_2CO), 7.38—7.68 (3 H, m, ArH), and 8.02—8.13 (1 H, d, *J* 7 Hz, ArH); *m/e* 185(32) (*M*), 157(100), and 129(10).

4-Benzoyl-2,2-dimethyl-3-phenylbutyronitrile O-carboxymethyloxime. This compound gave the keto-nitrile (31%) and *4-cyano-4-methyl-3-phenylvalerophenone azine* (27) (7%) as yellow needles, m.p. 185—188 °C (from petroleum–chloroform) (Found: *M* + 2, 496.3129. $C_{38}H_{40}N_4$ requires *M* + 2, 496.3129), $\nu_{max.}$ 2 240 cm^{-1}; δ ($CDCl_3$) 1.08 (6 H, s, 2Me), 1.36 (6 H, bs, 2Me), 2.97—3.44 (6 H, m, $2CH_2CH$), and 7.08—7.51 (20 H, m, ArH).

2-Hydroxy-2-methylacenaphthylen-1(2H)-one (29). A solution of methylmagnesium iodide [prepared from methyl iodide (10.4 g) and magnesium (1.5 g) in ether (100 ml)] was added dropwise to a stirred solution of acenaphthylene-1,2-dione (7.28 g, 0.04 mol) in THF (600 ml) at 4 °C. The reaction mixture was heated under reflux for 30 min and then allowed to cool to room temperature during 3 h before it was hydrolysed with aqueous ammonium chloride. After removal of THF the solution was extracted with ether and the ethereal extracts were concentrated. The starting material (1.2 g) which precipitated was collected and the filtrate gave *2-hydroxy-2-methylacenaphthylen-1(2H)-one* (2.45 g, 31%), m.p. 120—125 °C (from petroleum–ethyl acetate) (Found: C, 78.6; H, 5.4%; *M*+, 198.0680. $C_{13}H_{10}O_2$ requires C, 78.8; H, 5.1%; *M*, 198.0680), δ ($CDCl_3$), 1.67 (3 H, s, Me), 3.11 (1 H, s, OH), and 7.6—8.11 (6 H, m, ArH); $\nu_{max.}$ 3 420 and 1 700 cm^{-1}.

1-Acetyl-8-cyanonaphthalene (31) (cf. *ref.* 14). A solution of the oxime of 2-hydroxy-2-methylacenaphthylen-1-one (210 mg, 0.96 mmol) (prepared in the usual way from the corresponding ketone but not purified) and methanesulphonyl chloride (120 mg, 1.05 mmol) in pyridine was heated under reflux for 1 h. Water and 2M-hydrochloric acid were added and the resultant solution was extracted with chloroform. Evaporation of solvent gave a dark red oil, crystallisation of which from petroleum–benzene gave *1-acetyl-8-cyanonaphthalene* (100 mg, 53%), m.p. 98—100 °C (Found: C, 80.1; H, 4.6; N, 6.9%; *M*+, 195.0686. $C_{13}H_9NO$ requires C, 80.0; H, 4.70; N, 7.2%; *M*, 195.0684), $\nu_{max.}$ 2 220 and 1 680 cm^{-1}; δ ($CDCl_3$) 2.81 (3 H, s, Me), 7.48—7.64 (3 H, m, 2,4,5-ArH), and 7.95—8.15 (3 H, m, 3,6,7-ArH); *m/e* 195(20%) (*M*).

Treatment of this ketone (100 mg, 0.47 mmol) with hydroxylamine hydrochloride (40 mg, 0.56 mmol) and sodium acetate (100 mg) gave *1-imino-3-methyl-1H-benz[de]isoquinoline N-oxide* (33) (28 mg, 25%) as green crystals, m.p. 165—169 °C (from chloroform–petroleum) (Found: *M*+, 210.0791. $C_{13}H_{10}N_2O$ requires *M*, 210.0793), $\nu_{max.}$ 1 585, 1 575, and 1 525 cm^{-1}; δ ($CDCl_3$) 2.66 (3 H, s, Me), 7.46—7.94 (6 H, m, NH, ArN), and 8.36 (1 H, d, *J* 8 Hz, ArH), *m/e* 210(45%) (*M*).

In 2M-aqueous ethanolic sodium hydroxide the keto-nitrile gave *3-aminophenalen-1-one* (36) as orange crystals, m.p. 131—134 °C (Found: C, 80.0; H, 4.9; N, 6.9%; *M*+, 195.0686. $C_{13}H_9NO$ requires C, 80.0; H, 4.70; N, 7.2%; *M*, 195.0684), $\nu_{max.}$ 3 320, 3 170, and 1 632 cm^{-1}; δ ($CDCl_3$) 5.94 (1 H, s, 2-H), 7.66—7.76 (2 H, m, ArH), and 8.10—8.46 (4 H, m, ArH); *m/e* 195(100%) (*M*).

Reactions of 1,8-Dicyanonaphthalene.[22]—(i) *With t-butyl adamantane-1-percarboxylate.* A solution of 1,8-dicyanonaphthalene (112 mg, 0.63 mmol) and t-butyl adamantane-1-percarboxylate (266 mg, 1.06 mmol) in benzene (20 ml) was heated under reflux for 1 h. The residue obtained on removal of solvent was chromatographed on silica (t.l.c.) using methanol–chloroform (2 : 98) to give two *adamantan-1-yl-1,8-dicyanonaphthalenes* (14%), m.p. 275—277 °C and *ca.* 250 °C (*M*+, 312.1628 and *M*+, 312.1625. $C_{22}H_{20}N_2$ requires *M*, 312.1626); $\nu_{max.}$ (KBr) 2 220 cm^{-1} (both).

(ii) *With butyl-lithium.* A stirred suspension of 1,8-dicyanonaphthalene (65 mg, 0.37 mmol) in ether (30 ml) was treated with 1.16M butyl-lithium in pentane (3.0 ml) at 0 °C under nitrogen for 3 h. Work-up in the usual way and purification of the crude product on silica (t.l.c.) with methanol–chloroform (2 : 98) gave a mixture of *4-amino-1,6-di-t-butyl-5-azophenalene* and *6-amino-1,4-di-t-butyl-5-azaphenalene*, (43) and (42), as an unstable yellow oil (Found: *M*+, 293.2016 and *M*+ − C_4H_8, 237.1390. $C_{20}H_{25}N_2$ requires *M*, 293.2017 and *M* − C_4H_8, 237.1391); $\nu_{max.}$ (C_2H_5OH) 252 and 396; $\nu_{max.}$ (CCl_4) 3 510, 3 410, 1 641, and 1 598 cm^{-1}; δ (two stereoisomers) 0.80 and 0.87 (9 H, each s, 1-Bu^t), 1.58 (9 H, s, 4-Bu^t), 3.46 (1 H, d, *J* 6 Hz, 1-H), 4.37 (2 H, bs, NH_2), 6.1 (1 H, m, 2-H), 6.6 (1 H, d, *J* 10 Hz, 3-H), 7.0—7.3 (2 H, m, 8- and 7-H), and 8.1 (1 H, m, 9-H).

Treatment of this product with acetic anhydride in pyridine at room temperature gave the acetyl derivative as an unstable yellow oil, $\nu_{max.}$ 3 250, and 1 665 cm^{-1}; δ 0.78, 0.85 (9 H, each s, Bu^t), 1.6 (9 H, s, Bu^t), 2.26, 2.31 (3 H, each s, Me), 3.52, 3.82 (1 H, each d, *J* 6 Hz, CH), *ca.* 6.3 (1 H, m, =CH), *ca.* 6.7 (1 H, m, =CH), 7.2—7.5 (3 H, m, ArH), 7.72 (1 H, bs, NH), and *ca.* 8.25 (1 H, m, ArH).

(iii) *With hydroxylamine.* A solution of 1,8-dicyanonaphthalene (285 mg, 1.60 mmol), hydroxylamine hydrochloride (290 mg, 4.17 mmol), and sodium acetate (342 mg, 4.17 mmol) in ethanol–water (40 ml) was heated under reflux for 4 h. The crude product (213 mg) on cooling was collected and recrystallised from ethanol to give *naphthalimide dioxime* (39) as yellow needles, m.p. 238—239 °C. The ethanol of crystallisation was removed by drying the crystals at 80 °C for 6 h (Found: C, 63.4; H, 4.3; N, 18.5%; *M*+, 227.0692. $C_{12}H_{19}N_3O_2$ requires C, 63.4; H, 4.0; N, 18.5%; *M*, 227.0694); $\nu_{max.}$ (KBr) 3 410, 3 150, 1 645, and 1 611 cm^{-1}; δ 7.62 (2 H, t, *J* 8 Hz, ArH), 8.03 (2 H, d, *J* 10 Hz, ArH), 8.12 (2 H, d, *J* 10 Hz, ArH), and 8.95 (1 H, bs, NH).

(iv) *With peroxides.* Treatment of 1,8-dicyanonaphthalene (1 mol) with (a) an excess of acetyl peroxide in hot

benzene, (b) an excess of benzoyl peroxide in benzene under reflux, (c) solid benzoyl peroxide (2 mol) at 200 °C for 5 min, and (d) di-t-butyl peroxide (30 mol) at 126 °C for 20 h, gave either starting material (a) and (b) or starting material and intractable gum (c) and (d).

Reaction of 2-Cyanonaphthalene with t-Butyl Adamantane-1-percarboxylate.—A solution of 2-cyanonaphthalene (215 mg, 1.4 mmol) and t-butyl adamantanepercarboxylate (461 mg, 1.8 mmol) in dry benzene (60 ml) was refluxed for 30 min. The residue obtained on removal of solvent was chromatographed on silica (t.l.c.) using benzene to give a mixture of two products. The mixture showed $\nu_{max.}$ 2 220 (C≡N) and 1 708 cm^{-1} (C=O) and from the mass spectrum it was found to be composed of *adamantyl-2-cyanonaphthalene* (Found: M^+, 287.1673. $C_{21}H_{21}N$ requires M, 287.1673) and *adamantyl-2-naphthoate* (Found: M^+, 306.1622. $C_{21}H_{22}O_2$ requires M, 306.1619).

Copolymerisations.—(i) A mixture of freshly distilled acrylonitrile (24.5 g, 0.462 mol) and methyl vinyl ketone (8.1 g, 0.116 mol) and azobisisobutyronitrile (19 mg) was heated at 60—70 °C for 7 under nitrogen. The reaction mixture was poured into dimethylformamide. The jelly which separated was removed, and the filtrate was dropped into methanol giving a colourless precipitate which showed i.r. absorption at 2 240 (CN) and 1 710 (CO) cm^{-1}. A similar product was obtained when benzoyl peroxide was used as initiator and the reaction mixture was heated for 1 h at 65—68 °C.

(ii) Copolymerisation of methylacrylonitrile and methyl vinyl ketone as in (i) gave a copolymer with $\nu_{C\equiv N}$ 2 230 and $\nu_{C=O}$ 1 712 cm^{-1}. The copolymers were dried at 65 °C for 5 h.

Preparation and Oxidation of Polymeric O-Carboxymethyloximes.—General procedure. The copolymer (0.3 g) and amino-oxyacetic acid hemihydrochloride (0.3 g) in pyridine (10 ml) were heated at 85 °C for 3 h. After cooling, the reaction mixture was poured into dilute hydrochloric acid. The precipitate was soluble in hot, dilute aqueous sodium hydroxide and showed $\nu_{max.}$ 2 240 (C≡N) and 1 740 cm^{-1} (C=O).

The acid copolymer (1 g) in 0.1M-sodium hydroxide solution (15 ml) was oxidised with potassium persulphate (0.4 g) in water (20 ml) in the usual way. The copolymer produced after boiling the solution for 5 min was collected and examined by i.r. spectroscopy.

Crystal Structure Determination of Compound B (20).—An almost cubic fragment of dimension 0.2 mm was cut from a large crystal and mounted directly on a Nonius CAD-4 diffractometer. The cell parameters were found by least-squares from the setting angles of 25 reflections.

Crystal data: M = 303.3, monoclinic, a = 14.061(1), b = 7.391(1), c = 14.701(2) Å, β = 95.39(1)°, U = 1 520.9 Å^3, Z = 4, D_c = 1.325 g cm^{-3}, D_m = 1.30 g cm^{-3}, $F(000)$ = 648, Cu-K_α radiation (Ni filter) λ = 1.5418 Å, μ = 7.68 cm^{-1}, space group $P2_1/n$.

Data were collected for $\theta < 76°$ and 2 569 intensities (from a total of 3 182) had $I > 3\sigma I$ and were used in the refinement. The structure was solved routinely by the centrosymmetric direct methods routine of SHELX and refined by full-matrix least-squares. The differentiaton between oxygen and nitrogen was quite clear from the isotropic temperature factors when all the heteroatoms were refined as nitrogen. At the appropriate stage a difference map convincingly revealed the hydrogen atoms which lead to the formulation of the molecule as the nitrone (20). In the final stages of the refinement 12 very strong reflections, flagged as ' too strong ' by the diffractometer software, were omitted from the calculations. At convergence, with hydrogen atoms treated isotropically and other atoms anisotropically, R was 3.8%.

Table 1 gives the fractional co-ordinates of the non-hydrogen atoms and Figure 1 shows the crystallographic numbering and the bond lengths. Table 2 has the non-hydrogen bond angles. Tables of the temperature factors, the hydrogen co-ordinates, and the dimensions involving hydrogen, and calculated and observed structure factors are deposited as a Supplementary publication [SUP No. 23019 (23 pp.)].*

TABLE 1

Fractional co-ordinates ($\times 10^4$) with standard deviations in parentheses

Atom	x/a	y/b	z/c
N(1)	8 779(1)	3 664(2)	1 998(1)
O(1)	8 349(1)	5 316(1)	1 874(1)
N(2)	9 397(1)	4 667(2)	3 460(1)
O(2)	9 272(1)	6 521(1)	3 274(1)
N(3)	7 633(1)	2 667(2)	952(1)
O(3)	8 779(1)	5 142(2)	4 799(1)
C(1)	8 403(1)	2 299(2)	1 522(1)
C(2)	8 819(1)	425(2)	1 590(1)
C(3)	9 822(1)	465(2)	2 093(1)
C(4)	9 866(1)	1 648(2)	2 945(1)
C(5)	9 209(1)	976(2)	3 639(1)
C(6)	9 304(1)	2 120(2)	4 500(1)
C(7)	9 122(1)	4 093(2)	4 268(1)
C(8)	9 638(1)	3 617(2)	2 670(1)
C(9)	10 478(1)	4 537(2)	2 262(1)
C(10)	11 252(1)	5 112(2)	2 844(1)
C(11)	12 026(1)	5 933(3)	2 493(1)
C(12)	12 035(1)	6 162(3)	1 566(2)
C(13)	11 288(2)	5 549(4)	986(1)
C(11)	10 499(1)	4 760(3)	1 333(1)
C(15)	8 813(2)	−470(3)	653(2)
C(16)	8 648(1)	1 464(3)	5 198(1)

TABLE 2

Bond angles in degrees, with standard deviations in parentheses

O(1)–N(1)–C(8)	115.6(1)	O(3)–C(7)–N(2)	121.4(1)
O(1)–N(1)–C(1)	117.7(1)	C(7)–N(2)–C(8)	129.6(1)
C(1)–N(1)–C(8)	126.7(1)	C(7)–N(2)–O(2)	116.0(1)
N(1)–C(1)–C(2)	122.7(1)	O(2)–N(2)–C(8)	113.3(1)
N(1)–C(1)–N(3)	116.2(1)	N(2)–C(8)–N(1)	106.3(1)
N(3)–C(1)–C(2)	121.1(1)	N(2)–C(8)–C(4)	110.6(1)
C(1)–C(2)–C(3)	110.4(1)	N(2)–C(8)–C(9)	108.7(1)
C(1)–C(2)–C(15)	111.7(2)	N(1)–C(8)–C(4)	109.5(1)
C(3)–C(2)–C(15)	111.8(1)	N(1)–C(8)–C(9)	109.7(1)
C(2)–C(3)–C(4)	111.9(1)	C(4)–C(8)–C(9)	112.0(1)
C(3)–C(4)–C(5)	112.5(1)	C(8)–C(9)–C(10)	118.9(1)
C(3)–C(4)–C(8)	109.6(1)	C(8)–C(9)–C(14)	122.0(1)
C(5)–C(4)–C(8)	111.2(1)	C(10)–C(9)–C(14)	119.1(1)
C(4)–C(5)–C(6)	111.5(1)	C(9)–C(10)–C(11)	120.2(2)
C(5)–C(6)–C(7)	110.4(1)	C(10)–C(11)–C(12)	120.2(2)
C(5)–C(6)–C(16)	111.9(1)	C(11)–C(12)–C(13)	120.0(2)
C(7)–C(6)–C(17)	111.0(1)	C(12)–C(13)–C(14)	120.1(2)
C(6)–C(7)–N(2)	116.4(1)	C(13)–C(14)–C(9)	120.4(2)
C(6)–C(7)–O(3)	122.1(1)		

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* For details of the Supplementary publication Scheme, see Notice to Authors No. 7, in *J. Chem. Soc., Perkin Trans. 1*, Index issue, 1980.

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