Oxidative Rearrangement of *N*-Aminopyrazoles to 1,2,3-Triazines

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When 1-amino-3,5-dimethylpyrazole or 1-amino-3-methoxyindazole is oxidised with lead(IV) acetate, the *N*-amino group forms the central nitrogen (N-2) of the triazine which is formed.

N-Amino heterocycles show a fascinating diversity of behaviour on oxidation.[1] The reaction is usually assumed to proceed by the intermediate formation of *N*-nitrenes, some of which may be detected spectroscopically, or in acidic media stabilised as the diazenium ions. However, they more usually undergo immediate reaction, and in these cases the nitrenes should be considered as reasonable hypotheses rather than proven intermediates. For the purposes of the discussion which follows, we shall assume their formation, and that they occupy a key position in the reaction pathway.

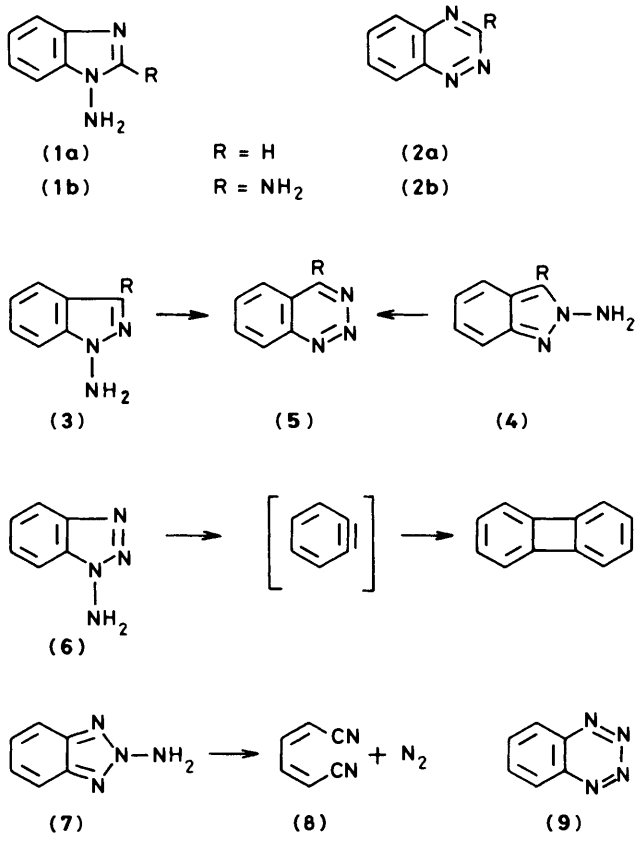
It is convenient to group the nitrenes according to the preferred type of reaction they undergo, although sometimes one nitrene will show more than one type of reaction, and often structurally closely related compounds react by different routes, suggesting that the reaction pathways actually followed may not energetically be greatly favoured over other routes which are in practice not observed. Three main classes can be discerned, as follows.

(a) *Rigid nitrenes.* These show little or no tendency to fragment (mode b) or rearrange (mode c), and when presented with a suitable reagent undergo nitrene addition reactions, *e.g.* forming *N*-aminoaziridines with olefins, and *N*-aminosulphoximines with sulphoxides. Without added nitrene traps, the oxidation often results simply in deamination.

(b) *Fragmenting nitrenes.* In these cases nitrene generation is followed by extrusion of dinitrogen. The remaining fragments may recombine, or undergo disproportionation or further fragmentation, reactions characteristic of free radicals. Dimerisation, to form tetrazenes, is frequently observed as a side-reaction of the fragmenting nitrenes, and also of the rigid types. In some cases this may not be a true nitrene dimerisation, but a trapping of the nitrene by the amine, followed by oxidation of the tetrazane so formed.

(c) *Rearranging nitrenes.* These quickly undergo ring enlargement, by (apparent) migration to the nitrene nitrogen of a group attached to the adjacent substituted atom.

Nitrenes derived from aromatic *N*-amino heterocycles are represented in all three classes, and it is not obvious what decides which pathway is to be taken. Thus, 1-aminobenzimidazole (**1a**) forms a 'rigid nitrene', and does not rearrange to 1,2,4-benzotriazine (**2a**).[2] Both 1-amino (**3**) and 2-amino (**4**) indazoles rearrange on oxidation to form 1,2,3-benzotriazines (**5**),[3] while both 1-and 2-aminobenzotriazoles (**6**) and (**7**) fragment, in distinctly different ways, the former generating benzyne, the latter producing muconononitrile (**8**).[4] Substitution, too, can affect the reaction pathway. Thus, 1,2-diaminobenzimidazole (**1b**) rearranges efficiently on oxidation to the aminobenzotriazine (**2b**),[5] and we find that, although most *N*-aminopyrazoles give 1,2,3-triazines,[6] the 3,4,5-triphenyl compound does not, forming instead a 'rigid nitrene'. 1-Aminopyrazole itself forms only a very small yield of 1,2,3-triazine on lead (IV) acetate oxidation, but considerably more (18%) when nickel peroxide is used as oxidant.[7,8] However, nickel peroxide is ineffective in forming triazines from other aminopyrazoles which give moderate to good yields when lead(IV) acetate is used:[8] in these cases the nickel peroxide deaminates the aminopyrazole—typical rigid nitrene behaviour. This rather strange dependence on oxidant should sound a warning against the presumption of nitrene intermediates in all the reactions studied.



Observing that the two isomeric aminoindazoles (**3**) and (**4**) followed an apparently similar path, to an identical product (**5**), while the aminobenzotriazoles (**6**) and (**7**) follow different fragmentation routes, the Norwich authors formed the hypo-

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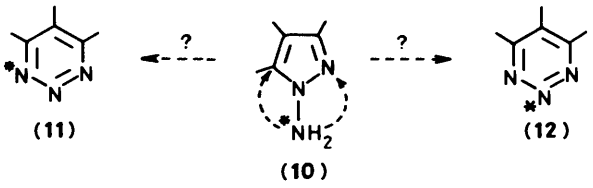
Table 1. ^{15}N Chemical shifts (p.p.m. downfield from external $MeNO_2$) and assignments of some 1,2,3-triazine derivatives

Compound (-triazine)	Chemical shift 1-N	2-N	3-N
4,6-Dimethyl	3.8	78.6	3.8
4-Methyl	12.5	79.9	3.6
4-Methylbenzo	15.9	66.6	−16.1
4-Methoxybenzo	5.1	61.2	−66.3

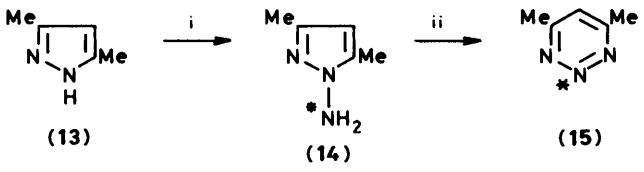
thesis that the 1-aminobenzotriazole (**6**) may be oxidised with rearrangement, to form benzotetrazine (**9**), transiently, which immediately fragments to lose two molecules of nitrogen. (This possibility was suggested earlier.[4]) However, if (**6**) does form benzotetrazine, evidently (**7**) does not, as the products of oxidation are not the same. Seeking the simplest interpretation of these results, they reasoned that since of the four aminoazoles (**3**), (**4**), (**6**), and (**7**), the one which behaves anomalously (**7**) is the only one in which the nitrogen atom carrying the amino group is flanked by two other nitrogens, the explanation may be that *the nitrene nitrogen, when formed, can cyclise only towards carbon, never towards nitrogen.* In terms of the simpler aminopyrazole→1,2,3-triazine rearrangement, this leads to the prediction that the expected pathway, using labelled nitrogen atoms, is as (**10**)→(**11**), rather than as (**10**)→(**12**).* The experiments described in the next Section were then carried out. The results were quite unambiguous: in the rearrangement a new N–N bond is formed, as in (**10**)→(**12**); *the hypothesis outlined above is therefore completely incorrect.*



The Norwich group used ^{15}N n.m.r. to follow the course of the reactions. When their findings were presented at a meeting in Grasmere in 1985, they learnt that similar results, using chemical/mass spectrometric methods of analysis, had been obtained some years earlier in Liverpool.[9] A joint publication was therefore agreed upon.

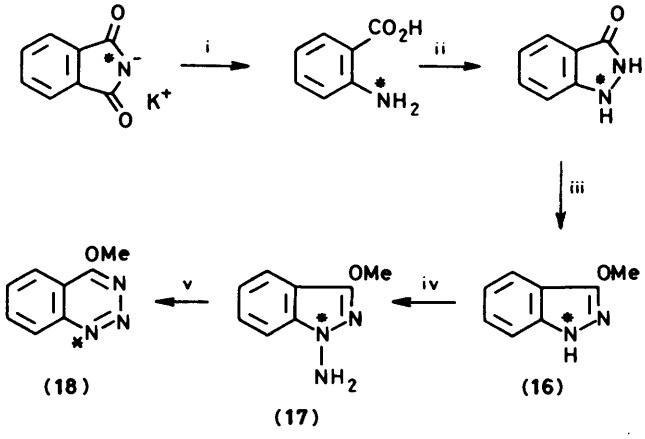
Results and Discussion

3,5-Dimethylpyrazole (**13**) was aminated with ^{15}N-enriched chloramine. Oxidation of the aminopyrazole (**14**) using lead(IV) acetate formed the dimethyltriazine (**15**) containing the excess label only at N-2, as shown by ^{15}N n.m.r. spectroscopy (Scheme 1 and Table 1). In the product (**15**) the lowfield signal (78.6 p.p.m. downfield of $MeNO_2$) was intensified. This is assigned to N-2 because (*a*) in the natural abundance spectrum the highfield signal (3.8 p.p.m.) is some twice the intensity of the lowfield signal; (*b*) in the ^{15}N n.m.r. spectrum of 4-methyl-1,2,3-triazine there are one lowfield and two highfield signals; (*c*) the central nitrogen of a 1,2,3-triazine is expected, by calculation[10] and by analogy with our and others' work[11] in the series of 1,2,3-benzotriazines to be deshielded, with respect to the signals from the other two.



Scheme 1. *Reagents:* i, NaH; $*NH_2Cl$; ii, $Pb(OAc)_4$

3-Methoxyindazole was prepared with ^{15}N enrichment at the 1- and 2-positions, separately, the 1-labelled compound (**16**) from potassium[^{15}N]phthalimide as in the indicated route (Scheme 2), the 2-labelled using sodium[^{15}N]nitrite in the diazotisation stage. 1-Amination proceeded in good yield using hydroxylamine *O*-sulphonic acid, and on oxidation of the amine (**17**) the label was found to be entirely at the 1-position of the benzotriazine (**18**). The 2-labelled aminoindazole analogously formed [3-^{15}N]-4-methoxy-1,2,3-benzotriazine, as expected. [2-^{15}N]-4-Methoxy-1,2,3-benzotriazine (**20**) was prepared from 2-labelled 1,2,3-benzotriazin-4-one. The ^{15}N n.m.r. chemical shifts of compounds relevant to the present work are listed in Table 1.

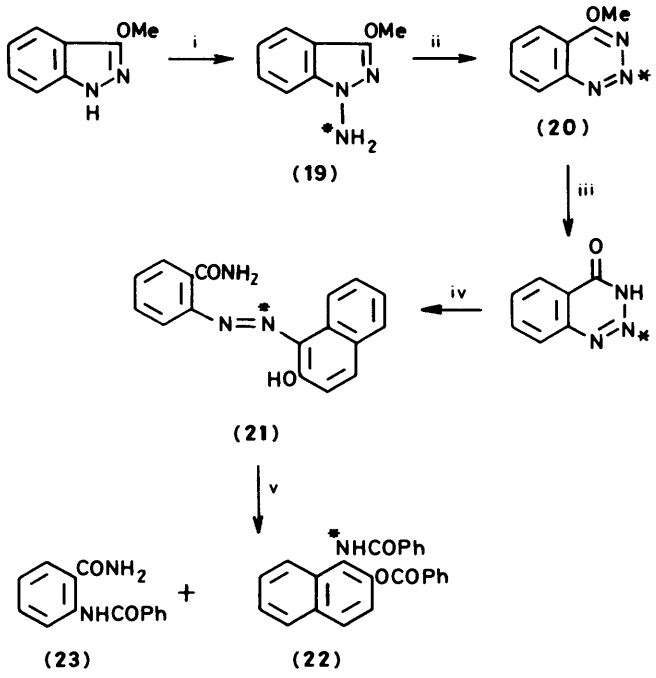


Scheme 2. *Reagents:* i, NaOBr; ii, (a) HNO_2, (b) $NaHSO_3$; iii, CH_2N_2; iv, H_2NOSO_3H; v, $Pb(OAc)_4$

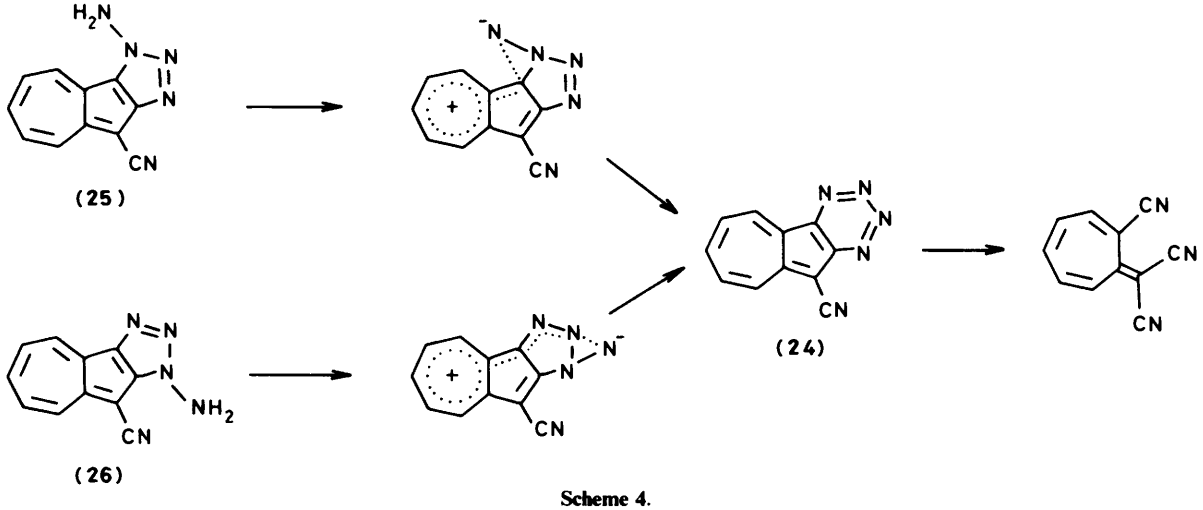
In the Liverpool experiments with 3-methoxyindazole, the unlabelled material was aminated using [^{15}N]chloramine (95% enrichment), giving the labelled amine (**19**) which was oxidised to the benzotriazine (**20**). That the label in (**20**) was exclusively at N-2 was shown by demethylation and coupling with 2-naphthol, followed by reductive cleavage of the azo-compound (**21**) and location of the ^{15}N-label in the (benzoylated) aminonaphthol (**22**) only; the benzoylanthranilamide (**23**) proved to be completely unlabelled, by mass spectrometry.

In the two cases examined, therefore, we have established that the amino nitrogen on oxidation becomes incorporated into the triazine ring as N-2. As to the mechanism of the reaction, we prefer not to speculate at this stage. In connection with the benzotetrazine intermediate in benzyne formation, Murata and co-workers[12] recently postulated the fused tetrazine (**24**) as a common intermediate in the oxidiative decomposition of the two aminotriazoloazulenes (**25**) and (**26**). In these reactions the expected aryne was not formed; instead the putative tetrazine ring fragmented to two cyano groups and one dinitrogen molecule. The authors' proposal seems attractive; we note, however, that they suggest different modes for the nitrene incorporation in the two cases (Scheme 4). In the light of our results, we believe it more likely that the nitrene nitrogen would

* It was pointed out by Atkinson (ref. 1, p. 268) that no experiments to determine the direction of this rearrangement have so far been published.



Scheme 3. *Reagents:* i, $*NH_2Cl$; ii, $Pb(OAc)_4$; iii, BBr_3; iv, 2-naphthol, H^+; v, (a) Zn–HOAc; (b), PhCOCl–pyridine



Scheme 4.

be included in the tetrazine ring between two nitrogen atoms, in each case. Clearly, a labelling study would provide useful insight into this reaction.

In the Experimental section we give details of an attempt to prepare triphenyl-1,2,3-triazine from 1-amino-3,4,5-triphenylpyrazole. The failure is certainly not owing to any instability in the triazine, which was the first example in the monocylic series to be prepared.[13] We also found difficulty in oxidising 1-aminopyrazole to the parent 1,2,3-triazine: nickel peroxide, which was successfully used by two other groups,[7,8] in our hands gave only a small yield of 1-prop-2-ynylideneaminopyrazole, which had also been isolated by Neunhoeffer *et al.*[8]

Experimental

M.p.s were determined on a Kofler hot-stage apparatus, using standardised thermometers, and so are 'corrected'. ^1H N.m.r. spectra were taken on Perkin-Elmer R12 or JEOL FX-100 FT spectrometers. ^{15}N.m.r. spectra were recorded in $CDCl_3$ with tris(acetylacetonato)chromium(III), at 18.25 MHz using a Bruker WH-180, and at 40.55 using a Bruker WH-400, spectrometer. Chemical shifts are given in p.p.m. downfield from $SiMe_4$ (^1H) or external $MeNO_2$ (^{15}N). The mass spectral instrumentation and techniques used in Liverpool are described elsewhere.[14]

[2-^{15}N]-4,6-*Dimethyl*-1,2,3-*triazine* (**15**).—Ammonium chloride (25% ^{15}N; 1.6 g) was added to a vigorously stirred mixture of Et_2O (160 ml) and 10% aqueous NaOH (4 ml), chilled to −12 °C. Stirring was continued while 1M-sodium hypochlorite (30 ml, containing 30 g ice) was dropped in over 20 min, the temperature being maintained below −9 °C. The layers were separated and the ether layer was washed with saturated aqueous NaCl and dried over $CaCl_2$ at −78 °C for 2 h. Iodometric assay showed the chloramine to be 0.087M in the ether (46% yield).

Sodium hydride (0.27 g) was added to 3,5-dimethylpyrazole[15] (1.0 g) in dry ether (40 ml). After 10 min under reflux the mixture was cooled in ice and the suspension added to the chloramine solution. The mixture was allowed to warm to room temperature and then stirred for 24 h. Removal of solvent left a mixture of the pyrazole (**13**) and the *N*-amino compound (**14**) which was separated by chromatography [silica gel, eluting with EtOAc–light petroleum (2:5)]. Recrystallisation (EtOAc), using unlabelled 1-amino-3,5-dimethylpyrazole for entrainment, eventually gave the labelled [1-^{15}N]amine (1.45 g, 2.5% enriched in ^{15}N), which was oxidised [$Pb(OAc)_4$][6] to the dimethyltriazine (**15**) (0.55 g, 39%), m.p. 92—93 °C (lit.,[8] m.p. 94 °C; the m.p. 159 °C of ref. 6 was reported in error[16]).

[1-^{15}N]-4-*Methoxy*-1,2,3-*benzotriazine* (**18**).—Potassium [^{15}N]phthalimide (1.0 g) was converted into [^{15}N]-2-aminobenzoic acid by the method of Holt and Bulloch.[17] This was recrystallised from water, entraining with unlabelled material, to provide 10% [^{15}N]-2-aminobenzoic acid (3.4 g). This was diazotised at −5 to 0 °C in 5% aqueous hydrochloric acid (30 ml) with sodium nitrite (1.9 g). Sodium sulphite (11 g) in water (50 ml) was added and the mixture was stirred for 2 h. Concentrated hydrochloric acid (8 ml) was added, and after the mixture had been stirred for a further 8 h at 20 °C it was heated to reflux for 3 h, treated with charcoal (3 g), filtered, cooled, and neutralised with aqueous sodium hydroxide. The [1-^{15}N]-indazolin-3-one (1.43 g, 43%) which separated, was collected, dried, and treated with ethereal diazomethane to provide [1-

^{15}N]-3-methoxyindazole (1.04 g, 65%, 10% in ^{15}N at N-1), which was separated from the more polar *N*-methylated isomer by short column chromatography (Al_2O_3). Amination was carried out by the procedure of Adger *et al.*[3] using hydroxylamine *O*-sulphonic acid (4.5 g), giving the 1-amino compound (**17**) (0.7 g, 60%), m.p. 107 °C (lit.,[3] 108 °C). This was diluted with unlabelled material, and oxidised with lead(IV) acetate,[3] to give [1-^{15}N]-4-methoxy-1,2,3-benzotriazine (**18**) (0.28 g, 59%, 3% in ^{15}N at N-1), m.p. 103.5—105 °C (lit.,[3] m.p. 105.5—106.5 °C).

[2-^{15}N]-4-*Methoxy*-1,2,3-*benzotriazine*.—2-Aminobenzamide (4.0 g) in 3% aqueous hydrochloric acid (30 ml) was treated with sodium nitrite (5% ^{15}N) (2.1 g) at −5 °C. After the mixture had been stirred for 0.5 h it was basified with 5% aqueous sodium hydroxide and filtered. Addition of 30% aqueous hydrochloric acid precipitated the [2-^{15}N]-1,2,3-benzotriazin-4(3*H*)-one (2.75 g, 64%). This was heated under reflux for 4 h in pyridine (75 ml) with phosphorus pentasulphide (4.5 g) and sodium hydrogen carbonate (9.2 g). The mixture was cooled, diluted with water (100 ml), and extracted with toluene (3 × 100 ml). The toluene layers were combined, washed with water (3 × 50 ml), dried ($MgSO_4$), filtered, and evaporated under reduced pressure to give a residue which was recrystallised from ethanol to provide the thione (1.2 g, 40%). This was dissolved in absolute methanol (50 ml) containing sodium methoxide from sodium (0.6 g), and treated with methyl iodide (2 ml) for 2 h at 20 °C with stirring. Solid CO_2 (20 g) was then slowly added, and the precipitated inorganic material was removed by filtration. The filtrate was evaporated and the residue was recrystallised from cyclohexane, to give the methoxy compound (0.76 g, 64%), 5%-^{15}N at N-2, m.p. 105—106 °C.

[3-^{15}N]-4-*Methoxy*-1,2,3-*benzotriazine*.—The synthesis for the 1-labelled compound (**18**) was followed, but employing normal 2-aminobenzoic acid (3.4 g) and sodium [^{15}N]nitrite (5%) (1.9 g). No entrainment was used in the isolation; the methoxy compound (0.07 g, 2% overall), 5%-^{15}N at N-3, m.p. 102—104 °C was obtained.

Amination of 3-Methoxyindazole with Labelled Chloramine.[9]—[^{15}N]Ammonium chloride (95%) was converted into [^{15}N]chloramine in 61% yield (iodometric assay) as described above. Reaction[3] of 3-methoxyindazole (0.53 g) containing *ca.* 12% 1-amino-3-methoxyindazole with the ethereal [^{15}N]chloramine gave the 1-amino compound (**19**) (0.56 g) containing 83.5 ± 2% ^{15}N at the amine group (m.s.). Oxidation[3] of (**19**) (0.39 g) with lead(IV) acetate gave the methoxybenzotriazine (**20**) (0.34 g, 90%) containing 83 ± 3% of one ^{15}N atom (m.s.).

Demethylation of (**20**) (0.30 g) to 1,2,3-benzotriazin-4-one (0.18 g, 67%) was accomplished using boron tribromide.[18]*

The benzotriazinone (0.18 g) was coupled with 2-naphthol (0.18 g) in acidic solution, from which the azo product (**21**) (m.p. 227 °C), containing 84 ± 4% ^{15}N-incorporation (m.s.) was precipitated. The azo compound was reduced by zinc dust and acetic acid, and the reduction products were benzoylated and separated to give: (a) 1-benzamido-2-naphthyl benzoate (**22**) (1.8 mg, 0.5%), m.p. 216—218 °C (lit.,[19] m.p. 226.5 °C); (b) 2-benzoylaminobenzamide (**23**) (37 mg, 65%), m.p. 212—214 °C (lit.,[20] m.p. 215—216 °C). The incorporation of ^{15}N in these two products was 83 ± 3% and 0 ± 1% respectively (m.s.).

1-*Amino*-3,4,5-*triphenylpyrazole*.—3,4,5-Triphenylpyrazole[21] (5.9 g) in water (40 ml) and ethanol (170 ml) was treated with sodium hydroxide (5 g) and hydroxylamine *O*-sulphonic acid (13.6 g), the latter added portionwise, the temperature being maintained at 70—75 °C. After the mixture had been stirred for 20 min it was cooled and the precipitate was collected, washed with water, and recrystallised from ethanol, to provide the *aminopyrazole* (4.74 g, 76%) as needles, m.p. 193.5 °C (Found: C, 81.5; H, 5.8; N, 13.9. $C_{21}H_{17}N_3$ requires C, 81.0; H, 5.5; N, 13.5%); *m/z* 311 (M^+, 100%).

The amine formed an *anisylidene derivative*, m.p. 163—164 °C (ethanol), *m/z* 429 (M^+, 100%) (Found: C, 80.8; H, 5.5; N, 9.65. $C_{29}H_{23}N_3O$ requires C, 81.1; H, 5.4; N, 9.8%).

Oxidation of 1-*Amino*-3,4,5-*triphenylpyrazole*.—(a) *Alone*. To a stirred, ice-cold solution of the amine (0.12 g, 0.4 mmol) in dichloromethane (40 ml), lead(IV) acetate (0.22 g, 0.5 mmol) was added over 20 min. The mixture was stirred and allowed to warm over 30 min. Glycerol (2 drops) was added to destroy excess of oxidant, and the lead salts were removed by filtration. The filtrate was evaporated and chromatographed (SiO_2; diethyl ether–light petroleum 1:2) to provide two products: (i) R_F = 0.7, yellow oil (22 mg), decomposing with time and tentatively identified as bis(3,4,5-triphenylpyrazol-1-yl)diazene (18%); *m/z* 295 ($Ph_3C_3N_2^+$), 178 ($Ph_2C_2^+$, 100%), M^+ not found; (ii) R_F = 0.4; 3,4,5-triphenylpyrazole (74 mg, 63%), m.p. 262—265 °C (lit.,[21] m.p. 265 °C).

(b) *In dimethyl sulphoxide*. Lead(IV) acetate (1.95 g, 4.4 mmol) was added in portions over 25 min to a stirred solution of the *N*-aminopyrazole (1.0 g, 3.2 mmol) in dry dimethyl sulphoxide (20 ml). The deep brown mixture was stirred for a further 10 min and then poured into water (150 ml) and extracted with chloroform (3 × 70 ml). The chloroform layers were combined and washed with water, dried, and evaporated. The residue was crystallised from ethanol, and the mother liquors from the crystallisation were evaporated and chromatographed (SiO_2; diethyl ether–light petroleum, 1:4) to provide three products: (i) R_F = 0.8; diphenylacetylene (17 mg, 3%), m.p. 60—61 °C, identical with a commercial sample; (ii) R_F = 0.1; 3,4,5-triphenylpyrazole (120 mg, 13%); (iii) R_F = 0; S,S-*dimethyl*-N-(3,4,5-*triphenylpyrazol*-1-*yl*)*sulphoximine*, m.p. 196—197 °C (ethanol–benzene, 2:1), identical with the bulk product from the first crystallisation (total 702 mg, 57%); *m/z* 387 (M^+), 296, 178 ($Ph_2C_2^+$, 100%), 103 ($PhCN^+$), 78 (Me_2SO^+); δ($CDCl_3$) 3.25 (SMe_2, 6 H) and 3.0—3.5 (15 H) (Found: C, 71.6; H, 5.6; N, 10.55; S, 8.2. $C_{23}H_{21}N_3OS$ requires C, 71.3; H, 5.5; N, 10.85; S, 8.3%).

Pyrolysis of S,S-*Dimethyl*-N-(3,4,5-*triphenylpyrazol*-1-*yl*)-*sulphoximine*.—The sulphoximine (70 mg, 0.18 mmol) was pyrolysed at 260 °C and 0.03 Torr in the apparatus described earlier.[22] From the product mixture was isolated only diphenylacetylene (12 mg, 37%) and the starting sulphoximine (44%). Benzonitrile was also present (identified by smell, before chromatography). No triphenyl-1,2,3-triazine was detected; in other experiments this was found not to be completely decomposed under the same conditions.

Acknowledgements

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* The Norwich group find that this conversion can be effected in good yield using sodium hydroxide in ethanol–water (9:1).

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