# 1,2,3-Triazine

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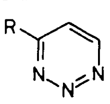
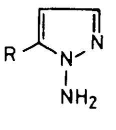
*Summary* 1,2,3-Triazine was obtained by nickel peroxide oxidation of *N*-aminopyrazole.

1,2,3-TRIAZINE (**1**) has not previously been prepared, although it is interesting chemically and physically and expected to be reasonably stable.[1] In a previous communication we reported the synthesis of alkyl-substituted monocyclic 1,2,3-triazines using the oxidation of *N*-aminopyrazoles with lead tetra-acetate, but the method was unsuccessful when applied to the synthesis of (**1**) from *N*-aminopyrazole (**2**).[2] We report in this paper the synthesis of (**1**) by oxidation of (**2**) with nickel peroxide.[3]

A dilute solution of (**2**) (2·69 g) in $CH_2Cl_2$ (220 ml)–AcOH† (2·2 g) was oxidized with nickel peroxide (17 g, activity 2·7 mg-atom oxygen/g) which was added in small portions at 0 °C. After filtration and evaporation of the solvent, the mixture was chromatographed over silica-gel and the crystalline fraction was purified by sublimation (room temp./0·1 mmHg) and recrystallization. The yield of pure (**1**) was 0·48 g (18%) and the compound has m.p. 69·5—71·0 °C (colourless plates from $Et_2O$). Its physical data‡ are in agreement with structure (**1**) and are analogous to those of the 4-methyl derivative (**3**) which was similarly obtained from nickel peroxide oxidation of 1-amino-5-methylpyrazole (**4**). The mass spectrum of (**1**) showed the typical fragment peaks of 1,2,3-triazines.[1]



(1) R = H
(3) R = Me



(2) R = H
(4) R = Me

The available data do not permit the evaluation of the degree of electron delocalization and aromaticity of (**1**), and, unfortunately, attempts at crystallographic analysis of (**1**) have been unsuccessful because of its instability under *X*-ray irradiation.

Finally, oxidation of (**2**) with active $MnO_2$, HgO, or $AgCO_3$–Celite, *etc.* did not afford isolable amounts of (**1**).

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† A trace of $CF_3COOH$ could also be used. When the acid was absent, the reaction proceeded very slowly.

‡ Spectral data (**1**): $\lambda_{max}$ (EtOH) 232(sh), 288 ($\epsilon$ 860), and 325(sh) nm; $\nu_{max}$ (KBr) 3045(m), 1565(s), 1440(m), and 1385(m) $cm^{-1}$; $\delta_H$ 9·06 (2H, d, 4- and 6-H, *J* 6·0 Hz) and 7·45 (1H, d, 5-H, *J* 6·0 Hz); $\delta_C$ ($CDCl_3$, $Me_4Si$) 117·9 (C-5, $J_{CH}$ 175·0 Hz) and 149·7 p.p.m. (C-4 and -6, *J* 187·5 Hz); *m/e* (rel. int./%), ionisation at 70 eV, 81 ($M^+$, 47), 53 ($M^+ - N_2$, 69), 27 (HCN, 13), and 26 ($C_2H_2$, 100). (**3**): $\lambda_{max}$ (EtOH) 288(sh), 286 ($\epsilon$ 510), and 313(sh) nm; $\nu_{max}$ (KBr) 3055(m), 1550(s), 1412(m), and 1380(w) $cm^{-1}$: $\delta_H$ 8·92 (1H, d, 6-H, *J* 6·0 Hz), 7·33 (1H, d, 5-H, *J* 6·0 Hz), and 2·70 (3H, s, $CH_3$); $\delta_C$ ($CDCl_3$, $Me_4Si$) 21·4 (4-$CH_3$, *J* 129·8 Hz), 117·8 (C-5, *J* 172·1 Hz), 148·8 (C-6, *J* 184·3 Hz), and 159·7 p.p.m. (C-4, s); *m/e* (rel. int./%), ionisation at 70 eV, 95 ($M^+$, 13) 67 ($M^+ - N_2$, 26), 40 [$M^+ - (N_2 + HCN)$, 100], 27 (HCN, 18), and 26 ($C_2H_2$, 22).

[1] R. J. Kobylecki and A. McKillop, *Adv. Heterocycl. Chem.*, 1976, **19**, 215; H. Neunhoeffer, *Chem. Heterocycl. Compd.*, 1978, **33**, 3, and references cited therein.

[2] A. Ohsawa, H. Arai, H. Ohnishi, and H. Igeta, *J. Chem. Soc., Chem. Commun.*, 1980, 1182.

[3] L. F. Fieser and M. F. Fieser, 'Reagents for Organic Synthesis,' 1967, p. **731**.