

in 50 ml. of benzene was added to the hot mixture and refluxing was continued for 18.5 hours. At this point a hydrolyzed sample of the reaction mixture was no longer alkaline to phenolphthalein and gave only a slight purple color with ferric chloride. Ether and dilute hydrochloric acid were added and the ethereal extract was washed with sodium bicarbonate and dried. Distillation gave 3.77 g. (32.2%) of the keto nitrile, b.p. 182–185.5° at 22 mm. A redistilled sample gave a negative ferric test and crystallized from petroleum ether (b.p. 20–40°) in colorless needles, m.p. 42–42.5°.

The semicarbazone was recrystallized from aqueous methanol; m.p. 203.5–204°.

Some Aldehydic Hydrazones of Triaminoguanidine

As potential coupling components in the formation of triformazans the derivatives listed in Table I were prepared. The general method was by refluxing for 10 to 15 minutes equimolar quantities of triaminoguanidine nitrate, dissolved in water, and the carbonyl component, dissolved in ethanol. Those derivatives which formed oils under these conditions were isolated as picrates. The hydrazones were crystallized from water or ethanol or mixtures of the two solvents, and occasionally from pyridine, which solvent usually removed the nitric acid and formed the free base of the hydrazone. Terephthalaldehyde and hydratropic aldehyde reacted anomalously.

TABLE I^{1,2}
TRIAMINOQUANYLHYDRAZONES (R₁CH=N—NH)₂—C=N—N=CH—R₁·HNO₃

Carbonyl compound	Empirical formula of hydrazone	M.p., °C.	Yield, ^b %	Nitrogen analyses, %	
				Calcd.	Found
Acrolein	C ₁₀ H ₁₉ N ₇ O ₆ ^{c,m}	Not below 360 ^{o,d}	60	30.9	31.4
4-Chlorobenzaldehyde	C ₂₂ H ₂₀ Cl ₃ N ₇ O ₄ ^{a,l}	159	95	17.7	17.9
Cinnamaldehyde	C ₂₈ H ₂₉ N ₇ O ₄ ^{a,l}	147	85	18.6	18.5
2,4-Dihydroxybenzaldehyde	C ₂₂ H ₂₀ N ₆ O ₁₁ ^{e,l}	218 ^d	69	15.1	14.5
2,3-Dimethoxybenzaldehyde	C ₂₈ H ₃₃ N ₇ O ₉ ^l	153	98	16.0	15.4
4-Dimethylaminobenzaldehyde	C ₂₈ H ₃₈ N ₁₀ O ₄ ^{a,l}	200	96	24.2	24.2
2,4-Dinitrobenzaldehyde	C ₂₂ H ₁₆ N ₁₃ O ₁₆ ^p	249	36	26.0	25.7
Formaldehyde	C ₁₀ H ₁₈ N ₉ O ₉ ^{f,l}	157	81	31.1	31.5
Furfural	C ₁₆ H ₁₆ N ₆ O ₄ ^{a,g,l}	82	90	23.8 ^r	24.5
2-Hydroxybenzaldehyde	C ₂₂ H ₂₁ N ₇ O ₆ ^l	145	90	20.5	20.2
4-Hydroxy-3-methoxybenzaldehyde	C ₂₈ H ₂₆ N ₆ O ₈ ^{a,k}	220	96	16.6	16.6
4-Isopropylbenzaldehyde	C ₃₁ H ₃₉ N ₇ O ₈ ^{h,l}	147	90	17.6	18.2
4-Methoxybenzaldehyde	C ₂₅ H ₂₉ N ₇ O ₇ ^{a,l}	148	81	18.2	18.5
2-Nitrobenzaldehyde	C ₂₂ H ₂₁ N ₉ O ₈ ^{i,a,k}	201	97	23.5	23.4
3-Nitrobenzaldehyde	C ₂₂ H ₁₉ N ₉ O ₇ ^{a,g,k}	232	84	24.2 ^q	23.6
Piperonal	C ₂₅ H ₂₂ N ₆ O ₇ ^{a,g,k}	223	93	16.2	15.8
Δ-3-Tetrahydrobenzaldehyde	C ₂₈ H ₃₅ N ₉ O ₇ ^{j,l}	185	91 ^j	20.6	20.7
2-Thiophene aldehyde	C ₁₆ H ₁₆ N ₇ S ₂ O ₈ ^l	153	98	21.0	21.4

^a Analysis corresponds to a monohydrate. ^b These yields include working up of all mother liquors, etc. ^c Analysis corresponds to a dihydrate. ^d Substance fuses at ca. 120° in its water of crystallization, resolidifies and then behaves as described. ^e Full analysis corresponds to hydrazone (free base) pentahydrate. Thus, calcd.: C, 47.4; H, 5.4. Found: C, 47.5; H, 5.0. Picrate (m.p. 205°) calcd. for C₂₃H₂₃O₁₃N₉: N, 18.1; found: N, 17.8. ^f Isolated as picrate. ^g Isolated as free base. ^h Picrate, m.p. 199°. *Anal.* Calcd. for C₃₇H₄₁N₉O₇: N, 17.9. Found: N, 17.8. ⁱ Analysis corresponds to dihydrate. ^j Yield is for crude material. Analysis is for picrate, for which substance m.p. 185°; calcd.: C, 55.2; H, 5.7. Found: C, 55.3; H, 5.7. ^k Recrystallized from pyridine. ^l Recrystallized from aqueous ethanol. ^m Recrystallized from water. ⁿ Insoluble in most organic solvents. ^o Calcd.: C, 50.7; H, 3.6. Found: C, 50.6; H, 3.4. ^p Calcd.: C, 54.4; H, 3.7. Found: C, 54.0; H, 4.3.

Anal. Calcd. for C₁₁H₁₆O₃N₄: C, 52.4; H, 6.4; N, 22.2. Found: C, 52.4, 52.3; H, 6.5, 6.5; N, 22.6, 22.4.

DEPARTMENT OF CHEMISTRY
SMITH COLLEGE
NORTHAMPTON, MASS.

MILTON D. SOFFER
ROBERTA A. STEWART

RECEIVED JULY 10, 1952

DEPT. OF CHEMISTRY
UNIVERSITY COLLEGE
CORK, IRELAND

F. L. SCOTT
M. CASHMAN
J. REILLY

RECEIVED MAY 20, 1952

(1) All m.p.s. are uncorrected.

(2) Analyses by Drs. Weiler and Strauss, Oxford.