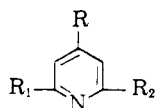


TABLE I
DERIVATIVES OF PICOLINIC ACID AND PYRIDINE-2,6-DICARBOXYLIC ACID OF THE STRUCTURE



R	R ₁	R ₂	Start- ing Mate- rial	Yield, ^a %	M.P.	Recryst. from	Calcd., % N	Found, % N	Empirical Formula
CH ₃ O	CONH ₂	CONH ₂	^b	90	>300°	H ₂ O-AcOH	21.5	21.3	C ₈ H ₉ N ₃ O ₃
CH ₃ O	CONHC ₆ H ₅	CONHC ₆ H ₅	^b	80	275-277°	Dioxane	12.1	11.8	C ₂₀ H ₁₇ N ₃ O ₃
C ₂ H ₅ O	CONH ₂	CONH ₂	III	70	289°	H ₂ O	20.1	20.4	C ₉ H ₁₁ N ₃ O ₃
C ₂ H ₅ O	CONHC ₆ H ₅	CONHC ₆ H ₅	III	80	258-259°	EtOH	11.7	11.4	C ₂₁ H ₁₉ N ₃ O ₃
Cl	Cl	COOH	V	80	114-116° ^o	H ₂ O ^d	7.30	7.11	C ₆ H ₃ Cl ₂ NO ₂
Cl	Cl	COOCH ₃	V	90	78.5-79.5° ^e	H ₂ O-MeOH	6.79	6.48	C ₇ H ₃ Cl ₂ NO ₂
Cl	Cl	CONH ₂	V	80	176.5-178.5° ^f	H ₂ O-EtOH	14.7	14.5	C ₈ H ₄ Cl ₂ N ₂ O
Cl	Cl	CONHC ₆ H ₅	V	75	172.5-174.5° ^c	EtOH	10.5	10.3	C ₁₂ H ₈ Cl ₂ N ₂ O
Cl	COOH	COOH	IV	60	218-219° ^g	H ₂ O	^h	^h	C ₇ H ₄ ClNO ₄
Cl	CONH ₂	CONH ₂	IV	95	>300°	H ₂ O	21.1	20.6	C ₇ H ₆ ClN ₃ O ₂
Cl	CONHC ₆ H ₅	CONHC ₆ H ₅	IV	65	272°	AcOH	11.9	11.5	C ₁₃ H ₁₄ ClN ₃ O ₂

^a Round figures. ^b 4-Methoxypyridine-2,6-dicarboxylic acid dichloride. ^c Lit. 111-112°. ^d Also sublimed *in vacuo*. ^e Lit. 73-74°. ^f Lit. 172-174°. ^g Lit. 220° (dec.). ^h Calcd.: C, 38.28; H, 2.75. Found: C, 38.04; H, 2.86.

boiling up to 110°/4 mm. and 1.0 g. of a residue which solidified on cooling. Samples of the two products were methanolized, the former giving *methyl 4,6-dichloropicolinate* of m.p. 78-79°, while the latter yielded *dimethyl 4-chloropyridine-2,6-dicarboxylate* of m.p. 143-144°. No depression of these melting points was observed on admixture with authentic samples.

Derivatives of substituted pyridinecarboxylic acids. The various acid chlorides reported above were converted to a number of derivatives. Hydrolyses and alcoholyses were carried

out by mixing the reactants without a solvent. The amides and anilides were prepared by treating benzene solutions of the acid chlorides with ammonia and aniline, respectively. Analyses and more preparative information is contained in Table I.

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(13) A. P. Sedgwick and N. Collie, *J. Chem. Soc.*, 67, 401 (1895).

[CONTRIBUTION FROM THE ROHM & HAAS COMPANY]

Olefinic Derivatives of 2,4-Diamino-s-triazines

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The reaction of *N*-alkylaminoalkyl vinyl ethers with cyanogen chloride gave the corresponding cyanamides. Amidonitriles containing vinyl ether or methacryloyl groups were obtained respectively by the successive cyanoalkylation and acylation of aminoethyl vinyl ether or the reaction of aminonitriles with methacryloyl chloride. Condensation of these cyanamides or amidonitriles with dicyandiamide gave the related derivatives of 2,4-diamino-*s*-triazine, a new group of triazines which undergo addition polymerization.

Olefinic derivatives of 2,4-diamino-*s*-triazines are potentially monomers from which cross-linked polymers may be prepared by successive alternate polymerization procedures. The few compounds of this type which have been described are limited to derivatives having the olefinic group joined directly to the heterocyclic nucleus.¹

Three new classes of olefinic triazines have been prepared whose common structural feature is separation of the olefin group from the heterocyclic ring

by a short chain containing oxygen, nitrogen, or both. Two of these classes are vinyl ethers, the third derivatives of methacrylamide. By appropriate selection of starting materials, a wide variety of monomeric triazines were obtained. These compounds showed good addition polymerization and copolymerization characteristics and could be cured by cross-linking reactions to insoluble polymers.

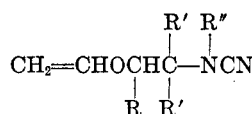
N-Vinoxyalkylcyanamides (I) were formed by the cyanation of appropriately substituted aminoalkyl vinyl ethers with cyanogen chloride. Subsequent condensation with dicyandiamide in the

(1) J. T. Thurston, U. S. Patent 2,461,943 (Feb. 15, 1949); C. G. Overberger and S. L. Shapiro, *J. Am. Chem. Soc.*, 76, 1061 (1954).

TABLE I
 N-ALKYLAMINOALKYL VINYL ETHERS^a

	B.P., °C(Mm.)	n_D^{25}	d_4^{25}	Nitrogen	
				Calcd.	Found
C ₂ H ₅ NHCH ₂ CH ₂ OCH=CH ₂	74(87)	1.4277	0.8519	12.2	12.0
(CH ₃) ₂ CHNHCH ₂ CH ₂ OCH=CH ₂	79(75)	1.4267	0.8400	10.8	11.2
CH ₃ NHCH ₂ CH(CH ₃)OCH=CH ₂	76(120)	—	—	12.2	12.1
(CH ₃) ₃ CNHCH ₂ CH ₂ OCH=CH ₂	76(43)	1.4282	0.8356	—	^b
C ₆ H ₁₁ NHCH ₂ CH ₂ OCH=CH ₂	70(2)	—	—	—	^c
(CH ₃) ₃ CCH ₂ C(CH ₃) ₂ NHCH ₂ CH ₂ OCH=CH ₂	109(20)	1.4462	0.8515	7.0	6.9
(CH ₃) ₃ CCH ₂ CH(CH ₃)CH ₂ NHCH ₂ CH ₂ OCH=CH ₂	91(2.4)	1.4649	0.8450	6.6	6.5
NH ₂ C(CH ₃) ₂ CH ₂ OCH=CH ₂	70(120)	1.4270	0.8498	—	^d

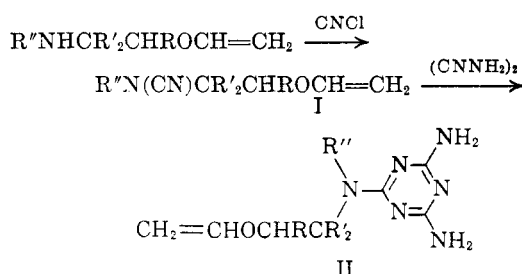
^a The compounds and the data were supplied by W. H. Watanabe, Guy Murdoch, and H. J. Schneider, of this laboratory. ^b 98% pure by vinyl ether determination. ^c Crude distillate, 88% pure by vinyl ether determination. ^d 97% pure by vinyl ether titration.

 TABLE II
 VINOXYALKYL CYANAMIDES


R	R'	R''	Yield, Method ^a %	B.P., °C.(Mm.)	n_D^{25}	Nitrogen	
						Calcd.	Found
H	H	CH ₃	A 93	84-87(1.6)	1.4551 ^b	22.2	22.0
H	H	C ₂ H ₅	B 77	85-88(0.3)	1.4535	20.0	19.2
H	H	(CH ₃) ₂ CH	B 79	77-78(0.2)	1.4510	18.2	17.9
H	H	(CH ₃) ₃ C	A 92	92-95(1.5)	1.4556	16.6	16.4
H	H	C ₆ H ₁₁	A 79	103-105(0.3)	1.4826	14.4	14.3
H	H	(CH ₃) ₃ CCH ₂ C(CH ₃) ₂	A 70	120-125(0.6)	1.4672	12.5	12.3
H	H	(CH ₃) ₃ CCH ₂ CH(CH ₃)CH ₂	A 74	128-132(0.5)	1.4577	11.8	11.7
CH ₃	H	CH ₃	A 90	86-93(0.8)	1.4524	20.0	19.8
H	CH ₃	H	A 83	108-110(2)	1.4590 ^c	20.0	19.8

^a Method A: ClCN process; method B: *t*-butylhypochlorite—NaCN process. ^b d_{25}^{25} 0.9884. ^c d_{25}^{25} 0.9760.

presence of alcoholic alkali² gave 2,4-diamino-6-*N*-alkyl-*N*-vinoxyalkylamino-8-triazines (II).



The intermediate cyanamides were obtained in satisfactory yields (Table II). A convenient alternative to the use of cyanogen chloride involved the treatment of mixtures of the amines and aqueous sodium cyanide with *t*-butyl hypochlorite. The cyanamide produced from aminoethyl vinyl ether polymerized at room temperature. The corresponding melamine (II, R, R', R'' = H) was therefore prepared by the reaction of the amine with 2-

chloro-4,6-diaminotriazine.³ The previously observed stability of secondary *t*-alkyl cyanamides⁴ allowed the preparation of a cyanamide (I, R, R'' = H, R' = CH₃) and its corresponding melamine from 2-amino-2-methylpropyl vinyl ether.

Formation of the substituted melamines (Table VI) was strongly influenced by branching on the carbon atoms immediately adjacent to the amine nitrogen.⁵ Excellent yields were obtained from unbranched cyanamides, while moderate branching led to reduced conversion. Frequently unreacted cyanamide could be recovered. The starting cyanamides were quantitatively recovered when the alkyl group (I, R') was *t*-butyl or 1,1,3,3-tetramethylbutyl.

Another general procedure utilized nitriles (III) obtained by the cyanoalkylation of aminoethyl vinyl ether with cyanohydrins or acrylonitriles (Table III). These aminonitriles could not be converted directly into triazines since they decomposed

(2) W. Zerweck and W. Brunner, U. S. Patent 2,302,162 (Nov. 17, 1942); J. K. Simons, U. S. Patent 2,532,519 (Dec. 5, 1950); D. W. Kaiser, U. S. Patent 2,567,847 (Sept. 11, 1951).

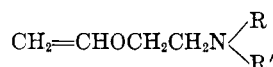
(3) D. W. Kaiser, J. T. Thurston, J. R. Dudley, F. C. Schaeffer, I. Hechenblekner, and D. Holm-Hansen, *J. Am. Chem. Soc.*, **73**, 2984 (1951).

(4) N. M. Bortnick, U. S. 2,606,923 (May 13, 1950).

(5) L. J. Exner and P. L. de Benneville, *J. Am. Chem. Soc.*, **75**, 4666 (1953).

TABLE III
 VINOXYALKYLAMINONITRILES
 $\text{CH}_2=\text{CHOCH}_2\text{CH}_2\text{NHR}$

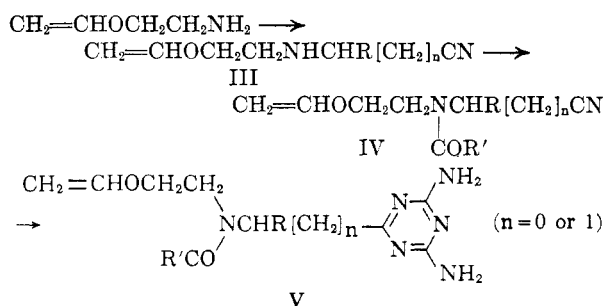
R	B.P., °C.(Mm.)	Yield	n_D^{25}	Nitrogen	
				Calcd.	Found
—CH ₂ CN	123–128(18)	75	1.4563	22.2	21.8
—CH(CH ₃)CN	68–72(0.4)	87	1.4503	20.0	19.7
—CH ₂ CH ₂ CN	79–81(0.4)	70	1.4599	20.0	19.8
—CH—CH(CH ₃) ₂ CN	77–82(0.6)	93	1.4499	16.7	16.6

 TABLE IV
 VINOXYALKYLAMIDONITRILES


R	R'	Yield, %	B.P., °C.(Mm.)	n_D^{25}	Nitrogen	
					Calcd.	Found
CH ₂ CN	CHO	97	^a	1.4702	18.2	18.1
	COOC ₂ H ₅	100	^a	1.4546	14.1	13.6
	COCH ₃	62	113–125(0.25)	1.4760	16.7	16.4
CH(CH ₃)CN	COOC ₂ H ₅	100	^a	1.4525	13.2	12.9
	COCH ₃	88	110–115(0.2)	1.4710	15.4	15.3
	COC ₆ H ₅	100	^a	1.4286	11.5	11.2
CH ₂ CH ₂ CN	CHO	100	^a	1.4880	16.7	16.5
	COOC ₂ H ₅	91	107–112(0.2)	1.4590	13.2	13.0
	COC ₂ H ₅	50	125(0.25)	1.4776	14.3	14.3
	COC ₆ H ₅	100	^a	—	11.5	11.2
	COC ₁₀ H ₂₁	86	^a	—	7.4	7.0
—CH—CH(CH ₃) ₂ CN COCH ₂ CN	COOC ₂ H ₅	97	85–90(0.15)	1.4510	11.7	11.7
	H	99	^a	1.5242	18.2	17.6

^a Reaction concentrates.

under the alkaline conditions of the condensation. By blocking the nitrogen atom with an acyl group, however, amidonitriles (IV) were formed which could be converted to triazines. The intermediate amides were prepared by the treatment of the aminonitriles (IV) with acyl chlorides, ethyl chloroformate, or methyl formate (Table IV). Many of these products could not be distilled, but were obtained as high purity crudes which could be used in the condensation with dicyandiamide to give 2,4-diamino-6-*N*-vinoxylethyl-*N*-acylamidoalkyltriazines (V) (Table VII).



Compounds of type V are fully substituted amides. However, this was not always required. An amidonitrile was obtained in a single step by the

aminolysis of methyl cyanoacetate with aminoethyl vinyl ether and was successfully converted to a triazine containing a partially substituted amide.

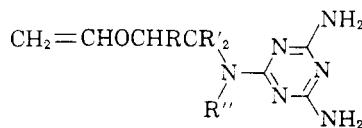
Amidonitriles were also used as intermediates for the synthesis of methacrylamidotriazines. The reaction of methacryloyl chloride with aminonitriles⁶ gave methacrylamidonitriles (Table V) which were converted without difficulty into the desired 2,4-diamino-6-methacryloamidoalkyl-*s*-triazines.

 TABLE V
N-CYANOALKYLMETHACRYLAMIDES

R	R'	Yield	M.P., °C.	Nitrogen	
				Calcd.	Found
H	CH ₂ CH ₂ CN	87	46–48	20.3	20.1
H	C(CH ₃) ₂ CN ^a	81	102–104	18.4	18.2
CH ₃	CH ₂ CH ₂ CN	95	^b	18.4	18.1
C ₆ H ₁₁	CH ₂ CN	91	73–75	13.6	13.6
C ₆ H ₁₁	CH ₂ CH ₂ CN	95	43–44	12.7	12.5

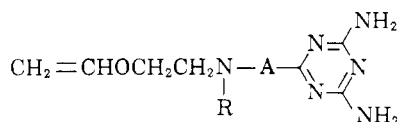
^a See reference 6. ^b B.p. 113–116°(1 mm.), n_D^{25} 1.4755.

(6) R. Jacobson, *J. Am. Chem. Soc.*, **67**, 1996 (1945).

TABLE VI
 N-ALKYL-N-VINOXYALKYLMELAMINES


R	R'	R''	Yield, %	M.P.	Nitrogen	
					Calcd.	Found
H	H	H	^a	148-151	42.8	42.3
H	H	CH ₃	83	137-138	40.0	39.9
H	H	C ₂ H ₅	81	141 ^b	37.5	37.1
H	H	(CH ₃) ₂ CH	28	143-145	38.3	38.5
H	H	C ₆ H ₁₁	42	144-146	30.2	29.8
H	H	(CH ₃) ₃ CCH ₂ CH(CH ₃)CH ₂	63	72-78	25.3	25.2
CH ₃	H	CH ₃	50	95-97 ^c	37.5	37.4
H	CH ₃	H	33	96-98 ^d	37.5	37.3

^a Prepared from diaminochlorotriazine. ^b Recrystallized from 2-butanol. ^c From toluene. ^d From benzene.

 TABLE VII
 N-VINOXYALKYLAMIDOGUANAMINES


A	R	Yield, %	M.P., °C	Nitrogen	
				Calcd.	Found
-CH ₂ -	CHO	40	194-196 ^a	35.3	34.7
	COOC ₂ H ₅	84	147-149	29.8	29.5
	COCH ₃	92	167-168	33.4	32.6
-CH(CH ₃)-	COOC ₂ H ₅	80	140-142	28.4	27.7
	COCH ₃	62	152-154	31.6	31.0
	COC ₆ H ₅	72	190-193	25.6	25.5
-CH ₂ CH ₂ -	CHO	90	145-146 ^a	33.4	33.4
	COOC ₂ H ₅	93	134-136	28.4	28.5
	COC ₆ H ₅	40	156-158	25.6	25.1
	COC ₁₄ H ₃₁	63	112-115 ^b	18.1	18.4
>CH[CH(CH ₃) ₂]	COOC ₂ H ₅	79	141-142 ^c	25.9	26.0
-COCH ₂	H	19	180-182 ^a	35.2	35.9

^a Recrystallized from water; ^b From ethanol; ^c From isopropyl alcohol.

All of the compounds underwent vinyl polymerization and copolymerization in the presence of free radical catalysts. The azo catalysts, α,α' -azodiisobutyronitrile and the azodiisobutyric esters, were particularly useful in the polymerization. The polymers were water-insoluble solids which were solubilized by reaction of the triazine nucleus with formaldehyde. Alkoxyalkyl ethers soluble in common solvents were obtained by acid-catalyzed treatment of these hydroxymethylated polymers with alcohols. Films prepared from these alkoxyalkyl ether polymers catalyzed with strong acids could be insolubilized by heating. Similar effects were observed with copolymers of the triazines with other vinyl monomers, notably acrylic esters and acrylonitrile.

EXPERIMENTAL⁷

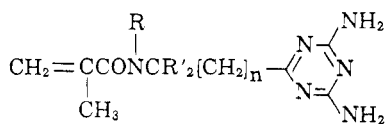
Starting materials. Aminoethyl vinyl ether and its homologs were prepared by the addition of acetylene to alkanol-

amines.⁸ The physical properties of hitherto unreported compounds are listed in Table I.

Vinoxyalkylcyanamides (I). (a) *N-Methyl-N-2-vinoxyethylcyanamide (Method A).* A solution of *N*-methylaminoethyl vinyl ether (404 g., 4 moles) in benzene (1660 ml.) was stirred in a 5-liter, 3-necked round bottom flask fitted with an addition funnel, efficient stirrer, thermometer, and reflux condenser cooled by circulated ice water. A solution of potassium carbonate (300 g.) in water (217 ml.) was added rapidly, followed by liquid cyanogen chloride (246 g., 4.0 moles). The temperature was kept between 10 and 20°. The addition of cyanogen chloride was completed in 75 min.

(7) The assistance of A. J. McFaul, G. E. Gantert, L. J. Exner, and Rita Cerruti in the preparation of specific compounds and to R. P. Fellmann, D. Falgiatore, and L. Souder in polymer preparations is gratefully acknowledged. We are especially indebted to W. H. Watanabe, Guy Murdoch, and H. J. Schneider who supplied the vinyl ethers.

(8) W. Reppe, U. S. Patent 1,959,927 (May 22, 1934); W. Reppe and O. Hecht, U. S. Patent 2,157,347 (May 9, 1939); A. E. Favorskii and M. F. Shostakovskii, *J. Gen. Chem. (USSR)*, 13, 1 (1943); W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, 79, 2825 (1957).

TABLE VIII
 METHACRYLAMIDOGUANAMINES


R	R'	n	Yield, %	M.P., °C.	Nitrogen	
					Calcd.	Found
H	H	1	78	184-185	37.8	37.0
H	CH ₃	0	51 ^{a,b}	175-177 ^c	35.6	35.3
CH ₃	H	1	64	256-257 ^d	35.6	35.4
C ₆ H ₁₁	H	0	82	273-274 ^d	29.0	29.0
C ₆ H ₁₁	H	1	68	220-221 ^d	27.6	27.5

^a Recrystallized from water. ^b Monohydrochloride, obtained from 0.5N hydrochloric acid, no m.p. below 260°. *Anal.* Calcd. for C₁₀H₁₇N₅OCl: Cl, 13.0; found 12.5. ^c Recrystallized from ethanol. ^d From methanol.

After stirring for 2 hr., the slurry was filtered and the solid was washed with benzene. The oil layer obtained from the combined filtrates was distilled to give the oily, colorless product (468 g., 93% yield, b.p. 84-87° (1.6 mm.)). The infrared spectrum showed an intense, sharp peak at 2210 cm.⁻¹, characteristic of cyanamides, and a strong olefinic band at 1624 cm.⁻¹

(b) *N*-Isopropyl-*N*-2-vinoxyethylcyanamide (Method B). A solution of 96% sodium cyanide (28.1 g., 0.55 mole) in water (200 ml.) was stirred and cooled in an ice bath at 15°. 2-*N*-Isopropylaminoethyl vinyl ether (64.5 g., 0.5 mole) was added rapidly, then *t*-butyl hypochlorite (60 g., 0.55 mole) during 3 hr., with the temperature held at 15°. After 4 hr. of additional stirring, the oil layer was removed and combined with toluene extracts (3 × 25 ml.) of the aqueous layer. Distillation gave the colorless, oily product which weighed 76 g. (79%), b.p. 77-78° (1.5 mm.).

Vinoyalkylamidonitriles (III). (a) *N*-2-Vinoyethylglycinonitrile. Glycolonitrile (163 g., of 70% aqueous solution, 2 moles) was added rapidly to aminoethyl vinyl ether (174 g., 2 moles) at 20-30°. After stirring for 5 hr., benzene (300 ml.) was added. The water layer was removed and the benzene solution was distilled to give 190 g. of a colorless oil, b.p. 123-128° (18 mm.). Infrared analysis showed the expected peaks at 3320 (amine stretch), 2235 (C≡N), and 1618 (C=C) cm.⁻¹

(b) 3-*N*-2'-Vinoyethylaminopropionitrile.⁹ Acrylonitrile (106 g., 2 moles) was added to aminoethyl vinyl ether (174 g., 2 moles) with cooling. After 2 hr. of stirring, the orange residue was distilled in two portions after removal of volatile starting materials; the product was obtained as a colorless oil, 196 g., (70%), b.p. 79-81° (0.4 mm.).

N-Vinoyalkylamidonitriles (IV). (a) *N*-Vinoyethyl- α -cyanoacetamide. The addition of aminoethyl vinyl ether (43.5 g., 0.5 mole) to methyl cyanoacetate (49.5 g., 0.5 mole) was accompanied by the evolution of heat. Methanol (100 ml.) was added and the solution was allowed to stand for several days. Evaporation of solvent under reduced pressure gave 78 g. (100%) of a red, viscous oil.

(b) *N*-Vinoyethyl-*N*-cyanomethylformamide. Methyl formate (120 g., 2 moles) and *N*-vinoyethylglycinonitrile (120 g., 1 mole) were refluxed for 8 hrs. Evaporation of excess methyl formate gave a brown oily residue which weighed 150 g. (97%), n_D^{25} 1.4702. The material could not be distilled without extensive decomposition. The reaction concentrate was sufficiently pure for further reaction.

(c) *N*-Vinoyethyl-*N*- β -cyanoethylacetamide. Acetyl chlo-

ride (39.3 g., 0.5 mole) was added slowly to a solution of 3-*N*- β -vinoyethylaminopropionitrile (70 g., 0.5 mole) and triethylamine (50.4 g., 0.5 mole) in benzene (150 ml.) at 15-25° with cooling. Stirring was continued overnight. The partially solid mixture was filtered; triethylamine hydrochloride was washed with benzene. The combined filtrates were evaporated at reduced pressure to give an oily residue (93 g.), which was distilled to give a pale yellow oil weighing 80.5 g. (88%), b.p. 110-115° (0.2 mm.).

(d) *Ethyl N*- β -cyanoethyl-*N*-vinoyethylcarbamate. Ethyl chloroformate (95.4 g., 0.88 mole) was added slowly to a mixture of 3-*N*- β -vinoyethylaminopropionitrile (123 g., 0.88 mole), sodium bicarbonate (74 g., 0.88 mole), and water (275 ml.) at 15-25°. After standing overnight, the mixture was separated. The aqueous layer was extracted twice with 50-ml. portions of chloroform. The extract was combined with the oil layer and the solvent was removed at reduced pressure to give 183 g. (97%) of a red oily residue. Distillation of 60 g. gave 56 g. of a pale yellow oil, b.p. 107-112° (0.2 mm.).

N-Cyanoalkylmethacrylamides. *N*-Cyclohexyl-*N*-cyanoethylmethacrylamide. A solution of cyclohexylaminoacetone nitrile¹⁰ (138 g., 1 mole) in an equal weight of benzene was added to a solution of methacryloyl chloride (52 g.) in benzene (60 ml.) at 40-50° in 90 min. After stirring three hours longer, the slurry was filtered and the solid washed with benzene. The filtrates were washed with dilute hydrochloric acid and with water. Decolorization with Nuchar and evaporation gave 93 g. of the white solid product, m.p. 73-75°.

Other *N*-alkylmethacrylamidonitriles were prepared by this method. α -Methacrylamidoisobutyronitrile and β -methacrylamidopropionitrile were obtained by the method of Jacobson.⁶ The solid collected by filtering the reaction slurry was washed with potassium carbonate to dissolve the aminonitrile hydrochloride, then with water. The crude products, which were insoluble in either benzene or water, were purified by recrystallization from water.

Condensation with dicyandiamide. 2-*N*-Methyl-*N*-vinoyethylamino-4,6-diamino-*s*-triazine. A slurry of *N*-methyl-*N*-vinoyethylcyanamide (302 g., 2.4 moles), dicyandiamide (240 g., 2.82 moles), and isopropanol was stirred and heated to reflux. The heating bath was removed and a solution of potassium hydroxide (48 g.) in isopropanol (400 g.) was added in 20 min. Vigorous boiling occurred during the addition of catalyst and was controlled by occasional cooling. Heating and stirring was continued for 6.5 hr. The hot mixture was filtered to remove insoluble materials which were washed with 100 ml. of hot isopropanol. The combined filtrates were cooled. The product which separated was collected and washed with warm water to remove some color and unreacted dicyandiamide. After drying, the crystalline white solid weighed 418 g. (83%), m.p. 137-138°.

Other triazines were prepared in a similar manner. The product often separated in pure state and required no further treatment. In some instances, recrystallization was necessary; the solvents used are indicated in the tables. Analogous melamines bearing a long *N*-alkyl group, such as 3,5,5-trimethylhexyl, were extremely soluble in all organic solvents and the crude reaction product could not be purified.

2,4-Diamino-6-*N*-vinoyethylamino-*s*-triazine. A mixture of aminoethyl vinyl ether (17.4 g., 0.2 mole), 2-chloro-4,6-diaminotriazine (29 g., 0.2 mole), sodium carbonate (11 g.), and water (150 ml.) was heated under reflux for 4 hr. The red solid was collected and washed with water and hot ethyl acetate to give 21 g. (53%) of a slightly tan solid, insoluble in most solvents, m.p. 148-151°.

Anal. Calcd. for C₇H₁₂N₆O: N, 42.8. Found: N, 42.3.

Polymerization of 2-N-methyl-N-vinoyethylamino-4,6-diamino-s-triazine. A solution of 2-*N*-methyl-*N*-vinoyethyl-

(9) H. Bruson, U. S. Patent 2,601,251 (June 24, 1952) has cited this compound without describing its synthesis or properties.

(10) L. J. Exner, P. L. de Benneville, and L. S. Luskin, *J. Am. Chem. Soc.*, 75, 4841 (1953).

amino-4,6-diamino-s-triazine (21.5 g.) in an equal amount of dimethylformamide was heated under nitrogen in a citrate bottle in the presence of dimethyl α,α' -azodiisobutyrate (0.32 g.) at 75° for 16 hr. The polymer was precipitated from the viscous solution on the addition of acetone, and filtered. It was washed with hot acetone and hot isopropyl alcohol to remove monomer. The dry polymer weighed 20 g. (93%). It was insoluble in common solvents, but dissolved in formic or acetic acid and in dilute aqueous mineral acids, using at least equivalent amounts of acid.

Similar polymers were also obtained from *N*-methyl-*N*-2-vinoxypropyl-melamine, *N*-1,1-dimethyl-2-vinoxyethyl-melamine, *N*-cyclohexyl-*N*-vinoxyethylmelamine, and methacrylamidoisobutyroguanamine in 40, 74, 52, and 90% yields, respectively.

Hydroxymethylation of polymer from N-methyl-N-vinoxyethylmelamine. The polymelamine (2.1 g., 0.01 mole) was heated with a solution of 36% aqueous formaldehyde (8.2 g., 0.1 mole) and water (10 ml.) made slightly basic with sodium carbonate. After 10 min. at 80–90° and 10 min. at 60°, the clear solution was cooled and carefully acidified with 10 ml. of 0.5*N* hydrochloric acid (0.005 mole). The resulting solution could be diluted further without separation of insoluble material.

Reaction of hydroxymethylated polymer with alcohols. A solution was prepared as before from the polymelamine (2.1 g.) and 37% aqueous formaldehyde solution (5 g., 0.06 mole). Methanol (about 5 ml.) was added until turbidity appeared and the pH was adjusted to 5.0 with formic acid.

After heating at 60° for 10 min., more methanol was added and the heating repeated. Evaporation to dryness gave a clear, viscous oil soluble in alcohols.

The resin, when repeatedly evaporated with 13-g. portions of *n*-butanol to remove water and methanol, gave a clear, viscous oil soluble in xylene. The original polymer and its hydroxymethylated derivative are insoluble in xylene.

Copolymer of methyl methacrylate and methacrylamidoisobutyroguanamine. A solution of methyl methacrylate (95 g., 0.95 mole) and methacrylamidoisobutyroguanamine (11.8 g., 0.05 mole) in 2-ethoxyethyl acetate (131 g.) was heated at 100° in a nitrogen atmosphere, using benzoyl peroxide (2 g.) as initiator. Additional initiator (0.4 g. total) in the same solvent (15 g.) was added during the heating period of 4.5 hr. A portion of the final, very viscous solution was treated with excess hot methanol to precipitate polymer. A dry, brittle solid, soluble in ethoxyethyl acetate, was obtained. Analysis indicated that a true copolymer had been produced; N, calcd. 3.9; found, 3.3. A portion of the copolymer solution was mixed with a 40% solution of formaldehyde in butanol (20% by weight of polymer solids) and paratoluenesulfonic acid (1% based on polymer solids). The resultant mixture was filmed and baked at 150° for 30 min. to give films of extreme hardness (8H-Koh-i-noor pencil) and exceptional resistance to lacquer solvents.

Copolymers containing 10 mole per cent of the guanamine were also prepared and possessed similar properties.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BRITISH COLUMBIA]

Reaction of Aromatic Ketoximes with Carbon Monoxide and Hydrogen¹

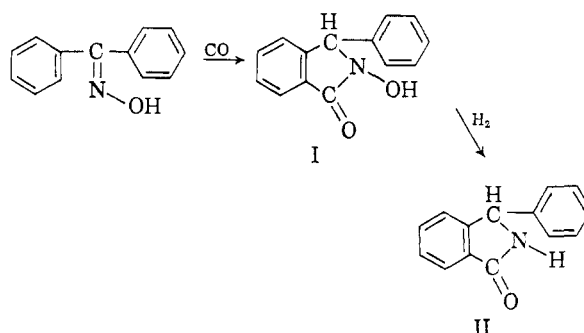
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A new synthesis of 3-phenyl, 3-methyl, and 3-benzylphthalimidine as well as of 3-phenyl-3,4-dihydroisocarbostyryl has been achieved by application of the oxo reaction to aromatic ketoximes. Carbon monoxide and hydrogen also reacted with methyl phenyl ketoxime to give a dimer described tentatively as 3,4-dimethyl-3,4-diphenyl-2-azetidione. The infrared spectra of the phthalimidines, isocarbostyryl, and the dimer product are described.

The oxo reaction² is an established procedure for converting olefins to aldehydes or alcohols. The application of this reaction to several aromatic ketoximes is here described.

Benzophenone oxime reacted with carbon monoxide and hydrogen (98.5:1.5) at 4100 p.s.i. and at 250° in the presence of preformed dicobalt octacarbonyl as catalyst to yield 3-phenylphthalimidine (II) in about 80% yield. The structure of II was established by direct comparison with an authentic sample of 3-phenylphthalimidine.³ Presumably 3-phenylphthalimidine was produced from the expected *N*-hydroxyphthalimidine (I) by reduction



of the latter with hydrogen. The infrared absorption data of 3-phenylphthalimidine are recorded in the experimental. Our observations (absorption at 1675 and 1600 cm.⁻¹) agree with the bands for an α - β -unsaturated lactam reported by Edwards and Singh.⁴ *o*-Benzoylbenzoic acid oxime also gave 3-phenylphthalimidine in almost quantitative yield.

When methyl phenyl ketoxime reacted with

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(2) I. Wender, H. W. Sternberg, and M. Orchin, *Catalysis*, edited by P. H. Emmett, Reinhold Publishing Corp., New York, N. Y., 1957, Vol. 5, p. 73.

(3) R. E. Rose, *J. Am. Chem. Soc.*, **33**, 388 (1911).

(4) O. E. Edwards and Tara Singh, *Can. J. Chem.*, **32**, 683 (1954).