ketone, but whether this actually is a reaction of CF_2 and not of its precursor is not certain: P. Hodge, J. A. Edwards, and J. H. Fried, *Tetrahedron Lett.*, 5175 (1966).

(7) (a) C. Ainsworth, *Can. J. Chem.*, **43**, 1607 (1965); (b) R. Madhavan and V. R. Srinivasan, *Indian J. Chem.*, **7**, 760 (1969).

(8) At 80°, the reaction of $PhHgCCl_2Br$ with mesityl oxide and methyl acrylate gave only the respective dichlorocyclopropanes: D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, **87**, 4259 (1965).

(9) D. Seyferth and R. L. Lambert, Jr., *J. Organometal. Chem.*, **16**, 21 (1969).

(10) H. Bock, G. Rudolph, and E. Baltin, *Chem. Ber.*, **98**, 2054 (1965).

(11) D. von der Brück, R. Bühler, and H. Plieninger, *Tetrahedron*, **28**, 791 (1972).

Hydrogen Cyanide Chemistry. VIII. New Chemistry of Diaminomaleonitrile. Heterocyclic Synthesis[1]

R. W. Begland, D. R. Hartter, F. N. Jones, D. J. Sam, W. A. Sheppard,*
O. W. Webster, and F. J. Weigert

Contribution No. 2112 from the Central Research Department, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware 19898.

Received March 25, 1974

Alkyl derivatives of diaminomaleonitrile (DAMN), are prepared by direct methylation and by reduction of Schiff bases. Cyclic anhydrides and DAMN produce amide acids. 2,3-Dicyanodiazepines and 2,3-dicyanodihydrodiazepines are prepared by condensation of DAMN with 1,3-diketones or other carbonyl derivatives. 2-Substituted 4,5-dicyanoimidazoles are prepared by improved cyclization procedures of Schiff bases and amides of DAMN. Tetrasubstituted pyrazines are prepared by condensation of DAMN with diimines prepared from alcohols and cyanogen.

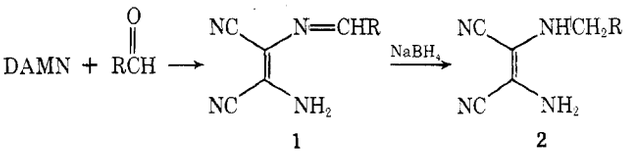
Diaminomaleonitrile (DAMN), a weakly basic diamine resembling *o*-phenylenediamine in reactivity, can be prepared directly from hydrogen cyanide by oligomerization[2] and indirectly by hydrogenation of diiminosuccinonitrile.[3] DAMN has been proposed to be an essential intermediate to purines in prebiotic origin of life[4] and has been used to prepare a variety of heterocyclic compounds, including 4,5-dicyanoimidazoles,[5,6] 5,6-dicyanopyrazines,[1,7] and purines[8] (including caffeine[5]), as well as amides[5,7a,9] and Schiff bases.[7a,9] We now report synthesis of new alkyldiaminomaleonitriles and seven-membered diazaheterocycles from DAMN; also we have extended the synthesis of five- and six-membered heterocycles and Schiff bases from DAMN.

Results and Discussion

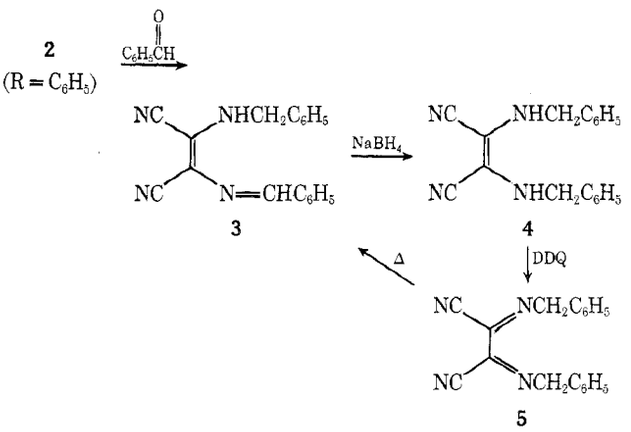
Schiff Bases of Diaminomaleonitrile. DAMN condenses rapidly with aliphatic and simple aromatic aldehydes in methanol without a catalyst.[7a,9] However, if the aldehyde is substituted by a strong electron-withdrawing group, acid catalysis (sulfuric acid) is required to make the condensation proceed at a reasonable rate. For amides, phosphorus oxychloride promotes condensation and the product may be isolated as a hydrochloride.

***N*-Alkyldiaminomaleonitriles.** Di-(*tert*-octylamino)-maleonitrile has been prepared indirectly from reaction of diisobutene, hydrogen cyanide, and hydrogen fluoride.[10] *N*-Alkyldiaminomaleonitriles (alkyl group is ethyl, isopropyl, *tert*-butyl, and cyclohexyl) and *N,N'*-dialkyldiaminomaleonitriles (alkyl group is isopropyl and cyclohexyl) have been prepared in low yield from *N*-alkyliminoacetonitriles.[11] Di-(*tert*-butylamino)maleonitrile was obtained in low yield by oligomerization of *tert*-butyl isocyanide with hydrogen chloride followed by hydrolysis.[12]

DAMN can be converted indirectly to an *N*-alkyl derivative **2** by conversion to Schiff base **1** followed by reduction. *N*-Benzyldiaminomaleonitrile results from a benzaldehyde anil (**1**, R = C_6H_5) and *N*-alkyldiaminomaleonitriles are prepared from aliphatic aldehydes (R = cyclohexyl and *tert*-butyl). Schiff base **1** does not react with a second mole of aldehyde but *N*-benzyldiaminomaleonitrile (**2**, R = C_6H_5) forms Schiff base **3**, which can be reduced

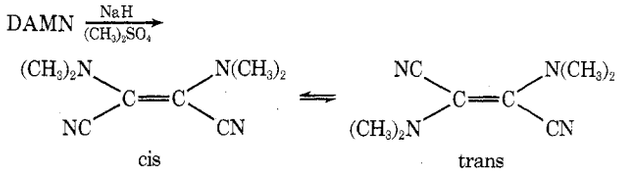


to *N,N'*-dibenzyldiaminomaleonitrile (**4**). This new DAMN derivative was oxidized to dibenzyldiiminosuccinonitrile (**5**), which on standing isomerizes to **3** and an



isomer that also is reduced to **4**. Schiff base **3** has four possible isomeric forms about the imine and the carbon–carbon double bond. The structure of the intermediate **1** was established as the Schiff base rather than the isomeric dihydroimidazole by the presence of a low-field =CH proton in the nmr.

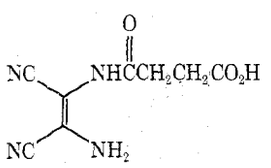
Direct tetramethylation of DAMN was accomplished by reaction of DAMN with excess sodium hydride at −30 to −20° to form the colorless monoanion followed by treatment with dimethyl sulfate at −10°. Nmr showed the



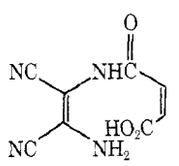
product to contain about 15% bis(dimethylamino)fumaronitrile (trans), and pure bis(dimethylamino)maleonitrile (cis) was isolated by low-temperature crystallization. On slow distillation of the crude reaction product, the cis isomer isomerizes to the lower boiling trans isomer.[13] Both cis and trans forms *isomerize* to the equilibrium mixture, 43% trans. The isomerization in DMSO at 105° is slow unless iodine is added as a catalyst. This is in marked contrast to DAMN, in which the cis configuration is much more stable than the trans[14] and is similar to bis(methylmercapto)maleonitrile and bis(methylmercapto)fumaronitrile, where the cis and trans forms equilibrate at 191° in 9 hr (melt, iodine catalysis) to 32% trans.[15] The cis and trans assignments of the tetramethylated products are based on their dipole moments in dioxane (Table I) and are similar to the bis(methylmercapto)dicyanoethylenes.[15] The C=C stretch absorption for the methylated cis isomer is as expected (see Table I). The strong absorption for the trans isomer is not normal (note trans methylmercapto derivatives) and could result if the double bond is slightly twisted or if one of the dimethylamino groups is held out of plane of the molecule by steric interaction. The dipole moment of 2.78 D for the trans isomer is higher than expected (calculated value employing group moments for the aromatic series is 1.50). The calculated value for the cis isomer (9.78 D) is also higher than the measured value (calculated value for DAMN is 9.62 D; these high values could result from use of group moments that are determined from aromatic systems). The steric interaction of dimethylamino groups is expected to be much more significant than for the methylmercapto group. The marked stability of cis over trans isomers in diaminodicyanoethylenes is not understood but may be analogous to the 1,2-dithiodicyanoethylenes.[15]

Amides and Ureas from Diaminomaleonitriles. Amides of DAMN have been reported from reaction of acyl halides and anhydrides with DAMN.[5,6,7a,9,16]

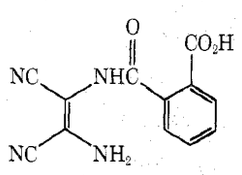
Some new amides with free acid groups (**6**, **7**, and **8**) are readily prepared by reaction of succinic, maleic, and phthalic anhydride with DAMN. With phthalic anhydride the imide **9** was also isolated in 21% yield.



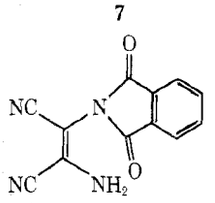
6



7



8



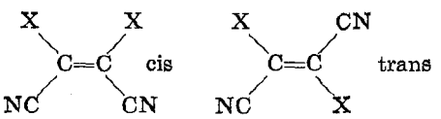
9

The acrylamide of DAMN was formed from acryloyl chloride and DAMN. Low molecular weight polyamides can be prepared from reaction of DAMN with diacid chlorides and will be described in other publications.

DAMN with phenyl isocyanate gives a monourea **10** at room temperature in CH_3CN and a diurea **11** in DMF at 80°.

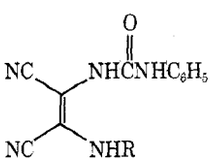
Synthesis of Heterocycles. Five-Membered Rings. The synthesis of 4,5-dicyanoimidazoles[5,6] has been extended to preparation of a series of 2-alkyl and 2-aryl derivatives. The Schiff bases **1** from condensation of DAMN with aldehydes can be oxidized to imidazoles **12** by reagents such as diiminosuccinonitrile (DISN) or dichlorodicyanoquinone (DDQ). A series of 2-aryl-4,5-dicyanoimidazoles was prepared to determine the structure of products from reaction of diazodicyanoimidazole with halobenzenes.[17]

Table I
Dipole Moments and Infrared Absorption of 1,2-Dicyanoethylene Derivatives

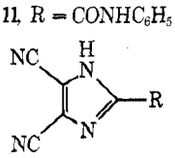


X	Isomer	Dipole moment, D	C=C stretch, cm^{-1}	Registry no.
NH_2	Cis	7.9[a]	1626 (s)	1187-42-4
$N(CH_3)_2$	Cis	6.98	1605 (s)	51801-84-4
	Trans	2.78	1600 (s)	51801-85-5
SCH_3	Cis	5.08	1493 (s)	7373-02-6
	Trans	1.57	None	7373-03-7

[a] R. L. Webb, S. Frank, and W. C. Schneider, *J. Amer. Chem. Soc.*, **77**, 3491 (1955).

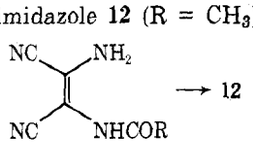


10, R = H
11, R = $CONHC_6H_5$



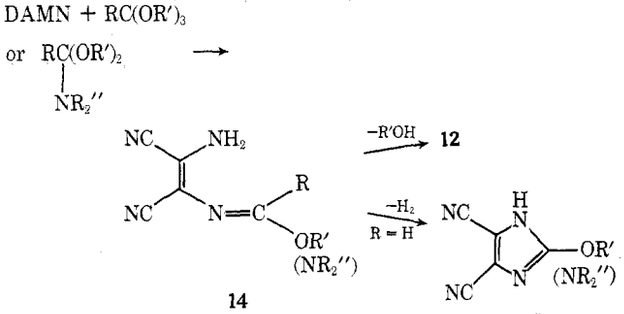
12

Condensation of DAMN with acid chlorides or anhydrides gives 1:1 products **13** which for R = CH_3 can be dehydrated to the imidazole **12** (R = CH_3). Imidazoles can



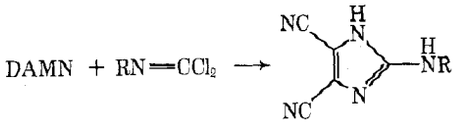
13

be produced from DAMN in one step from ortho esters[5] or imino ether hydrochlorides.[6] If the initial condensation of DAMN and ortho esters or ortho amides is run under mild conditions, the intermediate alkoxy imine or amidine **14** can be isolated. Amidines, **14**, can also be made by treatment of DAMN with *N,N*-dialkylamides and $POCl_3$. Oxidation of **14** leads to a new family of 2-heterosubstituted imidazoles **15**.[18] Other N-substituted aminoimidazoles **16**



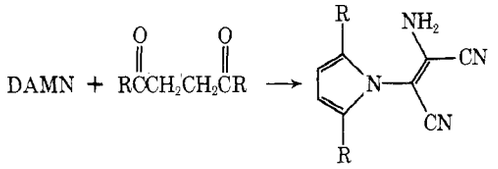
14 **15**

can be prepared from DAMN and isocyanide dichlorides. The parent 2-amino-4,5-dicyanoimidazole (**16**, R = H) is prepared from DAMN and cyanogen chloride and is used to prepare the reactive diazodicyanoimidazole.[17]



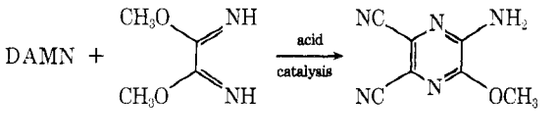
16

DAMN reacts with 1,4-diketones to give substituted pyrroles **17**.



17, R = CH_2, C_6H_5

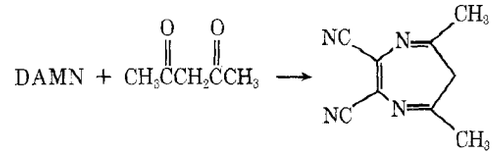
Six-Membered Rings. The synthesis of aminocyanopyrazines by condensation of DAMN with DISN is a major synthetic development.[1] The condensation of DAMN with 1,2-dimethoxy-1,2-diiminoethane (methanol–cyanogen adduct) leads to tetrasubstituted pyrazine **18**. As in



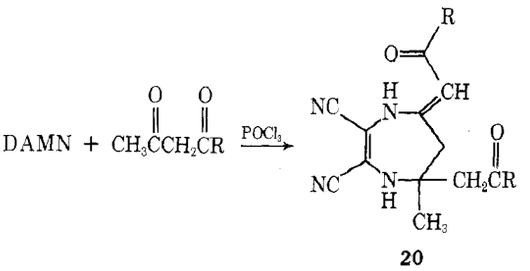
18

DISN–DAMN condensation, the amount of acid is critical to control the condensation to give a single major product. The synthesis of 5,6-dicyano-2-arylpyrazines[19] has been extended to preparation of 2-methyl-5,6-dicyanopyrazine by condensation of α-chloroacetone or pyruvaldehyde with DAMN.

Seven-Membered Rings. DAMN condenses with acetylacetone to give the 6*H*-1,4-diazepine **19**. Benzoylacetophenone and β-keto esters give uncyclized products under mild conditions, but methyl acetoacetate and *N,N*-dimethylacetoacetamide gave the tetrahydro-6*H*-1,4-diazepine **20** when phosphorus oxychloride was used as catalyst.



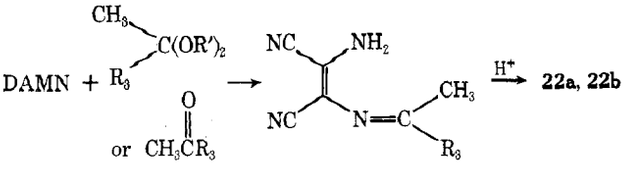
19



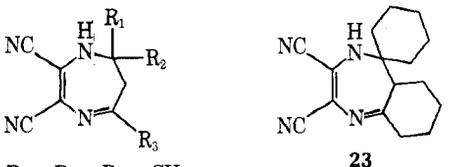
20

R = OCH_3 or $N(CH_3)_2$

Under very mild conditions the Schiff base from DAMN and acetophenone ketal **21** (R_3 = C_6H_5) can be isolated, but it readily hydrolyzes in moist air. However, with an acid catalyst DAMN condenses with 2 mol of ketones or their ketals to give a variety of 1,7-dihydro-6*H*-1,4-diazepines (**22a, 22b**), including the unusual spiro dihydrodiazepine **23** from cyclohexanone. Dihydrodiazepines (**22a, 22c, 22d, 22f**) can also be produced from DAMN and α,β-unsaturated ketones. However, cinnamaldehyde gives only the Schiff base.[9] The diazepine **24b** was produced from



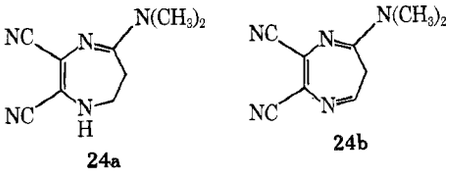
21



23

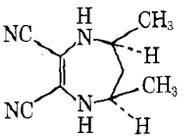
22a, R_1 = R_2 = R_3 = CH_3
b, R_1 = CH_3; R_2 = R_3 = C_6H_5
c, R_1 = R_2 = H; R_3 = CH_3
d, R_1 = H; R_2 = C_6H_5; R_3 = CH_3
e, R_1 = H; R_2 = R_3 = CH_3
f, R_1 = H; R_2 = R_3 = C_6H_5

condensation of DAMN with *N,N*-dimethylacrylamide to give **24a** followed by oxidation with DDQ.



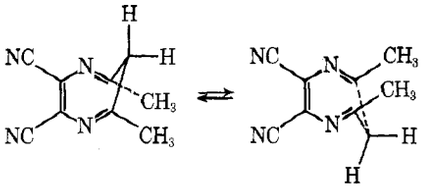
24a **24b**

Diazepine **19** was reduced to the 1,4,5,7-tetrahydro-6*H*-1,4-diazepine **25**, which is a cyclic dialkyl DAMN derivative. Only the cis product was formed, since the proton nmr showed multiplets of equal intensity for the two C-6 protons. Compound **25** oxidized readily to the dihydrodiazepine **22e**.

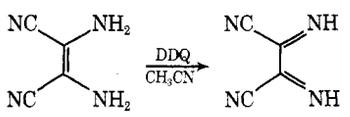


25

The room-temperature pmr spectrum of diazepine **19** showed only a single line which resolved at low temperature (−30° in acetonitrile solution) to the expected singlet for the two methyl groups and an AB δ 1.94 and 4.41 (J_{AB} = 10 Hz) for the methylene. The low-temperature chemical shift and the coalescence temperature (about room temperature) indicate a moderately low free energy of activation for the ring-inversion process. A similar nmr spectrum was observed for a benzodiazepine derivative.[20]

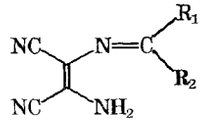


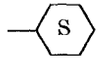
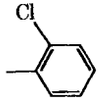
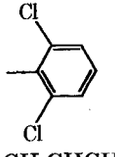
Oxidation and Hydrolysis of Diaminomaleonitrile. The chlorination of DAMN led to dichlorodiiminosuccinonitrile, presumably by initial oxidation of DAMN to DISN.[3] Direct oxidation of DAMN to DISN has been accomplished in essentially quantitative yield by treatment of DAMN with DDQ in acetonitrile.



DAMN DISN

Table II
Diaminomaleonitrile Schiff Bases and Amidines[a]



R_1	R_2	Registry no.	Method[b]	Yield, %	Crystn soln	Mp, °C	Ir, cm^{-1}	Nmr, δ
CH_2CH_3	H	51801-86-6	A	68	Ether–hexane	71–72	3425, 3300, 2250, 2210, 1630, 1610, 1470, 1380, 1100, 893	
$CH(CH_3)_2$	H	51801-87-7	A	87	Ether–hexane	82–83	3425, 3320, 2250, 2210, 1610, 1460, 1385, 1315, 975	($CDCl_3$) 1.10 (6 H, d, CH_3), 2.50 (1 H, m, CH), 5.37 (2 H, br s, NH_2), 7.85 (1, H, d, CH)
$C(CH_3)_3$	H	51801-88-8	A	85	Hexane	86–88	3425, 3300, 2250, 2210, 1620, 1465, 1385, 1360, 943, 916	($CDCl_3$) 1.10 (s, 3 CH_3), 5.40 (2 H, br s, NH_2), 7.78 (s, CH)
$CH(CH_2)_3CH_3$ CH_2CH_3	H	51801-89-9	A	81	Hexane	51–52	3425, 3330, 3175, 2210, 1610, 1000–900 (br)	
	H	51801-90-2	A	60	Ether–hexane	89–90	3425, 3300, 2250, 2210, 1610, 1590, 1460, 1380, 1360	
	H	51801-91-3	B	89	THF–anisole	222–223	3464, 3426, 3334, 2240, 2204, 1608, 1604, 1590, 1570, 1563	
	H	51801-92-4	B	88	Ethyl acetate	199–200	3455, 3320, 2240, 2200, 1610, 1578, 1548	
CH_2CHCH_3 OH	H	51801-93-5	A	79	THF–hexane	133–135	3225, 3125, 2200, 1640, 1600, 1460, 1380, 1140, 1110, 1075, 955, 930	1.00 (3 H, d, CH_3), 2.35 (2 H, t, CH_2), 3.88 (1 H, m, (CHO), 4.60 (1 H, d, OH), 7.35 (2 H, br s, NH_2), 7.68 (1 H, t, CH)
C_6H_5	CH_3	51802-34-7	B	65	Petroleum ether	123–123.5		
CF_3	H	51801-94-6	B	28	Benzene	154–155	3375, 3270, 3150, 2195, 1640, 1620, 1580	7.7 (1 H, m)
$N(CH_3)_2$	H	51801-95-7	C	60	Benzene	152–154	3570, 3450, 2270, 2250, 1610, 1430, 1350, 1270, 1240, 1120, 890	2.95, 3.08 (ss, 2 CH_3), 5.83 (NH_2), 7.59 (s, =CH)
$N(CH_3)_2$	CH_3	51801-96-8	C	54	Benzene	110–112	3400, 3300, 2205, 2195, 1565	2.15 (s, 3 H), 3.05 (s, 6 H), 4.4 (m, 2 H)
$N(CH_2CH_3)_2$	CH_3	51801-97-9	D	57	Methanol–ether	185–186	3600, 3360, 2240, 1640, 1600	1.1 (t, J = 6 Hz, 6 H), 2.2 (s, 3 H), 3.6 (m, 4 H), 8.4 (m, 2 H)
$N(CH_2CH_3)_2$	$CH_2CH_2CH_3$	51801-98-0	D	27	Methanol–ether	188–189	3300–3000, 2185, 1640, 1585	0.9–1.7 (m, 11 H), 2.3–2.6 (m, 2 H), 3.4–3.7 (m, 4 H), 8.5 (br, 2 NH)

$N(CH_3)_2$	CH_2CH_3	51801-99-1	D	35	Methanol–ether	185–186	3300, 3150, 2230, 1650, 1600	1.35 (t, J = 7.5 Hz, CH_3), 2.80 (q J = 7.5 Hz, CH_2) 3.45 (br, NCH_3)
[c]	H	51802-00-7	B	100	None	>280	3425, 3300, 3195, 2240, 2210, 1605, 1570, 1510	Insoluble
		51802-01-8	C	55	Benzene	159–160	3450, 3360, 2225, 2210, 1620, 1590, 1575	2.1 (m, 2 H), 2.8 (m, 2 H) 2.91 (s, 3 H), 3.49 (t, 2 H), 5.2 (m, 2 H)
		51802-02-9	C	67	Benzene	132–135	2980, 2210, 1640, 1605, 1565	3.10 (s, 12 H), 7.98 (s, 2 H)

[a] Satisfactory analytical data for C, H, and N were reported for all new compounds listed in the table. [b] See Experimental Section for general procedure. [c] From terephthalaldehyde.

Hydrolysis of DAMN in alkali solution leads to glycine, ammonia, and carbon dioxide or with barium hydroxide to oxalic acid, ammonia, and carbon dioxide.[21a] With alkaline peroxide, DAMN is quantitatively converted to oxamide.[21b]

Experimental Section

The ir spectra were obtained on a Perkin-Elmer Model 21 spectrometer; the uv spectra on a Cary Model 14; the nmr spectra on a Varian A-60; and the mass spectra on a Du Pont CEC 21-110B high-resolution double-focusing instrument. Where a number of compounds were made by a more or less standard procedure a typical method is given and the compounds are listed in tables. The petroleum ether used boiled at 37–50°.

Diaminomaleonitrile Schiff Bases and Amidines (Table II). Method A. Aldehyde plus DAMN in Methanol, No Catalyst. See ref 7a and 9.

Method B. Acid Catalysis. 2-Amino-3-(2,2,2-trifluoroethylideneamino)maleonitrile (1, R = CF_3). To a solution of 5.4 g (0.05 mol) of DAMN in 100 ml of THF was added 5 drops of H_2SO_4. Fluoral gas (9.8 g, 0.10 mol) was passed over the solution and maintained in the flask with a Dry Ice condenser. After a mild exotherm, the resulting solution was stirred for 4 hr and stripped and the resulting solid–oil was dried on a porous plate to give a white solid. Recrystallization from benzene gave 2.64 g (28%) of white needles: mp 154–155° dec; ir (Nujol) 3375, 3270, 3150, 2195, 1640, 1620, and 1580 cm^{-1}; nmr (acetone-d_6) δ 7.7 (multiplet).

Method C. Amide Condensation, Phosphorus Oxychloride Catalysis. 2-Amino-3-(*N,N*-dimethylaminoethylideneamino)-maleonitrile (14). To a solution of 4.0 g (0.037 mol) of DAMN in 30 ml of dimethylacetamide at 10° was added dropwise over 10 min 4.8 g (0.031 mol) of $POCl_3$. The temperature rose to 30° and a precipitate formed. After 1.5 hr 400 ml of cold water was added and the resulting solution was neutralized with concentrated ammonium hydroxide. The precipitate was collected, dissolved in 150 ml of chloroform, and dried over anhydrous $MgSO_4$ and the solvent was removed to give 3.5 g (54%) of 2-amino-3-(*N,N*-dimethylaminoethylideneamino)maleonitrile.

Method D. Amide Condensation, Phosphorus Oxychloride Catalysis, Hydrochloride Isolation. 2-Amino-3-(*N,N*-diethylaminobutylideneamino)maleonitrile Hydrochloride (14). To a solution of 10.8 g (0.10 mol) of DAMN and 20 g of *N,N*-diethylbutyramide in 100 ml of THF was added 10 ml of $POCl_3$ over 10 min. After stirring for 1.5 hr the resulting tan solid was collected and recrystallized from methanol–ether.

These and other Schiff bases and amidines prepared by these methods are listed in Table II.

Alkyl Derivatives of Diaminomaleonitrile (Table III). Method A. Reduction of Diaminomaleonitrile Schiff Bases. *N*-Benzyldiaminomaleonitrile (2, R = C_6H_5). To a solution of 3.92 g (0.02 mol) of Schiff base (1, R = C_6H_5) in 50 ml of methanol and 75 ml of THF was added 0.76 g (0.02 mol) of sodium borohydride in portions. This solution was stirred for 15 min and poured into 500 ml of ice water. The resulting precipitate was collected and dried to give 3.63 g (90%) of 2 (R = C_6H_5) as a light tan powder. Recrystallization from ether–petroleum ether gave light yellow needles: mp 114–116°; ir (Nujol) 3450, 3355, and 3250 ($-NH_2$, NH), 2220 and 2210 (–CN), 1640, 1620, and 1590 cm^{-1} (C=C, C=N, $-NH_2$); uv (CH_3CN) 311 mμ (ϵ 15,800); nmr (acetone-d_6) δ 4.32 (s, 2), 4.9 (br, 3), 7.35 (s, 5). See Table III for analysis.

***N*-Benzyl-*N'*-benzylidinediaminomaleonitrile (3).** To a solution of 6.0 g (0.03 mol) of 2 in 100 ml of ether was added 3.7 g (0.035 mol) of benzaldehyde and 5 drops of concentrated H_2SO_4. A mild exotherm occurred and a yellow precipitate slowly formed. After 1 hr the solid was collected and rinsed with ether to give 8.2 g (95%) of 3. Recrystallization from ethyl acetate gave bright yellow crystals: mp 182.5–184.0°; ir (KBr) 3345 (NH), 3060 (=CH–), 2240 and 2200 (–C≡N), 1610, 1585, and 1500 cm^{-1} (C=C and C=N); uv (CH_3CN) 263 mμ (ϵ 15,600), 379 (28,600), 397 (22,500); nmr (DMSO-d_6) δ 4.64 (s, 2), 7.40 (m, 8), 8.10 (m, 2), 8.35 (s, 1), 8.75 (br, 1). For reduction of this compound see Table III.

Anal. Calcd for $C_{18}H_{14}N_4$: C, 75.5; H, 4.9; N, 19.6. Found: C, 75.6; H, 4.9; N, 19.7.

***N,N*-Dibenzyldiiminosuccinonitrile (5). Synthesis and Rearrangement to *N*-Benzyl-*N'*-benzylidinediaminomaleonitrile (3).** A solution of 2.88 g (0.01 mol) of 4 in 75 ml of benzene was cooled to 7° and added to a cold solution of 2.27 g (0.01 mol) of DDQ in 75 ml of benzene. Dihydrodichlorodicyanoquinone imme-

diately precipitated. The resulting mixture was stirred for 15 min and filtered cold and the benzene was removed under reduced pressure to give 2.60 g (91%) of 5 as a yellow powder: ir (Nujol) no -NH, 2240 and 2210 (weak, -CN), 1620, 1600, and 1580 cm^{-1} (-C=N and C_6H_5); nmr ($CDCl_3$) δ 5.21 (s, 4), 7.38 (s, 10).

Recrystallization of 5 from benzene gave complete conversion to 3. Upon standing at room temperature for several days or upon recrystallization from ether, 5 is converted into an unknown isomer of 3 and upon heating is converted to 3. The unknown isomer shows ir (KBr) 3310 (-NH), 3030 (=CH), 2240 and 2200 (-CN), 1620, 1590, and 1500 cm^{-1} (-C=N and C_6H_5); uv λ_{max} (CH_3CN) 265 mμ (ϵ 11,100), 367 (30,000).

Anal. Calcd for $C_{18}H_{14}N_4$: C, 75.5; H, 4.9; N, 19.6. Found: C, 75.3; H, 4.7; N, 19.7.

Method B. Alkylation of Diaminomaleonitrile. Bis(dimethylamino)maleonitrile and Bis(dimethylamino)fumaronitrile. A solution of 54.0 g (0.50 mol) of DAMN in 300 ml of glyme was added dropwise to a suspension of 2.5 mol of sodium hydride in 1 l. of glyme at −30 to −20°. Hydrogen (13.3 l.) was evolved. The reaction mixture was warmed to −10° and 237 ml (2.5 mol) of dimethyl sulfate was added over 3.0 hr. During the addition 38.2 l. of hydrogen was produced. The reaction mixture was stirred for 1 hr at −10° and filtered. The precipitate of unreacted sodium hydride and sodium methyl sulfate was washed with 500 ml of glyme and the combined filtrate and wash was concentrated at room temperature to about 250 ml of solution containing dimethyl sulfate, bis(dimethylamino)maleonitrile, and bis(dimethylamino)fumaronitrile (nmr). The ratio of maleo- to fumaronitrile product was 85:15. On cooling the mixture to −80° bis(dimethylamino)maleonitrile crystallized (44.3 g, 54%). An analytical sample was recrystallized at −80° from glyme: mp 35–36°; ir (KBr) 2985, 2200, 1605, 1480, 1460, 1380, 1175, 1135, 1105, 1060, 1030, 870 cm^{-1}; uv λ_{max} (CH_2Cl_2) 328 nm (ϵ 8540); dipole moment 6.98 D (dioxane); nmr ($CDCl_3$) δ 2.75 (s).

The mother liquor from the crystallization of the cis-methylated product was slowly distilled through a spinning band column (5 hr). Bis(dimethylamino)fumaronitrile (33.0 g, 40%), bp 89° (0.25 mm), was obtained. An analytical sample was obtained by recrystallization from glyme at −80°: mp 46–47.5°; ir (KBr) 2940, 2875, 2840, 2790, 2230, 2175, 1600, 1450, 1400, 1290, 1105 cm^{-1}; uv λ_{max} (CH_2Cl_2) 318 nm (ϵ 9360); dipole moment 2.78 D (dioxane); nmr ($CDCl_3$) δ 2.82 (s). See Table III for analysis.

Isomerization of Bis(dimethylamino)maleonitrile and -fumaronitrile. A solution of 0.10 g of bis(dimethylamino)maleonitrile and 1 ml of deuterated DMSO was heated at 105–110° for 3 days. Nmr showed the sample to be 38% isomerized to the fumaronitrile. A crystal of iodine was added and heating continued at 105–110° for 4.5 hr. Nmr showed the sample to be 44% trans.

The above experiment was repeated with bis(dimethylamino)-fumaronitrile. After 3 days 30.6% of the cis isomer was present. After an additional 4.5 hr with iodine present, the equilibrium point with 42% trans and 58% cis isomer was reached.

Diaminomaleonitrile Succinamide (6). A solution of 5.4 g (50 mmol) of DAMN and 5.0 g (50 mmol) of succinic anhydride in 150 ml of THF was refluxed for 20 hr. The solvent was removed at reduced pressure, leaving 10.3 g of crude 6 which was recrystallized from THF, 9.1 g (87%) of white powdery crystals: mp 183–186°; uv (CH_3CN) 288 mμ (ϵ 13,300); ir (KBr) 3400–2500 (NH_2, NH, OH, CH), 2248, 2210 (C≡N), 1690 (acid C=O), 1671, 1522 (RNCO–), 1636 (NH_2), 1608 cm^{-1} (C=C); nmr (DMSO-d_6) δ 2.54 (s, 4), 6.97 (s, 2), 9.15 (s, 1), 11.78 (broad s, 1).

Anal. Calcd for $C_8H_8O_3N_4$: C, 46.2; H, 3.9; N, 26.9. Found: C, 46.2; H, 4.0; N, 27.1.

Diaminomaleonitrile Maleamide (7). Under similar conditions maleic anhydride gave a monoamide: mp 185–198° from anisole; 70% yield; uv (CH_3CN) 393 mμ (ϵ 19,700), 295 (4930), 256 (4960); ir (KBr) 3400–3100 (OH, NH_2, NH), 2240, 2200 (C≡N), 1786, 1751, 1690 (C=O), 1635, 1594, 1560, 1528 cm^{-1} (NH, C=C, N=C and/or $RCOO^-$); nmr (DMSO-d_6) δ 6.31 (d, 1, J = 6 Hz), 7.10 (d, 1, J = 6 Hz), 7.53 (s, broad, 4).

Anal. Calcd for $C_8H_6O_3N_4$: C, 46.6; H, 2.9; N, 27.2. Found: C, 46.7; H, 2.9; N, 27.2.

Diaminomaleonitrile Phthalamide (8). Refluxing phthalic anhydride and DAMN in THF for 20 hr gave a 24% yield of the phthalamide 8: mp 181°; uv (CH_3CN) 382 mμ (ϵ 14,500), 285 (6900), 265 (8820); ir (KBr) 3400, 3295, 3195 (NH_2, NH, OH), 2200 (C≡N), 1760, 1675, 1625 (C=O, NH_2), 1545 cm^{-1} (C=N); nmr (DMSO-d_6) δ 7.7 (m, 6), 8.0 (m, 2).

Anal. Calcd for $C_{12}H_8O_3N_4$: C, 56.3; H, 3.2; N, 21.9. Found: C, 56.4; H, 3.1; N, 21.9.

Diaminomaleonitrile Phthalimide (9). From the mother liquor of 8 was isolated 21% 9 by dissolving in DMF, precipitating with H_2O, and recrystallizing from CH_3OH: mp 275° dec; uv (CH_3CN) 287 mμ (ϵ 14,900), 217 (38,600); ir (KBr) 3350, 3295, 3240, 3176 (NH_2), 2242, 2216 (C≡N), 1787, 1720 (C=O), 1647 (NH_2), 1598 cm^{-1} (C=C); nmr (DMSO-d_6) δ 8.02 (s, 4), 8.33 (s, 2).

Anal. Calcd for $C_{12}H_6O_2N_4$: C, 60.5; H, 2.5; N, 23.5. Found: C, 59.9; H, 2.6; N, 23.1.

Diaminomaleonitrile Acrylamide. This amide was made from DAMN and acryloyl chloride in THF at 0–10° and was isolated as the hydrochloride salt. The monohydrate, mp 151.5–152°, crystallized from water in 52% yield: ir 3545, 3345, 3185, 2250, 2200, 1685, 1660, 1625, 1610, 1530 cm^{-1}; nmr (DMSO-d_6) δ 3.35 (s, NH), 5.63 (d, d, J = 7, 9 Hz, 1 H), 6.1 (m, 2 H), 7.05 (s, NH + OH).

Anal. Calcd for $C_7H_6N_4O \cdot H_2O$: C, 47.3; H, 4.5; N, 31.5. Found: C, 47.3; H, 4.1; N, 31.3.

The water was removed from the monohydrate by heating under reduced pressure.

Anal. Calcd for $C_7H_6N_4O$: C, 51.9; H, 3.7. Found: C, 51.8; H, 3.7.

Phenylurea Derivative of Diaminomaleonitrile (10). A solution of 1.08 g (10 mmol) of DAMN and 2.38 g (20 mmol) of phenyl isocyanate was kept for 20 hr at 25° as crystals slowly separated. The mixture was warmed on steam bath for 1.5 hr. The solid monoadduct, mp 180–210° dec, was collected and dried, yield 2.1 g (93%).

Anal. Calcd for $C_{11}H_9N_5O$: C, 58.2; H, 4.0; N, 30.8. Found: C, 58.3; H, 4.0; N, 31.1.

Bis(phenylurea) Derivative of Diaminomaleonitrile (11). A mixture of 3.36 g of DAMN, 12 g of phenyl isocyanate, and 40 ml of DMF was stirred at 80° for 4 hr. The dark red solid was collected and digested with warm acetonitrile. Filtration and drying gave 8.7 g of pale yellow crystals, ir (KBr) CN very weak, 1685, 1670, 1610, 970, 750, 695 cm^{-1}.

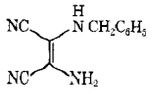
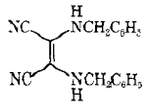
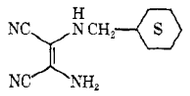
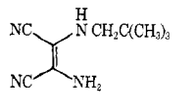
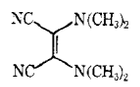
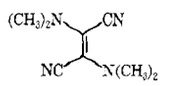
Imidazoles (12) from Diaminomaleonitrile (Table IV). Method A. Oxidation of Diaminomaleonitrile Schiff Base with Dichlorodicyanoquinone. 2-(2-Chlorophenyl)-4,5-dicyanoimidazole (12, R = 2-ClC_6H_4). A solution of 38 g (0.16 mol) of Schiff base from DAMN and 2-chlorobenzaldehyde and 38 g (0.16 mol) of 2,3-dichloro-5,6-dicyanoquinone (DDQ) in 1200 ml of CH_3CN was refluxed for 4 days. The solution was evaporated to dryness and the residual solid was slurried at reflux with 3 l. of benzene and filtered to remove the insoluble hydroquinone. The benzene filtrate was concentrated at reduced pressure, affording about 30 g of 2-(2-chlorophenyl)-4,5-dicyanoimidazole. Recrystallization from CH_2Cl_2–ether gave 24.8 g (66%) of 12 (R = 2-ClC_6H_4) as white needles: mp 205–208° dec; uv λ_{max} (CH_3CN) 264 mμ (ϵ 17,050); ir (KBr) 3290 (NH), 3080 (CH), 2240 (C≡N), 1590, 1568, 1543, 1508 cm^{-1} (C=C and/or C=N). See Table III for analysis.

Method B. *In Situ* Formation of Diaminomaleonitrile Schiff Base and Oxidation with Diiminosuccinonitrile. 2-*tert*-Butyl-4,5-dicyanoimidazole [12, R = $C(CH_3)_3$]. A solution of 25.9 g of pivaldehyde, 32.4 g of DAMN, 31.8 g of diiminosuccinonitrile (DISN), and 5.0 g of oxalic acid in 1 l. of anhydrous acetonitrile was refluxed under N_2 for 17 hr. The dark solution was preadsorbed on 140 g of Silicar CC-7 and chromatographed. Elution with chloroform gave a viscous, oily solid which was recrystallized from ether–hexane to give 30.0 g (57%) of colorless 2-*tert*-butyl-4,5-dicyanoimidazole, mp 150–151°. See Table III for analysis.

Method C. Reaction of *N,N*-Dialkylamides with Diaminomaleonitrile. 4,5-Dicyanoimidazole (12, R = H). A solution of 10.8 g (0.10 mol) of DAMN in 75 ml of dimethylformamide was cooled in an ice bath and 10.0 g (0.065 mol) of $POCl_3$ was added dropwise below 10°. The solution was heated to 160° over 1 hr and cooled to approximately 100° and most of the solvent was removed under vacuum. Water (100 ml) was added; the solution was warmed to 70° and filtered and the aqueous filtrate was extracted nine times with 200-ml portions of ether. The combined ether extracts were dried over $MgSO_4$ and the ether was removed to give 10.7 g (90%) of 4,5-dicyanoimidazole.[7a]

2-Aminoimidazoles. 2-*tert*-Butylamino-4,5-dicyanoimidazole [16, R = $C(CH_3)_3$]. To a solution of 8 g of *tert*-butyl isocyanide dichloride in 100 ml of THF was added 5.0 g of DAMN. The temperature rose to 43° and a precipitate formed. Upon stirring for 18 hr the precipitate redissolved and the resulting dark solution was preadsorbed and chromatographed on Silicar. Chloroform elution gave 0.94 g (11%) of **16**, R = $C(CH_3)_3$, as white crystals from ether–petroleum ether: mp 171.0–172.5°; ir (Nujol) 3311 (-NH), 2250 (-CN), 1645 cm^{-1} (C=C or C=N); nmr (acetone-d_6) δ 1.41 (s, 9), 6.10 (br, 1).

Table III
Alkyl Derivatives[a] of Diaminomaleonitrile

Compd	Registry no.	Method[b]	Yield, %	Crystn soln.	Mp, °C	Formula	Anal, % Carbon Calcd	Carbon Found	Hydrogen Calcd	Hydrogen Found	Nitrogen Calcd	Nitrogen Found
	51802-03-0	A	91	Ether–petroleum ether	114–116	$C_{11}H_{10}N_4$	66.7	66.6	5.1	5.1		
	51802-04-1	A	75	Ether–petroleum ether	76–79	$C_{18}H_{16}N_4$	75.0	74.6	5.6	5.5	19.4	19.6
	51802-05-2	A	67	CH_2Cl_2–hexane	133–134	$C_{11}H_{16}N_4$	64.7	64.5	7.9	7.8	27.4	27.5
	51802-06-3	A	87	CH_2Cl_2–hexane	165–166	$C_9H_{14}N_4$	60.7	60.4	7.9	7.8	31.4	31.3
		B	94	Glyme	35–36	$C_8H_{12}N_4$	58.5	58.1	7.4	7.4	34.1	34.6
		B	94	Glyme	46–47.5	$C_8H_{12}N_4$	58.5	58.5	7.4	7.2	34.1	34.0

[a] Structures were confirmed by nmr and ir. [b] See Experimental Section for general procedure.

Anal. Calcd for $C_9H_{11}N_5$: C, 57.1; H, 5.9; N, 37.0. Found: C, 56.6; H, 6.3; N, 37.7.

2-Anilino-4,5-dicyanoimidazole (16, R = C_6H_5). A solution of 4.3 g (0.04 mol) of DAMN and 6.2 g (0.035 mol) of phenyl isocyanide dichloride in 100 ml of THF was refluxed for 1 hr, stirred at room temperature for 18 hr, and chromatographed on Silicar. Chloroform–ether elution gave 2.82 g (39%) of **16** as white crystals from chloroform: mp 210–213° dec; ir (KBr) δ 3225 and 3115 (–NH), 2240 and 2230 (–CN), 1635, 1610, 1590, 1550, 1520, and 1500 cm^{-1} (C=C and C=N); uv (CH_3CN) 256 mμ (ϵ 21,700), 309 (9200); nmr (DMSO-d_6) δ 7.0–7.6 (m, 6), 9.6 (br, 1).

Anal. Calcd for $C_{11}H_7N_5$: C, 63.2; H, 3.4; N, 33.5. Found: C, 62.9; H, 3.6; N, 33.1.

2-Amino-4,5-dicyanoimidazole (16, R = H). To a solution of 89.8 g (1.46 mol) of cyanogen chloride in 2.0 l. of THF at 3° was added 157.7 g (1.46 mol) of DAMN. The solution was slowly (1 hr) warmed to reflux temperature (about 50°), and at this point occasional cooling was necessary to control the reflux rate. After an additional 1 hr the mixture was cooled to 0° and 1500 ml of ether was added. The hydrochloride of the imidazole was collected on a filter and was added to 3250 ml of water containing 120 g of sodium acetate. 2-Amino-4,5-dicyanoimidazole (142.6 g, 75% yield) precipitated. This product was purified by dissolving it in a solution of 1099 g of sodium bicarbonate in 2150 ml of water and treating with carbon black. White 2-amino-4,5-dicyanoimidazole (106 g) was reprecipitated by adding 250 ml of 6 *N* HCl. An analytical sample was recrystallized from CH_3CN: mp 270° dec; ir (KBr) 3487, 3380, 3280, 3225, 3030, 2860, 2740, 2650, 2230, 1660, 1600, 1560, 1460, 1410, 1370, 1316, 1280, 1090, 1050, 910, 790, 735 cm^{-1}.

Anal. Calcd for $C_5H_3N_5$: C, 45.1; H, 2.3; N, 52.6. Found: C, 45.3; H, 2.4; N, 52.6.

α-Amino-β-(*N*-2,5-dimethylpyrryl)maleonitrile (17, R = CH_3). A solution of 16.2 g (0.15 mol) of DAMN, 17.1 g (0.15 mol) of hexane-2,5-dione, and 1.0 g of *p*-toluenesulfonic acid in 600 ml of benzene was refluxed for 24 hr under a Dean-Stark trap. The reaction mixture was concentrated *in vacuo* to give 30 g of yellow solid. This material was dissolved in 200 ml of ether, treated with Darco, and recrystallized from ether–hexane. The yield of pale yellow product was 24.6 g (88%): mp 166.0–166.5°; ir (Nujol) 3450, 3330, 3225, 2220, 1640, 1600, 1410, 1380, 1315, 1220 cm^{-1}; nmr (DMSO-d_6) δ 2.08 (s, CH_3), 5.88 (s, CH), 7.73 (s, NH_2).

Anal. Calcd for $C_{10}H_{10}N_4$: C, 64.5; H, 5.4; N, 30.1. Found: C, 64.4; H, 5.3; N, 30.1.

α-Amino-β-(*N*-2,5-diphenylpyrryl)maleonitrile (17, R = C_6H_5). A solution of 10.8 g (0.10 mol) of DAMN, 23.8 g (0.10 mol) of 1,4-diphenylbutane-1,4-dione, and 1.0 g of *p*-toluenesulfonic acid in 400 ml of acetonitrile was refluxed for 17 hr. The reaction mixture was concentrated *in vacuo* to give 32 g of yellow solid. This material was dissolved in 200 ml of THF, treated with Darco, and recrystallized from THF–hexane. The yield of pale yellow product was 27.0 g (87%): mp 198–199°; ir (Nujol) 3450, 3330, 2220, 1610, 1590, 1370, 1315, 1075 cm^{-1}; nmr (DMSO-d_6) δ 6.55 (s, CH), 7.45 (s, aromatic), 8.08 (s, NH_2).

Anal. Calcd for $C_{20}H_{14}N_4$: C, 77.4; H, 4.6; N, 18.1. Found: C, 77.7; H, 4.6; N, 18.3.

Pyrazines from Diaminomaleonitrile. 2-Amino-3-methoxy-5,6-dicyanopyrazine (18). A mixture of 55.5 g (0.20 mol) of diaminomaleonitrile tosylate and 23.2 g (0.20 mol) of 1,2-dimethoxy-1,2-diiminoethane[22] in 800 ml of THF was stirred for 3 days, filtered, and stripped. The resulting solid was slurried with water, collected, and recrystallized from ethyl acetate to give 24.5 g (70%) of light tan crystals of **18**: mp 211.5–213.0°; ir (KBr) 3413, 3345,, and 3185 (–NH_2), 2240 (–CN), 1650, 1570, 1550, and 1520 cm^{-1} (C=C, C=N, –NH_2); uv (CH_3CN) 215 mμ (ϵ 20,900), 296 (19,600); nmr (DMSO-d_6) δ 4.06 (s, 3), 8.1 (br, 2).

Anal. Calcd for $C_7H_5ON_5$: C, 48.0; H, 2.9; N, 40.0. Found: C, 48.2; H, 2.9; N, 40.1.

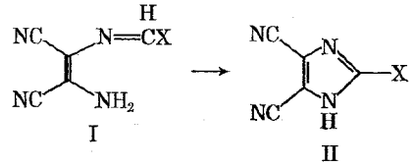
2-Methyl-5,6-dicyanopyrazine. A. From Chloroacetone. A suspension of 10.8 g (0.1 mol) of DAMN, 20 g of chloroacetone, and 100 ml of ethanol was stirred overnight at room temperature. Silicar was added to the dark solution and the solution was stripped to dryness and chromatographed. Eluting with benzene gave the product, which was recrystallized from carbon tetrachloride to give 2.2 g of pale yellow solid: mp 97°; ir (KBr) 3058, 2922, 2242, 1552, 1518, 1438 cm^{-1}; nmr ($CDCl_3$, TMS) δ 2.79 (s, CH_3), 8.82 (s, =CH); uv λ_{max} (CH_3CN) 280 mμ (ϵ 6320), 237 (11,000).

Anal. Calcd for $C_7H_4N_4$: C, 58.4; H, 2.8; N, 39.0. Found: C, 57.8; H, 2.6; N, 39.2.

B. From Pyruvaldehyde. A solution of 54 g of DAMN, 100 g of 40% aqueous pyruvic aldehyde, and 750 ml of ethanol was refluxed for 3 hr, treated with 25 g of Darco, and filtered. On cooling the product crystallized and was recrystallized from CCl_4, giving 59.5 g (80%) of light tan solid.

Diazepine Derivatives from Diaminomaleonitrile. 2,3-Dicyano-5,7-dimethyl-6*H*-1,4-diazepine (19). A mixture of 21.6 g (0.2 mol) of DAMN, 20.0 g (0.2 mol) of acetylacetone, 0.5 g of oxalic acid, and 200 ml of benzene was refluxed in a 1-l. flask with a Dean-Stark trap. In a few minutes, half the expected 7.2 ml of water was collected. After 3 hr, the mixture was cooled and filtered. The solid was rinsed with hexane and dried to give 32.9 g (96%) of product which was purified by dissolving in hot acetonitrile, decolorizing with Darco, and cooling to give colorless crystals, mp 199–200° dec, ir 2250, 1600, 1375, 1260 cm^{-1}.

Table IV
2-Substituted 4,5-Dicyanoimidazoles[a]



X	Registry no. I	Registry no. II	Prepn method[b]	Yield, %	Crystn soln	Mp, °C	Ir, cm⁻¹	Nmr, δ
o-C_6H_4F	51802-07-4	40953-38-6	A[c]	25	Acetone–benzene	246–247	3150, 2220, 1610, 1300, 1230, 1210, 1090, 965, 825, 770, 740	fmr 115.6
m-C_6H_4F	51802-08-5	40953-39-7	A[c]	29	Benzene	198–200	3150, 2220, 1580, 1310, 1263, 1200, 970, 890, 875, 800, 730	fmr 112.9
p-C_6H_4F	51802-09-6	40953-40-0	A[c]	24	Acetone–benzene	220–221	3150, 2220, 1600, 1285, 1235, 1160, 1110, 960, 845, 735	fmr 109.2
o-C_6H_4Cl		41021-16-3	A	66	CH_2Cl_2–ether	211–212	3270, 2220, 1310, 1225, 1115, 1050, 960, 780, 755, 735, 695, 685	
m-C_6H_4Cl	51802-10-9	40953-41-1	A	40	Acetone–benzene	227–228.5	3200, 2220, 1300, 1125, 1095, 1085, 975, 805, 795, 725, 690, 680	
p-C_6H_4Cl	51802-11-0	40953-42-2	A	33	CH_3CN	300–301	3200, 3100, 2260 2240, 1600, 1310, 1280, 1120, 1110, 1095, 1015, 965, 845, 832, 760, 735	
2,6-$C_6H_3Cl_2$		51802-37-0	A	65	Benzene	143–144.5	3210, 2255, 2240, 1590, 1560, 1550, 1510, 962, 795, 783, 720	
o-C_6H_4Br	51802-12-1	40953-43-3	A	34	$CHCl_3$–petroleum ether	182–183	3300, 2240, 1300, 1220, 1100, 1035, 1025, 960, 778, 745, 732	
m-C_6H_4Br	51802-13-2	51802-38-1	A	50	$CHCl_3$–petroleum ether	212–213	3150, 2260, 2230, 1570, 1300, 1120, 1080, 1000, 975, 800, 773, 727	
p-C_6H_4Br	51802-14-3	40953-44-4	A	50	CH_3CN	226 dec	3150, 3050, 2280, 2210, 1600, 1300, 1270, 1115, 1100, 1070, 1010, 990, 840, 830, 815, 730	
o-$C_6H_4CF_3$	51802-15-4	51802-39-2	A	51	$CHCl_3$–petroleum ether	92–93.5	3600, 2270, 1310, 1280, 1240, 1230, 1210, 1060, 1040, 970, 780, 770, 760, 740, 735, 730	fmr 57.80
m-$C_6H_4CF_3$	51802-16-5	40953-37-5	A	64	$CHCl_3$–hexane	205–206	3300, 3200, 2240, 1550, 1330, 1180, 1160, 1125, 1115, 1085, 1075, 970, 900, 820, 760, 725	fmr 62.41
p-$C_6H_4CF_3$	51802-17-6	51802-40-5	A	55	$CHCl_3$	251–252	3200, 2250, 1570, 1320, 1180, 1140, 1120, 1065, 1010, 960, 858, 843, 750, 728, 710, 695	fmr 62.45
CF_3		51802-41-6	A	50	Sublimed	86–88	3200–2300, 2250, 1570, 1515	
$CH_2CH_2CH_3$	51802-18-7	51802-42-7	B	37	Ether–hexane	142–143	3225–2270 (br), 2250, 1565, 1530, 1300, 1265, 1090	($CDCl_3$) 1.07 (3 H, t, CH_3), 1.90 (2 H, sextet, CH_2), 2.91 (2 H, t, CH_2), 11.67 (s, NH)
$C(CH_3)_3$		51802-43-8	B	57	Ether–hexane	150–151	3225, 3225–2500 (br), 2220, 1490, 1350, 1280, 1260, 1210, 1005	1.43 (9 H, s, CH_3), 11.67 (s, NH)
$CHCH_2CH_2CH_3$ | CH_3	51802-19-8	51802-44-9	B	37	Ether–hexane	75–76	3225, 3225–2325 (br), 2220, 1560, 1515, 1280, 1090, 1010	0.8–2.0 (10, H, m), 3.10 (1 H, q, CH), 11.43 (s, NH)

Cyclohexyl	40953-36-4	B	41	Ether–hexane	150–152	3030–2325 (br), 2220, 1575, 1530, 1460, 1380, 1300, 1250, 1060, 1040, 995, 900	1.0–2.5 (10 H, m, CH_2), 2.90 (1H, broad, CH)
$CH_3CH(OH)–CH_3$	51802-45-0	B	44	Ether–hexane	125–126	3330–2500 (br), 2220, 1515, 1460, 1380, 1310, 1290, 1120, 1100, 1030, 940, 850	1.08 (3 H, d, CH_3), 2.72 (2 H, d, CH_2), 3.92 (1 H, CH), OH and NH broad
Cyclopropyl	51802-20-1	B	96		169–172	2800–2500, 2210, 1570, 1525	0.7–0.9 (m, 4 H), 1.7–2.1 (m, 1 H,
$OCH_2CH=CH_2$	51802-21-2	A	27	Water	95–97	3225, 3125, 2260, 1590, 1540, 1315, 1280, 1265, 1135, 1090, 1060, 1010, 965, 935, 925, 825	7.25 (NH + OH), 6.13 (m, =CH), 5.48 (d, J = 18 Hz, m, =CH), 5.57 (d, J = 7 Hz, m, J = 1 Hz, =CH), 5.02 (d, J = 7 Hz, CH_2)
OCH_2CH_3	51802-22-3	A	54	Water	98–99	3330, 2700, 2250, 1640, 1610, 1470 1450, 1390, 1360, 1315, 1080, 1060, 1015, 1010, 1000, 760, 735	1.45 (t, J = 7 Hz, CH_3), 3.88 (q, J = 7 Hz, CH_2), 10.3 (s, NH)
$N(CH_3)_2$	51802-49-4	A	34	Water	164–166 dec	3225, 2270, 2250, 1650, 1330, 1030, 925)	2.98 (s, 6 H), 11.7 (br, NH)
$(CH_2)_4CN(CH_3)_2$ (=O)	51802-23-4	C	27	CH_2Cl_2–benzene	153.5–155.0	2900–2500, 2265, 1610, 1510	1.4–1.7 (m, 4 H), 2.1–2.7 (m, 4 H), 2.78 (s, 3 H), 2.93 (s, 3 H), 12.5 (br, NH)

[a] Satisfactory analytical data for C, H, and N were reported for all new compounds listed in the table. [b] See Experimental Section for general procedure. [c] Base extraction procedure in separation of product resulted in considerable loss of product.

Anal. Calcd for $C_9H_8N_4$: C, 62.7; H, 4.7; N, 32.6. Found: C, 62.5; H, 4.7; N, 32.3.

2,3-Dicyano-4,5,6,7-tetrahydro-5,7-dimethyl-1*H*-1,4-diazepine (25). To a slurry of 5.00 g (0.029 mol) of **19** in 200 ml of methanol was added 1.14 g (0.03 mol) of $NaBH_4$ in three portions. The temperature rose from 25° to 40° and the solid dissolved. Most of the solvent was removed, 300 ml of water was added, and the resulting solution was extracted with two 400-ml portions of ethyl acetate. Removing the solvent gave nearly colorless product which was recrystallized from ether to give 4.39 g (85%) of **26** as colorless needles: mp 158–160°; ir (KBr) 3370 (–NH), 2985, 2950, and 2890 (CH), 2210 (–CN), 1630 cm^{-1} (–C=C–); uv (CH_3CN) 208 mμ (ε 10,500), 314 (13,300); nmr (CD_3CN) δ 1.15 (m, 1) 1.17 (d, J = 6.2 Hz, 6), 1.5 (m, 1), 2.5–3.0 (m, 2), 4.45 (br, 2).

Anal. Calcd for $C_9H_{12}N_4$: C, 61.3; H, 6.9; N, 31.8. Found: C, 61.1; H, 6.9; N, 32.0.

2,3-Dicyano-5,7-dimethyl-6,7-dihydro-1*H*-1,4-diazepine (22e). To a slurry of 1.76 g (0.01 mol) of **25** in 50 ml of benzene at 10° was added 2.27 g (0.01 mol) of DDQ in 100 ml of benzene. The resulting mixture was stirred for 15 min, filtered to remove dihydrodichlorodicyanoquinone and stripped to dryness without warming. The infrared spectrum of the crude product showed no diimine. Recrystallization from benzene gave 1.46 g (84%) of tan crystals: mp 143–145°; ir (KBr) 3205 (–NH), 2240 and 2210 (–CN), 1620, 1560, and 1530 cm^{-1} (C=C and –C=N); uv (CH_3CN) 255 mμ (ε 3060), 337 (9700); nmr (acetone-d_6) δ 1.28 (d, J = 6.5 Hz, 3), 2.17 (s, 3), 2.78 (m, 2), 3.9 (br, 1), 7.2 (br, 1).

Anal. Calcd for $C_9H_{10}N_4$: C, 62.1; H, 5.8; N, 32.2. Found: C, 62.3; H, 5.9; N, 32.1.

2,3-Dicyano-5,7,7-trimethyl-6,7-dihydro-1*H*-1,4-diazepine (22a). To a solution of 2.50 g (0.023 mol) of DAMN and 10 ml of acetone in 50 ml of THF was added 5 drops of concentrated sulfuric acid. The resulting solution was stirred for 3 days and filtered to remove 0.71 g (0.003 mol) of diaminomaleonitrile sulfate. Removal of the solvent and recrystallization from methylene chloride gave 3.35 g (89.5%) of **22a** as light yellow needles: mp 181–182° from CH_2Cl_2; ir 3305, 3205 (NH), 2990, 2875 (CH); 2240, 2200 (C≡N); 1630, 1555 (C=C, C=N); 1395, 1375 cm^{-1} (H_3CCCH_3); uv λ_{max} (CH_3CN) 225 mμ (ε 2680), 335 (9400); nmr (DMSO-d_6) δ 1.18 (s, 6 H), 2.16 (s, 3 H), 2.63 (s, 2 H), 8.35 (s, 1 H, NH); high-resolution mass spectrum molecular ion m/e 188.1058 (calcd for $C_{10}H_{12}N_4$, 188.1062).

Anal. Calcd for $C_{10}H_{12}N_4$: C, 63.8; H, 6.4; N, 29.8. Found: C, 63.8; H, 6.6; N, 30.1.

Dicyanodihydrodiazepine (23) from Cyclohexanone. The reaction of DAMN with cyclohexanone under similar conditions gave dicyanodihydrodiazepine (**23**), 89% yield, mp 193–194°, from chloroform–ether as yellow needles: ir (KBr) 3285 (NH), 2960, 2930, and 2855 (NH), 2960, 2930, and 2855 (CH), 3065 and 3015, 2210 (–CN), 1610, 1557, and 1518 cm^{-1} (C=N, C=C); uv (CH_3CN) 222 mμ (ε 11,600), 343 (9000); nmr (DMSO-d_6) δ 1.0–2.1 (broad peak centered at δ 1.40, m, 17), 2.1–2.3 (br, 2), 7.88 (s, 1).

Anal. Calcd for $C_{16}H_{20}N_4$: C, 71.6; H, 7.5; N, 20.9. Found: C, 71.6; H, 7.7; N, 21.0.

2,3-Dicyano-6,7-dihydro-7-methyl-5,7-diphenyl-1*H*-1,4-diazepine (22b). The reaction of DAMN with acetophenone ethylene ketal gave **22b** in 72% yield: mp 158–159.5° from ether; ir (KBr) 3325 (NH), 3040 (aromatic =CH), 2930 (–CH), 2230 and 2210 (–CN), 1592, 1582, 1530, 1492 cm^{-1} (C=C, C=N); uv (CH_3CN) 254 mμ (ε 11,900), 375 (13,900); nmr (CD_3CN) δ 1.69 (s, 3), 2.87 (d, J = 14 Hz, 1), 3.90 (d, J = 14 Hz, 1), 7.0–7.5 (m, 10).

Anal. Calcd for $C_{20}H_{16}N_4$: C, 76.9; H, 5.2; N, 17.9. Found: C, 77.3; H, 5.4; N, 18.1.

2,3-Dicyano-4,5,6,7-tetrahydro-5,*N*,*N*-trimethyl-7-dimethylcarbamoyl-1-1*H*-1,4-diazepin-5-acetamide [20, R = $N(CH_3)_2$]. To a solution of 5.4 g (0.05 mol) of DAMN in 30 ml of *N*,*N*-dimethylacetoacetamide was added 2 g of $POCl_3$ over 30 sec. The temperature rose to 97°; the reaction mixture was stirred until cool and the resulting solid was collected. Recrystallization from ethyl acetate gave 9.1 g (55%) of **20** as a yellow powder: mp 178–179°; ir (Nujol) 3200, 2200, 2190, 1630, 1575, 1520 cm^{-1}; nmr ($CDCl_3$) δ 1.40 (s, 3), 2.5–2.8 (m, 4), 2.95–3.05 (m, 12), 5.0 (s, 1), NH's not seen.

Anal. Calcd for $C_{16}H_{22}O_2N_6$: C, 58.2; H, 6.7; N, 25.4. Found: C, 58.1; H, 6.7; N, 25.1.

2,3-Dicyano-4,5,6,7-tetrahydro-5-methyl-7-methoxycarbonylmethylene-1*H*-1,4-diazepin-5-acetic acid (20, R = OCH_3). To a solution of 5.4 g (0.05 mol) of DAMN in 40 ml of methyl acetoacetate was added dropwise over 5 min 3.0 g of $POCl_3$. The temperature reached 45° during the addition. After stirring for 1 hr the solution was poured into 200 ml of ice water. The resulting

precipitate was collected and recrystallized from benzene to give 3.9 g (25%) of **20** (R = OCH_3) as yellow crystals: mp 150–152°; ir (Nujol) 3250, 2205 (w), 2195, 1715, 1650, 1600, 1530 cm^{-1}; nmr (DMSO-d_6) δ 1.19 (s, 3), 2.52 (s, 2), 2.78 (s, 2), 3.53 (broad peak, 6), 4.75 (s, 1), 7.55 (br, 1, exchanges with D_2O), 8.72 (br, 1, exchanges with D_2O).

Anal. Calcd for $C_{14}H_{16}O_4N_4$: C, 55.3; H, 5.3; N, 18.4. Found: C, 55.4; H, 5.3; N, 18.7.

Diaminomaleonitrile Acetophenone Schiff Base 21. A solution of 10.8 g (0.10 mol) of DAMN, 26.4 g (0.22 mol) of acetophenone, and 5 drops of sulfuric acid in 300 ml of THF was stirred at room temperature for 20 hr, filtered, and stripped to dryness, giving a yellow oil. The oil was dissolved in petroleum ether and upon standing 1.6 g of yellow needles grew from solution. Recrystallization from ether gave light yellow needles: mp 123.0–123.5°; ir (Nujol) 3445 and 3280 ($-NH_2$), 2230 and 2190 (-CN), 1591, 1567, and 1548 cm^{-1} (NH_2, C=C and/or C=N); uv (CH_3CN) 258 mμ (ϵ 13,450), 283 (10,400), 360 (12,300); nmr (CD_3CN) δ 2.47 (s, 3), 5.61 (br, 2), 7.45 (m, 3), 7.94 (m, 2).

Anal. Calcd for $C_{12}H_{10}N_4$: C, 68.55; H, 4.79; N, 26.65. Found: C, 68.53; H, 4.80; N, 27.03.

2,3-Dicyano-5-dimethylamino-1,7-dihydro-6*H*-1,4-diazepine (24a). To a solution of 10.0 g of DAMN and 12.0 g of *N,N*-dimethylacrylamide in 100 ml of THF was added 10 ml of $POCl_3$ over 15 min. The resulting solution was stirred for 4 hr as a tan precipitate formed. This solid was collected (6.5 g) and recrystallized from methanol–ether to give 3.5 g of the hydrochloride as colorless crystals, mp 234–236° dec. The hydrochloride was dissolved in water and neutralized with NH_4OH to give an immediate yellow precipitate. Recrystallization from chloroform gave the diazepine **24a** as yellow needles: mp 190–192°; ir (Nujol) 3280, 2195, 1580, 1540, 1510 cm^{-1}; nmr (acetone-d_6) δ 2.9 (m, 2), 3.03 (s, 6), 3.55 (m, 2).

Anal. Calcd for $C_9H_{11}N_5$: C, 57.1; H, 5.9; N, 37.0. Found: C, 57.1; H, 5.6; N, 37.4.

2,3-Dicyano-5-dimethylamino-6*H*-1,4-diazepine (24b). A solution of 0.68 g (3.0 mmol) of DDQ in 25 ml of benzene was added to 0.59 g (3.0 mmol) of **24a** in 100 ml of benzene. The solution turned green and then to a yellow slurry over 1 hr. After stirring for 18 hr the solution was filtered to remove dihydrodichlorodicyanoquinone. Concentration and recrystallization from benzene gave 0.52 g (88%) of **24a** as colorless crystals: mp 130–132°; ir (KBr) 2220, 1595, 1570, 1480 cm^{-1}; nmr ($CDCl_3$) δ 3.17 (s, 3), 3.26 (s, 3), 3.2 (2 H under singlets), 6.96 (t, J = 5.5 Hz, 1).

Anal. Calcd for $C_9H_9N_5$: C, 57.8; H, 4.9; N, 37.4. Found: C, 57.6; H, 4.8; N, 37.5.

2,3-Dicyano-5-methyl-6,7-dihydro-1*H*-1,4-diazepine (22c). A solution of 10.8 g (0.100 mol) of DAMN and 7.00 g (0.100 mol) of methyl vinyl ketone in 200 ml of absolute ethanol was refluxed for 5 hr. Twenty grams of Silicar was added and the solution was stripped to dryness. Chromatography with ether and THF gave crude product, which was recrystallized from THF–petroleum ether, giving light yellow needles: mp >290°; 5.0 g (31%); ir (Nujol) 3220, 2270, 2220, 1640, 1590, 1560, 1370, 1330, 1320, 1220, 1010, 980 cm^{-1}; nmr (DMSO-d_6) δ 2.1 (s, CH_3), 2.65 (m, CH_2), 3.4 (m, CH_2), 8.3 (broad singlet, NH); uv (CH_3CN) 338 mμ (ϵ 9080), 258 (2720).

Anal. Calcd for $C_8H_8N_4$: C, 60.0; H, 5.0; N, 35.0. Found: C, 59.6; H, 5.0; N, 34.6.

2,3-Dicyano-5-methyl-7-phenyl-6,7-dihydro-1*H*-1,4-diazepine (22d). A solution of 5.4 g (0.050 mol) of DAMN, 7.3 g (0.050 mol) of benzalacetone, 1 g of oxalic acid, and 200 ml of absolute ethanol was refluxed for 4 hr. A yellow solid was deposited after 1 hr. The solution was cooled to 0° and the product was collected by filtration and washed with ether. The solid was recrystallized from acetone–petroleum ether, giving 7.0 g (60% yield) of pale yellow crystals: mp 200–202°; ir 3225, 2275, 2220, 1640, 1370, 1330, 1320, 1280, 850, 700 cm^{-1}; nmr (DMSO-d_6) δ 1.73 (s, CH_3), 3.0 (AB of ABX, 2 H), 5.07 (br, CH), 7.3 (m, 5 H), 8.65 (br, NH).

Anal. Calcd for $C_{14}H_{12}N_4$: C, 71.2; H, 5.08; N, 23.7. Found: C, 71.1; H, 5.16; N, 23.8.

2,3-Dicyano-5,7-diphenyl-6,7-dihydro-1*H*-1,4-diazepine (22f). A solution of 5.4 g (0.050 mol) of DAMN, 10.4 g (0.050 mol) of chalcone, and 15 drops of cooncentrated sulfuric acid in 250 ml of THF was refluxed for 3 days. The products were preadsorbed on Silicar CC-7 and chromatographed. Methylene chloride eluted a sticky orange solid which crystallized when triturated with ether. Recrystallization from ether gave 5.0 (33% yield) of yellow solid: mp 156–161°; ir 3225, 3075, 2220, 1560, 1350, 1330, 1220, 925, 780, 765, 750, 705, 690 cm^{-1}; nmr (DMSO-d_6) δ 3.20 (d, J = 14 Hz, 1 H), 3.75 (d, d, J = 14, 5 Hz, 1 H), 5.17 (d, J = 5 Hz, 1 H), 7.2–7.7 (m, 10 H), 9.12 (s, NH); uv (CH_3CN) λ_{max} 378 nm (ϵ 13,100), 256 (12,600).

Anal. Calcd for $C_{19}H_{14}N_4$: C, 76.5; H, 4.7; N, 18.8. Found: C, 76.1; H, 4.8; N, 18.7.

Oxidation of Diaminomaleonitrile to Diiminosuccinonitrile with Dichlorodicyanobenzoquinone. A mixture of 3.24 g (30 mmol) of DAMN and 6.78 (30 mmol) of dichlorodicyanobenzoquinone in 75 ml of acetonitrile was stirred at room temperature for 30 min. Dichlorodicyanohydroquinone (6.53 g, 95%) was removed by filtration. The filtrate yielded 3.32 g of residue which was DISN containing a small amount of dichlorodicyanohydroquinone according to its infrared spectrum.

Registry No.—3, 51802-24-5; **5,** 51802-51-8; **6,** 51802-25-6; **7,** 51802-26-7; **8,** 51802-27-8; **9,** 51802-28-9; **10,** 51802-29-0; **11,** 51802-30-3; **12** (R = H), 1122-28-7; **14** (R = R″ = CH_3), 51801-96-8; **14** (R = Pr; R″ = Et)·HCl, 51802-31-4; **16** [R = $C(CH_3)_3$], 51802-52-9; **16** (R = C_6H_5), 51802-53-0; **16** (R = H), 40953-34-2; **17** (R = CH_3), 51802-32-5; **17** (R = C_6H_5), 51802-33-6; **18,** 51802-54-1; **19,** 51802-55-2; **20** [R = $N(CH_3)_2$], 51802-56-3; **20** (R = OCH_3), 51802-57-4; **21,** 51802-34-7; **22a,** 51802-58-5; **22b,** 51802-59-6; **22c,** 51802-60-9; **22d,** 51802-61-0; **22e,** 51802-62-1; **22f,** 51802-63-2; **23,** 51802-64-3; **24a,** 51802-65-4; **24b,** 51802-66-5; **25,** 51802-35-8; propionaldehyde, 123-38-6; isobutyraldehyde, 78-84-2; pivaldehyde, 630-19-3; 2-ethylhexanal, 123-05-7; cyclohexanecarboxaldehyde, 2043-61-0; 2-chlorobenzaldehyde, 89-98-5; 2,6-dichlorobenzaldehyde, 83-38-5; 3-hydroxybutyraldehyde, 107-89-1; acetophenone, 98-86-2; fluoral, 75-90-1; *N,N*-dimethylformamide, 68-12-2; *N,N*-dimethylacetamide, 127-19-5; *N,N*-diethylacetamide, 685-91-6; *N,N*-diethylbutyramide, 1114-76-7; *N,N*-dimethylpropionamide, 758-96-3; terephthalaldehyde, 623-27-8; *N*-methyl-2-pyrrolidinone, 872-50-4; benzaldehyde, 100-52-7; succinic anhydride, 108-30-5; maleic anhydride, 108-31-6; phthalic anhydride, 85-44-9; diaminomaleonitrile acrylamide, 51802-36-9; acryloyl chloride, 814-68-6; phenyl isocyanate, 103-71-9; *tert*-butyl isocyanide, 7188-38-7; phenyl isocyanide dichloride, 622-44-6; cyanogen chloride, 506-77-4; 2,5-hexanedione, 110-13-4; 1,4-diphenyl-1,4-butanedione, 495-71-6; 1,2-dimethoxy-1,2-diiminoethane, 30986-09-5; chloroacetone, 78-95-5; acetylacetone, 123-54-6; acetone, 67-64-1; cyclohexanone, 108-94-1; acetophenone, 98-86-2; *N,N*-dimethylacetoacetamide, 2044-64-6; methyl acetoacetate, 105-45-3; *N,N*-dimethylacrylamide, 2680-03-7; methyl vinyl ketone, 78-94-4; benzalacetone, 122-57-6; chalcone, 94-41-7; DISN, 28321-79-1.

References and Notes

(1) Part VII: R. W. Begland, D. R. Hartter, D. S. Donald, A. Cairncross, and W. A. Sheppard, *J. Org. Chem.*, **39**, 1235 (1974).
(2) (a) H. Bredereck, G. Schmötzer, and E. Oehler, *Justus Liebigs Ann. Chem.*, **600**, 81 (1956); (b) T. Okada and N. Asai, U. S. Patent 3,701,797 (1972); *Chem. Abstr.*, **74**, 22456h (1971); (c) O. W. Webster, U. S. Patent 3,629,318 (1971); *Chem. Abstr.*, **76**, 13864d (1972).
(3) O. W. Webster, D. R. Hartter, R. W. Begland, W. A. Sheppard, and A. Cairncross, *J. Org. Chem.*, **37**, 4133 (1972).
(4) R. M. Lemmon, *Chem. Rev.*, **70**, 103 (1970).
(5) D. W. Woodward, U. S. Patent 2,534,331 (1950); *Chem. Abstr.*, **45**, 5191 (1951).
(6) H. Bredereck and G. Schmötzer, *Justus Liebigs Ann. Chem.*, **600**, 95 (1956).
(7) (a) L. E. Hinkel, G. O. Richards, and O. Thomas, *J. Chem. Soc.*, 1432 (1937); (b) R. P. Linstead, E. G. Noble, and J. M. Wright, *ibid.*, 911 (1937).
(8) (a) H. Wakamatsu, Y. Yamada, T. Saito, I. Kumashiro, and T. Takenishi, *J. Org. Chem.*, **31**, 2035 (1966); (b) Y. Yamada, I. Kumashiro, and T. Takenishi, *Bull. Chem. Soc. Jap.*, **42**, 1454 (1969).
(9) P. S. Robertson and J. Vaughan, *J. Amer. Chem. Soc.*, **80**, 2691 (1958).
(10) L. de Vries, *J. Org. Chem.*, **36**, 3442 (1971); J. H. Boyer and H. Dabek, *Chem. Commun.*, 1204 (1970).
(11) J. P. Ferris, D. B. Donner, and W. Lotz, *J. Amer. Chem. Soc.*, **94**, 6968 (1972).
(12) J. Honzl and P. Křivinka, *Tetrahedron Lett.*, 2357 (1970).
(13) Bis(dimethylamino)fumaronitrile has been prepared also from α,α-difluorotrimethylamine and hydrogen cyanide or sodium cyanide by Dr. C. W. Tullock of this laboratory.
(14) Y. Yamada, N. Nagashima, Y. Iwashita, A. Nakamura, and I. Kumashiro, *Tetrahedron Lett.*, **43**, 4529 (1968).
(15) H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Amer. Chem. Soc.*, **84**, 4756 (1962).
(16) (a) E. Grischkevitsch-Trochimovski, *Rocz. Chem.*, **8**, 1965 (1928); (b) H. Bredereck, G. Schmötzer, and H.-J. Becher, *Justus Liebigs Ann. Chem.*, **600**, 87 (1956).
(17) W. A. Sheppard and O. W. Webster, *J. Amer. Chem. Soc.*, **95**, 2695 (1973).
(18) F. J. Weigert, U. S. Patent 3,778,446 (1973); *Chem. Abstr.*, **80**, 59941n (1974).
(19) W. Eckert and F. Quint, U. S. Patent 2,200,689 (1940); *Chem. Abstr.*, **34**, 6455 (1940).
(20) A. Mannschreck, G. Rissmann, F. Vögtle, and D. Wild, *Chem. Ber.*, **100**, 335 (1967).
(21) (a) C. Bedel, *C. R. Acad. Sci.*, **176**, 168 (1923). (b) This experiment was performed by D. W. Woodward of these laboratories.
(22) H. Weidinger and J. Kranz, *Chem. Ber.*, **97**, 1599 (1964).