Chemistry of 1,3-Butadiene-2,3-dicarbonitrile. 1

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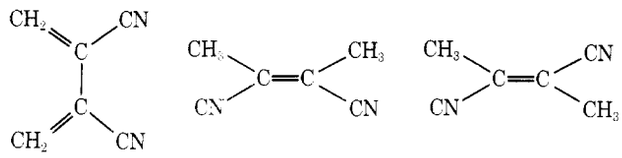
Hydrogenation of butadiene-1,2-dicarbonitrile (1) yielded *cis*- and *trans*-2-butene-2,3-dicarbonitrile, while bromine or chlorine gave 1,4-dihalo-2-butene-2,3-dicarbonitrile. Reaction of 1 with methanolic hydrogen halide gave 2,3-bis(halomethyl)succinimide. Secondary amines easily added to 1, resulting in formation of *cis*- and *trans*-1-amino-2-butene-2,3-dicarbonitriles, which underwent an amine-catalyzed tautomerization to 1-amino-1-butene-2,3-dicarbonitriles. Hydrolysis of the latter gave 2,3-dicyanobutyraldehyde. Also described are the preparation of 1-methoxy-2-butene-2,3-dicarbonitrile, 2,3-dicyano-1,4-butanedithiol diacetate, disodium 2,3-dicyano-1,4-butanedisulfonate, and 1-(*p*-toluenesulfonyl)-2-butene-2,3-dicarbonitrile by reaction of 1 with methanol, thiolacetic acid, sodium bisulfite, and *p*-toluenesulfinic acid, respectively. Hydration of 1 with sulfuric acid gave the diamide 23, and conditions are described for the Ritter reaction of 1.

The reactions of 1,3-butadiene-2-carboxylic and -2,3-dicarboxylic acid derivatives have received little attention. Some work has been reported on the chemistry of the esters of the diacid[1] and with certain derivatives of the monoacid.[2] Convenient syntheses of dienes of these types, especially the diacid derivatives, have been developed recently,[3,4] and definitive chemistry of 1,3-butadiene-2,3-dicarbonitrile (1) is beginning to appear.[3]

For some time we have been interested in the chemistry of 1. Befitting such a multifunctional molecule, this diene possesses a diverse, often unique reactivity. This report will be concerned with solvolytic and conventional double-bond addition reactions that 1 undergoes, while its behavior as a strongly electron-deficient diene will be dealt with separately.

Results and Discussion

Hydrogenation. Catalytic reduction of 1 occurred under mild conditions to give *cis*- and *trans*-2-butene-2,3-dicarbonitrile (2 and 3, respectively) as the major products.[5] Al-



1 2 3

though these products have been described previously,[6] it is nevertheless appropriate to relate their spectral properties (Table I) to isomer structure, since such data were important in defining the structures of other products obtained in this study.

The absorption in the infrared region due to carbon–carbon double bond stretching (at ca. 1600 cm^{-1}) is normally substantial only with symmetrically substituted olefins. Since 3 is symmetric in so far as the dipole may be affected, while 2 is not, only the latter (i.e., symmetrically substituted maleonitriles vis a vis isomeric fumaronitriles) will exhibit a (relatively) significant absorption in this region.

From the NMR data in Table I, the salient observations are: (a) the resonances for the hydrogens in 3 are shifted downfield relative to those for 2, because both cyano groups participate in deshielding the methyl groups to a larger extent in the former than in the latter; and (b) steric perturbations of the relatively bulky adjacent methyl groups in 2 shift this (methyl carbon) resonance upfield relative to that of 3, as normally observed in systems such as this.[7]

Since the spectral data are thus in agreement with the structures of the known 2 and 3, comparison of similar data from other cis,trans pairs prepared in this work permitted structural assignments to be made with a reasonable level of confidence. Accordingly, cis structures were assigned to those isomers having a relatively significant absorption at ca. 1600 cm^{-1} and exhibiting resonances from the hydrogens on the allylic carbons slightly upfield those of the trans isomers. (These criteria resulted in the cis structure being assigned the isomer having the lower up; this is normally expected.)

Halogenation and Hydrohalogenation. Under ultraviolet irradiation, diene 1 underwent ready addition of one molecule of bromine to give 1,4-dibromo-2-butene-2-3-dicarbonitrile (4). Even with excess bromine, 4 was the only observed product. Without light, the addition was very slow. The reaction was not affected by the addition of hydrogen bromide, lithium bromide, or aluminum chloride. Although thin-layer chromatography (TLC) indicated that two products were formed (closely related isomers, since the ^1H NMR spectrum of the mixture was a single peak), careful and repeated attempts to separate by HPLC were not successful. In an analogous manner, 1 underwent reaction with chlorine to give 1,4-dichloro-2-butene-2,3-dicarbonitrile (5). All attempts to add iodine to 1 failed.

The diene 1 was relatively inert to hydrogen chloride in an aprotic solvent, even under irradiation or in the presence of stannic chloride. However, in hot methanol addition of 2 mol of the acid occurred with concurrent reaction of the nitrile groups to yield, after hydrolysis, 20–25% of 2,3-bis(chloromethyl)succinimide (7) of undetermined stereochemistry. The dibromo analogue 6 was formed in low yield (at room temperature) in a similar manner. Ethanolic hydrogen chloride failed to react with 1 after several days at room temperature. In a further study of related systems, 4 failed to undergo solvolysis (at the nitrile group) with either hydrogen halide in methanol. Thus, recovery of 4 was nearly quantitative after treatment with methanolic hydrogen bromide at 50 °C.

The reactivity of 1 toward hydrogen halide only in the presence of methanol suggests that reaction at the nitrile group to yield a cyclic imido chloride or ester may precede or is at least involved in the addition to the double bond. Lending support to this is the observed lability (toward dimerization and polymerization) of the imide and anhydride of 1,3-butadiene-2,3-dicarboxylic acid,[8] suggesting a highly reactive system in structures such as these (and the proposed cyclic imide intermediate). The resistance of 4 toward solvolysis with methanolic hydrogen halide suggests further that the overall reaction (i.e., formation of 6 and 7) may occur as a more-or-less concerted addition-solvolysis process, or at least a closely related sequential process. Otherwise, the exact process for the moment remains obscure.

Results of attempts to use the dibromo derivative 4 as a reactive intermediate were disappointing. While reaction with various nucleophilic reagents (e.g., cyanide, sulfide, thiourea, acetate, and amines) occurred, giving generally intensely

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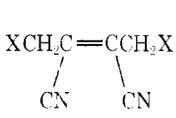
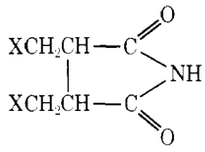
Table I. Properties of Products from Hydrogenation of Diene 1

	Product 2	Product 3
Yield, % (by VPC)	35	52
Mp.,[a] °C	40–46	81.5–82.5
IR absorption, cm^{-1}		
CN	2220	2220
C=C	1620	
^1H NMR ($CDCl_3$) δ (ppm)		
CH_3	2.07 (s)	2.27 (s)
^{13}C NMR ($CDCl_3$) δ (ppm)		
CH_3	17.46	20.16
C=C	124.80	124.92
CN	117.26	116.19

[a] Lit. mp for 2 48 °C and for 3 81 °C; see ref 6.



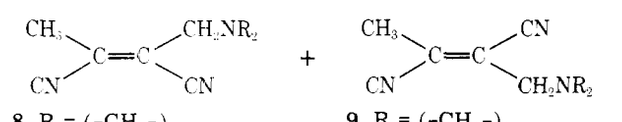
4, X = Br
5, X = Cl



6, X = Br
7, X = Cl

colored reaction solutions, discrete reaction products could not be isolated. For example, *tert*-butylamine in acetonitrile underwent a rapid and exothermic reaction with **4** to give *tert*-butylammonium bromide almost quantitatively; however, attempts to isolate anything from the tarry residual product by a variety of methods were fruitless.

Addition of Amines. Diene **1** has marginal stability in the presence of bases.[9] However, as the result of the polarization induced by the two strongly electronegative nitrile groups, it undergoes facile addition reactions with secondary amines. Thus, with piperidine in benzene at room temperature, a 72% yield of a 1:3 mixture of *cis*- and *trans*-1-(1-piperidino)-2-butene-2,3-dicarbonitrile (**8** and **9**, respectively) was isolated. Similarly, morpholine gave a 55% yield of *cis*- and *trans*-1-(1-morpholino)-2-butene-2,3-dicarbonitrile (**10** and **11**, respectively). Dimethylamine gave the analogous products **12** and **13**, although only the latter was characterized. Pyrrolidine



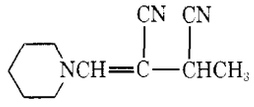
8, R = $(-CH_2-)_5$
10, R = $[-(CH_2)_2O(CH_2)_2-]$
12, R = CH_3

9, R = $(-CH_2-)_5$
11, R = $[-(CH_2)_2O(CH_2)_2-]$
13, R = CH_3

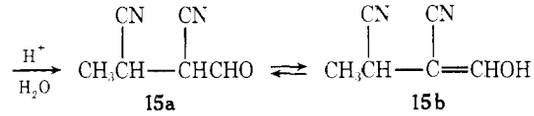
and di-*n*-octylamine underwent similar reaction with **1**, but the oily products appeared to be less stable and were not rigorously identified. Diphenylamine underwent reaction with **1** in hot acetic acid in the presence of copper or cupric acetate,[10] but a complex reaction mixture resisted separation and purification by a number of means.[11]

While both **8** and **9** were formed under mild conditions, **9** was thermally favored. Thus, reaction of **1** with piperidine at higher temperatures (e.g., in hot benzene) gave only **9** (by TLC and NMR), and mixtures of **8** and **9** yielded only **9** upon distillation. The trans isomer **9** was reasonably stable thermally. Although no similar study was made of the other amine derivatives, it is assumed that the trans adducts were similarly favored (and yield data supported this; see Experimental Section).

In addition to this thermal cis to trans isomerization, the mixed adducts **8** and **9** underwent a base-catalyzed tautomerization to the cyanoenamine **14**, 1-(1-piperidino)-1-butene-2,3-dicarbonitrile, by treatment with, e.g., hot piperidine. The same product **14** was obtained when the diene **1** was added directly to an excess of the hot amine. The structure of **14** was proven by both spectral and chemical means. It exhibited intense absorption in the infrared region at ca. 1640^{-1} cm, characteristic of a strongly polarized double bond, and a singlet resonance (^1H NMR) corresponding to one hydrogen in the olefinic region.[12] The product **14** underwent facile acid-catalyzed hydrolysis to give 2,3-dicyanobutyraldehyde (**15a**). From both IR and NMR data, this was found to be in



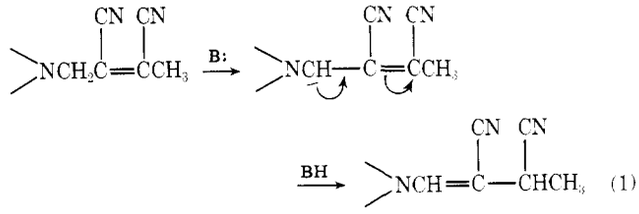
14



15a **15b**

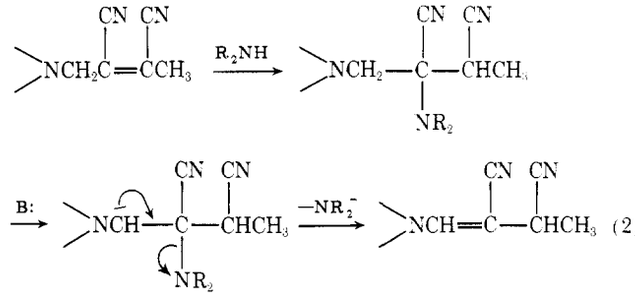
dynamic equilibrium with its enol **15b**, with the latter predominant (see Experimental Section).

The initial formation of the adducts **8** and **9** was very fast (by NMR monitoring; complete in a short time, even at 0 °C), while the tautomerization, a (1,3)-prototropic shift, was considerably slower. With catalytic amounts of piperidine (in hot toluene), the tautomerization was very slow, while in hot piperidine itself, the **9** → **14** process was complete in 20 min. Furthermore, there was no formation of **14** from **9** in hot triethylamine, which approximates piperidine in base strength. Assuming that there is no significant difference in the activity of these two amines due to steric differences, this latter finding precludes the formation of **14** by a simple proton removal and subsequent isomerization (eq 1). An alternative mechanism



(1)

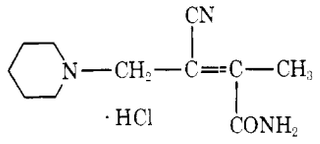
may be an addition–elimination process, in which another molecule of the secondary amine adds (at the carbon β to the amine) to the initial 1,4 adduct, as reported for the similar reaction of butadiene-2-carbonitrile,[2d] followed by proton abstraction and elimination (eq 2).[13]



(2)

Isomerization of the mixed piperidine adducts **8** and **9** with di-*n*-propylamine resulted also in the formation of **14** (by VPC), in addition to a number of other products which were not readily separated or identified. Similarly, treatment of the mixed morpholine adducts **10** and **11** with hot piperidine gave (by TLC) a complex mixture of at least four products.[14] While these results suggested the complexity of the process, because discrete reaction products could not be isolated, no further light was shed on the tautomerization mechanism.

The adduct **9** underwent reaction with methanolic hydrogen chloride to give 77% of the hydrochloride of an apparently isomerically pure cyanoamide, tentatively assigned the structure **16**, 1-(1-piperidino)-2-cyano-2-butene-3-carboxamide hydrochloride.[15]



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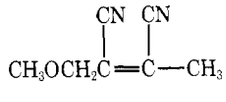
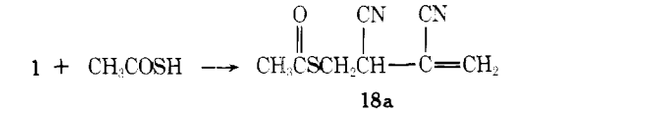


17

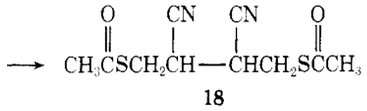
While secondary amines generally gave well-characterized addition products with **1**, reactions with primary amines were more complex. Thus, methylamine yielded viscous, variously colored (dark) products (by liquid chromatographic separation) of limited stability that gave spectral (IR) evidence for the presence of amine, nitrile, and enamine groups. With *tert*-butylamine, monitoring by ^1H NMR showed that adduction was complete in 10 min. Further reaction occurred, but discrete products could not be separated, although again spectral evidence suggested that cyanoenamines were formed.

Addition of Alcohol The reaction of **1** with methanol, in the presence of 1,8-bis(dimethylamino)naphthalene, a strongly basic but weakly nucleophilic amine catalyst, gave a modest yield of **17**, 1-methoxy-2-butene-2,3-dicarbonitrile, as a 1:3 mixture of cis,trans isomers. There was no reaction in the absence of catalyst. Under identical conditions, treatment with ethanol resulted in polymerization of **1**. Polymerization also occurred in methanol in the presence of the similar catalysts 2,2,6,6-tetramethylpiperidine and 1,5-diazabicyclo[4.3.0]non-5-ene, and no **17** could be isolated.

Reaction with Sulfur Nucleophiles The diene **1** underwent ready reaction with thiolacetic acid in THF; analysis (VPC) showed that reaction was complete in a few minutes, even at 0 °C, and that two major (volatile) products were formed. Interestingly, no reaction occurred in dichloromethane, suggesting that the process may be free radical and depends on a trace of peroxide present in the ether (THF) solvent for initiation. A small amount of a crystalline product was isolated that was apparently 2,3-dicyano-1,4-butanedithiol diacetate (**18**). Although the NMR spectrum of the major oily product indicated the presence of terminal methylene and acetyl groups, there were other resonances that could not be assigned to a simple structure such as the monoadduct 2,3-dicyano-3-butene-1-thiol acetate (**18a**) (see Experimental Section). This major product(s) thus remains unidentified. No attempt was made to add simple mercaptans to **1**.



18a



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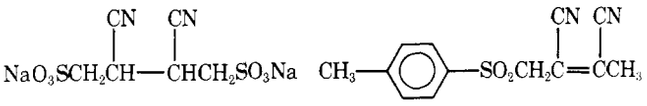
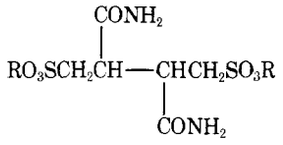
The diene **1** reacted exothermally with 2 equiv of sodium bisulfite to give a high yield of **19**, disodium 2,3-dicyano-1,4-butanedisulfonate. The reaction was much more complex when only 1 equiv of sodium bisulfite was used, giving discoloration and insoluble, apparently polymeric products. Sodium *p*-toluenesulfinate was sufficiently basic to polymerize diene **1** in aqueous solution. However, in acetic acid at ca. 70 °C, reaction occurred to give 96% of 1-(*p*-toluenesulfonyl)-2-butene-2,3-dicarbonitrile, **20**, as a 2:1 mixture of the cis,trans isomers.



19 **20**

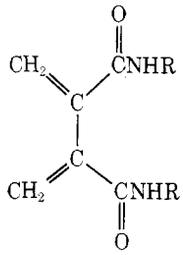


21, R = Na
22, R = CH_3

The salt **19** underwent a complex reaction with methanolic hydrogen chloride. Two products were isolated in low yield which were assigned the structures disodium 2,3-dicarbamoyl-1,4-butanedisulfonate (**21**) and the corresponding dimethyl ester **22**.[16] A sulfonic acid ion-exchange resin apparently converted **19** to the free acid, but no attempt was made to rigorously purify or characterize the waxy solid product.

Hydrolysis and Similar Reactions The best method found for the hydration of the cyano groups of **1** was by treatment of a sulfuric acid solution of **1** with ice. This afforded 1,3-butadiene-2,3-dicarboxamide (**23**) in ca. 50% yield. Although more severe treatment with sulfuric acid yielded a product that gave spectral evidence for the presence of acid groups, no rigorous attempt was made to prepare the diacid from **1**.

Interestingly, solutions of **1** in acetic acid or in formic acid failed to undergo any apparent reaction with sulfuric acid. However, in the presence of a suitable substrate, these conditions allowed a successful Ritter reaction to occur. Thus, in 97% formic acid the diene **1** gave *N,N'*-di-*tert*-butyl-1,3-butadiene-2,3-dicarboxamide, **24**, and *N,N'*-bis(2-methyl-2-butyl)-1,3-butadiene-2,3-dicarboxamide, **25**, with *tert*-butyl alcohol and 2-methyl-2-butene, respectively.



23, R = H
24, R = $C(CH_3)_3$
25, R = $C(CH_3)_2CH_2CH_3$

Conclusions

Although 1,3-butadiene-2,3-dicarbonitrile, **1**, is potentially a useful intermediate to numerous types of derivatives, its value is limited by its propensity to polymerize or otherwise form often intractable products under free-radical or basic conditions. Where these processes are rapid, e.g., addition of thiolacetic acid or secondary amines, monomeric products may often be isolated in good yield; this indicates perhaps that polymerization is a slower process than addition, at least under the described conditions.

In the studies that gave characterizable products, two types of additions were noted. Thus, hydrogen, halogen, arenesulfinic acid, and amines gave 1,4 addition products, while hydrogen halide, bisulfite, and apparently thiolacetic acid gave 1,2 addition products. Especially striking are the results with the grossly similar sodium bisulfite and arenesulfinic acid, yielding **19** and **20**, respectively. We have no explanation for this diverse behavior at present.

Experimental Section[17]

2-Butene-2,3-dicarbonitrile (2 and 3). About 20 mL of freshly distilled tetrahydrofuran (THF) was mixed with ca. 0.25 g of 10% palladium on charcoal in a Brown Hydrogenator. The catalyst was treated with hydrogen, and a solution of 1.0 g of **1** in 20 mL of THF containing 2 drops of glacial acetic acid was added. Hydrogen uptake was complete in about 1 h. Products were separated by liquid chromatography on silica gel, eluting with a mixture of cyclohexane and dichloromethane. Physical and spectral properties of the products are given in Table I.

1,4-Dibromo-2-butene-2,3-dicarbonitrile (4). A solution of 10.0 g (0.096 mol) of **1** in 100 mL of chloroform was stirred in a Pyrex flask under irradiation by a (external) UV light source while a solution of 17 g (0.106 mol) of bromine in 40 mL of chloroform was added dropwise over a 30-min period; the temperature was kept at 19–20 °C by cooling in a water bath. After another 90 min, the solvent was removed under aspirator pressure. The residue, an orange mixture of crystals in an oil, was dissolved in dichloromethane (Norit); chilling at −20 °C gave 21.1 g (83%) of yellow, crystalline **4:** mp 106–112 °C (from a mixture of dichloromethane and hexane); IR (KBr) 2270 (CN) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.43 (s, CH_2). Anal. Calcd for $C_6H_4Br_2N_2$: C, 27.30; H, 1.53; Br, 60.55; N, 10.61. Found: C, 27.28; H, 1.48; Br, 58.9; N, 10.69.

1,4-Dichloro-2-butene-2,3-dicarbonitrile (5). A solution of 4.6 g (0.044 mol) of **1** in 100 mL of chloroform, in a Pyrex flask, was stirred at 30–35 °C under irradiation from a (external) UV source while chloride was added through a gas dispersion tube. When an excess of chlorine was present (persistent yellow color; after ca. 3 h), the addition of the gas was terminated, and the reaction solution was allowed to stand overnight at room temperature. After removing a small amount of an insoluble material, hexane was added to the solution to the cloud point. Several crops of crystals were obtained by chilling to −20 °C and addition of more hexane to give a total of ca. 7.3 g (94%) of **5;** this solid discolored upon standing. Sublimation (high vacuum) gave a white, crystalline product, mp 102–103.5 °C, that retained its white color; IR (KBr) 2270 (CN) cm^{-1}; ^1H NMR ($CDCl_3$; run on the crude product) δ 4.45 (s, CH_2) and 3.0 (impurity). Anal. Calcd for $C_6H_4Cl_2N_2$: C, 41.18; H, 2.30; Cl, 40.51; N, 16.01. Found: C, 40.81; H, 2.54; Cl, 40.29; N, 15.43.

2,3-Bis(chloromethyl)succinimide (7). A solution of 9.0 g (0.086 mol) of **1** in 150 mL of methanol was stirred under nitrogen while a slow stream of anhydrous hydrogen chloride was added through a gas dispersion tube. No provision was made for cooling the reaction, and the gas was added for a total of 7–8 h (no attempt was made to meter the flow). The solvent was stripped under aspirator pressure. The residual paste was taken up in 100 mL of water. After allowing the mixture to stand overnight at room temperature, the product was extracted into methylene chloride. After drying (mole sieve), decolorizing (Norit A), and concentration, chilling the solution to −20 °C gave 3.77 g (23%) of **7:** mp 121–123 °C (from methylene chloride); IR (KBr) 3226 (NH), 1695 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.8 (broad s, 1, NH), 4.0 (CH_2 portion of an $A_2B_2X_2$ pattern, 4), 3.4 (CH portion of an $A_2B_2X_2$ pattern, 2). Anal. Calcd for $C_6H_7NO_2Cl$: C, 36.76; H, 3.60; Cl, 36.17; N, 7.15. Found: C, 36.93; H, 3.81; Cl, 36.9; N, 6.99.

2,3-Bis(bromomethyl)succinimide (6). A solution of 4.0 g (0.038 mol) of **1** in 100 mL of methanol was treated with gaseous hydrogen bromide in a manner similar to that described for the preparation of **7.** Addition required 2 h, and the temperature was kept at 20–27 °C. After concentrating the reaction solution to a volume of ca. 50 mL under aspirator pressure, 100 mL of water was added. A small amount (0.48 g, 4%) of (probably) 4-bromo-2-bromomethyl-3-cyanobutyramide was removed: IR (KBr) 3280 and 3180 (NH_2), 2270 (CN), 1665 and 1615 (amide) cm^{-1}. Anal. Calcd for $C_6H_8Br_2N_2O$: C, 25.38; H, 2.84; Br, 56.34; N, 9.86. Found: C, 27.7; H, 2.8; Br, 56.3; N, 9.9. After removal of this product, the yellow aqueous filtrate was extracted with dichloromethane. Evaporation of the extracts gave an oil. Addition of ether gave 0.62 g (6%) of **6:**[18] mp 129–130 °C; IR (KBr) 3225 and 3075 (NH_2), 1820, 1785, and 1710 (imide) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.0 (broad s, 0.7, NH), 3.8 (m, 4, CH_2), 3.5 (m, 2.3, CH), 1.7 (impurity, 5% of H). Anal. Calcd for $C_6H_7Br_2NO_2$: Br, 56.08. Found: Br, 55.1.

1-Piperidino-2-butene-2,3-dicarbonitrile (8 and 9). A solution of 1.53 g (0.015 mol) of **1** in 50 mL of benzene was stirred under nitrogen while 1.25 g (0.015 mol) of freshly distilled piperidine was added over a 10–15-min period. The slightly exothermic reaction (temperature rose about 5 °C) was accompanied by a color change from yellow to gray-green; continued stirring at room temperature for an hour gave a further color change to purple, then red, and finally dark red. After allowing the mixture to stand overnight at room temperature, the black solution was filtered to remove 0.04 g of a polymeric product; about 0.6 g of mixed **8** and **9,** mp 58–65 °C, was recovered from the mother liquor. Chromatographic separation (on silica gel, eluting with a mixture of hexane and ether) gave, first, **9:** mp 67.0–68.5 °C; IR (KBr) 2245 (CN) and 1625 (weak, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.30 (m, 2, CH_2C=),[19] 2.4 (m, 4, ring CH_2N), 2.20 (m, 3, CH_3),[19] 1.5 (m, ring CH_2, 6). Anal. Calcd. for $C_{11}H_{15}N_3$: C, 69.81; H, 7.99; N, 22.20. Found: C, 69.50; H, 8.18; N, 21.73. After elution of **9, 8** was collected: mp 46–48 °C; IR (KBr) 2220 (CN) and 1625 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.20 (m, 2, CH_2C=),[19] 2.4 (m, 4, ring CH_2N), 2.10 (m, 3, CH_3),[19] 1.5 (m, 6, CH_2). In another run, **8** and **9** were obtained in ca. 18 and 54% yields, respectively.

1-(1-Morpholino)-2-butene-2,3-dicarbonitrile (10 and 11). A solution of 2.19 g (0.021 mol) of **1** in 80 mL of THF was stirred while 1.74 g (0.020 mol) of morpholine was added as described for the preparation of **8** and **9.** After 24 h at room temperature, the blue solution was treated with Norit. The resulting amber solution was stripped under aspirator pressure to give 3.6 g of a dark solid. Recrystallization from hexane gave a mixture of white, crystalline **10** and **11** in a total yield of 2.18 g (55%): mp 79–83 °C; IR (KBr) 2220 (CN) and 1650 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.75 (m, 4, CH_2O), 3.4 (m, CH_2C=, 2),[19] 2.6 (m, ring CH_2N, 4), 2.35 (m, CH_3, 3)[19] with minor resonances at δ 3.25, 2.90, 2.18, and 1.7; mass spectrum *m/e* (rel intensity) 191 (18), 105 (47), 100 (85), 86 (86). Anal. Calcd for $C_{10}H_{13}N_3O$: C, 62.87; H, 6.76; N, 22.00. Found: C, 63.22; H, 6.74; N, 22.40. TLC analysis of the crystalline product showed two components, one greatly preponderant. Chromatography on silica gel (eluting with a mixture of cyclohexane and ether) of a 0.2-g sample gave 0.185 g of white, crystalline **11,** mp 84–85.5 °C, with ^1H NMR resonances identical to the major resonances described above for the mixture, and 0.019 g of **10** as a colorless oil; ^1H NMR ($CDCl_3$) δ 3.25 and 2.18 (for the "non-morpholine" portion of the spectrum).

1-(Dimethylamino)-2-butene-2,3-dicarbonitrile (12 and 13). A solution of 0.47 g (0.0045 mol) of **1** in 50 mL of THF was treated with 130 mL (0.0054 mol) of gaseous dimethylamine in the manner described for the preparation of **8** and **9.** The solvent was removed under aspirator pressure from the red-brown reaction solution after 3 h to give 0.64 g of a residual oil. High vacuum sublimation gave 0.34 g of a (wet) white solid mixed with 0.08 g of a yellow oil.[20a] The former, recrystallized from a mixture of methylene chloride and hexane, gave 0.17 g (25%) of (probably) **13:** mp 34.5–35.5 °C; IR (KBr) 2220 (CN), 1620 (weak, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.35 (s with a shoulder,[20b] 2, CH_2C=) and 2.33 (s, 9, CH_3C= and CH_3N); mass spectrum *m/e* (rel intensity) 149 (1.3), 58 (100). Anal. Calcd for $C_8H_{11}N_3$: C, 64.40; H, 7.43; N, 28.17. Found: C, 64.4; H, 7.4; N, 28.3.

1-(1-Piperidino)-1-butene-2,3-dicarbonitrile (14). Piperidine (17 g) was stirred at 80 °C while 2.0 g (0.019 mol) of **1** was added over a 2-min period. After an hour, the brown solution was evaporated in a stream of nitrogen. The residual oil was extracted with hexane, and the hexane solution was distilled to give 1.53 g (43%) of **14:** bp 156 °C (0.9 mmHg); mp 70.8–71.5 °C (ether); IR (KBr) 2270 and 2175 (CN), 1640 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.55 (s, 1, HC=), 3.1–3.6 (m, 5, CH_2N and HCC=), 1.6 (m, 6, ring CH_2), 1.5 (d, 3, CH_3). Anal. Calcd for $C_{11}H_{15}N_3$: C, 69.81; H, 7.99; N, 22.20. Found: C, 70.01; H, 7.98; N, 21.81.

2,3-Dicyanobutyraldehyde (15a) and 2,3-Dicyano-1-buten-1-ol (15b). The cyanoenamine **14,** 0.22 g (0.0012 mol), was added to 5 mL of 7% hydrochloric acid. The solid dissolved in about an hour. The colorless solution was extracted with ether. After drying (calcium chloride), evaporation gave 0.08 g (ca. 50%) of **15** as a colorless oil: IR (neat) 3225 (OH), 2775 and 1665 (aldehyde), 2220 (and "shoulder" ca. 2280, CN) cm^{-1}; ^1H NMR (acetone-d_6) δ 7.5 (s superimposed on a broad resonance, 1.67, HC=O and HC(OH)=C), 4.0 and 3.7 (2 "quartets" in a 1.4:1 integral ratio, 1, HCCN),[21] 1.45 (d, 3, CH_3).

1-(1-Piperidino)-2-cyano-2-butene-3-carboxamide Hydrochloride (16). A solution of 2.0 g (0.011 mol) of **9** in 75 mL of methanol was stirred in an ice bath while gaseous hydrogen chloride was added; the temperature rose to 58 °C during the (2 h) addition. The volatiles were removed under aspirator pressure to give 2.8 g of a cream-colored solid. The latter was stirred for 30 min or so with water and then the water was removed in vacuo. The product was dissolved in a mixture of ethanol and isopropyl alcohol. Cooling to −20 °C and addition of ether gave 1.97 g (77%) of **16:** mp 165–166 °C dec; IR (KBr) 3330, 3125, 1695, and 1610 (amide), broad absorption at 1850–2350 (salt), 2220 (CN) cm^{-1}; ^1H NMR (D_2O) δ 3.95 (s, 2, NCH_2C=), 3.2 (m, 4, ring CH_2N), 2.2 (s, 3, CH_3), 1.6 (m, 6, ring CH_2). Anal. Calcd for $C_{11}H_{17}N_3O$·HCl: C, 54.21; H, 7.44; N, 17.24. Found: C, 54.41; H, 7.35; N, 16.91.

1-Methoxy-2-butene-2,3-dicarbonitrile (17). To a stirred refluxing solution of 0.1 g of 1,8-bis(dimethylamino)naphthalene in 50 mL of methanol and 20 mL of acetonitrile was added 2.0 g (0.019 mol)

of 1 in a mixture of 25 mL each of methanol and acetonitrile over a 50-min period. The dark-brown solution was stripped under aspirator pressure, and the residue was extracted twice each with hexane and with ether. Removal of the solvent from the combined extracts gave 0.9 g of a yellow oil, which, by VPC, showed two major and at least six minor components. The major (oily) products, amounting to 73 and 22%, respectively, of the product mixture, were separated by chromatography on silica gel (eluting with a mixture of hexane and ether) and shown to be *trans*- and *cis*-**17**, respectively. *cis*-**17**: IR (neat) 2220 (CN), 1640 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.16 (s, 2, CH_2O), 3.34 (s, 3, CH_3O), and 2.14 (s, 3, CH_3C). *trans*-**17**: IR (KBr) (practically identical to that for *cis*-**17**); ^1H NMR ($CDCl_3$) δ 4.27 (s, 2, CH_2O), 3.42 (s, 3, CH_3O), and 2.30 (s, 3, CH_3C).

Addition of Thiolacetic Acid to 1. A solution of 0.99 g (0.0095 mol) of 1 in ca. 40 mL of THF was stirred in an ice bath while 1.59 g (0.021 mol) of thiolacetic acid was added rapidly. After a few minutes (VPC showed complete reaction of 1 in less than 5 min), distillation from a water bath at 30 °C through a short-path column under high vacuum removed the solvent and excess thiolacetic acid. The residue, 2.0 g of an orange, viscous oil, was purified by dry-column chromatography (on silica gel). From 0.76 g of the oil was obtained, as one fraction, 0.13 g of a crystalline solid mixed with an oil. Removal of the oil by washing with ether gave 0.016 g of 2,3-dicyano-1,4-butanedithiol diacetate (**18**): IR (KBr) 2270 (CN), 1695 (broad and strong, ester) cm^{-1}. Anal. Calcd for $C_{10}H_{12}N_2O_2S_2$: C, 46.85; H, 4.72; N, 10.93. Found: C, 47.25; H, 4.93; N, 11.44. Another fraction from the separation was 0.22 g of a pale yellow oil (unstable on the VPC injection port): IR (neat) 3175 (HC=?), 2250 (CN), 1710 (ester) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.3 (s, 1.23, H_2C=), 3.8 (m, 1.46), 3.4 (s, 0.77), 3.3 (d, 0.69), and 2.4 (s, 3, CH_3C=O).

Disodium 2,3-Dicyano-1,4-butanedisulfonate (19). A solution of 8 g (0.077 mol) of sodium bisulfite in 50 mL of water was stirred at room temperature with a solution of 3.3 g (0.032 mol) of 1 in 200 mL of ether. The ether layer immediately became yellow but became colorless again in 90 min; VPC analysis showed that reaction of 1 was complete. The aqueous phase was separated, and the water was removed in vacuo with gentle heating. The residual solid, 12.2 g (quantitative yield), was the trihydrate of the salt **19**: mp 225 °C dec; IR (KBr) 2270 (CN); ^1H NMR (D_2O) δ 4.8 (s, 6, H_2O), 4.0 (m, 2, CH), and 3.6 (m, 4, CH_2). Anal. Calcd for $C_6H_6N_2Na_2O_6S_2{\cdot}3H_2O$: C, 19.68; H, 3.30; N, 7.65; S, 17.51. Found: C, 19.76; H, 2.98; N, 7.63; S, 18.1. Bis(*S*-benzylisothiuronium) salt of **19** (poor mp, dec): Anal. Calcd for $C_{22}H_{28}N_6O_6S_4$: C, 44.13; H, 4.38; N, 14.04; S, 21.42. Found: C, 44.10; H, 4.61; N, 13.62; S, 20.9.

1-(*p*-Toluenesulfonyl)-2-butene-2,3-dicarbonitrile (20). A solution of 2.0 g (0.019 mol) of 1 in 35 mL of glacial acetic was stirred at 60 °C while a solution of 7.1 g (0.04 mol) of sodium *p*-toluenesulfinate in 25 mL of acetic acid and 10 mL of water was added dropwise during 20–25 min. The reaction was exothermic (temperature rose to ca. 85 °C), and the solution was allowed to stand at room temperature overnight. Analysis (by TLC) showed no 1 was present, and two products were formed in a 2:1 ratio in a crude yield of 96%. These were separated by preparative TLC. *cis*-**20** (80% pure by NMR): mp 138–150 °C; IR (KBr) 2250 (CN) 1625 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.65 (A_2B_2 pattern, 4, aromatic H), 4.10 (s, 2, CH_2), 2.48 (s, 3, aromatic CH_3), and 2.14 (s, 3, allylic CH_3). Anal. Calcd for $C_{13}H_{12}N_2O_2S$: C, 59.98; H, 4.65; N, 10.76; S, 12.32. Found: C, 59.32; H, 4.52; N, 10.42; S, 12.2. *trans*-**20** (90% pure by NMR): mp 135.5–139 °C; IR (KBr) 2245 (CN) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.65 (A_2B_2 pattern, 4, aromatic H), 4.20 (s, 2, CH_2), 2.50 (s, 3, aromatic CH_3), and 2.32 (s, 3, allylic CH_3).

Reaction of 19 with Methanolic Hydrogen Chloride. A suspension of 4.0 g (0.011 mol) of **19** in 75 mL of methanol was stirred at 50 °C (cooling as required) while gaseous hydrogen chloride was introduced for 2 h. The volatiles were removed under aspirator pressure. Water (50 mL) was added to the residual paste, and the mixture was stirred for 45 min. The white opalescent suspension was treated with aqueous sodium hydroxide to pH 8. Dimethyl 2,3-dicarbam-oyl-1,4-butanedisulfonate (**22**) was removed as an insoluble white solid, 0.28 g (8%): mp 185 °C with (acidic) gaseous dec; IR (KBr) 3450 and 3330 (NH_2), 1670 (C=O), 1350 and 1160 (sulfonate) cm^{-1}. Anal. Calcd for $C_8H_{16}N_2O_8S_2$: C, 28.91; H, 4.85; N, 8.43. Found: C, 28.10; H, 5.01; N, 8.46. After removal of **22**, the aqueous filtrate was diluted with ethanol and cooled to give 0.65 g (15%) of a hydrate of disodium 2,3-dicarbamoyl-1,4-butanedisulfonate (**21**): IR (KBr) 3450 and 3330 (NH_2), 1665 (carbonyl), 1330 and 1200 (latter very strong and broad, sulfonate) cm^{-1}. Anal. Calcd for $C_6H_{10}N_2Na_2O_8S_2{\cdot}2.5H_2O$: C, 18.32; H, 3.84; N, 7.12. Found: C, 18.78; H, 4.03; N, 7.19.

1,3-Butadiene-2,3-dicarboxamide (23). A solution of 5.0 g (0.048 mol) of 1 in methylene chloride was filtered to remove a trace of polymer. The solvent was evaporated, and the residual 1 was added to 20 mL of 96% sulfuric acid. Solution occurred rapidly with little, if any, exotherm. The water-white solution was allowed to stand overnight at room temperature, becoming slightly discolored. It was then poured over 100 g of crushed ice. The resulting solid was filtered and washed well with cold water then THF and ether to give 2.97–3.25 g (44–56%) of **23** (about 1.0 g of unreacted 1 was recovered from the wash solutions, resulting in 55–70% net yields). This product was sparingly soluble in boiling water and was recovered as small, off-white crystals: mp 300 °C dec (ammonia evolved); IR (KBr) 3330 and 3125 (NH_2), 1665 and 1610 ($CONH_2$), 950 (=CH_2) cm^{-1}; mass spectrum *m/e* (rel intensity) 140 (5.2), 123 (32), 80 (21), 52 (100). Anal. Calcd for $C_6H_8N_2O_2$: C, 51.42; H, 5.75; N, 19.99. Found: C, 50.94; H, 5.64; N, 19.61.

***N,N'*-Di-*tert*-butyl-1,3-butadiene-2,3-dicarboxamide (24).** A solution of 2.6 g (0.025 mol) of 1 and 10 mL of *tert*-butyl alcohol in 50 mL of 97% formic acid was stirred under reflux (55–60 °C) for 20 h. A small amount of insoluble polymer was removed, and the water-white solution was poured into 500 mL of ice–water. The mixture was extracted three times with ether. After drying (magnesium sulfate), removal of the ether gave a solid residue. This was triturated with hexane,[22] and the residual material was digested with ether, leaving 0.59 g of **24** as an insoluble material and another 0.36 g of **24** (15% total yield) was recovered from the ether: fine white plates, mp 174–176 °C (from THF and ether at −70 °C); IR (KBr) 3250 (NH), 3030 (H-C=), 1550, 1610, and 1640 (CONH), 925 (=CH_2, with overtone at 1850) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.05 and 5.55 (2 doublets, 4, =CH_2), 5.80 (s, 2, NH), 1.30 (s, 9, CH_3); ^{13}C NMR ($CDCl_3$) δ165.4 (C=O), 143.2 (—C=), 123.9 (CH_2=), 51.7 (CN), 28.6 (CH_3); mass spectrum *m/e* (rel intensity) 252 (2.2), 180 (13), 179 (10), 124 (100).

***N,N'*-Bis(2-methyl-2-butyl)-1,3-butadiene-2,3-dicarboxamide (25).** A solution of 2.0 g (0.019 mol) of 1 and 10 g of 2-methyl-2-butene in 50 mL of 97% formic acid was stirred under gentle reflux for 24 h. Treating the reaction solution as described for the preparation of **24** gave 3.0 g of a residual solid. This was recrystallized from a mixture of THF and hexane at −70 °C to give 0.50 g (a second crop of 0.25 g; total yield of 15%) of **25**: mp 142–143 °C (ether–THF at −70 °C); IR (KBr) 3225 (NH), 3125 (HC=), 1610 and 1560 (CONH), 925 (=CH_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.09 and 5.51 (2 doublets, 4, =CH_2), 5.77 (s, 2, NH), 1.77 (q, 4, CH_2), 1.34 (s, 12, CH_3), and 0.83 (t, 6, CH_3). Anal. Calcd for $C_{16}H_{28}N_2O_2$; C, 68.52; H, 10.06; N, 9.99. Found: C, 68.06; H, 10.15; N, 10.10.

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Registry No.—**1**, 19652-57-4; **2**, 6613-46-3; **3**, 6613-47-4; **4**, 59967-74-7; **5**, 59967-75-8; **6**, 64754-45-6; **7**, 64754-44-5; **8**, 58390-02-6; **9**, 58390-03-7; **10**, 64754-46-7; **11**, 64754-47-8; **12**, 64754-48-9; **13**, 64754-49-0; **14**, 64754-50-3; **15b**, 64754-51-4; **16**, 64754-52-5; *cis*-**17**, 64754-53-6; *trans*-**17**, 64754-54-7; **18**, 64754-55-8; **19**, 64771-38-6; **19** bis(*S*-benzylisothiuronium) salt, 64754-57-0; *cis*-**20**, 64754-58-1; *trans*-**20**, 64754-40-1; **21**, 64754-41-2; **22**, 64754-42-3; **23**, 64754-43-4; **24**, 64754-33-2; **25**, 64761-50-8; 4-bromo-2-bromomethyl-3-cyanobutyramide, 64784-28-7; piperidine, 110-89-4; morpholine, 110-91-8; dimethylamine, 124-40-3; thiolacetic acid, 507-09-5; methanol, 67-56-1; sodium bisulfite, 7631-90-5; sodium p-toluenesulfinate, 824-79-3; *tert*-butyl alcohol, 75-65-0; 2-methyl-2-butene, 513-35-9; 2-cyano-3-(*tert*-butylcarbamoyl)-1,3-butadiene, 64754-34-3.

References and Notes

(1) W. L. Bailey, R. L. Hudson, and E. T. Yates, *J. Org. Chem.*, **28**, 828 (1963).
(2) (a) E. Müller, R. Mayer-Mader, and K. Dinges, 163rd National Meeting of the American Chemical Society, April 1972, Preprint of INDE-44; (b) C. S. Marvel and N. O. Buice, *J. Am. Chem. Soc.*, **71**, 37 (1949); (c) M. Tanaka, *Kogyo Kagaku Zasshi*, **60**, 1509 (1957); *Chem. Abstr.*, **53**, 18925 (1959); (d) M. Tanaka and M. Yubio, *ibid.*, **61**, 714 (1958); *Chem. Abstr.*, **55**, 10313 (1961).
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(4) (a) R. L. Cobb and J. E. Mahan, *J. Org. Chem.*, **42**, 2829 (1977); (b) R. L. Cobb and J. E. Mahan, unpublished observations.
(5) Minor products (7 and 5% yields by VPC) containing nonconjugated nitrile groups and no unsaturation (by IR and NMR) were formed. For these mixed products: mp 44–45 °C; ^1H NMR ($CDCl_3$) δ 2.80 (m, 2) 1.53 (d, 6); ^{13}C NMR ($CDCl_3$) δ 29.8 (CH), 15.8 (CH_3). Although the expected by-products are the diastereomers of butane-2,3-dicarbonitrile [lit. mp 56–58 °C and 45–46 °C for *d,l* and meso isomers, respectively; see R. P. Linstead and M.

Whalley, *J. Chem. Soc.*, 3722 (1955)] the NMR spectra of such a mixture should be more complicated than that obtained.

(6) W. F. Beech and H. A. Piggott, *J. Chem. Soc.*, 423 (1955).

(7) Further corroboration of this assignment is the slight shift in the opposite direction observed for the nitrile carbons. Although not as well demonstrated, steric perturbations apparently shift sp carbon resonances in a direction opposite to that found for sp^3 carbons. See, e.g., G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, p 130.

(8) See ref 4a and references cited therein.

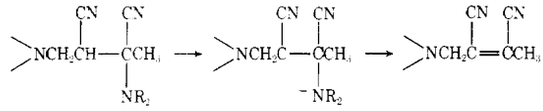
(9) It is appropriate to note that the diene 1 undergoes facile polymerization to give an intractable and often dark-colored product under such diverse conditions as solution in or contact with dimethylformamide, dimethyl sulfoxide, triphenylphosphine, some samples of ethanol, acetone, acetonitrile, amine vapors, aqueous alkali, and often with alkali–metal salts of weak acids.

(10) These conditions allow a "normal" addition of diphenylamine to acrylonitrile; see, e.g., R. C. Cookson and F. G. Mann, *J. Chem. Soc.*, 67 (1949), and J. T. Braunholtz and F. G. Mann, *ibid.*, 1817 (1953).

(11) By column chromatography, a small amount of an oily cyano (by IR) product was isolated which exhibited ^1H NMR resonances at δ 7.0–7.6 and 1.2–1.9 (a pair of doublets superimposed on a multiplet) in a proton ratio of 3–4:1. The resonances of the nonaromatic protons are too far upfield to correspond to any conceivable structure containing Ar_2NCH_2 and HCCN groups.

(12) While both *E* and *Z* isomers of **14** are possible, the single olefinic resonance suggests that only one is present. No attempt was made to determine this further.

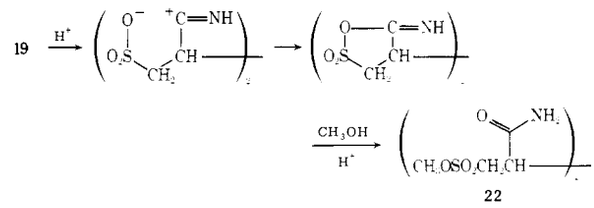
(13) Addition of the amine at the γ position (cf. eq 2), which may also occur, would not be observed, since proton abstraction and elimination would result in formation of the starting adduct



(14) Separation of these products by TLC was unsatisfactory. Analysis (by IR) of two isolated fractions showed strong cyanoenamine absorptions at ca. 2170 and 1640 cm^{-1}, but NMR studies of these same materials were equivocal. Crude product from a similar reaction of **10** and **11** with methylamine and with *tert*-butylamine also gave spectral evidence for the presence of a cyanoenamine.

(15) We are grateful to a referee for suggesting that amine participation would activate the γ nitrile to protonation and hydrolysis, yielding **16** rather than the alternative 1-(1-piperidino)-3-cyano-2-butene-2-carboxamide.

(16) Formation of a sulfonate ester by this means is unprecedented. If this structure is correct, a mechanism involving participation of the sulfonate and cyano groups may be visualized:



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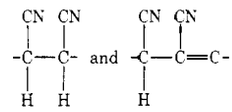
(17) Melting points (uncorrected) were recorded on a Mel-Temp apparatus; IR spectra were obtained on a Perkin-Elmer Model 137 Infracord; NMR spectra (vs. internal Me_4Si) were determined on Varian T60 and CFT20 instruments; mass spectra were recorded on a CEC 110B instrument (70 eV).

(18) There was insufficient material for a careful analysis. However, the data available give substantial confirmation of the structure.

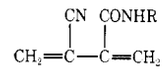
(19) The resonances for the methyl and allylic methylene hydrogens were complicated by long-range coupling effects.

(20) (a) Although not investigated, this oil may have been largely **12.** (b) The shoulder on this resonance may be due to the presence of **12** as an impurity.

(21) The broad resonance at δ 7.5 is due to active proton exchange, while the narrow singlet at δ 7.5 represents the aldehydic and enolic protons. The two "quartets" at δ 3.7 and 4.0 are due to the methine hydrogens of respectively, and the integral ratio (1:1.4) suggests that the latter (enol form) predominates in the equilibrium.



(22) Cooling the hexane extracts at −70 °C gave 0.44 g of a white crystalline solid which may have been the cyanoamide related to **24**



IR (KBr) 3225 (NH), 2275 (CN), 1640 and 1650 (CONH), 960, 925 (CH_2=) cm^{-1}.

Chemistry of 1,3-Butadiene-2,3-dicarbonitrile. 2. Reactions with Dienophiles

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Reaction of butadiene-2,3-dicarbonitrile (1) with diazomethane yielded the bipyrazoline **2,** which lost nitrogen thermally to give the bicyclopropane **3.** With ethyl diazoacetate, **1** gave the bipyrazoline **7,** but the major product was an intractable solid. **1** yielded the expected (4 + 2) cycloadducts with maleic anhydride, *N*-ethylmaleimide, methyl acrylate, acrylonitrile, 1-cyanovinyl acetate, ethyl vinyl ether, divinyl ether, 1-methoxycyclohexene, dimethylisobutenylamine, and 1-methoxycyclohexene. With furan, **1** gave both 1:1 benzofuran and 2:1 dibenzofuran types of adducts; with *N*-methylpyrrole, only the corresponding 2:1 type of adduct was isolated. With dimethyl acetylenedicarboxylate, **1** gave dimethyl 4,5-dicyanophthalate.

Because of its multifunctionality, the chemistry of 1,3-butadiene-2,3-dicarbonitrile (**1**) is rich and varied. It undergoes reactions characteristic of a conjugated diolefin,[1,2] an activated olefin,[3,4] and a nitrile.[3] As a strongly electron-deficient diene, **1** is an example of the less-studied class of dienes which exhibit an "inverse electron demand" in Diels–Alder reactions.[5] These are considered to undergo normal (2 + 4) cycloadditions only with electron-rich dienophiles, although other types of cycloadditions, e.g., (3 + 2), are not necessarily subject to these electronic restrictions. While some Diels–Alder reactions of **1** have been reported,[4] we wish to describe here the results of our study utilizing **1** as a diene in both (3 + 2) and (4 + 2) cycloaddition processes.

(3 + 2) Cycloadditions. The diene **1** underwent facile reaction with diazomethane to give 3,3′-bi(1-pyrazolinyl)-3,3′-dicarbonitrile (**2**) as a mixture of (probably) two (chiral) isomers. While there were subtle differences in the ^1H NMR spectra of these products (only one of which was isolated in

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