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Dimerizations of Electronegatively Substituted Dienes

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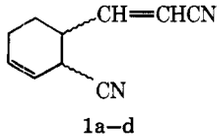
Structures have been assigned to four Diels–Alder dimers of 1-cyanobutadiene and two dimers of 2-fluorobutadiene by NMR techniques. Diradical stabilities can account for the structural change in the dimers of 2-fluorobutadiene and 2-cyanobutadiene. A new eight-membered ring dimer of 2-cyanobutadiene has been isolated, and some chemistry of the cyanobutadienes and their dimers is described.

The major product of the thermal dimerization of butadiene, 4-vinylcyclohexene, is derived from a 2 + 4 cycloaddition.[1] Minor amounts of the 2 + 2 product 1,2-divinylcyclobutane and its Cope rearrangement product 1,5-cyclooctadiene are also found.[1] 2-Methylbutadiene[2] and 2-chlorobutadiene[3] dimerizations have also been studied in detail. Before modern spectroscopic tools for structure identification were available, the dimerizations of 1-[4] and 2-cyanobutadienes[5] and 2-fluorobutadiene[6] were reported.

In this paper we present spectral evidence which revises the structures of the 1-cyanobutadiene and 2-fluorobutadiene dimers. A new 2-cyanobutadiene dimer has been isolated and characterized, and some chemistry of the cyanobutadiene dimers is presented.

1-Cyanobutadiene Dimerization. Heating 1-cyanobutadiene either neat or in *N*-methylpyrrolidinone solution at a pot temperature of 200 °C until no further reflux occurs followed by vacuum distillation gives a mixture of four major 1-cyanobutadiene dimers (**1a–d**). Gas chromatography on a 1,4-cyclohexane–dimethanol succinate column revealed many more minor peaks, all of which had the empirical formula of cyanobutadiene dimers by GC/MS. Only the four major products were characterized. Heating either pure *cis*- or pure *trans*-1-cyanobutadienes gives two major products from each with no crossover.

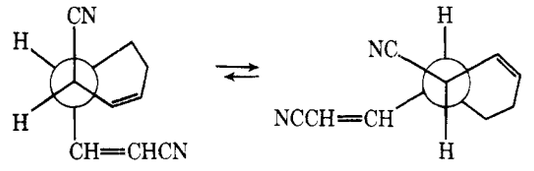


1a–d

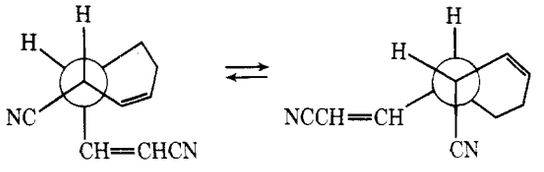
Pure samples of two of the four isomers could be isolated. Isomer **1a**, the lowest boiling, could be purified by distillation. Isomer **1b** crystallized from the crude liquid on extended standing. Isomers **1c** and **1d** could be concentrated by preparative GC but not completely separated. By ^{1}H NMR isomers **1a** and **1b** have cis-substituted external double bonds while the other two are trans.

The ring configurations are inferred from the general pattern of the NMR spectrum of the aliphatic region. The cis isomers should be flexible and invert between two relatively equally populated twist chair conformations. The conformation of the trans isomers should be biased toward a diequatorial orientation. Isomers **1a** and **1d** show only two multiplets for the CH_2CH_2 protons while isomers **1b** and **1c** show three resonances in the ratio 2:1:1. The former are assigned to cis isomers and the latter two to trans. The four dimers are present in essentially equal amounts when formed from mixed *cis*- and *trans*-1-cyanobutadienes.

Palladium-catalyzed hydrogenation at room temperature

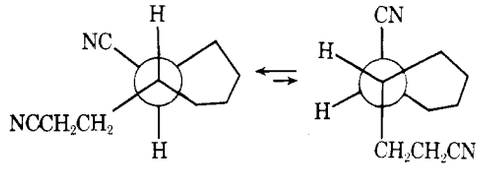


1b and 1c
trans

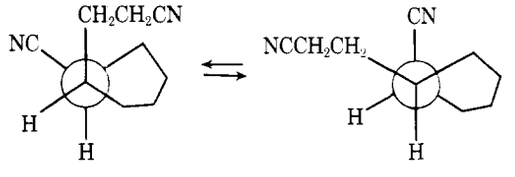


1a and 1d
cis

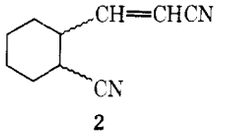
gives dihydro derivatives **2** in which the ring double bond is saturated. At slightly higher temperatures the cyanovinyl group is reduced to a cyanoethyl group **3.** The two tetrahydro compounds **3** were separated by preparative gas chromatography on an XE-60 column. The isomer with the earlier retention time shows an NMR spectrum characteristic of a relatively flexible cis isomer **3a**, while the second isomer shows many individual resonances characteristic of a trans form **3b.**



trans
3b

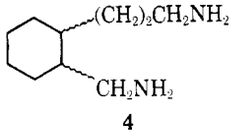


cis
3a

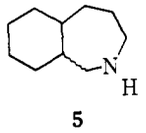


2

Hydrogenation of **1** with Raney nickel or cobalt gives a mixture of two isomeric diamines **4** and two perhydroazepines **5.**

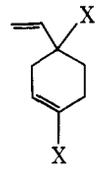


4

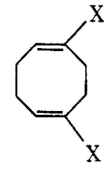


5

2-Cyanobutadiene Dimerization. Letting inhibited 2-cyanobutadiene stand at room temperature gives relatively pure 1,4-dicyano-4-vinylcyclohexene (**6a**),[5] but when the diene is heated, the product is considerably more complex. The lowest boiling and still the major component is **6a,** but a second product **7b** can be obtained in pure form as a high-boiling fraction. The intermediate fraction is quite complex, and no pure cyanobutadiene dimers were isolated. The proton NMR of **7b** resembled that of 1,6-dichloro-1,5-cyclooctadiene (**7a**) quite closely,[3b] suggesting the two products have similar



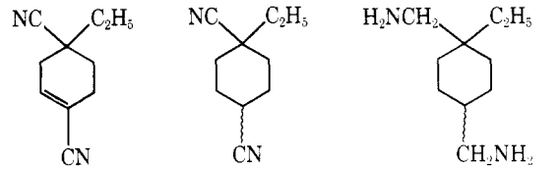
6a, X = CN
b, X = F



7a, X = Cl
b, X = CN
c, X = F

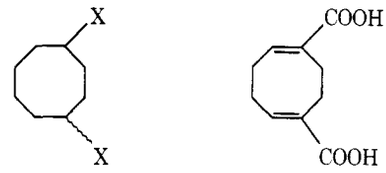
structures. Decoupling the olefinic protons gave two singlets for the aliphatic protons. The 1,5-disubstituted isomer would be inconsistent with this observation.

Dimer **6a** can be hydrogenated in steps. Room temperature, 40 psi hydrogen, and a palladium catalyst give dihydro compound **8.** Palladium at room temperature and 100 psi gives the tetrahydro compounds **9.** Raney nickel at 1500 psi and 135 °C gives the mixed diamines **10.**



8 9 10

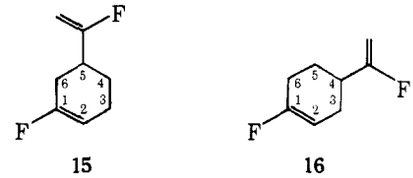
Cyanobutadiene dimer **7b** can be reduced with a palladium catalyst to the saturated dinitriles, **11a,** or with Raney nickel to the diamines **11b.** Hydrolysis yields the dicarboxylic acid **12.**



11a, X = CN
b, X = CH_2NH_2

12

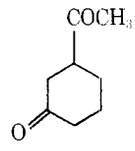
2-Fluorobutadiene. Fluorobutadiene, like other butadienes, dimerizes on standing. Gas chromatography of the crude liquid residue showed one dimer peak but fluorine NMR showed two pairs of signals in the ratio of ca. 4:1. Fractional distillation gave analytically pure fluorobutadiene dimer with an unchanged fluorine NMR spectrum. That these four signals are attributable to two isomers each with two nonequivalent fluorines is suggested by heating the monomer to 100 °C overnight. In addition to polymer, the same four signals are seen, in a different ratio, with the same peaks predominating, but still in two pairs. From these data symmetrical structures such as **7c** are eliminated. The proton NMR spectrum gives the ratio of olefinic to aliphatic protons as three to seven eliminating such possible structures as **6b** which have four vinyl protons. Two possibilities remain for the two isomers fluoro(fluorovinyl)cyclohexenes **15** and **16** as discussed previously.[6] The carbon NMR (Table I) is useful in distinguishing these possibilities.



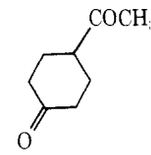
15 16

The major isomer shows four aliphatic resonances: two doublets of doublets, a doublet, and a broad singlet. A combination of chemical shift and coupling constant arguments can be used to assign these four resonances to their proper

carbons in one of the two possibilities **15** and **16**. Two-bond, carbon–fluorine coupling is reasonably invarient at ~20 Hz.[7] Thus the two low-field resonances are either C-5 and C-6 of **15** or C-4 and C-6 of **16**. Four-bond, carbon–fluorine coupling is generally small.[7] Simple doublets would therefore be expected for C-4 and C-6 of **16**, while the three-bond couplings of C-3 and C-5 in **15** should be discernible and are. Three-bond carbon–fluorine coupling is angle dependent and maximum in the trans arrangement.[7b] From models in the twist chair conformation with the fluorovinyl group equatorial the dihedral angle between the external fluorine and ring carbons 4 and 6 is near 120° accounting for the small couplings to both these carbons. The trans three-bond couplings involving F-1 are both 9 Hz (C-3 and C-5). The fluorobutadiene dimers were hydrolyzed with concentrated sulfuric acid at room temperature to diketones **17** and/or **18**. The carbon NMR spectrum



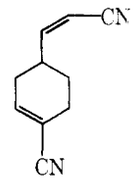
17



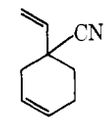
18

showed 8 peaks which is consistent with the "meta" structure **17** for the diketone and **15** for the major fluorobutadiene dimer, reversing the previous assignment.[6]

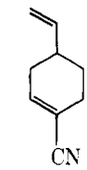
Reaction Products from Different Dienes. By taking advantage of the differing rates of dimerization of various butadienes mixed adducts can be formed. For example *cis*-1-cyanobutadiene is very reluctant to dimerize because of steric hindrance in the cisoid form of the diene component. On the other hand 2-cyanobutadiene is an avid diene. Adding 2-cyanobutadiene slowly to a hot solution of *cis*-1-cyanobutadiene leads to a moderate yield of dinitrile **19** as well as some **6a**. Adding 2-cyanobutadiene to hot butadiene forms the two adducts **20** and **21** in the ratio 1:3.



19



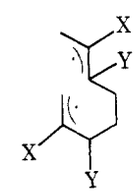
20



21

Discussion

The dimerizations of the various 2-substituted butadienes show remarkable variations. We do not wish to debate the "concertedness" of the 2 + 4 cycloaddition reactions, but whether diradical character is produced in the transition state or not, the formation of products can often be deduced by considering the stability of supposed intermediate radicals. The major dimers from 2-cyanobutadiene and 2-fluorobutadiene have opposite orientations at both such centers. If the cyanobutadiene dimers are explained by the stabilizing effect

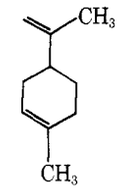


X = F; Y = H
X = H; Y = CN

of α-cyano groups, by contrast, α-fluorovinyl radicals may not be stabilized. This is consistent with the observation that while vinyl fluoride gives significant head-to-head incorporation when polymerized under radical conditions[8] acrylonitrile gives a much more uniform head-to-tail polymer.[9] The two isomers of 2-chlorobutadiene dimer analogous to **15** and **16** together comprised ca. 30% of the dimerization product.[3a] At 1 atm they were present in approximately equal amounts, but at 10 000 atm the "meta" isomer was formed in twice the yield of the "para" isomer.[3b] There was no single major product as four-, six-, and eight-membered ring dimers were formed in nearly equal amounts, and all possible isomers of the 2 + 4 cycloadduct are present or implied. The major 2-methylbutadiene dimer[2] **22** corresponds to a structure not encountered from electronegatively substituted butadienes.

Table I. Carbon-13 NMR Parameters of 2-Fluorobutadiene Dimer **15**

Assignment	Chemical shift, ppm	C–F couplings, Hz
3	22	8.8
4	25.5	Broad singlet
6	29.1	25, 3
5	37.4	27, 9
β	88.6	20.6
2	101.8	16
1	158.5	254
α	169.1	257



22

A molecular orbital theory has been proposed which predicts the regioselectivity of the Diels–Alder reaction.[11]

Three modifications are presented requiring varying degrees of computation of the preferred Hückel wave functions. The favored version appears to be the one of intermediate complexity requiring only the HOMO and LUMO wave functions and energies.

The theory successfully predicts the structures of cyanobutadiene dimers but fails with the 2-halobutadienes and 2-methylbutadiene. For 2-chloro-, 2-fluoro-, and 2-methylbutadiene the predicted dimer has the analogous structure to that from 2-cyanobutadiene.

In spite of the differences observed, one should not attempt to read too much into them. The energy differences of the transition states to account for these selectivities could be less than 5 kcal/mol and to accurately predict the relative stabilities of transition states to this accuracy is difficult at present.

Experimental Section

Cyanobutadienes and their dimers were prepared as previously described.[10] Melting and boiling points are uncorrected. NMR spectra were obtained on Varian A60, HA100, HR220, and XL100 instruments. Infrared spectra were obtained as mulls on a Perkin-Elmer 21 instrument.

4(2-Cyanovinyl)-3-cyanocyclohex-1-ene (1). A mixture of *cis*- and *trans*-1-cyanobutadiene was heated at reflux until the temperature of the solution reached 200 °C. The mixture of four cyanobutadiene dimers was isolated by distillation, bp 120–160 °C (0.3 mm).

NMR Characterization of 1-Cyanobutadiene Dimers (220 MHz, $CDCl_3$). Dimer A: δ 6.62 (t, J = 9, 1 H), 6.02 (d, J = 10 Hz, t, J = 4 Hz, d, J = 2 Hz, 1 H), 5.68 (m, 1 H), 5.50 (d, J = 9 Hz, 1 H), 3.34 (s, $W_{1/2}$ = 12 Hz, 1 H), 3.10 (t, J = 5 Hz, t, J = 10 Hz, 1 H), 2.23 (m, 2 H), 1.85 (m, 2 H). **Dimer B:** δ 6.39 (t, J = 9 Hz, 1 H), 6.00 (m, 1 H), 5.64 (m, 1 H), 5.52 (d, J = 9 Hz, 1 H), 3.20 (m, 1 H), 3.10 (m, 1 H), 2.20

(m, 2 H), 1.84 (m, 1 H), 1.63 (m, 1 H). **Dimer C:** δ 6.68 (d, d, J = 16, 8 Hz, 1 H), 6.20 (m, 1 H), 5.68 (m, 1 H), 5.59 (d, J = 16 Hz, 1 H), 3.26 (d, J = 9 Hz, 1 H), 2.73 (m, 1 H), 2.23 (m, 2 H), 1.95 (m, 1 H), 1.61 (m, 1 H). **Dimer D:** δ 6.75 (d, d, J = 16, 8 Hz, 1 H). 5.98 (m, 1 H), 5.72 (m, 1 H), 5.59 (d, J = 16 Hz, 1 H), 3.25 (d, J = 10 Hz, 1 H), 2.73 (m, 1 H), 2.23 (m, 2 H), 1.82 (m, 2 H).

1-(2-Cyanovinyl)2-cyanocyclohexane (2). A solution of 16 g of 1 in 30 mL of ethanol was shaken for 1 h under 40 psi of H_2 with 100 mg of 5% Pd/C. The catalyst was filtered and the product was distilled giving 14.3 g of colorless liquid: bp 100–120 °C (0.1 mm); IR 3.3, 3.4, 3.5, 4.45, 6.85, 6.96, 11.4, 11.55, 13.7 μm; ^{1}H/NMR (CCl_4/Me_4Si) δ 5.4–6.2 (pseudo-AB, 2 H); 3.0, 3.3 (broad singlets, total 1 H), 1–2.6 (aliphatic, 9 H). Anal. Calcd for $C_{10}H_{12}N_2$: C, 75.0; H, 7.5; N, 17.5. Found: C, 74.6; H, 7.6; N, 17.6.

1-(2-Cyanoethyl)-2-cyanocyclohexane (3). A solution of 10 g of 1 in 40 mL of ethanol and 0.2 g of 5% Pd/C was hydrogenated at room temperature and 1000 psi. The catalyst was filtered and the solution was distilled giving 7.6 g of colorless liquid: bp 114–122 °C (0.1 mm); IR (neat) 3.39, 3.47, 4.45 μm. **3a:** NMR ($CDCl_3$) δ 1.31 (m, 1 H), 1.70 (m, 7H), 2.01 (d, J = 9 Hz, 1 H), 2.95 (s, $W_{1/2}$ = 9, 1 H). **3b:** NMR ($CDCl_3$) δ 1.30, 1.61, 1.79, 1.99 (d, d, J = 4, 12.5 Hz), 2.10 (m), 2.25 (d, J = 4 Hz, t, J = 12 Hz, 1 H), 2.38 (t, J = 6 Hz, 1 H); IR 3.39, 3.47, 4.45 μm. Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.1; H, 8.6. Found: C, 74.5; H, 8.0.

1-(3-Aminopropyl)-2-(aminomethyl)cyclohexane (4). Perhydro-2-benzazepine (5). A solution of 60 g of 1 in 600 mL of THF with 1 g of 5% Pd/C and 25 g of Raney cobalt was pressured to 1000 psi with H_2 and heated at 50 °C for 2 h then at 135 °C for 8 h. The catalysts were filtered and the solvent was removed on a rotary evaporator. The residue was dried over CaH_2 and distilled through an 18 in. spinning band column giving 50 g of colorless liquid: bp 100–117 °C (1 mm); IR 2.94, 3.02, 3.40, 3.47, 6.20 μm; ^{1}H NMR (CCl_4/Me_4Si) δ 0.88 (s, 2 NH_2), 2.58 (t, 2 CH_2N), 0.9–1.9 (m, 14 H, aliphatic). Anal. Calcd for $C_{10}H_{22}N_2$: C, 70.6; H, 12.9; N, 16.5. Found: C, 70.8; H, 12.2; N, 16.7.

The fore run, bp 74–80 °C (0.3 mm) yield ca. 10%, consisted of 2-azabicyclo[5.4.0]undecane. Anal. Calcd for $C_{10}H_{19}N$: C, 78.4; H, 12.5. Found: C, 78.1; H, 12.3. Higher boiling material consisted of dimeric triamines, bp 225–235 °C (0.4 mm).

1,4-Dicyano-4-vinylcyclohex-1-ene (6a): NMR ($CDCl_3$) δ 2.08 (m, 2 H), 2.6 (m, 4 H), 5.2–6.0 (m, 3 H), 6.65 (m, =CH).

1,6-Dicyano-1,5-cyclooctadiene (7b) Distillation of crude 2-cyanobutadiene dimer gave a high boiling fraction, 130 °C 50 (μm), which crystallized on standing: mp 122.5–124 °C (MeOH); IR 3.30, 3.34, 3.40, 3.43, 3.49, 3.52, 4.51, 6.12 μm; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 6.51 (t, broad, J = 7 Hz, 2 =CH), 2.71 (s, 2 CH_2), 2.61 (virtually coupled triplet, J = 7 Hz, 2 CH_2); yield ca. 10%. Anal. Calcd for $C_{10}H_{10}N_2$: C, 75.1; H, 6.4; N, 17.7. Found: C, 75.8; H, 6.2; N, 17.8.

1,4-Dicyano-4-ethylcyclohex-1-ene (8). A mixture of 15.8 g of **6a,** 30 mL of ethanol, and 95 mg of 5% Pd/C was shaken at room temperature with 40 psi of hydrogen for 2 h. The catalyst was filtered, the ethanol was removed on a rotary evaporator, and the residue was distilled, giving 14.6 g of colorless liquid, bp ~100 °C (1 mm), which solidified on standing: mp 75–77 °C; IR 3.25, 3.33, 3.38, 3.44, 4.45, 4.48, 6.05, and 7.30 μm; NMR (CCl_4) δ 6.53 (m, 1), 1.12 (t, J = 7 Hz, CH_3), 1.46–4.58 (aliphatic multiplet). Anal. Calcd for $C_{10}H_{12}N_2$: C, 75.0; H, 7.6; N, 17.5. Found: C, 74.7; H, 7.5; N, 17.6.

1,4-Dicyano-4-ethylcyclohexane (9). A solution of 75 g of **6a** in 750 mL of ethanol with 3 g of 5% Pd/C was hydrogenated at 100 psi and room temperature. The catalyst was filtered and the ethanol was removed on a rotary evaporator and the residue was distilled giving 63 g of product as a colorless liquid, bp 112–121 °C (0.4 mm), which solidified on standing: mp 65–66 °C; IR 3.38, 3.48, 4.46, and 7.23 μm; NMR (CCl_4) only aliphatic absorptions. Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.1; H, 8.6. Found: C, 73.8; H, 8.8.

1,4-Bis(aminomethyl)-1-ethylcyclohexane (10). In a bomb was placed 16 g of **6a,** 200 mL of THF, 1.5 g of 5% Pd/C, and 10 g of Raney cobalt. The bomb was cooled, evacuated, and pressured to 500 psi of H_2. After 1 h hydrogen was vented and 50 g of ammonia distilled in. The bomb was pressured to 1500 psi of H_2 and heated at 135 °C for 8 h.

The catalyst was filtered and the solvent was stripped on a rotary evaporator and the residue distilled giving 10.3 g of diamine as colorless liquid: bp 82–88 °C (0.2 mm); IR 2.94, 3.02, 3.42, 3.48, and 6.15 μm; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 1.00 (s, NH), 2.43, 2.60 (s, s, CH_2N), 0.6–1.7 (m, aliphatic), 2.55 (m, $HCCH_2N$). Anal. Calcd for $C_{10}H_{22}N_2$: C, 70.6; H, 12.9; N, 16.5. Found: C, 70.3; H, 12.9; N, 16.0.

1,4-Dicyanocyclooctane (11a). 7b (10 g), 0.5 g of 5% Pd/C, and 30 mL of THF were heated at 100 °C under 1000 psi of H_2. The catalyst was removed and 7.1 g of product distilled as a colorless liquid: bp 125 °C (20 μm); IR 3.39, 3.47, 4.46 μm; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 2.83 (broad, 2 H), 1.5–2.0 (m, 12 H). Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.1; H, 8.6; N, 17.3. Found: C, 75.7; H, 8.6; N, 17.4.

1,4-Bis(aminomethyl)cyclooctane (11b). Dinitrile **7b** (10 g), 20 mL of THF, 5 g of Raney cobalt, and 10 g of ammonia were heated at 135 °C for 8 h under 1000 psi of H_2. Catalyst was separated and 7.5 g of product distilled as a colorless liquid: bp 90 °C (0.25 mm); IR 2.97, 3.04, 3.42, 3.47, 6.25 μm; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 1.07 (s, 4 NH), 1.5 (broad, 14 H), 2.4–2.6 (broad 4 H). Anal. Calcd for $C_{10}H_{22}N_2$: C, 70.6; H, 12.9; N, 16.5. Found: C, 70.4; H, 12.1; N, 16.4.

1,5-Cyclooctadiene-1,6-dicarboxylic Acid (12). A solution of 10 g of dicyanocyclooctadiene **7b** and 20 g of sodium hydroxide in 100 mL of H_2O was refluxed overnight with N_2 sparging. After acidifying with HCl a white solid formed which was filtered and recrystallized from water giving 13.2 g of product: mp 178–180 °C; IR 3.38, 3–4, 5.92, 6.16, 10.65 μm. Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.2; H, 6.2. Found: C, 61.5; H, 5.9.

2-Fluorobutadiene Dimer (15). A cylinder of 2-fluorobutadiene in toluene had been stored at room temperature for at least 4 years. Material boiling below room temperature under an oil pump vacuum was transferred to another cylinder and the nonvolatiles were recovered by decanting the liquid contents. No solid polymer was observed. 2-Fluorobutadiene dimers were separated from toluene by distillation through an 18 in. spinning band column: bp 53 °C (26 mm); IR 3.27, 3.39, 3.48, 5.85, 5.97, 8.83, 11.93 μm; ^{19}F NMR (CCl_4/$CFCl_3$) major isomer δ −100.8 (d, d, d, d, J = 50, 19, 12, 2 Hz), −102.1 (d, J = 16 Hz, broad), minor isomer δ −99.7, −102.3; ^{1}H NMR (CCl_4/Me_4Si) δ 1.2–2.9 (m, 7 H), 4.20 (d, d, J = 8, 2.6 Hz, 1 H), 4.48 (d, d, J = 50, 2.6 Hz, 1 H), 5.20 (d, J = 16 Hz, m, CH=CF). Anal. Calcd for $(C_4H_5F)_n$: C, 66.6; H, 7.0; F, 26.4. Found: C, 66.5; H, 7.0; F, 26.2.

Hydrolysis of 2-Fluorobutadiene Dimer (17). To 10 mL of concentrated sulfuric acid at room temperature was added with stirring 5 mL of a 50% solution of 2-fluorobutadiene dimer in toluene. The red solution was stirred for 1 h at room temperature and then poured onto 100 mL of ice. The aqueous solution was extracted with two 100-mL portions of dichloromethane. The organic phase was dried with magnesium sulfate and concentrated on a rotary evaporator. The diketone was purified by preparative gas chromatography on a 6 ft × 0.25 in. column of 10% SE-30/Chromosorb W-HP programmed from 75 to 190 °C at 10 °C/min and a flow rate of 60 cm^3/min. The retention time was 12 min: ^{13}C NMR ($CDCl_3$) δ 209.6, 208.2, 50.7, 42.3, 40.7, 28.0, 27.0, 24.6; mol wt (MS) 168.

1-Cyano-4-(2-cyanovinyl)cyclohex-1-ene (19). To 44 g of *cis*-1-cyanobutadiene at 75 °C was added dropwise with stirring 44 g of 2-cyanobutadiene. The solution was heated at 75 °C overnight. GC showed essentially equal amounts of **6a** and **19.** Slow distillation through a spinning band column gave **19** as a colorless liquid: bp 116–121 °C (0.3 mm); IR 3.25, 3.40, 4.50, 6.08, 6.15, 13.25 μm; NMR (CCl_4/Me_4Si) δ 1.4–3.0 (m, 7 H), 5.37 (d, J = 11 Hz), 6.20 (d, d, J = 11, 9.5 Hz), 6.55 (m). Anal. Calcd for $C_{10}H_{10}N_2$: C, 75.9; H, 6.4; N, 17.7. Found: C, 75.8; H, 6.5; N, 18.0.

4-Vinyl-4-cyanocyclohex-1-ene (20). In a 400-mL bomb was placed 200 mL of butadiene. At 100 °C a solution of 50 g of 2-cyanobutadiene and 1 g of hydroquinone in 100 mL of ether was added over a 6-h period. Heating was continued 1 h longer. The solvent was removed on a rotary evaporator and the residue was distilled on an 18 in. spinning band column to give two fractions: **20,** 8 g; bp 93–97 °C (17 mm); IR 3.28, 3.40, 3.49, 4.47, 6.03, 6.08, 10.12, 10.79 μm; NMR δ 1.5–2.5 (6 H), 5.1–5.9 (5 H). Anal. Calcd for $C_9H_{11}N$: C, 81.2; H, 8.3; N, 10.5. Found: C, 81.1; H, 8.3; N, 10.7.

4-Vinyl-1-cyanocyclohex-1-ene (21). Continued distillation from the synthesis of **20** gave **21:** bp 103 °C (17 mm); 24 g; IR 3.24, 3.41, 4.51, 6.09, 10.07, 10.90 μm; NMR olefinic–aliphatic = 4:7. Anal. Calcd for $C_9H_{11}N$: C, 81.2; H, 8.3; N, 10.5. Found: C, 80.9; H, 8.2; N, 10.3.

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Registry No.—*cis*-**1,** 63763-44-8; *trans*-**1,** 63783-45-9; *cis*-**2,** 63730-78-9; *trans*-**2,** 63730-79-0; **3a,** 63730-80-3; **3b,** 63730-81-4; *cis*-**4,** 63730-82-5; *trans*-**4,** 63730-83-6; *cis*-**5,** 63730-84-7; *trans*-**5,** 63730-85-8; **6a,** 63730-86-9; **7b,** 63730-87-0; **8,** 63730-88-1; *cis*-**9,** 63730-89-2; *trans*-**9,** 63730-90-5; *cis*-**10,** 63730-91-6; *trans*-**10,** 63730-92-7; *cis*-**11a,** 63730-93-8; *trans*-**11a,** 63730-94-9; *cis*-**11b,** 63730-95-0; *trans*-**11b,** 63730-96-1; **12,** 63730-97-2; **15,** 63730-98-3; **17,** 15040-97-8; **19,** 63730-99-4; **20,** 63731-00-0; **21,** 63731-01-l; **21,** 63731-01-1; *cis*-1-cyanobutadiene, 2180-69-0; *trans*-1-cyanobutadiene, 2180-68-9; 2-

fluorobutadiene, 381-61-3; 2-cyanobutadiene, 5167-62-4; butadiene, 106-99-0.

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Acylanthranils. 5. Reaction of Acetylanthranil with β-Substituted Amines that Associate by Intramolecular Hydrogen Bonding[1]

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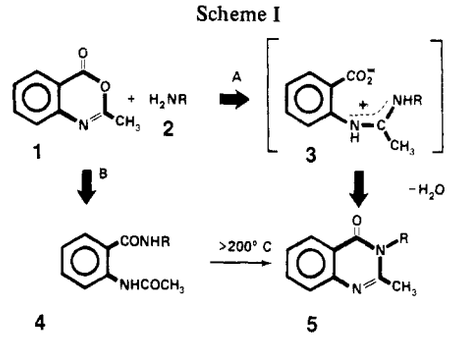
The reaction of acetylanthranil (1) with anthranilic acid (**2a**) in toluene follows pathway B to give *o*-(*o*-acetamidobenzamido)benzoic acid (**4a**), but in a polar solvent it follows pathway A to give *N*-(2-carboxyphenyl)-2-methylquinazol-4-one (**5a**), as shown in Scheme I. Similarly, reaction of 1 with ethanolamine (**2b**) neat follows pathway B to give the corresponding *o*-acetamidobenzamide **4b**, but in pyridine it follows pathway A to give the corresponding quinazolone **5b**. This change in selectivity with change in solvent is attributed to steric hindrance that is manifested by the amine when it is held in a cyclic configuration by intramolecular hydrogen bonding, but which is precluded when the reaction is made to occur in a polar solvent.

It was reported by us[2] that acetylanthranil (1) reacts with anilines to give the corresponding acetamidine intermediate **3** via pathway A as shown in Scheme I, but that anthranilic acid is an exception, which gives the corresponding *o*-acetamidobenzamide **4a** via pathway B. Since it was shown subsequently[3,4] that 1 reacts with aliphatic amines via pathway A preferentially unless steric hindrance on the part of the amine causes the reaction to occur via the slower alternate pathway B, it might be reasonable to attribute the exception with anthranilic acid to classical bulk interference by the ortho substituent were it not for the observation that other ortho-substituted anilines, such as 2,4,6-trimethylaniline, 2,6-diethylaniline, and *o*-anisidine, follow pathway A exclusively to give the corresponding quinazolone **5** in very good yields.

These results indicate that an ortho substituent per se does not interfere with the approach of the amino group to the 2 position of acetylanthranil. Neither can this exception be attributed to simple decreased reactivity of the aniline, owing to the electronegative withdrawing effect of a carboxylic acid group, because it was observed[2] that other similarly substituted anilines, such as *p*-aminobenzoic acid and *m*-trifluoromethylaniline, also follow pathway A exclusively, despite the retarding effect of the electronegative substituent, and like anthranilic acid, required several hours for reaction completion at reflux in toluene.

We postulated, therefore, that this observed exception in selectivity in a nonpolar solvent was caused by the direct association of the *o*-carboxylic acid group with the nucleophilic amine group to form a relatively rigid six-membered ring by intramolecular hydrogen bonding. In this form the anthranilic acid molecule resembles geometrically, but not electronically, heterocyclic secondary amines, which have been shown to exhibit steric hindrance in this reaction.[4] It is reasonable to expect, therefore, that so long as the geometric integrity of this quasi-heterocyclic amine structure remains intact, it should encounter about the same magnitude of steric hindrance in its approach to the electrophilic center at the 2 position of acetylanthranil as that encountered by a true cyclic secondary amine such as pyrrolidine and piperidine, which follow pathway B.

Scheme I



Others have shown[5] that *o*-aminobenzoic acids do indeed exhibit intramolecular hydrogen bonding, especially when dissolved in nonpolar solvents, and that the magnitude of force supporting the cyclic configuration is 7–14 kcal.[6] It is assumed that this force is sufficient to ensure the integrity of the quasi-cyclic amine structure in its reaction with acetylanthranil in a nonpolar solvent.

If this hypothesis is correct, then it also follows that pathway A should be favored, when reaction of anthranilic acid with 1 is made to occur in a polar solvent such as acetic acid, which would preclude the formation of the quasi-heterocyclic amine structure, **2a**, by salt formation and strong intermolecular association with the solvent to give an open structure, **2a'**, as shown in Scheme II. Equilibrium dissociation of the salt form **2'** makes available for reaction with 1 the free base form, **2a''**, in low concentration, but not fettered by the *o*-carboxylic acid group, which is still associated with the solvent by strong intermolecular hydrogen bonding. In the form of **2a''**, an-