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FLUORINE-CONTAINING 1,1-DICYANOETHYLENES: THEIR PREPARATION,
DIELS-ALDER REACTIONS, AND DERIVED NORBORNENES AND NORBORNANES

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SUMMARY

Several new 1,1-dicyanoethylenes, which are potent dienophiles, were prepared in two or more steps by the condensation of fluorocarbonyl compounds with malononitrile. These include $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{R}_f$ (R_f is CF_3 , C_2F_5 , and C_3F_7) obtained from perfluorocarboxylic acid esters, $\text{KCH}(\text{CN})_2$ and PCl_5 , and $\text{CF}_3(\text{CF}_2\text{Cl})\text{C}=\text{C}(\text{CN})_2$ from $\text{CF}_3\text{COCF}_2\text{Cl}$ and malononitrile. Reaction of cyclopentadiene with these new dienophiles, and also with the known $(\text{CF}_3)_2\text{C}=\text{C}(\text{CN})_2$, $\text{ClHC}=\text{C}(\text{CN})_2$, and $\text{Cl}_2\text{C}=\text{C}(\text{CN})_2$, gave dicyanonorbornenes. Addition of chlorine, bromine, or hydrogen to the norbornenes gave norbornanes. Many of these compounds are exceptionally toxic. For example, 2,2-dicyano-5,6-dichloro-3,3-bis(trifluoromethyl)norbornane has an approximate lethal dose for rats of only 0.2 mg/kg, indicating it to be one of the most potent synthetic oral toxins known.

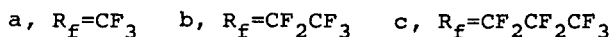
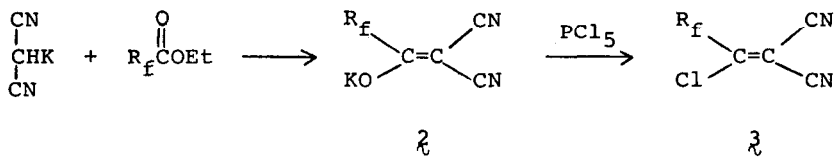
INTRODUCTION

Earlier [1], we reported the preparation of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (λ), an exceptionally reactive, electron-poor olefin. In the course of a routine investigation of the biological properties of this olefin and several of its derivatives, we found that the norbornene (ρ , X=Y=CF₃) derived from λ and cyclopentadiene had a surprising high degree of toxicity for rodents. To further investigate this phenomenon, we have extended our study of the Diels-Alder reactions of λ and other known dicyanoolefins, and have also prepared and investigated the chemistry of several new fluorine-containing 1,1-dicyanoethylenes.

RESULTS AND DISCUSSION

Preparation of new 1,1-dicyanoethylenes

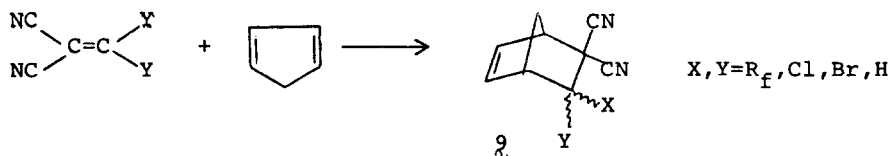
Three new 1,1-dicyano-2-(perfluoroalkyl)-2-chloroethylenes (λ) were prepared from malononitrile and esters of perfluorocarboxylic acids. The potassium salt of malononitrile was condensed with the ester to give a salt of a β,β -dicyano- α -(perfluoroalkyl)vinyl alcohol (ρ). These vinyl alcohols were then treated with PCl₅ to give moderate yields of the dicyanoolefin λ . In one case, a chlorine adduct of the olefin was also obtained.



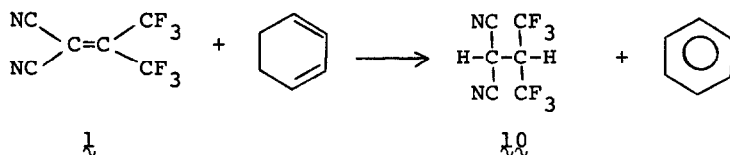
The other olefins used in this study, $\text{Cl}_2\text{C}=\text{C}(\text{CN})_2$ and $\text{HClC}=\text{C}(\text{CN})_2$, were prepared by literature methods [3].

Diels-Alder reactions

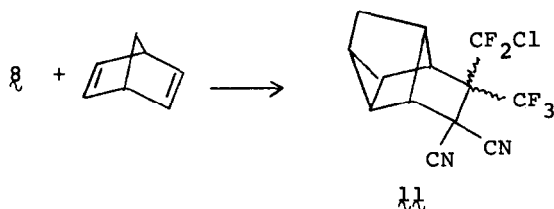
All of the 1,1-dicyanoethylenes investigated are reactive dienophiles in the Diels-Alder reaction. They react rapidly at 0-25° with cyclopentadiene to give 2,2-dicyanonorbornenes (**9**) and with linear 1,3-dienes to give substituted cyclohexenes. Even sluggish 'dienes' such as anthracene and 9-bromoanthracene react readily. In most cases, a transient color due to a π -complex was formed during the reaction. A crude observation of the relative rates of reaction of the various dicyanoolefins with cyclopentadiene, as judged by the fading of the π -complex color, indicated the order of reactivity is approximately $\text{TCNE} > \text{1} > \text{8} > \text{3} > \text{4} > \text{Cl}_2\text{C}=\text{C}(\text{CN})_2 > \text{ClHC}=\text{C}(\text{CN})_2$.



Surprisingly, no adduct was formed from the reaction of **1** with 1,3-cyclohexadiene. Instead, an oxidation-reduction reaction occurred and the dicyanoethane **10** and benzene were formed. Thus, it appears that **1** is also a potent oxidizing agent, and this property predominates when the diene is easily oxidized.



In addition to being a reactive dienophile in the Diels-Alder reaction, olefin \mathfrak{g} is also a potent dienophile in the homo-Diels-Alder reaction with norbornadiene, being more reactive than TCNE [4] but less reactive than \mathfrak{h} [1].



One diene, 1-chloro-1,3-butadiene, reacted with \mathfrak{h} to give a mixture of 2 + 4 ($\mathfrak{h}\mathfrak{h}$) and 2 + 2 ($\mathfrak{h}\mathfrak{h}$) adducts.

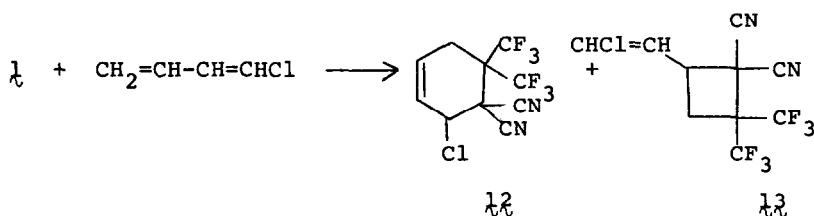


Table I contains a list of the Diels-Alder reactions and the products obtained in this study.

Toxicity of 2,2-Dicyanonorbornenes and Norbornanes

All of the 2,2-dicyanonorbornenes prepared in this study appear to be exceptionally toxic compounds with an oral LD_{50} in mice < 4 mg/kg. 2,2-Dicyano-3,3-bis(trifluoromethyl)norbornene (\mathfrak{g} , $\text{X}=\text{Y}=\text{CF}_3$) has an approximate oral lethal dose (ALD) of only 1.5 mg/kg, indicating it to be more toxic than sodium cyanide by an order of magnitude. The other norbornenes listed in Table I were also more toxic than sodium cyanide [5].

TABLE I

Diels-Alder Reactions of 2,2-Dicyanoethylenes with 1,3-Dienes

Olefin	Diene	Product Name	No. Yield	Reaction Solvent	Work-Up Method	Yield
1	1,3-cyclopentadiene	3,3-Bis(trifluoromethyl)bicyclo[2.2.1]hept-5-ene-2,2-dicarbonitrile	9a	pentane	A	83
3a	"	3-Chloro-3-(trifluoromethyl)bicyclo[2.2.1]hept-5-ene-2,2-dicarbonitrile	9b	pentane	A	71
3b	"	3-Chloro-3-(pentafluoroethyl)bicyclo[2.2.1]hept-5-ene-2,2-dicarbonitrile	9c	pentane	B	95
3c	"	3-Chloro-3-(heptafluoropropyl)bicyclo[2.2.1]hept-5-ene-2,2-dicarbonitrile	9d	pentane	C	92
4	"	3-Bromo-3-(trifluoromethyl)bicyclo[2.2.1]hept-5-ene-2,2-dicarbonitrile	9e	pentane	A	95
8	"	3-(Chlorodifluoromethyl)-3-(trifluoromethyl)bicyclo[2.2.1]hept-5-ene-2,2-dicarbonitrile	9f	pentane	A	78
CHCl=C(CN) ₂	"	3-Chlorobicyclo[2.2.1]hept-5-ene-2,2-dicarbonitrile	9g	cyclo-pentadiene	C	22
CCl ₂ =C(CN) ₂	"	3,3-Dichlorobicyclo[2.2.1]hept-5-ene-2,2-dicarbonitrile	9h	CH ₂ Cl ₂	C	70
1	1,3-butadiene	6,6-Bis(trifluoromethyl)cyclohex-3-ene-1,1-dicarbonitrile	16	pentane	A	60
1	Isoprene	4 (and 3)-Methyl-6,6-bis(trifluoromethyl)cyclohex-3-ene-1,1-dicarbonitrile	17	pentane	A	83
1	2,3-dimethylbutadiene	3,4-Dimethyl-6,6-bis(trifluoromethyl)cyclohex-3-ene-1,1-dicarbonitrile	18	CFCl ₃	C	82
1	1,3-pentadiene	2-Methyl-6,6-bis(trifluoromethyl)cyclohex-3-ene-1,1-dicarbonitrile	19	pentane	C	63

λ	trans, trans-2, 4-hexadiene	2, 5-Dimethyl-6, 6-bis (trifluoromethyl) cyclohex-3-ene-1, 1-dicarbonitrile	20	pentane	C	58
λ	1, 3-hexadiene	2-Ethyl-6, 6-bis (trifluoromethyl) cyclohex-3-ene-1, 1-dicarbonitrile	21	pentane	A	84
λ	1, 3-octadiene	2-n-Butyl-6, 6-bis (trifluoromethyl) cyclohex-3-ene-1, 1-dicarbonitrile	22	pentane	C	67
λ	2, 3-dichloro-1, 3-butadiene	3, 4-Dichloro-6, 6-bis (trifluoromethyl) cyclohex-3-ene-1, 1-dicarbonitrile	23	xylene	A	60
λ	anthracene	9, 10-Dihydro-12, 12-bis (trifluoromethyl) -9, 10-ethanoanthracene-11, 11-dicarbonitrile	24	CS ₂	C	95
λ	9-bromoanthracene	9-Bromo-9, 10-dihydro-12, 12-bis (trifluoromethyl) -9, 10-ethanoanthracene-11, 11-dicarbonitrile	25	neat 100°	A	86
λ	anthracene	9, 10-Dihydro-12-(chlorodifluoromethyl) -12-(trifluoromethyl) -9, 10-ethanoanthracene-11, 11-dicarbonitrile	26	benzene	C	67
λ	anthracene	9, 10-Dihydro-12-chloro-12-(trifluoromethyl) -9, 10-ethanoanthracene-11, 11-dicarbonitrile	27	benzene	A	91
λ	2, 4-dimethyl-3-methylenepenta-1, 4-diene	3 (and 4) -methyl-4 (and 3) -isopropenyl-6, 6-bis (trifluoromethyl) cyclohex-3-ene-1, 1-dicarbonitrile	28	pentane	C	83
λ	28	C ₂₀ H ₁₂ F ₁₂ N ₂ (unknown structure)	29	none	A	45

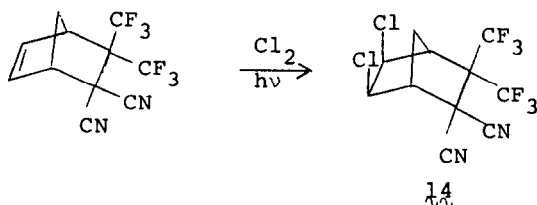
TABLE II
 Characterization of Diels-Alder Adducts

Compound No.	Formula	Recrystallizing Solvent	mp (bp) °C	¹⁹ F NMR, δ ppm	Analysis ^a
2a	C ₁₁ H ₆ F ₆ N ₂	CCl ₄	182-3	-58.2, -62.7 ^b	C, H, F, N
2b	C ₁₀ H ₆ ClF ₃ N ₂	hexane	168-170	-67.0 (93%), -68.6 (7%) ^b	C, H, Cl, F, N
2c	C ₁₁ H ₆ ClF ₅ N ₂	distilled	(94-96/0.6 mm)	-76.7, -105.6 ^b	C, H, Cl, F, N
2d	C ₁₂ H ₆ ClF ₇ N ₂	none	34-36	-81.2, -102.3, -128.1 ^b	C, H, Cl, F, N
2e	C ₁₀ H ₆ BrF ₃ N ₂	hexane	177-179	-63.8 (95%), -65.6 (5%) ^b	C, H, Br, F, N
2f	C ₁₁ H ₆ ClF ₅ N ₂	hexane	160-161	-45.2, -58.7 (41%) ^b -48.3, -61.3 (59%)	C, H, Cl, F, N
2g	C ₉ H ₇ ClN ₂ ^f	benzene	68-88		C, H, N
2h	C ₉ H ₆ Cl ₂ N ₂	hexane	149-151		C, H, N
2i	C ₁₀ H ₆ F ₆ N ₂	hexane	158-159	-67.7 ^b	C, H, F, N
2j	C ₁₁ H ₈ F ₆ N ₂	hexane	50-63	-67.0 (75%), -66.9 (25%) ^c	C, H, F, N
2k	C ₁₂ H ₁₀ F ₆ N ₂	pentane	57-58	-67.7 ^d	C, H, F, N
2l	C ₁₁ H ₈ F ₆ N ₂	hexane	95-98	-65.8, -67.7 ^c	C, H, F, N

20	$C_{12}H_{10}F_6N_2$	pentane	136-137	-62.6, -67.7 ^b	C, H, F, N
21	$C_{12}H_{10}F_6N_2$	hexane	110-111	-65.7, -67.6 ^c	C, H, F, N
22	$C_{14}H_{14}F_6N_2$	hexane	101-102	-65.7, -67.7 ^c	C, H, F, N
23	$C_{10}H_4Cl_2F_6N_2$	hexane	74-75	-67.4 ^b	C, H, Cl, F, N
24	$C_{20}H_{10}F_6N_2$	benzene	185	-60.9 ^c	C, H, F, N
25	$C_{20}H_9BrF_6N_2$	pentane wash	110-112	-60.8 ^c	C, H, Br, F, N
26	$C_{20}H_{10}ClF_5N_2$	hexane	150	-44.1, -58.1 ^e	Cl, N
27	$C_{19}H_{10}ClF_3N_2$	benzene	186-187	-66.6 ^e	N
28	$C_{14}H_{12}F_6N_2$	pentane	36-40	-67.4 (93%), -67.2 (7%)	C, H, F, N
29	$C_{20}H_{12}F_{12}N_4$	ethanol	175-176	-59.3 ^e , -65.9, -61.3, -64.0 ^e	C, H, F, N

(a) Analyses indicated were within 0.4% of the theoretical value. (b) Solvent, $CFCl_3$.
(c) Solvent, acetone- d_6 . (d) Solvent, $CDCl_3$. (e) Solvent, $DMSO-d_6$. (f) 1H NMR indicates
a 1:1 mixture of isomers.

Removal of the double bond of the 2,2-dicyanonorbornenes (Table I) by hydrogenation, chlorination, or bromination produced a series of 2,2-dicyanonorbornanes listed in Table II. For example, **9** ($X=Y=CF_3$) reacts with chlorine under radical conditions to give exclusively exo-cis-5,6-dichloro-2,2-dicyano-3,3-bis(trifluoromethyl)norbornane (**14**). Bromination in pentane also gives the exo-cis-dibromide (**15**).



These 2,2-dicyanonorbornanes are as toxic or more toxic than the corresponding norbornenes. For example, norbornane **14** is one of the most potent synthetic oral toxins known (ALD in rats of only 0.2 mg/kg). [5]. Great care should be taken in handling these compounds to avoid accidental poisoning.

EXPERIMENTAL

Proton NMR spectra were obtained on a Varian A-60 instrument with TMS as an internal standard. Fluorine NMR spectra were obtained on a Varian XL-100 instrument operated at 94.1 MHz using $CFCl_3$ as an internal standard. Downfield shifts are reported as positive values.

1,1-Dicyano-2-chloro-2-(trifluoromethyl)ethylene (3a) (nc)

Potassium, 40 g (1-g atom), was dissolved in 750 ml ethanol, and a solution of 66 g (1 mole) of malononitrile in 150 ml ethanol was added. Methyl trifluoroacetate, 141 g (1.1 mole), was then added rapidly, and the resulting mixture was refluxed for 2 hr and then evaporated to dryness under reduced pressure to give 200 g (100%) of the potassium salt of β,β -dicyano- α -(trifluoromethyl)vinyl alcohol as an off-white crystalline solid: mp 165-170°; ^{19}F NMR (CD_3CN) δ -73.1 ppm (s); ir(KBr) 4.52 μ (C \equiv N) and 6.22 μ (C=C).

Anal. Calcd for $\text{C}_5\text{F}_3\text{KN}_2\text{O}$: C, 30.00; F, 28.48; N, 14.00;

K, 19.53.

Found: C, 30.30; F, 28.38; N, 14.05;

K, 20.00.

This salt (200 g, 1 mole) was mixed with 250 g (1.2 mole) of phosphorous pentachloride and was heated in a simple still until no further distillation occurred. The distillate was redistilled to give: (a) 35 g of phosphorous trichloride, bp 75-83°; (b) 78 g of phosphorous oxychloride, bp 100-110°; (c) 29.66 g of 3a as a colorless liquid, bp 139-140°; ^{19}F NMR (CCl_3F) δ -65.7 ppm (s); ir (l) 4.43 μ (CN) and 6.23 μ (C=C); and (d) 15.7 g of 1,1-dicyano-1,2,2-trichloro-3,3,3-trifluoropropane (nc); colorless solid, bp 149-150°, mp 104-106°; ^{19}F NMR (CCl_3F) δ -71.1 ppm (s); ir (CCl_4) 4.43 μ (CN).

Anal. Calcd for $\text{C}_5\text{ClF}_3\text{N}_2(\text{C})$: C, 33.27; Cl, 19.64; F, 31.57;

N, 15.52.

Found: C, 33.17; Cl, 19.58; F, 31.39;

N, 15.57.

Anal. Calcd for $C_5Cl_3F_3N_2$ (d): C, 23.89; Cl, 42.30; F, 22.67;
N, 11.14.

Found: C, 24.19; Cl, 42.43; F, 22.61;
N, 11.25.

1,1-Dicyano-2-chloro-2-(pentafluoroethyl)ethylene (3b) (nc)

Potassium, 16 g (0.4 mole), was dissolved in 300 ml ethanol, and a solution of 26.4 g (0.4 mole) of malononitrile in 60 ml ethanol was added. To this solution was added dropwise 76.8 g (0.4 mole) of ethyl pentafluoropropionate, and the reaction mixture was stirred at room temperature for 2 hr and then evaporated to dryness under reduced pressure to give 99.1 g of crude potassium salt of β,β -dicyano- α -(pentafluoroethyl)vinyl alcohol (nc) as a light yellow crystalline solid: mp 238-240°; ir(KBr) 4.52 μ (CN) and 6.27 μ (C=C); ^{19}F NMR (DMSO) δ -81.9 ppm (t, J = 1.6 Hz, 3F) and -117.8 ppm (q, J = 1.6 Hz, 2F).

Anal. Calcd for $C_6F_5KN_2O$: C, 28.81; F, 37.97; N, 11.20.

Found: C, 28.91; F, 37.89; N, 11.33.

A mixture of 88 g (0.35 mole) of this salt with 88 g (0.42 mole) of phosphorous pentachloride was heated in a simple still at 50 mm pressure until no further distillate was formed. Redistillation gave 27.1 g (34%) of 3b as a colorless liquid: bp 79-80° (50 mm); ir (l) 4.43 μ (CN) and 6.27 μ (C=C); ^{19}F NMR (CCl_3F) δ -82.4 ppm (t, J = 2 Hz, 3F) and -112.4 ppm (q, J = 2 Hz, 2F).

Anal. Calcd for $C_6ClF_5N_2$: C, 31.26; Cl, 15.38; F, 41.21;
N, 12.15.

Found: C, 31.47; Cl, 15.67; F, 40.96;
N, 12.14.

1,1-Dicyano-2-chloro-2-(heptafluoropropyl)ethylene (3c) (nc)

Potassium, 4 g (0.1 mole), was dissolved in 75 ml ethanol, and then a solution of 6.6 g (0.1 mole) of malononitrile in 15 ml ethanol was added. While the reaction mixture was still warm, 23 g (0.1 mole) of methyl perfluorobutyrate was added dropwise. The mixture was stirred for 2 hr at room temperature and then evaporated to dryness under reduced pressure to give 27.36 g of the potassium salt of β,β -dicyano- α -(perfluoropropyl)vinyl alcohol (nc) as a cream-colored solid: mp 127-130°; ^{19}F NMR (DMSO) δ -79.9 ppm (3F), -115.7 ppm (2F) and -126.3 ppm (2F); ir(KBr) 4.50 μ (CN) and 6.29 μ (C=C).

Anal. Calcd for $\text{C}_7\text{F}_7\text{KN}_2\text{O}$: C, 28.01; F, 44.30; K, 13.03;

N, 9.33.

Found: C, 28.10; F, 44.02; K, 12.98;

N, 9.26.

A mixture of 24 g (0.082 mole) of this salt and 21 g (0.1 mole) of phosphorous pentachloride was heated in a simple still at 50 mm pressure. The distillate (up to 90°/50 mm) was redistilled to give phosphorous oxychloride and 5.05 g of 3c as a colorless liquid: bp 86° (45 mm); ir (l) 4.45 μ (CN) and 6.29 μ (C=C); ^{19}F NMR (CCl_3F) δ -80.77 ppm (3F), -109.4 ppm (2F) and -124.7 ppm (2F).

Anal. Calcd for $\text{C}_7\text{ClF}_7\text{N}_2$: C, 29.97; Cl, 12.64; F, 47.41;

N, 9.99.

Found: C, 30.03; Cl, 12.74; F, 47.19;

N, 10.11.

1,1-Dicyano-2-bromo-2-(trifluoromethyl)ethylene (4) (nc)

A mixture of 14.44 g (0.08 mole) of 3a and 13.9 g (0.16 mole) of lithium bromide was heated to 120°. The pressure was reduced, and the material that distilled out was condensed in an ice-cooled trap. Redistillation gave 12.83 g (71%) of 4 as a colorless liquid: bp 55-56° (10 mm); ^{19}F NMR (CCl_3F) δ -63.8 ppm (s).

Anal. Calcd for $\text{C}_5\text{BrF}_3\text{N}_2$: C, 26.69; Br, 35.52; F, 25.33; N, 12.45.

Found: C, 26.51; Br, 35.31; F, 25.21; N, 12.31.

1,1-Dicyano-2-(chlorodifluoromethyl)-2-(trifluoromethyl)ethylene (8) (nc)

A mixture of 75 g (1.14 mole) of malononitrile, 4 g zinc chloride, and 165 g (0.9 mole) of chloropentafluoroacetone was heated in a 300-ml pressure vessel at 80° for 8 hr. The vessel was cooled and vented, and 236 g of crude 3-chloro-3,3-difluoro-1-hydroxy-2-trifluoromethyl-1,1-propanedinitrile was obtained as a liquid residue. The liquid was mixed with 454 g (3.2 mole) of phosphorous pentoxide, and the mixture was heated in a simple still until no further distillate was collected. Redistillation gave 103 g of 8 as a colorless liquid: bp 133-133.5°; ^{19}F NMR (CCl_3F) δ -53.2 ppm (q, J = 10 Hz, 2F) and δ -61.0 ppm (t, J = 10 Hz, 3F); ir (l) 4.44 μ ($\text{C}\equiv\text{N}$) and 6.14 μ ($\text{C}=\text{C}$).

Anal. Calcd for $\text{C}_6\text{ClF}_5\text{N}_2$: C, 31.26; Cl, 15.38; F, 41.21; N, 12.15.

Found: C, 31.33; Cl, 15.64; F, 41.02; N, 12.43.

4-(N,N-Dimethylamino)- α -(trifluoromethyl)- β , β -dicyanostyrene
(δ_a) (nc)

A 9.03-g (0.05 mole) sample of δ_a was added dropwise to a solution of 6.06 g (0.05 mole) of N,N-dimethylaniline in 30 ml of pyridine. The reaction mixture was cooled with an ice bath to keep the temperature between 35-45°. After the addition, the reaction mixture was stirred at room temperature for 1 hr, and then mixed with 30 ml acetic acid and 200 ml water. The orange solid that precipitated was collected on a filter, washed thoroughly with water, and then recrystallized from benzene-hexane to give 11.23 g of (δ_a) as dark-orange crystals: mp 116-118°; ^{19}F NMR (acetone- d_6) δ -59.3 ppm (t, J = 1.2 Hz); ^1H NMR (acetone- d_6) δ 3.16 ppm (s, 6H) and 6.86 + 7.63 ppm (4H, aromatic); uv(acetone) λ_{max} 480 m μ (ϵ 23,600); uv(Freon 113) λ_{max} 456 m μ (ϵ 25,000).

Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{F}_3\text{N}_3$: C, 58.87; H, 3.80; F, 21.49;
N, 15.84.

Found: C, 58.61; H, 3.57; F, 21.25;
N, 16.00.

4-(N,N-Dimethylamino)- α -(pentafluoroethyl)- β , β -dicyano-
styrene (δ_b) (nc)

A 10.37-g (0.045 mole) sample of δ_b was added dropwise to a solution of 5.45 g (0.045 mole) of N,N-dimethylaniline in 30 ml pyridine. The reaction mixture was cooled to keep the temperature between 35-45°. The reaction mixture was stirred for 1 hr and then mixed with 30 ml acetic acid and 200 ml water. This mixture was extracted with four 100-ml portions of CCl_3F . The extracts were combined, washed with water, dried (MgSO_4), and then evaporated to dryness under reduced pressure. The semi-solid residue was stirred with

200 ml pentane, and the undissolved solid was collected on a filter and washed with pentane. There was obtained 10.95 g of (6b) as shiny black crystals: mp 59-60°; ^{19}F NMR (acetone- d_6) δ -82.1 ppm (t, $J = 2.7$ Hz, 3F) and -110.6 ppm (m, 2F); uv (acetone) λ_{max} 490 m μ (ϵ 20,600); uv (Freon 113) λ_{max} 465 m μ (ϵ 21,600).

Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{F}_5\text{N}_3$: C, 53.34; H, 3.20; F, 30.13;
N, 13.33.

Found: C, 53.11; H, 3.18; F, 31.09;
N, 13.33.

Tetraethylammonium 2-Trifluoromethyl-1,1,3,3-tetracyanopropenide (5) (nc)

A solution of 3.3 g (0.05 mole) of malononitrile in 20 ml ethanol was added dropwise to a solution prepared by dissolving 2 g (0.05 mole) of potassium in 50 ml ethanol. The resulting solution was cooled to 5°, and 4.5 g (0.025 mole) of C_2F_6 was added dropwise. The reaction mixture was warmed to room temperature and filtered, and the filtrate was evaporated to dryness under reduced pressure. The solid residue was dissolved in 50 ml of water, filtered again, and the filtrate was mixed with a solution of 5.0 g of tetramethylammonium chloride in 10 ml of water and then cooled. The solid that precipitated was collected on a filter, washed with cold water, and then recrystallized from water (activated charcoal) to give 3.3 g of 5 as yellow needles: mp 170-172°; ^{19}F NMR (acetone- d_6) δ -60.4 ppm (s); uv (ethanol) λ_{max} 386 m μ (ϵ 26,700) and 372 m μ (ϵ 26,400); ir (KBr) 4.53 μ (C \equiv N) and 6.52 μ (C=C).

Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{F}_3\text{N}_5$: C, 50.88; H, 4.27; F, 20.12;
N, 24.72.

Found: C, 50.78; H, 4.16; F, 20.02;
N, 24.73.

Reaction of λ with 1,3-Cyclohexadiene

A solution of 6.42 g (0.03 mole) of λ in 10 ml pentane was added dropwise to a solution of 3.2 g (0.04 mole) of 1,3-cyclohexadiene in 20 ml pentane at 10°. An orange color formed, which slowly faded when the reaction mixture was warmed to room temperature. The reaction mixture was distilled to give 4.0 g of pink liquid, bp 49-55° (1.0 mm) that solidified on cooling. Recrystallization from chloroform-pentane gave 3.5 g of 1,1-dicyano-2,2-bis(trifluoromethyl)ethane (nc) ($\lambda\lambda$) as colorless needles: mp 39-40°; ^{19}F NMR (CD_3CN) δ 5.05 ppm (d, J = 3 Hz, 1H) and 6.32 ppm (septet of d, J = 7, 3 Hz, 1H).

Anal. Calcd for $\text{C}_6\text{H}_2\text{F}_6\text{N}_2$: C, 33.35; H, 0.93; F, 52.75;
N, 12.97.

Found: C, 33.44; H, 1.17; F, 52.75;
N, 12.62.

Reaction of ξ with Norbornadiene

A solution of 11.5 g (0.05 mole) of ξ and 11.5 g (0.1 mole) of norbornadiene in 25 ml of hexane was allowed to stand at room temperature for 20 hr. The dark brown crystals that formed were filtered off and washed with pentane (15.26 g). The product was chromatographed over Al_2O_3 (ether) to remove the color. There was obtained 10.7 g of 8,8-dicyano-9-(chlorodifluoromethyl)-9-(trifluoromethyl)tetracyclo[2.2.1.-1^{2,1}.2^{3,5}]nonane ($\lambda\lambda$) (nc) (62:38 mixture of isomers) as colorless crystals: mp 107-109°; ^{19}F NMR (acetone- d_6) 62% isomer, δ -62.3 ppm (CF_3) and -44.2 ppm (CF_2Cl), 38% isomer, δ -57.7 ppm (CF_3) and -49.1 ppm (CF_2Cl); ir(KBr) 4.43 μ (CN).

Anal. Calcd for $C_{13}H_8ClF_5N_2$: C, 48.39; H, 2.50; Cl, 10.99;
F, 29.44; N, 8.68.

Found: C, 48.00; H, 2.72; Cl, 10.87;
F, 29.15; N, 8.45.

Reaction of I with 1-Chlorobutadiene

A mixture of 5.31 g (0.06 mole) of 1-chloro-1,3-butadiene and 6.42 g (0.63 mole) of I was allowed to remain at room temperature for 20 hr. The two products that formed were separated on a preparative G.C. column (25% DC-200 on Gas Chrom. Z at 180° with flow rate of 400 ml/min.). There was obtained (16.3 min.) 3.1 g of 2-(2-chlorovinyl)-4,4-bis-(trifluoromethyl)cyclobutane-1,1-dicarbonitrile (I^3) (nc) as a colorless liquid: n_D^{25} 1.4179; ir (l) 3.22 and 3.28 μ (=CH), 4.43 μ (CN), 6.14 μ (C=C) and 10.32 μ (trans CH=CH); ^{19}F NMR (CCl_3F) δ -68.7 and -70.2 ppm (qs, J = 10 Hz, 3F each) ^1H NMR (CCl_3F) δ 2.80 ppm (m, 2H), 4.47 ppm (q, 1H), 5.99 ppm (t, J = 7.5 Hz, 1H) and δ 6.56 ppm (d of d, J = 7.5, 1.5 Hz, 1H).

Anal. Calcd for $C_{10}H_5ClF_6N_2$: C, 39.69; H, 1.67; Cl, 11.72;
F, 37.67; N, 9.26.

Found: C, 39.72; H, 1.72; Cl, 11.81;
F, 37.49; N, 8.99.

Also obtained (23.8 min) was 1.2 g of 2-chloro-6,6-bis-(trifluoromethyl)cyclohex-3-ene-1,1-dicarbonitrile (I^2) (nc) as a colorless solid: mp 88-90°; ir(KBr) 3.23 μ (=CH), 4.43 μ (C \equiv N) and weak 6.01 (C=C); ^{19}F NMR (CCl_3D) δ -65.7 and 68.4 ppm (qs, J = 11.5 Hz, 3F each); ^1H NMR (CCl_3D) δ 2.87 ppm (m, 2H), 5.06 ppm (m, 1H) and 5.96 ppm (s, 2H).

Anal. Calcd for $C_{10}H_5ClF_6N_2$: C, 39.69; H, 1.67; Cl, 11.72;
F, 37.67; N, 9.26.

Found: C, 29.78; H, 1.91; Cl, 11.81;
F, 37.60; N, 9.13.

Diels-Alder Reactions of 2,2-Dicyanoethylenes (Table I)

The reactions listed in Table I were conducted by mixing the diene with the dicyanoolefin in a solvent at 0-25°, unless otherwise noted. Three different work-up procedures were used, and are illustrated by the following.

Procedure A. A mixture of 6.75 g (0.03 mol) of I in 10 ml pentane was added dropwise to a solution of 6 ml cyclopentadiene in 20 ml pentane at 20°. The yellow color that first formed faded rapidly. The mixture was cooled, and the solid precipitate was collected on a filter and recrystallized to give 8.26 g of II .

Procedure B. Cyclopentadiene, 5 ml, was added to a solution of 6.0 g (0.026 mol) of III in 25 ml pentane. The reaction mixture was distilled to give 8.6 g of II as a colorless liquid.

Procedure C. A solution of 1.8 g (0.01 mol) of anthracene and 2.14 g (0.01 mol) of I in 100 ml carbon disulfide was allowed to remain at room temperature (25°) until the initial purple color faded. The reaction mixture was evaporated to dryness under reduced pressure, and the residue was recrystallized to give 3.7 g of II as colorless needles.

Bromination of Norbornenes (Table III)

5,6-Dibromo-3,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane-2,2-dicarbonitrile (IV of Table III) was prepared by mixing 2.4 g (0.015 mol) of bromine with a solution of 4.2 g (0.015 mole) of I in 38 ml chloroform. After 3 hrs, the

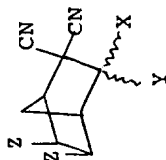


TABLE III
2,2-Dicyanonorbornanes

Compound No.	Structure X, Y, Z	Formula	Yield %	Recryst. Solvent	Mp °C	¹⁹ F NMR, δ ppm	Analysis
34	CF ₃ , CF ₃ , Cl	C ₁₁ H ₆ Cl ₂ F ₆ N ₂	75	heptane	124-126	-59.7, -64.9 ^e	C, H, Cl, F, N
35	CF ₃ , CF ₃ , Br	C ₁₁ H ₆ Br ₂ F ₆ N ₂	92	CCl ₄	163-165	-59.0, -64.1 ^e	Br
36	CF ₃ , CF ₃ , H	C ₁₁ H ₈ F ₆ N ₂	76	hexane	175-176	-60.3, -64.8 ^b	C, H, F, N
37	CF ₃ , CF ₂ Cl, Cl	C ₁₁ H ₆ Cl ₃ F ₅ N ₂ ^b	70	hexane	115-117	-49.1, -63.3 ^c -43.8, -56.5 ^{d, g}	C, H, Cl, F, N
38	CF ₃ , CF ₂ Cl, Br	C ₁₁ H ₆ Br ₂ ClF ₅ N ₂ ^b	85	hexane	133-135	-49.5, -62.0 ^{c, f} -44.3, -57.1 ^d	Br
39	CF ₃ , CF ₂ Cl, H	C ₁₁ H ₈ ClF ₅ N ₂ ^b	70	hexane	134-151	-45.9, -62.7 ^{c, f} -49.6, -58.3 ^d	C, H, Cl, F, N
40	CF ₃ , Cl, Cl	C ₁₀ H ₆ Cl ₃ F ₃ N ₂	80	benzene	118-119	-65.6 ^b	C, H, F, Cl, N
41	CF ₃ , Cl, Br	C ₁₀ H ₆ ClBr ₂ F ₃ N ₂	90	benzene	156-158	-65.5 ^f	Br
42	CF ₃ , Br, Cl	C ₁₀ H ₆ BrCl ₂ F ₃ N ₂	71	CCl ₄	111-113	-63.1 ^e	C, H, N
43	Cl, Cl, Cl	C ₉ H ₆ Cl ₃ N ₂	64	heptane	98-100	-	C, H, N

(a) Analyses indicated were within 0.4% of the theoretical value. (b) Obtained as a mixture of two isomers. (c) Major isomer. (d) Minor isomer. (e) Solvent, CDCl₃. (f) Solvent, acetone-d₆. (g) Solvent, DMSO-d₆.

bromine color had faded. The solution was evaporated to dryness under reduced pressure, and the residue was recrystallized to give 30 as colorless crystals, ^1H NMR (CDCl_3) δ 2.77 ppm (AB, $J = 13$ Hz, 2H), 3.28 ppm (m, 1H), 3.46 ppm (m, 1H) and 4.73 ppm (AB, $J = 7$ Hz, 2H).

In the same manner, 33 was prepared from 2f, and 36 was prepared from 2b.

Chlorination of Norbornenes (Table III)

5,6-Dichloro-3,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane-2,2-dicarbonitrile (14 of Table III) was prepared by slowly distilling 2 ml (measured at -78°) of chlorine into a solution of 7.0 g (0.025 mole) of 2a in 100 ml carbon tetrachloride. The reaction mixture was irradiated with a 275 watt sun lamp for 2 hrs. The solvent was evaporated at reduced pressure, and the residue was recrystallized from heptane to give 14 as colorless crystals.

In the same manner, 32, 35, 37, and 38 were prepared from 2f, 2b, 2e, and 2h respectively.

Hydrogenation of Norbornenes (Table III)

3,3-Bis(trifluoromethyl)bicyclo[2.2.1]heptane-2,2-dicarbonitrile (31) was prepared by shaking a solution of 5.6 g (0.02 mol) of 2a in 100 ml ethanol containing 0.1 g PtO_2 catalyst under 40 lb/in² hydrogen pressure for 30 min. The solution was filtered, and the filtrate was evaporated to dryness under reduced pressure. The residue was recrystallized from hexane to give 4.3 g of 31 as white plates. In the same manner, 34 was prepared from 2f.

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