sulfate. The solvent was removed leaving 26.4 g. of an oil, impact sensitivity 6 cm. using a 2-kg. weight.[7]

This oil was dissolved in 360 ml. of acetic anhydride and 30 ml. of concd. sulfuric acid was added dropwise with stirring. The temperature was kept at −10 to −20° during the addition, and then at 0° for 2 hr. The reaction mixture was poured into 1.5 l. of ice water, and the gummy residue which separated was filtered off, dissolved in methylene chloride, dried with sodium sulfate, and the solvent was removed.

The residue (10.2 g.) was heated at reflux for 2 hr. in a mixture of 370 ml. of methanol and 17 ml. of concd. hydrochloric acid. The product was stripped under vacuum and recrystallized twice from methylene chloride to yield 3.55 g. of 4,6,6-trinitro-4-aza-1,2-heptanediol (11% over-all yield if it is assumed that the condensation product consisted entirely of 6,6-dinitro-4-aza-1,2-heptanediol), m.p. 60°, with a crystalline phase change at 50°.

Anal. Calcd. for $C_6H_{12}N_4O_8$: C, 26.87; H, 4.48; N, 20.89. Found: C, 26.81; H, 4.79; N, 20.79.

2,2-Dimethyl-4-(2,4,4-trinitro-2-azapentyl)dioxalane (IV).—To a solution of 3.00 g. (0.0112 mole) of 4,6,6-trinitro-4-aza-1,2-heptanediol in 200 ml. of dry acetone was added slowly, with stirring, 1.67 g. (0.0177 mole) of boron trifluoride etherate. The temperature of the solution was kept below 20° by means of an ice bath. After 5 min. the solution was poured into 100 ml. of ice water and a solid crystallized. This solid was filtered, dried, and recrystallized from isopropyl ether to give 2.55 g. (74% yield) of 2,2-dimethyl-4-(2,4,4-trinitro-2-azapentyl)dioxalane, m.p. 84.5–86°.

Anal. Calcd. for $C_9H_{16}N_4O_8$: C, 35.07; H, 520; N, 18.39. Found: C, 34.93; H, 5.00; N, 18.21.

6-Nitroxy-2,2,4,8,10,10-hexanitro-4,8-diazaundecane (V) by Nitration of I.—The condensation product of 3-amino-1,2-propanediol and 2,2-dinitropropanol (25 g., 0.11 mole as 6,6-dinitro-4-aza-1,2-pentanediol) was added dropwise to a mixture of 125 ml. of 100% nitric acid and 115 ml. of concd. sulfuric acid at 55°, and the mixture was heated at this temperature for an additional 3 hr. The reaction mixture was then added to 2 l. of ice and water. The product was filtered and slurried with 1.5 l. of boiling ethylene dichloride. A small amount of insoluble residue was filtered from the hot solution, and the filtrate was concentrated and cooled. The product which crystallized was filtered and washed with a small amount of ether to yield 7.6 g. (28% yield assuming this condensation product was pure 6,6-dinitro-4-aza-1,2-heptanediol) of 6-nitroxy-2,2,4,8,10,10-hexanitro-4,8-diazaundecane, m.p. 158–159°. An analytical sample was recrystallized from ethylene dichloride.

Anal. Calcd. for $C_9H_{15}N_9O_{15}$: C, 22.08; H, 3.07; N, 25.77. Found: C, 22.42; H, 3.03; N, 25.29.

6-Nitroxy-2,2,4,8,10,10-hexanitro-4,8-diazaundecane (V) from 1,3-Diamino-1-propanol.—1,3-Diamino-2-propanol (7 g., 0.0556 mole) was added slowly to a swirled suspension of 17.3 g. (0.112 mole) of 2,2-dinitropropanol (96% assay) in 20 ml. of water. An oil formed, which was separated from the aqueous layer and dried under vacuum. The residue weighed 10.9 g. (55.4% yield). This oil was dissolved in 10 ml. of acetic anhydride and 105 ml. of 100% nitric acid was added dropwise, with stirring, while the temperature was kept at 0–5°. The solution was stirred at 0° for an additional 2 hr. and then was poured over 2 l. of crushed ice. The ice was allowed to melt, and the water was decanted from a gum-like residue. This residue was recrystallized from ethylene chloride, to yield 6.1 g. of V, (40.5% yield assuming the condensation product was pure 6-hydroxy-2,2,10,10-tetranitroundecane), m.p. 158–159°. A mixed melting point with the above product gave no depression.

6-Acetoxy-2,2,4,8,10,10-hexanitro-4,8-diazaundecane (VI).—6-Nitroxy-2,2,4,8,10,10-hexanitro-4,8-diazaundecane (7.6 g., 0.0155 mole) was dissolved in 80 ml. of acetic anhydride and 8 ml. of concd. sulfuric acid was added dropwise while the temperature of the solution was kept at −10 to −20°. The solution was stored at 0° for 24 hr. and then was poured in to 2l. of ice water. The gum-like precipitate was recrystallized from methylene chloride to yield 6.5 g. (0.0134 mole, 86% yield) of 6-acetoxy-2,2,4,8,10,10-hexanitro-4,8-diazaundecane, m.p. 145°.

Anal. Calcd. for $C_{11}H_{18}N_8O_{14}$: C, 27.16; H, 3.71; N, 23.05. Found: C, 26.92; H, 3.31; N, 23.41.

6-Hydroxy-2,2,4,8,10,10-hexanitro-4,8-diazaundecane (VII).—6-Acetoxy - 2,2,4,8,10,10 - hexanitro - 4,8 - diazaundecane (6.5 g., 0.0134 mole) was heated under reflux for 4 hr. in a mixture of 390 ml. of methanol and 40 ml. of concd. hydrochloric acid. The volatile materials were removed under vacuum and the residue was recrystallized from methylene chloride to yield 2.7 g. (0.0061 mole, 45.4% conversion, 61% yield) of 6-hydroxy-2,2,4,8,10,10-hexanitro-4,8-diazaundecane, m.p. 168.5–169°. Some starting material, 6-acetoxy-2,2,10,10-tetranitro - 4,8 - dinitrazeundecane (1.6 g., 0.0033 mole) was recovered upon concentration of the filtrate.

Anal. Calcd. for $C_9H_{16}N_8O_{13}$: C, 24.32; H, 3.60; N, 25.22. Found: C, 24.51; H, 3.43; N, 25.37.

Acknowledgment.—We are indebted to the Office of Naval Research for the financial support of this work.

(7) Bureau of Mines Bulletin No. 346.

Variations of Alkyl Groups in 4-(4-Dialkylaminostyryl)quinolines[1,2]

CARL TABB BAHNER, LYDIA MOORE RIVES, EMMA BROWN SENTER, WILLIAM LONGMIRE, HAROLD KINDER, DOROTHY BETTIS BALES, FRED HANNAN, BOBBY PETTYJOHN, WILLIAM K. EASLEY, LOVELY FREE, AND HUGH FREE

Department of Chemistry, Carson-Newman College, Jefferson City, Tenn.

Received November 13, 1961

Although slight modifications in the structure of aminostyrylquinolines sometimes destroy their antitumor effects, the replacement of the dimethylamino group in 4-(4-dimethylaminostyryl)quinoline by an $—NH_2$, and $—N(C_2H_5)CH_2C_6H_5$ or an $—N{=}CH—C_6H_4—N(CH_3)_2$, produced compounds with good antitumor activity.[3–6] A series of dialkylaminostyryl compounds, listed in Table I, has been prepared in order to determine the optimum chain length. In the course of these preparations, three monoalkylamino compounds were obtained as by-products and others were then sought.

A number of Schiff bases were prepared by treating 4-(4-aminostyryl)quinoline with a variety

(1) This research was aided by grants from the American Cancer Society and the National Institute of Health.

(2) Presented in part at the Southeastern Region Meeting of the American Chemical Society in Birmingham, Ala., November, 1960.

(3) C. T. Bahner, Lydia Moore Rives, Emma Brown Senter, Dorothy Bettis Bales, Fred Hannan, and Bobby Pettyjohn, *J. Org. Chem.*, **23**, 1060 (1958).

(4) Margaret Reed Lewis, Boland Hughes, Aubrey L. Bates, and Carl Tabb Bahner, *Cancer Res*, **20**, 691 (1960).

(5) A. Haddow, private communication.

(6) K. Sugiura, private communication.

TABLE I
AMINOSTYRYL COMPOUNDS

No.	Alkyl Group on Amino Nitrogen	Formula	M.P.	Reaction Time, Hr.[a]	Yield, %	Calcd. C	Calcd. H	Found C	Found H
	A. 4-(4-Aminostyryl)quinolines								
1	*N,N*-Dipropyl	$C_{23}H_{26}N_2$	76–77	1.5	33	83.61	7.93	83.27	7.80[b]
2	*N,N*-Diallyl	$C_{23}H_{22}N_2$	82.0–83.5	1.5	13	84.64	6.79	84.63	6.65[b]
3	*N,N*-Dibutyl	$C_{25}H_{30}N_2$	81–83	2	23	83.75	8.44	84.16	8.43[c]
4	*N,N*-Diisobutyl	$C_{25}H_{30}N_2$	94.5–95.0	2		83.75	8.44	83.61	8.43[b]
5	*N,N*-Di-*sec*-butyl	$C_{25}H_{30}N_2$	96.0–96.5	3.5					[b,d]
6	*N,N*-Diamyl	$C_{27}H_{34}N_2$	88–89	2	14	83.88	8.86	84.05	8.95[b,e]
7	*N,N*-Dihexyl	$C_{29}H_{38}N_2$	23.0–25.5	2		84.00	9.24	83.79	9.40[b]
8	*N,N*-Diheptyl	$C_{31}H_{42}N_2$	Oil	1	26	84.10	9.56	83.90	9.53[b,f]
9	*N,N*-Dioctyl	$C_{33}H_{46}N_2$	Oil	1.5	31	84.21	9.85	84.51	9.93[b,g]
10	*N,N*-Dinonyl	$C_{35}H_{50}N_2$	Oil	4[h]		84.28	10.10	84.45	10.13[b]
11	*N,N*-Didecyl	$C_{37}H_{54}N_2$	Oil	5[i]	50[j]				
12	*N,N*-Dioctadecyl	$C_{53}H_{86}N_2$	52–53	6[k]	14	84.73	11.54	85.02	11.49[b]
13	*N,N*-Dibenzyl	$C_{29}H_{22}N_2$	99–100	1[l]	8	87.28	6.14	87.18	6.03[b]
14	*N*-Benzyl-*N*-methyl	$C_{24}H_{20}N_2$	118.0–118.5	15.5[m]	8	85.68	6.33	85.49	6.12[b]
15	*N*-Monomethyl	$C_{18}H_{16}N_2$	137–138	1[n]	26	83.04	6.20	82.98	5.99[b]
16	*N*-Monobutyl	$C_{21}H_{22}N_2$	128–130	2		83.40	7.33	83.37	7.27[b]
17	*N*-Monohexyl	$C_{23}H_{26}N_2$	97–98	2	2[o]	83.62	7.93	83.95	7.89[b]
18	*N*-Monoheptyl	$C_{24}H_{28}N_2$	98–99	1	0.4[o]				[b,p]
19	*N*-Monooctyl	$C_{25}H_{30}N_2$	112–113	1.5	2[o]	83.75	8.43	83.88	8.74[b,q]
20	*N*-Methyl-*N*-(2-*N'*,*N'*-diethylaminoethyl)	$C_{24}H_{29}N_3$	54–55	3[r]	12	80.18	8.13	79.91	8.07[b]
21	*N*-Ethyl-*N*-(2-*N'*,*N'*-diethylaminoethyl)	$C_{25}H_{31}N_3$	72–73	7[r]	20	80.38	8.37	80.61	8.39[b]
22	*N*-Ethyl-*N*-(3-*N'*,*N'*-dimethylaminopropyl)	$C_{24}H_{29}N_3$		3[r]	10	80.18	8.13	80.00	8.34[b]
23	*N*-Methyl-*N*-carboxymethyl	$C_{20}H_{18}N_2O_2$	236–237	3[s]	20	75.45	5.70	75.16	6.00[c]
24	*N*-*n*-Butyl-*N*-2-cyanoethyl	$C_{24}H_{25}N_3$	115–116	3	70	81.10	7.09	80.99	7.03[b]
25	*N*-*n*-Butyl-*N*-2-carboxyethyl	$C_{24}H_{26}N_2O_2$	181–182	0.5	52	76.96	7.01	77.26	7.11[c]
	B. 1-(4-Aminostyryl)isoquinolines								
26	None	$C_{17}H_{14}N_2$	196.7–197.7	2	28	82.90	5.72	82.95	5.60[b]
27	*N*-Benzyl-*N*-ethyl	$C_{25}H_{22}N_2$	118.0–119.5	2	8	85.67	6.64	85.70	6.44[c]
	C. Schiff Bases from 4-(4-Aminostyryl)quinoline and:								
28	2-Thiophenaldehyde	$C_{22}H_{16}N_2S$	132	Method A	58	77.61	4.70	77.53	4.79[c]
29	2-Furfuraldehyde	$C_{22}H_{16}N_2O$	125	Method A	8	81.45	4.93	81.71	4.98[c]
30	3,4-Diethoxybenzaldehyde	$C_{28}H_{26}N_2O_2$	147	Method A	73	79.60	6.24	79.59	6.14[c]
31	4-*N,N*-Dimethylamino-3-methylbenzaldehyde	$C_{27}H_{25}N_3$	114	Method A	3	82.85	6.39	83.29	6.10[c]
32	4-*N,N*-Bis-2-chloroethylaminobenzaldehyde	$C_{28}H_{25}N_3Cl_2$	160–161	Method A Method B	41 83	Cl—14.95		Cl—14.68[c]	
	D. Schiff Base from 4-(4-Aminostyryl)pyridine and:								
33	4-*N,N*-Bis-2-chloroethylaminobenzaldehyde	$C_{24}H_{23}N_3Cl_2$	179–180	Method A Method C	47 62	Cl—16.71		Cl—16.82[c]	

[a] At 150–160° unless otherwise indicated. [b] Analyses by Galbraith Microanalytical Laboratories. [c] Analyses by Weiler and Strauss. [d] N: Calcd., 7.82; found, 8.01. [e] N: Calcd., 7.25; found, 7.14. [f] N: Calcd., 6.33; found, 6.55. [g] N: Calcd., 5.95; found, 6.07. [h] At 150–170°. [i] At 160–165°. [j] Isolated and analyzed as maleate salt. See Table II. [k] At 157–176°. [l] At 185–190°. [m] Used lepidine zinc chloride complex instead of hydrochloride and heated at 110°. [n] At 143–158°. [o] By product. [p] N: Calcd., 8.14; found, 8.18. [q] N: Calcd., 7.82; found, 7.83. [r] Dry HCl was passed into the reaction mixture during heating. [s] The required 4-(*N*-methyl-*N*-carboxymethylamino)benzaldehyde was obtained in 33% yield as tan needles, m.p. 223–224°, by heating 0.080 mole 4-*N*-methylaminobenzaldehyde with 0.080 mole bromoacetic acid 2 hr. at 100° and recrystallizing the solid three times from water. *Anal.*: Calcd. for $C_{10}H_{11}NO_3$: C, 62.16; H, 5.74. Found: C, 62.18; H, 5.59. Because of the high melting point of the aldehyde, a small amount of dimethylformamide was used as solvent for the reaction with lepidine hydrochloride. [t] Prepared by refluxing for 6 hr. a mixture containing 10.0 g. of 4-[4-(*N*-*n*-butyl-*N*-2-cyanoethylamino)styryl]quinoline and 25 g. of sodium hydroxide in 150 ml. of methanol and 50 ml. of water, neutralizing with acetic acid, washing the orange crystals with water, and recrystallizing twice from benzene.

of aldehydes, in the hope that one of them might lead to a more favorable distribution of the compound in the animal.

Quinoline derivatives with an *N,N*-dialkylamino-alkylamino group have found favor as antimalarials.[7] Three styrylquinolines containing such groups were prepared. It seemed desirable to examine also compounds with a carboxyl group

(7) R. M. Acheson, "An Introduction to the Chemistry of Heterocyclic Compounds," Interscience Publishers, New York, 1960, p. 228.

TABLE II
SALTS OF 4-(4-AMINOSTYRYL)QUINOLINES

Base No.	M.P.	Formula	Calcd. C	Calcd. H	Calcd. N	Found[a] C	Found[a] H	Found[a] N
			Picrates					
5	231–232	$C_{31}H_{33}N_5O_7$	63.36	5.66		63.10	5.51	
6	186	$C_{33}H_{37}N_5O_7$	64.37	6.06	11.38	64.27	5.96	11.10
7	185–186	$C_{35}H_{41}N_5O_7$	65.30	6.38	10.88	64.97	6.55	10.71
8	181	$C_{37}H_{45}N_5O_7$	66.15	6.75		66.15	6.56	
9	159–160	$C_{39}H_{49}N_5O_7$	66.93	7.06	10.00	66.41	6.91	9.96
20	225–226	$C_{36}H_{35}N_9O_{14}$	52.90	4.31		53.09	4.39	
22	239–240	$C_{36}H_{35}N_9O_{14}$	52.90	4.31		53.05	4.39	
			Malate					
[b]	180	$C_{25}H_{28}N_2O_5$	68.78	6.47		68.27	6.72	
			Maleate					
[b]	183	$C_{25}H_{26}N_2O_4$	71.75	6.26		71.81	6.25	
7	133	$C_{33}H_{42}N_2O_4$	74.68	7.98		74.44	8.01	
8	115	$C_{35}H_{46}N_2O_4$	75.25	8.30		75.19	8.46	
10	103	$C_{39}H_{54}N_2O_4$	76.17	8.85		76.06	8.70	
11	106–107	$C_{41}H_{58}N_2O_4$	76.60	9.09		76.45	9.10	
			Fumarates					
[b]	200	$C_{25}H_{26}N_2O_4$	71.75	6.26		72.05	6.45	
[b]	200	$C_{46}H_{48}N_4O_4$	76.65	6.71		76.76	6.75	
7	112	$C_{62}H_{80}N_4O_4$	78.63	8.51		78.29	8.55	
9	104	$C_{70}H_{96}N_4O_4$	79.50	9.15		79.37	8.91	

[a] Analyses by Weiler & Strauss, Oxford, England. [b] 4-(4-Diethylaminostyryl)quinoline.

on an alkyl radical. 4-[4-(*N*-*n*-Butyl-*N*-2-cyanoethylamino)styryl] quinoline was hydrolyzed to 4-[4-(*N*-*n*-butyl-*N*-2-carboxyethylamino)-styryl] quinoline. 4-[4-(*N*-Methyl-*N*-carboxymethylamino)styryl] quinoline, which may be considered as a substituted glycine, was prepared from the corresponding aldehyde by condensation with lepidine hydrochloride. The presence of the carboxyl group on the side chain increased the solubility in water. 4-[*N*,*N*-Bis(2-chloroethyl)amino]benzaldehyde was used to make a styrylquinoline because the compound so produced would contain two antitumor groupings and might be more effective for that reason. Popp[8] has reported several derivatives prepared from this aldehyde that were active against tumors.

In order to facilitate purification and handling of the basic compounds that were oils at room temperature, several types of salts were prepared (Table II).

Experimental

Dipropylaniline was purchased from Distillation Products Industries, dibutyl-, di-*sec*-butyl-, diamyl-, dinonyl-, didecyl-, and dioctadecylanilines from K & K Laboratories and diallylaniline was purchased from Peninsular Chemresearch, Inc. Dihexyl-, diheptyl-, dioctyl-, and diisopropylaniline were prepared by alkylating aniline with the appropriate halides. The dialkylaminoalkylanilines were prepared by refluxing an amyl alcohol solution of the appropriate dialkylaminoalkyl chloride and the aniline over anhydrous sodium carbonate. (Amyl alcohol gave better yields than ethyl alcohol.) The dialkylanilines were converted to aldehydes by the process of Champaigne and Archer[9] except that the mixture of dimethylformamide, phosphorus oxychloride, and dialkylaniline was heated at 105–110°. The period of heating was doubled for *N*,*N*-dioctadecylaniline. *N*-Benzyl-*N*-methylaminobenzaldehyde and *N*,*N*-dibenzylaminobenzaldehyde were prepared by William K. Easley, L. Free, and Hugh Free at East Tennessee State College. Attempts to prepare monoalkylaminobenzaldehydes from the corresponding anilines by reaction with alloxan and treatment with hot sulfuric acid by the method of Bohringer and Sohn[10] produced little if any of the desired products.

p-*N*-Monomethylaminobenzaldehyde and *p*-*N*-monobutylaminobenzaldehyde were prepared from the corresponding *N*-alkylformanilides by treatment with phosphoryl chloride and phosphorus pentachloride according to the method of Vilsemeier and Haack.[11] The aldehydes were converted into styrylquinolines by heating with lepidine hydrochloride.

The solid styrylquinolines were purified by recrystallization from isohexane or mixed octanes. In addition, chromatography on silica gel or alumina and purification through conversion to the salts were employed. The latter two methods were especially valuable for the products which melted below room temperature.

The dark red salts were prepared by mixing concd. alcoholic solutions of the acid and base, cooling, filtering, and recrystallizing. The bases reacted with picric and maleic acids in a mole to mole ratio, but with fumaric acid some salts contained 2 moles of base per mole of acid, probably because the carboxyl groups are farther apart in the latter acid so that the introduction of the second large molecule of base is less difficult. Tartaric acid tended to give gels instead of satisfactory crystalline salts.

4-{4-[*N*,*N*-Bis(2-chloroethyl)amino]styryl}quinoline.—A mixture of 3.7 g. (0.010 mole) of lepidine picrate with 2.5 g. (0.010 mole) of 4-[*N*,*N*-bis(2-chloroethyl)amino]-benzaldehyde was heated 1.5 hr. in an oil bath at 150–

(8) Frank D. Popp, *J. Org. Chem.*, **26**, 1566 (1961); see also W. C. J. Ross, G. P. Warwick, and J. J. Roberts, *J. Chem. Soc.*, 3110 (1955).

(9) E. Campaigne and W. L. Archer, *Org. Syntheses*, **33**, 27 (1953).

(10) Bohringer and Sohn (DRP 108026).

(11) A. Vilsmeier and A. Haack, *Ber.*, **60B**, 119–122 (1927).

160°. A solution of the red solid in a minimum amount of hot dimethylformamide when cooled in a freezer deposited 2.7 g. of crude product, m.p. 221°. The product after four recrystallizations from dimethylformamide and washing with acetone was obtained as reddish green crystals; yield, 1.3 g.; 21.6%, m.p. 241°.

Anal. Calcd. for $C_{27}H_{23}N_5Cl_2O_7$: C, 54.01; H, 3.86. Found: C, 53.74, 54.03; H, 4.23, 4.39.[12]

The picrate was neutralized with ammonium hydroxide and the precipitate was recrystallized from octane to yield yellow crystals, m.p. 115–116°.

Anal. Calcd. for $C_{21}H_{20}N_2Cl_2$: Cl, 19.10. Found: 19.25, 19.19.[13]

Schiff Bases.—A mole to mole mixture of 4-aminostyryl base and the aldehyde was heated 10–20 min. without solvent (method A), or dissolved in a minimum volume of methanol (method B), or the aldehyde was added slowly with stirring at 110° to a solution of the amine in a minimum amount of dimethylformamide, then heated 15 min. at 120°–130° (method C). The crude product was precipitated by addition of water and was recrystallized from octane or from methanol.

(12) Analyses by Weiler and Strauss, Oxford, England.

(13) Analyses by Galbraith Laboratories, Knoxville, Tenn.

Base-Catalyzed Ring Opening of Diethyl 1,1,2,2-Tetracyanocyclopropane-3,3-dicarboxylate

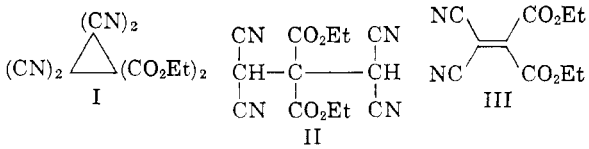
T. H. REGAN

Explosives Department, Experimental Station Laboratory, E. I. du Pont de Nemours & Co., Wilmington, Del.

Received November 13, 1961

Polycarboxylic esters of cyclopropane are generally stable to bases with respect to ring cleavage.[1] Hydrolysis is often accompanied by decarboxylation but the cyclopropane ring remains intact unless very vigorous reaction conditions are employed. Herewith is reported an example of a cyclopropane ring cleavage under very mild conditions.

Diethyl 1,1,2,2 - tetracyanocyclopropane - 3,3-dicarboxylate (I) was synthesized using the technique of Mariella and Roth.[2] Condensation of malonitrile and diethyl ketomalonate catalyzed by a trace of piperidine yielded diethyl dihydroxymalonate and an intermediate, presumably II. Attempted isolation of this intermediate gave instead a compound assigned the structure diethyl 1,1 - dicyanoethylene - 2,2 - dicarboxylate (III).[3]



I II III

(1) W. E. Truce and L. B. Lindy, *J. Org. Chem.*, **26**, 1464 (1961).

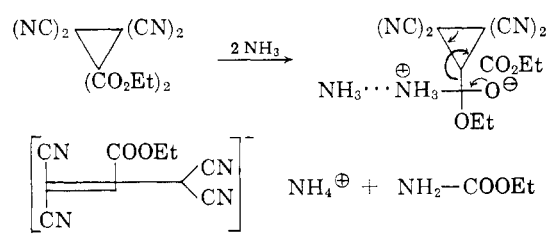
(2) R. P. Mariella and A. J. Roth, *J. Org. Chem.*, **22**, 1130 (1957).

(3) This compound was originally prepared by W. T. Tsatsos of the Central Research Dept., E. I. du Pont de Nemours & Co., *via* the condensation of malonitrile and diethylketomalonate.

Structural assignment was made on the basis of elementary analysis, infrared absorption, and reaction with anthracene to form initially the π-complex and then the Diels-Alder adduct. The reaction with anthracene is analogous to the reactions of tetracyanoethylene with aromatic compounds[4] to give the π-complexes and, where favorable, the Diels-Alder adducts.

Treatment of an ethanol solution of intermediate II with bromine gave the cyclic diester I in 87% yield.[5] When the diester I was added to aqueous or methanolic ammonia, a deep orange solution formed, but no tractable product could be isolated. In anhydrous ether, ammonolysis of the diester gave a nearly quantitative yield of an orange crystalline solid. The orange compound was soluble in water and alcohol and insoluble in nonpolar organic solvents. Its aqueous solutions gave instantaneous colored precipitates on addition of organic bases, *e.g.*, quinoline. The infrared spectrum had a sharp, intense nitrile band at 2190 cm.$^{-1}$ (4.57 μ), no absorption between 1710 and 1650 cm.$^{-1}$, but a strong band at 1510 cm.$^{-1}$ (6.62 μ). Cyclopropane nitriles absorb in the region 2250 cm.$^{-1}$ (4.45μ) and those containing carbethoxy groups characteristically have very weak nitrile bands[6]—*e.g.*, the diester I has only a barely perceptible nitrile band at 2240 cm.$^{-1}$ (4.46 μ). This sharp increase in nitrile band intensity coupled with the shift to lower frequency corresponds to the nitrile absorption of cyanopropenide ions as exhibited by sodium pentacyanopropenide and similar ions[7] which have high intensity absorption in the 2190-cm.$^{-1}$ (4.57μ) region. The polycyanopropanides also exhibit a strong low fequency shift in the C=C-stretching band from the region near 1625 cm.$^{-1}$ (6.1μ) to the region 1550–1400 cm.$^{-1}$ (6.45–7.41 μ)[7]; and in addition they form colored precipitates with organic bases such as quinoline.

These data lead to the structural assignment for the orange compound as ammonium 1,1,3,3-tetracyano-2-carbethoxypropenide. Further buttressing evidence is the fact that the ethereal



(4) T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald, and H. E. Winberg, *J. Am. Chem. Soc.*, **80**, 2775 (1958).

(5) This compound was first synthesized in very small yield by Dr. R. M. Scribner of the Central Research Dept., E. I. du Pont de Nemours & Co., using the procedure of L. Ramberg and S. Widequist, *Arkiv. für Kemi*, **12A**, No. 22 (1937); **12B**, No. 37 (1941).

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., Wiley, New York, 1958, p. 266.

(7) C. E. Looney and J. R. Downing, *J. Am. Chem. Soc.*, **80**, 2840 (1958).