Presumed Ethyl 2-Acetoxymercuri-2-deoxy-3,4,6-tri-O-acetyl-β-D-glucoside (IIIa).—A filtered solution of 6.4 g. (0.02 mole) of mercuric acetate (Mallinckrodt, anal. reag.) in 100 ml. of anhydr. ethanol was added to a solution of 5.45 g. (0.02 mole) of D-glucal 3,4,6-triacetate in the same solvent. Formation of white needles was observed within 5 min. at room temp., after which the reaction mixture was refrigerated for 2 hr. A first crop (4 g.) was collected, washed with cold isopropyl alcohol and then 30–60° petroleum ether. A second crop (1.2 g.) was obtained by concentrating combined filtrate and washings to 50 ml., adding 30 ml. of 30–60° petroleum ether and refrigerating for 1 hr. Three recrystallizations of the combined crops from isopropyl alcohol provided 4.5 g. (39%) of white crystals melting at 172–173.5°. The infrared spectrum of this compound is very similar to that of III. *Anal.*[28] Calcd. for $C_{16}H_{24}O_{10}Hg$: C, 33.30; H, 4.19; Hg, 34.77; EtO, 7.81. Found: C, 33.43; H, 4.41; Hg, 34.65; EtO, 7.70.

Presumed Ethyl 2-Chloromercuri-2-deoxy-3,4,6-tri-O-acetyl-β-D-glucoside (IVa).—A solution of 2.9 g. (0.005 mole) of IIIa in 50 ml. of 95% ethanol was treated with 5 ml. of satd. aq. NaCl. After 2 hr. at rm. temp. and overnight refrigeration, 1.25 g. of white crystals melting at 138–144° was collected. Evaporation to dryness of the filtrate, extraction of the resulting residue with $CHCl_3$, evaporation to dryness of the extract and recrystallization from isopropyl alcohol–30–60° petroleum ether of the remaining solid provided 1.15 g. of crystals melting at 139–145°. The combined crops were recrystallized three times from isopropyl alcohol–petroleum ether to yield 2.0 g. of long, fine, white needles melting at 146–147° and with an infrared spectrum very similar to that of IV. *Anal.*[27] Calcd. for $C_{14}H_{31}O_8$: HgCl: C, 30.38; H, 3.82; Hg, 36.25; EtO, 8.14. Found: C, 30.57; H, 4.02, Hg, 36.40; EtO, 8.21.

Presumed Isopropyl 2-Acetoxymercuri-2-deoxy-3,4,6-tri-O-acetyl-β-D-glucoside IIIb.—The procedure was the same as for the preparation of IIIa except that isopropyl alcohol (Baker, anal. reag.) was used in place of ethanol. Two recrystallizations from isopropyl alcohol–30–60° petroleum ether provided a 40% yield of white needles melting at 190–191°. The infrared spectrum of IIIb is similar to those of III and IIIa. *Anal.*[27] Calcd. for $C_{17}H_{26}O_{10}Hg$: C, 34.55; H, 4.43; Hg, 33.94. Found: C, 34.70; H, 4.63; Hg, 33.76.

Infrared spectra were obtained on Nujol mulls with a model 21C Perkin–Elmer spectrophotometer.

Melting points were determined in a Thomas–Hoover apparatus and are not corrected.

[CONTRIBUTION NO. 658 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

Cyanocarbon Chemistry. XIX.[1,2] Tetracyanocyclobutanes from Tetracyanoethylene and Electron-rich Alkenes

BY J. K. WILLIAMS, D. W. WILEY AND B. C. MCKUSICK

RECEIVED NOVEMBER 13, 1961

1,1,2,2-Tetracyanocyclobutanes are formed in high yield under very mild reaction conditions by the cycloaddition of tetracyanoethylene to electron-rich alkenes such as methyl vinyl ether and *p*-methoxystyrene. 1,1,2-Tricyanocyclobutanes are formed similarly from tricyanoethylene.

The thermal addition of allenes, fluoroalkenes and ketenes to alkenes to give cyclobutanes has been extensively investigated in the last few years and is now one of the most important routes to cyclobutanes, some of which are useful as precursors of alicyclic compounds.[3,4] Tetracyanoethylene, a reactive dienophile in the Diels–Alder reaction,[5] has been observed to form cyclobutane derivatives with a few 1,3-diene systems to which Diels–Alder addition is difficult or impossible.[6]

It has now been found that tetracyanoethylene readily forms 1,1,2,2-tetracyanocyclobutanes (I) with a variety of electron-rich alkenes.[7] Tricyanoethylene behaves similarly. As will be described in a subsequent paper, these polycyanocyclobutanes are good sources of 1,1,2-tricyanobutadienes and other acyclic products *via* ring-opening reactions.

I

X = RO–, RS–, R(R′CO)N–, $C_6H_5SO_2N(R)$–, *p*-ROC_6H_4–

In striking contrast to cycloaddition reactions of allenes, fluoroalkenes and ketenes, which require several hours of heating at 100–225°, the cycloaddition reactions of tetracyanoethylene generally occur rapidly and in high yield at 0–30°. The reactions are easy to follow because tetracyanoethylene forms highly colored π-complexes with alkenes[8]; when the color fades, the cycloaddition reaction is over. Thus, addition of methyl vinyl ether to a tetrahydrofuran solution of tetracyanoethylene at room temperature caused the solution to become deep orange; heat was evolved, the orange color faded to pale green in the course of half an hour, and 1,1,2,2-tetracyano-3-methoxycyclobutane was isolated as a colorless solid in 90% yield.

Vinyl ethers, vinyl sulfides, N-vinylamides and N-vinylsulfonamides all form tetracyanocyclobutanes with tetracyanoethylene as illustrated in Table I. The vinyl group can be substituted; thus, dihydropyran gives a bicyclic adduct (II), as does the 1,2-dialkoxyethylene 2,2-dimethyldioxole, and 4-methylenedioxolane forms a spiro

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(1) Paper XVIII, J. R. Roland and B. C. McKusick, *J. Am. Chem. Soc.*, **83**, 1652 (1961).

(2) Presented at the St. Louis Meeting of the American Chemical Society, March, 1961.

(3) J. D. Roberts and C. M. Sharts, "Cyclobutane Derivatives from Thermal Cycloaddition Reactions" in "Organic Reactions," John Wiley and Sons, Inc., in press.

(4) Recently, the thermal reaction of isobutenylamines with electrophilic olefins such as methyl acrylate and diethyl maleate has been reported to give cyclobutanes; K. C. Brannock, A. Bell, R. D. Burpitt and C. A. Kelly, *J. Org. Chem.*, **26**, 625 (1961).

(5) W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).

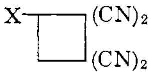
(6) A. T. Blomquist and Y. C. Meinwald, *ibid.*, **81**, 667 (1959); J. K. Williams, *ibid.*, **81**, 4013 (1959); D. S. Matteson, J. J. Drysdale and W. H. Sharkey, *ibid.*, **82**, 2853 (1960); K. Hafner and J. Schneider, *Ann.*, **624**, 37 (1959).

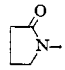
(7) We are greatly indebted to Prof. Saul Winstein of the University of California at Los Angeles for first suggesting this reaction.

(8) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

TABLE I

PROPERTIES OF 1,1,2,2-TETRACYANOCYCLOBUTANES

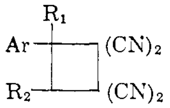


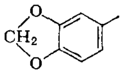
X	Yield, %	M.p., °C.	Carbon, %		Hydrogen, %		Nitrogen, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
CH_3O-	90	158–159.5[d]	58.1	58.1	3.3	3.3	30.1	30.0
CH_3CH_2O-[e]	82	140–141[d]	59.7	59.8	4.5	4.0	27.9	27.8
$C_6H_5CH_2O-$	83	148–150[d]	68.7	68.6	3.8	3.8	21.4	21.3
$ClCH_2CH_2O-$	77	105–106[d]	51.2	51.1	3.0	3.1	23.9	23.9
	90	130–130.5[a]	60.3	60.5	3.8	3.9	29.3	29.5
$C_6H_5SO_2\overset{CH_3}{\overset{\vert}{N}}-$	94[b]	130–145 d.[a]	55.4	54.7	3.4	3.3		
$C_6H_5CH_2S-$	83	119.5–121[c] 123–124.5[c]	64.7	65.0	3.6	3.2	20.1	20.4

[a] Recrystallization was conducted at room temperature by diluting an acetonitrile solution of the cyclobutane with ether. [b] The product was unstable; the analytical sample darkened at room temperature even when protected from the atmosphere. [c] Crystallized from a 1,2-dichloroethane–cyclohexane mixture. The two isomorphs had essentially the same infrared spectra in Nujol mulls. They were interconvertible by appropriate seeding. The higher melting form crystallized as cubes; the lower melting form crystallized as needles and was analyzed. [d] Recrystallized from 1,2-dichloroethane. [e] Mol. wt. calcd. 201, found 201.

TABLE II

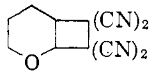
PROPERTIES OF 1,1,2,2-TETRACYANO-3-ARYLCYCLOBUTANES



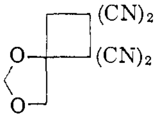
Ar	R_1	R_2	Yield, %	M.p., °C.	CH_3CN λ_{max}, mμ (ε)	Carbon, %		Hydrogen, %		Nitrogen, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
$p\text{-}CH_3OC_6H_4-$	H	H	93	182–183[a]	238 (13,000) 272 (1,630) 282 (1,210)	68.7	68.6	3.9	3.9	21.4	21.5
$p\text{-}CH_3OC_6H_4-$	H	$-CH_3$	85	135–136[b]	239 (13,600) 272 (1,640) 282 (1,190)	69.6	69.7	4.4	4.5	20.3	20.9
$p\text{-}CH_3OC_6H_4-$	CH_3	H	69	148–150[c]	232 (10,700) 277 (1,530) 283 (1,240)	69.6	69.7	4.4	4.5		
$p\text{-}CH_3O_6H_4-$	CH_3	CH_3	45	131–133[b]	232 (10,900) 277 (1,420) 283 (1,190)	70.3	70.5	4.9	5.1		
	H	CH_3	100	199.5–200[d]		66.2	66.1	3.5	3.7	19.3	19.2
$o\text{-}CH_3OC_6H_4-$	CH_3	H	63	162–162.5[e]		69.6	69.7	4.4	4.4	20.3	20.0

[a] Recrystallized from 1,2-dichloroethane. [b] Recrystallized from benzene. [c] Recrystallized from methyl ethyl ketone–methanol. [d] Recrystallized from 1,2-dichloroethane–cyclohexane. [e] Recrystallized from 1,2-dichloroethane–ether,

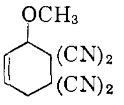
adduct (III). However, with 1-methoxy-1,3-butadiene, tetracyanoethylene reacts to give the Diels–Alder adduct 1,1,2,2-tetracyano-3-methoxy-4-cyclohexene (IV). These results and the fact that 4,5-dimethylenedioxolane also forms a Diels–Alder adduct (V) with tetracyanoethylene,[9] indicate that Diels–Alder addition of tetracyanoethylene is favored over cycloaddition when both are possible.



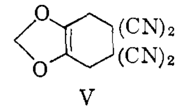
II



III

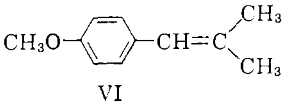


IV

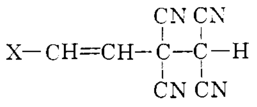


V

The electron-donating group need not be attached directly to the double bond undergoing cycloaddition. Its effect may be transmitted through a benzene ring, as is illustrated by the adducts with alkoxystyrenes listed in Table II. Compound VI, having a double bond hindered by



VI



$X-CH=CH-\underset{CN}{\overset{CN}{C}}-\underset{CN}{\overset{CN}{C}}-H$

VII

two methyl groups in the β-position, gave a deep-blue π-complex with tetracyanoethylene just as did the less hindered alkoxystyrenes of Table II, but it failed to give a cycloaddition product.

A cyclobutane structure for the adducts listed in Table I is supported by their composition and molecular weight and by the fact that they show no absorption in the double-bond stretching region

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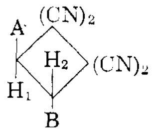
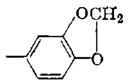
[9] J. B. Miller, *J. Org. Chem.*, **25**, 1279 (1960).

TABLE III

N.M.R. SPECTRA OF TETRACYANOCYCLOBUTANES—
CHEMICAL SHIFTS[a] AND SPIN-SPIN COUPLING CONSTANTS



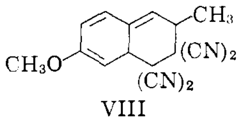
Compound		Chemical shifts in τ(p.p.m.)				Spin-spin coupling constants in c./s. (calcd.)
A =	B =	A	H_1	H_2	B	
H	OCH_3	6.53 8-line pattern	6.97	5.15 4-line pattern	6.57	ABX system with OCH_3 absorption at 6.57 τ obscuring one peak in AB pattern, J_{AH_1} = 14, J_{AH_2} = 7.8 $J_{H_1H_2}$ = 9.2
H	OCH_2CH_3	6.24 8-line pattern	6.66	4.83 4-line pattern	CH_2–, quadruplet at 6.05 CH_3–, triplet at 8.63	ABX system with OCH_2 absorption overlapping AB pattern, J_{CH_2,CH_3} = 7.5, J_{AH_1} = 13.5, J_{AH_2} = 7.4, $J_{H_1H_2}$ = 8.6
H	p-$CH_3OC_6H_4$–	6.36 8-line pattern	6.61	5.15 4-line pattern	CH_3O–, 6.38 Aromatic H-symmetrical pattern at 2.71	ABX system with OCH_3 absorption at 6.38 τ obscuring two peaks in AB pattern, J_{AH_1} = 13, J_{AH_2} = 9.5, $J_{H_1H_2}$ = 11.5 Aromatic mainly w,s,s,w quartet with 21 c./s. splitting between strong peaks and 40 c./s. splitting between weak peaks
CH_3	p-$CH_3OC_6H_4$–	8.43 doublet	5.90 w,s (split into quartets)	5.50 w,s	CH_3O–, 6.18 Aromatic H-symmetrical pattern at 2.70	AB type quartet with H_1 portion being further split into quartets, partially obscured by OCH_3 absorption at 6.18 τ, $J_{H_1H_2}$ = 13, J_{H_1,CH_3} = 6, J_{H_2,CH_3} = ~0 Aromatic mainly w,s,s,w quartet with 20 c./s. splitting between strong peaks and 40 c./s. splitting between weak peaks
CH_3		8.47 doublet	5.93 w,s (split into quartets)	5.50 w,s	–OCH_2O–, 3.93 Aromatic H-complex at 3.0	AB type quartet with H_1 portion being furth serplit into quartets, $J_{H_1H_2}$ = 12, J_{H_1,CH_3} 5, = J_{H_2,CH_3} = ~0

[a] Nuclear magnetic resonance spectra were taken at 60 Mc. using deuterioacetone as solvent with tetramethylsilane as an internal reference. Chemical shifts are recorded in τ-values; G. V. D. Tiers, *J. Phys. Chem.*, 62, 1151 (1958).

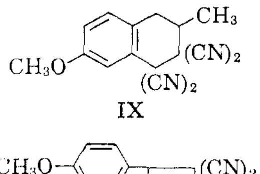
of the infrared. This transparency in the 6 μ region eliminates structures such as VII.

The n.m.r. spectra of the tetracyanoethylene adducts of methyl and ethyl vinyl ethers show the characteristic spin-spin coupling pattern of an ABX system along with methoxy and ethoxy groups, respectively (see Table III and discussion in Experimental Section). The CH_2–CH relationship of the three hydrogens along with the position of their absorption are completely in accord with the assigned cyclic structure.

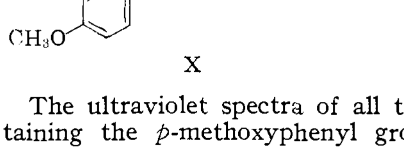
The problem of the structure of the adducts formed from the styrene derivatives listed in Table II is complicated by the possibility that they could be conventional Diels–Alder adducts. Thus, using the adduct from anethole as an example, the structures to be considered are VIII, IX, X and XI.



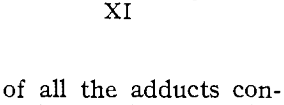
VIII



IX



X



XI

The ultraviolet spectra of all the adducts containing the p-methoxyphenyl grouping resemble the spectrum of p-methylanisole closely and are dissimilar to that of anethole.[10] These data made structures VIII and X unlikely. Permanganate oxidation of the anethole adduct gave a low yield of anisic acid, thus supporting structure XI and eliminating structure IX, which should give 4-methoxyphthalic acid upon oxidation. The infrared spectra of the p-methoxyphenyl adducts all show the 12 μ band indicative of a p-disubstituted benzene. In addition, the n.m.r. spectrum of the anethole adduct shows a symmetrical weak–strong–strong–weak quartet in the aromatic region corresponding to a p-disubstituted benzene. As is discussed in detail in the Experimental section, the rest of the spectrum can be reasonably interpreted as showing the methoxy group and the structural grouping of –CHCHCH$_3$ (see Table III). Additional confirmation of the cyclobutane structure XI is provided by the n.m.r. spectrum of the p-methoxystyrene adduct, which shows characteristic absorption for the p-methoxyphenyl group along with the spin–spin coupling pattern for an ABX system as also seen in the vinyl ether adducts.

In one instance an anomalous cycloaddition took place. When tetracyanoethylene was allowed to react with 2-ethoxy-3,4-dihydro-2H-pyran (XII), two products were obtained having infrared spectra so similar as to suggest that they were stereoisomers. That the products were not

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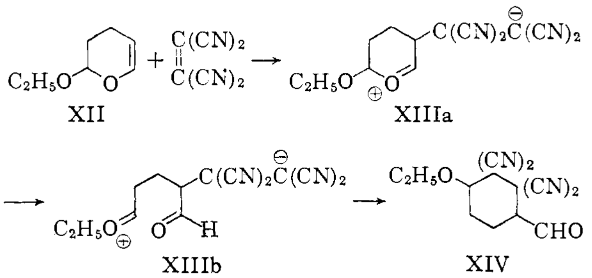
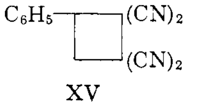
(10) p-Methyl anisole: λ_{max} 223 (ϵ 8350), 278 (1850), 286 (1540). Anethole: λ_{max} 259 (19,800), sh 290 (2520), sh 307 (1240).

the two stereoisomers of the expected cyclobutane was suggested by absorption bands in the infrared spectra of both substances near 3.73 and 5.78 μ, and by a proton magnetic resonance absorption of the lower melting, more soluble isomer at 0.77 τ strongly indicative of an aldehyde group. On the basis of these data, it is likely that the structure of the product is XIV (stereoisomers).

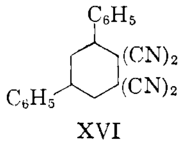
This anomalous reaction can be rationalized by assuming initial reaction to form an intermediate dipolar species XIIIa with a carbonium ion stabilized by an adjacent oxygen atom. Rearrangement of XIIIa to the carbonium ion XIIIb with loss of stereochemistry can then be followed by cyclization to XIV.



Tetracyanoethylene was unreactive toward styrene at room temperature, but reaction did take place in refluxing xylene. None of the expected cyclobutane XV was isolated from the complex reaction mixture. Instead we obtained benzalmalononitrile (15% yield) and an adduct of one molecule of tetracyanoethylene to two molecules of styrene (18% yield). The adduct may have the cyclohexane structure XVI. A probable explanation of the formation of benzalmalononitrile is that the cyclobutane XV actually did form, but was unstable at 140° and cracked to benzalmalononitrile and vinylidene cyanide. In support of this, the anethole adduct XI slowly cracks at 177° and one of the products appears to be p-methoxybenzalmalononitrile.

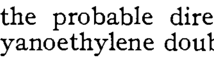


XV

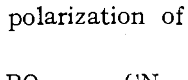


XVI

Tricyanoethylene[11] also reacts with vinyl ethers. Thus, benzyl vinyl ether and methyl vinyl ether reacted with tricyanoethylene to give solid adducts probably having the tricyanocyclobutane structure XVI. The assignment of a cyclobutane structure to these adducts rests largely on the spectral data, which show no olefinic unsaturation. Structure XVII is favored over structure XVIII on the basis of the probable direction of polarization of the tricyanoethylene double bond.



XVII

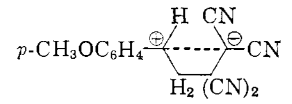


XVIII

The cycloaddition of tetracyanoethylene to electron-rich olefins is strongly influenced by solvents. For example, the addition of p-methoxystyrene to a solution of tetracyanoethylene in nitromethane caused an immediate deep blue color due to the formation of π-complex. In one minute, the solution is colorless and the reaction is complete. *Qualitative* observations of this kind using a series of solvents showed times required for the disappearance of blue color varying from 12 sec. in formic acid to 6×10^5 sec. (7 days) in toluene with intermediate times of 3×10^2 sec. for nitrobenzene, 8×10^3 sec. in ethanol, 8×10^4 sec. in ethyl acetate, and 2×10^4 sec. in ether. The reaction is so slow in carbon tetrachloride and cyclohexane that even after one month the blue π-complex color still persisted.

These qualitative data strongly suggest that the reaction mechanism involves charge separation in the rate-determining step with a transition state or intermediate such as XIX. Some support of the charged intermediate is seen in the anomalous reaction of 2-ethoxy-3,4-dihydro-2H-pyran with tetracyanoethylene to give the stereoisomers of XIV; a concerted, one-step process should show more steric control.

Further studies on the mechanism of the cycloaddition reactions of tetracyanoethylene are in progress and will be reported in a future publication.



XIX

Experimental

Preparation of Alkenes.—N-Methyl-N-vinylbenzenesulfonamide was prepared by ethynylation of N-methylbenzenesulfonamide.[12]

Dehydration of the appropriate carbinols as described in the literature gave 2-(4-methoxyphenyl)-propene, 2-(4-methoxyphenyl)-2-butene[13] and 2-(2-methoxyphenyl)-propene.[14] The other alkenes used in this work were obtained from commercial sources.

Preparation of 1,1,2,2-Tetracyanocyclobutanes.—The tetracyanocyclobutanes were most commonly prepared by adding a 5–20% excess of an alkene to a solution of tetracyanoethylene in tetrahydrofuran at room temperature. The characteristic color of the π-complex of the components appeared at once; vinyl ethers gave a red-orange color, alkoxystyrenes a blue one. The reaction was sometimes rapid enough to be exothermic, in which case the mixture was cooled to hold the temperature at 0–30°. Disappearance of the characteristic color of the complex, which required anything from a few minutes to a day, was a good indication that the reaction was over. The method of isolation of the product varied. Occasionally the product crystallized from the reaction mixture. Frequently it could be made to crystallize by diluting the reaction mixture with petroleum ether. Alternatively, the tetrahydrofuran was removed by vacuum distillation at room temperature, and the residue, if not crystalline, was triturated with benzene or 1,2-dichloroethane to induce crystallization. The crystalline product obtained, however, was recrystallized from inert solvents such as benzene or 1,2-dichloroethane.

In a typical example, 21.6 g. (0.30 mole) of ethyl vinyl ether was added to a solution of 32 g. (0.25 mole) of tetracyanoethylene in 250 ml. of tetrahydrofuran cooled in an ice-bath. The dark red-orange solution was cooled in the ice-bath for 5 minutes, at which point the deep color had faded, and the original exothermic reaction seemed to be over. The reaction mixture was allowed to stand at 25°

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[11] C. L. Dickinson, D. W. Wiley and B. C. McKusick, *J. Am. Chem. Soc.*, **82**, 6132 (1960).

[12] T. L. Cairns and J. C. Sauer, *J. Org. Chem.*, **20**, 627 (1955).

[13] A. Klages, *Ber.*, **37**, 3987 (1904).

[14] V. Auwers, *Ann.*, **413**, 303 (1917).

for 67 hours to ensure completeness of reaction. The resultant mixture, now dark green, was diluted with 500 ml. of petroleum ether. The solid that precipitated was collected; weight 36 g. The filtrate was reduced to a volume of about 50 ml. on a steam-bath and then diluted with 150 ml. of petroleum ether to give an additional crop of dark green crystals that weighed 10.7 g.; total crude yield 46.7 g. (93%). Two recrystallizations from 1,2-dichloroethane afforded 41.2 g. (82%) of colorless 1,1,2,2-tetracyano-3-ethoxycyclobutane (Table I) melting at 137–140°. A sample prepared for analysis by two further recrystallizations from 1,2-dichloroethane melted at 140–141°. The infrared spectrum had bands at 4.45 (–CN), 7.27 ($-CH_3$) and 8.83 μ (C–O–C).

The properties and analytical data for most of the cyclobutanes are listed in Tables I and II.

1-(*p*-Anisyl)-2-methyl-3,3,4,4-tetracyanocyclobutane (X).—The adduct from anethole and tetracyanoethylene, prepared by the standard procedure, has an ultraviolet spectrum (Table II), an infrared spectrum and a proton n.m.r. spectrum consistent with the assigned cyclobutane structure. The infrared spectrum has bands at 4.45 (unconjugated C≡N), 6.17 and 6.57 μ (phenyl), and 11.85 μ (*p*-disubstituted benzene). The adduct, m.p. 135–136°, can be sublimed at 177° (0.1 mm.), but sublimation is accompanied by a small amount of decomposition. The characteristic smell of anethole can be detected, tetracyanoethylene (identified by color tests) collects above the adduct on the walls of the subliming tube and the sublimed adduct contains about 1% of material having the λ_{max}^{EtOH} 348 mμ characteristic of *p*-methoxybenzalmalononitrile.[15]

Permanganate oxidation helped substantiate the cyclobutane structure. Five grams of the powdered adduct was added to a solution of 28.5 g. of potassium permanganate and 3.5 g. of sodium bicarbonate in 750 ml. of water, and the mixture was stirred vigorously at room temperature for 3 days. The excess potassium permanganate was destroyed by addition of 4 g. of sodium bisulfite (a slight excess). Twenty five grams of diatomaceous earth was stirred into the mixture, and the mixture of diatomaceous earth and manganese dioxide was separated by filtration and washed with water. The combined filtrates were concentrated to a volume of 150 ml. by distillation at 20 mm. and then acidified with concentrated hydrochloric acid and stored at 0° for 24 hours. Filtration separated 291 mg. of anisic acid, which was recrystallized from benzene to give 253 mg. (9%). It was identified by direct comparison of its melting point (183–185°) and infrared spectrum with those of an authentic sample.

7,7,8,8-Tetracyano-2-oxabicyclo[4.2.0]octane (II).—To a solution of 1.28 g. of tetracyanoethylene in 10 ml. of tetrahydrofuran was added 2 ml. of dihydropyran. The deep red-brown solution became slightly warm, and after 0.5 hour crystals began to form. After the reaction mixture had been allowed to stand at 25° for 1.5 hours, it was diluted with 15 ml. of ether, and the solid which formed was collected and washed with ether to give 2.0 g. (94%) of 7,7,8,8-tetracyano-2-oxabicyclo[4.2.0]octane as pale yellow cubes that decomposed at 171°. Two recrystallizations from acetonitrile gave material melting at 173–176° dec.

Anal. Calcd. for $C_{11}H_8N_4O$: C, 62.3; H, 3.8; N, 26.4; mol. wt., 212. Found: C, 62.5; H, 3.8; N, 26.4 mol. wt., 210.

6,6,7,7-Tetracyano-3,3-dimethyl-2,4-dioxabicyclo[3.2.0]heptane.[16]—2,2-Dimethyl-1,3-dioxole[17] (0.52 ml., about 0.005 mole) was added to a solution of 0.64 g. (0.005 mole) of tetracyanoethylene in 5 ml. of tetrahydrofuran. A deep violet color developed at once, and after 20 minutes crystals began to appear. After 2.5 hours, the suspension was sky-blue in color. Diethyl ether (10 ml.) was added and 0.96 g. (84%) of the adduct was separated by filtration, washed with diethyl ether, and air-dried. The adduct had a light blue color caused by a trace of impurity.

Anal. Calcd. for $C_{11}H_8O_2N_4$: C, 57.9; H, 3.5. Found: C, 58.0; H, 3.7.

2,2,3,3-Tetracyano-6,8-dioxaspiro[3:4]octane (III).[18]—To a solution of 14.1 g. (0.11 mole) of tetracyanoethylene in 60 ml. of tetrahydrofuran was added 11.5 g. (0.137 mole) of 4-methylenedioxolane[19] prepared by the method of Radcliffe and Mayes.[20] The solution became hot and instantly turned reddish-orange, then yellow, within 1 minute. As the mixture cooled to room temperature, crystals formed. The mixture was allowed to stand overnight, and then the crystals were collected by filtration and washed with a little tetrahydrofuran–petroleum ether (1:1 by volume) to yield 11.56 g. of 2,2,3,3-tetracyano-6,8-dioxaspiro[3.4]octane, m.p. 152° dec. The filtrate was diluted with an equal volume of petroleum ether, and the crystalline precipitate was collected to yield an additional 8.62 g. of product, m.p. 152° dec., total yield 86%. After four recrystallizations from 1,2-dichloroethane an analytical sample was obtained melting at 167° dec.

Anal. Calcd. for $C_{10}H_6N_4O_2$: C, 56.1; H, 2.8; N, 26.2; mol. wt., 214. Found: C, 56.0; H, 3.1; N, 26.2; mol. wt., 215, 227.

2,2,3,3-Tetracyano-4-ethoxycyclohexanecarboxaldehyde (XIV).—To a solution of 25.6 g. of tetracyanoethylene in 100 ml. of tetrahydrofuran was added 27 g. of 2-ethoxy-3,4-dihydro-2H-pyran (XII). After about 10 minutes the mixture became slightly warm. It was allowed to stand for 3 hours and then diluted with 300 ml. of petroleum ether. The solid that precipitated was collected and washed with ether to give 47 g. (92%) of material melting at 121–133°. This crude product was dissolved in 120 ml. of 1,2-dichloroethane and diluted while warm with 50 ml. of ether. The solid that crystallized weighed 18.1 g., m.p. 142–156° (A). When the liquors were evaporated, 16 g. of pink solid was obtained that gave 12 g. of material, m.p. 128–133°, after three recrystallizations from 1,2-dichloroethane (B). An additional recrystallization of B from the same solvent afforded an analytical sample as needles, m.p. 127–136° dec.

The infrared spectrum of A had bands at 3.64 and 5.78 μ $(\overset{\overset{O}{\|}}{C}\text{–H})$ and at 4.44 μ (–CN). The spectrum of B showed absorption at 3.68, 5.78 and 4.45 μ.

A sample of A was prepared for analysis by recrystallization from ethyl acetate to give large, hexagonal prisms, m.p. 157–171° dec.

Anal. Calcd. for $C_{13}H_{12}N_4O_2$: C, 60.9; H, 4.7; N, 21.9. Found (A): C, 61.1; H, 4.8; N, 22.1. Found (B): C, 60.8; H, 4.6; N, 22.1.

3-Methoxy-4,4,5,5-tetracyano-1-cyclohexane (IV).—To a slurry of 12.8 g. (0.1 mole) of tetracyanoethylene in 200 ml. of CH_2Cl_2 was added 12.6 g. (0.15 mole) of 1-methoxy-1,3-butadiene in 50 ml. of CH_2Cl_2. After 1.5 hours, the colorless solution was concentrated *in vacuo*, and the residue taken up in 65 ml. of hot benzene. The adduct, which separated upon cooling, was filtered and washed with a small amount of benzene to give 16.1 g. (76%) of 3-methoxy-4,4,5,5-tetracyano-1-cyclohexene, m.p. 112.4–114°. An analytical sample was obtained by recrystallizations from benzene and sublimation at 95° (0.05 mm.), m.p. 112.8–113.6°.

The infrared spectrum has characteristic absorption bands at 4.41 (w, unconjugated CN) and 6.02 μ (—CH═CH—). The proton magnetic resonance spectrum in deuterioacetone is consistent with assigned structure with absorption peaks at 3.90 (—CH═CH—), 5.13 ($>CHOCH_3$), 6.13 ($—OCH_3$) and 6.50 τ (satd. $—CH_2—$); relative intensities are 2:1:3:2, respectively.

Anal. Calcd. for $C_{11}H_8N_4O$: C, 62.3; H, 3.8; N, 26.4. Found: C, 62.2; H, 3.9; N, 26.2.

1-Benzyloxy-2,2,3-tricyanocyclobutane.—To a solution of 2.0 g. of tricyanoethylene in 2 ml. of ether was added a solution of 2.61 g. of benzyl vinyl ether in 3 ml. of ether. After the reaction mixture stood at room temperature for 4 hours, the solid that had precipitated was collected and washed with a small amount of cold ether. This tan crystalline material, m.p. 100–108°, weighed 3.42 g. (74%). A dark,

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[15] G. N. Sausen, V. A. Engelhardt and W. J. Middleton, *J. Am. Chem. Soc.*, **80**, 2815 (1958).

[16] We are indebted to Dr. N. G. Field of du Pont's Textile Fibers Department for this experiment.

[17] N. G. Field, *J. Am. Chem. Soc.*, **83**, 3504 (1961).

[18] We are indebted to Dr. J. B. Miller, Explosives Department, E. I. du Pont de Nemours and Co., for this experiment.

[19] H. O. Fischer, E. Baer and L. Feldmann, *Ber.*, **63**, 1738 (1930).

[20] M. R. Radcliffe and W. G. Mayes, U. S. Patent 2,445,733 (1948).

tarry contaminant was only difficultly removed by several recrystallizations from tetrahydrofuran–cyclohexane mixtures. The recrystallized material appeared to undergo decomposition during heating since the melting point fell to 96–109°. However, recrystallization from ether gave an analytidal sample of 1-benzyloxy-2,2,3-tricyanocyclobutane as white needles melting at 115–116°. The ultraviolet spectrum in ethanol showed only the low intensity fine-structure bands characteristic of benzenoid absorption.

Anal. Calcd. for $C_{14}H_{11}N_3O$: C, 70.9; H, 4.7; N, 17.7; mol. wt., 237. Found. C, 70.6; H, 4.7; N, 17.7; mol. wt., 229.

1-Methoxy-2,2,3-tricyanocyclobutane.—A solution of 5.8 g. of methyl vinyl ether in 10 ml. of tetrahydrofuran was added with cooling and stirring to 7.73 g. of tricyanoethylene. The resulting solution was cooled below 35° until the reaction was no longer exothermic and was then allowed to stand overnight at room temperature. The resulting orange solution was concentrated under vacuum and chilled. The resulting pasty mass was washed with a small amount of cold ether to give 10.55 g. of crystalline, tan material, m.p. 70–95°. Recrystallization from ether, ethylene chloride and 1:1:1 tetrahydrofuran–ethylene chloride–cyclohexane all gave crystals, m.p. 100–110°, which were contaminated by small amounts of brown gum. Sublimation attempts gave a sticky solid with an infrared spectrum essentially identical to the crystalline material. It appeared that lengthy heating was always accompanied by the formation of amorphous tan material which coated the surface of the crystals. The melting point could be raised by successive recrystallizations from ethylene chloride, decanting the mother liquors off the crystals and washing the surface free of the amorphous material with additional cold solvent. An analytical sample of 1-methoxy-2,2,3-tricyanocyclobutane melted at 114–116°. The infrared spectrum showed a band at 4.44 μ (unconjugated –CN) and had no strong absorption from there to 6.8 μ.

Anal. Calcd. for $C_8H_7N_3O$: C, 59.6; H, 4.4; N, 26.1. Found: C, 59.4; H, 4.6; N, 26.1.

Reaction of Tetracyanoethylene with Styrene.—A mixture of 2.56 g. (0.02 mole) of tetracyanoethylene, 5.20 g. (0.05 mole) of styrene and 10 ml. of xylene was heated at reflux for 4 hours. The black mixture was then mixed with 150 ml. of petroleum ether (30–60°) with stirring. The black solid that formed was separated by filtration to give a pale yellow filtrate. Concentration of the filtrate gave an orange oil. This oil was dissolved in 5 ml. of hot cyclohexane and cooled to give 0.46 g. of almost colorless needles, m.p. 75–80°. Recrystallization from cyclohexane and sublimation gave a white solid, m.p. 85–86°, identified by mixed m.p. and infrared spectrum as benzalmalononitrile.

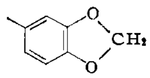
The dried black solid above was mixed with 30 g. of alumina and added to the top of an alumina column (90 g., acid Woelm, Activity I) constructed in benzene. The column was developed with 1:1 benzene–ethylene chloride. A total of 1500 ml. of solution was required to move a yellow band off the column while a dark brown band had moved two-thirds of the way down the column. Further development of the column gave only tarry residue. Concentration of the initial 1500 ml. of yellow solution afforded 3.2 g. of a slightly gummy, bright yellow-orange residue. Washing with very small amounts of cold methylene chloride removed the colored impurities to give 1.7 g. of colorless solid, m.p. 155–180°. Successive rechromatography of the white material always yielded a product contaminated by yellow impurities. Three recrystallizations from 10:7 ethanol–ethylene chloride gave 1.2 g. of long, colorless, fluffy needles, m.p. 193–194° (with slow decomposition occurring at 180°), having the composition of an adduct of one molecule of tetracyanoethylene and two molecules of styrene. The ultraviolet spectrum in methylene chloride contained only the low-intensity fine-structure bands characteristic of benzenoid absorption. When ethanol was used as solvent, strong absorption bands at 208 and 235 mμ appeared. The intensity of these bands increased as a function of time indicating that the molecule was reacting slowly with the solvent. The infrared spectrum was strikingly similar to that of 1-phenyl-2,2,3,3-tetracyanocyclopropane,[21] differing only slightly in relative band positions and intensities and having an additional strong band at 6.87 μ characteristic of the $-CH_2-$ deformation vibration. The compound may be 1,1,2,2-tetracyano-3,5-diphenylcyclohexane (XVI).

Anal. Calcd. for $C_{22}H_{16}N_4$: C, 78.5; H, 4.8; N, 16.7. Found: C, 78.3; H, 4.8; N, 16.9.

N.m.r. Spectra of Tetracyanocyclobutanes.—The proton magnetic resonance absorption spectra were taken at 60 Mc. using deuterioacetone as solvent with tetramethylsilane as an internal standard. The data are recorded in Table III. The first three compounds in the table, where A = H, showed the characteristic 12-line ABX pattern.[22] The X-proton quartet at low field in relation to the AB pattern consisted of 4 lines with the middle two so close together as to almost appear as a triplet. However, analyses of the AB patterns gave the listed spin-spin coupling constants and reconstruction of the X-proton quartets from these values agreed very closely with the observed patterns. The *cis-trans* assignments listed were made on the assumption $J_{trans\text{-HH}} > J_{cis\text{-HH}}$, and were consistent with these three examples.

The n.m.r. spectrum of the anethole adduct (A = CH_3, B = *p*-anisyl) is interpreted to consist of aromatic H at 2.70, CH_3O at 6.18 and CH_3 (doublet) at 8.43 τ. The rest of the spectrum consists of an AB-type quartet with the components of the doublet associated with H_1 proton being split into quartets by the methyl group. The fine structure of these quartets was partially obscurred by the OCH_3 absorption but could be seen clearly in the related iso-safrole adduct (where A = CH_3,

B =



The coupling constants are approximate.

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[21] S. Widequist, *Arkiv. Kemi. Mineral Geol.*, **20B**, No. 4, 8 (1945).

[22] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw–Hill Book Co., Inc., New York, N. Y., 1959, pp. 132–138.