Tetracyanoethylene Oxide. IV. Nucleophilic Ring Opening

W. J. LINN AND E. CIGANEK

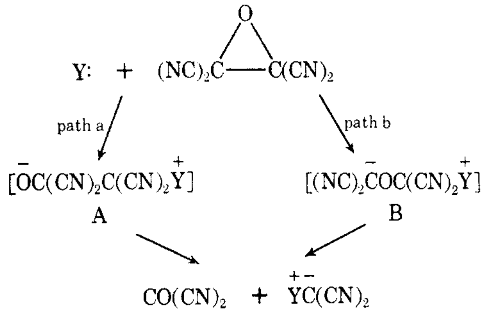
Contribution No. 1473 from the Central Research Department,
E. I. du Pont de Nemours and Company, Wilmington, Delaware

Received June 28, 1968

Most reactions of nucleophiles with tetracyanoethylene oxide (TCNEO) involve fragmentation of the ring. Examples are given of reactions with amines, thiocarbonyl compounds, benzylideneaniline, and benzophenone azine. The amine reaction gives the same products as the reaction of the amines with carbonyl cyanide. The products from TCNEO and thiocarbonyl compounds depend on the substituents attached to the thiocarbonyl group. Thus, thiourea gives a stable thiouronium ylide whereas with thiobenzophenone, sulfur is eliminated with the formation of a dicyanoethylene. The reaction of TCNEO with benzylideneaniline takes two pathways. One gives an addition product with loss of hydrogen cyanide. The second involves ring scission to form a 1,3 dipole that adds a second molecule of benzylideneaniline. The benzophenone azine reaction, however, takes a different course and gives nitrogen, 1,1-dicyano-2,2-diphenylethylene, and the epoxide of this olefin. Acetic anhydride and acetyl chloride add to TCNEO to give ring-opened products without fragmentation. Benzaldehyde and TCNEO form a 1:1 addition product believed to be a cyclic acetal.

The oxirane ring of tetracyanoethylene oxide (TCNEO) is extremely susceptible to nucleophilic attack. A common result is cleavage into the elements of carbonyl cyanide and dicyanomethylene. Examples of reactions with pyridines and alkyl sulfides have been given.[1] These reactions may be concerted, *i.e.*, both bonds may break simultaneously. However, if the process is stepwise, an initial attack on carbon can be followed by one of two different reaction sequences, either of which could lead to the same ultimate products (Scheme I). The two paths differ in the order in which the C–C and C–O bonds break. These paths can only be distinguished if it is possible to intercept either A or B.

SCHEME I



We have now observed additional examples of nucleophilic ring-opening reactions of TCNEO. Although some of these are similar to the earlier reported reactions and involve rupture of two bonds, there are two clear-cut instances that follow path a. There are cases also suggesting that path b ring opening can occur, but these are ambiguous. Negative charge is stabilized in both A and B, and a delicate balance may be swung in either direction depending upon the attacking reagent.

Another difficulty is the possibility of nucleophilic attack on oxygen. Brown and Cookson[2] isolated an unsymmetrical adduct of TCNEO to the 9,10 positions of anthracene. This was attributed to initial attack on oxygen, but it is not possible to distinguish this from a path a reaction.

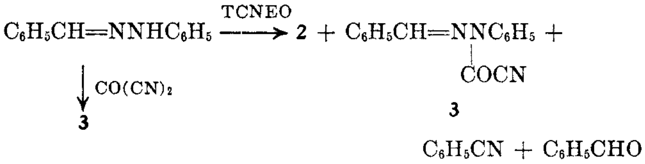
Reaction with Amines.—Nothing can be inferred about the direction of ring opening of TCNEO by amines. Both a C–C and a C–O bond are broken. Whereas the previously reported reaction with pyridine derivatives is fairly clean, reaction with simple primary, secondary, and tertiary amines is more complex. Yields of products are generally low and it is often not possible to account for all the molecular fragments.

One of the reaction products of TCNEO and aniline is N-(cyanoformyl)aniline (**1**). This is also obtained from reaction of carbonyl cyanide and aniline,[3] and it is likely that the TCNEO reaction also involves the intermediacy of carbonyl cyanide. The complexity of the reaction is indicated by the isolation, in small yields, of the anil of carbonyl cyanide (**2**). An oxidation must be involved to explain this product.

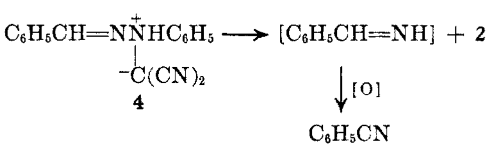
Closely related to this reaction is that of TCNEO with benzaldehyde phenylhydrazone. The anil **2** is also a product of this reaction along with 1-cyanoformyl-1-phenyl-2-benzylidenehydrazine (**3**) and small amounts of benzonitrile and benzaldehyde. The structure of **3** was established by an independent synthesis from the hydrazone with carbonyl cyanide and the anil **2** was prepared from malononitrile and nitrosobenzene.

The initial reaction presumably results in the scission of TCNEO into carbonyl cyanide and the unstable zwitterion **4**. The carbonyl cyanide produced in this first step is undoubtedly the source of **3**, whereas the breakdown of **4** may be responsible for formation of carbonyl cyanide anil and benzonitrile. The complications in such a process are indicated by the low yields of all the products.

$$C_6H_5NH_2 \xrightarrow{TCNEO} \underset{\mathbf{1}}{C_6H_5NHCOCN} + \underset{\mathbf{2}}{C_6H_5N{=}C(CN)_2}$$



$$\begin{array}{l} C_6H_5CH{=}NNHC_6H_5 \xrightarrow{TCNEO} \mathbf{2} + C_6H_5CH{=}\underset{\substack{|\\ COCN \\ \mathbf{3}}}{N}C_6H_5 + \\ \quad \downarrow CO(CN)_2 \\ \quad \mathbf{3} \qquad\qquad\qquad\qquad C_6H_5CN + C_6H_5CHO \end{array}$$



$$\begin{array}{l} C_6H_5CH{=}N\overset{+}{\underset{\substack{| \\ ^{-}C(CN)_2 \\ \mathbf{4}}}{N}}HC_6H_5 \longrightarrow \underset{\substack{\downarrow [O] \\ C_6H_5CN}}{[C_6H_5CH{=}NH]} + \mathbf{2} \end{array}$$

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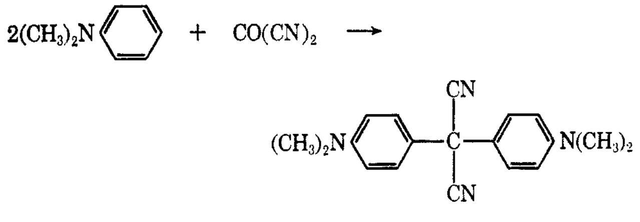
[1] W. J. Linn, O. W. Webster, and R. E. Benson, *J. Am. Chem. Soc.*, **87**, 3651 (1965).

[2] P. Brown and R. C. Cookson, *Tetrahedron*, **24**, 2551 (1968).

[3] R. Malachowski and J. Jankiewicz-Wasowska, *Roczniki Chem.*, **25**, 34 (1951).

Products of the reaction of a tertiary aliphatic amine, *e.g.*, triethylamine, with TCNEO are unstable and decompose on attempted purification. It was expected, however, that from dimethylaniline one might obtain bis(*p*-dimethylaminophenyl)dicyanomethane (**5**), the product of condensation of the amine and carbonyl cyanide.[3] This is the case although the yields from TCNEO are small and no products were isolated to account for the remainder of the molecule.



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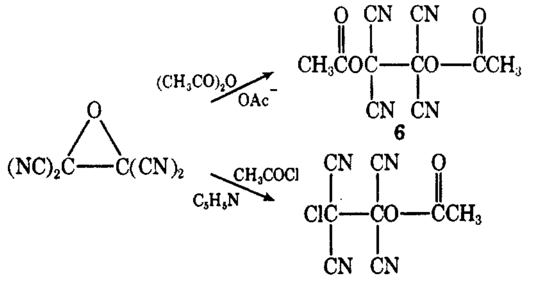
Reaction with Acetic Anhydride and Acetyl Chloride.—These reactions afforded the first example of nucleophilic ring opening of TCNEO proceeding *via* path a, the C–C bond remaining intact. Addition of a catalytic amount of acetate ion to a solution of TCNEO in acetic anhydride results in the precipitation of the diacetate of tetracyanoethylene glycol (**6**), identified on the basis of elemental analysis and spectra. Similarly, **7** is obtained when a drop of pyridine is added to a suspension of TCNEO in acetyl chloride.



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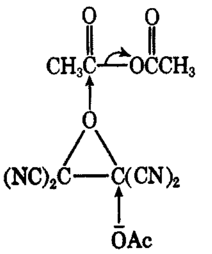
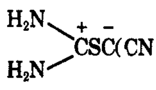
The preservation of the carbon–carbon bond of the epoxide ring is probably due to solvation by large amounts of the anhydride or acetyl chloride which can trap the anion as soon as it develops.



Reaction with Unsaturated Nucleophiles.—The ability of TCNEO to add to double and triple bonds[4] led to the investigation of molecules containing other types of unsaturation. Some preliminary work of this kind has been reported.[5] However, each system behaves differently and there are interesting aspects to each.



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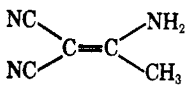

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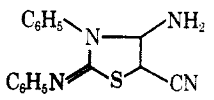

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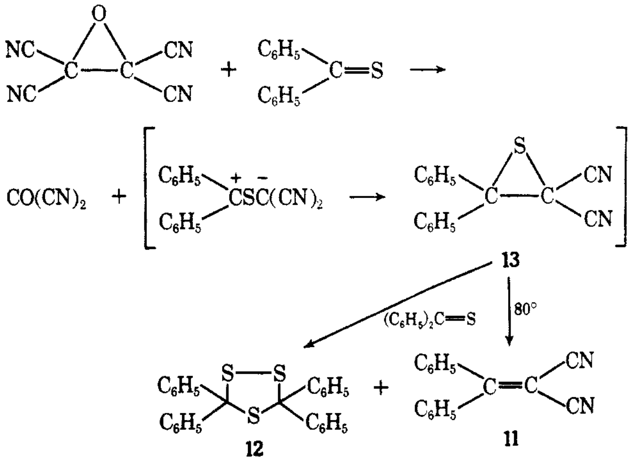
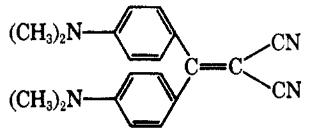
Middleton has described the reaction of 2,2-dicyano-3,3-bis(trifluoromethyl)ethylene oxide with thiocarbonyl compounds.[6] Tetracyanoethylene oxide reacts similarly with thiourea, thioacetamide, and N,N′-diphenylthiourea to give compounds **8**–**10**, respectively. Side reactions involving carbonyl cyanide were avoided by using ethanol as a solvent, which reacts with carbonyl cyanide to yield ethyl cyanoformate and hydrogen cyanide. TCNEO also reacts rapidly with thiobenzophenone in boiling benzene giving 1,1-diphenyl-2,2-dicyanoethylene (**11**) in 68% yield. The reaction occurs more slowly at room temperature in acetonitrile or in ethanol. In the latter instance 3,3,5,5,-tetraphenyl-1,2,4-trithiolane (**12**) can be isolated in substantial yield. This compound has been reported[7] as a minor product in the autoxidation of thiobenzophenone. At elevated temperatures the trithiolane decomposes into thiobenzophenone and sulfur; thus it was not isolated in the reaction at 80°.

SCHEME II



A possible mechanism for these reactions involves an unstable dicyano episulfide **13** (Scheme II). Reaction between 4,4′-bis(dimethylamino)thiobenzophenone (**14**) and TCNEO occurs even at −50° yielding the corresponding dicyanoethylene derivative **15** in 79% yield; elemental sulfur was also isolated.



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Reaction with Carbonyl Groups.—Unlike the thiocarbonyl compounds, benzaldehyde reacts with TCNEO only at elevated temperature. A 1:1 adduct could be isolated in about 10% yield. Because of the reaction conditions, it was first assumed that the mechanism of the reaction was similar to that observed for the addi-

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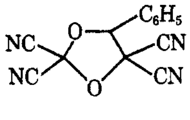
[4] W. J. Linn and R. E. Benson, *J. Am. Chem. Soc.*, **87**, 3657 (1965).

[5] E. Ciganek, *J. Org. Chem.*, **30**, 4198 (1965).

[6] W. J. Middleton, *ibid.*, **31**, 3731 (1966).

[7] A. Schönberg, O. Schütz, and S. Nickel, *Chem. Ber.*, **61**, 2175 (1928); H. Staudinger and H. Freudenberger, *ibid.*, **61**, 1838 (1928).

tion of TCNEO to olefins.[8] Therefore the expected product was the dioxolane **16**. However, mild hydrolysis of the adduct with dilute hydrochloric acid gives benzaldehyde in good yield.[9] It is conceivable that hydrolysis of **16** could give benzaldehyde, although this does not seem probable in view of the mild conditions employed. Therefore the hydrolysis experiment favors the alternative structure **17**. Spectral characterization does not distinguish between **16** and **17**. The single proton on the five-membered ring shows a sharp resonance peak at τ 3.08. This may be contrasted with the hydrogen in the ethylene acetal of benzaldehyde which has its resonance at τ 4.50.[10] Although this downfield shift could be interpreted in favor of structure **16**, the chemical evidence that points to **17** is stronger. This reaction, therefore, is evidently a second example of ring opening of TCNEO *via* path a in which the carbon–oxygen bond is preferentially broken.



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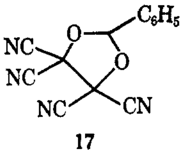

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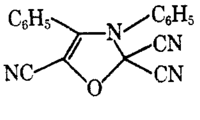
Reaction with Schiff Bases.—Two crystalline products are isolated from the reaction of TCNEO with benzylideneaniline in benzene at reflux temperature. The major product (25% yield) has the composition of a 1:1 adduct which has lost one molecule of hydrogen cyanide. It is unlikely that this product arises from addition of benzylideneaniline to a species derived from predissociation of the carbon–carbon bond of the epoxide. This mechanism has been shown to operate in addition of TCNEO to olefins,[8] but at an appreciable rate only above 100°. In this case, nucleophilic attack on carbon followed by ring closure and loss of HCN could only occur with opening of the carbon–carbon bond of the epoxide ring which would give **18**. Opening of the carbon–oxygen bond would give rise to a five-membered ring that could not eliminate HCN. We cannot, however, rule out a structure (**18a**) in which the ring has opened unsymmetrically by nucleophilic attack on oxygen. However, the longer wavelength absorption of the product (λ_{max} 332 mμ) favors structure **18** which has the ring oxygen in conjugation with the double bond and nitrile group. The alternative structure should have an ultraviolet spectrum similar to that of *cis*-cinnamonitrile (λ_{max} 273 mμ) or 2-phenyl-1-cyclohexenecarbonitrile (λ_{max} 251 mμ).[11] Neither of these has a longer wavelength absorption. The second product, found in only 8% yield, is 1,2,3,4-tetraphenyl-5,5-dicyanoimidazolidine (**19**). The latter assignment is based on analysis, spectral evidence, and acid hydrolysis to aniline and benzaldehyde. A reasonable mechanism for the formation of the minor product **19** is *via* a 1,3-dipolar intermediate **20** which can add another molecule of the Schiff base. Evidence for this intermediate is furnished by carrying out the reaction of TCNEO and benzylideneaniline in the presence of dimethyl acetylenedicarboxylate. The *only* product isolated (in 62% yield) is a colorless, crystalline compound to which structure **21** is assigned on the basis of analytical and spectral data. The product loses hydrogen cyanide readily on heating to form the pyrrole **22** in 72% yield.



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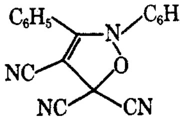
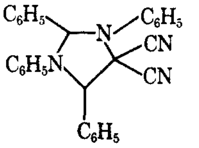


18a



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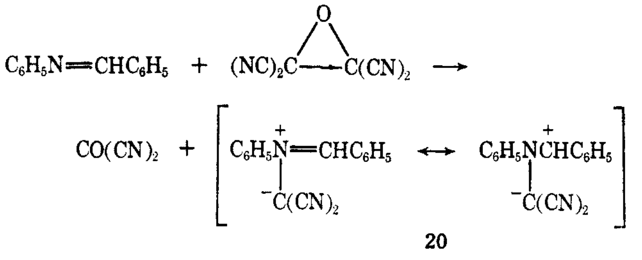

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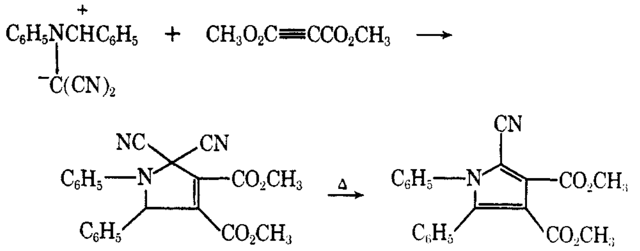
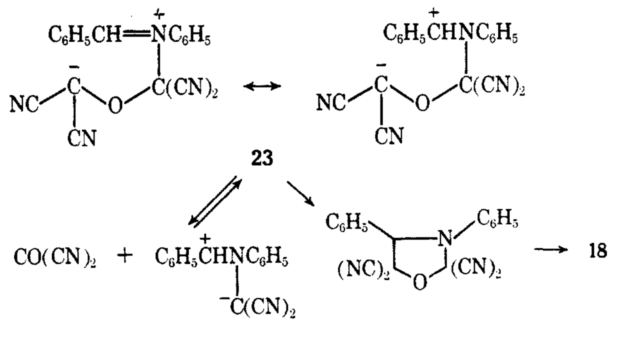


21 **22**

This experiment provides strong evidence for the dipole **20** as an intermediate in the reaction, but it is of interest that the adduct **18** is *not* formed in the presence of the added acetylenic dipolarophile. The fragmentation reaction which leads to the intermediate 1,3 dipole may be reversible (Scheme III). When the acetylenic ester is present, the dipolar addition reaction is faster than ring closure. In the absence of the acetylene, ring closure competes with the addition of benzylideneaniline, a poorer dipolarophile. Another possible explanation of the results could involve addition of dimethyl acetylenedicarboxylate to **23** followed by elimination of carbonyl cyanide to give **21**.

SCHEME III



A somewhat related reaction is that of TCNEO and benzophenone azine. The reaction occurs smoothly in boiling benzene. Nitrogen is evolved nearly quantitatively (91%), and two crystalline products are formed.

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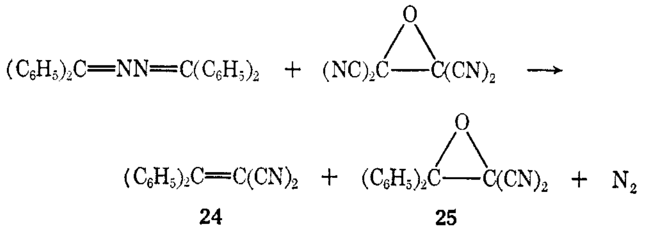
(8) W. J. Linn, *J. Am. Chem. Soc.*, **87**, 3665 (1965).

(9) A referee suggested the hydrolysis experiment.

(10) B. A. Arbuzov, Yu. Yu. Samitov, and L. K. Yieldasheva, *Izv. Akad. Nauk, SSSR Ser. Fiz.*, **27**, 89 (1963) (for the English translation, see *Bull. Acad. Sci. USSR, Phys. Ser.*, **27**, 95 (1963)).

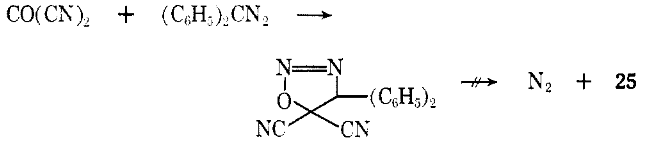
(11) W. E. Parham, W. N. Moulton, and A. Zuckerbraun, *J. Org. Chem.*, **21**, 72 (1956).

One was identified as 1,1-dicyano-2,2-diphenylethylene (**24**) by an independent synthesis from benzophenone and malononitrile. The other product was believed to be 1,1-diphenyl-2,2-dicyanoethylene oxide (**25**), but attempts to synthesize it by direct oxidation of the olefin were unsuccessful. This was not unexpected because alkaline epoxidation of 1,1-dicyanoethylenes invariably gives the epoxyamide.[12]



24 **25**

This same product is obtained from reaction of diphenyldiazomethane and TCNEO. One might suspect that **25** was formed from diphenyldiazomethane and carbonyl cyanide in this latter reaction. However, it has been shown in this laboratory that carbonyl cyanide adds to diphenyldiazomethane giving **26** which is thermally stable and does not decompose to **25** and nitrogen on heating.[13] The structure of the product **25** was established by elemental analysis and spectra combined



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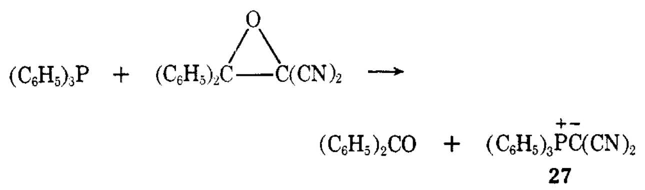
with the observation that reaction with triphenylphosphine gives benzophenone and triphenylphosphonium dicyanomethylide (**27**).



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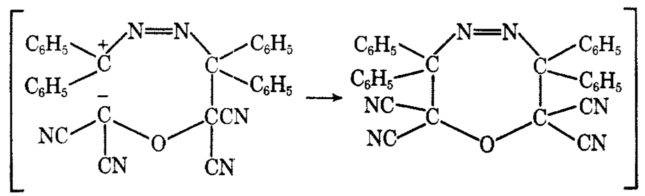
The mechanism of formation of **25** in the reaction of diphenyldiazomethane and TCNEO is unknown. Possibly, the active reactant is benzophenone azine (the decomposition product of diphenyldiazomethane), although the olefin **24** was not actually identified as the other reaction product. No evidence is at hand that bears on the mechanism of the azine reaction, but the seven-membered ring **28** is a possible method of combining the fragments in the proper order to give the observed products.



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Experimental Section

Reaction of TCNEO and Aniline.—A solution of 1.86 g (0.02 mole) of freshly distilled aniline in 15 ml of ether was cooled in an ice bath, and 1.44 g (0.01 mole) of TCNEO was added all at once. The reaction mixture was stirred for 1.5 hr, and the resulting yellow solution was evaporated to leave 2.78 g of light orange solid. This product was dissolved in hot benzene and the solution was cooled. The precipitated solid was collected by filtration. The light-colored product, mp 123–126°, weighed 0.92 g (63%). The reported melting point of N-(cyanoformyl)-aniline is 123–126°.[2] The infrared spectrum of the product was identical with that of N-(cyanoformyl)aniline prepared by the reaction of carbonyl cyanide and aniline. Attempts to purify the product by repeated recrystallization led to a gradual lowering of the melting point. Malachowski[2] reports neither further purification nor analysis of N-(cyanoformyl)aniline, but does report reaction with ammonia to give phenylurea. Our product also reacts with ammonia to give phenylurea, identical with an authentic sample.

In another experiment a solution of 1.31 g (0.0141 mole) of aniline in 5 ml of tetrahydrofuran was added, all at once, to a cold (−30°) solution of 2.03 g (0.0141 mole) of TCNEO in 15 ml of tetrahydrofuran. The mixture was stirred at −20° for 5 min and at room temperature for 3 hr. The solvent was removed at room temperature leaving 3.88 g of a pale yellow semisolid. Immediate chromatography of 1.80 g of this product over Florisil gave 0.12 g of yellow crystals (eluted with benzene-hexane, 3:2) having an infrared spectrum identical with that of carbonyl cyanide anil (see below). The yield was 12%. When this reaction was carried out in the presence of yellow mercuric oxide under otherwise identical conditions, the yield of carbonyl cyanide anil was 15%.

Reaction of TCNEO with Benzaldehyde Phenylhydrazone.—To a boiling solution of 3.60 g (0.025 mole) of TCNEO in 50 ml of benzene was added, over 1.5 hr, a solution of 3.90 g (0.025 mole) of benzaldehyde phenylhydrazone in 50 ml of benzene and 20 ml of tetrahydrofuran. The reaction mixture was then heated at reflux for 1 hr. The cooled mixture was concentrated (rotary evaporator) leaving a dark semisolid. Chromatography on Florisil (elution with benzene-methylene chloride, 3:1) gave 1.01 g (52% crude yield) of a partially crystalline yellow compound and 1.97 g (63% crude yield) of a pale yellow solid. The former, on crystallization from cyclohexane, gave bright yellow plates of carbonyl cyanide anil: mp 63–64° (sealed tube); ultraviolet spectrum (in cyclohexane), λ_{max} 367 mμ (ϵ 4900), 281 (5300), and 235 sh (5600); infrared spectrum ($CHCl_3$), 2225 (m), 1550 (s), 1160 cm^{-1} (vs).

Anal. Calcd for $C_9H_5N_3$: C, 69.67; H, 3.27; N, 27.08; mol wt, 155. Found: C, 69.70; H, 3.43; N, 27.28; mol wt, 160 (boiling point elevation in benzene).

The second product was recrystallized from benzene-cyclohexane to give pale yellow needles of 1-(cyanoformyl)-1-phenyl-2-benzylidenehydrazine: mp 154–154.5°; ultraviolet spectrum (in cyclohexane), λ_{max} 289 mμ (ϵ 21,500); infrared spectrum (KBr), 2240 (w), 1690 cm^{-1} (s).

Anal. Calcd for $C_{15}H_{11}N_3O$: C, 72.27; H, 4.95. Found: C, 72.27; H, 4.34.

The reaction was repeated by heating 1.57 g of TCNEO and 2.00 g of benzaldehyde phenylhydrazone in 8 ml of benzene under reflux for 30 min. The flask was then connected to a cold trap, and the volatile products were distilled at 0.4-mm pressure, first at room temperature and then at elevated temperature. The distillate was transferred to a volumetric flask and diluted to 10.0 ml with benzene. Gas chromatographic analysis of this solution was carried out using a 30% silicone oil coumn at 150°. It was shown to contain about 130 mg of a mixture of benzonitrile and benzaldehyde (ratio 4.9:1). A small amount of this mixture was collected and the components were identified by mass spectroscopy.

Carbonyl Cyanide Anil from Malononitrile and Nitrosobenzene.—A mixture of 2.3 g of potassium cyanide, 16 ml of *t*-butyl alcohol, 4 ml of water, 20 ml of ether, and 20 ml of benzene was cooled to −5°, and a solution of 3.1 g (0.047 mole) of malononitrile and 5.0 g (0.047 mole) of nitrosobenzene in 15 ml of benzene and 15 ml of ether was added. The temperature was kept below −5° during the addition, which took 15 min. Stirring at −5° was then continued for 5 min, and a 15% aqueous sodium chloride solution (100 ml) was added. The layers were separated, and the aqueous phase was extracted with 15 ml of

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[12] G. B. Payne, *J. Org. Chem.*, **26**, 662 (1961).

[13] We are indebted to Dr. E. L. Martin for this experiment.

ether followed by 15 ml of benzene. The combined organic phases were washed with water, 10% potassium carbonate solution, and concentrated sodium chloride solution and dried over $MgSO_4$. Removal of the solvents left 4.84 g of a dark liquid which was chromatographed on 130 g of Florisil. The first 600 ml of *n*-hexane–benzene (4:1) eluted 1.79 g of carbonyl cyanide anil containing 3% nitrosobenzene as shown by gas chromatography on a 30% silicone grease column at 155°. An additional 0.41 g of an 80:20 mixture of the anil and nitrosobenzene was eluted with the next 300 ml of the same solvent mixture. The total yield of the anil in both fractions was 2.07 g (29%). Crystallization of the first fraction from cyclohexane gave 1.29 g of the pure anil, mp 63–64°. Another 0.44 g was obtained from the mother liquor and second fraction. The total weight of purified product was 1.73 g (24%). The product was identical with the carbonyl cyanide anil obtained from aniline and TCNEO and from benzaldehyde phenylhydrazone and TCNEO as shown by comparison of the infrared spectra and by mixture melting point determinations.

1-Cyanoformyl-1-phenyl-2-benzylidenehydrazine from Benzaldehyde Phenylhydrazone and Carbonyl Cyanide.—To a vigorously stirred solution of 8.50 g (0.043 mole) of benzaldehyde phenylhydrazone in 25 ml of glacial acetic acid, 25 ml of benzene, and 40 ml of tetrahydrofuran was added, over 15 min, a solution of 3.68 g (0.046 mole) of carbonyl cyanide in 20 ml of benzene. The temperature was kept below −3° during the addition. The yellow solution was then stirred at 0° for 20 min; the solvent was removed and the residue was dried under high vacuum over solid potassium hydroxide. Crystallization from 250 ml of ethanol gave 8.93 g (83%) of 1-(cyanoformyl)-1-phenyl-2-benzylidenehydrazine, mp 153–154°, identical with the product obtained from TCNEO and benzaldehyde phenylhydrazone (see above).

Anal. Calcd for $C_{15}H_{11}N_3O$: C, 72.27; H, 4.45; N, 16.86; mol wt, 249. Found: C, 72.33; H, 4.49; N, 16.71; mol wt, 267.

Bis(*p*-dimethylaminophenyl)dicyanomethane from TCNEO and Dimethylaniline.—A solution of 2.53 g (0.021 mole) of dimethylaniline in 5 ml of glacial acetic acid was cooled in an ice bath. To this solution 1.00 g (0.007 mole) of TCNEO was added in small portions. The reaction mixture first turned light green, then a very dark green, and finally reddish brown. After a short time a yellow solid began to precipitate. After 1 hr this yellow solid was collected by filtration and dried to give 0.45 g of crude product. In a similar preparation which had been allowed to stand for only 10 min, the crude product weighed 0.23 g. These two solids were combined, boiled with ethanol, and filtered. The insoluble portion, 0.37 g, was recrystallized from *n*-butyl alcohol to give light yellow crystals of bis(*p*-dimethylaminophenyl)dicyanomethane, mp 195–196°. This material was identified by comparison of its infrared spectrum with that of an authentic sample.[8]

Bis(*p*-dimethylaminophenyl)dicyanomethane from Carbonyl Cyanide and Dimethylaniline.—The addition of N,N-dimethylaniline to a solution of carbonyl cyanide in acetic acid results in a strongly exothermic reaction and the production of deep yellow solutions from which greenish yellow crystals separate. Recrystallization of the crystals does not remove the color but passage of a methylene chloride solution of the compound over neutral alumina removes a small amount of an intensely yellow impurity. Colorless crystals, mp 192–193°, can be obtained from the colorless solution obtained by chromatography.[14]

Anal. Calcd for $C_{19}H_{20}N_4$: C, 74.97; H, 6.62; N, 18.41. Found: C, 74.93; H, 6.71; N, 18.35.

Tetracyanoethylene Glycol Diacetate.—To a solution of 2.88 g (0.02 mole) of TCNEO and 10 ml of acetic anhydride was added two small drops of pyridine in 1.0 ml of glacial acetic acid. A precipitate began to form after approximately 15 min. The reaction mixture was stirred overnight at room temperature and then filtered. The solid was washed with water and air dried to give 3.52 g of crude product which was recrystallized from ethylene dichloride to give 3.24 g (66%) of colorless crystals of tetracyanoethylene glycol diacetate, mp 194.5–195°.

Anal. Calcd for $C_{10}H_6N_4O_4$: C, 48.78; H, 2.45; N, 22.76. Found: 48.94; H, 2.57; N, 23.15.

The proton magnetic resonance spectrum in deuterioacetone shows only a single peak at τ 7.38.

2-Chlorotetracyanoethyl Acetate.—A suspension of 2.88 g (0.02 mole) of TCNEO in 15 ml of acetyl chloride was cooled in an ice bath and stirred. One drop of pyridine was added. After approximately 5 min all the TCNEO had gone into solution. The pale yellow reaction mixture was allowed to stand in the ice bath for 1 hr and then poured onto cracked ice to hydrolyze the excess acid chloride. The solid was collected by filtration, air dried, and recrystallized from carbon tetrachloride to give 2.03 g of tan needles, mp 85.5–90°. Repeated recrystallization gave an analytical sample, mp 90–91°.

Anal. Calcd for $C_8H_3ClN_4O_2$: C, 43.16; H, 1.81; Cl, 15.93. Found: C, 43.48; H, 1.58; Cl, 15.68.

The proton resonance spectrum in CD_3Cl shows only a single peak at τ 7.54.

S-Thiouroniodicyanomethanide (8).—A solution of 5.79 g (0.0402 mole) of TCNEO in 50 ml of ethanol was cooled to −10°; thiourea (3.05 g, 0.0402 mole) was added, with stirring, the temperature being kept below −5°. The resulting faintly yellow solution was concentrated to dryness (rotary evaporator) and the residue was dried under high vacuum. The yield of crude S-thiouroniodicyanomethanide was 5.51 g (98%). The infrared spectrum was identical with that of an authentic sample.[6]

2-Amino-1,1-dicyanopropene (9).—To a cold stirred solution of 1.91 g (0.0133 mole) of TCNEO in 15 ml of ethanol was added, over a period of 20 min, 1.00 g (0.0133 mole) of thioacetamide. The temperature was kept below 0°; after *ca.* 10 min, a yellow precipitate formed. The mixture was stirred at 0° for another 10 min and then filtered to give 0.83 g of a yellow solid, and from the filtrate, 0.88 g of an ill-smelling semisolid. Both products had similar infrared spectra. A small sample of the solid was heated in ethanol and the solution was decanted from the rubberlike insoluble material (presumably sulfur). On cooling, 2-amino-1,1-dicyanopropene deposited as colorless needles. Its infrared spectrum was identical with an authentic sample prepared by Middleton.[6]

4-Amino-5-cyano-3-phenyl-2-phenylimino-2,3-dihydrothiazole (10).—To a stirred solution of 3.00 g (0.0208 mole) of TCNEO in 50 ml of ethanol was added, over 20 min, 4.75 g (0.0208 mole) of finely powdered N,N′-diphenylthiourea. The temperature was kept below 30° during the addition. The mixture was stirred at room temperature for 1 hr, and the yellow precipitate was collected by filtration. The yield of 4-amino-5-cyano-3-phenyl-2-phenylimino-2,3-dihydrothiazole was 4.57 g (75%). Its infrared spectrum was identical with that of a sample prepared by Middleton.[6]

Reaction of TCNEO with Thiobenzophenone in Benzene at 80°.—The reaction was carried out in a 100-ml three-necked flask fitted with pressure-equalizing dropping funnel and a 15-cm Vigreux column set up for distillation. To a boiling solution of 3.50 g (0.0243 mole) of TCNEO in 50 ml of benzene was added with stirring, over 10 min, a solution of 4.30 g (0.0218 mole) of thiobenzophenone in 50 ml of benzene. Nitrogen was passed through the reaction mixture, and solvent was distilled continuously during and for about 15 min after the addition. A total of 60 ml of a yellow distillate was collected. The reaction mixture was concentrated to dryness (rotary evaporator), the distillate being caught in a solid carbon dioxide–acetone trap. The two distillates were combined and diluted to 100 ml with benzene. Analysis by gas chromatography (30% Triton X-305 on 60–80-mesh acid-washed Firebrick at 52°) showed this solution to contain *ca.* 0.2 g (10%) of carbonyl cyanide (identification by retention time only). The brown semisolid residue, on chromatography over Florisil, gave 3.40 g (68% yield) of 1,1-dicyano-2,2-diphenylethylene (elution with benzene), the infrared spectrum of which was identical with that of an authentic sample (see below). A small amount (0.21 g) of 3,3,5,5-tetraphenyl-1,2,4-trithiolane was also obtained (see below).

Reaction of TCNEO with Thiobenzophenone in Acetonitrile at Room Temperature.—A solution of 2.95 g (0.0149 mole) of thiobenzophenone and 2.50 g (0.0173 mole) of TCNEO in 30 ml of purified acetonitrile was stirred at room temperature under nitrogen for 24 hr. The yellow precipitate which had formed in the dark green solution was collected by filtration. The yield of crude 3,3,5,5-tetraphenyl-1,2,4-trithiolane so obtained was 1.08 g (51%). It was purified by chromatography over Florisil (elution with benzene–methylene chloride, 7:3) and crystallization from methylene chloride–petroleum ether (30–60°) to give colorless crystals, mp 122–124° dec, lit.[7] mp 124°.

Anal. Calcd for $C_{26}H_{20}S_3$: C, 72.85; H, 4.71; S, 22.44. Found: C, 72.72; H, 4.62; S, 22.45.

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[14] We are indebted to Dr. E. L. Martin for this experiment. Malachowski[8] reports that this product melts at 192–193°.

The filtrate was concentrated to dryness (rotary evaporator) and part of the residue was chromatographed over Florisil, yielding 165 mg (extrapolated yield: 48%) of 1,1-dicyano-2,2-diphenylethylene, identified by its infrared spectrum (see below). TCNEO was recovered in 54% yield by sublimation of the other part of the residue.

A similar run, using ethanol instead of acetonitrile as the solvent, gave 1,1-dicyano-2,2-diphenylethylene in 47% yield and 3,3,5,5-tetraphenyl-1,2,4-trithiolane in 53% yield; the latter had to be isolated by chromatography; it did not precipitate from the ethanol solution.

1,1-Dicyano-2,2-diphenylethylene.—Dry ammonia was passed into a solution of 54 g of benzophenone (0.31 mole) and 20 g of malononitrile (0.30 mole) in 180 ml of anhydrous ethanol for 1 hr. The mixture was left standing at room temperature for 4 days, but no 1,1-dicyano-2,2-diphenylethylene crystallized as claimed by previous workers.[15] The solution was poured into 400 ml of water and the mixture was extracted with three 150-ml portions of benzene; the combined extracts were washed with 10% potassium hydroxide solution, water, and concentrated sodium chloride solution, and dried over magnesium sulfate. Removal of the solvent left 62 g of a pale yellow liquid to which 50 ml of ethanol was added. After standing at room temperature for 20 hr, the colorless crystals of 1,1-dicyano-2,2-diphenylethylene, mp 140–141.5° (lit.[15] mp 136°), were collected by filtration. A further crop was obtained by adding 50 ml of petroleum ether (30–60°) to the mother liquor and keeping the mixture in a cold room for 20 hr; total yield: 8.91 g (12%). An analytical sample, mp 141–142°, was obtained by two crystallizations from ethanol; ultraviolet spectrum (in cyclohexane), λ_{max} 315 mμ (ϵ 15,800), 275 sh (10,500), and 228 (10,400).

Anal. Calcd for $C_{16}H_{10}N_2$: C, 83.46; H, 4.38; N, 12.17. Found: C, 83.97; H, 4.46; N, 12.09.

1,1-Dicyano-2,2-bis(4-dimethylaminophenyl)ethylene (15).—A mixture of 10.0 g (0.035 mole) of 4,4′-bis(dimethylamino)-thiobenzophenone, 10.0 g of malononitrile, 5.0 g (0.036 mole) of anhydrous potassium carbonate, and 100 ml of *n*-propyl alcohol was stirred under reflux for 1 hr. The reaction mixture was cooled with ice, 100 ml of water was added, and the precipitate was collected by filtration, washed with cold water and methanol, and dried. The 1,1-dicyano-2,2-bis(4-dimethylaminophenyl)ethylene so obtained (10.80 g, 97%) had mp 254–257°; it was 97% pure as indicated by its ultraviolet spectrum. Recrystallization from glacial acetic acid (40 ml/g) gave purple crystals of the pure product, mp 259–260°, in 82% yield (overall); ultraviolet spectrum (in acetonitrile), λ_{max} 430 mμ (ϵ 48,550), 320 (4000), 310 (3700), 265 (22,900).

Anal. Calcd for $C_{20}H_{20}H_4$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.85; H, 6.42; N, 17.68.

Reaction of TCNEO with 4,4′-Bis(dimethylamino)thiobenzophenone.—A solution of 0.92 g (0.0064 mole) of TCNEO in 5 ml of tetrahydrofuran and 10 ml of ethanol was cooled to around −50°, and a solution of 1.53 g (0.0054 mole) of 4,4′-bis(dimethylamino)thiobenzophenone in 30 ml of chloroform was added with vigorous stirring over 25 min. The red color of the thioketone changed to green immediately. The mixture was allowed to warm to room temperature (1 hr); it was then stirred at room temperature for 30 min. The solvents were removed leaving 1.95 g of a brown semisolid. A small amount (46 mg) of this solid was dissolved in 50 ml of acetonitrile; the insoluble portion (3.7 mg of a rubber-like material) contained 88.8% sulfur as shown by microanalysis; total yield of elemental sulfur: 140 mg (81%). The acetonitrile solution had an ultraviolet spectrum identical with that of 1,1-dicyano-2,2-bis(4-dimethylaminophenyl)ethylene: the *k* value of the 430-mμ band was 120, indicating that the product contained 1.52 g (89% yield) of the ethylene derivative. Recrystallization of 1.31 g of the crude product from 40 ml of glacial acetic acid gave 0.90 g (79%) of 1,1-dicyano-2,2-bis(4-dimethylaminophenyl)ethylene as purple crystals, mp 256–258°. The infrared spectrum was identical with that of an authentic sample prepared as described in the preceding experiment.

4,4,5,5-Tetracyano-2-phenyl-1,3-dioxolane (17).—A reaction vessel containing 3.00 g (0.0208 mole) of TCNEO in 25 ml of freshly distilled benzaldehyde was alternately evacuated and flushed with nitrogen. It was heated at 100–110° for 18 hr. Most of the benzaldehyde was evaporated at reduced pressure, and the residual solid was dried on a porous plate. The dried residue was sublimed at 80–90° (0.1 mm) until sublimation ceased. This first fraction was mainly recovered TCNEO as indicated by the infrared spectrum. However, some of the desired adduct was present. The sublimation was continued at 110°. The second fraction contained essentially no TCNEO. This product was recrystallized once from 2-propanol to give 0.62 g of brown needles which were sublimed at 190° (0.1 mm) to give 0.53 g (10%) of colorless crystals, mp 140–142°. Further recrystallization from 2-propanol raised the melting point to 141–142°.

Anal. Calcd for $C_{13}H_6N_4O_2$: C, 62.40; H, 2.42; N, 22.39; mol wt, 250. Found: C, 62.15; H, 2.48; N, 22.11; mol wt, 238–240.

Acid Hydrolysis of Benzaldehyde–TCNEO Adduct.—A suspension of 0.101 g of the 1:1 adduct of TCNEO and benzaldehyde in 5 ml of 5% hydrochloric acid was warmed overnight on a steam bath in a nitrogen atmosphere. The solid disappeared and was replaced by small drops of oil immiscible in the aqueous phase. The mixture smelled strongly of benzaldehyde. The reaction mixture was extracted with methylene chloride and the extract was dried with Drierite. Gas chromatography of the extract on a 6 ft × 0.25 in. column of XE-60 on Gas Chrom RA at 145° and a helium flow of 100 ml/min showed, besides the methylene chloride peak, a component eluting at 4.4 min. An authentic sample of benzaldehyde in methylene chloride also eluted at 4.4 min. Removal of the solvent with a rotary evaporator left a small residue which was dissolved in 6 ml of 50% aqueous ethanol. The solution was heated to boiling for 0.5 min after the addition of two drops of phenylhydrazine. Cooling the solution caused the precipitation of pale yellow needles which weighed 0.050 g (63%) and melted at 153–155°. Recrystallization from 50% aqueous ethanol raised the melting point to 155–156.5°. An authentic sample of benzaldehyde phenylhydrazone had the same melting point and the infrared spectra of the two samples were identical.

Reaction of TCNEO and Benzylideneaniline.—The reaction was carried out in a 500-ml, three-necked flask fitted with gas-inlet tube, two 125-ml dropping funnels, and a 20-cm Vigreux column connected to a 1000-ml receiving flask, the contents of which (45 g of dimethylaniline in 100 ml of glacial acetic acid) was cooled with ice and stirred. To 500 ml of boiling benzene in the three-necked flask were added separately and with stirring, solutions of 25.5 g (0.18 mole) of TCNEO in 75 ml of tetrahydrofuran and of 46.5 g (0.26 mole) of benzylideneaniline (Eastman White Label, mp 53–54°) in 200 ml of benzene. Nitrogen was passed through the reaction mixture, and solvent was distilled out continuously. Addition of the two solutions was complete after 50 min. Benzene (100 ml) was added and solvent distillation was continued for 25 min, when the volume of the dark green reaction mixture was *ca.* 200 ml. It was cooled with ice and the yellow precipitate was collected by filtration. It weighed 13.3 g (25%). Crystallization from 85 ml of acetonitrile gave 9.05 g of yellow needles of 2,2,4-tricyano-1,5-diphenyl-Δ^4-oxazoline (18), mp 232.5–234° (sealed tube). Further recrystallization did not increase the melting point. The infrared spectrum (KBr) showed bands at 2230, 1685, and 955 cm^{-1}; ultraviolet spectrum (in acetonitrile), λ_{max} 252 mμ (ϵ 21,600) and 332 (6500); nmr spectrum, two peaks (each split at least into a doublet) at τ 2.29 and 2.50 (ratio of areas 1:1).

Anal. Calcd for $C_{18}H_{10}N_4O$: C, 72.47; H, 3.38; N, 18.78; mol wt, 298. Found: C, 72.62; H, 3.30; N, 18.79; mol wt, 319 (ebullioscopically in benzene).

The mother liquor was concentrated, using a rotary evaporator, and to the residue (56.78 g of a black oil) was added, with stirring with a glass rod, 200 ml of boiling ethanol. The cooled mixture was filtered to give 21.16 g of a light tan solid, which was chromatographed on 300 g of Florisil. A pale yellow solid (8.47 g) was eluted with benzene. It was crystallized from acetonitrile, giving 6.48 g (8.5% yield) of 1,2,3,4-tetraphenyl-5,5-imidazolidinedicarbonitrile (19) as almost colorless plates, mp 209–211° (sealed tube). The analytical sample melted at 210–211°; ultraviolet spectrum (in acetonitrile), λ_{max} 237 mμ (ϵ 19,300) and 287 sh (1900); infrared spectrum, weak CN band at 2240 cm^{-1} (in KBr); nmr spectrum (in acetonitrile), singlets at τ 3.92 and 3.34 (area $\sim$1 each) and a very complex spectrum from 2.4 to 3.2 (area $\sim$20).

Anal. Calcd for $C_{29}H_{22}N_4$: C, 81.66; H, 5.20; N, 13.14; mol wt, 426. Found: C, 81.89; H, 5.29; N, 13.17; mol wt, 451 (ebullioscopically in benzene).

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(15) R. Schenck and H. Finken, *Ann. Chem.*, **462**, 27 (1928).

The contents of the receiving flask (containing the reaction product of dimethylaniline with carbonyl cyanide) were concentrated to dryness using a rotary evaporator. The residual yellow crystals were heated with 30 ml of ethanol and collected by filtration to give 5.73 g (11%) of bis(*p*-dimethylaminophenyl)-dicyanomethane identified by comparison of its infrared spectrum with that of an authentic sample (see above).

Reaction of TCNEO with Benzylideneaniline and Dimethyl Acetylenedicarboxylate.—The apparatus used was a 100-ml, three-necked flask fitted with magnetic stirrer, gas-inlet tube, 100-ml dropping funnel, and a 15-cm glass spiral column set for distillation. To a stirred boiling solution of 3.24 g (0.0225 mole) of TCNEO and 6.40 g (0.045 mole) of dimethyl acetylenedicarboxylate in 50 ml of benzene was added, over 70 min, a solution of 4.10 g (0.0225 mole) of benzylideneaniline in 50 ml of benzene. Nitrogen was passed through the reaction mixture, and solvent was distilled into a receiving flask (containing 8 g of dimethylaniline in 15 ml of glacial acetic acid) at about the same rate as benzylideneaniline solution was added. Thirty milliliters of benzene was then added, and distillation of solvent was continued for 30 min. The reaction mixture, on cooling with ice, deposited 4.67 g of light tan crystals of dimethyl 2,2-dicyano-1,5-diphenyl-Δ^3-3,4-pyrrolinedicarboxylate (**21**), mp 174–176° dec. From the filtrate, on evaporation to dryness and chromatography on Florisil, an additional 0.73 g of the diester was obtained. The analytical sample, prepared by two recrystallizations from benzene, melted at 175° dec; ultraviolet spectrum (in acetonitrile), $\lambda_{\max}$ 230 mμ (ϵ 16,000), shoulders at 265 (2800) and 272 (2500); infrared spectrum (KBr), 2240 (w), 1750, 1730 (s) cm^{-1}.

Anal. Calcd for $C_{22}H_{17}N_3O_4$: C, 68.21; H, 4.43; N, 10.85; mol wt, 387. Found: C, 68.48; H, 4.56; N, 10.71; mol wt, 429.

The yield of bis(*p*-dimethylaminophenyl)dicyanomethane, isolated from the contents of the receiving flask as described for the reaction of TCNEO with benzylideneaniline, was 1.60 g (23%).

No **19** was obtained in the chromatography, nor was any **18** isolated by sublimation of a small sample of the evaporated filtrate (before chromatography) at 180° and 0.3 mm.

Thermal Decomposition of 21.—A sample of 0.61 g of the pyrroline **21** in a 10-ml flask was evacuated to 120 Torr and slowly heated in an oil bath. Smooth evolution of hydrogen cyanide started at 171° (bath temperature). After 20 min a temperature of 185° had been reached and no gas was being evolved. On cooling, 0.53 g of a colorless solid was obtained. This was recrystallized from 4 ml of benzene–cyclohexane (3:1) to give 0.40 g (71%) of dimethyl 1,2-diphenyl-5-cyano-3,4-pyrroledicarboxylate (**22**): mp 151–152°; ultraviolet spectrum (in acetonitrile); $\lambda_{\max}$ 285 mμ (ϵ 10,000), 235 (22,000); infrared spectrum (KBr), 2240, 1740, and 1725 cm^{-1}.

Anal. Calcd for $C_{21}H_{16}N_2O_4$: C, 69.99; H, 4.48; N, 7.77; mol wt, 360. Found: C, 70.56; H, 4.43; N, 7.86; mol wt (ebullioscopic in benzene), 370, 371.

Reaction of TCNEO with Diphenyldiazomethane.—To a stirred boiling solution of 1.35 g (0.0094 mole) of TCNEO in 40 ml of benzene was added, over 30 min, a solution of 1.81 g (0.0093 mole) of diphenyldiazomethane in 30 ml of benzene. The mixture was then heated under reflux for 10 min. A total of 200 ml (88%) of nitrogen was evolved. In a second experiment, solvent was distilled continuously during the addition; no carbonyl cyanide was detected in the distillate. The solvent was removed at reduced pressure to give 3.19 g of a dark semisolid, part of which (1.66 g) was chromatographed over Florisil (45 g). In the first 200 ml of benzene, 0.40 g (17%) of 1,1-dicyano-2,2-diphenylethylene oxide was eluted. Two recrystallizations from benzene gave an analytical sample: mp 166–167°; ultraviolet spectrum (in cyclohexane), $\lambda_{\max}$ 269 mμ (ϵ 685), 262 (850), 258 (750), 256 (755), 226 (11,900); infrared spectrum (KBr), 2245, 1590, 1500, 1240, 1230, 1225, 910, and 885 cm^{-1}.

Anal. Calcd for $C_{16}H_{10}N_2O$: C, 78.03; H, 4.10; N, 11.38; mol wt, 246. Found: C, 78.13; H, 4.12; N, 11.28; mol wt, 261.

An unstable yellow oil was obtained by further elution with benzene and benzene–methylene chloride.

Reaction of 1,1-Dicyano-2,2-diphenylethylene Oxide (25) with Triphenylphosphine.—A mixture of 0.22 g (0.00093 mole) of 1,1-dicyano-2,2-diphenylethylene oxide, 0.44 g (0.0015 mole) of triphenylphosphine, and 3 ml of 1,2-dichloroethane was heated under reflux for 1 hr. Removal of the solvent (rotary evaporator) gave a dark oil, which was dissolved in 2 ml of hot benzene. Addition of 2 ml of hot cyclohexane and cooling gave 0.20 g of triphenylphosphonium dicyanomethylide.[16] The mother liquor was concentrated to dryness and the residue was chromatographed over Florisil. Triphenylphosphine (0.19 g) was eluted with the first 36 ml of benzene–*n*-hexane (1:1). Another 60 ml of the same solvent mixture eluted 0.15 g (92% yield) of benzophenone, identified by its infrared spectrum. A small quantity (*ca.* 0.03 g) of triphenylphosphonium dicyanomethylide (**27**) was eluted with methylene chloride–tetrahydrofuran (4:1). The total yield of **27** was 0.23 g (79%).

Reaction of TCNEO with Benzophenone Azine.—The reaction was carried out in a 100-ml three-necked flask fitted with a pressure-equalizing dropping funnel and a reflux condenser, the top of which was attached, through a drying tube, to a 100-ml gas buret. To a boiling solution of 1.68 g (0.0117 mole) of TCNEO in 15 ml of benzene was added, over 8 min, a solution of 1.40 g (0.00389 mole) of benzophenone azine in 20 ml of benzene, and the mixture was then heated under reflux until gas evolution ceased (3 hr). A total of 86 ml (at 24°, 91% of the theoretical amount) of nitrogen was evolved. The solvent was removed (rotary evaporator), leaving 2.99 g of a tan solid. Chromatography over Florisil gave 0.73 g (76%) of 1,1-dicyano-2,2-diphenylethylene oxide (eluted with benzene–hexane, 2:3) and 0.79 g (88%) of 1,1-dicyano-2,2-diphenylethylene (eluted with benzene). The two products were identified by comparison of their infrared spectra with those of samples prepared previously (see above).

Registry No.—TCNEO, 3189-43-3; **2**, 19769-98-3; **3**, 19769-99-4; **6**, 19770-00-4; **7**, 19770-01-5; **14**, 1226-46-6; **15**, 19770-02-6; **17**, 19770-03-7; **18**, 19770-04-8; **19**, 19769-85-8; **21**, 19769-86-9; **22**, 19769-87-0; **25**, 19769-88-1; aniline, 62-53-3; benzaldehyde phenylhydrazone, 588-64-7; acetic anhydride, 108-24-7; acetyl chloride, 75-36-5; thiobenzophenone, 1,450-31-3; benzylideneaniline, 538-51-2; diphenyldiazomethane, 883-40-9; benzophenone azine, 983-79-9.

Acknowledgment.—We are indebted to Dr. R. E. Benson for many helpful discussions in connection with this work.

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[16] L. Hoerner and H. Oediger, *Chem., Ber.*, **91**, 437 (1958).