of triethylamine–phenylborane, and 24.9 g. (0.15 mole) of N,N′-diallylpiperazine was slowly distilled at atmospheric pressure. After the flask temperature reached 120°, the remaining toluene was removed under reduced pressure. The residual white solid was dissolved in benzene and precipitated by pouring the solution into a large volume of pentane. The mixture was filtered and dried, yielding 28.8 g. (75%) of a stable white solid which melted completely over the temperature range of 208–230°.

Anal. Calcd. for $C_{16}H_{25}BN_2$: C, 75.01; H, 9.83; B, 4.22; N, 10.94. Found: C, 75.11; H, 9.77; B, 4.27; N, 10.70; mol. wt., 660 (vapor pressure osmometer).

Treatment of 1-*sec*-Butyl-5-phenyl-1-aza-5-borabicyclo[3.3.0]-octane under Reaction Conditions.—A solution of 100 ml. of toluene and 2.3 g. of 1-*sec*-butyl-5-phenyl-1-aza-5-borabicyclo-[3.3.0]octane was refluxed for 36 hr. The toluene was distilled at atmospheric pressure until the flask temperature reached 120°. The remaining toluene was removed under reduced pressure and the residual liquid was distilled giving only one fraction at 120° (0.1 mm.). The flask temperatures ranged from 160 to 230° during the distillation. A small amount of acetone was added to the liquid distillate and the solution was cooled in a Dry Ice–acetone bath yielding 2.1 g. of white solid, m.p. 58.8–60.9°.

Progress of the Reaction of Triethylamine–Phenylborane and Diallyl-*n*-propylamine as Followed by Infrared Absorption.—A solution of 2.0 l. of toluene, 28.8 g. (0.15 mole) of triethylamine–phenylborane, and 20.8 g. (0.15 mole) of diallyl-*n*-propylamine was placed in a three-neck flask fitted with a serum cap and a thermometer. The flask was connected to the distillation apparatus and slowly heated. Samples of 30 ml. each were withdrawn at various temperatures and immediately cooled. The samples were then concentrated to 1 ml. under reduced pressure and the infrared spectra of the samples were taken using a cell of 0.0258-mm. cell width. All spectra were obtained using this cell in order to assure uniformity. The intensity of the boron–hydrogen absorption at 4.3 μ (2330 cm.$^{-1}$) was measured from the base line to the peak. The following intensities were observed at the respective temperatures: 24°, 55%; 47°, 49%; 60°, 35%; 73°, 25%; 90°, 22%; 112°, 8%; and after refluxing for 1.5 hr. at 112°, 0%.

N.m.r. Data.—The proton magnetic resonance spectral data for three of the 1,2-azaborolidines (based on structure III) are as follows (peak assignment, τ, and peak area): for 1-ethyl-2-phenyl-, 1, 3.33, 5.0; 4 and 5, 7.41, 4.0; 3, 8.79, —; 2, 9.12, —; 6, 9.52, 7.53 (combined areas for 2, 3, and 6); for 1-*sec*-butyl-2-phenyl-, 1, 3.14, 5.2; 5, 6.70, 1.0; 4, 7.28, 2.0; 3, 8.63, —; 2, 9.04, —; 6, (hidden), —; 8, 9.30, 8.5 (combined areas for 2, 3, 6 and 8); and for 1,2-diphenyl-, 1, 3.06 and 3.42, 9.2; 4, 6.88, 2.0; 2, and 3, 8.70, 3.8.

The proton magnetic resonance spectral data for three of the 1-aza-5-borabicyclo[3.3.0]octanes are as follows: for 1-ethyl-5-phenyl-, 1, 3.01, 5.0; 4 and 5, 7.02, 1.1[18]; 4 and 5, 7.89, —; 3, 8.34, 7.9[18] (combined areas for 3, 4, and 5); 2, 9.20, —; 6, 9.68, 8.4[18] (combined areas for 2 and 6); for 1-*sec*-butyl-5-phenyl-, 1, 2.78, 4.9; 4 and 5, 7.30, 5.2; 3, 8.20, 5.4[18]; 2, 6, and 8, 9.09, 7.9[18]; 7, 9.82, 3.0; and for 1, 5-diphenyl-, 1,3.19, 10.0; 4, 6.76, 4.0; 3, 7.87, 4.0; 2, 8.92, 4.4.

Acknowledgment.—We are extremely grateful to the National Lead Foundation for financial support of this research in the form of a fellowship. We are also grateful to Dr. George L. K. Hunter, Citrus Experiment Station, Winter Haven, Florida, for mass spectral data, to Dr. P. E. Slade, Chemstrand Research Center, Durham, North Carolina, for thermal gravimetric analyses, and to Dr. George D. Price, Glidden Company, Baltimore, Maryland, for certain infrared spectra.

[18] Partial overlap of peaks made individual peak areas somewhat uncertain.

Dicyanodiazomethane[1]

ENGELBERT CIGANEK

Contribution No. 1105 from the Central Research Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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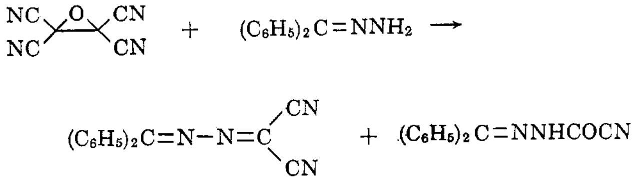
Dicyanodiazomethane, a highly electrophilic diazoalkane, has been prepared by lead tetraacetate oxidation of carbonyl cyanide hydrazone. Its properties are described. Some of its more unusual reactions include the diazo coupling with dimethylaniline, reaction with diazofluorene and diphenyldiazomethane to yield mixed azines, and the dehydrogenation of primary and secondary alcohols.

During an investigation of the chemistry of tetracyanoethylene epoxide,[2] a route to carbonyl cyanide hydrazone was discovered. This new hydrazone proved to be a convenient intermediate for the synthesis of dicyanodiazomethane, a molecule of interest both as an example of a highly electronegatively substituted diazoalkane and as a precursor of the heretofore unknown dicyanocarbene. The present paper is concerned with the synthesis and properties of dicyanodiazomethane as well as with its reactions to the extent that they do not involve a carbene intermediate. Reactions of dicyanocarbene will be described elsewhere.

Carbonyl Cyanide Hydrazone.—Tetracyanoethylene epoxide (TCNEO) has been shown to add to olefinic, acetylenic, and aromatic hydrocarbons yielding derivatives of tetracyanofuran.[2] Reactions of the epoxide with certain nucleophiles, on the other hand, proceed with cleavage of the molecule into carbonyl cyanide and products that are formally the adducts of dicyanocarbene to the nucleophile employed.[2] To determine the course of the reaction with a compound having both unsaturated and nucleophilic character, TCNEO was allowed to interact with benzophenone hydrazone. The products of this reaction, which occurred at 0°, were 1,1-dicyano-4,4-diphenyl-2,3-diazabutadiene (1)



1 (27%) 2 (45%)

and 1-cyanoformyl-2-diphenylmethylenehydrazine (2). The structures of the two products were determined by independent syntheses. Compound 2 was prepared in 77% yield by the reaction of benzophenone hydra-

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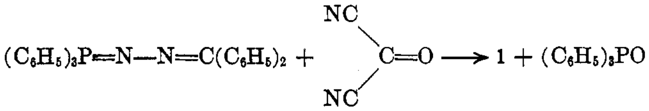
[1] A preliminary report on the preparation of dicyanodiazomethane appeared: E. Ciganek, *J. Am. Chem. Soc.*, **87**, 652 (1965).

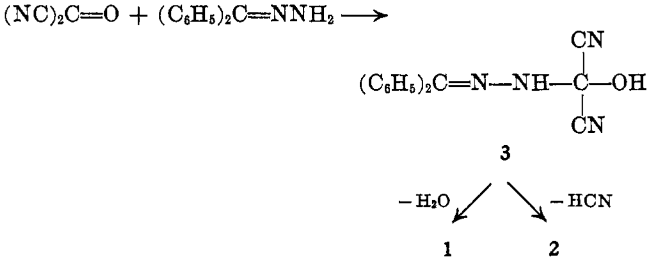
[2] W. J. Linn, O. W. Webster, and R. E. Benson, *ibid.*, **85**, 2032 (1963).

zone with carbonyl cyanide.[3] The mixed azine **1** was obtained in 71% yield by the interaction of benzophenone triphenylphosphazine with carbonyl cyanide at 0°. Similar Wittig-type reactions of phosphazines with aldehydes have been reported, but they required elevated temperatures; ketones were found to be unreactive.[4]



$$(C_6H_5)_3P{=}N{-}N{=}C(C_6H_5)_2 + (NC)_2C{=}O \longrightarrow 1 + (C_6H_5)_3PO$$

The isolation of 1-cyanoformyl-2-diphenylmethylenehydrazine (**2**) from the reaction of TCNEO with benzophenone hydrazone is easily explained as a result of the intermediate formation of carbonyl cyanide which reacts further to give **2**. The mechanism of the formation of **1** is less obvious, but the observation[5] that both **1** and **2** are formed when benzophenone hydrazone is added to an excess of carbonyl cyanide in the presence of acetic acid may indicate a common intermediate, **3**. The dicyanomethylene fragment of TCNEO was unaccounted for; the product of the addition of TCNEO to the C=N double bond was not found among the products.

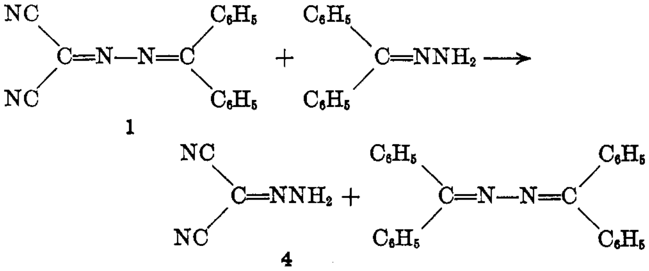


$$(NC)_2C{=}O + (C_6H_5)_2C{=}NNH_2 \longrightarrow (C_6H_5)_2C{=}N{-}NH{-}C(CN)_2{-}OH$$

3

$-H_2O$ → 1; $-HCN$ → 2

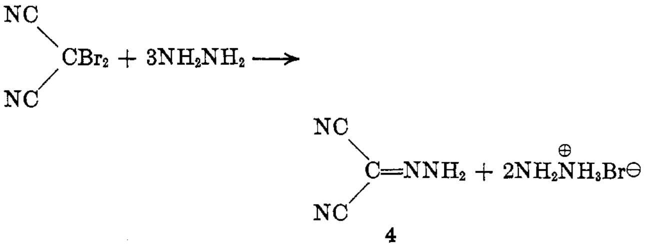
The chance observation that benzophenone azine, rather than **1**, was produced when TCNEO was allowed to react with an *excess* of benzophenone hydrazone, led to an investigation of the reaction of the hydrazone with the mixed azine **1**. This reaction occurred at room temperature and yielded carbonyl cyanide hydrazone (**4**, 70%) in addition to benzophenone azine (93%).



$$(NC)_2C{=}N{-}N{=}C(C_6H_5)_2 + (C_6H_5)_2C{=}NNH_2 \longrightarrow (NC)_2C{=}NNH_2 + (C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2$$

There appears to be no precedent for this rather unexpected azine–hydrazone interchange reaction. A somewhat related reaction is the formation of hydrazones from azines and hydrazine at elevated temperatures.[6]

Although carbonyl cyanide hydrazone could be prepared in fairly large amounts in this way, the required chromatographic separation and the low yield of **1** in the first step made a more direct synthesis of **4** desirable.[7] This was realized by the interaction of dibromomalononitrile (readily prepared by the bromination of malononitrile) with excess anhydrous hydrazine in tetrahydrofuran at −70°.[8] In addition to hydrazine hydrobromide and undetermined amounts of malononitrile, carbonyl cyanide hydrazone was obtained in 35–40% yield. The success of this reaction is surprising in view of the highly positive character of the bromine atoms in dibromomalononitrile. The related diethyl dibromomalonate[9] and ethyl dibromocyanoacetate,[10] on the other hand, are reduced by hydrazine to the corresponding malonic and cyanoacetic esters. Hydrazone formation has been reported, however, in other similar cases.[11] Reaction of dibromomalononitrile with unsymmetrically disubstituted hydrazines such as 1,1-dimethylhydrazine, 1,1-diphenylhydrazine, and N-aminopiperidine in the presence of triethylamine gave the corresponding N,N-disubstituted carbonyl cyanide hydrazones in high yields (78–89%). Methylhydrazine, on the other hand, failed to give carbonyl cyanide N-methylhydrazone; reaction of methyl hydrazinecarboxylate with dibromomalononitrile produced carbonyl cyanide N-methoxycarbonylhydrazone in 13% yield. Spectral data of these hydrazones are given in the Experimental Section.



$$(NC)_2CBr_2 + 3NH_2NH_2 \longrightarrow (NC)_2C{=}NNH_2 + 2NH_2\overset{\oplus}{N}H_3Br^{\ominus}$$

Carbonyl cyanide hydrazone (**4**) is a colorless crystalline compound which may be sublimed without decomposition at 90° under reduced pressure. Its stability is probably a consequence of extensive delocalization of the unshared electron pair on the amino nitrogen into the cyano groups. The high dipole moment of the compound (5.82 D.) and its ultraviolet spectrum [$\lambda_{\max}^{\mathrm{MeCN}}$ 282 mμ (ε 13,500)] are evidence for such an effect as is the n.m.r. spectrum which displays a broad singlet at τ 0.28 (in tetrahydrofuran). The amino protons in hydrazones usually occur at higher field.[12] The mass spectrum of carbonyl cyanide hydrazone shows, in addition to the parent peak, strong peaks at *m/e* 66, 65, and 64 (malononitrile) and 28 (nitrogen).

Dicyanodiazomethane.—Initial attempts to oxidize carbonyl cyanide hydrazone to dicyanodiazomethane

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[3] In this as in other reactions, *e.g.*, with amines or alcohols, carbonyl cyanide acts like an acid chloride: *cf.* R. Malachowski and J. Jankiewicz-Wasowska, *Roczniki Chem.*, **25**, 35 (1951); *Chem. Abstr.*, **47**, 10483 (1953).

[4] H. J. Bestmann and H. Fritzsche, *Chem. Ber.*, **94**, 2477 (1961).

[5] S. Proskow, unpublished results.

[6] *Cf.*, for instance, T. Curtius and H. Franzen, *Ber.*, **35**, 3234 (1902).

[7] Carbonyl cyanide hydrazone cannot be prepared by the direct interaction of carbonyl cyanide with hydrazine; *cf.* footnote 3.

[8] This reaction was first carried out by Dr. T. H. Regan of the Explosives Department.

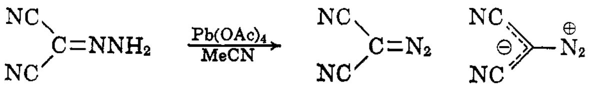
[9] E. L. Hirst and A. K. McBeth, *J. Chem. Soc.*, **121**, 904 (1922); for further examples of dehalogenations by hydrazine, see A. Furst, R. C. Berlo, and S. Hooton, *Chem. Rev.*, **65**, 51 (1965).

[10] E. Ciganek, unpublished results.

[11] S. Ruhemann and K. J. P. Orton, *J. Chem. Soc.*, **67**, 1002 (1895); H. P. Gallus and A. K. McBeth, *ibid.*, 1810 (1937).

[12] The shifts (τ, 10% solution in tetrahydrofuran) of the amino protons in benzophenone hydrazone and fluorenone hydrazone are 4.40 and *ca.* 3.0 (under the aromatic protons), respectively. The higher-field absorption of the former compound may be due to the lack of coplanarity of the phenyl groups with the C=N double bond, precluding efficient delocalization of the unshared pair of electrons on the amino nitrogen into the phenyl groups.

(**5**) were unsuccessful. Standard oxidizing agents such as mercuric, manganese, and silver oxides either did not react or effected decomposition of the hydrazone into nitrogen and malononitrile. The desired diazo compound was eventually obtained in almost quantitative yield by employing lead tetraacetate in acetonitrile.[13] This reagent has subsequently proved useful also in the preparation of bis(phenylsulfonyl)diazomethane,[16] bis(trifluoromethyl)diazomethane,[17] and cyanotrifluoromethyldiazomethane[18] from their respective hydrazones. Its application will be limited, however, to the synthesis of diazo compounds that are stable to acetic acid, a by-product of the oxidation.



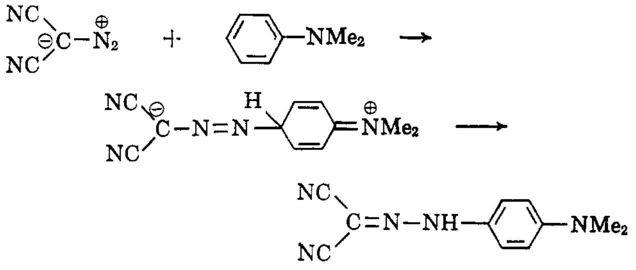
5 **5b**

Dicyanodiazomethane is a pale yellow crystalline solid, milligram quantities of which melt with decomposition at about 75°. Larger amounts explode violently when heated to that temperature; in addition, the compound has borderline sensitivity to static electricity. *The solid diazo compound should thus be handled only with proper safety precautions.* No explosions were encountered with solutions of dicyanodiazomethane. Despite its low molecular weight of 92, dicyanodiazomethane has negligible vapor pressure at room temperature.[19] The dipole moment of 3.8 D. and the position of the diazo band in the infrared spectrum at 2140 cm.$^{-1}$ also point to a considerable contribution of the diazonium methylid structure **5b** to the ground state of dicyanodiazomethane. The high symmetry of the molecule is reflected in the simplicity of its infrared spectrum, which contains only four bands at 2225, 2140, 1240, and 1215 cm.$^{-1}$ (in KBr). The ultraviolet spectrum in acetonitrile shows absorption at 241 mμ (ε 12,400) and 313 mμ (ε 107) with a shoulder at 370 mμ (ε 50). Dicyanodiazomethane is soluble in polar organic solvents but virtually insoluble in saturated hydrocarbons. It is remarkably stable toward acids; a solution in 2 *N* sulfuric acid in acetonitrile still showed 87% of the initial extinction at 241 mμ after standing at room temperature for 16 hr.[20] Addition of concentrated sulfuric acid to solid dicyanodiazomethane, however, resulted in an explosion. Dicyanodiazomethane is readily attacked by bases; triphenylphosphine and Grignard reagents react below room temperature with the formation, respectively, of carbonyl cyanide triphenylphosphazine (**6**) and (after hydrolysis) of substituted carbonyl cyanide hydrazones, **7**. The formation of hydrazones from diazo compounds and Grignard reagents has been reported previously[21]; it is noteworthy that attack of the base on the cyano groups occurred, if at all, only to a small extent.

$Ph_3\overset{\oplus}{P}-N=N-\overset{\ominus}{C}(CN)_2$ **6**

$(NC)_2C=NNHR$ **7**, R = Me, C_6H_5

Addition of excess N,N-dimethylaniline to solid dicyanodiazomethane resulted in a rapid reaction (accompanied by gas evolution) from which carbonyl cyanide *p*-N,N-dimethylaminophenylhydrazone (**8**) and bis(*p*-N,N-dimethylaminophenyl)malononitrile (**11**) were obtained in 27 and 19% yields, respectively. The *ortho* isomer of **8** was not formed. Compound **8** is the product of an azo coupling reaction of dicyanodiazomethane.[22] The formation of **11** is less easily explained. The intermediacy of carbonyl cyanide, which is known[3] to react with N,N-dimethylaniline to give **11**, is unlikely in view of the observed resistance of dicyanodiazomethane to autoxidation. A pos-



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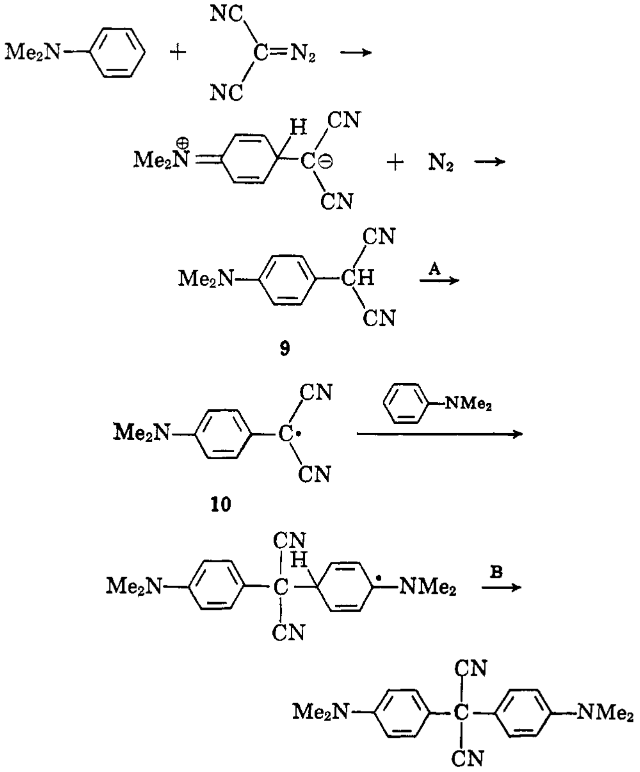

9

10

11

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[13] Lead tetraacetate oxidation of hydrazones to yield diazo compounds does not appear to have been reported previously. *Cf.*, however, the preparation of diacyl diimides from diacyl hydrazides using this reagent.[14] Azoacetates were obtained when N-mono- or N,N-disubstituted ketohydrazones were oxidized with lead tetraacetate.[15]

[14] R. A. Clement, *J. Org. Chem.*, **25**, 1724 (1960).

[15] D. C. Iffland and E. Cerda, *ibid.*, **28**, 2767 (1963); D. C. Iffland, L. Salisbury, and W. T. Schafer, *J. Am. Chem. Soc.*, **83**, 747 (1961).

[16] J. Diekmann, *J. Org. Chem.*, **28**, 2933 (1963), and private communication.

[17] D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, **86**, 657 (1965).

[18] S. Proskow, to be published.

[19] Dicyanodiazomethane can be kept under 0.1-mm. pressure at room temperature for extended periods without noticeable loss of weight.

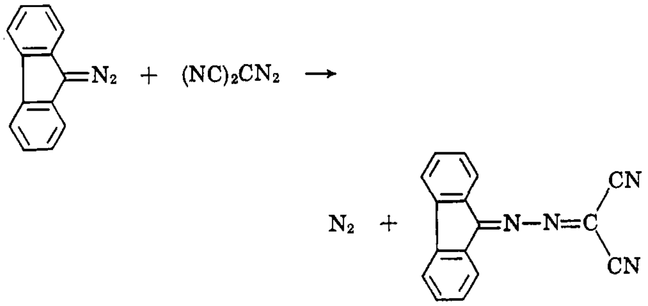
[20] Electron-withdrawing substituents as a rule enhance the acid stability of diazo compounds: *cf.*, for instance, F. Klages and K. Bott, *Chem. Ber.*, **97**, 735 (1964); F. Klages, K. Bott, and P. Hegenberg, *Angew. Chem.*, **74**, 725 (1962).

[21] G. H. Coleman, H. Gilman, C. E. Adams, and P. E. Pratt, *J. Org. Chem.*, **3**, 99 (1938); L. Canonica and C. Tedeschi, *Gazz. chim. ital.*, **84**, 175 (1954).

[22] A number of negatively substituted aliphatic diazo compounds have recently been reported to undergo diazo coupling: *cf.* M. Regitz and G. Heck, *Chem. Ber.*, **97**, 1482 (1964), and references cited therein.

sible mechanism for the formation of **11** is shown above. Excess dicyanodiazomethane probably acts as the oxidizing agent in steps A and B. The mechanism involving two one-electron transfers is preferred over a two-electron oxidation of **9** to yield a positively charged intermediate which would be very unstable in view of the high electron demand of the two cyano groups. Radicals of type **10** have been shown to be fairly stable.[23]

Dicyanodiazomethane and 9-diazofluorene reacted rapidly at room temperature with the formation of nitrogen and 1-dicyanomethylene-2-fluoren-9-ylidinehydrazine, **12**. Similarly, diphenyldiazomethane gave the mixed azine **1**. Product **12** was identified by independent synthesis from fluorenone triphenylphosphazine and carbonyl cyanide in analogy to the preparation of **1**. Mixed azines have been obtained previously in the interaction of certain diazo ketones with diazoethane[24a] and of a number of negatively substituted diazo compounds with diphenyldiazomethane.[24b] A probable mechanism involves electrophilic attack of dicyanodiazomethane on 9-diazofluorene followed by, or concurrent with, loss of nitrogen. A stepwise mechanism would involve intermediate **13**. The less nucleophilic diazo compounds ethyl diazoacetate and diethyl diazomalonate did not react with dicyanodiazomethane at room temperature. Interestingly, diethyl diazomalonate also failed to react with diphenyldiazomethane in refluxing acetonitrile. Only benzophenone azine (the decomposition product of diphenyldiazomethane) and unreacted diazo ester were isolated.



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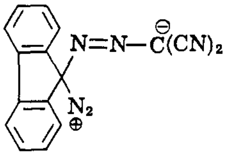

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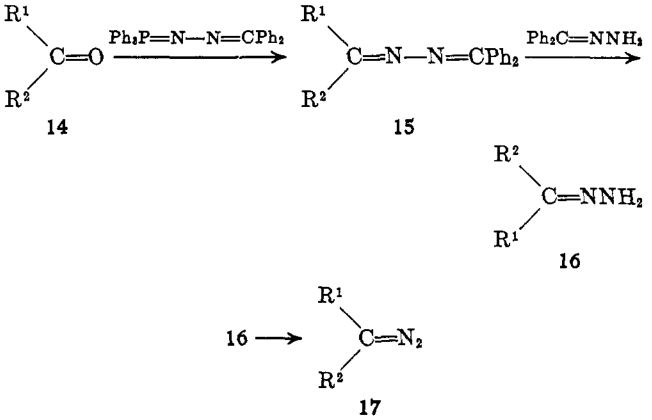
Dicyanodiazomethane was found to be completely inactive as a "1,3-dipolarophile." It failed to react with norbornene, dimethyl acetylenedicarboxylate, and benzalaniline in the temperature range in which it is stable (below *ca.* 50° in solution). This is in agreement with the finding[25] that the reactivity of substituted diazo compounds in 1,3 dipolar additions decreases with increasing delocalization of the negative charge on the carbon atoms into the substituents.

Dicyanodiazomethane reacts slowly at room temperature with methanol and isopropyl alcohol to give carbonyl cyanide hydrazone in 30 and 36% yield, respectively. The disappearance of the diazo compound, determined ultraviolet spectroscopically over the first 40 hr., followed pseudo-first-order kinetics with half-lives that were identical within experimental error (26 and 24 hr., respectively). In the case of the reaction with isopropyl alcohol, acetone was isolated in 8% yield in the form of its 2,4-dinitrophenylhydrazone. This dehydrogenation reaction, which appears not to have been observed with other diazoalkanes, reflects the highly electrophilic character of dicyanodiazomethane.

The possibility of preparing other substituted diazoalkanes from the respective carbonyl compounds in analogy to the synthesis of dicyanodiazomethane from carbonyl cyanide was investigated briefly. Both diethyl mesoxalate (**14**, $R^1 = R^2 = COOEt$) and benzoyl cyanide (**14**, $R^1 = CN$; $R^2 = C_6H_5$) reacted with benzophenone triphenylphosphazine with the formation of the corresponding mixed azines **15**, neither of which, however, underwent the azine–hydrazone interchange reaction with benzophenone hydrazone. The reaction between phosgene and benzophenone triphenylphosphazine occurred at 0° and triphenylphosphine oxide was obtained in almost 100% yield; the only other product isolated was benzophenone, probably formed by hydrolysis of the unstable 1,1-diphenyl-4,4-dichloro-2,3-diazabutadiene (**15**, $R^1 = R^2 = Cl$). The successful preparation of trifluoromethylcyanodiazomethane (**17**, $R^1 = CF_3$; $R^2 = CN$) from trifluoroacetyl cyanide (**14**, $R^1 = CF_3$; $R^2 = CN$) by this route will be reported elsewhere.[18]



Experimental Section[26]

1,1-Dicyano-4,4-diphenyl-2,3-diazabutadiene (1). A. From Tetracyanoethylene Epoxide and Benzophenone Hydrazone.—A solution of 2.18 g. (1.51×10^{-2} mole) of tetracyanoethylene epoxide (TCNEO) in 10 ml. of tetrahydrofuran (THF) was cooled with an ice bath, and a solution of 2.40 g. (1.22×10^{-2} mole) of benzophenone hydrazone in 25 ml. of THF was added, with stirring, over a period of 1 hr. Stirring was then continued for 75 min. at ice-bath temperature and for 1 hr. at room temperature. The solvent was removed (rotary evaporator), leaving 4.73 g. of a dark semisolid. Chromatography of 1.43 g. of the crude product mixture on Florisil gave 0.38 g. of crude 1,1-dicyano-4,4-diphenyl-2,3-diazabutadiene (**1**, eluted with benzene–

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[23] H. D. Hartzler, to be published.

[24] (a) P. Yates, D. G. Farnum, and D. W. Wiley, *Tetrahedron*, **18**, 881 (1962), and references cited therein; (b) A. Schönberg and K. Junghans, *Chem. Ber.*, **98**, 820 (1965).

[25] R. Huisgen and R. Fleischmann, cited by R. Huisgen, *Angew. Chem.*, **75**, 742 (1963).

[26] Melting points and boiling points are uncorrected. N.m.r. spectra were determined on a Varian, Inc., A-60 spectrometer, infrared spectra on a Perkin-Elmer 21 spectrometer, and the ultraviolet spectra on a Cary 14 spectrometer of the Applied Physics Corp.

hexane 4:1) and 0.42 g. (45% yield) of crude 1-cyanoformyl-2-diphenylmethylenehydrazine (2, eluted with methylene chloride–ether 9:1). The former product was crystallized from 2 ml. of cyclohexane, giving 0.26 g. (27%) of the diazabutadiene 1, m.p. 92–95°, in the form of orange needles. An analytical sample, obtained by crystallization from cyclohexane, had m.p. 95–96.5°.

Anal. Calcd. for $C_{16}H_{10}N_4$: C, 74.39; H, 3.91; N, 21.71; mol. wt., 258.27. Found: C, 74.31; H, 4.04; N, 21.66. mol. wt. (ebullioscopically in ethylene chloride) 269, 280.

The ultraviolet spectrum (in cyclohexane) had λ_{max} 230 mμ (ϵ 12,900), 275 (sh) (9700), and 335 (13,200). The latter band trails into the visible region (ϵ at 400 mμ, 1000; at 500 mμ, 17). The infrared spectrum (in KBr) had CN at 2230 (w) cm.$^{-1}$.

With a 100% excess of benzophenone hydrazone, under otherwise identical conditions as above, no 1,1-dicyano-4,4-diphenyl-2,3-diazabutadiene was isolated. The products were benzophenone azine (33%) and 1-cyanoformyl-2-diphenylmethylene hydrazine (33%) (yields based on benzophenone hydrazone).

B. From Carbonyl Cyanide and Benzophenone Triphenylphosphazine.—To a suspension of 3.00 g. (6.6 × 10^{-3} mole) of benzophenone triphenylphosphazine[27] in 30 ml. of chloroform was added at room temperature, with stirring and under nitrogen, a solution of 1.02 g. (1.27 × 10^{-2} mole) of carbonyl cyanide[28] in 10 ml. of THF. The mixture turned orange and became homogeneous after a few minutes; after standing at room temperature for 30 min., the solvent was removed under reduced pressure, and the residual brown oil (3.42 g.) was chromatographed on Florisil. 1,1-Dicyano-4,4-diphenyl-2,3-diazabutadiene (1, 1.20 g., 71%) was eluted with *n*-hexane–benzene (1:1) followed by triphenylphosphine oxide (1.37 g., 75%) which came off the column with methylene chloride–THF (7:3). The products were identified by their infrared spectra.

1-Cyanoformyl-2-diphenylmethylenehydrazine (2).—To a solution of 8.7 g. (4.4 × 10^{-2} mole) of benzophenone hydrazone in 25 ml. of anhydrous benzene and 25 ml. of glacial acetic acid was added, with vigorous stirring, a solution of 3.8 g. (4.7 × 10^{-2} mole) of carbonyl cyanide in 20 ml. of dry benzene. The temperature was kept below 0° during the addition, which took 10 min. The mixture was then stirred at 0° for 10 min., the solvents were removed, and the residue was dried under high vacuum over potassium hydroxide. Crystallization from 250 ml. of ethanol gave 8.5 g. (77% yield) of 1-cyanoformyl-2-diphenylmethylenehydrazine (2), m.p. 180–182° dec.

Anal. Calcd. for $C_{15}H_{11}N_3O$: C, 72.28; H, 4.45; N, 16.86; mol. wt., 249.26. Found: C, 72.54; H, 4.59; N, 16.88; mol. wt., 246 252 (ebullioscopically in benzene).

The ultraviolet spectrum (in cyclohexane) had λ_{max} 289 mμ (ϵ 19,300) and 225 mμ (sh) (ϵ 13,900). The infrared spectrum (in KBr) showed bands at 3170, 2240, and 1710 cm.$^{-1}$.

Carbonyl Cyanide Hydrazone (4) from 1,1-Dicyano-4,4-diphenyl-2,3-diazabutadiene (1).—A solution of 3.00 g. (11.6 mmoles) of 1,1-dicyano-4,4-diphenyl-2,3-diazabutadiene (1) and 3.00 g. (15.3 mmoles) of benzophenone hydrazone in 40 ml. of THF was left standing at room temperature for 12 hr. Removal of the solvent gave 6.00 g. of a yellow solid from which, in a different experiment, benzophenone azine was isolated in 93% yield by chromatography on Florisil (elution with benzene). In the present experiment the solid was stirred with 60 ml. of benzene at room temperature, and the insoluble material was chromatographed on Florisil. Benzophenone azine was eluted with benzene–methylene chloride (1:1) followed by 0.72 g. of a brown solid (eluted with THF); the latter (0.52 g.), on sublimation at 0.1 mm. and 80° bath temperature, gave 0.44 g. (56%) of carbonyl cyanide hydrazone, m.p. 122–124° dec. after crystallization from benzene. In scaled up runs, yields of 70% of carbonyl cyanide hydrazone were obtained.

Anal. Calcd. for $C_3H_2N_4$: C, 38.30; H, 2.14; N, 59.56; mol. wt., 94.08. Found: C, 38.39; H, 2.52; N, 59.74; mol. wt., 93 (cryoscopically in dioxane).

The ultraviolet spectrum (in acetonitrile) had λ_{max} 282 mμ (ϵ 13,500) and 233 mμ (ϵ 1500). The infrared spectrum (in Nujol) had ν_{max} 3400, 3270, 3170, 2225 (doublet), 1650, 1500, and 1460 cm.$^{-1}$, among others: mass spectrum (115° inlet temperature) *m/e* 94 (parent), 66, 65, 64 (malononitrile), and 28 (nitrogen). The n.m.r. spectrum (10% in tetrahydrofuran) showed a singlet at τ 0.28, width at half-height 15 c.p.s. The dipole moment was 5.82 D. (at 25° in dioxane).

Carbonyl Cyanide Hydrazone (4) from Dibromomalononitrile.—To a vigorously mechanically stirred solution of 55.35 g. (1.73 moles) of anhydrous hydrazine in 100 ml. of methanol and 900 ml. of THF was added, over a period of 3 hr., a solution of 129.1 g. (0.577 mole) of dibromomalononitrile[29] in 450 ml. of THF. The temperature was kept below −70° during the addition. A total of 4100 cc. (29%) of a gas was evolved; a sample collected after *ca.* 25% of the dibromomalononitrile had been added was shown by mass spectroscopy to be a mixture of air and nitrogen. The mixture was stirred at −70° for 2 hr., allowed to warm to −10°, and filtered. The insoluble material was washed with THF and dried, giving 122.0 g. (94%) of crude hydrazine hydrobromide. The combined filtrates were concentrated to *ca.* 200 ml. Florisil (70 g.) was added and the rest of the solvent was removed. The residue was added to a column packed with 150 g. of Florisil. Elution with 600 ml. of methylene chloride–THF (1:1) and removal of the solvents gave a dark semisolid. Sublimation of this material first gave a considerable amount of malononitrile (at 60°, 0.2 mm.); the bath temperature was then increased to 80° and the first crop of carbonyl cyanide hydrazone, still containing some malononitrile, was also discarded. Continued sublimation gave 21.19 g (39%) of carbonyl cyanide hydrazone having a slightly brown color. Resublimation gave 19.52 g. (36%) of an almost colorless crystalline product.

Carbonyl Cyanide N,N-Dimethylhydrazone.—To a mechanically stirred solution of 26.95 g. (0.449 mole) of 1,1-dimethylhydrazine in 150 ml. of dry THF was added, over a period of 1 hr., a solution of 32.17 g. (0.144 mole) of dibromomalononitrile[29] in 50 ml. of THF; the temperature was kept below −60° during the addition. After stirring at −70° for 2 hr., the mixture was allowed to warm to room temperature and filtered. The solids were washed with THF, and the combined filtrate and washings were concentrated to dryness. Short-path distillation of the residue at 0.5 μ and a bath temperature of 80–95° gave 15.55 g. (88%) of carbonyl cyanide dimethylhydrazone, $n^{25}D$ 1.5533, as a pale-yellow oil.

Anal. Calcd. for $C_5H_6N_4$: C, 49.17; H, 4.95; N, 45.88; mol. wt., 122.13. Found: C, 48.82; H, 4.81; N, 46.73; mol. wt., 131 (ebullioscopically in benzene).

The ultraviolet spectrum (in acetonitrile) had λ_{max} 300 mμ (ϵ 17,500) and 232 mμ (ϵ 1350); the infrared spectrum (neat) 2210 (s), 2000 (sh) (s), and 1540 cm.$^{-1}$ (vs), among others; the n.m.r. spectrum (neat) singlet at τ 6.62 (half-band width 2 c.p.s.).

N-(Dicyanomethyleneimino)piperidine.—To a mechanically stirred mixture of 20.00 g. (0.20 mole) of N-aminopiperidine, 46.85 g. (0.40 mole) of anhydrous triethylamine, and 250 ml. of THF was added at −70°, over a period of 2 hr., a solution of 44.8 g. (0.20 mole) of dibromomalononitrile in 200 ml. of THF. The temperature was kept at −70° for an additional 30 min.; the mixture was allowed to come to room temperature and filtered. The solids were washed with THF and the filtrate and washings were concentrated to dryness leaving 33.9 g. of a dark oil. Short-path distillation of 20.6 g. of this product at 0.5 μ and 100° bath temperature gave 15.55 g. (78% yield) of N-(dicyanomethyleneimino)piperidine as a yellow oil, $n^{24}D$ 1.5759.

Anal. Calcd. for $C_8H_{10}N_4$: C, 59.24; H, 6.21; N, 34.55; mol. wt., 162.19. Found: C, 59.18; H, 6.13; N, 34.91; mol. wt., 162 (osmometrically in benzene).

The ultraviolet spectrum (in acetonitrile) had λ_{max} 305 mμ (ϵ 21,400) and 238 mμ (ϵ 1900); the infrared spectrum (neat) 2220 (s), 2195 (m), and 1525 (vs) cm.$^{-1}$, among others.

Carbonyl Cyanide N,N-Diphenylhydrazone.—A solution of 1.50 g. (2.78 × 10^{-2} mole) of sodium methoxide in 10 ml. of methanol was added to a solution of 6.00 g. (2.71 × 10^{-2} mole) of 1,1-diphenylhydrazine hydrochloride in 40 ml. of methanol. After stirring at room temperature for 10 min., 100 ml. of THF and 5.5 g. (5.44 × 10^{-2} mole) of triethylamine were added and the mixture was cooled to −70°. During 1 hr., a solution of 6.05 g. (2.72 × 10^{-2} mole) of dibromomalononitrile in 30 ml. of THF was added dropwise, with stirring, keeping the temperature below −70°. After stirring at that temperature for 30 min. more, the mixture was allowed to come to room temperature. Evaporation of the filtered solution gave 10.50 g. of a gray solid. A sample of 9.42 g. of this product was washed with water, dried,

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[27] H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 619 (1919).

[28] W. J. Linn, O. W. Webster, and R. E. Benson, *J. Am. Chem. Soc.*, **87**, 3651 (1965); W. J. Linn, U. S. Patent 3,115,517 (1963).

[29] K. Torssell and K. Dahlquist, *Acta Chem. Scand.*, **16**, 346 (1962).

and crystallized from 30 ml. of isopropyl alcohol to give 5.25 g. (89% yield) of carbonyl cyanide diphenylhydrazone in the form of yellow crystals, m.p. 131.5–133.0°. Recrystallization gave an analytical sample, m.p. 132.5–133°.

Anal. Calcd. for $C_{15}H_{10}N_4$: C, 73.15; H, 4.10; N, 22.76; mol. wt., 246.26. Found: C, 72.92; H, 4.13; N, 22.66; mol. wt., 231 (ebullioscopic in benzene).

The ultraviolet spectrum (in acetonitrile) had λ_{max} 348 mμ (ε 18,300), 250 (sh) (6600), and 232 (8900); the infrared spectrum (KBr) 2220 (m–s), 2205 (m), 1500 (vs), and 1490 (vs) cm.$^{-1}$, among others.

Carbonyl Cyanide N-Methoxycarbonylhydrazone.—To a mechanically stirred suspension of 4.500 g. (50.0 mmoles) of methyl hydrazinecarboxylate and 10.100 g. (0.100 mole) of triethylamine in 150 ml. of THF was added, over a period of 1.5 hr., a solution of 1.202 g. (50.0 mmoles) of dibromomalononitrile[29] in 50 ml. of THF, keeping the temperature below −70°; *ca.* 380 cc. of a gas (0.31 mole at 25°) was evolved. After stirring at −70° for 2 hr., the mixture was warmed to −10° and filtered; evaporation of the solvent gave 9.86 g. of a black tar. Chromatography of 6.738 g. of this product on 70 g. of Florisil and elution with 600 ml. of methylene chloride–THF (95:5) gave 1.567 g. of a yellow semisolid. Addition of 2 ml. of methylene chloride, filtration, and washing the insoluble material with methylene chloride gave 679 mg. (13%) of carbonyl cyanide N-methoxycarbonylhydrazone, m.p. 110.5–111.5° (unchanged by crystallization from isopropyl alcohol).

Anal. Calcd. for $C_5H_4N_4O_2$ (152.11): C, 39.48; H, 2.65; N, 36.83. Found: C, 39.55; H, 2.69; N, 36.81.

The ultraviolet spectrum (acetonitrile) had λ_{max} 280 mμ (ε 18,100). The infrared spectrum (KBr) showed bands at 3180 (m), 3010 (w), 2260 (w), 2240 (w), 1775 (vs), 1535 (s), and 1515 (vs), cm.$^{-1}$, among others. The n.m.r. spectrum (in CD_3CN) had a singlet at τ 6.14 (three protons) and a broad band at τ −0.58 (one proton).

Dicyanodiazomethane.—*Caution:* Solid dicyanodiazomethane is a potent explosive which has borderline sensitivity to static electricity. It should be handled only behind a shield and while wearing protective clothing. A sample of 15.0 mmoles (weight after removal of the acetic acid) of lead tetraacetate was kept under high vacuum at room temperature for 30 min. to remove the acetic acid present in commercial preparations. Anhydrous acetonitrile (60 ml.) was then added with the exclusion of moisture, and the mixture was stirred at room temperature for 5 min. and then cooled with an ice bath. A solution of 1.23 g. (13.1 mmoles) of carbonyl cyanide hydrazone in 20 ml. of acetonitrile was added over a period of 10 min. The ice bath was removed, and the mixture was stirred for 2 hr. Water (2 ml.) was added, stirring was continued for 15 min., and the lead diacetate was removed by filtration. The filtrate and two washings (5-ml. portions of acetonitrile) were concentrated to dryness using a rotary evaporator at room temperature. The residual yellow solid was kept under 0.1-mm. vacuum at room temperature for 30 min. Ether (100 ml.) was then added, the solid was scraped from the walls using a plastic spatula, and the suspension was stirred vigorously for *ca.* 5 min. to effect dissolution of the diazo compound. The filtered mixture was concentrated to dryness (rotary evaporator), leaving 1.16 g. (96%) of essentially pure dicyanodiazomethane. An analytical sample was prepared by cooling a saturated (at room temperature) solution in ether to −30°, filtering under nitrogen, washing the precipitate with cold ether, and drying. Dicyanodiazomethane melts at *ca.* 75° (hot stage) with gas evolution. Larger amounts explode when heated to this temperature.

Anal. Calcd. for C_3N_4: C, 39.14; N, 60.86; mol. wt., 92.06. Found: C, 39.63; H, 61.56[30]; mol. wt., 92 (cryoscopically in dioxane).

Stability of Dicyanodiazomethane toward Sulfuric Acid.—Dicyanodiazomethane (112 mg.) was dissolved in 25 ml. of a solution of 5.05 g. of concentrated sulfuric acid in 50.0 ml. of anhydrous acetonitrile (2.06 *N* H_2SO_4). Ultraviolet spectra were taken at intervals and the concentration of dicyanodiazomethane was determined by the extinction coefficient of the 243-mμ band. After 16.5 hr. at room temperature, 87% of the initial amount of the diazo compound was still present. A 2.06 *N* sulfuric acid solution in acetonitrile, after standing at room temperature for 17 hr., showed absorption at 243 mμ corresponding to less than 3% of the absorption of the diazo compound. Ether (50 ml.) was added to the acidic solution of the dicyanodiazomethane, and the mixture was washed five times with water and dried ($MgSO_4$). To the filtered solution was added 888 mg. of triphenylphosphine. After 1 hr. at room temperature, the solvents were removed leaving a yellow solid, which on chromatography gave triphenyl phosphine (eluted with benzene) and 128 mg. (30% yield, eluted with methylene chloride–THF 1:1) of carbonyl cyanide triphenylphosphazine (see below), identified by its infrared spectrum.

Carbonyl Cyanide Triphenylphosphazine (6).—To a solution of 74 mg. of dicyanodiazomethane in 5 ml. of ether was added a solution of 222 mg. of triphenylphosphine in 3 ml. of ether. The pale yellow precipitate which formed immediately was collected after 1 hr. and washed with ether: yield 230 mg. (82%), m.p. 171–173° dec.

Anal. Calcd. for $C_{21}H_{15}N_4P$: C, 71.19; H, 4.27; N, 15.81; P, 8.74; mol. wt., 354.32. Found: C, 71.40; H, 4.48; N, 15.62; P, 8.33; mol. wt., 340, 376 (ebullioscopically in benzene).

Carbonyl Cyanide N-Phenylhydrazone (7, R = C_6H_5).—To a solution of dicyanodiazomethane, prepared from 1.01 g. (1.07×10^{-2} mole) of carbonyl cyanide hydrazone, in 50 ml. of ether was added, over a period of 5 min., 4.0 ml. of ethereal 3 *M* phenylmagnesium bromide solution (1.18×10^{-2} mole). The reaction was exothermic and a brown precipitate formed immediately; the temperature was kept below 30°. The mixture was stirred at room temperature for 30 min., concentrated ammonium chloride solution was added, the layers were separated, and the aqueous layer was extracted with 30 ml. of benzene and 30 ml. of methylene chloride. The combined extracts were washed with water and dried ($MgSO_4$). Removal of the solvents gave 1.85 g. of a semisolid. Chromatography of 1.78 g. of this product on Florisil gave 1.16 g. (66% yield) of crude carbonyl cyanide phenylhydrazone eluted with 300 ml. of benzene followed by 150 ml. of benzene–methylene chloride (1:1) and 150 ml. of methylene chloride. Crystallization from isopropyl alcohol gave the pure hydrazone, the infrared spectrum of which was identical with that of an authentic sample.[31]

Carbonyl Cyanide N-Methylhydrazone (7, R = Me).—The procedure was that described for the preparation of carbonyl cyanide N-phenylhydrazone (see above). Removal of the solvents gave 587 mg. (from 857 mg. of carbonyl cyanide hydrazone, 60% yield) of crude carbonyl cyanide N-methylhydrazone. Sublimation at 70–75° bath temperature and 0.2-mm. pressure followed by crystallization from benzene gave the pure hydrazone in the form of off-white crystals, m.p. 99–101° dec.

Anal. Calcd. for $C_4H_4N_4$: C, 44.44; H, 3.73; N, 51.83; mol. wt., 108.10. Found: C, 44.85; H, 3.89; N, 51.89; mol. wt., 99, 103.

The infrared spectrum (in KBr) had bands at 3200 (s), 3080 (w–m), 3000 (w), 2250 (w), 2220 (s), 2205 (m), 1565 (s), and 1555 (s) cm.$^{-1}$, among others. The ultraviolet spectrum (in acetonitrile) had λ_{max} 300 mμ (ε 15,900) and 228 mμ (ε 900); the n.m.r. spectrum [in $(CD_3)_2CO$] a singlet at τ 6.99 (three protons) and a broad singlet at τ 0.75 (one proton). Carbonyl cyanide methylhydrazone turns dark on standing at room temperature.

Reaction of Dicyanodiazomethane with 9-Diazofluorene and Diphenyldiazomethane.— A solution of 163 mg. (8.5 mmoles) of 9-diazofluorene in 3 ml. of THF was added at room temperature to a solution of 78 mg. (8.5 mmoles) of dicyanodiazomethane in 2 ml. of acetonitrile. Nitrogen was evolved immediately. The solvents were removed after standing at room temperature for 4 hr., leaving 222 mg. of a purple solid, the infrared spectrum of which was identical with that of 1-dicyanomethylene-2-fluoren-9-ylidinehydrazine (**12**, see below). Recrystallization of 208 mg. of the product from 2 ml. of benzene gave 145 mg. (71%) of the pure compound, m.p. and m.m.p. 171–172°.

In a similar experiment, 1,1-dicyano-4,4-diphenyl-2,3-diazabutadiene (**1**) was obtained in 82% yield from 0.571 g. of dicyanodiazomethane and 1.06 g. of diphenyldiazomethane in acetonitrile at room temperature.

1-Dicyanomethylene-2-fluoren-9-ylidinehydrazine (12) from Fluorenone Triphenylphosphazine and Carbonyl Cyanide.—A solution of 1.57 g. (1.96×10^{-2} mole) of carbonyl cyanide[28] in 15 ml. of THF was added to a cooled (Dry Ice–acetone) suspension of 7.11 g. (1.57×10^{-2} mole) of fluorenone triphenylphosphazine[27] in 25 ml. of THF. The mixture was stirred while the bath was allowed to come to room temperature (1 hr.);

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(30) In view of the explosive character of dicyanodiazomethane, this analysis is considered satisfactory.

(31) A. Hantzsch and K. J. Thompson, *Ber.*, **38**, 2266 (1905).

it was then stirred an additional 30 min. The dark purple, homogeneous solution was concentrated to dryness and the residue (8.36 g.) was chromatagraphed over Florisil (250 g.). Crude 1-dicyanomethylene-2-fluoren-9-ylidenehydrazine (3.44 g., 86% yield) was eluted with 700 ml. of benzene–methylene chloride (1:1). Crystallization from 30 ml. of benzene gave 2.94 g. (73%) of the pure product, m.p. 171–172°, in the form of red needles. An analytical sample, obtained by crystallization from benzene, had m.p. 171.5–172°.

Anal. Calcd. for $C_{16}H_8N_4$: C, 74.99; H, 3.15; N, 21.7;8 mol. wt., 256.26. Found: C, 75.16; H, 3.61; N, 21.52; mol. wt., 271, 262 (ebullioscopically in ethylene chloride).

The ultraviolet spectrum (in acetonitrile) had λ_{max} 240 mμ (ϵ 28,700), 270 (31,800), and 358 (15,800) with a long trail into the visible spectrum: ϵ at 400 mμ, 5300; at 500 mμ, 230. The infrared spectrum (in KBr) had bands at 2230 (CN), 1610, 1590, 1490, 1470, and 1450 cm.$^{-1}$.

Reaction of Dicyanodiazomethane with N,N-Dimethylaniline. A. In N,N-Dimethylaniline.—To 601 mg. of solid dicyanodiazomethane was added 15 ml. of freshly distilled N,N-dimethylaniline and the mixture was stirred at room temperature overnight. Nitrogen evolution began after a short induction period but stopped again after *ca.* 60% of the calculated amount had been given off. Removal of most of the amine left 1.720 g. of a dark semisolid. Chromatography of 221 mg. of this product over Florisil (7 g.) gave 50 mg. (19%) of bis(*p*-N,N-dimethylaminophenyl)malononitrile (11),[3] eluted with benzene and identified by its infrared spectrum, and 48 mg. (27% yield) of a red solid, eluted with methylene chloride, the infrared spectrum of which was that of carbonyl cyanide *p*-N,N-dimethylaminophenylhydrazone.[32] The *ortho* isomer (see below) was present, if at all, to the extent of less than 2% as determined by n.m.r. spectroscopy.

B. In Acetonitrile.—A solution of 364 mg. (3.96 mmoles) of dicyanodiazomethane in 4 ml. of acetonitrile was added at room temperature during 10 min. to a stirred solution of 748 mg. (6.18 mmoles) of N,N-dimethylaniline in 4 ml. of acetonitrile. The first few drops caused a red coloration which faded immediately; later a green precipitate formed and eventually the whole mixture turned dark purple. After stirring at room temperature for 2 hr., the solvent and excess dimethylaniline were removed under vacuum and the residue was chromatographed as under A, giving 287 mg. (24%) of bis(*p*-N,N-dimethylaminophenyl)-malononitrile and *ca.* 100 mg. of a purple oil, part of which may have been carbonyl cyanide *p*-N,N-dimethylphenylhydrazone as indicated by its infrared spectrum.

Carbonyl Cyanide *o*-Dimethylaminophenylhydrazone.—A solution of 5.9 g. (0.16 mole) of hydrogen chloride in 50 ml. of anhydrous ethanol was added, with cooling, to a solution of 20.2 g. (0.15 mole) of N,N-dimethyl-*o*-phenylenediamine[33] in 200 ml. of ethanol. To the mixture was then added, over a period of 20 min., with continued cooling, 24.6 g. (0.21 mole) of isoamyl nitrite. After stirring at ice-bath temperature for 3 hr., a solution of 18 g. (0.27 mole) of malononitrile in 300 ml. of water was added, followed by 14 g. (0.17 mole) of sodium acetate. Stirring in the cold was continued for 2 hr.; the precipitate was collected by filtration, washed with 30% aqueous alcohol and water, and dried, giving 26.1 g. (82%) of carbonyl cyanide *o*-dimethylaminophenylhydrazone in the form of an olive green solid, m.p. 114–115°. Recrystallization from isopropyl alcohol gave olive green crystals, m.p. 114–115°.

Anal. Calcd. for $C_{11}H_{11}N_5$: C, 61.95; H, 5.20; N, 32.84; mol. wt., 213.24. Found: C, 62.14; H, 5.22; N, 32.73; mol. wt., 212, 214 (ebullioscopically in benzene).

The ultraviolet spectrum (in acetonitrile) had a shoulder at 245 mμ (ϵ 8400) and λ_{max} 277 mμ (ϵ 3100) and 379 mμ (ϵ 16,700); the latter band trails into the visible region, ϵ_{450} 1400.

Reaction of Dicyanodiazomethane with Methanol.—A solution of 504 mg. of dicyanodiazomethane in 100.0 ml. of methanol was left standing at room temperature for 147 hr. The disappearance of the diazocompound, determined by ultraviolet spectroscopy, followed pseudo-first-order kinetics during the first 41 hr., the half-life being *ca.* 26 hr. Removal of the solvent and sublimation of the residue gave a 30% yield of carbonyl cyanide hydrazone, identified by its infrared spectrum.

Reaction of Dicyanodiazomethane with Isopropyl Alcohol.—A solution of 544 mg. of dicyanodiazomethane in 100.0 ml. of isopropyl alcohol (spectro grade) was left standing at room temperature for 5 days. The disappearance (ultraviolet spectrum) of the diazo compound followed pseudo-first-order kinetics (determined for the first 40 hr.) with a half-life of *ca.* 24 hr. The solvent was removed by evaporation under vacuum, the distillate being collected in a trap cooled with Dry Ice–methanol. Chromatography of the residue on Florisil gave 198 mg. (36% yield) of carbonyl cyanide hydrazone, eluted with methylene chloride. With benzene–methylene chloride (1:1) there was eluted 170 mg. of a pale yellow liquid of unknown structure. To the isopropyl alcohol distillate was added 15 ml. of a 2,4-dinitrophenylhydrazine solution. After standing at room temperature for 72 hr., the mixture was concentrated to *ca.* 40 ml. and poured onto ice. The filtrate and washings were extracted with methylene chloride until the aqueous layer was almost colorless; the dried extracts were concentrated to dryness and the residue was combined with the precipitate from above. Chromatography on Florisil gave 113 mg. (8% yield) of acetone 2,4-dinitrophenylhydrazone, m.p. and m.m.p. 15–126°.

Preparation of 1,1-Bis(ethoxycarbonyl)4,4-diphenyl-2,3-diazabutadiene. A. Directly from Benzophenone Hydrazone and Diethyl Mesoxalate.—A mixture of 16.46 g. (8.4 × 10^{-2} mole) of benzophenone hydrazone, 14.61 g. (8.4 × 10^{-2} mole) of diethyl mesoxalate, and 80 ml. of benzene was refluxed under a Dean–Stark trap for 18 hr. About 2 ml. of water was collected. The solvent was removed, the residue was dissolved in 70 ml. of hot ethanol, and the solution was seeded with a crystal of the product. The yield of 1,1-bis(ethoxycarbonyl)-4,4-diphenyl-2,3-diazabutadiene (yellow crystals), m.p. 76–77°, was 21.31 g. (72%). An analytical sample, m.p. 79–80°, was prepared by two recrystallizations from ethanol.

Anal. Calcd. for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95; mol. wt., 352.38. Found: C, 68.14; H, 5.57; N, 7.97; mol. wt., 353, 350 (ebullioscopic in benzene).

The ultraviolet spectrum (in cyclohexane) had λ_{max} 267 mμ (ϵ 17,400) and 310 mμ (sh) (ϵ 7200, trails into the visible spectrum, ϵ_{400} 410). The infrared spectrum (in KBr) showed CO at 1740 and 1715 cm.$^{-1}$.

B. From Benzophenone Triphenylphosphazine and Diethyl Mesoxalate.—To a stirred suspension of 7.93 g. (1.74 × 10^{-2} mole) of benzophenone triphenylphosphazine[27] was added, at 30–40° (no reaction occurred at 0°), a solution of 3.02 g. (1.74 × 10^{-2} mole) of diethyl mesoxalate in 10 ml. of THF. The phosphazine went into solution within *ca.* 30 min. Removal of the solvent gave 11.59 g. of a mixture of colorless crystals and a yellow oil. Chromatography of 2.05 g. of this mixture on Florisil (43 g.) gave 697 mg. of 1,1-bis(ethoxycarbonyl)-4,4-diphenyl-2,3-diazabutadiene (63% yield), eluted with methylene chloride and identified by comparison of its infrared spectrum with that of an authentic sample (see bove). THF–methylene chloride (3:7) eluted first a fraction of 600 mg. of a yellow semisolid, presumably a mixture of the mixed azine and triphenylphosphine oxide, followed by 544 mg. (72%) of pure triphenylphosphine oxide, identified by its infrared spectrum.

1,1,4-Triphenyl-4-cyano-2,3-diazabutadiene.—A solution of 5.103 g. (3.90 × 10^{-2} mole) of benzoyl cyanide and 17.80 g. (3.90 × 10^{-2} mole) of benzophenone triphenylphosphazine[27] in 100 ml. of THF was heated under reflux for 30 min. and then allowed to stand at room temperature for 3 days. Removal of the solvent gave 23.19 g. of an orange oil. Part of this product (20.14 g.) was dissolved in 50 ml. of hot ethanol; on cooling, a precipitate of yellow needles formed. Water (30 ml.) was added and the precipitate was filtered, washed with 70% aqueous alcohol, and dried, giving 8.93 g. (85%) of 1,1,4-triphenyl-4-cyano-2,3-diazabutadiene, m.p. 110–110.5°; recrystallization (ethanol) gave an analytical sample, m.p. 109.5–110.0°.

Anal. Calcd. for $C_{21}H_{15}N_3$: C, 81.53; H, 4.89; N, 13.59; mol. wt., 309.35. Found: C, 81.75; H, 5.12; N, 13.76; mol. wt., 299 (cryoscopically in benzene).

The ultraviolet spectrum (cyclohexane) had λ_{max} 338 mμ (ϵ 22,700) and shoulders at 280 mμ (ϵ 11,000) and 233 mμ (ϵ 12,800). The infrared spectrum (KBr) showed CN at 2220 (w) cm.$^{-1}$.

1,1,4-Triphenyl-4-cyano-2,3-diazabutadiene did not react with benzophenone hydrazone (no solvent) at 120° during 10 hr.

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