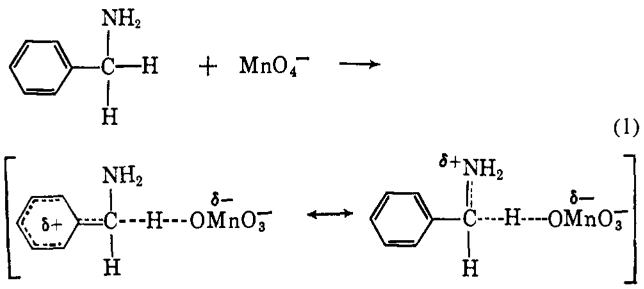
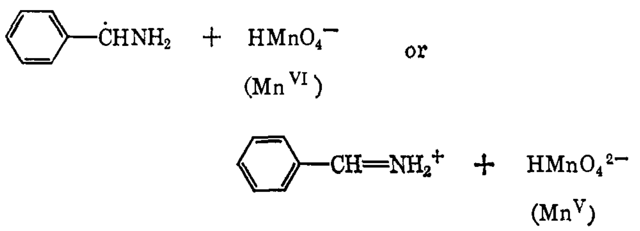


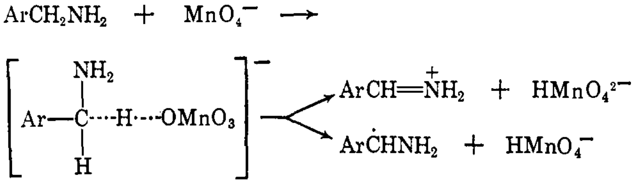
(1)

The fairly good $\rho\sigma^+$ correlation is also in agreement with hydride transfer since the positive charge in the protonated amine can be dispersed to the aromatic ring.[26]



The ρ^+ is quite small, however (−0.28), and furthermore three of the substituents (m-NO_2, p-NO_2, and m-CF_3) give much faster rates than their substituent constants would lead one to predict.

One can rationalize the activation due to p-NO_2 by saying that a hydrogen atom transfer also takes place in this case since the intermediate radical could disperse its odd electron to the substituent ($O_2NC_6H_4\dot{C}HNH_2 \longleftrightarrow \cdot O_2N{=}C_6H_4{=}CNNH_2$). The activation by m-NO_2 and m-CF_3 is more troublesome. Possibly the distinction between hydrogen atom and hydride ion transfer is not clear-cut. To be sure, one path leads to a radical intermediate and the other to a cation intermediate and this means that two distinct paths can be envisaged for the over-all reaction. However, the structure of the activated complex will be almost identical for the two paths and it seems preferable to consider a single activated complex whose decomposition to the two types of products is nicely balanced. The decomposition route would be influenced by many factors, including probability, vibrational effects in the activated complex, and the electronic effect of any substituents. The radical would be subject to immediate further oxidation (presumably to the imine conjugate acid) and the manganese species to disproportionation.



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(26) The odd electron may also be dispersed but whether a $\rho\sigma^+$ correlation would be expected is less certain, although precedents for such an effect do exist.[27]

(27) G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958); E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 394 (1960); G. A. Russell and R. C. Williamson, Jr., *ibid.*, **86**, 2357 (1964).

Dicyanocarbene[1]

Engelbert Ciganek

Contribution No. 1134 from the Central Research Department,
Experimental Station, E. I. du Pont de Nemours & Company Inc.,
Wilmington, Delaware. *Received October 4, 1965*

Abstract: Dicyanocarbene, generated thermolytically from dicyanodiazomethane, inserts into the primary, secondary, and tertiary C–H bonds of n-butane and isobutane in the relative ratios of 1:4.6:12.0. Addition of the carbene to *cis*- and *trans*-2-butene proceeds nonstereospecifically, the formation of nonstereospecific adducts increasing with increasing dilution of the butenes with cyclohexane. At high dilution, an identical mixture containing 70% *trans*- and 30% *cis*-2,3-dimethyl-1,1-dicyanocyclopropane is obtained from either of the two isomeric olefins. Addition of dicyanocarbene to acetylenes yields 3,3-dicyanocyclopropenes. The nmr spectra of some of the products are discussed.

Dicyanocarbene is of interest as a highly electrophilic divalent species.[2] Its study became feasible with the recent synthesis of dicyanodiazomethane.[3] The present paper describes the reactions of dicyanocarbene with saturated hydrocarbons and with olefinic and acetylenic compounds.

Results

Dicyanodiazomethane (**1**) loses nitrogen readily, either on heating to about 70°, or on irradiation with ultraviolet light. In view of the facile thermal decomposition, this method of generating dicyanocarbene was used almost exclusively. In the single exception, namely in the decomposition of dicyanodiazomethane in benzene,[1] both methods gave the same product in identical yields. No solvent could be found that did not react with dicyanocarbene. Reactions were thus carried out using the substrates as

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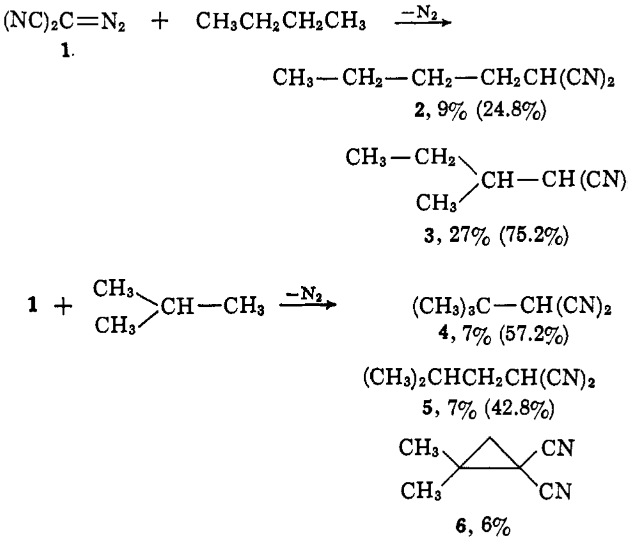
(1) A preliminary communication describing the addition of dicyanocarbene to aromatic hydrocarbons appeared in *J. Am. Chem. Soc.*, **87**, 652 (1965).

(2) For an excellent review on carbenes, see W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

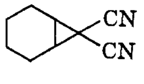
(3) E. Ciganek, *J. Org. Chem.*, **30**, 4198 (1965).

solvents. In the case of gaseous substrates, sufficiently high pressures were applied to ensure liquid phases at the decomposition temperature whenever possible.

Reactions with Saturated Hydrocarbons. Generation of dicyanocarbene in aliphatic hydrocarbons resulted in the formation of alkylmalononitriles; thus, with cyclohexane, cyclohexylmalononitrile was formed in 42% yield. In these reactions, yields were generally low, probably due to the virtual insolubility of dicyanodiazomethane in saturated hydrocarbons. The selectivity of dicyanocarbene in insertion reactions was determined by decomposing dicyanodiazomethane in *n*-butane and isobutane. The results are summarized below. The relative ratios of the insertion products, determined gas chromatographically, are given in parentheses; the values represent averages of two experiments in each case. After correction for the number of different types of bonds available, the relative rates for the insertion of dicyanocarbene into primary, secondary, and tertiary C–H bonds are calculated to be 1:4.6:12.0. The alkylmalononitriles **2**, **3**, **4**, and **5** were identified by comparison of their infrared spectra with those of authentic samples prepared by standard methods. The 1,1-dicyano-2,2-dimethylcyclopropane (**6**), isolated from the thermolysis of **1** in isobutane, had infrared and nmr spectra identical with those of the dicyanocarbene–isobutene adduct. The isobutane used contained less than 0.01% isobutene, and no enrichment of isobutene was observed in the recovered isobutane. At least three additional products of unknown structures were formed, in *ca.* 15% yield, in the thermolysis of dicyanodiazomethane in *n*-butane.



Reactions with Olefins. Decomposition of dicyanodiazomethane in olefins produced 1,1-dicyanocyclopropanes; insertion of dicyanocarbene into allylic C–H bonds occurred in the case of olefins with such bonds. Thermolysis of **1** in ethylene gave large amounts of black intractable polymeric solids in addition to 1,1-dicyanocyclopropane (18% yield), probably because the reaction was carried out above the critical temperature of ethylene. The cyclopropane was identical with an authentic sample prepared by dehydration of 1-cyanocyclopropanecarboxamide. Thermolysis of **1** in cyclohexene produced 7,7-dicyanonorcarane (**7**) and 2-cyclohexenylmalononitrile (**8**) in 61 and 24% yields, respectively; with tetramethylethylene as the substrate, the yields of addition product **9** and insertion product **10** were 54 and 40%, respectively. Addition of dicyanocarbene to the double bonds in *cis*- and *trans*-2-butene proceeded nonstereospecifically as shown in Table I. Neither the 2-butene nor the two 1,1-dicyano-2,3-dimethylcyclopropanes **11** and **12** were isomerized under the conditions of the thermolysis. On gas-phase pyrolysis at 300–500°, **11** and **12** rearranged to 2-butylidenemalononitrile, (**13**). Authentic samples of **11** and **12** were not available, but their structures followed from their nmr spectra (see the Experimental Section) and their mode of formation. The identities and stereochemistry of the insertion products **14** were not established rigorously; their nmr spectra (Experimental Section) were those expected for 2-butenylmalononitriles, and the fact that the two insertion products obtained from *cis*- and *trans*-2-butene had different retention times on gas chromatography indicated that little or no isomerization had taken place in the insertion step. In the experiments using cyclohexane as the diluent, the corrected ratios of addition to the 2-butenes to insertion into cyclohexane



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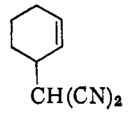

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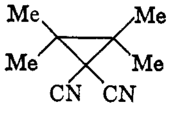

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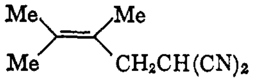

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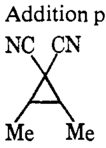
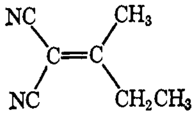
Table I. Addition of Dicyanocarbene to *cis*- and *trans*-2-Butene

Olefin	Dilution[a]	Addition products[b]  11	 12	Ratio of addition to insertion[c]
cis-2-Butene	Neat	92	8	92:8
	1:10	60	40	94:6
	1:100	30	70	>98:2[e]
trans-2-Butene	Neat	6	94	88:12[d]
	1:10	22	78	94:6
	1:100	30	70	>98:2[e]

[a] Ratio of 2-butene to cyclohexane. [b] Relative ratio determined gas chromatographically; uncorrected for possible differences in thermal conductivity. [c] Ratio of *cis*- and *trans*-2,3-dimethyl-1,1-dicyanocyclopropanes to 2-butenylmalononitriles. [d] The value of 12% includes an impurity of unknown structure which may not be an insertion product; see the Experimental Section. [e] No 2-butenylmalononitriles could be detected; limit of detection *ca.* 2%.



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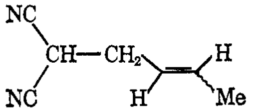
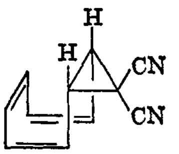


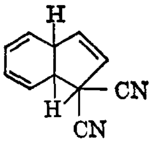
14

increased from *ca.* 4:1 in 10% dilution to *ca.* 15:1 in 1% dilution. These values are probably not very accurate because of fairly large possible errors in the dilution ratios (see the Experimental Section), but the observed trend to increased addition to insertion ratios with decreasing 2-butene concentrations is outside the error limits. Thermolysis of **1** in tetrachloroethylene gave 1,1-dicyano-2,2,3,3-tetrachlorocyclopropane in 29% yield; with butadiene, 1,1-dicyano-2-vinylcyclopropane was isolated in 25% yield. Dicyanocarbene added to both the aromatic and olefinic double bonds of styrene. The isomeric vinylnorcaradienes polymerized rapidly at room temperature and were not isolated; 1,1-dicyano-2-phenylcyclopropane was obtained in 32% yield.

Thermolysis of **1** in cyclooctatetraene at 80° produced a mixture of two isomeric adducts, tentatively assigned structures **15** and **16**, in 70 and 18% yields, respectively.



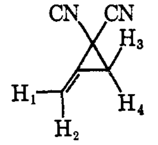
15



16

The ultraviolet spectrum of **15** ($\lambda_{max}^{cyclohexane}$ 242 mμ (ε 3400)) is that expected for the bicyclo[6.1.0]nonatriene chromophore.[4] Its nmr spectrum in perdeuterioacetone shows the two cyclopropyl protons as a just barely split singlet (width at half-height 1.9 cps) at τ 7.43 and the olefinic protons as a multiplet at τ 3.9 to 4.4. The spectrum is practically identical with that of 9,9-dichlorobicyclo[6.1.0]nonatriene.[4] Compound **15** rearranged to **16** on heating to 190° for 1 hr. The assignment of structure **16** to this product is based on the fact that 8,9-dihydroindenes have been obtained by thermal rearrangement of a number of bicyclo[6.1.0]-nonatrienes.[4–6] The ultraviolet spectrum of **16** ($\lambda_{max}^{cyclohexane}$ 218 mμ (ε 3900), 255 (4600), 264 (4400), and a shoulder at 274 (2400)) is similar to that of 1-ethoxycarbonyl-8,9-dihydroindene.[6] The nmr spectrum of **16** shows the two methine protons as fairly broad (widths at half-height 4 cps) singlets at τ 6.15 and 5.97, the olefinic protons on C_2 and C_3 as a doublet (separation 1.5 cps) at 4.53, and the four diene protons as a multiplet at 3.5 to 4.0. Apparent evidence against structure **16** is the observed failure of the product to undergo Diels–Alder addition with dimethyl acetylenedicarboxylate at 90° and the fact that neither palladium in boiling xylene nor 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in benzene at 80° effected dehydrogenation to give 1,1-dicyanoindene. However, it has been noted previously that proximity of a number of cyano groups tends to impart unusual properties to double bonds.[7] The rate of rearrangement of **15** to **16** was low at 160° and essentially zero at 80°. The fact that **16** was nevertheless isolated from the decomposition of dicyanodiazomethane in cyclooctatetraene at 80° may be explained by assuming that the initially formed vibrationally excited molecules of adduct **15** are only inefficiently deactivated by collision with the solvent.

Dicyanocarbene was found to add to allene to give the monoadduct **17** in 28% yield. The structure follows unambiguously from the nmr spectrum which shows a doublet, split into triplets, centered at τ 3.97 (H_1), a doublet split into triplets centered at 4.20 (H_2), and a doublet, split into doublets, at 7.57 (H_3 and H_4). The following splitting constants were derived. $J_{1,2} = 2.2$ cps, $J_{1,(3,4)} = 3.2$ cps, and $J_{2,(3,4)} = 2.7$ cps. The lowest field signal was assigned to H_1 since it is closer to the cyano groups than H_2, but these assignments may actually be reversed.



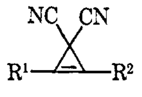
17

$(NC)_2C{=}N{-}N(COOEt)_2$

18

Thermolysis of dicyanodiazomethane in diethyl azodicarboxylate gave carbonyl cyanide N,N-diethoxycarbonylhydrazone (**18**) in 56% yield. The ultraviolet spectrum of **18** (λ_{max}^{MeCN} 283 mμ (ε 10,200) and 255 mμ (ε 6600)) rules out the diaziridine structure expected from addition of dicyanocarbene to the N–N double bond of the azodiester. Hydrazones analogous to **18** have been obtained previously in reactions of diazo compounds with diethyl azodicarboxylate, and the nature of the intermediate has been determined.[8]

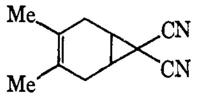
Reactions with Acetylenes. The 3,3-dicyanocyclopropenes **19**, **20**, and **21** were obtained in 11, 56, and 77% yields by thermolysis of dicyanodiazomethane in acetylene, methylacetylene, and dimethylacetylene. The low yield of **19** is in part due to the fact that, because of the hazards involved, the reaction was carried out in acetonitrile solution. The formation of small amounts of insertion products was observed in the reactions with methyl- and dimethylacetylene. The stability of the three cyclopropenes increases with increasing substitution; thus, **19** decomposed on attempted analysis by gas chromatography at 130° whereas **21** was recovered unchanged after heating to 150° for 6 hr. In the infrared spectrum of **19**, the carbon–carbon stretching band is found at 1670 cm^{-1}; two bands, at 1760 and 1825 cm^{-1} in **20**, and at 1880 and 1935 cm^{-1} in **21**, occur in the spectra of the substituted cyclopropenes.[9] Increasing substitution decreased the reactivity of the cyclopropenes in Diels–Alder additions to 2,3-dimethylbutadiene: **19** added rapidly at 76° to give the 7,7-dicyanonorcarene **22**;



19; $R^1{=}R^2{=}H$

20; $R^1{=}H$; $R^2{=}CH_3$

21; $R^1{=}R^2{=}CH_3$



22

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[4] T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **86**, 5194 (1964).

[5] E. Vogel, *Angew Chem.*, **73**, 548 (1961); E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Letters*, 673 (1963).

[6] K. F. Bangert and V. Boekelheide, *J. Am. Chem. Soc.*, **86**, 905 (1964).

[7] *Cf.* for instance the inactivity of 1,1,3,3-tetracyano-1,3,3a,7a-tetrahydroisobenzofuran in Diels–Alder additions: W. J. Linn and R. E. Benson, *ibid.*, **87**, 3657 (1965).

[8] E. Fahr, *Angew. Chem.*, **76**, 505 (1964); H. Staudinger and A. Gaule, *Ber.*, **49**, 1961 (1916).

[9] The large dependence on substitution of the band in the double-bond stretching region of cyclopropenes has been noted previously: K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961); W. von E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960); G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 99 (1963).

the reaction between the diene and **20** required heating to 120° and no reaction occurred when 2,3-dimethylbutadiene and **21** were heated to 150° for 6 hr.[10]

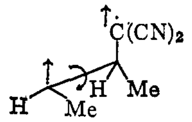
Discussion

While the intervention of free divalent species in α-elimination reaction is still subject to controversy in certain cases,[11,12] the intermediacy of carbenes in photolytic or thermolytic decompositions of diazo compounds is more generally accepted.[15] The possibility that the dicyanocyclopropanes isolated from the thermolysis of dicyanodiazomethane in olefins resulted from loss of nitrogen from initially formed pyrazolines is considered excluded by the isolation of insertion products from these reactions and by the consistent failure to obtain pyrazolines at temperatures just below the decomposition temperature of dicyanodiazomethane. This is in agreement with the finding[3] that dicyanodiazomethane is completely inactive as a 1,3-dipolarophile.

Dicyanocarbene displays moderate selectivity in its insertion reactions into carbon–hydrogen bonds; it is less selective than photolytically generated diethoxycarbonylcarbene, but more so than ethoxycarbonylcarbene.[16] Since singlet-to-triplet transition appears to occur at a rate comparable to that of addition and insertion reactions of dicyanocarbene (see below), part of the insertion products may be formed by a hydrogen abstraction–radical recombination mechanism involving triplet dicyanocarbene.[17] An indication for the intervention of triplet dicyanocarbene is the isolation of the cyclopropane **6** from the reaction of the carbene with isobutane. This product probably arises by the addition of dicyanocarbene to isobutene, formed by abstraction of hydrogen from the substrate by triplet dicyanocarbene followed by disproportionation of the resulting *t*-butyl radical.

The observed product composition in the thermolysis of dicyanodiazomethane in *cis*- and *trans*-2-butene[19] is consistent with increasing amounts of triplet dicyanocarbene forming and reacting as the medium is changed from pure olefin to a 1% olefin solution in cyclohexane.

Most collisions of the initially formed singlet carbene lead to addition in neat *cis*- and *trans*-2-butene and the amount of nonstereospecific products is small. With added cyclohexane, which reacts with dicyanocarbene at a lower rate than the butenes, collisional deactivation allows singlet-to-triplet transition to become competitive with singlet addition. The observed identical ratios of addition products obtained from either olefin in high dilution indicate that only the triplet is involved to a significant amount in these cases. In addition, it



23

shows that rotation around the C–C bond in the diradical **23**, the initial adduct of triplet dicyanocarbene to *cis*- (as pictured) or *trans*-2-butene, is rapid compared to spin inversion and recombination. The 30:70 ratio of **11**:**12** is a measure of the equilibrium concentrations of the rotomers of **23**. The observation that the relative rate of insertion into the C–H bonds of both cyclohexane and the two 2-butenes decreases as increasing amounts of triplet are formed shows that the singlet is more efficient in net insertions, or less efficient in net additions, than the triplet.

The ground state of dicyanocarbene thus is a triplet, as expected on the basis of Skell's rationalizations,[20] and as found experimentally by observation of the epr spectrum of dicyanocarbene generated photolytically at low temperatures.[21] The above explanation assumes spin conservation in the thermolytic formation of dicyanocarbene from dicyanodiazomethane;[22] it is also based on the notion[23] that singlet carbenes add stereospecifically, and triplet carbenes nonstereospecifically, to double bonds. The dilution experiments seem to bear out this latter hypothesis.

Nmr Spectra

The reactions of dicyanocarbene yielded a number of compounds, the nmr spectra of which are of general interest. Although the spectra have not been analyzed to determine the effect of two cyano groups on the coupling constants in cyclopropanes,[24] some observations on the chemical shifts in these compounds are reported here.[25] Secondary protons in 1,1-dicyanocyclopropanes absorb at τ 7.5 to 8.5, ranging from 8.57 in neat 1,1-dicyanocyclopropane (**24**) to 7.57 in 1,1-dicyano-2-methylenecyclopropane. Tertiary protons occur at τ 6.5 to 8.25, depending on the nature and stereochemistry of the substituents. Thus, the tertiary

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[10] In the case of 1,2-diphenylcyclopropenes, increasing substitution on C-3 also decreases dienophilic reactivity: M. A. Battiste, *Tetrahedron Letters*, 3795 (1964).

[11] This aspect of carbene chemistry has been reviewed by W. Kirmse, *Angew. Chem.*, 77, 1 (1965).

[12] The formation of 1,1-dicyano-2,2,3,3-tetramethylcyclopropane by treatment of bromomalononitrile with triethylamine in the presence of tetramethylethylene has recently been postulated to proceed by way of dicyanocarbene.[13] This species has also been mentioned as an intermediate by E. Müller and co-workers,[14] but no details as to its generation were given.

[13] J. S. Swensen and D. J. Renaud, *J. Am. Chem. Soc.*, **87**, 1394 (1965).

[14] H. D. Spanagel and E. Müller, quoted by E. Müller, *et al.*, *Tetrahedron*, **21**, 227 (1965).

[15] The concept of free divalent species as intermediates in the decomposition of diazo compounds in condensed phases has recently also come under attack: G. v. Bünau, P. Potzinger and G. O. Schenck, *Tetrahedron*, **21**, 1293 (1965).

[16] W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **83**, 1989 (1961).

[17] In analogy to methylene,[18] only singlet dicyanocarbene is assumed to be capable of one-step insertion into C–H bonds.

[18] K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *J. Am. Chem. Soc.*, 84, 1015 (1962).

[19] The dilution experiments were suggested by Professor P. S. Skell, to whom we are also indebted for helpful discussions. After this work had been completed, similar observations were reported for the addition reactions of fluorenylidene and carbethoxynitrene: M. Jones, Jr., and K. R. Rettig, *ibid.*, **87**, 4013 (1965); W. Lwowski and J. S. McConaghy, Jr., *ibid.*, **87**, 5490 (1965).

[20] R. M. Ettner, H. S. Skovronek, and P. S. Skell, *ibid.*, **81**, 1008 (1959); P. S. Skell and J. Klebe, *ibid.*, **82**, 247 (1960).

[21] E. Wasserman, L. Barash, and W. A. Yager, *ibid.*, **87**, 2075 (1965).

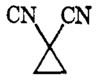
[22] Evidence for the direct formation of both singlet and triplet propargylene in the condensed-phase *photolysis* of the corresponding diazo compound has recently been presented: J. V. Gramas, Ph.D. Thesis, The Pennsylvania State University, 1965; *cf.* R. A. Bernheim, R. J. Kempf, J. V. Gramas, and P. S. Skell, *J. Chem. Phys.*, 43, 196 (1965).

[23] P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956); *cf.*, however, P. P. Gaspar and G. S. Hammond, ref 2, Chapter 12.

[24] (a) T. Schaefer, F. Hruska, and G. Kotowycz, *Can. J. Chem.*, 43, 75 (1965); (b) S. L. Manatt, D. D. Elleman, and S. J. Brois, *J. Am. Chem. Soc.*, **87**, 2220 (1965), and references cited there.

[25] All spectra were determined in $CDCl_3$ solution unless stated otherwise.

cyclopropyl protons in 7,7-dicyanonorcaradienes[1] absorb at τ 6.5 to 7, the ones in the cyclooctatetraene adduct **15** at 7.3. The corresponding signals occur at τ 7.87 in *cis*-1,1-dicyano-2,3-dimethylcyclopropane (**11**) and at 8.25 in the *trans* isomer **12**. The two geminal cyano groups thus cause a downfield shift of *ca.* τ 1–1.5 units. The ring protons in neat methyl 1-cyano-1-cyclopropylcarboxylate (**25**) occur at τ 8.42, actually at somewhat lower field than in 1,1-dicyanocyclopropane. It is of interest to note that the signal due to the cyclopropyl protons in **25** is a sharp singlet, even though one should expect an A_2B_2 pattern. The shifts of the two nonequivalent secondary protons in 1,1-dicyano-2-phenylcyclopropane also are almost identical. The C^{13}–H coupling constant in **24** is 173 cps, that in **25** is 170 cps. In both cases, the C^{13} satellites are triplets with indications of further splitting and with apparent coupling constants of 9 cps. The correlation of $J_{C^{13}-H}$ with s character[26] would assign 35% s character to the C–H bonds in **24**, a somewhat higher value than usually observed in cyclopropanes.[27]



24

25

The two vinylic protons in 3,3-dicyanocyclopropene (**19**) absorb at τ 2.78, the one in the methyl derivative **20** at 3.31 (both neat). This compares with τ 2.99 in the parent cyclopropene.[28] The C_{13}–H coupling constant in **19** is 255 cps, which would correspond[26] to 51% s character. $J_{C^{13}-H}$ in 3,3-dimethylcyclopropene has been reported[29] to be 220 cps. The C^{13} satellites in **19** are just barely split into doublets, with $J_{1,2} = 0.4$ cps. Although it may not be permissible, in view of the electronegativity of the substituents, to conclude that $J_{1,2}$ in cyclopropene itself will be in the same range, the small value of the vicinal coupling constant in **19** correlates well with the reported decrease of $J_{1,2}$ in cyclic olefins with decreasing ring size.[30–32] Thus, $J_{1,2}$ is 10.8 cps in cycloheptene,[32] 9.6 cps in cyclohexene,[31] 5.4 cps in cyclopentene,[31] and 2.7 cps in cyclobutene.[33] It has been suggested,[33] however, that $J_{1,2}$ may pass zero on going from cyclopentene to cyclobutene; a continuing trend would then give cyclopropene a $J_{1,2}$ more negative than −2.7 cps. A value of 0.5–1.5 cps for $J_{1,2}$ in 3,3-dimethylcyclopropene has been estimated;[31] direct determination of this coupling constant was complicated by the interaction of the vinylic with the methyl protons.

Experimental Section[34]

Thermolysis of Dicyanodiazomethane in Cyclohexane. Dicyanodiazomethane, prepared from 934 mg of carbonyl cyanide hydrazone,[3] was suspended in 50 ml of cyclohexane. The vigorously stirred mixture was heated slowly to the boiling point, then refluxed until nitrogen evolution ceased. The solvent was removed (rotary evaporator), leaving 1.373 g of a dark liquid. Short-path distillation (80° bath temperature, 0.1 mm pressure) gave 630 mg (42% yield) of cyclohexylmalononitrile, identified by comparison of its infrared spectrum with that of an authentic sample (see below).

Cyclohexylmalononitrile. A solution of 5.93 g of cyclohexylidenemalononitrile[35] in 50 ml of ethyl acetate was hydrogenated with 0.9 g of palladium-on-charcoal (10%) catalyst. The hydrogenation was still proceeding at a fairly rapid rate when it was stopped after 1.17 mole equiv had been taken up. Removal of the solvent from the filtered solution gave 5.85 g of a colorless oil, the infrared spectrum of which displayed strong N–H absorption at 3500 and 3400 cm^{-1}; some unreacted starting material was also present. Chromatography of 5.60 g of the product over alumina (160 g, Woelm, neutral, activity 1, elution with 500 ml of benzene–*n*-hexane 9:1) followed by distillation gave 2.32 g (40%) of cyclohexylmalononitrile, bp 81–83° (0.3 mm), n^{26}D 1.4663–1.4667.

Anal. Calcd for $C_9H_{12}N_2$: C, 72.93; H, 8.16; N, 18.90. Found: C, 72.87; H, 8.19; N, 18.61.

The infrared spectrum showed CN at 2250 cm^{-1}. The nmr spectrum (in $CDCl_3$) showed a doublet centered at τ 6.24 (J = 5.5 cps, 1 H) and two broad bands at 8.1 and 8.7 (11 H).

Thermolysis of Dicyanodiazomethane in *n*-Butane. A sample of dicyanodiazomethane, prepared from 836 mg of carbonyl cyanide hydrazone,[3] was placed in a 400-ml stainless steel cylinder. *n*-Butane (200 g, 99% purity) was added, and the cylinder was heated to 70° for 1 hr. The excess butane was allowed to escape slowly, and the product was taken up in tetrahydrofuran. The solution was concentrated to *ca.* 3 ml by distillation and then analyzed by gas chromatography[34] at 160°. The volatile components consisted of 70.5% of a mixture of *sec*-butylmalononitrile (**3**) and *n*-butylmalononitrile (**2**), and 29.5% of at least three compounds having longer retention times. The average ratio of **3**:**2** (three determinations) was 75.9:24.1. A mixture of 71.3% *sec*-butylmalononitrile and 28.7% *n*-butylmalononitrile gave peak areas of 70.2 and 29.8%, respectively (average of four determinations), giving rise to correction factors of 1.016 for *sec*- and 0.963 for *n*-butylmalononitrile. The corrected product ratio was thus 76.9% of **3** to 23.1% of **2**. Short-path distillation of the products at 80° bath temperature and under 1.3 mm of pressure gave 575 mg of a pale yellow oil. The yield of *n*-butylmalononitrile thus was 9%, that of *sec*-butylmalononitrile 27%. In a second experiment, the corrected ratio of **3**:**2** was 73.5:26.5. The *sec*-butylmalononitrile and *n*-butylmalononitrile were collected by preparative gas chromatography[34] at 170° and identified by comparison of their infrared spectra with those of authentic samples (see below).

***n*-Butylmalononitrile (2).** Using the method of Russell and Hitchins,[36] diethyl *n*-butylmalonate was converted in 51% over-all yield into *n*-butylmalononitrile, bp 106° (12 mm), n^{27}D 1.4245 (lit[37] bp 46–48° (0.01 mm), n^{20}D 1.4292). The nmr spectrum (neat) shows a triplet centered at τ 6.12 (J = 6.5 cps, 1 H) and complex multiplets at 8–9.2 (9 H).

***sec*-Butylmalononitrile (3).** A mixture of 79 g (1.1 moles) of methyl ethyl ketone, 66 g (1.0 mole) of malononitrile, 1 g of β-alanine, 10 ml of glacial acetic acid, and 250 ml of benzene was heated under reflux under a Dean–Stark trap for 5 hr. *Ca.* 20 ml of water was collected. The cooled mixture was washed with water (five 50-ml portions) and concentrated sodium chloride solution, dried, and distilled. The yield of 2-butylidenemalononitrile, bp 62° (1.0 mm), n^{25}D 1.4685 (lit[38] bp 102° (8 mm)), was 107 g (89%).

Anal. Calcd for $C_7H_8N_2$: C, 69.97; H, 6.71; N, 23.32. Found: C, 69.79; H, 6.88; N, 23.15.

The ultraviolet spectrum showed $\lambda_{max}^{cyclohexane}$ 232 mμ (ε 12,600). The nmr spectrum (neat) showed a singlet at τ 7.68 (3 H), a triplet centered at 8.72 (J = 8 cps. 3 H), and a quartet centered at 7.35

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[26] N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959); J. N. Shoolery, *ibid.*, **31**, 1427 (1959).

[27] $J_{C^{13}-H}$ in cyclopropane is 161 cps;[26] in the series cyclopropane, ethylenimine, and ethylene oxide, $J_{C^{13}-H}$ increases with increasing electronegativity of the heteroatom.[24b]

[28] K. B. Wiberg and B. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961); measured in 15% carbon tetrachloride solution.

[29] G. L. Closs, *Proc. Chem. Soc.*, 152 (1962).

[30] O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963).

[31] P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963).

[32] G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963).

[33] S. Borcić and J. D. Roberts, *ibid.*, **87**, 1056 (1965).

[34] Melting points and boiling points are uncorrected. Nmr spectra were measured with a Varian A-60 spectrometer, infrared spectra with a Perkin-Elmer 21 spectrometer, and ultraviolet spectra with a Cary 14 spectrometer of the Applied Physics Corp. Gas chromatographic analyses were carried out using 200 × 0.6 cm Pyrex or copper columns containing 30% of Dow Corning FS 1265 silicone oil on 60–80 mesh Chromosorb P, unless otherwise specified. For preparative gas chromatography, 3.6 m × 0.9 cm copper columns containing the same stationary phase were used. The samples were eluted with helium and detected with a thermal conductivity cell.

[35] A. C. Cope and K. E. Hoyle, *J. Am. Chem. Soc.*, **63**, 733 (1941).

[36] P. B. Russell and G. H. Hitchins, *ibid.*, **74**, 3443 (1952); P. B. Russell, *ibid.*, **72**, 1853 (1950).

[37] V. Schmidt and H. Kubitzek, *Chem. Ber.*, **93**, 866 (1960).

[38] J. D. Kendall, H. G. Suggate, and J. H. Mayo, British Patent 704, 770 (1954); *Chem. Abstr.*, **48**, 9850 (1954).

(J = 8 cps, 2 H). There is some secondary splitting in both the CH_2 and CH_3 of the ethyl group.

A solution of 84 g of 2-butylidenemalononitrile in 200 ml of ethanol was hydrogenated in a Parr shaker, using 3 g of palladium on carbon (10%) as the catalyst. After 24 hr, about 130% of 1 mole of hydrogen had been taken up and further uptake was very slow. The mixture was filtered, ice and ether (200 ml) were added to the filtrate, the mixture was shaken, and the layers were separated. The aqueous layer was extracted with 200 ml of benzene. The combined extracts were washed with 50 ml of 10% hydrochloric acid, three 50-ml portions of water, and concentrated sodium chloride solution, and dried ($MgSO_4$). Distillation gave 33.8 g of a fraction boiling at 61–70° (1.0 to 0.8 mm), $n^{26}D$ 1.4277. This material showed strong absorption at 3300 cm^{-1} in the infrared spectrum due to an N–H containing impurity, which could not be removed by redistillation. The material was passed through a column of 100 g of aluminum oxide (Woelm, neutral, activity 1) and eluted with 50 ml of cyclohexane followed by 400 ml of benzene. Distillation gave 24.1 g (28% yield) of pure *sec*-butylmalononitrile, bp 70° (2.0 mm), $n^{26}D$ 1.4255.

Anal. Calcd for $C_7H_{10}N_2$: C, 68.82; H, 8.25; N, 22.93. Found: C, 69.21; H, 8.21; N, 22.90.

The nmr spectrum (neat) showed a doublet centered at τ 6.17 (J = 5 cps, 1 H), multiplets at 7.6 to 8.3 (1 H) and 8.3 to 8.7 (2 H), a doublet centered at 8.85 (J = 6.5 cps, 3 H), and a triplet, split further, centered at 9.05 (J = 6.5 cps, 3 H).

Thermolysis of Dicyanodiazomethane in Isobutane. A sample of dicyanodiazomethane,[3] prepared from 1.47 g of carbonyl cyanide hydrazone, was decomposed in isobutane and the products were analyzed as described for the thermolysis of *n*-butane (see above). The volatile products contained 71% of a mixture of *t*-butylmalononitrile (**4**) and isobutylmalononitrile (**5**), 25% of 1,1-dicyano-2,2-dimethylcyclopropane (**6**), and 4% of two unidentified products. The ratio of **4**:**5** (average of three determinations) was 56.5:43.5. Correction factors for an authentic mixture of 52.5% **4** and 47.5% **5** were found to be 1.027 and 0.971, respectively. The corrected ratio of *t*-butylmalononitrile to isobutylmalononitrile in the product was thus 57.9:42.1. Short-path distillation gave 375 mg of a colorless oil. The yields were thus: *t*-butylmalononitrile, 7%; isobutylmalononitrile, 7%; and 1,1-dicyano-2,2-dimethylcyclopropane, 6%. In a second experiment, the corrected ratio of **4**:**5** was 56.5:43.5. In a third run, isobutane of high purity (Phillips research grade, 99.97%) was used. Gas chromatographic analysis of the isobutane before and after pyrolysis showed the presence of less than 0.01% of isobutene. The yield of the cyclopropane **6** was the same as in the first two experiments. Products **4**, **5**, and **6** were isolated by preparative gas chromatography[34] and identified by their infrared spectra.

***t*-Butylmalononitrile (4).** To a solution of 0.65 mole of methylmagnesium iodide in 500 ml of ether (Arapahoe Chemical Co.) was added. over a period of 1 hr, a solution of 51.0 g (0.48 mole) of isopropylidenemalononitrile[35] in 150 ml of benzene. The mixture was then heated under reflux for 1 hr, poured onto ice, and acidified with 25% sulfuric acid. The aqueous layer was extracted with benzene (three 50-ml portions), and the combined ether layer and benzene extracts were washed with water, 5% sodium bicarbonate solution, and concentrated sodium chloride solution, then dried. Distillation gave 28 g (48%) of *t*-butylmalononitrile, bp 90–100° (11–20 mm). The yield is by no means optimal since because of the high melting point considerable difficulties were encountered in the distillation, which was stopped before all the product had been collected. Crystallization from *n*-hexane gave a waxy solid which changed to a free-flowing liquid at 85° (lit[39] mp 84°).

Anal. Calcd for $C_7H_{10}N_2$: C, 68.82; H, 8.25; N, 22.93. Found: C, 69.17; H, 8.24; N, 23.08.

The nmr spectrum (in $CDCl_3$) shows singlets at τ 6.45 (1 H) and 8.80 (9 H).

Isobutylmalononitrile (5). Using the procedure described for the preparation of *n*-butylmalononitrile, diethyl isobutylmalonate was converted to isobutylmalononitrile in 44% over-all yield. The product had bp 103° (14 mm), $n^{25}D$ 1.4234 (lit[40] bp 222°). The nmr spectrum (neat) showed a triplet centered at τ 6.18 (J = 7 cps, 1 H); a multiplet centered at 8.2 (3 H), and a doublet centered at 9.05 (J = 5.5 cps, 6 H).

Thermolysis of Dicyanodiazomethane in Ethylene. A mixture of 1.890 g of dicyanodiazomethane and 80 g of ethylene, contained in a 400-ml stainless steel cylinder, was heated to 70° for 1 hr. The cylinder was rinsed out with tetrahydrofuran; there was a large amount of a black insoluble solid. Removal of the solvent and short-path distillation of the residue (0.2 mm, 80° bath temperature) gave 386 mg of a yellow oil containing 86% of 1,1-dicyanocyclopropane as determined by gas chromatography[34] at 140°, yield 18%. A sample of the cyclopropane was isolated by preparative gas chromatography and identified by comparison of its infrared spectrum with that of an authentic sample (see below).

1,1-Dicyanocyclopropane. An intimate mixture of 7.57 g of finely powdered 1-cyano-1-cyclopropanecarboxamide[41] and 30 g of phosphorus pentoxide was heated to 165–170° under 8–10 mm of pressure for 1 hr; the distillate (3.78 g) was collected in a trap cooled with Dry Ice–acetone. Redistillation gave 3.45 g (54% yield) of 1,1-dicyanocyclopropane, bp 76° (5.0 mm), $n^{25}D$ 1.4460.

Anal. Calcd for C_5H_4N: C, 65.20; H, 4.38; N, 30.42. Found: C, 65.22; H, 4.63; N, 30.60.

The nmr spectrum (neat) showed a singlet at τ 8.57. The C^{13} satellites were separated by 173 ± 1 cps. They were triplets, the center components of which were split further. Separation of the two outer components of the triplets was 18.4 cps. The C^{13} satellites of methylene chloride, used as external standard, were separated by 177.7 ± 0.5 cps (lit[42] 178.24 cps).

Thermolysis of Dicyanodiazomethane in Isobutene. Using the procedure described for *n*-butane, dicyanodiazomethane, prepared[3] from 2.206 g of carbonyl cyanide hydrazone, was heated to 70° with 100 ml of isobutene for 1 hr. Short-path distillation (0.5 mm, 70° bath temperature) gave 1.85 g of a colorless semisolid, which was shown by gas chromatography[34] at 168° to be a mixture of 92% (60% yield) 1,1-dicyano-2,2-dimethylcyclopropane and 8% (5% yield) of a second product believed to be 2-methyl-2-propenylmalononitrile (multiplets of equal intensities at τ 4.7 and 5.0 in the nmr spectrum). Low-temperature crystallization from methanol gave pure 1,1-dicyano-2,2-dimethylcyclopropane in the form of colorless crystals, mp 39–40°.

Anal. Calcd for $C_7H_8N_2$: C, 69.97; H, 6.71; N, 23.32. Found: C, 70.07; H, 6.96; N, 23.57.

There was only end absorption in the ultraviolet spectrum. The nmr spectrum (in $CDCl_3$) showed sharp singlets at τ 8.34 (2 H) and 8.54 (6 H).

Thermolysis of Dicyanodiazomethane in Neat *cis*-2-Butene. A sample of 1.077 g of dicyanodiazomethane was placed in a 400-ml stainless steel cylinder. One hundred grams of *cis*-2-butene (Matheson CP grade, *ca.* 99.6% pure by gas chromatography, the 0.4% impurity probably being the *trans* isomer as judged by its retention time) was added and the cylinder was heated to 70° for 1 hr. The excess *cis*-2-butene was allowed to evaporate slowly; gas chromatography of the effluent gases showed that no isomerization had taken place. Short-path distillation of the residue gave 1.019 g of a liquid boiling at *ca.* 45–50° (0.3 mm). Gas chromatography[34] (at 130°) of the products before and after distillation showed the presence of three compounds in the ratio 8:7:85 (in the order of increasing retention times). They were isolated by preparative gas chromatography[34] at 160°. The 8% component (liquid) showed bands in the infrared spectrum at 3070, 2280, and 1660 cm^{-1}, among others; its nmr spectrum showed a multiplet at τ 3.8 to 4.8 (2 H), a triplet centered at 6.22 (J = 7 cps, 1 H), a triplet centered at 7.17 (2 H), and a doublet centered at 8.24 (J = 6 cps, 3 H). The data strongly suggest this compound to be 2-butenylmalononitrile (presumably *cis*), yield 6%. The infrared spectrum of the 7% component (colorless solid) was identical with that of *trans*-2,3-dimethyl-1,1-dicyanocyclopropane (see below, yield 5%). Trap-to-trap distillation of the 85% component gave a colorless solid, mp 30–32°.

Anal. Calcd for $C_7H_8N_2$: C, 69.97; H, 6.71; N, 23.32. Found: C, 69.91; H, 6.96; N, 22.99.

The infrared spectrum (melt) showed bands at 2990, 2950, 2900, 2250, 1610 (weak), 1470, 1460, 1395, 1090, 1075 1050, 1005, and 795 cm^{-1}, among others. The band at 1610 cm^{-1} and a weak band at 233 mμ in the ultraviolet spectrum were probably due to *ca.* 1% (from the extinction coefficient) of 2-butylidenemalononitrile formed by thermal rearrangement during isolation. The nmr spectrum ($CDCl_3$) shows a doublet centered at τ 8.73 (J = 6 cps, shoulders on the insides, 6 H) and a ten-band symmetrical multiplet centered at 7.87 (2 H). These data suggest *cis*-2,3-dimethyl-1,1-dicyanocyclopropane as the structure of the 85% component;

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[39] P. Boldt and L. Schulz, *Naturwissenschaften*, **51**, 288 (1964).

[40] P. Henry, *Jahresber. Fortschr. Chem.*, 640 (1889).

[41] H. C. H. Carpenter and W. H. Perkin, *J. Chem. Soc.*, **75**, 921 (1899).

[42] G. V. D. Tiers, *J. Phys. Chem.*, **64**, 373 (1960).

yield 66%; ratio of *cis*-:*trans*-2,3-dimethyl-1,1-dicyanocyclopropane 12.1:1. In a second run, this ratio was 12.5:1.

Thermolysis of Dicyanodiazomethane in Neat *trans*-2-Butene. Dicyanodiazomethane (1.642 g) was decomposed in *trans*-2-butene (Matheson CP, containing *ca.* 0.5% of the *cis* isomer) as described above for *cis*-2-butene. Analysis of the effluent gas showed again that no isomerization of the *trans*-2-butene had taken place. Short-path distillation gave 1.800 g of a colorless liquid, bp *ca.* 45-50° (0.4 mm); gas chromatography before and after distillation showed the presence of three components in the ratio 14:81:5 (in the order of increasing retention times). The 14% component had a retention time *ca.* 2 min shorter than the 8% component in the products from *cis*-2-butene. The products were isolated by gas chromatography[34] at 160°. The 14% component (colorless liquid) showed bands at 3050, 2280, and 1660 cm^{-1}, among others, in the infrared spectrum. The nmr spectrum (in $CDCl_3$) showed a multiplet at τ 3.8 to 4.6 (2 H), a triplet (J = 6.5 cps) centered at 6.21, a triplet (J = 6.5 cps) centered at 7.30 (2 H), and a doublet (J = 5 cps) centered at 8.22 (3 H), in agreement with *trans*-2-butenylmalononitrile being the structure of this compound. Additional fairly strong bands at τ 8.7 to 9.1 must have been due to the presence of an impurity. The 5% component (colorless solid) had an infrared spectrum identical with that of *cis*-2,3-dimethyl-1,1-dicyanocyclopropane (4% yield). Trap-to-trap distillation of the 81% component gave a colorless solid, mp 28-29°.

Anal. Calcd for $C_7H_8N_2$: C, 69.97; H, 6.71; N, 23.32. Found: C, 70.09; H, 6.74; N, 23.27.

The infrared spectrum (melt) showed bands at 2990, 2950, 2900, 2250, 1470, 1455, 1390, 1090, 1055, 1005, 940, and 830 cm^{-1}, among others. There was only end absorption in the ultraviolet spectrum. The nmr spectrum (in $CDCl_3$) showed a seven-band multiplet at τ 8.1 to 8.4 (2 H) and an unsymmetrical doublet (J = 5 cps) centered at 8.63 (6 H). These data are in agreement with the structure assignment of *trans*-2,3-dimethyl-1,1-dicyanocyclopropane to the 81% component; yield 68%; ratio of *trans*-:*cis*-2,3-dimethyl-1,1-dicyanocyclopropane 16.2:1. In a second run, this ratio was 16.0:1.

Thermolysis of Dicyanodiazomethane in *cis*- and *trans*-2-Butene in the Presence of Cyclohexane. Mixtures of 400-600 mg of dicyanodiazomethane and 150 ± 1 g (1.79 moles) of distilled cyclohexane were placed in 400-ml stainless steel cylinders. *cis*- or *trans*-2-butene (10 ± 1 g, 0.18 mole or 1 ± 0.1 g, 0.018 mole) was added and the mixtures were heated to 70° for 1 hr. The cyclohexane was removed and the residues were analyzed as described for the runs in the neat butenes. The residues were short path distilled. Yields (2-butene, dilution, per cent *trans*-2,3-dimethyl-1,1-dicyanocyclopropane, per cent *cis*-2,3-dimethyl-1,1-dicyanocyclopropane, per cent cyclohexylmalononitrile): *trans*, 1:10, 12, 4, 41; *trans*, 1:100, 5, 2, 40; *cis*, 1:10, 6, 10, 40; *cis*, 1:100, 4, 1, 49. The yields are rounded off; the accurate ratios of **11**:**12** are listed in Table I. The cyclopropanes **11** and **12** were isolated and identified by their infrared spectra in all runs except in the thermolysis of dicyanodiazomethane in *trans*-2-butene:cyclohexane 1:100.

Thermal Stability of *cis*- and *trans*-2,3-Dimethyl-1,1-dicyanocyclopropane. Pure samples of the two isomers were heated to 120° for 2 hr. Gas chromatographic analysis showed that no isomerization had occurred; the limit of detection of the other isomer was below 1% in each case.

Pyrolysis of *cis*- and *trans*-2,3-Dimethyl-1,1-dicyanocyclopropane. The samples (10 μl) were injected into a pyrolysis column packed with 20-mesh quartz chips. The column was connected to a 1-m gas chromatography column packed with cyanoethylated pentaerythritol on firebrick (for the analysis of the *cis* isomer and its pyrolysis product) or tricresyl phosphate on firebrick (for the analysis of the *trans* isomer and its product). The column temperature was 162° in both cases. The contact times were *ca.* 0.2-0.3 min. *cis*-2,3-Dimethyl-1,1-dicyanocyclopropane (which contained 7% of the *trans* isomer and 8% of 2-butenylmalononitrile) was unaffected at a pyrolysis temperature of 225°. Starting at *ca.* 300°, 2-butylidenemalononitrile was observed in addition to unreacted starting material; at 450° the ratio of unreacted cyclopropane to product was 5:95. At 500°, complete conversion was obtained, but the product partially decomposed further; at 600°, 2-butylidenemalononitrile was also completely absent. The infrared spectrum of the product collected at a pyrolysis temperature of 450° was that of 2-butylidenemalononitrile with additional bands at 1780 (w), 1550 (m), 1230 (m), 1050 (m), 980 (s), and 830 cm^{-1} (s).

trans-2,3-Dimethyl-1,1-dicyanocyclopropane (containing 5% of the *cis* isomer and 13% of 2-butenylmalononitrile) also was unaffected at 225°. Rearrangement had occurred to the extent of 83% at 450°; the infrared spectrum of the product was that of 2-butylidenemalononitrile with additional bands at 1050, 940, and 890 cm^{-1}.

Thermolysis of Dicyanodiazomethane in Tetramethylethylene. A suspension of 580 mg of dicyanodiazomethane in 50 ml of tetramethylethylene was heated slowly to the boiling point and then refluxed for 30 min. The calculated amount of nitrogen was evolved. Most of the solvent was removed by distillation, and the residue was chromatographed over 10 g of Florisil. The material eluted with 15 ml of benzene and then 150 ml of methylene chloride was a pale yellow oil (after removal of the solvents) which weighed 917 mg. Gas chromatography[34] at 173° showed its major components to be two compounds (41 and 55%), which were separated by preparative gas chromatography. The 41% component was identified as 2,3-dimethyl-2-butenylmalononitrile by comparison of its infrared spectrum with that of an authentic sample (see below). The 55% component (1,1-dicyano-2,2,3,3-tetramethylcyclopropane) was a solid, mp 51-52°, after two recrystallizations from *n*-hexane (lit[13] mp 51.5-52.0°).

Anal. Calcd for $C_9H_{12}N_2$: C, 72.93; H, 8.16; N, 18.90; mol wt, 148.20. Found: C, 73.06; H, 8.37; N, 18.98; mol wt., 162, 153.

The nmr spectrum (in $CDCl_3$) showed only one sharp singlet at τ 8.60. In the ultraviolet spectrum (in cyclohexane) only end absorption, ϵ_{210} 98, is observed. These data unambiguously establish the structure of 1,1-dicyano-2,2,3,3-tetramethylcyclopropane for the 55% component. The total yields were: 2,3-dimethyl-2-butenylmalononitrile, 40%; 1,1-dicyano-2,2,3,3-tetramethylcyclopropane, 54%. The yields are based on the assumption that gas chromatographic analysis showed all components of the crude product mixture. The nmr spectrum of the crude product mixture supports this assumption, since it showed only the bands due to the two major identified compounds (ratio 42:58).

2,3-Dimethyl-2-butenylmalononitrile. A mixture of 100 g (0.56 mole) of N-bromosuccinimide, 50 g (0.60 mole) of tetramethylethylene, 250 ml of carbon tetrachloride, and 200 mg of benzoyl peroxide was heated under reflux for 4 hr. The mixture was irradiated with a G.E. sunlamp for the last 2 hr. Distillation of the filtered solution gave 14.6 g (16%) of 1-bromo-2,3-dimethyl-2-butene, bp 67-68° (40 mm), n^{25}D 1.4937 (lit[43] bp 65-66° (40 mm), n^{20}D 1.4948). The nmr spectrum showed a singlet at τ 6.0 (2 H) and two bands at 8.30 and 8.33 (9 H).

To a suspension of 4.65 g (53 mmoles) of sodiomalononitrile in 35 ml of THF, kept at 50°, was added, over a period of 25 min, a solution of 7.50 g (43 mmoles) of 1-bromo-2,3-dimethyl-2-butene in 20 ml of THF. The mixture was filtered after stirring at 50° for 30 min. Benzene (100 ml) was added to the filtrate, which was washed with water, dried, and distilled, giving 3.11 g (46%) of 2,3-dimethyl-2-butenylmalononitrile, bp 72-74° (0.45 mm), n^{26}D 1.4632.

Anal. Calcd for $C_9H_{12}N_2$: C, 72.93; H, 8.16; N, 18.90. Found: C, 72.61; H, 8.06; N, 18.62.

Ultraviolet spectrum (in cyclohexane) showed only end absorption, ϵ_{210} 5600. The nmr spectrum (in $CDCl_3$) showed a triplet centered at τ 6.14 (J = 8 cps, 1 H), a doublet centered at 7.18 (J = 8 cps, 2 H), and a singlet (with a barely visible shoulder) at 8.23 (9 H).

The semisolid pot residue, on crystallization from methanol, gave 0.58 g (11%) of bis(2,3-dimethyl-2-butenyl)malononitrile, mp 67-67.5°.

Anal. Calcd for $C_{15}H_{22}N_2$: C, 78.21; H, 9.63; N, 12.16; mol wt, 230.34. Found: C, 78.17; H, 9.48; N, 11.96; mol wt, 202, 210.

The nmr spectrum ($CDCl_3$) shows a singlet at τ 7.14 (4 H) and partially split singlets at 8.05 (6 H) and 8.18 (12 H).

Thermolysis of Dicyanodiazomethane in Cyclohexene. A vigorously stirred suspension of dicyanodiazomethane[8] (prepared from 1.97 g of carbonyl cyanide hydrazone) in 130 ml of freshly distilled cyclohexene was heated slowly to the boiling point and then refluxed for 5 min. Removal of the solvent and short-path distillation of the residue gave 2.61 g of a semisolid (85% yield). Gas chromatography,[34] at 173°, of the crude products before distillation showed the presence of two components (28 and 72%, respectively); these were separated by preparative gas chromatography. The 28% component was essentially pure 2-cyclohexenylmalononitrile as determined by comparison of the infrared and mass spectra with those of an authentic sample (see below). Weak

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[43] K. Ziegler, A. Späth, E. Schaaf, W. Schumann, and E. Winkelmann, *Ann.*, **551**, 80 (1942).

additional bands in the infrared spectrum and small differences in the relative abundance of some ions in the mass spectrum may indicate the presence of other isomer(s). The 72% component had mp 62–63° after recrystallization from cyclohexane.

Anal. Calcd for $C_9H_{10}N_2$: C, 73.94; H, 6.89; N, 19.17; mol wt, 146.19. Found: C, 73.91; H, 6.74; N, 18.93; mol wt, 154, 147.

The nmr spectrum shows only a complex multiplet at τ 7.6 to 8.7. The ultraviolet spectrum (in cyclohexane) shows only end absorption (ϵ_{210} 69). The infrared spectrum showed $\nu_{\max}^{\text{KBr}}$ 3030, 2940, 2860, 2255, and 1030 cm^{-1}, among others. These data strongly support the structure assignment of 7,7 dicyanonorcarane to the 72% component; yields 2-cyclohexenylmalononitrile, 24%; 7,7-dicyanonorcarane, 61% (based on carbonyl cyanide hydrazone).

2-Cyclohexenylmalononitrile. To a suspension of 32.0 g (0.36 mole) of sodiomalononitrile in 300 ml of THF was added, at 50–53° over a period of 75 min, a solution of 54.0 g (0.34 mole) of 3-bromocyclohexene[43] in 100 ml of THF. *Ca.* 200 ml of THF was then removed by distillation at reduced pressure; benzene (200 ml) was added to the cooled residue, which was then filtered. The filtrate and two washings (100 ml of benzene and 50 ml of ether) were washed with water and dried. Distillation gave 29.5 g (60%) of 2-cyclohexenylmalononitrile, which was contaminated by *ca.* 0.5% of malononitrile as shown by gas chromatography. Redistillation gave the pure product, bp 75° (0.15 mm), n^{25}D 1.4834.

Anal. Calcd for $C_9H_{10}N_2$: C, 73.94; H, 6.89; N, 19.17; mol wt, 146.19. Found: C, 74.16; H, 6.77; N, 19.44; mol wt, 147, 151.

The infrared spectrum (neat) showed $\nu_{\max}$ 3030, 2910, 2250, and 1650 cm^{-1}, among others. The ultraviolet spectrum (in cyclohexane) showed only end absorption, ϵ_{210} 58. The nmr spectrum (neat) shows four bands at τ 3.8 to 4.5 (2 H), a doublet centered at 6.10 (J = 6 cps, 1 H), a broad band at 7.2 (1 H), and a multiplet at 7.8 to 8.7 (6 H).

The residue from the distillation (10.70 g), on crystallization from methanol, gave 6.46 g (17%) of bis(2-cyclohexenyl)malononitrile, mp 108–112°. An analytical sample, prepared by repeated crystallizations from cyclohexane, had mp 113–115°.

Anal. Calcd for $C_{15}H_{18}N_2$: C, 79.60; H, 8.02; N, 12.38; mol wt, 226.31. Found: C, 79.72; H, 8.01; N, 12.52; mol wt, 221, 231.

The nmr spectrum (in $CDCl_3$) shows a multiplet at τ 3.7 to 4.4 (4 H), a broad band at 7.2 (2 H), and a multiplet at 7.7 to 8.6 (12 H).

Thermolysis of Dicyanodiazomethane in Tetrachloroethylene. A solution of 1.245 g of dicyanodiazomethane in 80 ml of freshly distilled tetrachloroethylene was heated slowly to 60° and kept at that temperature until nitrogen evolution became very slow. After a further 10 min at 80°, the solvent was removed under reduced pressure, leaving 2.542 g of a dark semisolid. Chromatography of 1.685 g of this product on Florisil (50 g) gave 38 mg of a colorless, fragrant liquid of unknown structure, eluted with *n*-hexane, followed by 586 mg (29% yield) of 1,1,2,2-tetrachloro-3,3-dicyanocyclopropane (eluted with *n*-hexane–benzene 4:1). Recrystallization from cyclohexane gave an analytical sample, mp 126–127°.

Anal. Calcd for $C_5Cl_4N_2$: C, 26.12; Cl, 61.69; N, 12.19; mol wt, 229.89. Found: C, 26.27; Cl, 61.15; N, 12.01; mol wt, 200, 197.

The ultraviolet spectrum (in cyclohexane) showed only end absorption, ϵ_{210} 1100. The infrared spectrum showed $\nu_{\max}^{\text{KBr}}$ 2260 (m), 1265 (m), 1230 (m), 1210 (w), 985 (w), 935 (s), 895 (vs), sh 880 (s), 850 (vs), 700 (m), and 675 (vs) cm^{-1} (all bands listed).

Decomposition of Dicyanodiazomethane in Butadiene. The procedure used was that described for the pyrolysis of the diazo compound in *n*-butane. The product, after removal of the THF, was a dark oil (1.189 g from 1.72 g of carbonyl cyanide hydrazone) which on short-path distillation gave 0.564 g of a pale yellow liquid, bp *ca.* 50–60° (0.4 mm), the infrared spectrum of which was identical with that of an authentic sample of 1,1-dicyano-2-vinylcyclopropane except for additional bands at 1780 (m), 1700 (m), 1620 (w), 1180 (m), and 890 (w). Gas chromatography[34] at 160° showed the presence of 97.3% of 1,1-dicyano-2-vinylcyclopropane (retention time 18.6 min) in addition to peaks after 5.4 (0.15%), 7.1 (0.1%), 9.8 (0.05%), 13.1 (1.5%), and 26.6 min (1.0%). The yield of 1,1-dicyano-2-vinylcyclopropane was 25%.

1,1-Dicyano-2-vinylcyclopropane. Reaction of 1,4-dibromo-2-butene and malononitrile with freshly precipitated silver oxide according to the method of Korte, *et al.*,[44] gave 1,1-dicyano-2-vinylcyclopropane in 45% yield, bp 54° (0.4 mm), n^{24}D 1.4773 to 1.4776.

Anal. Calcd for $C_7H_6N_2$: C, 71.17; H, 5.12; N, 23.71. Found: C, 71.05; H, 5.10; N, 23.50.

The ultraviolet spectrum (in cyclohexane) showed only end absorption, ϵ_{226} 118, ϵ_{214} 1180, and ϵ_{209} 2360. The nmr spectrum (neat) showed multiplets at τ 4.0 to 5.1 (3 H), 6.9 to 7.5 (1 H), and 7.9 to 8.3 (2 H). The infrared spectrum (neat) showed $\nu_{\max}$ 3120 (m), 3040 (m), 2250 (s), and 1645 (m) cm^{-1}, among others.

Thermolysis of Dicyanodiazomethane in Styrene. A solution of 820 mg of dicyanodiazomethane in 60 ml of freshly distilled styrene was heated to 80° for 30 min. Most of the styrene was removed under 0.3 mm of pressure, leaving 1.600 g (106%) of a dark oil still containing a small amount of styrene. The ratio of 1,1-dicyano-2-phenylcyclopropane to the mixture of vinyl-7,7-dicyanonorcaradienes, as determined by nmr spectroscopy, was about 2:3. This value was arrived at by taking the ratio of the areas (M) of the two bands due to the two C_3 protons in 1,1-dicyano-2-phenylcyclopropane to the area of all bands in τ 6.5–7.0 region (1 and 6 protons of the norcaradienes) from which $M/2$ had been deducted (the proton on C_2 in 1,1-dicyano-2-phenylcyclopropane absorbs at τ 6.8). On standing overnight, part of the crude product polymerized. A sample of this mixture (1.211 g) was separated into a benzene-insoluble polymer and a benzene-soluble dark oil (768 mg). The latter (707 mg) was chromatographed over Florisil (3 g); 331 mg of 1,1-dicyano-2-phenylcyclopropane (32% yield) were eluted with 170 ml of benzene–methylene chloride (7:3). Short-path distillation (0.15 mm, bath temperature 120°) gave a sample which apparently was still slightly impure (*cf.* the analysis), but which showed only one band in the gas chromatogram.

Anal. Calcd for $C_{11}H_8N_2$: C, 78.55; H, 4.79; N, 16.66. Found: C, 78.87; H, 5.02; N, 16.03.

Due to lack of material, no further purification was attempted.

The nmr spectrum (in $CDCl_3$) showed a doublet of equal intensity centered at τ 7.95, separation 9 cps, the higher field component being again split into a doublet (separation *ca.* 1 cps); total area 2 H; a triplet centered at 6.83 (J = 9 cps, 1 H), the central band is split again into a doublet (separation 1 cps); and a doublet centered at 2.73 (5 H). The near-infrared spectrum (in CCl_4) showed bands, among others, at 1.625 and 2.21 μ. The ultraviolet spectrum showed $\lambda_{\max}^{\text{cyclohexane}}$ 272 mμ (ϵ 160), 266 (240), 259 (240), and 219 (6200). The infrared spectrum showed $\nu_{\max}$ 3110 (m), 3030 (m), 2250 (s), 730 (s), and 695 (s) cm^{-1}, among others.

Thermolysis of Dicyanodiazomethane in Cyclooctatetraene. A suspension of 1.573 g of dicyanodiazomethane in 75 ml of freshly distilled cyclooctatetraene was heated slowly to 60° and then kept at this temperature until nitrogen evolution stopped. Most of the solvent was removed by distillation followed by evaporation using a rotary evaporator, leaving 2.891 g of a dark semisolid. The nmr spectrum of this material showed the ratio of 9,9-dicyanobicyclo[6.1.0]nona-2,4,6-triene (**15**) to 9,9-dicyanobicyclo[4.3.0]nona-2,4,7-triene (**16**) to be 3.88:1 (unchanged in a second experiment). Chromatography of 1.013 g of the crude product over Florisil and elution with hexane-benzene 1:1, 35:65, and pure benzene gave first a mixture of the two isomers followed by pure **15**. The total amount eluted was 951 mg; the yields of **15** and **16** were thus 70 and 18%, respectively. An analytical sample of **15**, mp 148.5–149.5°, was obtained by crystallizations from isopropyl alcohol and benzene–cyclohexane.

Anal. Calcd for $C_{11}H_8N_2$: C, 78.55; H, 4.79; N, 16.66; mol wt, 168.19. Found: C, 78.39; H, 4.73; N, 16.76; mol wt, 177, 166.

The infrared spectrum showed $\nu_{\max}^{\text{KBr}}$ 3010 (m), 2970 (sh), 2245 (s), 1645 (w–m), and 1620 (w–m) cm^{-1}, among others. The ultraviolet spectrum showed $\lambda_{\max}^{\text{cyclohexane}}$ 242 mμ (ϵ 3400). The nmr spectrum (in perdeuterioacetone) showed a multiplet at τ 3.9 to 4.4 (6 H) and a singlet at 7.43 (2 H, half-band width 1.9 cps).

Pure **16** was obtained by thermal rearrangement of **15** (see below).

Thermal Rearrangement of 9,9-Dicyanobicyclo[6.1.0]nona-2,4,6-triene (15). Preparation of 9,9-Dicyanobicyclo[4.3.0]nona-2,4,7-triene (16). 9,9-Dicyanobicyclo[6.1.0]nona-2,4,6-triene was recovered unchanged when refluxed in benzene for 100 min. A mixture of **15** and **16** was obtained when **15** was heated to 165° for 30 min. A sample of 531 mg of **15** was sealed in a Carius tube and heated to 190° for 1 hr. Chromatography of the product on Florisil (elution with benzene) gave 380 mg (72%) of 9,9-dicyanobicyclo[4.3.0]nona-2,4,7-triene (**16**). An analytical sample, mp 100–100.5°, was prepared by crystallization from cyclohexane.

Anal. Calcd for $C_{11}H_8N_2$: C, 78.55; H, 4.79; N, 16.66. Found: C, 78.63; H, 4.63; N, 16.63.

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[44] F. Korte, D. Scharf, and K. H. Büchel, *Ann.*, **664**, 97 (1963).

The infrared spectrum showed ν_{max}^{KBr} 3100, 3030, 2950, 2250, 1695, 1635, and 1605 cm^{-1}, among others. The ultraviolet spectrum (in cyclohexane) showed a shoulder at 274 mμ (ε 2400), λ_{max} 264 mμ (ε 4400), 255 (4600), and 218 (3900). The nmr spectrum (in CDCl$_3$) showed fairly broad singlets at τ 6.15 and 5.97 (1 H each, half-band width 4 cps), a doublet at 4.53 (2 H, separation 1.5 cps), and a multiplet at 3.5 to 4.0 (4 H).

Thermolysis of Dicyanodiazomethane in Allene. A mixture of dicyanodiazomethane (prepared from 1.736 g of carbonyl cyanide hydrazone) and 30 g of allene was heated to 70° in a stainless steel cylinder for 1 hr. The dark oil which remained after removal of the excess allene was chromatographed over Florisil; elution with benzene–hexane (1:1) gave, first, 28 mg of a colorless oil, followed by 569 mg of a pale yellow oil contained in 350 ml of effluent. Short path distillation of this oil gave 532 mg (28% yield) of 1,1-dicyano-2-methylenecyclopropane, bp *ca.* 28° (0.15 mm), n^{25}D 1.4708.

Anal. Calcd for $C_4H_4N_2$: C, 69.21; H, 3.88; N, 26.91. Found: C, 69.37; H, 4.13; N, 26.93.

The infrared spectrum (neat) showed bands at 3090 (m–s), 3020 (m–s), 2260 (s), 1860 (w–m), 1765 (m), 1550 (m–w), 1405 (s), 1225 (s), 930 (vs), 845 (m–w), 745 (m), and 685 (m–w) cm^{-1}, among others. The ultraviolet spectrum (in acetonitrile) shows only end absorption with a shoulder at 233 mμ. The mass spectrum (150° inlet temperature) shows the parent ion at *m/e* 104; the most abundant peak has *m/e* 77 (parent minus HCN).

Thermal Decomposition of Dicyanodiazomethane in Diethyl Azodicarboxylate. A solution of 1.692 g of dicyanodiazomethane in 30 ml of freshly distilled diethyl azodicarboxylate was heated to 80°; the nitrogen evolution, which was rather slow up to this temperature suddenly became very vigorous. A total of 500 ml (110%) of gas was evolved. Removal of the substrate (0.15 mm pressure, 90° bath temperature) gave 3.628 g of a purple liquid; 2.476 g of this product was short path distilled (0.4-μ pressure, 80° bath temperature) giving 1.685 g (56%) of carbonyl cyanide N,N-bis-(ethoxycarbonyl)hydrazone in the form of a yellow oil which did not solidify at Dry Ice temperature. Further purification was effected by chromatography over Florisil (elution with *n*-hexane–benzene 1:1), giving an almost colorless product.

Anal. Calcd for $C_9H_{10}N_4O_4$: C, 45.38; H, 4.24; N, 23.52; mol wt, 228.20. Found: C, 45.46; H, 4.26; N, 23.33; mol wt, 238.

The ultraviolet spectrum showed λ_{max}^{MeCN} 283 mμ (ε 10,200) and 255 mμ (ε 6600). The nmr spectrum (in CDCl$_3$) showed a triplet centered at τ 8.58 (6 H J = 7.2 cps) and a quartet centered at 5.49 (J = 7.2 cps, 4 H); there was no indication of two different ethyl groups being present. The infrared spectrum (neat) showed ν_{max} 3010, 2970, 2240, 1785, and 1550 cm^{-1}, among others.

Thermal Decomposition of Dicyanodiazomethane in Acetylene. Acetylene (*ca.* 25 g) was added to a solution of dicyanodiazomethane (prepared from 2.585 g of carbonyl cyanide hydrazone) in 50 ml of anhydrous acetonitrile contained in a 400-ml stainless steel pressure tube. The molar ratio of acetonitrile to acetylene was thus *ca.* 1:1. The mixture was heated to 60° for 3 hr. Removal of the solvent by distillation under reduced pressure (55° bath temperature) left 3.130 g of a very viscous black tar. Chromatography over 90 g of Florisil and elution with methylene chloride gave 362 mg of crude 3,3-dicyanocyclopropene in the form of a brown oil. The infrared spectrum of this product was identical with that of the distilled product (see below). Short-path distillation (0.3 mm pressure, 60–75° bath temperature gave 0.28 g of a pale yellow liquid (11% yield) which solidified when cooled with ice and remelted at about room temperature. It appeared to turn brown quite rapidly at room temperature.

Anal. Calcd for $C_5H_2N_2$: C, 66.66; H, 2.24; N, 31.10. Found: C, 66.90; H, 2.81; N, 30.45.

Because of lack of material, no further purification was attempted.

The mass spectrum (most abundant ions) had *m/e* 90 (parent), 89, 64, 63, 38, 37, and 26. Weak bands of *m/e* higher than 91 indicated the presence of impurities. The ultraviolet spectrum showed λ_{max}^{MeOH} 290 mμ (k = 0.83) and 255 mμ (sh, k = 0.99), both probably due to an impurity; end absorption ϵ_{225} 165, ϵ_{210} 670). The infrared spectrum (neat) showed bands at 3135 (s), 2250 m), 1670 (m), 1120 (m), 1075 (m), 995 (m), 850 (m), and 660 (s) cm^{-1} (all bands listed). The nmr spectrum (neat) showed a singlet at τ 2.78. The C^{13} satellites were separated by 255 cps; they were doublets, $J_{1,2} = 0.38 \pm 0.05$ cps. The C^{13} satellites of chloroform, used as external standard, were separated by 208 cps (lit[42] 209.17 cps).

Reaction of 3,3-Dicyanocyclopropene with 2,3-Dimethylbutadiene. A mixture of 58 mg of 3,3-dicyanocyclopropene and 3 ml of freshly distilled 2,3-dimethylbutadiene was heated under reflux for 45 min. Removal of the solvent gave 108 mg of colorless crystals (98% yield), the infrared spectrum of which was identical with that of the purified product (see below). The nmr spectrum (in CDCl$_3$) showed a singlet at τ 8.38 (half band width 2.7 cps, 6 H) and a broad band at 7.6 (half band width *ca.* 7 cps, 6 H). Crystallization from 2 ml of methanol gave 52 mg (47%) of 3,4-dimethyl-7,7-dicyanobicyclo[4.1.0]hept-3-ene, mp 144°.

Anal. Calcd for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02; N, 16.27. Found: C, 76.26; H, 6.90; N, 16.13.

The infrared spectrum showed ν_{max}^{KBr} 3060, 2990, 2900, 2840, 2240, 1430, 1230, 1140, 1065, 1045, 1030, and 840 cm^{-1}

Thermolysis of Dicyanodiazomethane in Methylacetylene. Dicyanodiazomethane, prepared from 1.758 g of carbonyl cyanide hydrazone, was heated to 70° with 100 g of methylacetylene for 1 hr. Removal of the excess acetylene and short-path distillation of the residue gave 1.092 g of a yellow oil, bp *ca.* 50–55° (0.3 mm), n^{25}D 1.4518.

Anal Calcd for $C_6H_4N_2$: C, 69.22; H, 3.88; N, 26.91. Found: C, 68.43; H, 4.20; N, 24.94.

The infrared spectrum showed bands at 3170 (s), 3010 (w), 2960 (w), 2255 (s), 1825 (m), 1760 (m), and 720 (s, broad) cm^{-1}, among others. The ultraviolet spectrum showed a weak band at 284 mμ (k = 0.73) in addition to end absorption. The mass spectrum shows the parent ion at *m/e* 104, the most abundant ion having *m/e* 77. The nmr spectrum (neat) showed a quartet centered at τ 3.31 (J = 1.5 cps, 1 H) and a doublet centered at 7.85 (J = 1.5 cps, 3 H) in addition to weak bands at 4.7, 5.5, and 6.6. The product thus appears to be mostly 1-methyl-3,3-dicyanocyclopropene. Partial decomposition occurred when it was analyzed by gas chromatography.

Reaction of 1-Methyl-3,3-dicyanocyclopropene with 2,3-Dimethylbutadiene. No reaction occurred when a sample of the cyclopropene was refluxed with excess 2,3-dimethylbutadiene for 1 hr. Heating to 120° for 2 hr in a Carius tube followed by chromatography on Florisil gave a crystalline product (eluted with benzene) which was crystallized twice from cyclohexane, affording colorless crystals of 1,3,4-trimethyl-7,7-dicyano-3-norcarene, mp 99–100°.

Anal. Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04; mol wt, 186.25. Found: C, 77.30; H, 7.63; N, 15.09; mol wt, 193.

The ultraviolet spectrum (in cyclohexane) showed only end absorption, ϵ_{212} 1860, ϵ_{224} 186. The infrared spectrum (KBr) had bands at 3030, 2980, 2910, 2880 (sh), 2840 (sh), and 2230 cm^{-1}, among others; there was no absorption in the C=C stretching region.

Thermal Decomposition of Dicyanodiazomethane in 2-Butyne. A solution of dicyanodiazomethane (prepared from 1.826 g of carbonyl cyanide hydrazone) in 100 g of 2-butyne was placed in a stainless steel cylinder and heated slowly to 70°; after 1 hr at that temperature, most of the 2-butyne was removed by distillation (low-temperature still). Evaporation to dryness (rotary evaporator) gave 2.147 g of a brown solid; gas chromatography[34] at 150° showed two volatile components, one having a retention time of 14.9 min (relative peak area 3%), the other 36.2 min (area 97%). An authentic sample of 2-butynylmalononitrile (see below) had a retention time of 14.8 min. The nmr and infrared spectra of the crude product were identical with those of pure 3,3-dicyano-1,2-dimethylcyclopropene. Chromatography of 2.102 g of the crude product on Florisil (elution with 300 ml of methylene chloride) gave 1.798 g of a yellow solid; assuming this to be essentially a mixture of only two products and using the ratio obtained by gas chromatography, the yield of 1,2-dimethyl-3,3-dicyanocyclopropene (**21**) is 77%; that of 2-butynylmalononitrile, 2%. Crystallizations from isopropyl alcohol and cyclohexane–benzene gave an analytical sample of **21**, mp 67°.

Anal. Calcd for $C_7H_6N_2$: C, 71.17; H, 5.12; N, 23.71; mol wt, 118.13. Found: C, 71.52; H, 5.27; N, 23.56; mol wt, 113, 114.

The infrared spectrum showed ν_{max}^{KBr} 3000 (w), 2950 (w), 2860 (w), 2240 (s), 1935 (m), 1880 (w), 1435 (s), 1370 (m), 1155 (s), 1125 (m), 1080 (vs), 1020 (m), 760 (s), and 730 (s) cm^{-1}; in CHCl$_3$) 2230 and 1925 cm^{-1}, among others. The ultraviolet spectrum (in cyclohexane) showed only end absorption, ϵ_{205} 910, ϵ_{210} 425, ϵ_{215} 141. The nmr spectrum (in CDCl$_3$) showed only one singlet at τ 7.78.

2-Butynylmalononitrile. To a mixture of 38 g of a sodium hydride suspension in mineral oil[45] (53.5%, 0.85 mole) and 400 ml of anhydrous THF was added 56 g (0.85 mole) of malononitrile in 200 ml of THF. The suspension was then heated to reflux and a solution of 189 g (0.85 mole) of 2-butyn-1-ol tosylate[46] in 400 ml of THF was added over a period of 1 hr. After heating to reflux for an additional 3 hr, 500 ml of benzene was added to the cooled mixture which was then filtered. The solids were washed with 1 l. of benzene and 200 ml of ethanol. The combined filtrates were washed with water and concentrated sodium chloride solution and dried. Removal of the solvents gave two layers; the lower layer was shown by gas chromatography to be a mixture of 16% of malononitrile, 21% of 2-butynylmalononitrile, and 63% of bis(2-butynyl)malononitrile; some mineral oil was also present. Repeated distillation using a spinning-band column gave pure 2-butynylmalononitrile, bp 82° (1.2 mm), n^{24}D 1.4612, which solidified on standing at room temperature.

Anal. Calcd for $C_7H_6N_2$: C, 71.17; H, 5.12; N, 23.71; mol wt, 118.13. Found: C, 71.44; H, 5.26; N, 23.67; mol wt, 119, 117.

The nmr spectrum (in $CDCl_3$) shows a triplet at τ 5.96 (1 H, $J = 6$ cps), seven bands at 7.1 (2 H, presumably two doublets, $J = 6$ cps, split again with $J = 2.5$ cps), and a triplet centered at 8.1 (3 H, $J = 2.5$ cps).

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(45) The mineral oil interferes seriously with the purification of the products and should be removed in any repetitions of this preparation.

(46) A. Marszak-Fleury, *Ann. Chim.* (Paris), [13] 3, 656 (1958).

Adamantyloxycarbonyl, a New Blocking Group. Preparation of 1-Adamantyl Chloroformate[1]

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Contribution from the Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana. *Received December 22, 1965*

Abstract: 1-Adamantyl chloroformate was prepared from 1-adamantanol and phosgene. The chloroformate was allowed to react with amino acids to give the corresponding 1-adamantyloxycarbonyl (*t*-AdOC) derivatives. Several of them could be obtained in crystalline form while the corresponding *t*-butyloxycarbonyl derivatives have either not been reported or have been described as oils or amorphous solids. The adamantyloxycarbonylamino acids are cleaved by acid-catalyzed solvolysis with trifluoroacetic acid to yield the free amino acids. Adamantyl chloroformate forms mixed carbonic–carboxylic anhydrides with triethylamine salts of N-protected amino acids which give peptide derivatives on reaction with amino acid esters.

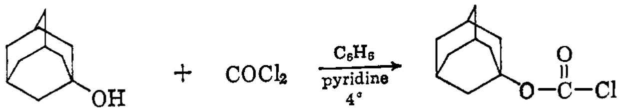
Considerable progress has been made in recent years in finding groups that can be used to block amino and hydroxy functions temporarily and can subsequently be removed under mild (solvolytic) conditions.[2]

The *t*-butyloxycarbonyl group proved to be particularly useful in peptide synthesis.[3a]

Because of the difficulty in the preparation and the lack of stability of *t*-butyl chloroformate,[3b] and because of the failure of this compound to react in even moderate yields with aniline or methyl glycinate,[3a] *t*-butyl azidoformate[4] or *t*-butyl *p*-nitrophenyl carbonate[3a] are widely used to introduce the *t*-butyloxycarbonyl group.[5]

The ease with which *t*-butylcarbamates are cleaved to yield free amino functions relates to the tendency of the *t*-butyl group to form a carbonium ion which in turn can lose a proton to yield isobutene. Adamantane forms a relatively stable carbonium ion at the bridgehead tertiary carbon[6] which can accept anions from the reaction mixture but cannot lose a proton to form an olefin.

It has been possible to prepare 1-adamantyl chloroformate (1-adamantyloxycarbonyl chloride) in crystalline form by allowing 1-hydroxyadamantane[6] to react with excess phosgene in a benzene solution in the presence of pyridine.



Crystalline 1-adamantyl chloroformate, mp 45–46°, was obtained from petroleum ether at −20°. Its structure is supported by analytical and infrared data. Further confirmation of the structure was obtained in two ways. First, reaction with hydrazine gave the crystalline carbazate, mp 142°, which was found to be identical with samples prepared from 1-adamantyl *p*-nitrophenyl carbonate[7] and from O-1-adamantyl S-methylthiolcarbonate.[8]

Secondly, reaction of the chloroformate and ammonia gave 1-adamantylcarbamate which was found to be identical with a sample prepared from 1-adamantyl phenyl carbonate.[9]

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(1) Presented in part before the Division of Biological Chemistry, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, Abstracts, p 44C.

(2) For reviews see (a) J. Rudinger, *Pure Appl. Chem.*, 7, 335 (1963); (b) R. A. Boissonnas, *Advan. Org. Chem.*, 3, 159 (1963).

(3) (a) G. W. Anderson and A. C. McGregor, *J. Am. Chem. Soc.*, 79, 6180 (1957), and numerous applications by other authors since then; (b) A. R. Choppin and J. W. Rogers, *ibid.*, 70, 2967 (1948).

(4) L. A. Carpino, C. A. Giza, and B. A. Carpino, *ibid.*, 81, 955 (1959).

(5) Recently *t*-butyl cyanoformate (L. A. Carpino, *J. Org. Chem.*, 29, 2820 (1964), and M. Leplawy and W. Stec, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, 12, 21 (1964)) and *t*-butyl iminodicarboxylate (L. A. Carpino, *J. Org. Chem.*, 29, 2820 (1964)) have been suggested for the same purpose.

(6) R. C. Fort and P. von R. Schleyer, *Chem. Rev.*, 64, 277 (1964).

(7) Prepared from adamantyl alcohol and *p*-nitrophenyloxycarbonyl chloride by the general method of Anderson and McGregor.[3a]

(8) Prepared from adamantyl alcohol and S-methylchlorothiolformate by the general method of L. A. Carpino, *J. Org. Chem.*, 28, 1910 (1963).

(9) Prepared from adamantyl alcohol and phenyloxycarbonyl chloride by the general method of McLamore, *ibid.*, 20, 3791 (1955).