added, the mixture was heated to 165°, and treated dropwise, over a 2-hr. period, with one mole of dimethyl disulfide at such a rate that the reaction temperature was maintained above 150°. The mixture was stirred at reflux for an additional 14 hr. and the organic layer was withdrawn, washed with a small amount of saturated sodium sulfate solution, and fractionated. There was obtained 33 g. (21%) of 4-methylmercapto-3-cresol, b.p. 108–109° (1 mm.); benzenesulfonate, m.p. 79–80°; phenyl carbamate, m.p. 106–107°.

4-Methylmercaptophenol (Phosphoric Acid Method).—A mixture of 45 g. of phosphorus pentoxide, 155 g. of 85% phosphoric acid, and 47 g. of phenol was treated over a 2-hr. period with 94 g. of dimethyl disulfide at such a rate that a temperature of 150–155° was maintained. Heating was continued for two additional hours after which the catalyst layer was withdrawn. The organic layer was washed with saturated sodium sulfate solution and fractionated to give 33 g. (47%) of 4-methylmercaptophenol, b.p. 146–148 (10 mm.). The recovered catalyst layer (after heating in an open flask to 180°), 47 g. of phenol, and 94 g. of dimethyl disulfide when treated as previously described in two consecutive experiments yielded 42 g. (60%) and 49 g. (70%) of 4-methylmercaptophenol, respectively.

4-Methylmercaptophenol (Ion-Exchange Method).—A mixture of 94 g. of phenol and 60 g. of resin AG50-X12 (Bio-Rad Laboratories) was treated dropwise, with stirring at 150°, with 75 g. of dimethyl disulfide during 4 hr. The reaction mixture was heated for two additional hours, cooled, and filtered. The resin was washed with five 100-ml. portions of chloroform, and the combined filtrates were fractionated to yield 43 g. (31%) of 4-methylmercaptophenol.

4-Methylmercaptophenol (Sulfuric Acid Method).—A mixture of one mole of phenol and 0.5 mole of concentrated sulfuric acid was heated rapidly to 170° and then cooled to 155°. One mole of dimethyl disulfide was added to the reaction mixture at such a rate that a reaction temperature of 150–155° was maintained. The reaction mixture was heated at 160–170° for an additional 2 hr. and treated as in the ion-exchange method. There was obtained 12 g. (8%) of 2-methylmercaptophenol, b.p. 115–117° (14 mm.), and 65 g. (46%) of 4-methylmercaptophenol, b.p. 146–148° (10 mm.); benzenesulfonate, m.p. 57–58°; phenyl carbamate, m.p. 145–146°.

4-Methylmercapto-2,6-diisopropylphenol (Sulfenyl Chloride Method).—A freshly prepared solution of 0.74 mole of methanesulfenyl chloride in 60 ml. of carbon tetrachloride was added during 30 min. to a solution of 0.37 mole of 2,6-diisopropylphenol in 60 ml. of dry carbon tetrachloride while the reaction temperature was maintained at −20° during the addition. The reaction mixture was then allowed to warm to room temperature. It was stirred overnight, washed with saturated sodium sulfate solution, and fractionated to give 32 g. (48%) of 4-methylmercapto-2,6-diisopropylphenol, b.p. 164–165 (12 mm.).

4-Methylmercaptophenol (Hydrolysis of 4-Bromothioanisole).—A mixture of 0.2 mole of 4-bromothioanisole, 200 ml. of 10% sodium hydroxide, 7.5 g. of copper oxide, and 2.5 g. of copper powder was heated in a rocking autoclave at 200–225° for 3 hr. A maximum pressure of 560 p.s.i. developed. The reaction mixture was allowed to cool and was extracted with 20 ml. of benzene to remove unchanged 4-bromothioanisole. Upon acidification of the alkaline solution, an oil separated, which was fractionated to yield 22 g. (79%) of 4-methylmercaptophenol.

Bis(2-bromoalkyl)malononitriles by Addition of Dibromomalononitrile to Alkenes

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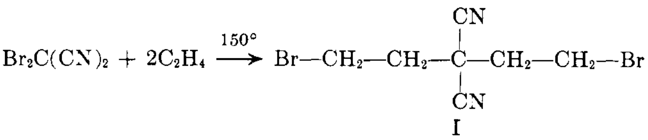
The addition of dibromomalononitrile to olefins is catalyzed by free-radical initiators and some metal halides. The structures of the products are consistent with a free radical mechanism.

Although dibromomalononitrile was reported over sixty years ago[1] little is known of its reactivity.[2,3] The discovery of its reaction with copper powder to yield tetracyanoethylene[4] has prompted study of its reactions with unsaturated compounds. Reaction with cyclohexene in the presence of copper powder was found[4] to yield cyclohexylidenemalononitrile, believed to result from initial formation of 7,7-dicyanobicyclo[4.1.0]heptane followed by thermal rearrangement. It was suggested that this reaction and the formation of tetracyanoethylene may have proceeded through intermediate formation of dicyanocarbene.[4]

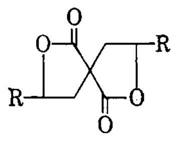
It has now been found that dibromomalononitrile reacts with terminal olefins to yield primarily 1:2 adducts.[5] Thus, dibromomalononitrile adds to ethylene at 150° under a pressure of 1000 atm. to give 1,5-dibromo-3,3-dicyanopentane (I) in 71% yield.



$$Br_2C(CN)_2 + 2C_2H_4 \xrightarrow{150^\circ} Br{-}CH_2{-}CH_2{-}\underset{CN}{\overset{CN}{C}}{-}CH_2{-}CH_2{-}Br$$

I

The structure is assigned on the basis of the A_2B_2 pattern of the n.m.r. spectrum. Chemical confirmation of the structure was provided by conversion of I to the known spirolactone IIa.[6]



IIa, R = H
IIb, R = n-C_4H_9

1-Hexene, styrene, and 3-methylenecyclobutanecarbonitrile reacted with dibromomalononitrile at 60–80° to give 1:2 adducts. The reaction product of 1-hexene with dibromomalononitrile is more complex than that with ethylene in giving two isomeric products whose structures could differ in the mode of addition to 1-hexene (III, IV, or V) or in the diastereomeric forms of the adducts.

The structural question was conveniently resolved by n.m.r. spectroscopy which showed III to be the structure of both isomers. It seems most likely that the products isolated are the *meso* and *d,l* forms of III.

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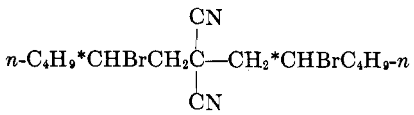
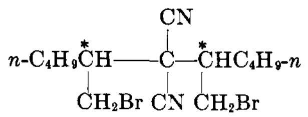


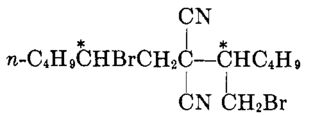
$$n\text{-}C_4H_9{}^*CHBrCH_2C(CN)_2{-}CH_2{}^*CHBrC_4H_9\text{-}n$$

III



$$n\text{-}C_4H_9\overset{*}{C}H(CH_2Br){-}C(CN)_2{-}\overset{*}{C}H(CH_2Br)C_4H_9\text{-}n$$

IV

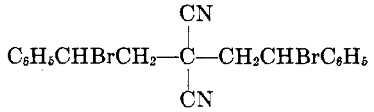


$$n\text{-}C_4H_9\overset{*}{C}HBrCH_2C(CN)_2{-}\overset{*}{C}H(CH_2Br)C_4H_9$$

V

Both isomers could be converted to diastereomeric lactones IIb.

The styrene–dibromomalononitrile adduct was similarly shown to be 1,5-dibromo-1,5-diphenyl-3,3-dicyanopentane (VI). The isomers were not separated in this case, but the methylene groups appear as an overlapping pair of doublets in the n.m.r. spectrum, thus leading to the belief that diastereomers were formed.



$$C_6H_5CHBrCH_2{-}C(CN)_2{-}CH_2CHBrC_6H_5$$

VI

The addition of dibromomalononitrile to olefins is catalyzed by a variety of agents as shown by data in Table I for the reaction of dibromomalononitrile in refluxing 1-hexene.

TABLE I

YIELDS OF DIBROMOMALONONITRILE-1-HEXENE ADDUCTS WITH VARIOUS INITIATORS

Initiator (g.)	Total yield of adduct g.	%
Benzoyl peroxide (0.1)	2.94	16.3
Copper powder (0.1)	18.0	92
Azobis(α,γ-dimethylvaleronitrile) (0.2)	19.1	97.5
$FeCl_3$ (0.2)	12.1	61.5
$SnCl_4$ (0.1)	1.95	9.9
$AlCl_3$ (0.2)	2.53	12.9
None	0	0

The n.m.r. spectra of all products showed them to have the structure III. The high yields obtained with copper and the azonitrile initiator suggest a free-radical mechanism, akin to that used to explain the radical-chain addition of carbon tetrachloride to olefins.[7] The products have structures consistent with this mechanism. Initiation by ferric chloride probably also is by a free-radical mechanism, for ferric chloride has been shown[8] to function as a free-radical generator in an oxidation–reduction process culminating in the addition of halogen compounds to olefins. The mechanism by which stannic chloride and aluminum chloride bring about addition is obscure, but it is probably ionic rather than free-radical in character. The small yield obtained in the presence of benzoyl peroxide is readily explained by the low rate of radical generation from this initiator at the boiling point of 1-hexene.

It is likely that the reaction of cyclohexene with dibromomalononitrile[4] also involves initial radical-chain addition of dibromomalononitrile to the double bond, and that dicyanocarbene is not involved. It follows that this reaction cannot be taken as evidence that tetracyanoethylene is formed from dibromomalononitrile and copper *via* dicyanocarbene.[9]

Experimental

Melting points were uncorrected except as noted. The n.m.r. spectra were obtained on a Varian Associates A-60 spectrometer; chemical shifts are given in τ values[10] relative to tetramethylsilane as an internal standard. Infrared spectra were determined on a Perkin-Elmer Model 21 double beam spectrometer by Miss Naomi Schlichter.

1,5-Dibromo-3,3-dicyanopentane (I). **A.**—Dibromalononitrile[1] (22.4 g., 0.1 mole) and 150 ml. of benzene were heated in a 400-ml., stainless steel pressure vessel with ethylene at 150° and 1000-atm. pressure for 16 hr. The benzene was removed from the reaction product by distillation. The residual brown oil crystallized on standing overnight. Recrystallization of this crude 1,5-dibromo-3,3-dicyanopentane from benzene gave 20 g. (71.5% yield) of white crystals, m.p. 59–60°. This material did not react with alcoholic silver nitrate.

Anal. Calcd. for $C_7H_8N_2Br_2$: C, 30.00; H, 2.86; N, 10.00; Br, 57.10; mol. wt., 280. Found: C, 30.15; H, 3.03; N, 10.21; Br, 57.07; mol. wt., 252.

B.—A preparation was carried out as previously described except that 0.5 g. of precipitated copper powder was added. This procedure yielded 4.0 g. (14%) of product that melted at 60–60.5° (corr.) after successive crystallizations from hexane and alcohol. The n.m.r. spectrum is a typical A_2B_2 spectrum with the centers of gravity of the two halves at τ 6.42 and 7.48. The splitting was complex. This shows the product has two kinds of methylene groups and confirms the structure as I.

2,7-Dioxaspiro[4.4]nonane-1,6-dione (II).—Hydrolysis of 1,5-dibromo-3,3-dicyanopentane was effected by dissolution of 1.0 g. in 3 ml. of concentrated sulfuric acid followed by careful dilution with 2.3 ml. of water. The mixture was heated on a steam bath until hydrogen bromide evolution ceased. It was then cooled and poured into 30 ml. of ice–water mixture. The aqueous mixture was then continuously extracted with chloroform, and the extract was then evaporated to dryness. The crude product was crystallized from benzene to give 0.33 g. (59%) of product melting at 108.5–108.8° (cor.) after slight softening at 98°. After a second crystallization from alcohol the material melted at 108.5–108.8° (cor.); lit.[6] m.p. 109–110°. The n.m.r. spectrum showed complex splitting of the methylene groups centered at τ 2.61 and 4.54. The infrared spectrum showed a γ-lactone carbonyl at 5.70 μ and an unexplained CH at 3.3μ in addition to the expected CH bands.

Anal. Calcd. for $C_7H_8O_4$: C, 53.84; H, 5.17. Found: C, 53.97; H, 5.68.

5,9-Dibromo-7,7-dicyanotridecane (III).—A flask fitted with a stirrer and reflux condenser was charged with 22.4 g. (0.10 mole) of dibromomalononitrile, 50 ml. of 1-hexene, and 0.5 g. of copper powder. This mixture was stirred and heated for 3 hr. in a bath at 80°. After cooling, the mixture was diluted with 100 ml. of acetone and filtered. The filtrate was evaporated to dryness to give 39 g. (100%) of a mixture of *meso* and *d,l* isomers of 5,9-dibromo-7,7-dicyanotridecane. The high-melting isomer was isolated from this mixture by two extractions of the solid with boiling hexane using 200 ml. of solvent for the first extraction and 70 ml. for the second. After each extraction the mixture was cooled to room temperature prior to filtering. The residue from the extractions was the high-melting isomer. It weighed 14.9 g. (38%), m.p. 119–122°. After crystallization from alcohol or hexane, the compound melted at 124–125°.

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(7) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 247 ff., Chap. 7.

(8) M. Asscher and D. Vofsi, *Chem. Ind.*, **209** (1962).

(9) We are indebted to Professor P. S. Skell of Pennsylvania State University for helpful discussions on the possible role of dicyanocarbene in reactions of dibromomalononitrile.

(10) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

Table II

Multiplicity	τ	Rel. intensity	Separation, c.p.s.
5	5.72	1	6
2	7.43	2	7
broad	8.11	4	...
broad	8.53		...
broad shoulder	8.98	5	...
1	9.07		...

The n.m.r. spectrum of this material is shown in Table II. This spectrum (Table II) is consistent only with structure III.

Anal. Calcd. for $C_{15}H_{24}N_2Br_2$: C, 45.92; H, 6.12; N, 7.14; Br, 40.82; mol. wt., 392. Found: C, 45.67; H, 6.31; N, 7.05; Br, 40.66; mol. wt. (ebull. benzene), 407.

The hexane extracts from the isolation of the high-melting isomer were combined and evaporated to dryness to give 20.8 g. (53%) of the low-melting isomer, m.p. 68–71°. The compound could be crystallized from hexane, alcohol, or petroleum ether, and melted at 76–77° after crystallization. It gave no reaction with sodium iodide in acetone on heating, nor did it react with alcoholic silver nitrate. The n.m.r. spectrum of the low-melting isomer was the same as that of the high-melting isomer except that the methylene doublet occurred at τ 7.37. Actually the lower-melting, more soluble isomer could not be entirely freed of the high-melting isomer, and the spectrum showed both doublets.

Anal. Calcd. for $C_{15}H_{24}N_2Br_2$: C, 45.92; H, 6.12; N, 7.14; mol. wt., 392. Found: C, 45.93; H, 6.14; N, 7.14; mol. wt. (f.p. benzene), 402.

The effects of various initiators were shown by a series of experiments in which 11.2 g. (0.05 mole) of dibromomalononitrile was refluxed for 3 hr. in 20 ml. of 1-hexene with a small amount of initiator. These data are summarized in Table I.

3,8-Di-*n*-butyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (IIb).—Three grams of the low-melting 5,9-dibromo-7,7-dicyanotridecane was dissolved in 10 ml. of concentrated sulfuric acid by gentle warming. After cooling, the solution was diluted with sufficient water to give a 70% sulfuric acid concentration and then heated for 1 hr. on a steam bath. During this period hydrogen bromide was evolved. The mixture was then poured on ice, and the precipitated solid was isolated by filtration and dried. After crystallization from hexane, the dilactone melted at 102.5–103°, yield 1.07 g. (52%). The infrared spectrum showed a 5.70 μ γ-lactone carbonyl absorption.

Anal. Calcd. for $C_{15}H_{24}O_4$: C, 67.13; H, 9.02; mol. wt., 268. Found: C, 67.03; H, 8.87; mol. wt., 283.

Hydrolysis of the high-melting 5,9-dibromo-7,7-dicyanotridecane with sulfuric acid in the same manner gave a dilactone melting at 117–118° after crystallization from ethanol. The infrared spectrum showed a 5.65-μ absorption for γ-lactone carbonyl.

Anal. Calcd. for $C_{15}H_{24}O_4$: C, 67.13; H, 9.02. Found: C, 66.73; H, 8.91.

1,5-Dibromo-1,5-diphenyl-3,3-dicyanopentane (VI).—A mixture of 2.24 g. (0.01 mole) of dibromomalononitrile, 2.1 g. (0.02 mole) of styrene, and a trace of copper powder was heated gently on a steam bath. After the mildly exothermic reaction subsided, the mixture was heated for one hour on the steam bath. It was then diluted with acetone and filtered, and the filtrate was evaporated to dryness. This left 2.3 g. of a mixture of isomers sintering above 105° and melting over the range 115–125°. After crystallization from alcohol, the mixture formed soft white plates melting over the range 134–140°.

The n.m.r. spectrum is shown in Table III.

Table III

Multiplicity	τ	Rel. intensity	Separation (c.p.s.)
1	2.60	5.2	...
3	4.81	0.9	7
2	7.15	2	8
	7.20		

Anal. Calcd. for $C_{19}H_{16}Br_2N_2$: N, 6.48; Br, 36.98. Found: N, 6.74; Br, 36.66.

1,3-Bis(1-bromo-3-cyanocyclobutyl)-2,2-dicyanopropane.—Dibromomalononitrile (4.48 g., 0.02 mole) and 3-methylenecyclobutanecarbonitrile (7.2 g., 0.08 mole) were mixed in a 100-ml. erlenmeyer flask, and a trace of copper powder was added. The reaction mixture was swirled manually and kept below 10° by intermittent immersion in a Dry Ice-acetone bath at −30° until the first separation of solid occurred and then was kept below 20°. About 40 min. was required for the reaction. The solid reaction mixture was taken up in acetone, filtered from the copper, and diluted with water to precipitate the adduct. The crude product from two runs was crystallized from aqueous acetone to yield 16.4 g. (56%) of 1,3-bis(1-bromo-3-cyanocyclobutyl)-2,2-dicyanopropane, m.p. 192–194°.

Anal. Calcd. for $C_{15}H_{14}N_4Br_2$: C, 43.92; H, 3.44; Br, 38.97; N, 13.66. Found: C, 43.38; H, 3.45; Br, 38.74; N, 13.66.

The Indirect Fluorination of Some Halogenated Aliphatic Nitriles[1]

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Received May 27, 1963

The reaction of argentic fluoride with dichloro- and difluoromalononitrile, tetrafluorosuccinonitrile, hexafluoroglutaronitrile and chlorodifluoroacetonitrile have been investigated. A number of interesting cyclization products have been identified including two new cyclic azoalkanes. The pyrolytic and spectroscopic properties of the latter have been examined.

Several fluorinating agents have been found effective in preparing highly fluorinated azoalkanes. Most notable among these are iodine pentafluoride,[2,3] argentic fluoride,[4,5] and elemental fluorine.[6,7] In addition, combinations such as argentous fluoride and bromine or sodium fluoride and chlorine have been successfully employed.[8] Recently Emeleus and Hurst[9] reported the first fluorinated cyclic azo system, $\underline{CF_2CF_2\text{—}N{=}N}$, by passing cyanogen over a heated bed of argentic fluoride.

During the course of the present research it was found that dichloro- and difluoromalononitrile undergo analogous cyclizations with argentic fluoride under autogenous pressure. The resulting new compounds were, respectively, 4,4-dichloro-3,3,5,5-tetrafluoro-1-pyrazo-

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[1] A portion of the research reported in this publication was supported by the Advanced Research Projects Agency to which grateful acknowledgment is hereby made.

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