diethyl ether was cooled at 0° and a 100% excess of diborane, generated externally from sodium borohydride and boron trifluoride etherate, was bubbled into the solution with a stream of nitrogen. The reaction mixture was allowed to stand at room temperature for 4 hr and most of the ether and excess diborane were removed by distillation under nitrogen. The residue was dissolved in 50 ml of dry chloroform and a 20% excess of *m*-chloroperbenzoic acid was added and allowed to stand for 24 hr. The solution was washed with several small portions of acidified 5% ferrous ammonium sulfate. The chloroform was removed under reduced pressure. The residue was dissolved in 30 ml of ether and 5 ml of pyridine and 10 ml of acetic anhydride was added and allowed to stand at room temperature for 16 hr. Direct analysis of the mixture by gas–liquid partition chromatography on a 30-ft 20% Carbowax 20M on firebrick column showed the presence of *cis*- and *trans*-4-*t*-butylcyclohexyl acetate in approximately a 65:35 ratio. No *cis*- or *trans*-3-*t*-butylcyclohexyl acetate was present.

A New Synthesis of Tetracyanocyclopropanes

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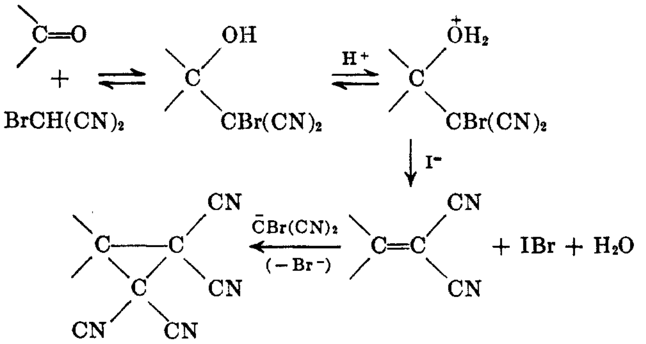
Received April 1, 1966

Alkylidenemalononitriles ($R_1R_2C{=}C(CN)_2$) are shown to react at room temperature with bromomalononitrile in aqueous ethanol to produce tetracyanocyclopropanes in good yields. Examples include $R_1 = CH_3$; $R_2 = CH_3$, C_2H_5, *n*- and *i*-C_3H_7, *n*-C_5H_{11}, aryl; and $R_1 = C_2H_5$; $R_2 = C_2H_5$, C_6H_5; $R_1 = R_2 =$ cyclopropyl. Spirocyclopropanes were obtained from cycloalkylidenemalononitriles with 5-, 6-, 10-, 12-, and 15-membered rings. In many instances this method provides a better route to tetracyanocyclopropanes than the Wideqvist reaction (carbonyl compound, bromomalononitrile, and iodide ion), which either fails altogether or, in the case of aryl methyl ketones, gives low yields. It probably represents the final stage of the Wideqvist reaction. The present reaction seems sensitive to steric factors, either proceeding poorly or failing altogether when R_1 and/or R_2 are long chains or highly branched. In two instances (2,3-benzocyclohexylidenemalononitrile and 2,3-benzocyclopentylidenemalononitrile) the substrate underwent bromination rather than cyclopropanization, although with the former the direction could be controlled by relatively minor changes in solvent polarity. Bromomalononitrile reacts with aqueous ethanol, either on prolonged standing or on reflux, to give 1,1-dicyano-2-amino-2-ethoxyethene.

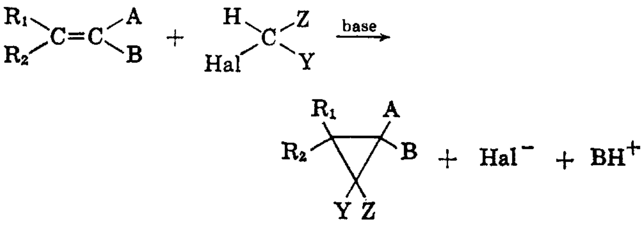
Wideqvist and Ramberg showed[1] that certain carbonyl compounds react with bromomalononitrile and iodide ion to produce tetracyanocyclopropanes. The reaction, now referred to as the Wideqvist reaction,[2] is fairly general,[3,4] although certain limitations were encountered which will be described in more detail below. It was suggested[3] that the Wideqvist reaction follows the scheme shown, the function of the iodide ion being to bring about an elimination reaction to form alkylidenemalononitrile. (See Scheme I.)

SCHEME I



In order to test the last step in this scheme, we have prepared a number of alkylidenemalononitriles and allowed them to react with bromomalononitrile in the absence of iodide ion. In many cases tetracyanocyclopropanes were formed quickly and in high yield; indeed, this procedure allows the preparation of a number of tetracyanocyclopropanes which cannot be obtained directly by the Wideqvist reaction, presumably because under the conditions normally used for that reaction the first equilibria shown in the scheme may be unfavorable.

It should be pointed out that the literature abounds in examples of syntheses of polyfunctional cyclopropanes by the base-catalyzed condensation of activated α,β-unsaturated systems with α-halo esters, ketones, nitriles, etc., followed by intramolecular dehydrohalogenation.[5-10] The present work involves a similar type of reaction except that base is omitted, because bromomalononitrile is a reasonably strong acid[11] which can furnish a sufficient concentration of bromodicyanocarbanion for reaction.[12]



(A, B, Y, and Z are generally electron-withdrawing groups)

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(1) L. Ramberg and S. Wideqvist, *Arkiv. Kemi*, **12A**, No 22 (1937); S. Wideqvist, *ibid.*, **20B**, No 4 (1945).

(2) H. Hart and F. Freeman, *J. Am. Chem. Soc.*, **85**, 1161 (1963).

(3) H. Hart and F. Freeman, *J. Org. Chem.*, **28**, 1220 (1963).

(4) R. M. Scribner, G. N. Sausen, and W. W. Prichard, *ibid.*, **25**, 1440 (1960).

(5) O. Widman, *Ber.*, **51**, 533, 907 (1918).

(6) R. Fraisse and R. Jacquier, *Bull. Soc. Chim.*, 986 (1957); R. Fraisse, *ibid.*, 1102 (1959); R. Fraisse and M. Guitard, *ibid.*, **418**, 788 (1960); 200 (1961).

(7) G. Westoo, *Acta Chem. Scand.*, **11**, 1290 (1957); **13**, 683, 689 (1959).

(8) D. T. Warner, *J. Org. Chem.*, **24**, 1536 (1959).

(9) M. Mousseron and R. Fraisse, *Compt. Rend.*, **248**, 887 (1959); M. Mousseron, R. Fraisse, R. Jacquier and G. Bonavent, *ibid.*, **248**, 1465, 2840 (1959).

(10) L. L. McCoy, *J. Am. Chem. Soc.*, **80**, 6568 (1958); L. L. McCoy, *J. Org. Chem.*, **25**, 2078 (1960); L. L. McCoy, *J. Am. Chem. Soc.*, **82**, 6416 (1960); L. L. McCoy, *ibid.*, **84**, 2246 (1962); L. L. McCoy, *J. Org. Chem.*, **29**, 240 (1964); L. L. McCoy and G. W. Nachtigall, *ibid.*, **27**, 4312 (1962).

(11) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).

(12) It should be noted that alkylidene bismalononitriles have been converted to tetracyanocyclopropanes by bromination: R. P. Mariella and A. J. Roth, III, *J. Org. Chem.*, **22**, 1130 (1957).

TABLE I
ALKYLIDENEMALONONITRILES
$R_1R_2C{=}C(CN)_2$

Compd	R_1	R_2	Yield, %	Bp (mm), °C	n_D (temp, °C)	Infrared[a]	Ultraviolet[b]	Nmr[c]
I[d]	CH_3	CH_3	74.8	75 (4)	1.4670 (23)		232 (4.08)	7.70 (s)
II[e]	CH_3	C_2H_5	37.5	82 (4)	1.4707 (19)	2250, 1600	232	8.82 (t, 3), 7.74 (s, 3), 7.41 (q, 2)
III[n]	CH_3	n-C_3H_7	69.8	92 (4)	1.4705 (21.5)	2230, 1598	234 (4.12)	9.01 (t, 3), 8.37 (m, 2), 7.76 (s, 3), 7.43 (t, 2)
IV	CH_3	i-C_3H_7	79.7	90 (4)	1.4707 (19)	2240, 1590	233 (4.14)	8.84 (d, 6), 7.84 (s, 3), 6.83 (se, 1)
V[d]	CH_3	t-C_4H_9	34.7	125–128 (8)	1.4778 (24)		238 (4.10)	8.62 (s, 9), 7.67 (s, 3)
VI[f]	CH_3	n-C_5H_{11}	60.9	113–114 (4)	1.4698 (20)	2250, 1600	235 (3.85)	9.08 (t, 3), 8.57 (m, 6), 7.76 (s, 3), 7.45 (t, 2)
VII[n]	C_2H_5	C_2H_5	70.8	84–89 (9)	1.4690 (24)	2240, 1591		8.82 (t, 6), 7.41 (q, 4)
VIII[g]	C_2H_5	n-C_4H_9	78.3	109–110 (4)	1.4705 (22)	2245, 1590	236 (4.09)	8.82 (m, 10), 7.46 (m, 4)
IX[h]	i-C_3H_7	i-C_3H_7	41.5	97–98 (4)	1.4714 (20)	2252, 1575	237.5 (4.15)	8.75 (d, 12), 6.95 (se, 2)
X	i-C_4H_9	i-C_4H_9	55.7	116–117 (4)		2225, 1587		9.00 (d, 12), 7.95 (m, 2), 7.48 (d, 4)
XI	n-C_5H_{11}	n-C_5H_{11}	46.3	145–146 (4)	1.4708 (20.5)	2250, 1591	238 (4.11)	9.08 (t, 6), 8.57 (m, 12), 7.44 (t, 4)
XII	Cyclo-C_3H_5	Cyclo-C_3H_5	17.7	mp 43–45		2205, 1530		8.78 (m, 8), 8.15 (m, 2)[i]
XIII	$-(CH_2)_4-$		22.1	113–114 (4)	1.4995 (23)	2250, 1618	238 (4.04)	8.11 (m, 4), 7.24 (m, 4)
XIV	$-CH(CH_3)CH_2CH_2CH(CH_3)-$		64.5[j]	109 (4)		2255, 1605		8.72 and 8.68 (d, 6), 8.13 (m, 4), 6.87 (m, 2)
XV[d,n]	$-(CH_2)_5-$		74.8	137 (10)	1.5119 (21)	2240, 1597	236 (4.28)	8.26 (m, 6), 7.39 (m, 4)
XVI	$-(CH_2)_4CH(CH_3)-$		71.6	120 (4)	1.5053 (25)	2244, 1593[m]		8.73 (d, 3), 8.27 (m, 6), 7.39 (m, 2), 6.82 (m, 1)[k]
XVII	$-(CH_2)_9-$		89.2	l		2255, 1583[m]	242	8.52–8.05 (m, 14), 7.27 (t, 4)[k]
XVIII	$-(CH_2)_{11}-$		l	l		2254, 1592[m]	241	8.60–8.41 (m, 18), 7.37 (t, 4)[k]
XIX	$-(CH_2)_{14}-$		l	l		2250, 1590[m]	239	

[a] C≡N and C=C frequencies in cm^{-1}, CCl_4 solution. [b] λ_{max} and log ϵ in ethanol. [c] Neat unless otherwise stated; τ relative to tetramethylsilane, with multiplicity and number of protons given in parentheses; s = singlet, d = doublet, t = triplet, q = quartet, se = septet, b = broad single band, m = multiplet. [d] F. S. Prout, *J. Org. Chem.*, **18**, 928 (1953). [e] J. D. Kendall, H. G. Suggate, and J. H. Mayo, British Patent 704,770 (March 3, 1954); *Chem. Abstr.*, **48**, 9850 (1954). [f] *Anal.* Calcd for $C_{10}H_{14}N_2$: C, 74.03; H, 8.70; N, 17.27. Found: C, 73.96; H, 8.88; N, 17.12. [g] *Anal.* Calcd for $C_{10}H_{14}N_2$: C, 74.03; H, 8.70; N, 17.27. Found: C, 74.06; H, 8.85; N, 17.15. [h] *Anal.* Calcd for $C_{10}H_{14}N_2$: C, 74.03; H, 8.70; N, 17.27. Found: C, 74.05; H, 8.83; N, 17.25. [i] In acetone-d_6. [j] A mixture of *trans* and *cis* isomers, in ratio 2:1, determined from nmr (8.72 = *cis*, 8.68 = *trans* methyls). [k] Carbon tetrachloride solution. [l] Not purified; used directly to prepare corresponding tetracyanocyclopropane. [m] Liquid film. [n] Reference 13.

Results and Discussion

Alkylidenemalononitriles were prepared from the corresponding ketones and malononitrile, using ammonium acetate and acetic acid as catalysts, benzene as solvent, and removing the water as it formed.[13] In general the yields were good and no difficulties were encountered. Alkylidenemalononitriles prepared for subsequent conversion to tetracyanocyclopropanes are listed, with some of their properties, in Table I. Although many of these are new compounds, only a few were analyzed. Others were identified *via* their nmr, ultraviolet, and infrared spectra, and by conversion to known or analyzed new tetracyanocyclopropanes.

Conversion of the alkylidenemalononitriles to tetracyanocyclopropanes was usually accomplished by reaction with an excess of bromomalononitrile in 50–95% aqueous ethanol at room temperature. All the products were crystalline and were separated by filtration and purified by recrystallization, usually from ethanol. Table V in the Experimental Section gives the details of these preparations. The yields and properties of the products are summarized in Table II. The structures of the products follow either from comparison with authentic samples prepared *via* the Wideqvist reaction or from analytical and spectral data.

Tetracyanocyclopropanes which are easily formed by this route, but which could not be obtained[3] by the usual Wideqvist conditions include those derived from dicyclopropyl ketone (XXVII), 3-heptanone (XXVI), and large-ring cyclic ketones (XXXI–XXXIII). The case of XXVII is particularly striking, a good yield being obtained from XII within 10 min at room temperature, but even the present route seems particularly sensitive to steric effects. For example, the yield decreased on substitution of a methyl group in the 2 position of cyclohexanone, from 97 to 39% (compare XXIX and XXX); two methyl groups, one each in the 2 and 5 positions of cyclopentanone (XIV), caused the cyclopropanization to fail. Although no cyclopropane could be obtained from the alkylidenemalononitrile derived from di-*n*-amyl ketone (XI), large-ring cyclic alkylidenemalononitriles (such as XVIII), in which the alkyl groups are pinned back, reacted readily. Other alkylidenemalononitriles listed in Table I which failed to give tetracyanocyclopropanes are all rather hindered (V, IX, and X).

A number of aryl methyl ketones are reported to react poorly, or not at all, in the Wideqvist reaction.[1,14] Since the corresponding alkylidenemalononitriles are

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

(14) For example, acetophenone gave only a 14% yield of a tetracyanocyclopropane, and methyl α-naphthyl ketone failed to react.[1]

TABLE II

3,3-DIALKYL-1,1,2,2-TETRACYANOCYCLOPROPANES

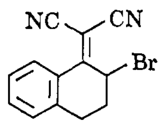
Compd	R_1	R_2	Yield, %	Mp, °C	Infrared^{a}	Nmr^{b}	% C		% H		% N	
							Calcd	Found	Calcd	Found	Calcd	Found
XX	CH_3	CH_3	86	206–208^{c}								
XXI	CH_3	C_2H_5	91	204–206^{d}	2265, 982	8.72 (t, 3), 8.23 (s, 3), 7.92 (q, 2)						
XXII	CH_3	n-C_3H_7	97.5	164–166^{e}	2280, 983	8.94 (t, 3), 8.23 (s, 3), 8.07 (m, 4)						
XXIII	CH_3	i-C_3H_7	97.4	201–202.5^{f}	2260, 983	8.82 (d, 6), 8.49 (s, 3), 8.32 (se, 1)^{g}						
XXIV	CH_3	n-C_5H_{11}	97.5	103–105	2280, 982	9.08 (t, 3), 8.73 (m, 6), 8.41 (s, 3), 8.27 (m, 2)^{g}	69.00	69.14	6.28	6.37	24.76	24.78
XXV	C_2H_5	C_2H_5	88.5	163–165^{h}	2276, 980	8.76 (t, 6), 7.96 (q, 4)						
XXVI	C_2H_5	n-C_4H_9	94.5	119–121	2275, 998	9.10–8.00 (m)	69.00	68.97	6.28	6.27	24.76	24.85
XXVII	Cyclo-C_3H_5	Cyclo-C_3H_5	62	185–187	2262, 1040	9.09 (m, 8), 8.76 (m, 2)	70.25	70.38	4.54	4.47	25.21	25.32
XXVIII	$-(CH_2)_4-$		52.6	240–243^{i}	2270, 968	7.91 (b)^{j}						
XXIX	$-(CH_2)_5-$		97.5	177–179^{k}	2260, 983	8.22 (m, 6), 7.97 (m, 4)						
XXX	$-(CH_2)_4CH(CH_3)-$		39.3	165–166	2275, 984	8.43 (d, 3), 8.22 (m, 6), 7.93 (m, 2), 7.36 (m, 1)	69.62	69.73	5.39	5.29	24.98	25.10
XXXI	$-(CH_2)_9-$		34.8	214–216	2280, 978	8.43 (b, 10), 8.03 (b, 8)^{g}	72.15	72.14	6.81	6.81	21.04	21.11
XXXII	$-(CH_2)_{11}-$		94	197–200	2265, 971	8.53 (b, 14), 8.09 (m, 8)	73.44	73.59	7.53	7.56	19.03	19.12
XXXIII	$-(CH_2)_{14}-$		36^{l}	111–112	2280, 973	8.64 (b, 20), 8.30 (b, 8)	74.96	74.86	8.39	8.38	16.65	16.61

[a] Nujol mull, C≡N, and band near 1000 cm^{-1}, possibly due to the cyclopropane ring. [b] Solvent is acetone-d_6 unless otherwise stated; for meaning of symbols, see footnote *c*, Table I. [c] Lit.[1] 209.5–210°. [d] Lit.[1] 202–202.5°. [e] Lit.[3] 167.5–168°. [f] Lit.[3] 187–188°. [g] In DMSO-d_6. [h] Lit.[3] 167–168°. [i] Lit.[3] 239–240°. [j] In DMSO-d_6 at 110° (CH_3NO_2, τ 5.67, reference). [k] Lit.[3] 180–181°. [l] Over-all, from ketone.

readily prepared from these ketones,[15] it seemed worthwhile to extend our method to such compounds. Table III lists the starting α-arylalkylidenemalononitriles, and Table IV gives the yields and properties of the tetracyanocyclopropanes prepared from them. The structures of the products are clear from their analytical and spectral properties.

The reaction proceeds well in most cases. Thus 3-methyl-3-phenyl-1,1,2,2-tetracyanocyclopropane (XLIII) can be obtained in 73% over-all yield from acetophenone, an improvement over the previous method.[14] Cyclopropane formation seems to proceed well with electron-withdrawing (m-Cl, XLVII) or electron-releasing (p-OCH_3, XLVI) groups on the aryl ring, although the reaction seems to be slower in the latter case (see Table V).

Exceptional Cases.—2,3-Benzocyclohexylidenemalononitrile (XLI) behaved in an exceptional manner, the reaction course being particularly sensitive to solvent and temperature. In 80% aqueous ethanol at room temperature the normal cyclopropanization occurred, L being obtained in reasonable yield. However, when the reaction of XLI with bromomalononitrile was carried out in 85% ethanol at reflux, or in 95% ethanol at room temperature, the cyclopropane L was not produced. Instead, needle-like crystals of a bromine-containing product, $C_{13}H_9BrN_2$, mp 135–138°, were obtained in 40–50% yield. In 90% ethanol at room temperature low yields (10–15%) of both products were obtained. Compound XLI and ethyl bromocyanoacetate also gave the same bromine-containing product, which is believed to be 6-bromo-2,3-benzocyclohexylidenemalononitrile (LI) on the following evidence.



LI

The infrared spectrum (Nujol) showed three absorption bands in the double-bond region at 1603, 1567 and 1543 cm^{-1} which are similar in shape and relative intensity to bands at 1599, 1564, and 1531 cm^{-1} in the starting material (XLI). The C≡N stretching frequency (2245 cm^{-1}) was much lower than in the corresponding cyclopropane (2265 cm^{-1}) or most other aryl alkyl tetracyanocyclopropanes (2262–2300 cm^{-1}; see Table IV) suggesting that the C≡N was conjugated with a carbon–carbon double bond (for example, $\nu_{C\equiv N}$ in the starting material, XLI, was 2230 cm^{-1}). The ultraviolet spectrum (see Experimental Section) also indicated an α,β-unsaturated nitrile, the maximum at 235 mμ being particularly characteristic of alkylidenemalononitriles (*cf.* Table I). Finally, the nmr spectrum, in hexadeuteriodimethyl sulfoxide, consisted of two multiplets at τ 7.55 and 6.94, a triplet at τ 4.36, and aromatic multiplets at τ 2.47 and 1.73, with relative areas 2:2:1:4. This spectrum is consistent with structure LI, or possibly with that of the 4-bromo isomer, LII. Of these, LI is preferred from a comparison of chemical shifts with those of a model compound. Thus the proton on C-1 of 1-bromotetralin (LIII)

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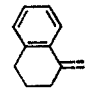
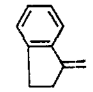
[15] D. T. Mowry, *J. Am. Chem. Soc.*, **67**, 1050 (1945).

TABLE III

α-ARYLALKYLIDENEMALONONITRILES

ArRC═C(CN)$_2$

Compd	Ar	R	Yield, %	Mp, °C	Nmr[a]
XXXIV	C_6H_5	CH_3	84.7	88–91[b]	7.58 (s, 3), 2.58 (m, 5)
XXXV[c]	C_6H_5	C_2H_5	64.9	65–67	8.92 (t, 3), 7.05 (q, 2), 2.55 (s, 5)[d]
XXXVI	p-$CH_3C_6H_4$	CH_3	78.5	96–98[e]	7.62 (s, 3), 7.42 (s, 3), 2.72 (d, 2), 2.42 (d, 2)
XXXVII	p-$CH_3OC_6H_4$	CH_3	59.7	77–79	7.39 (s, 3), 6.12 (s, 3), 2.94 (d, 2), 2.27 (d, 2)
XXXVIII	m-ClC_6H_4	CH_3	31.6	65–67	7.35 (s, 3), 2.37 (m, 4)
XXXIX	2-$C_{10}H_7$	CH_3	81.6	107–109	7.30 (s, 3) 2.35 (m), 2.00 (m), 1.74 (d) (last three total 7 protons)
XL	2-Thienyl	CH_3	61.2	83–86[f]	7.12 (s, 3), 2.52 (m), 1.76 (m) (last two total 3 protons)
XLI			59	108–109[g]	8.05 (m, 2), 7.09 (m, 4), 2.63 (m), 1.84 (m) (last two total 4 protons)
XLII			29.2	147–150[h]	

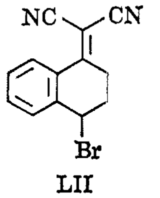
[a] In acetone-d_6 unless otherwise stated; for meaning of symbols, see footnote c, Table I. [b] Lit.[15] 94°. [c] Described by M. Bargain, *Compt. Rend.*, **255**, 1948 (1962), and **256**, 1990 (1963), but yield and melting point are not given. [d] Solvent is $CDCl_3$. [e] Lit.[15] 97°. [f] Lit.[15] 86°. [g] Lit.[15] 109°. [h] D. M. W. Anderson, F. Bell, and J. L. Duncan [*J. Chem. Soc.*, 4705 (1961)] reported mp 152°.

TABLE IV

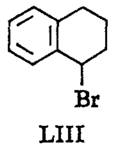
3-ARYL-3-ALKYL-1,1,2,2-TETRACYANOCYCLOPROPANES

							% C		% H		% N	
Compd	Ar	R	Yield, %	Mp, °C	Infrared[a]	Nmr[b]	Calcd	Found	Calcd	Found	Calcd	Found
XLIII	C_6H_5	CH_3	86.6	249–252[c,d]	2270, 988	8.13 (s, 3), 2.50 (m, 5)						
XLIV	C_6H_5	C_2H_5	17.8	225–227	2275, 990	8.89 (t, 3), 7.68 (q, 2), 2.21 (m, 5)	73.16	73.08	4.09	4.11	22.75	22.68
XLV	p-$CH_3C_6H_4$	CH_3	81.2	222–224	2262, 985	7.98 (s, 3), 7.62 (s, 3), 2.65 (d, 2), 2.18 (d, 2)	73.16	73.18	4.09	4.03	22.75	22.62
XLVI	p-$CH_3OC_6H_4$	CH_3	51.2	215–217	2300, 990	7.98 (s, 3), 6.15 (s, 3), 2.93 (d, 2), 2.14 (d, 2)	68.69	68.52	3.84	3.78	21.36	21.38
XLVII	m-ClC_6H_4	CH_3	68.1	206–208	2266, 988	7.93 (s, 3), 2.42, 2.05, 1.75 (m, 4)	63.05	62.26	2.65	2.81	21.01[e]	20.77
XLVIII	2-$C_{10}H_7$	CH_3	54.8	255–260[c]	2280, 985	7.84 (s, 3), 2.37, 2.02, 1.43 (m, 7)	76.58	75.03	3.57	3.54	19.85	19.50
XLIX	2-Thienyl	CH_3	22.1	207–210[c]	2275, 985	8.16 (s, 3), 2.87, 2.25 (m, 3)[f]	60.49	60.47	2.54	2.76	23.52[g]	23.52
L			54.2	167–170	2265, 968	h	74.40	74.31	3.90	3.98	21.69	21.53

[a] Nujol mull, C≡N, and band near 1000 cm^{-1}, possibly due to the cyclopropane ring. [b] Solvent is acetone-d_6 unless otherwise stated; for meaning of symbols see footnote c, Table I. [c] Decomposes. [d] Lit.[1] 225. [e] *Anal.* Calcd for Cl: 13.3. Found: 13.57. [f] In DMSO-d_6. [g] *Anal.* Calcd for S: 13.46. Found: 13.31. [h] Could not find suitable solvent.



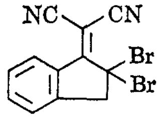
LII



LIII

appears as a triplet at τ 4.64;[16] if the unknown bromide had structure LII, the triplet in its nmr spectrum ought to appear at τ 4.64, whereas it actually appears considerably further down field, at τ 4.36. This is understandable if the correct structure is LI, where this proton is in the vicinity of the strongly electron-withdrawing nitrile groups.

Similar bromination, rather than cyclopropanization, occurred with 2,3-benzocyclopentylidenemalononitrile (XLII). The product of reaction with bromomalononitrile in 80% ethanol was a crystalline, off-white dibromo derivative, $C_{12}H_6Br_2N_2$, mp 208–211°. On the basis of infrared and ultraviolet spectra and mechanistic considerations, the structure is believed to be LIV.



LIV

Unfortunately a satisfactory nmr solvent could not be found.

It seems likely that this bromination is ionic, rather than free-radical, bromomalononitrile being a source of positive bromine.[17] One possible scheme is shown. In the presence of acid (bromomalononitrile has a p*K* of about 5 in water)[11] some 2,3-benzocyclohexylidenemalononitrile may be converted to its double-bond isomer, LV, which is attacked electrophilically by bromomalononitrile. It is probably significant that bromina-

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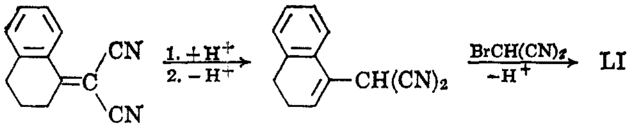
(16) We are indebted to Dr. Alan Sheller for preparing a sample of LIII from the corresponding alcohol and determining its nmr spectrum.

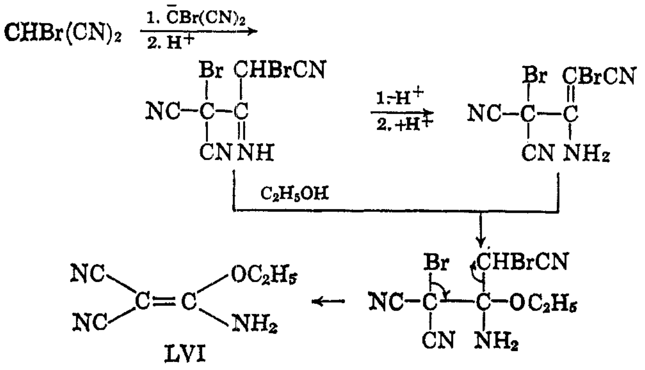
(17) It will, for example, oxidize iodide ion.[1]

tion occurs in less polar solvents, when bromomalononitrile is present largely as the acid, and that cyclopropanization, which requires nucleophilic attack on XLI by the bromodicyanocarbanion, is favored in more aqueous ethanol.


XLI LV

Reaction of Bromomalononitrile with Ethanol.—In some instances, reaction mixtures of alkylidenemalononitriles and bromomalononitrile which did not readily yield tetracyanocyclopropanes were allowed to stand at room temperature for as long as a month. During this time small amounts of a brownish precipitate formed which, on purification, was obtained as white crystals, mp 235–237°. The same substance was produced regardless of the structure of the recalcitrant alkylidenemalononitrile (V, IX, XI, and tetracyanoethylene), and presumably arose from a reaction of bromomalononitrile with ethanol. Accordingly, bromomalononitrile was refluxed for several hours with aqueous ethanol, and work-up led to an 8% yield of the same compound, which analyzed correctly for $C_6H_7N_3O$. The infrared spectrum (Nujol) had bands at 3355 and 3230 cm^{-1} (N–H), 2248 and 2205 cm^{-1} (C≡N), 1658, 1550, and 1503 cm^{-1} (C=C and/or N–H), and 1043 cm^{-1} (C–O–C). The compound had a single absorption band (in ethanol) at 253 mμ (ϵ 18,640). The nmr spectrum (in DMSO-d_6) showed a typical triplet and quartet for an ethoxyl group (τ 8.71, t, and 5.72, q; J = 7 cps) and a singlet at τ 1.45, in the area ratio 3:2:2. From these data, and comparison with the literature[18] the substance seems to be 1,1-dicyano-2-amino-2-ethoxyethene (LVI), which was previously[18] obtained by reaction of aqueous ammonia with one equivalent of dicyanoketene diethyl acetal. Possible schemes for the formation of LVI from bromomalononitrile and ethanol are shown in Scheme II.

SCHEME II



Extensions of the cyclopropanization reaction described in this paper and of the chemistry of tetracyanocyclopropanes are being explored.

TABLE V

EXPERIMENTAL DETAILS FOR PREPARATION OF TETRACYANOCYCLOPROPANES LISTED IN TABLES II AND IV[a]

Compd	Reactants, mmoles: Alkylidene-malono-nitrile	Reactants, mmoles: Bromo-malono-nitrile	Solvent[b]	Time[c]
XX[d]	4.72	6.90	5, 50	2 min, 30 min
XXI[d]	8.3	10.0	15, 80	few min, few hr
XXII	5.95	8.97	10, 75	few min
XXIII	3.73	6.00	12, 80	1 hr, 24 hr[e]
XXIV	7.71	10.0	10, 90	1 hr, few hr
XXV	10.1	13.8	15, 95	few hr
XXVI	6.17	10.3	15, 90	24 hr
XXVII	5.0	6.9	20, 60	10 min, 24 hr
XXVIII[f]	7.57	10.3	14, 85	30 min, few hr
XXIX[d]	6.84	11.07	15, 80	2 min, few hr
XXX	6.25	10.3	30, 95	16 hr, 48 hr
XXXI[d]	4.85	15.3	12, 95	15 min, few hr
XXXII[d]	2.17[g]	13.8	10, 95	1 hr, few hr
XXXIII	2.89[g]	13.8	15, 95	6 days[h]
XLIII[d]	5.96	10.0	40, 95	1.5 hr, 24 hr[i]
XLIV	5.0	8.0	20, 95	few days[j]
XLV	5.49	10.0	50, 95	15 hr, 18 hr[k]
XLVI	5.04	15.0	50, 95	20 hr, 44 hr[l]
XLVII	4.93	10.3	50, 95	2 hr, few hr
XLVIII[d]	4.58	15.0	50, 95	1 hr, 24 hr
XLIX	5.7	6.9	50, 95	30 min[m]
L	3.1	10.3	35, 80	6 hr, 12 hr[n]

[a] All reactions carried out at room temperature. The solvent for recrystallization of the product was 95% ethanol, unless otherwise stated. [b] First figure is volume in milliliters, second % aqueous ethanol. [c] First figure is time for first crystals to appear, second time elapsed before work-up. If only one figure is given it is the second of these. [d] Recrystallization solvent, ethanol–acetone. [e] At this time, 6.00 mmoles additional bromomalononitrile was added; product was collected daily for 5 days. [f] Recrystallization solvent acetone. [g] Millimoles of starting ketone. [h] At this time, 3 ml of water were added, and an oil was obtained which subsequently crystallized. [i] At this time, 10.0 mmoles additional bromomalononitrile was added; product was collected daily for 3 days. [j] Cooling in an ice bath led to deposition of crystals. [k] Added 6 mmoles additional bromomalononitrile, and collected second crop overnight. [l] Added 14 mmoles additional bromomalononitrile, and collected second crop 24 hr later. [m] Reaction mixture heated on steam bath for a few minutes. [n] Added 2 ml of water and collected second crop a few hour later.

Experimental Section[19]

Alkylidenemalononitriles.[13]—These were prepared by refluxing 0.1–0.2 mole each of ketone and malononitrile in 25–30 ml of benzene containing 1.5–3.0 g of ammonium acetate and 2–3 ml of acetic acid for several hours (up to 24), the water being removed periodically from a Dean-Stark trap until the theoretical amount was produced. The cooled reaction mixture was washed with water, dried, and distilled; products are listed in Table I.

α-Arylalkylidenemalononitriles.[15]—These were prepared as is described immediately above, but purified by recrystallization, usually from ethanol or ethanol–acetone mixtures (Table III).

Tetracyanocyclopropanes.—The general procedure was described in the text, but in each case conditions varied in some detail (relative amounts of reactants, solvent, reaction time). Table V contains the essential experimental details for the preparation of each tetracyanocyclopropane listed in Tables II and IV.

Bromination of 2,3-Benzocyclohexylidenemalononitrile (XLI).—A mixture of 0.6 g (3.1 mmoles) of XLI and 35 ml of 85% aqueous ethanol was warmed to effect solution, then 1.5 g (10.3 mmoles) of bromomalononitrile was added, and the solution refluxed for 4 hr. The dark residue which remained after the solvent was removed on a rotary evaporator was treated with Norit A and recrystallized from ethanol, giving 0.34 g (40.2%) of pinkish white crystals of 6-bromo-2,3-benzocyclohexylidenemalononitrile (LI), mp 135–138°.

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[18] W. J. Middleton and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2788 (1958).

[19] Analyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich. Melting points are uncorrected.

Anal. Calcd. for $C_{13}H_9BrN_2$: C, 57.16; H, 3.32; Br, 29.26; N, 10.26. Found: C, 57.33; H, 3.43; Br, 29.18; N, 10.20.

The infrared spectrum (Nujol) showed bands at 2245 (C≡N), 1603, 1567, 1543 (C=C), and 735 cm^{-1} (1,2-disubstituted benzene). The ultraviolet spectrum (ethanol) had λ_{max} at 322.5 mμ (ϵ 16,740) and 235 mμ (ϵ 6830). The nmr spectrum (in DMSO-d_6) had bands at τ 7.55 (m, 2), 6.94 (m, 2), 4.36 (t, J = 3.6 cps, 1), 2.47, and 1.73 (m, 4).

The same product was obtained in 48% yield when 10 mmoles of XLI, 30 mmoles of bromomalononitrile, and 70 ml of 95% ethanol were allowed to stand at room temperature for 2 weeks. It was also obtained, in 68.4% yield, when 5.2 mmoles of XLI and 20.8 mmoles of ethyl bromocyanoacetate in 50 ml of 95% ethanol were refluxed for 10 hr.

Reaction of 2,3-Benzocyclopentylidenemalononitrile (XLII) with Bromomalononitrile.—A mixture of 1 g (5.55 mmoles) of XLII, 100 ml of 95% ethanol, and 10 ml of water was heated to effect solution. Bromomalononitrile (3 g, 20.7 mmoles) was added, and the mixture was refluxed for 6 hr, during which time a precipitate formed. Cooling and filtration gave a small (about 10%) yield of a product believed to be 5,5-dibromo-2,3-benzocyclopentylidenemalononitrile (LIV), mp 208–211° (from acetone).

Anal. Calcd for $C_{12}H_6Br_2N_2$: C, 42.64; H, 1.79; Br, 47.28; N, 8.29. Found: C, 42.72; H, 1.52; Br, 47.65; N, 8.11.

The infrared spectrum (Nujol) had bands at 2240 (C≡N), 1599, 1568 (C=C), and 790 cm^{-1} (arom). The ultraviolet spectrum (ethanol) had λ_{max} at 346 mμ (ϵ 15,730), 337 mμ (ϵ 15,860), and 236 mμ (ϵ 7140). A suitable solvent for an nmr spectrum could not be found.

Reaction of Bromomalononitrile with Ethanol.—A solution of 5 g (34.5 mmole) of bromomalononitrile in 15 ml of 90% ethanol was refluxed for 8 hr, then evaporated to dryness. Water (30 ml) was added to the dark residue, and the mixture was cooled in an ice bath. The crystals which separated were treated with Norit A and recrystallized from ethanol, giving 0.2 g (8.4%) of 1,1-dicyano-2-amino-2-ethoxyethene (LVI), mp 235–237°.

Anal. Calcd for $C_6H_7N_3O$: C, 52.55; H, 5.15; N, 30.64. Found: C, 52.71; H, 5.07; N, 30.73.

The infrared spectrum (Nujol) had bands at 3355, 3230 (N-H), 2248, 2205 (C≡N), 1658, 1550, and 1503 cm^{-1} (C=C and/or N-H). The ultraviolet spectrum (ethanol) had a single λ_{max} at 253 mμ (ϵ 18,640). The nmr spectrum (in DMSO-d_6) had bands at τ 8.71 (t, J = 7.0 cps, 3), 5.72 (q, J = 7.0 cps, 2), and 1.45 (s, 2).

Acknowledgement.—We are indebted to the National Institutes of Health for a grant (GM11775) which supported this research.

Chemistry of *gem*-Dihalocyclopropanes. V.[1] Formation of Tricyclo[4.1.0.0^{4,6}]heptane and Derivatives

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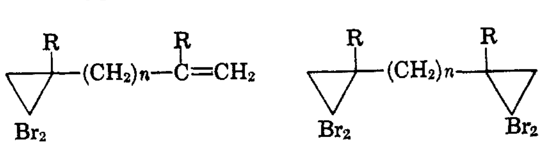
Received March 15, 1966

Reactions of 2-alkenyl-1,1-dibromocyclopropane (I) and bis(1,1-dibromocyclopropyl)alkane (II) with methyllithium have been studied. The corresponding allenes and diallenes were obtained from compounds I and II, respectively. In addition, from reactions of I (n = 2) and II (n = 2), the highly strained novel compound tricyclo[4.1.0.0^{4,6}]heptane and derivatives were obtained. These are probably formed by an intramolecular addition of a complexed carbene (carbenoid) intermediate.

Since the first allenic compound, *viz.*, allene itself, was synthesized one-hundred years ago[2] several methods for the preparation of this class of compounds have become available. Some of these methods are quite impractical because mixtures with the corresponding acetylenes and other isomers are frequently encountered. On the basis of prior work by Doering and LaFlamme,[3] a two-step synthesis of allenes from olefins was developed independently in this laboratory[4] and by Moore and co-workers.[5] The first step involves the preparation of *gem*-dibromocyclopropanes from olefins and dibromocarbene;[6,7] the addition of methyllithium to the bromides at temperatures between −78 and 0° gives, in a number of examples, allenes in excellent yields. This method has several advantages: olefins as starting materials, lenient reaction conditions, and the absence of acetylenic by-products being the most important. It is also the only practical method for the preparation of cyclic allenes. Hence, it was of interest to establish the generality of the reaction as a method for allene synthesis, and the present work[8] describes reactions of compounds of the general structures I and II where n >0. The expected allenes and diallenes would belong to a virtually unknown structural type.



I II

R=H or CH_3

The compounds to be studied became available by the addition of dibromocarbene to dienes,[9] and their reactions with methyllithium were carried out as already described.[4] The results from reactions of compounds of the general structure I are summarized in Table I.

As seen in Table I, all reactions afforded allenes and, except in the case of XIII, they constituted the main part of the reaction products. In those cases where the product consisted of a mixture the pure components were obtained by fractional distillation or preparative gas chromatography. Characterization of the allenes presented no difficulties. Besides elemental analysis the structures were assigned on the basis of

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[1] Part IV: L. Skattebøl, *J. Org. Chem.*, **31**, 1554 (1966).

[2] For a comprehensive review on allenes, see A. A. Petrov and A. V. Fedorova, *Russ. Chem. Rev.*, 1 (1964).

[3] W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958).

[4] L. Skattebøl, *Tetrahedron Letters*, 167 (1961); *Acta. Chem. Scand.*, **17**, 1683 (1963).

[5] W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); **27**, 4179 (1962); W. R. Moore, H. R. Ward, and R. F. Merrit, *J. Am. Chem. Soc.*, **83**, 2019 (1961).

[6] W. von E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6162 (1954).

[7] For a review of this reaction, see W. E. Parham and E. E. Schweizer, *Org. Reactions*, **13**, 55 (1963).

[8] Part of this investigation has appeared as a preliminary communication: L. Skattebøl, *Chem. Ind.* (London), 2146 (1962).

[9] L. Skattebøl, *J. Org. Chem.*, **29**, 2951 (1964).