g. of 40% formaldehyde (0.5 mole) in 50 cc. of concentrated hydrochloric acid at 55–70° during 12 hours.[11] The upper layer was taken up in pentane, washed with water, dried and distilled over anhydrous potassium carbonate. There was obtained 51 g. (58%) of chloromethyl-*p*-chlorotoluene, b.p. 75–75° at 1.5 mm., n^{20}_D 1.5560; and 8 g. (14%) of bis-(chloromethyl)-*p*-xylene, as crystalline residue which gave short white needles, m.p. 108–109°, on recrystallization from heptane.

Anal. Found: C, 48.45; H, 4.35; Cl, 47.38. Calcd. for $CH_3C_6H_2Cl(CH_2Cl)_2$ or $C_9H_9Cl_3$: C, 48.36; H, 4.06; Cl, 47.59.

Tschunker and Eichler[11] state that oxidation of the monochloromethylated compound yielded 2-chloro-5-methylbenzoic acid while reduction yielded 4-chloro-*m*-xylene, indicating that the compound (no physical properties of which are given in the patent) was 3-chloromethyl-4-chlorotoluene.

A solution of 15 g. (0.086 mole) of the chloromethylchlorotoluene in 29 g. of *p*-chlorotoluene was added during 1.5 hours to a stirred mixture of 58 g. (0.69 mole total) of *p*-chlorotoluene and 3 g. of ferric chloride at 28–29°. The product was stirred for an additional 50 minutes, after which the upper layer was separated from 5.5 g. of solid catalyst layer, treated in the usual manner and distilled, yielding 10.5 g. (60%) of XXII, b.p. 147–149° at 0.9 to 1.0 mm. (converts to 358–359° at 760 mm., 328–331° in a test-tube), n^{20}_D 1.5876 to 1.5891.

Infrared analysis of various fractions indicated that the product consisted essentially of one compound and that this was a component of the product obtained by the reaction of *p*-chlorotoluene with *t*-butyl chloride.

Nitration of various samples of XXII with 2:1 sulfuric acid–nitric acid yielded a dinitro derivative, m.p. 144° (recrystallized from Formula 30 alcohol).

Anal. Found: C, 50.68; H, 3.71; N, 8.17; Cl, 20.20. Calcd. for $C_{15}H_{12}Cl_2N_2O_4$: C, 50.72; H, 3.41; N, 7.88; Cl, 19.97.

Tetranitrodi-*p*-xylylmethane.—Nitration of VII with 2:1 nitrating mixture yielded a tetranitro derivative, m.p. 190°.

Anal. Found: C, 50.36; H, 4.03; N, 13.85. Calcd. for $C_{17}H_{16}N_4O_8$: C, 50.50; H, 3.98; N, 13.85.

DES PLAINES, ILL.

---

[11] E. Tschunker and F. Eichler, German Patent 509,149 (1930).

[CONTRIBUTION NO. 509 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Chemistry of Cyclobutanes. I. Synthesis of Methylenecyclobutanes

BY H. N. CRIPPS, J. K. WILLIAMS AND W. H. SHARKEY

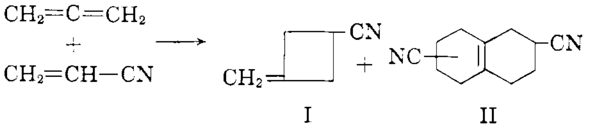
RECEIVED NOVEMBER 21, 1958

A new route to substituted methylenecyclobutanes has been discovered that involves cycloaddition of allenes to appropriately substituted olefins. This reaction has been used to prepare 3-methylenecyclobutanes substituted in the 1-position with nitrile, carboxyl, carboalkoxy, aldehyde and aryl groups. 2,6(and/or 2,7)-Disubstituted -1,2,3,4,5,6,7,8-octahydronaphthalenes were also obtained as secondary products. When substituted allenes were employed, products corresponding to cycloaddition to each double bond were usually obtained. In these cases reaction of the less substituted allenic double bond appeared to be favored.

The cycloaddition of tetrafluoroethylene, chlorotrifluoroethylene and 1,1-dichloro-2,2-difluoroethylene to olefins[1] has made a variety of fluorinated cyclobutanes readily available for study. However, the direct syntheses of simple non-fluorinated cyclobutanes has been limited to the dimerization of acrylonitrile,[2] methacrylonitrile,[3] allenes[4] and alkylketenes[5] and the addition of ketene to cyclopentadiene[6,7] and cyclohexadiene.[7]

Recently, a synthesis of non-fluorinated cyclobutanes[8] of breadth and simplicity comparable to the direct cycloaddition of fluoroölefins has been discovered. Allenes have been found to react with suitably substituted olefins at elevated temperatures to give alkylidenecyclobutanes. Alder and Ackermann[9] reported that allenes and maleic anhydride react to form 3-alkylidenecyclobutane-1,2-dicarboxylic anhydrides. Prior to Alder and Ackermann's report we had independently discovered the thermal cycloaddition of allenes to olefins and had found the reaction to be generally applicable to the preparation of a wide variety of substituted alkylidenecyclobutanes.

The thermal cycloaddition of allenes to substituted olefins is best exemplified by allene and acrylonitrile, which react smoothly to give a cyclobutane, I, and an octahydronaphthalene, II.



I II

Reaction conditions are 150–250° at autogenous pressure. The maximum pressure during reaction is in the range of 4–4.5 atm. When a large excess of acrylonitrile is used 3-methylenecyclobutanecarbonitrile (I) is formed in yields as high as 60%. The formation of the second product, 2,6(and/or 2,7)-dicyano-1,2,3,4,5,6,7,8-octahydronaphthalene (II), which is obtained in 15–25% yields under these conditions, will be discussed later.

The identity of the 1:1 adduct as 3-methylenecyclobutanecarbonitrile (I) was established by its conversion to known compounds. Catalytic hydrogenation of I gave a saturated nitrile that was hydrolyzed to 3-methylcyclobutanecarboxylic acid. The anilide of this acid, III, melted at 127–128°, which is in agreement with the melting point of 3-

---

[1] (a) D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, THIS JOURNAL, **71**, 490 (1949); (b) P. L. Barrick and R. D. Cramer, U. S. Patent 2,427,128 (1947); (c) P. L. Barrick, U. S. Patent 2,427,116 (1947); (d) J. Harmon, U. S. Patent 2,404,374 (1946).

[2] E. C. Coyner and W. S. Hillman, THIS JOURNAL, **71**, 324 (1949).

[3] C. J. Albisetti, D. C. England, M. J. Hogsed and R. M. Joyce, *ibid.*, **78**, 472 (1956).

[4] S. V. Lebedeff and B. K. Merezhkovskii, *J. Russ. Phys. Chem. Soc.*, **45**, 1249 (1913); S. V. Lebedeff, *ibid.*, **43**, 820 (1911).

[5] W. E. Hanford and J. C. Sauer, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 108–140.

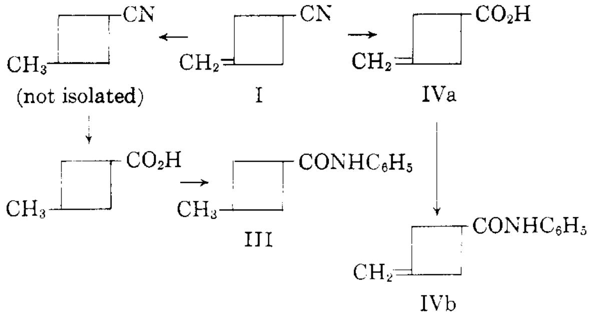
[6] B. T. Brooks and G. Wilbert, THIS JOURNAL, **63**, 879 (1941).

[7] A. T. Blomquist and J. Kwiatek, *ibid.*, **73**, 2098 (1951).

[8] H. N. Cripps, J. K. Williams and W. H. Sharkey, *ibid.*, **80**, 751 (1958).

[9] K. Alder and O. Ackermann, *Chem. Ber.*, **90**, 1697 (1957).

methylcyclobutanecarboxanilide reported by Kazanskii and Lukina.[10]



Hydrolysis of I gave 3-methylenecyclobutanecarboxylic acid (IVa) which formed an anilide (IVb) having the same melting point as that reported by Applequist and Roberts[11] for 3-methylenecyclobutanecarboxanilide.

Infrared and nuclear magnetic resonance (hereafter designated n.m.r.) spectra of I were consistent with the structure proposed. The infrared spectrum showed absorption at 4.45 μ for the nitrile group and at 5.95 μ and 11.30 μ for the terminal methylene group. The n.m.r. spectrum[12] (Fig. 1)

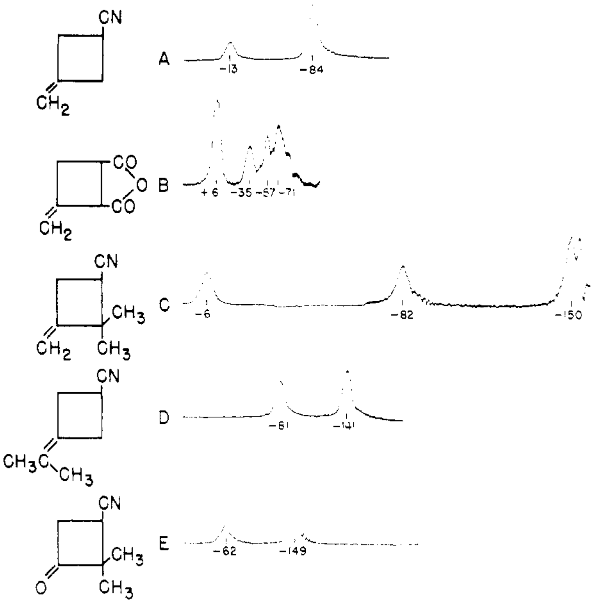
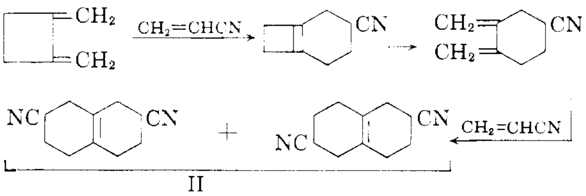


Fig. 1.—N.m.r. spectra of methylenecyclobutanes.

was composed of a methylene hydrogen peak at -13 c.p.s. of relative intensity 2, and a peak of intensity 5 at -84 c.p.s. corresponding to two ring $-CH_2-$ groups, and a $-CH-$ bearing the nitrile.

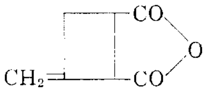
Under the synthesis conditions the dimerization of allene to 1,2-dimethylenecyclobutane[4,13,14] is a competing reaction. This apparently is the first step in the sequence leading to the octahydronaphthalene II. Succeeding steps are visualized as



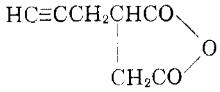
A similar series of reactions has been proposed[13] to explain the formation of 1,2,3,4,5,6,7,8-octahydronaphthalene-2,3,6,7-tetracarboxylic dianhydride from allene and maleic anhydride. The view that dimerization of allene is the key step in formation of the octahydronaphthalene is supported by the finding that the yield of II is profoundly influenced by the composition of the reaction mixture. For example, when a four molar excess of acrylonitrile was employed, the yield of I was 60% and that of II was 15–20%. However, when equimolar amounts of allene and acrylonitrile were used, compound I was obtained in only 5% yield and the yield of II was 75%.

The generality of the reaction of allene with substituted olefins to form methylenecyclobutanes is illustrated by the examples listed in Table I. Unsatured compounds containing such electronegative groups as nitrile, carboalkoxy, carboxyl and aldehyde undergo cycloaddition. Compounds containing an aromatic ring conjugated with the olefin, exemplified by styrene, 1,1-diphenylethylene, indene and 4-vinylpyridine, also react with allene to form cyclobutanes. In many of these cases the corresponding octahydronaphthalenes were isolated. These are described in Table II.

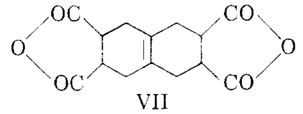
We have also studied the cycloaddition of allene to maleic anhydride. In this case the products were 3-methylenecyclobutane-1,2-dicarboxylic anhydride (V), propargylsuccinic anhydride (VI) and 1,2,3,4,5,6,7,8-octahydronaphthalene-2,3,6,7-tetracarboxylic dianhydride (VII).



V



VI



VII

Alder and Ackermann[9] identified V and VI through investigation of hydrogenated products. In our work the liquid portion of the reaction was carefully fractionated to separate V, b.p. 130° (10 mm.), from VI, b.p. 140° (10 mm.); V was characterized by its infrared spectrum, which contained bands at 5.96 and 10.95 μ for the exocyclic double bond and a doublet at 5.37 and 5.60 μ for the cyclic anhy-

---

(10) B. A. Kazanskii and M. Yu Lukina, *Izvest. Akad. Nauk, SSSR, Otdel. Khim. Nauk*, 47 (1951); *C. A.*, **46**, 4491 (1952); **45**, 2878 (1951).

(11) D. E. Applequist and J. D. Roberts, This Journal, **78**, 4012 (1956).

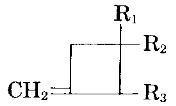
(12) We are indebted to Dr. W. D. Phillips of this Laboratory who determined and interpreted the n.m.r. spectra by means of a high resolution nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates, Palo Alto, Calif., operating at 40 Mc. and approximately 10,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the proton resonance of H_2O. Negative frequency displacements indicate resonances occurring at higher field relative to the reference.

(13) K. Alder and O. Ackermann, *Chem. Ber.*, **87**, 1567 (1954).

(14) A. T. Blomquist and J. A. Verdol, This Journal, **78**, 109 (1956).

TABLE I

CYCLOBUTANES FROM ALLENE AND UNSATURATED COMPOUNDS



Reactants[a] moles allene/moles olefin	Cyclobutane	Yield, %	B.p. °C.	B.p. Mm.	$n^{25}D$	Analyses Calcd. C	Calcd. H	Calcd. N	Calcd. Sapn. or neut. equiv.	Calcd. Mol. wt.	Found C	Found H	Found N	Found Sapn. or neut. equiv.	Found Mol. wt.
0.5/3 Methacrylonitrile[b]	**R_1 = CN; R_2 = CH_3; R_3 = H**	**62**	**58–58.5**	**21**	**1.4453**	**78.46**	**8.47**	..	...	107	78.48	8.54	..	...	97
0.25/0.5 α-Acetoxyacrylonitrile[c]	R_1 = CN; R_2 = $OCOCH_3$; R_3 = H	20	96–97	10	1.4515	...	..	9.26	...	151	...	..	9.54	...	154
0.5/2 Methyl acrylate[d]	R_1 = CO_2CH_3; R_2 = R_3 = H	25	56–59	20	1.4464	66.83	7.98	..	126.2	126.2	67 04	8.18	..	125	121
1/2 Acrylic acid[e]	R_1 = CO_2H; R_2 = R_3 = H	21	92	5	1.4668	64.27	7.19	..	112.1	...	64.39	7.35	..	112	..
0.5/1 Methyl methacrylate	R_1 = CO_2CH_3; R_2 = CH_3; R_3 = H	25	54–55	15	1 4432	68.54	8.63	..	140.2	140.2	68.89	8.73	..	140	137
2/4 Methacrolein[f]	R_1 = CHO; R_2 = CH_3; R_3 = H	6.7	43–44	25	....	76.40	9.08	..	...	...	76.25	9.12	..	...	..
2/2 Styrene[g]	R_1 = φ; R_2 = R_3 = H	22	90–90.5	16	1.5360	91.61	8.39	..	...	144.2	91.50	8.52	..	...	165
1/1.5 α-Methylstyrene[h]	R_1 = φ; R_2 = CH_3; R_3 = H	20	88	11	1.5263	91.08	8.92	..	...	158	90.94	8.99	..	...	164
0.5/1.34 Ethyl itaconate[i]	R_1 = $CH_2CO_2C_2H_5$; R_2 = $CO_2C_2H_5$ R_3 = H	32	110	5	1.4511	63 70	8.02	..	113.3	226.3	63.60	8.01	..	113	232
1/1 4-Vinylpyridine[j]	R_1 = C_5H_4N; R_2 = R_3 = H	23	113–115	17–18	1.5409	...	..	9.65	...	145.2	...	..	9.54	...	132
1/2 Ethyl fumarate	R_1 = R_3 = $CO_2C_2H_5$; R_2 = H	10.5	138–140	21–22	1.4486	62.25	7.60	..	106.1	212.2	62.65	7.87	..	109	205
0.5/1.5 Indene	2-Methylene-1,2,2a,7a-tetrahydro-7H-cyclobuta-[*a*]-indene	28	59–61	0.9	1.5595	92.26	7.74	..	...	156.2	92.32	7.97	..	...	169
1/3 Chloromaleic anhydride[k]	1(or 2)-Chloro-3-methylenecyclobutane-1,2-dicarboxylic anhydride	30	136	25	....	48.72	2.92	..	...	...	48.76	3.02	..	...	..
10/20 Maleic anhydride[l]	3-Methylenecyclobutane-1,2-dicarboxylic anhydride	..	130	10	1.4950	60.87	4.38	..	69.1	138.1	60.81	4.70	..	68.5	141

[a] Unless otherwise stated, reactants were heated with agitation at 200° for about 8 hours under autogenous pressure. Polymerization inhibitor was phenothiazine, hydroquinone or *t*-butyl catechol. [b] 225°, 12 hours. [c] 6 hours, 50 ml. of benzene solvent; α-acetoxyacrylonitrile prepared as described by Johnson and Newton in U. S. Patent 2,395,930, Nov. 5, 1946. [d] 13 hours. [e] 6 hours. [f] 6 hours, 300 ml. of benzene solvent. [g] 4 hours, 300 ml. of benzene solvent; [h] 190°, 4 hours. [i] 225°. [j] 150 ml. of benzene solvent. [k] 5 hours, 200 ml. of benzene solvent. [l] 2600 ml. of benzene solvent.

TABLE II

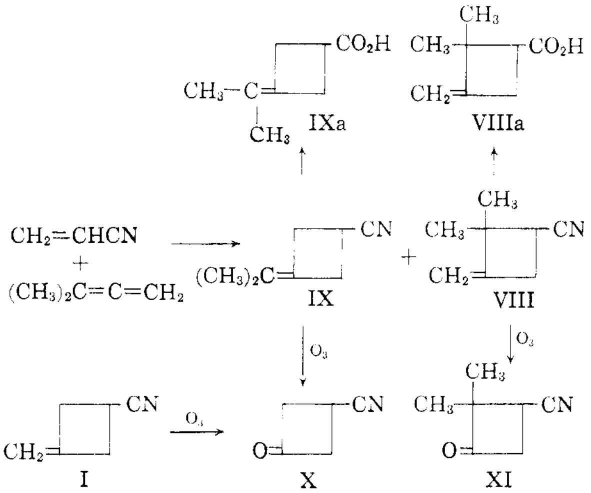
OCTAHYDRONAPHTHALENES FROM ALLENE AND UNSATURATED COMPOUNDS

Reactants[a] moles allene/moles unsaturated compound	1,2,3,4,5,6,7,8-Octahydronaphthalene	Yield, %	M.p., °C.	MCB[b] %	Analyses Calcd. C	Calcd. H	Calcd. N	Calcd. Sapn. or neut. equiv.	Calcd. Mol. wt.	Found C	Found H	Found N	Found Sapn. or neut. equiv.	Found Mol. wt.
1/1 Acrylonitrile[c]	2,6 (or 7)-Dicarbonitrile	75	143.5-144.5[f]	15	77.38	7.58	15.04		186	77.27	7.50	15.09		175
1/1 Methyl acrylate[c]	2,6 (or 7)-Bis-(methoxycarbonyl)	45	149-151[i]	13.2	66.64	7.99		126	252	66.54	7.94		120	255
1/2 Acrylic acid[e]	2,6 (or 7)-Dicarboxylic acid	4	248->300[f]	21										
1/1 Ethyl maleate[c]	2,3,6,7-Tetrakis-(ethoxycarbonyl)	28	100-102[g]		62.25	7.60		106	424	62.71	7.66		104	387
1/1 Methyl crotonate[d,e]	2,6 (or 7)-Dimethyl-3,7(or 6)-bis-(methoxycarbonyl)	25	87-92[h]	0	68.54	8.63				68.73	8.73			

[a] Unless otherwise noted, reactants were heated with agitation at 200° for about 8 hours under autogenous pressure in the presence of a polymerization inhibitor. [b] MCB, % yield of methylenecyclobutane; see Table I. [c] Benzene solvent, product same as reported by Alder and Ackerman.[14] [d] Benzene solvent. [e] Position of substituents not established; all products are isomeric mixtures. [f] See Experimental also. [g] Crystallized from ethanol. [h] Crystallized from methanol. [i] B.p. at 0.6 mm.; $n^{25}D$ 1.4970–1.4990.

dride group. The n.m.r. spectrum of V (Fig. 1B) contained a peak at +6 c.p.s. of relative intensity 2 for the exocyclic methylene hydrogens and three peaks at −35, −57 and −71 c.p.s. of relative intensity 4 for the four ring hydrogens. This cyclobutane has been examined in some detail and its chemistry will be described in succeeding papers.

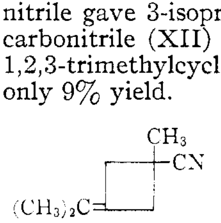
Investigation of unsymmetrically substituted allenes established that each double bond can participate in cycloaddition. At 200° and autogenous pressure, 1,1-dimethylallene combined with acrylonitrile to give 2,2-dimethyl-3-methylenecyclobutanecarbonitrile (VIII) in 30% yield and 3-isopropylidenecyclobutanecarbonitrile (IX) in 36% yield. Alkaline hydrolysis of these compounds gave acids VIIIa and IXa, respectively.



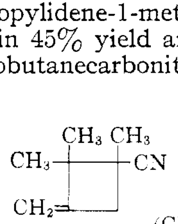
Compound IX was identified by ozonolysis to a cyanoketone, X, that was identical to the cyanoketone obtained by ozonolysis of 3-methylenecyclobutanecarbonitrile. This ketone had an infrared absorption band at 5.6 μ characteristic for the carbonyl group in cyclobutanones.[15]

Identification of VIII was based mainly upon spectral data. The infrared spectrum showed absorption at 5 95 and 11.37 μ as expected for exocyclic methylene and at 4.45 μ for nitrile. The n.m.r. spectrum had a resonance peak of approximate intensity 2 at −6 c.p.s. (Fig. 1C) for the methylene group, which is about the same frequency given by this group in 3 methylenecyclobutanecarbonitrile. The peak of intensity 3 at −82 c.p.s. corresponded to the hydrogens on the 1 and 4 carbon atoms and the doublet of intensity 6 at −148 and −152 c.p.s. is in the frequency range characteristic for methyl groups on saturated carbon. Apparently the nitrile group has an effect across space on the methyl that is on the same side of the plane of the ring, but has no effect on the *trans*-methyl group. Ozonolysis of VIII gave 2,2-dimethyl-3-cyanocyclobutanone (XI) which had infrared absorption at 5.6 μ characteristic for cyclobutanones. The n.m.r. pattern of XI (Fig. 1E) contained a peak at −62 c.p.s. of relative intensity 3 for the ring hydrogens and a peak at −149 c.p.s. of relative intensity 6 for the methyl hydrogens. Splitting of the resonance of the methyl hydrogens was not observed probably because of insufficient resolution.

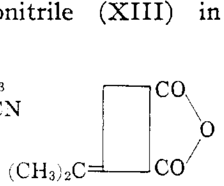
The relative proportion of isomers formed by substituted allenes appears to be associated with substitution about the double bond of the olefin. For example, 1,1-dimethylallene and methacrylonitrile gave 3-isopropylidene-1-methylcyclobutanecarbonitrile (XII) in 45% yield and 3-methylene-1,2,3-trimethylcyclobutanecarbonitrile (XIII) in only 9% yield.



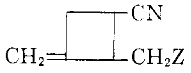
XII



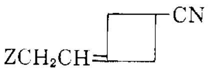
XIII



XIV



XV



XVI

$Z = OCOCH_3, CH(CO_2C_2H_5)_2$

Cycloaddition of 1,1-dimethylallene to maleic anhydride gave a single cyclobutane, XIV, which agrees with Alder and Ackermann's[9] findings.

The wide applicability of this new synthesis of alkylidenecyclobutanes is further illustrated by the reactions of 1-acetoxy-2,3-butadiene and diethyl 2,3-butadienylmalonate. These substituted allenes reacted with acrylonitrile to give mixtures of the isomeric cyclobutanes XV and XVI.

Experimental[16]

Preparation of 3-Methylenecyclobutanes.—Reaction of allene, prepared by the method of Gustavson and Demjanoff,[17] with substituted unsaturated compounds was accomplished at 200–225° and autogenous pressure. The preparation of these cyclobutanes is described in Table I. Synthesis of 3-methylenecyclobutanecarbonitrile, which is illustrative of the procedure followed, is described below.[18]

A 500-ml. stainless steel rocker bomb was charged with 212 g. (4 moles) of acrylonitrile, 40 g. (1 mole) of allene and 2 g. of hydroquinone. The bomb was heated at 200° with agitation for 10.5 hours. After cooling to room temperature the bomb was opened and the contents distilled to yield 120.4 g. of unreacted acrylonitrile and 55.4 g. (60.4%) of 3-methylenecyclobutanecarbonitrile (I), b.p. 64–65° (21 mm.), n^{25}_D 1.4595.

Anal. Calcd. for C_6H_7N: C, 77.38; H, 7.58; N, 15.04; mol. wt., 93; quant. hydrogenation, 0.0215 g. H_2/g. sample. Found: C, 77.24; H, 7.75; N, 15.02; mol. wt., 93, 94; quant. hydrogenation, 0.0236, 0.0230 g. H_2/g. sample.

The distillation flask contained 32.5 g. of a tan solid residue, m.p. 138–143°. Several recrystallizations from acetone followed by a recrystallization from isopropyl alcohol gave white needles of 1,2,3,4,5,6,7,8-octahydronaphthalene-2,6(or 2,7)-dicarbonitrile, m.p. 143.5–144.5°.

Anal. Calcd. for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04; mol. wt., 186. Found: C, 77.27; H, 7.50; N, 15.09; mol. wt., 175.

A mixture of 10.0 g. (0.054 mole) of crude octahydronaphthalenedicarbonitrile (m.p. 138–143°), 10.0 g. (0.25 mole) of sodium hydroxide, 50 ml. of water and 25 ml. of ethanol was heated under reflux for 16 hours. Acidification of the

---

(15) J. D. Roberts and C. W. Sauer, This Journal, **71**, 3925 (1947).

(16) Melting and boiling points are uncorrected.

(17) G. Gustavson and N. Demjanoff, *J. prakt. Chem.*, **38**, 202 (1888).

(18) Extreme care should be exercised in maintaining proper temperature control and agitation in these reactions. In one instance a violent explosion occurred when acrylonitrile was overheated. Use of an inert diluent, for example benzene, appears to lessen the danger of thermal decomposition of sensitive olefins.

cooled solution gave 13.7 g. of a mixture of tan isomeric acids (m.p. 250–260°). Five grams of the isomeric acids were dissolved in 25 ml. of hot (100°) dimethylformamide and the solution was diluted with 10 ml. of water. The solution was cooled slowly. A white solid (1.20 g.), m.p. above 300°, slowly crystallized.

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.09; H, 7.16.

The filtrate was heated on a steam-bath and diluted with 10 ml. of water. An acid (2.25 g.) separated that melted at 248–250°.

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.32; H, 7.22.

These acids could be position isomers, geometric isomers or both.

A mixture of 7.72 g. (0.034 mole) of the crude isomeric acids (m.p. 250–260°), 200 ml. of methanol and 1.0 g. of *p*-toluenesulfonic acid was heated under reflux for 16 hours. The reaction mixture was concentrated under reduced pressure to a volume of about 85 ml. and diluted with 200 ml. of water. Esters were removed by extraction with 200 ml. of ether. The ether solution was washed with 100 ml. of saturated aqueous sodium bicarbonate and then with 50 ml. of distilled water. After drying with anhydrous magnesium sulfate, ether was removed by distillation. The residue was a mixture of crude isomeric methyl esters (7.2 g., 83.2%).

A 6-inch Hevi Duty furnace was fitted with a 1-inch Pyrex tube containing an intimate mixture of 2.0 g. of 10% palladium-on-carbon and 8.0 g. of charcoal chips (6 mesh). The crude methyl esters (6.4 g.) and a slow stream of carbon dioxide were passed concurrently through the hot tube at 400° over a one-hour period. The product (1.55 g., 47%) was identified as naphthalene by mixed melting point and ultraviolet absorption.

3-Methylcyclobutanecarboxylic Acid.—A solution of 4.65 g. of 3-methylenecyclobutanecarbonitrile in 50 ml. of ethanol containing 0.5 g. of palladium oxide catalyst was placed in a pressure bottle and hydrogen admitted until one mole had been absorbed. The reaction mixture was filtered and ethanol was removed by distillation. To the residue (4.5 g.) was added a solution of 4.0 g. of sodium hydroxide in 25 ml. of water. After heating under reflux for 15 hours the reaction mixture was acidified with sulfuric acid. The acidified solution was extracted with ether. Removal of the ether by distillation gave an acid that was purified by fractional distillation. The fraction boiling at 108–108.5° (18 mm.), n^{25}_{D} 1.4351, was 3-methylcyclobutanecarboxylic acid (3.1 g., 62.5%). The neutral equivalent of this acid was 114.5, which is the theoretical value.

Identity of 3-methylcyclobutanecarboxylic acid was established by preparation of its anilide III, which after crystallization from ethanol melted at 127–128°.[10]

Anal. Calcd. for $C_{12}H_{15}NO$: N, 7.40. Found: N, 7.44.

The amide of 3-methylcyclobutanecarboxylic acid melted at 163–164° (the reported melting point[10] is 167°) after crystallization from water.

Anal. Calcd. for $C_6H_{11}NO$: N, 12.39. Found: N, 12.46.

3-Methylenecyclobutanecarboxylic Acid (IVa).—A mixture of 46.5 g. (0.5 mole) of 3-methylenecyclobutanecarbonitrile, 40 g. (1 mole) of sodium hydroxide and 200 ml. of water was heated under reflux for 24 hours. The reaction mixture was acidified with sulfuric acid and extracted in a continuous ether extractor for 23 hours. The ether was removed and the residue distilled to give 45 g. (56%) of 3-methylenecyclobutanecarboxylic acid, b.p. 119° (26 mm.), n^{25}_{D} 1.4672.

Anal. Calcd. for $C_6H_8O_2$: C, 64.27; H, 7.19; neut. equiv., 112.1; quant. hydrogenation, 0.0178 g. H_2/g. sample. Found: C, 64.39; H, 7.35; neut. equiv., 112.4; quant. hydrogenation, 0.0200 g. H_2/g. sample.

This compound was identical to the product obtained by the addition of allene to acrylic acid (see Table I) as judged by comparison of infrared spectra.

3-Methylenecyclobutanecarbonyl Chloride.—A mixture of 20 g. (0.178 mole) of 3-methylenecyclobutanecarboxylic acid and 36.4 g. (0.3 mole) of thionyl chloride was heated under reflux for three hours. Distillation gave 3-methylenecyclobutanecarbonyl chloride (16.4 g., 72%), b.p. 48–50° (16 mm.), n^{25}_{D} 1.4731. An anilide was prepared from this acid chloride. After recrystallization from alcohol this anilide melted at 145–148°.[11]

3-Cyanocyclobutanone (X).—Ozone generated in a Welsbach Ozonator (model T-19) was passed through a solution of 10 g. (0.108 mole) of 3-methylenecyclobutanecarbonitrile in 150 ml. of methylene chloride at −80° until the blue color of dissolved ozone persisted (about 2 hours were required). The mixture was purged with nitrogen and added with stirring to 500 ml. of distilled water. After stirring for about 16 hours the reaction mixture was heated under reflux for 20 minutes and cooled. The methylene chloride layer was separated, washed with 50 ml. of 10% aqueous ferrous sulfate solution, and dried with anhydrous calcium sulfate. Distillation through a short Vigreux column gave 3.47 g. (34%) of 3-cyanocyclobutanone that boiled at 109–113° (12 mm.) and melted at 49–50.5°.

Anal. Calcd. for C_5H_5ON: C, 63.15; H, 5.30; N, 14.73; mol. wt., 95.1. Found: C, 63.44; H, 5.23; N, 14.77; mol. wt., 93.

The semicarbazone of 3-cyanocyclobutanone melted at 208–210°.

Anal. Calcd. for $C_6H_8ON_4$: C, 47.37; H, 5.30. Found: C, 47.67; H, 5.28.

3-Methylenecyclobutane-1,2-dicarboxylic Anhydride (V).—A mixture of 400 g. (10 moles) of allene, 2000 g. (20.4 moles) of maleic anhydride, 2600 ml. of anhydrous benzene and 1 g. of hydroquinone was placed in a two-gallon autoclave and heated at 200° under autogenous pressure with stirring for 8 hours. The reaction mixtures from five such runs were combined and filtered to remove about 480 g. of crude 1,2,3,4,5,6,7,8-octahydronaphthalene-2,3,6,7-tetracarboxylic dianhydride (VII). After recrystallization from ethyl acetate this dianhydride melted at 240–242°.[13] Benzene and most of the unreacted maleic anhydride were removed by distillation at 7 mm. The residue was distilled through a 4-foot spinning band column to obtain 1694 g. (24.6%) of 3-methylenecyclobutane-1,2-dicarboxylic anhydride (V), b.p. 156–159° (28 mm.), n^{25}_{D} 1.4935–1.4952 (see Table I for analyses) and 608 g. (8.8%) of propargylsuccinic anhydride (VI), b.p. 168–171° (28 mm.); VI was crystallized from benzene to give material melting at 69–71°. Proparglysuccinic anhydride was identified by its infrared spectrum which showed the acetylenic hydrogen absorption at 3.05 μ and the cyclic anhydride doublet at 5.41 and 5.86 μ. Hydrogenation gave *n*-propylsuccinic anhydride having the same infrared spectrum as authentic material obtained by the hydrogenation of allylsuccinic anhydride.[19]

3 - Isopropylidenecyclobutanecarbonitrile (IX) and 2,2-Dimethyl-3-methylenecyclobutanecarbonitrile (VIII).—A mixture of 1,1-dimethylallene (132 g., 1.94 moles),[20] acrylonitrile (344 g., 6.5 moles) and phenothiazine (3.5 g.) was heated in a 1-l. stainless steel rocker bomb at 200° for 8 hours under autogenous pressure. Unreacted acrylonitrile was removed by distillation at atmospheric pressure and the residue was distilled through a 30-inch spinning band column. The product (158 g., 66.4%) was a mixture, b.p. 121–139° (100 mm.), of VIII and IX. Fractionation through a 30-inch column packed with glass helices gave 45 g. of 2,2-dimethyl-3-methylenecyclobutanecarbonitrile (VIII), b.p. 111° (100 mm.), n^{25}_{D} 1.4503, and 53 g. of 3-isopropylidenecyclobutanecarbonitrile (IX), b.p. 138° (100 mm.), n^{25}_{D} 1.4691.

Anal. Calcd. for $C_8H_{11}N$: C, 79.27; H, 9.15; N, 11.58. Found for VIII: C, 79.24; H, 9.26; N, 11.45. Found for IX: C, 78.99; H, 9.11; N, 11.76.

Absorption in the infrared spectrum of VIII occurred at 4.45 μ (-CN), at 5.95 and 11.37 μ ($>C{=}CH_2$), and at 7.25 and 7.35 μ ($>C(CH_3)_2$). The infrared spectrum of IX showed absorption at 4.45 (CN) and at 7.35 μ (CH_3). Its Raman spectrum had a band at 5.8 μ (1722 cm.$^{-1}$)(C=C). Ozonolysis of IX gave 3-cyanocyclobutanone, m.p. 49–50°, in 44% yield. The melting point of this compound was not depressed by admixture with 3-cyanocyclobutanone formed by ozonolysis of 3-methylenecyclobutanecarbonitrile.

3-Isopropylidenecyclobutanecarboxylic Acid (IXa).—A mixture of 21.8 g. (0.18 mole) of 3-isopropylidenecyclobutanecarbonitrile (IX), 15 g. of sodium hydroxide and 50 ml. of water was heated under reflux for 15 hours. The mixture was diluted with 100 ml. of water, treated with decolorizing

---

(19) K. Alder, F. Pasher and A. Schmitz, *Ber.*, **76B**, 27 (1943).

(20) Ya. I. Ginzburg, *J. Gen. Chem.* (*USSR*), **10**, 513 (1940); *C. A.*, **34**, 7843 (1940).

charcoal, filtered and acidified with hydrochloric acid. The solid acid that separated was dissolved in ether and dried over magnesium sulfate. When the ether was removed on the steam-bath, 21 g. (83%) of IXa remained that crystallized in cooling. After two recrystallizations from cyclohexane, this compound melted at 73.5–74.5°.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63; Found: C, 68.74; H, 8.67.

2,2-Dimethyl-3-methylenecyclobutanecarboxylic Acid (VIIIa).—2,2 - Dimethyl - 3 - methylenecyclobutanecarbonitrile (15 g., 0.124 mole) was heated under reflux in 20% aqueous sodium hydroxide solution until evolution of ammonia ceased. Upon acidification of the cooled mixture with hydrochloride acid, 15.1 g. of an oil separated that crystallized. Distillation of this crude material gave 11.7 g. (67.5%) of 2,2-dimethyl-3-methylenecyclobutanecarboxylic acid (VIIIa), b.p. 120° (19 mm.), m.p. 39.5–40°.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63; neut. equiv., 140. Found: C, 68.56; H, 8.85; neut. equiv., 139.

2,2-Dimethyl-3-cyanocyclobutanone (XI).—A solution of 24.4 g. (0.158 mole) of 2,2-dimethyl-3-methylenecyclobutanecarbonitrile in 300 ml. of methylene chloride was ozonized at −78°. The solution of ozonide was added to a mixture of 20 g. of zinc dust, 100 ml. of water and 100 ml. of glacial acetic acid at 40° After 15 minutes the ozonide was completely destroyed. The reaction mixture was extracted in a continuous extractor with methylene chloride for 23 hours. Removal of the solvent gave 13.8 g. (61%) of 2,2-dimethyl-3-cyanocyclobutanone (XI), b.p. 96–100° (10 mm.). A center cut, b.p. 96–98.5° (10 mm.), $n^{25}\text{D}$ 1.4509, was analyzed. The infrared spectrum had absorption at 4.5 μ for the nitrile, at 5.6 μ for the carbonyl and at 7.25 and 7.35 μ (doublet) for the *gem*-dimethyl. This cyclobutanone gave a semicarbazone, m.p. 193.5–194°.

Anal. Calcd. for C_7H_9ON: C, 68.27; H; 7.37; N, 11.37. Found: C, 68.15; H, 7.68; N, 11.36.

Anal. Calcd. for $C_8H_{12}ON_4$: C, 53.32; H, 6.71. Found: C, 53.40; H, 6.95.

Addition of 1,1-Dimethylallene to Methacrylonitrile.—A mixture of 132 g. (1.94 moles) of 1,1-dimethylallene, 400 g. (5.8 moles) of methacrylonitrile and 4 g. of phenothiazine was heated at 200° for 8 hours under autogenous pressure. Two such runs were combined and distilled to give 47.0 g. (9%) of 1,2,2-trimethyl-3-methylenecyclobutanecarbonitrile (XIII), b.p. 116–117° (100 mm.), $n^{25}\text{D}$ 1.4506–1.4529, and 224 g. (43%) of 3-isopropylidene-1-methylcyclobutanecarbonitrile (XII), b.p. 130–132° (100 mm.), $n^{25}\text{D}$ 1.4571. The infrared spectrum of XIII showed absorption·at 3.25 μ (vinyl hydrogen), at 4.48 μ (–CN) at 5.95 and 11.35 μ ($>C{=}CH_2$), at 7.26 μ (methyl) and at 7.20 and 7.32 μ (*gem*-dimethyl). Absorption in the infrared spectrum of XII occurred at 4.46 (–CN) and at 7.29 μ (methyl).

Anal. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69. Found for XIII: C, 80.16; H, 9.66. Found for XII: C, 80.30; H, 9.99.

3-Isopropylidenecyclobutane-1,2-dicarboxylic Anhydride (XIV).—A two-gallon, stainless steel autoclave was charged with 340 g. (5 moles) of 1,1-dimethylallene, 2210 g. (22.5 moles) of maleic anhydride and 1500 ml. of benzene. The mixture was heated with stirring at 200° for 8 hours under autogenous pressure. Distillation of the reaction mixture gave 382 g. (48.4%) of anhydride XIV, b.p. 152–153° (10 mm.), that solidified. After recrystallization from carbon tetrachloride there was obtained 251 g. (32.2%) of colorless cubes, m.p. 55–56°.

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.04; H, 6.07. Found: C, 64.85; H, 6.16.

The infrared spectrum of this compound was compatible with structure XIV. Absorption assignable to the terminal methylene group (11.3–11.5 μ) or the *gem*-dimethyl group (doublet 7.25, 7.35 μ) was not observed. Neither was such absorption detected in the infrared spectra of the crude reaction products.

Dimethyl 3-Isopropylidenecyclobutane-1,2-dicarboxylate.—A mixture of crude 3-isopropylidenecyclobutane-1,2-dicarboxylic anhydride (256 g., 1.54 moles), 900 g. of absolute methanol and 50 g. of methanol-washed Amberlite IR 120 ion exchange resin (H) was heated under reflux with stirring for 45 hours. The catalyst was removed by filtration and the excess methanol was removed by distillation at atmospheric pressure. The dimethyl 3-isopropylidenecyclobutane-1,2-dicarboxylate that remained was distilled through a 30-inch spinning band column to obtain eleven fractions boiling at 134–141° (10 mm.), $n^{25}\text{D}$ 1.4667–1.4719. The middle fractions (116 g., 36%), b.p. 136–138° (10 mm.), had a constant refractive index ($n^{25}\text{D}$ 1.4678). One of the middle fractions was analyzed. The infrared spectra of all fractions were consistent for the dimethyl ester of 3-isopropylidenecyclobutanecarboxylic acid and showed a band at 5.73 μ (ester carbonyl). Absorption in the 3.25 (vinyl hydrogen) and 11.25 μ (terminal methylene) regions was not observed.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.26; H, 7.60. Found: C, 62.23; H, 7.63.

Addition of Diethyl 2,3-Butadienylmalonate to Acrylonitrile.—A mixture of 106 g. (0.5 mole) of diethyl 2,3-butadienyl-malonate,[21] 106 g. (2 moles) of acrylonitrile and 2 g. of phenothiazine was heated in a stainless steel shaker tube at 200° for 5 hours at autogenous pressure. Acrylonitrile was removed from the reaction mixture by distillation at atmospheric pressure and the residue was fractionated through a 30-inch spinning band still to give 28 g., b.p. 176–179° (5 mm.) (A), 14 g., b.p. 179–182° (5 mm.) (B) and 23.5 g., b.p. 182–188° (5 mm.) (C).

Anal. Calcd. for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22. Found for A: C, 63.38; H, 7.24. Found for C: C, 63.49; H, 7.36.

Infrared spectra indicated that fraction A (absorption for $CH_2{=}C<$ at 5.95 and 11.25 μ) was primarily XV ($Z = CH(CO_2C_2H_5)_2$) and that fraction C (no 5.95 μ band, much weaker 11.25 μ band) was mainly XVI ($Z = CH(CO_2C_2H_5)_2$). Both fractions showed absorption for the nitrile group at 4.48 μ and for the carbonyl groups (ester) at 5.77 μ.

Addition of 1-Acetoxy-2,3-butadiene to Acrylonitrile.—A mixture of 168 g. (1.5 moles) of 1-acetoxy-2,3-butadiene,[21] 318 g. (6.0 moles) of acrylonitrile and 3.0 g. of phenothiazine was heated in a 1-l. stainless steel rocker bomb at 200° under autogenous pressure for 8 hours. Acrylonitrile was removed and the residue distilled to obtain 148 g. (62%) of an isomeric mixture of adducts boiling at 144–165° (21 mm.).

Anal. Calcd. for $C_9H_{11}NO_2$: C, 65.43; H, 6.71. Found: C, 65.40; H, 6.81.

This mixture of isomers was separated into a fraction, b.p. 144–145° (20 mm.) (A), a large intermediate fraction (B), and a fraction b.p. 160–161° (20 mm.) (C). Fraction A appeared to be largely XV ($Z = OCOCH_3$) on the basis of its infrared spectrum, which showed absorption at 3.25 μ (vinyl hydrogen) and at 11.24 μ (terminal methylene). These bands were absent in the infrared spectrum of fraction C, which was largely XVI ($Z = OCOCH_3$). Absorption at 4.45 μ (CN), at 5.74 μ (ester carbonyl) and at 5.92 μ ($C{=}C$) was present in the spectra of all fractions.

WILMINGTON 98, DEL.

---

[21] W. H. Carothers and G. A. Berchet, U. S. Patent 2,073,363 (1937).