The use of concentrated sulfuric acid for the hydrolysis of hindered esters is generally a useful method,[4] and it has been successful in the hydrolysis of certain compounds related to orsellinic acid ester.[5] When **4** was treated with concentrated sulfuric acid, a sulfonated product (**5**) was obtained even when the reaction period was as short as 15 min. This is not completely unexpected, since the ring is very highly activated toward electrophilic substitution. The product was obtained by salting out with sodium chloride. Carbon–hydrogen analysis of this compound indicates that a monosulfonation product is obtained and that the ester is converted to the acid (there is 1 mole of methyl alcohol/mole of compound in the crystalline product). No attempt was made to determine the position at which the substitution occurred. The compound gives a very intense violet ferric chloride test.

In order to avoid the sulfonation and still utilize the sulfuric acid method of hydrolyzing the ester to the acid, the hydrolysis was carried out on the dibromo ester **3** of Sonn. The corresponding acid **2** was obtained in 97% yield.

Using essentially the same method reported[3] for converting **3** to **4**, the new acid **2** was converted to orsellinic acid (**1**) in 70% yield. It should be noted that the melting point of the analytical sample reported in the Experimental Section is considerably higher than that reported in the literature.[6] The literature value apparently refers to the monohydrate; our recrystallized but undried product is also the monohydrate. Our analytical sample is the anhydrous compound.

Experimental Section

2,4-Dibromo-5-methyl-6-carboxycyclohexa-1,3-dione (2).— The dibromo ester **3** (3.56 g., 10 mmoles) was prepared according to Sonn[1] and dissolved in 10 ml. of concentrated sulfuric acid. The reaction mixture was allowed to stand at room temperature for 30 min. When the solution was poured over ice, a heavy white precipitate formed. The complete reaction mixture was then extracted three times with 25-ml. portions of ethyl ether. The dibromo acid was separated from any unreacted ester by extraction of the ether with 0.5 N sodium bicarbonate.

The sodium bicarbonate solution was acidified to pH 3 using 3 N hydrochloric acid to yield 3.18 g. (97% yield) of the dibromo acid, m.p. 212–213°. This product gave an intense violet ferric chloride test; the starting ester did not. Recrystallization of crude product from methyl alcohol gave a white crystalline solid, m.p. 213–213.5°, λ_{max}^{EtOH} 265 mμ (ϵ 8650) and 313 (5850).

Anal. Calcd. for $C_8H_8Br_2O_4$ (328.98): C, 29.21; H, 2.40 Found: C, 29.68; H, 2.05.

2,4-Dihydroxy-6-methylbenzoic Acid (Orsellinic Acid, 1).— A mixture of 0.827 g. (252 mmoles) of dibromo acid **2**, 2.20 g. of palladium–calcium carbonate catalyst,[7] and 14 ml. of 2 N sodium hydroxide was shaken under 40 p.s.i. of hydrogen for 6 hr. A weight of catalyst two to three times the dibromo acid weight was found to give better results than when lesser amounts were used.

The mixture was filtered to remove the reduced catalyst and cooled to 0°. Acidification to pH 3 with 2 N hydrochloric acid to precipitate the orsellinic acid gave no evidence of carbon dioxide evolution. The solid removed by filtration, m.p. 186–187°, 0.32 g. (70% yield), gave a positive ferric chloride test. Recrystallization from acetone and water gave fine white crystals, m.p. 197–198°, when dried for at least 48 hr. at <1.0 mm. at 34°, λ_{max}^{EtOH} 260 mμ (ϵ 9450) and 298 (6500).[8]

(4) M. Newman, *J. Am. Chem. Soc.*, **63**, 2431 (1941).
(5) K. Mosbach, personal communication.
(6) F. K. Beilstein, "Handbuch der organischen Chemie," Springer Verlag, Berlin, Vol. 10, 1927, p. 412; 1949, p. 272.
(7) M. Busch and H. Stöve, *Ber.*, **49**, 1063 (1916).
(8) *Cf.* C. A. Wachtmeister, *Acta Chem. Scand.*, **12**, 147 (1958).

Anal. Calcd. for $C_8H_8O_4$ (168.14): C, 57.17; H, 4.80. Found: C, 57.48; H, 5.04.

Sodium Salt of Monosulfonated Orsellinic Acid (5).— Concentrated sulfuric acid (2.0 ml.) was added to 0.60 g. of ethyl orsellinate. The reaction mixture was allowed to stand for 20 hr. and then poured over ice. The reaction mixture was then extracted three times with ethyl ether. Sodium bicarbonate was used to separate the acid from unreacted ester. Salting out with sodium chloride produced 0.25 g. (27% yield) of white solid. Recrystallization of the crude product from methanol gave a white crystalline solid.

Anal. Calcd. for $C_8H_7NaO_7S \cdot CH_3OH$ (302.24): C, 35.77; H, 3.67. Found: C, 36.00; H, 3.28.

Diels–Alder Reactions of Acrylic Acid Derivatives Catalyzed by Aluminum Chloride

Takashi Inukai and Michio Kasai

The Central Research Laboratories, Chisso Corporation, Kamariya, Kanazawa-ku, Yokohama, Japan

Remarkable acceleration of certain Diels–Alder reactions by aluminum chloride was first reported by Yates and Eaton.[1] Dienophiles tested by these workers were those activated by two carbonyl groups, for example, maleic anhydride, *p*-benzoquinone, and dimethyl fumarate. The scope of such catalyzed Diels–Alder reactions was extended to the cases of dienophiles with a single carbonyl function such as acrolein, methyl vinyl ketone, and acrylic acid, and also to the use of a variety of Friedel–Crafts catalysts for this type of reactions.[2,3] The general utility of these catalysts for preparation of the desired products is limited, however, owing to the instability of some dienes and dienophiles under the reaction conditions.[1,2]

We wish to report the aluminum chloride catalyzed diene syntheses with methyl acrylate, methyl methacrylate, and acrylonitrile as dienophiles and some observations relevant to such syntheses. The reaction between methyl acrylate and butadiene proceeds cleanly and smoothly at moderate temperatures in the presence of aluminum chloride to give methyl 3-cyclohexene-1-carboxylate in a high yield. Other Friedel–Crafts catalysts are of much less or practically no activity (Table I), in contrast to the general activity of these catalysts in the reactions with methyl vinyl ketone.[2,3] To carry out the reaction, a dienophile is mixed with aluminum chloride in a suitable solvent to form a complex[4] and the diene is then allowed to come into contact with the preformed complex, since undesirable side reactions may occur otherwise. Reactions of other combinations of diene and dienophiles are shown in Table II.

In all these cases resinous materials, which would be formed by the Friedel–Crafts reaction between butadiene and benzene (*vide infra*), or by the polymerization of diene, were not formed, presumably because aluminum chloride complexed with an ester group is not ca-

(1) P. Yates and P. Eaton, *J. Am. Chem. Soc.*, **82**, 4436 (1960).
(2) G. I. Fray and R. Robinson, *ibid.*, **83**, 249 (1961).
(3) R. Robinson and G. I. Fray, British Patent 835,840 (1960).
(4) Formation of a complex between aluminum chloride and an ester group has been shown, for example, by M. F. Lappert [*J. Chem. Soc.*, 817 (1961); 542 (1962)].

TABLE I

ACID-CATALYZED CONDENSATION REACTIONS BETWEEN
METHYL ACRYLATE AND BUTADIENE[a,b]

Expt. no.	Methyl acrylate, mole	Catalyst (mole)	Solvent, ml.	Time, hr.	Temp., °C.	Yield,[c] %
1	0.50	AlCl₃ (0.45)	300	4	50–60	92
2	0.50	AlCl₃ (0.05)	300	4	50–60	88
3	0.50	AlCl₃ (0.05)	250	3	10–20	65
4	0.50	AlCl₃ (0.05)	300	3	50–60	73
5[d]	0.54	None	20	96	Room temp.	0
6	0.30	SnCl₄ (0.03)	270	2	50–60	2
7	0.30	ZnCl₂ (0.03)	200	2	50–60	0
8	0.30	FeCl₃·6H₂O (0.03)	200	2	50–60	0
9	0.30	BF₃·OEt₂ (0.04)	230	2.5	50–60	10
10	0.30	TiCl₄ (0.30)	220	3	20	19

[a] Benzene was used as solvent in all experiments except expt. 4 where hexane was used instead. [b] An excess of butadiene was bubbled into the reaction mixture. [c] Based on methyl acrylate. [d] Control experiment carried out in an autoclave at room temperature; butadiene, 0.6 mole.

TABLE II

ALUMINUM CHLORIDE CATALYZED CONDENSATION
BETWEEN SOME α,β-UNSATURATED CARBOXYLIC ACID
DERIVATIVES AND 1,3-DIENES IN BENZENE[a]

Expt. no.	Diene	Dienophile	Reaction time, hr.	Yield,[b] %
11[c]	Isoprene	Methyl acrylate	3.5	59
12[d]	Butadiene	Ethyl crotonate	3	0
13[d]	Butadiene	Methyl methacrylate	2.5	57.5
14[c]	2,3-Dimethyl-butadiene	Methyl acrylate	5	74
15[c]	Butadiene	Acrylic acid	5	0
16[c,e]	Butadiene	Acrylic acid	1	18

[a] Mole ratio of dienophile–AlCl₃ was 10:1. Titanium tetrachloride was used in expt. 16. [b] Based on dienophile. [c] Reaction at 20°. [d] Reaction at 50–60°. [e] Acrylic acid was added to the mixture of butadiene and titanium tetrachloride; see Experimental Section.

pable of activating dienes toward these cationic reactions. Interestingly, even 2,3-dimethylbutadiene gave a good yield of adduct with only a slight indication of formation of a small amount of resin.[5]

No attempts have been made to determine the isomeric composition of the products from isoprene and methyl acrylate. Thermal condensation is reported to yield methyl 3- and 4-methyl-3-cyclohexene-1-carboxylates in a ratio of 30:70.[6] Our product may have a different isomeric composition in view of the fact that isoprene–methyl vinyl ketone reactions give different compositions depending on whether they proceed thermally or catalytically.[7]

The reaction using acrylonitrile and butadiene is shown in Table III. Here one needs an approximately equimolecular amount of aluminum chloride in order to obtain 3-cyclohexene-1-carbonitrile in a high yield, and therefore inevitably gets a large amount of tar suggestive of the Friedel–Crafts reaction between butadiene and solvent benzene. In fact, a mixture of isomeric diphenylbutanes was separated from the reaction mixture.[8]

(5) 2,3-Dimethylbutadiene is reported to give only polymer in attempted reaction with methyl vinyl ketone in the presence of titanium tetrachloride.[2]
(6) H. E. Hennis, J. Org. Chem., 28, 2570 (1963).
(7) E. F. Lutz and G. H. Bailey, J. Am. Chem. Soc., 86, 3899 (1964).
(8) The detailed study of the Friedel–Crafts reaction between benzene and butadiene is under way and will be shortly reported elsewhere.

TABLE III

ALUMINUM CHLORIDE CATALYZED CONDENSATION OF
ACRYLONITRILE WITH BUTADIENE[a]

Expt. no.	Acrylonitrile–AlCl₃, mole ratio	Time, hr.	Temp., °C.	Solvent, ml.	Yield,[b] %	Residue,[c] g.
17	10:1	4.5	60	200[d]	19	1.3
18	10:9	4	60	400[d]	86	80
19	10:9	1	20	300[d]	22	58
20	10:1	2.5	60	300[e]	0	0
21	10:1	3	40	200[f]	0	0
22	20:9	20	20	200[f]	42	8.4

[a] In each experiment 0.5 mole of acrylonitrile was used. An excess of butadiene was bubbled into the reaction mixture. [b] Based on acrylonitrile. [c] Reddish brown residue. [d] Benzene. [e] Hexane. [f] Methylene chloride.

Experimental Section[9]

Materials.—Methyl acrylate (b.p. 79.5°), methyl methacrylate (b.p. 45–45.5° at 100 mm.), and acrylonitrile (b.p. 76.6°) were obtained by distillation through a 30-cm. Vigreux column under a nitrogen atmosphere. Acrylic acid was prepared by a published procedure[10] and had b.p. 55–56° (25 mm). These were stored, with a small concentration of hydroquinone added, in a refrigerator for not more than 1 month and used as required without removing the inhibitor. Ethyl crotonate was of commercial C.P. grade and freshly distilled, b.p. 134–134.5°. Commercial butadiene of pure grade, 99+%, was dried by passing through molecular sieves (4A). Commercial isoprene, 95%, was used directly. 2,3-Dimethylbutadiene was prepared by a known method[11] and had b.p. 70.5–71.0°. Inorganic compounds used as catalysts were commercial materials of C.P. grade or higher and were used as obtained. Solvents were purified in the usual way and were anhydrous.

Reaction between Methyl Acrylate and Butadiene (Expt. 2).—To a stirred suspension of 6.8 g. (50 mmoles) of powdered anhydrous aluminum chloride and 250 ml. of benzene warmed to about 50° was added a solution of 43.2 g. (0.5 mole) of methyl acrylate in 50 ml. of benzene in 10 min. Aluminum chloride rapidly dissolved to form a slightly yellow clear solution. Butadiene, 1.6 moles, was bubbled through the solution with stirring during 4 hr., the temperature of the mixture being kept at 50–60° by external heating. The resulting solution was cooled and treated with dilute hydrochloric acid, and the benzene layer was washed with water and dried over anhydrous sodium sulfate. The benzene was removed by distillation at atmospheric pressure and the residue was distilled to yield, after an insignificant forerun, 61.8 g. (88%) of methyl 3-cyclohexene-1-carboxylate, b.p. 73.0–73.5° at 20 mm. (lit.[12] b.p. 80–82° at 23 mm.), n²⁰D 1.4602 (lit. n²⁵D 1.4575,[12] n²⁰D 1.4602[13]). The residue of distillation was less than 2 ml. with no indication of resin formation. Alkaline hydrolysis of the product yielded 3-cyclohexene-1-carboxylic acid, b.p. 129° at 20 mm. (lit.[14] b.p. 132.5–133° at 22 mm.), m.p. 19.8–21.2° (lit.[14] m.p. 17°), n²⁰D 1.4806 (lit.[14] n²⁰D 1.4812). The infrared spectrum was identical with that of an authentic sample,[14] and a mixture melting point determination showed no depression.

Reaction between Isoprene and Methyl Acrylate (Expt. 11).—To a stirred suspension of 4.3 g. (32 mmoles) of aluminum chloride and 250 ml. of benzene was added 26.1 g. (303 mmoles) of methyl acrylate in 30 ml. of benzene during 15 min. Gaseous isoprene, 20.9 g. (307 mmoles), was introduced into the resulting solution in 0.5 hr. and the mixture was let stand for an additional 3 hr. at 20°. The reaction mixture was worked up in the usual way and yielded 27.6 g. of a distillate, b.p. 91–93° at 20 mm.,

(9) All melting points are corrected. All boiling points are uncorrected and at atmospheric pressure unless otherwise specified.
(10) C. E. Rehberg, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 33.
(11) C. F. H. Allen and A. Bell, ref. 10, p. 312.
(12) W. J. Bailey and R. A. Baylouny, J. Am. Chem. Soc., 81, 2126 (1959).
(13) E. D. Bergmann and D. F. Herman, J. Appl. Chem. (London), 3, 42 (1953).
(14) A. A. Petrov and N. P. Sopov, J. Gen. Chem. USSR, 17, 2228 (1947); Chem. Abstr., 42, 4957 (1948).

n^{25}D 1.4603, n^{20}D 1.4621. This product, on gas–liquid partition chromatographic analysis,[15] showed a single peak of the same retention time as the isomeric mixture of methyl 3- and 4-methyl-3-cyclohexene-1-carboxylates, b.p. 91–93° at 20 mm. (lit.[6] b.p. 85–86° at 15 mm.), n^{25}D 1.4610, n^{20}D 1.4630 (lit. n^{25}D 1.4606,[6] n^{20}D 1.4655[16]), prepared by thermal condensation at 130–140° for 24 hr. On alkaline hydrolysis the product of the present experiment yielded, after repeated recrystallization from hexane,[6] 4-methyl-3-cyclohexene-1-carboxylic acid, m.p. 99.2–100.2° (lit.[6] m.p. 98.5–99° uncor.). A mixture melting point determination with an authentic sample[6] showed no depression.

Butadiene and Methyl Methacrylate (Expt. 13).—From 30.3 g. (303 mmoles) of methyl methacrylate in a similar way as in expt. 2 was obtained 26.7 g. (57.5%) of methyl 1-methyl-3-cyclohexene-1-carboxylate, b.p. 76–78° (20 mm.), n^{25}D 1.4565, n^{20}D 1.4600 (lit. b.p. 64–65° at 10 mm.,[17] n^{25}D 1.4568,[17] n^{20}D 1.4600[18]). Alkaline hydrolysis yielded 1-methyl-3-cyclohexene-1-carboxylic acid, m.p. 77–79° (from ligroin) (lit.[17] m.p. 78–79°).

2,3-Dimethylbutadiene and Methyl Acrylate (Expt. 14).—2,3-Dimethylbutadiene, 15.1 g. (184 mmoles), in 30 ml. of benzene was added in 5 min. to a solution prepared from 15.9 g. (185 mmoles) of methyl acrylate, 2.5 g. (19 mmoles) of aluminum chloride, and 280 ml. of benzene. The resulting mixture was stirred for 5 hr. at 20°, worked up in the usual way, and yielded on distillation 22.9 g. (74%) of methyl 3,4-dimethyl-3-cyclohexene-1-carboxylate, b.p. 104–106° (20 mm.), n^{25}D 1.4678.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.5; H, 9.6. Found: C, 71.4; H, 9.5.

A colorless viscous oil, 1.9 g., remained in the flask. Alkaline hydrolysis of the ester, with 30% aqueous sodium hydroxide on a boiling water bath, gave 3,4-dimethyl-3-cyclohexene-1-carboxylic acid, m.p. 80–82° (from hexane) (lit.[19] m.p. 83°).

Butadiene and Acrylic Acid (Expt. 16).—Butadiene, 5.4 l. (0.24 mole), was bubbled into a solution of 2.7 g. (14 mmoles) of titanium tetrachloride in 90 ml. of benzene at 20°. To this solution was added 5.1 g. (71 mmoles) of acrylic acid in 10 ml. of benzene in 5 min. at 20°, when the mixture turned to dark red. After stirring 1 hr. the mixture was decomposed with 30 ml. of water, and the benzene solution was washed with water, dried with anhydrous sodium sulfate, and distilled to yield 2.8 g. of a distillate, b.p. 75–128° at 19 mm. Gas–liquid partition chromatographic analysis using a 2.6-m. Silicone DC-550 column showed that it contained approximately 1.5 g. of 3-cyclohexene-1-carboxylic acid, yield 17%.

Reaction between Butadiene and Acrylonitrile (Expt. 18).—To a stirred suspension of 61 g. (457 mmoles) of aluminum chloride and 300 ml. of benzene was added 26.6 g. (502 mmoles) of acrylonitrile in 100 ml. of benzene at 60°. Aluminum chloride dissolved and a large amount of dark red precipitates was formed. Butadiene (0.9 mol.) was bubbled into the mixture in a period of 4 hr. and the reaction mixture was worked up as usual and distilled to yield (i) 2.3 g. of a forerun, b.p. <80° (20 mm.); (ii) 46.0 g. (86%) of 3-cyclohexene-1-carbonitrile, b.p. 80–87° (20 mm.); (iii) 24.7 g. of higher boiling materials, b.p. 90–155° (3 mm.); and (iv) 80 g. of viscous dark red residue. Fraction ii had n^{20}D 1.4742 (lit. b.p. 83° at 20 mm.,[14] n^{20}D 1.4736,[14] n^{20}D 1.4758[20]), and the gas chromatographic retention time and infrared spectrum were identical with those of the authentic sample[14] of 3-cyclohexene-1-carbonitrile. Fraction iii gave on vacuum distillation a center cut, b.p. 102–107° (1 mm.), a mixture of isomeric diphenylbutanes.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.4; H, 8.6; mol. wt., 210. Found: C, 91.7; H, 8.6; mol. wt., 201 (freezing point depression of benzene).

On gas–liquid partition chromatographic analysis using a 2.6-m. PEG-6000 column it gave three peaks, one of which coincided with that of 1,2-diphenylbutane. The infrared spectrum was similar to a superposition of the spectra of 1,1-diphenylbutane[21] and 1,2-diphenylbutane.[8]

(21) "Sadtler Standard Infrared Spectra," Midget Ed., Sadtler Research Laboratories, Philadelphia, Pa., 1959, Spectrum No. 9980.


Bredt Rule Interdictions of Cyclopropane Rearrangements. The Vinylnortricyclenes[1]

Jerome A. Berson and M. Robert Willcott[2]

Department of Chemistry, University of Wisconsin, Madison, Wisconsin

The Bredt rule[3-5] recognizes the extreme torsion imposed on a hypothetical double bond at the bridgehead of a small bicyclic system. If the "olefinic" carbons in such an environment use sp^2-hybrid orbitals for σ-bond formation, the p-orbitals to be used for π-bond formation are nearly orthogonal.[6] The geometry corresponds roughly to that of the transition state for thermal *cis–trans* olefin interconversion and consequently, if its electronic state is singlet, it lies some 60–65 kcal./mole above a hypothetical strainless species.[7] The much discussed[8] possibility that intersystem crossing to a triplet state might lower the energy of the twisted species provides a conceivable way of making this form more accessible, but no violations of the Bredt rule by such a device have ever been reported. In any case, even if the transition state enthalpy for "olefin" formation is lowered by intersystem crossing, the full effect will not be felt in the rate. Because of the change of multiplicity, the benefit is purchased at the expense of a severe drop in the pre-exponential term.[8] Thus, the net result would be that anti-Bredt species (*e.g.*, II) would be kinetically inaccessible by way of conventional olefin-forming reactions, for example, by vicinal elimination from a 1,2-disubstituted norbornane (I).
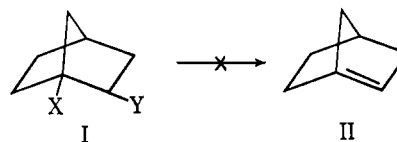
(1) We are grateful for grants from the Army Research Office (Durham) and the Camille and Henry Dreyfus Foundation which provided partial support of this work.

(2) National Institutes of Health Postdoctoral Fellow, 1964–1965.

(3) J. Bredt, *Ann.*, **437**, 1 (1924).

(4) For a review, see F. S. Fawcett, *Chem. Rev.*, **47**, 219 (1950).

(5) *Cf.* E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 298.

(6) (a) If the σ-bond is made from sp^3-hybrid orbitals, the situation is not nearly so bad, since the residual sp^2-orbitals are not orthogonal. To the extent that overlap and bond strength are porportional, these can form a bond about two-thirds as strong as an ordinary π-bond, as can be estimated from standard tables of overlap integrals[6b] and reasonable estimates of molecular geometry. (b) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(7) (a) J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *ibid.*, **23**, 315 (1955); (b) B. S. Rabinovitch and K. W. Michel, *J. Am. Chem. Soc.*, **81**, 5065 (1959).

(8) For reviews, see B. F. Gowenlock, *Quart. Rev.* (London), **14**, 133 (1960); R. B. Cundall, *Progr. Reaction Kinetics*, **2**, 167 (1964).

(15) Columns (2.6-m.) of PEG-600, Silicone DC-550, TCP, and DOP (Shimadzu Seisakusho Ltd., Kyoto) were ineffective in attempted separations of the isomers.

(16) I. N. Nazarov, Yu. A. Titov, and A. I. Kuznetsova, *Dokl. Akad. Nauk SSSR*, **124**, 586 (1959); *Chem. Abstr.*, **53**, 11268 (1959).

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