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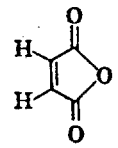
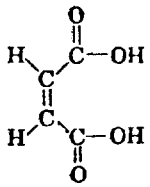
MALEIC ANHYDRIDE
AP-42 Section 5-24
Reference Number
4

MALEIC ANHYDRIDE, MALEIC ACID, AND FUMARIC ACID

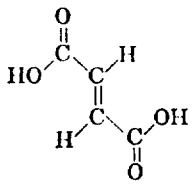
Maleic anhydride, maleic acid, and fumaric acid constitute a group of chemically related, industrially important chemicals. Maleic anhydride is the common name for 2,5-furandione; maleic acid is *cis*-butenedioic acid (IUPAC), and fumaric acid is the trans isomer.



maleic anhydride



maleic acid



fumaric acid

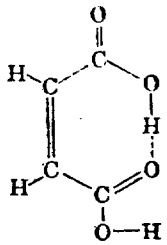
Maleic acid, as well as fumaric acid and maleic anhydride, were prepared and characterized for the first time by Pelouze (1) who in 1834 obtained these compounds by heating malic acid. Fumaric acid was first isolated from *Fumaria officinalis* and named in 1832 by Winckler (2). Pelouze (1) discussed it under the name of paramaleic acid.

Maleic acid assumed industrial importance much later after Weiss and Downs (3,4) prepared it by the catalytic oxidation of benzene. The acid became commercially available in 1928 and the anhydride in 1933.

Physical Properties

Physical constants (5–20), including thermal and solution properties, are listed in Table 1. Differences in the physical properties between maleic acid and fumaric acid reflect the difference between a *cis*-ethylenic and a *trans*-ethylenic system. The distinction is shown most clearly by the solubilities and the degrees of ionization in water. X-ray work on the crystal structure of maleic acid (16) shows an intramolecular hydrogen bond of 2.46 Å which accounts for the easier removal of the first proton compared to fumaric acid. The same hydrogen bonding accounts for the smaller second ionization constant of maleic acid in comparison to fumaric acid. These factors also help to explain the solubility differences.

Maleic anhydride is nearly planar with the anhydride oxygen tilted 0.03 Å from the plane of the ring(10). The heat of isomerization of fumaric to maleic acid is 5.46 kcal/mole (5) while the activation energy is 15.8 kcal/mole (21) for the conversion of maleic to fumaric acid.



Chemical Properties

The reactions of maleic anhydride and its derivatives have been reviewed extensively by Flett and Gardner (22). The initial site of attack is normally either at one

B. Dmuchovsky and J.E. Franz, "Maleic Anhydride", Kirk-Othmer Encyclopedia of Chemical Technology, Volume 12, John Wiley and Sons, Inc., New York, NY, 1967, pp. 819-837.

Table 1. Physical Properties of Fumaric Acid, Maleic Acid, and Maleic Anhydride

Property	Fumaric acid	Maleic acid	Maleic anhydride	Reference
melting point, °C	287	130–130.5	52.85	9,18
boiling point, °C	$165_{1.7}$ subl	138 dec	202	18
sp gr at 20/20°C, solid	1.635	1.590	1.48	19
molar volume	79	81		11
heat of formation, kcal/mole	−193.84	−188.95	−112.43	6,12
free energy of formation, kcal/mole	−156.70	−149.40		18
heat of combustion, kcal/mole	−319.01	−324.56	−332.29	6,13
heat of hydrogenation, kcal/mole	−31.15	−36.61		5,7
specific heat,				
solid			0.29	18a
liquid			0.40	18a
heat of vaporization, kcal/mole			13.1	14
heat of fusion, kcal/mole			3.262	9,15
heat of solution, kcal/mole		4.44		18a
heat of hydrolysis, kcal/mole			−8.33	18a
heat of neutralization, kcal/mole		30.32		18a
crystal structure		monoclinic	orthorhombic	10,16
space group		$P2_1/C$	$P2_12_12_1$	
a, Å		7.47	7.180	
b, Å		10.15	11.231	
c, Å		7.65	5.39	
dissociation constant, at 25°C				
K_1	9.57×10^{-4}	1.14×10^{-2}		17
K_2	4.13×10^{-5}	5.95×10^{-7}		18a
viscosity, mP			16.1	
60°C			10.7	
90°C			6.0	
150°C				18a
pH of water solutions				
1×10^{-2} molar	2.42			
5×10^{-3}	2.62			
1×10^{-4}	3.10			20
solubility, g/100 g soln				
water, at 25°C	0.70	44.1		
40°C	1.05	52.9		
60°C	2.34	59.8		
97.5°C		79.7		
100°C	8.93			
diethyl ether, at 25°C	0.71	7.57		
chloroform, at 25°C	0.02	0.011		
carbon tetrachloride, at 25°C	0.027	0.002		
benzene, at 25°C	0.003	0.024		
acetone, at 29.7°C	1.69	26.3		
xylene, at 29.7°C	0.027	0.0085	163.2[a]	
dipole moment (dioxane), at 25°, Debye	2.46	3.17		8
vapor pressure, mm Hg				19
at 44.0°C			1	
78.7°C			10	
111.8°C			40	
135.8°C			100	
179.5°C			400	
202.0°C			760	

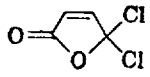
[a] In g/liter.

of the carbonyl groups, or at the C=C double bond, which is conjugated with the two C=O double bonds. Occasionally, participation of both the carbonyl and the olefin groups is observed.

CARBONYL GROUP REACTIONS

Dehydration. Maleic acid is converted to maleic anhydride by heating to 100°C. Fumaric acid has to be heated to 250–300°C to obtain maleic anhydride (23). Dehydration may also be accomplished at lower temperature with chemical dehydrating agents (24,25). Chemical or physical removal of the water (such as azeotropic distillation, etc) is necessary to prevent the reverse process.

Acid Chloride Formation. The monoacid chlorides of maleic and fumaric acids are not known. Fumaroyl chloride, ClOCH=CHCOCl, is prepared by heating fumaric acid with phthaloyl chloride, phosphorus pentachloride, or thionyl chloride in the presence of iron (26,27). Under similar conditions maleic acid or anhydride yield an isomeric dichlorolactone (27), often referred to as "maleyl chloride." Maleoyl chloride, the noncyclic form of this compound, is not known.



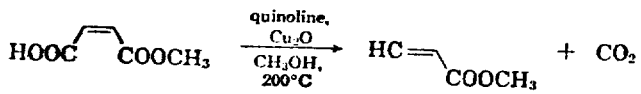
maleyl chloride

Esterification. Mono- and dialkyl maleates and fumarates are readily prepared (28,29) by heating the alcohol and maleic acid, maleic anhydride, or fumaric acid together in the presence of sulfuric acid. Aryl fumarates are generally prepared from fumaroyl chloride and phenols (30), whereas aryl maleates are obtained by the reaction of maleic anhydride with phenols in the presence of phosphorus pentoxide (30a) or polyphosphoric acid (30b).

Linear unsaturated polyesters (31) are obtained from glycols or epoxides (32). Ethylene glycol would give the repeating unit $+CH_2CH_2OCCH{=}CHCO+_n$.

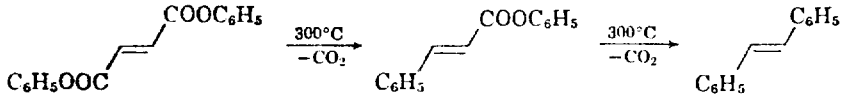
Amidation. Under suitable conditions ammonia, primary amines, and secondary amines yield mono- or diamides. The reaction of primary amines with maleic anhydride produces amic acids which can be dehydrated to imides (33), polyimides, or isoimides (34), depending on the conditions employed and on the nature of the amic acid. In general, amic acids yield imides in the presence of acetic anhydride and sodium acetate, whereas isoimides are produced when trifluoroacetic anhydride is used as the dehydrating agent. The unique character of trifluoroacetic anhydride in this reaction is not completely understood at the present time.

Decarboxylation. Under certain conditions irradiation of aqueous solutions of maleic acid produces acrylic acid (35). The decarboxylation is more readily accomplished by heating maleic acid or its monoalkyl esters in the presence of various catalysts (36).

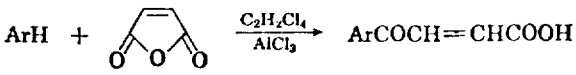


Maleic anhydride produces a friable black polymer and carbon dioxide when warmed with tertiary amines (37,38) or alkali. Once started, the decarboxylation is autocatalytic and results in explosions (39,40).

The pyrolytic decarboxylation of diaryl fumarates proceeds in a stepwise fashion to yield stilbenes (30).

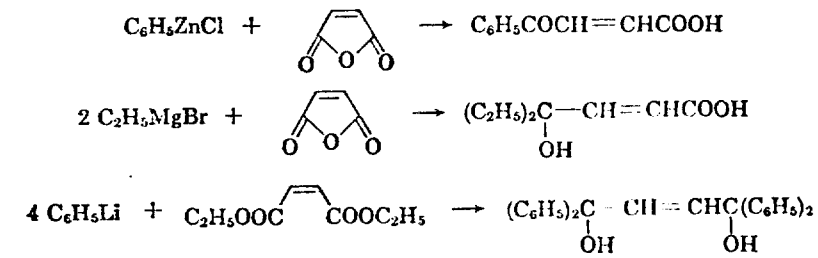


Acylation Reactions. Maleic anhydride reacts with aromatic hydrocarbons in the presence of strong acids ($AlCl_3$) to produce β-aroylacrylic acids (41,42). Best yields are obtained with solvents, such as chlorinated hydrocarbons, in which the maleic anhydride–aluminum chloride complex is soluble.



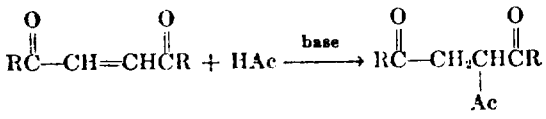
Diaroylethylenes (43) are obtained from fumaroyl chloride. Depending on the conditions used, the condensation of maleic anhydride with phenols in the presence of acids yields aroylacrylic acids (42,44), phenolmaleins (45), benzocyclopentanones (41), benzoquinones (41), chromanones (41), or coumarins (46).

Grignard and Related Reactions. The nucleophilic addition of a variety of organometallic reagents to the carbonyl groups of maleic anhydride and maleic esters has been described (22). Representative examples of these reactions are illustrated by the following equations:



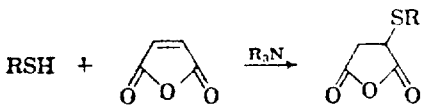
DOUBLE-BOND REACTIONS

Nucleophilic Reactions. Due to the electron-withdrawing capacity of the carbonyl groups in the conjugated maleic and fumaric systems, the β-carbon atom is highly susceptible to attack by nucleophilic reagents. This type of reaction has been studied extensively and is usually carried out under basic conditions according to the following general equation:



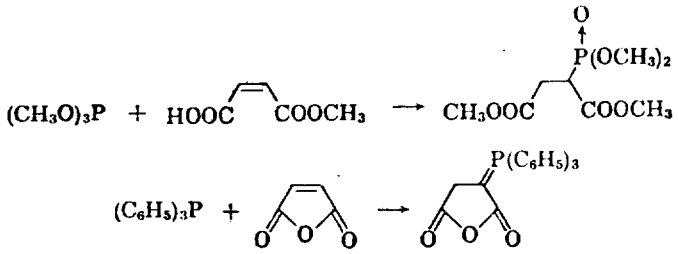
The addition of reagents, such as alcohols, ammonia, amines, sulfinic acids, thioureas, Grignard reagents, Michael reagents (ketoesters, malonic esters, nitriles, nitroparaffins), and alkali cyanides, has been adequately described (22). A wide variety of

thiol adducts of maleic anhydride have been prepared (47) and the mechanism of the reaction has been discussed (48,49).

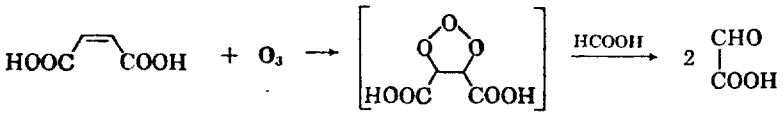


dl-alkylthiosuccinic anhydride

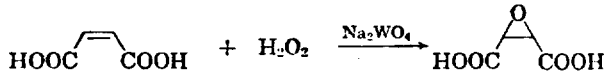
This reaction is essentially quantitative and has been used to measure the relative nucleophilicities of several thiolate anions. Phosphites (50,51) and phosphines (52) also react as nucleophiles with maleic anhydride and its derivatives to form stable adducts.



Electrophilic Reactions. Several electrophilic reagents attack the electron-deficient double bonds of maleic acid and its derivatives (22). The addition reactions of water, halogens, halogen acids, aromatic hydrocarbons, phenols, and sulfur trioxide are typical examples. A variety of products are obtained by the use of suitable oxidizing agents. Ozone produces good yields of glyoxalates provided formic acid is used as a solvent (53–55).

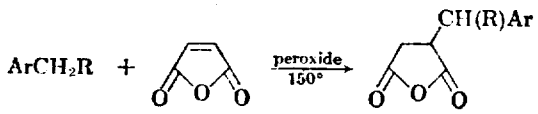


Hydrogen peroxide in the presence of osmium tetroxide or peroxytungstic acid (56) produces tartartic acid, HOOCCHOHCHOHCOOH. If the pH range in the latter reaction is maintained at 4.5–5, *cis*-epoxysuccinic acid is obtained (57).



The trans isomer is readily prepared by epoxidation of fumaric acid (57) or by fermentation of molasses with *Aspergillus fumigatus* (58). The epoxy acids are unusually acid-stable and can be converted to the corresponding esters, amides, and nitriles by conventional means.

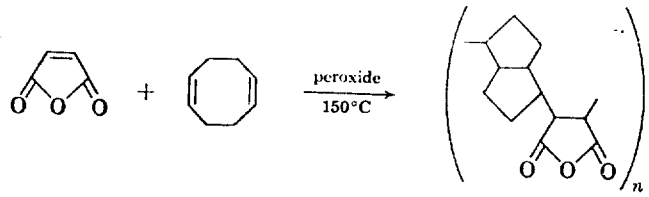
Free-Radical Reactions. The peroxide-catalyzed addition of alkylbenzenes to maleic anhydride produces aralkylsuccinic anhydrides (59).



Maleate esters are less reactive than fumarates in free-radical addition reactions. A kinetic study (60) of the addition of methyl radicals to these esters indicates that the transition state involving maleates is less resonance stabilized due to noncoplanarity of the carboxyl groups. Maleic anhydride, however, is planar and even more reactive than fumarate esters. The free-radical-initiated polymerization and copolymerization of fumarate and maleate esters has been extensively reviewed (31,61).

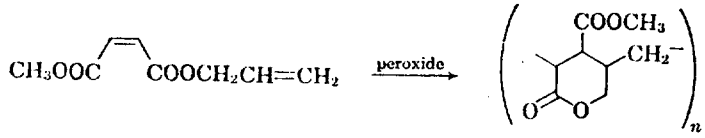
Maleic anhydride can be homopolymerized by gamma irradiation (^{60}Co), free-radical initiators, or ultraviolet irradiation (62). Gamma irradiation has also been utilized to homopolymerize diethyl fumarate (63).

The free-radical addition of maleic anhydride and its derivatives to various diolefins ("Butler" polymerization) has provided an interesting series of cyclic polymers (64,65).



cyclooctadiene

A similar reaction mechanism yields the following polymer:

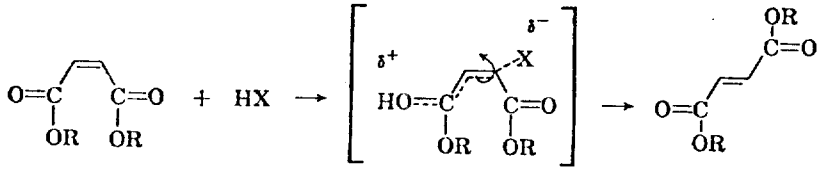


allyl methyl maleate

The free-radical additions of hexaphenylethane, benzoyl peroxide, and sulfur to maleic acid derivatives have been described (22).

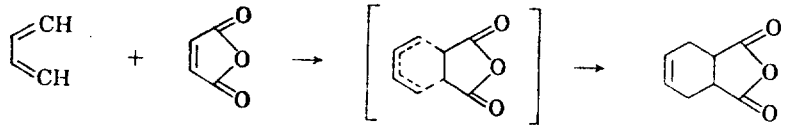
Isomerization. Maleic acid and its derivatives are isomerized to the trans isomers by a variety of physical and chemical methods (22). Commercially maleic acid is isomerized to fumaric acid by heat (66), hydrochloric acid (67), potassium bromate (68), a mixture of ammonium bromide and ammonium persulfate (69), and a large number of sulfur compounds, such as thiourea (70). Maleate esters are converted to fumarates with hydrochloric acid (28), phosphorus and sulfur halides (71), primary and secondary amines (72), and thiols (73).

The mechanism of the isomerization has been investigated (72,74,75) and the data indicate that a succinate intermediate is not involved. A transition state midway between sp^2 (trigonal) and sp^3 (tetrahedral) hybridization of one of the olefinic carbon atoms is postulated as the species which undergoes rotation.



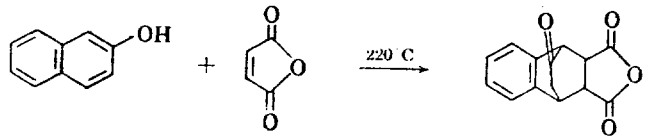
The photostationary equilibrium of fumarates and maleates has recently been studied (76). Sensitizers with triplet energy levels below 59 kcal/mole do not effect isomerization. The triplet energy level of maleates is estimated to be 72–77 kcal/mole, whereas for fumarates it is 61–67 kcal/mole. Therefore, sensitizers with triplet energy levels in the range 60–75 kcal/mole (eg, benzophenone) promote conversion of fumarate to maleate on irradiation.

Concerted Nonpolar Reactions. *1,4-Additions.* For a review of the Diels-Alder reaction of maleic anhydride and its derivatives, see reference 77. This reaction has been studied extensively and is represented by the formation of tetrahydrophthalic anhydride from butadiene.

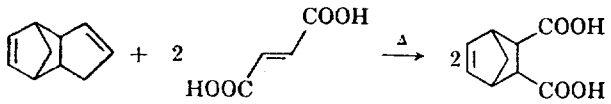


The mechanism of the reaction is still open to question but acids, peroxides, or light does not usually exert a catalytic effect. Rate studies (78,79) indicate that the reaction is facilitated by electron-donating substituents in the diene and by a cisoid structure. Other studies indicate that the reaction is concerted (80,81) and that in some cases a rate enhancement occurs even when the dienophile is the electron-rich substrate (82) ("inverse" Diels-Alder reaction). Thus, simple olefins surpass maleic anhydride in their rate of addition to hexachlorocyclopentadiene, but maleic anhydride adds to 9,10-dimethylanthracene 200,000 times faster than to cyclopentene.

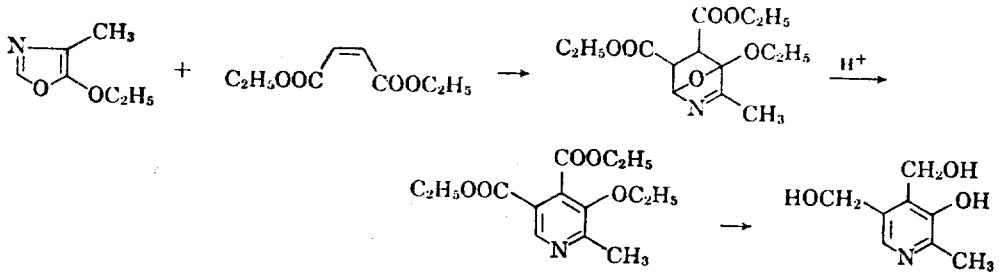
A number of novel Diels-Alder reactions have been described. 2-Naphthol (83) and certain hydroquinones (84,85) yield Diels-Alder adducts with maleic anhydride.



*Endo*methylenetetrahydrophthalic acid is formed directly from fumaric acid and dicyclopentadiene (86).

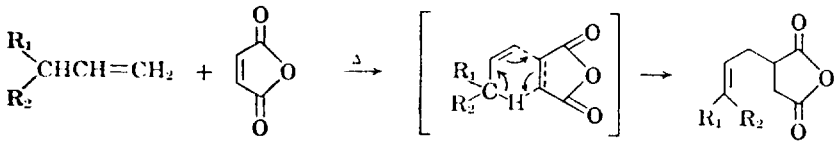


The addition of maleic esters and maleic anhydride to oxazoles (86) followed by dehydration provides a method for the synthesis of pyridoxol or vitamin B_6 (87).



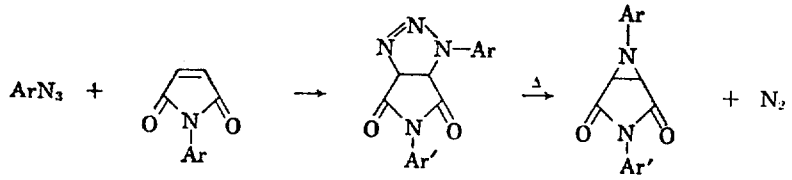
The Diels-Alder reaction of maleic derivatives has also been utilized in the preparation of polymers (88,89).

The formation of alkenylsuccinic anhydride from maleic anhydride and a monoolefin bears some similarity to the Diels-Alder reaction and is known as the "ene reaction" (90). It is now fairly well established that this reaction proceeds through a highly restricted cyclic transition state (91).

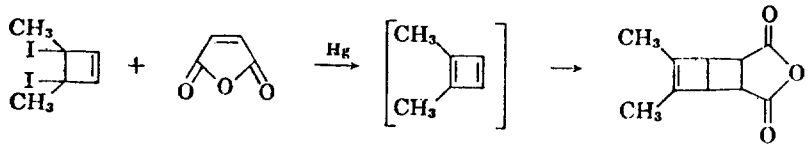


The double bond always undergoes a 1,2 shift and optically active olefins yield optically active products.

Other Cycloadditions. The formation of triazolines from maleic derivatives and azides (92) is an example of a concerted, 1,3-dipolar cycloaddition reaction (93).

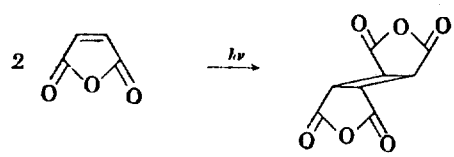


A possible 1,2 addition (94) is shown below:



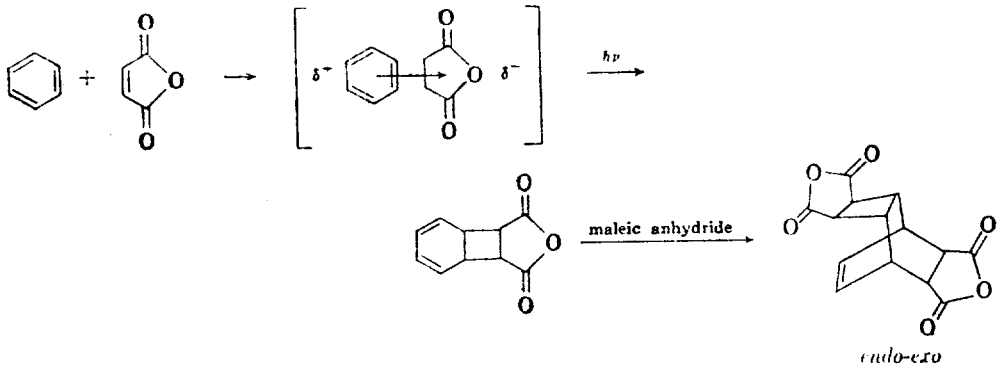
Photochemical Reactions. Cycloaddition reactions, which form four-membered rings, are common when unsaturated compounds are irradiated; but the formation of six-membered rings by a photo Diels-Alder reaction is rare (95). For molecular orbital explanation of these differences, see reference 96. The photoaddition of maleic anhydride to several aromatic derivatives has been studied (99–101).

The solid-state irradiation of fumaronitrile, dimethyl fumarate, or maleic anhydride has been reported (97) to yield cyclobutane derivatives.



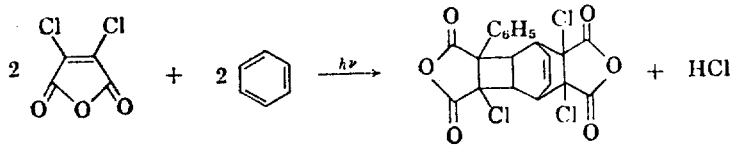
Similar cyclodimers are obtained from methylmaleic anhydride and *N*-phenylmaleimide (98).

In all cases the species activated by the light appears to be a charge-transfer complex between the anhydride and the hydrocarbon. The formation of a stable 2:1 photoadduct of benzene is illustrated in the following equations:

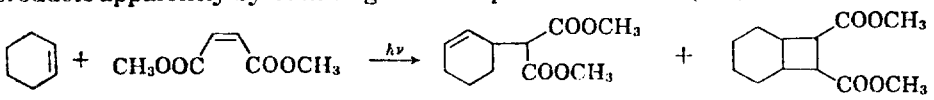


endo-exo

In the absence of a sensitizer the activated intermediate appears to be a singlet whereas the sensitized reaction apparently proceeds via a triplet. Similar photoadducts (102) have been prepared from several maleimides even though the latter compounds do not form charge-transfer complexes with the aromatic hydrocarbons. The reaction of dichloromaleic anhydride with benzene is reported to yield a 2:2 photoadduct (103).

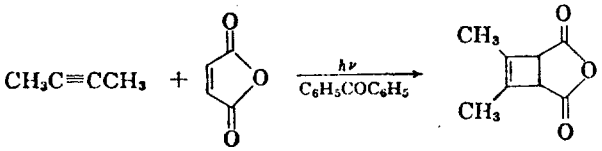


The irradiation of maleic anhydride and its esters in the presence of olefins has also been extensively studied (104–107). The reaction with cyclohexene produces a variety of products apparently by both singlet and triplet mechanisms (104).

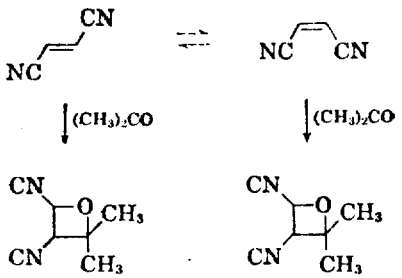


4 isomers

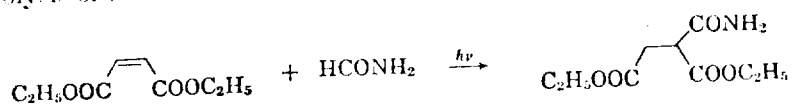
The sensitized photoaddition of maleic anhydride to dimethylacetylene produces a cyclobutene (108).



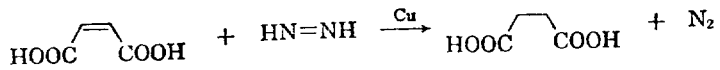
A mixture of oxetanes is the product when fumaronitrile is irradiated in acetone (109).



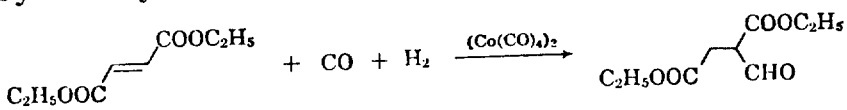
Photolysis of a formamide–dimethylmaleate mixture yields a 1,2 adduct (110).



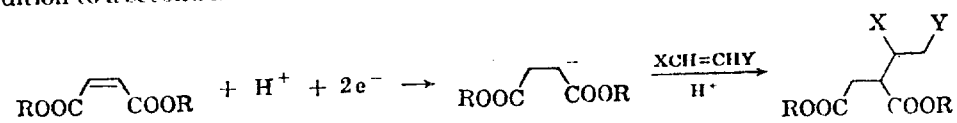
Reduction Reactions. The heterogeneous catalytic reduction of maleic acid and its derivatives gives succinates (22). Homogeneous reduction has also been accomplished by both chemical (111) and catalytic (112) methods. Diimide, prepared by the oxidation of hydrazine with air or peroxide (113), is an especially convenient reagent.



The reductive carbonylation ("oxo reaction") of diethyl fumarate is reported (114) to yield diethyl α-formylsuccinate.



The electrolytic reductive coupling of maleates (115) has been utilized recently as a novel method of preparing a large variety of interesting products. The mechanism of the reaction is believed to involve an anionic intermediate which undergoes a Michael addition to a second molecule of activated olefin.



X and/or Y are electron-withdrawing groups, such as CN, COOR, COR, etc.

Manufacture

Most of the maleic anhydride produced commercially is made by the catalytic oxidation of benzene in the vapor phase (3,116). Many other raw materials (116) have also been used; one manufacturer uses butene (117). Nearly any four- or five-carbon organic compound (except a paraffin) affords maleic anhydride in some yield, particularly furfural, crotonaldehyde, and olefins (116,118). Economics in the United States favor the use of benzene. A cost calculation (119) for production from benzene at 3.75¢/lb shows a cost of 11.3¢/lb at a rate of 10 million lb per year. Maleic anhydride is obtained as a by-product in the manufacture of phthalic anhydride.

The catalyst employed for the oxidation contains at least 70 wt % vanadium oxide. Most catalysts also use molybdenum oxide in the range of 25–30% (116). Several other oxides can be added, such as those of alkali metals, silver, phosphorus, titanium (120), nickel, or cobalt. The catalyst is generally deposited on an inert support made of silica, silica–alumina, or metal turnings (120,121). These supports are available in a wide variety of shapes and surface areas but are usually pellets of low surface area, about 1 m^2/g (116,122). The catalyst is prepared by impregnating the support with an aqueous solution or suspension of the preferred ingredients, concentrating to dryness and then heating to 450–500°C in a stream of gas (122).

The physical properties of a typical catalyst, consisting largely of vanadium and molybdenum oxides, were studied and it has been shown that 20% of the vanadium was reduced (122). The various additives are supposed to increase the activity of the catalyst, the yield of maleic anhydride, and the lifetime of the catalyst. Unlike the catalyst used for phthalic anhydride production the maleic anhydride catalyst cannot be regenerated.

The reaction is usually carried out as a fixed-bed process (123,124), although patents have been issued for a fluid-bed operation (125). The multitubular converter is equipped for cooling the tubes by means of circulating liquid mercury or molten salts (126). The need for efficient heat removal is dictated by the highly exothermic reaction which liberates 10,500–13,500 Btu per lb of benzene reacted.

A vapor mixture of 1.2–1.5 mole % benzene in air (127) is fed through the catalyst bed which is maintained at 300–400°C (127,128). The contact time ranges from 0.01–5.0 sec (126,127) at atmospheric pressure and can be changed according to the conversion and temperature. The yield of product depends upon the residence time and the temperature, as well as the catalyst composition (122). Up to 65 mole % maleic anhydride in the reaction mixture can be realized based on the benzene fed (122).

The effluent gases contain maleic anhydride, maleic acid, carbon dioxide, carbon monoxide, water, and unreacted benzene. The reaction mixture is passed through a cooler. If maleic acid is required the cooled gases are absorbed in water to yield a 40% solution which is purified with carbon, concentrated, and crystallized (129–131).

If maleic anhydride is wanted the cooled gases are partially condensed (132) at 60°C, which is slightly above the melting point of the anhydride. The remaining gases are absorbed in solvents from which the anhydride is recovered by dehydration and distillation. The condensed maleic anhydride and acid are dehydrated by vacuum or azeotropic distillation. Purification is effected by vacuum distillation or sublimation (129–131). Overall yield of the purified anhydride is 50–60% based on benzene.

Butenes are converted to maleic anhydride at 350°C using a catalyst consisting of the oxides of molybdenum, vanadium, and phosphorus, supported on silica gel. The reaction is carried out at 25–50 psi and at a contact time of 1.5 sec (117).

Fumaric acid is prepared from maleic acid by isomerization (133), using amine bases, mercaptans, heavy metal salts, mineral acids, disulfides, and other materials as catalysts. The conversion is carried out at atmospheric pressure at 40–60°C in a 10–20% hydrochloric acid solution. Fumaric acid precipitates from the aqueous medium and after separation is dried and purified by recrystallization or sublimation (134,135). Yields are nearly quantitative (136). It is possible to get fumaric acid directly from benzene oxidation without first isolating maleic acid if the effluent gases are scrubbed in aqueous hydrochloric acid.

Fermentation processes for fumaric acid are also available using glucose or molasses with strains of *Rhizopus nigricans* and *R. japonicus* (137).

Economic Aspects

United States production, sales, and selling price for maleic anhydride, fumaric acid, and dibutyl maleate and fumarate are shown in Table 2. Usage of these items is increasing steadily while, at the same time, the selling price is decreasing. The profit squeeze is evident when the selling price of 12¢/lb for maleic anhydride is compared to the calculated production cost of 11.3¢/lb. Table 3 shows the world production of maleic anhydride estimated from reports in several periodicals and scientific journals.

Table 2. Production and Sales, million lb/year (138)

Year	Production	Sales	Price, $/lb	Production	Sales	Price, $/lb
	Fumaric acid			*Maleic anhydride*		
1959	16.258	13.844	0.29	60.607	49.231	0.26
1960	23.423	16.739	0.27	90.128	51.710	0.24
1961	20.591	18.840	0.22	77.261	41.838	0.22
1962	24.432	20.033	0.19	83.966	46.286	0.17
1963	23.775	23.099	0.16	86.568	57.072	0.13
1964	30.145	23.629	0.16	118.109	67.792	0.12
1965[a]				122.861		
	Dibutyl fumarate			*Dibutyl maleate*		
1961	3.918					
1962	4.852					
1963	4.580	3.973	0.22	8.494	3.391	0.23
1964	5.143	4.630	0.21	6.052	3.653	0.22

[a] Estimated.

Table 3. Worldwide Production of Maleic Anhydride, metric tons (139)

Country	1961	1963
England	8,500	10,500
France	6,000	9,600
Belgium	5,600	5,600
Italy	12,000	27,500
United States	83,600	84,500
Canada	2,800	2,800
Brazil	480	480
Japan	16,200	14,280
Austria	1,200	1,200
Spain	600	2,100
West Germany	18,000	28,800
Total	185,040	187,360

Analytical Methods and Specifications

Maleic anhydride can be determined quantitatively even in the presence of maleic acid. One method (140) employs the reaction of the anhydride with a known excess of aniline to yield the half acid half anilide. The aniline consumed in the reaction is detected by titration with hydrochloric acid in a solution of ethylene glycol–isopropyl alcohol and is a measure of the anhydride present. A second method (141) requires addition of a measured excess of morpholine which produces the half acid half amide of maleic anhydride. The free acid and the acid formed by reaction are neutralized with sodium hydroxide. Carbon disulfide is added at the equivalence point to convert unreacted morpholine to the corresponding dithiocarbamic acid, which is then titrated potentiometrically with sodium hydroxide in nonaqueous media.

Maleic acid can be determined in the presence of the anhydride by the morpholine–CS_2 method (141) just described, or by direct titration using tri-*n*-propylamine or *N*-ethylpiperidine in acetone (142). Maleic acid can also be identified by hydrogenation (143) of the double bond using Raney nickel or platinum oxide in a nonreducible

solvent together with hydrogen. The number of moles of hydrogen uptake is equivalent to the number of moles of maleic acid. Bromine can be added to the double bond of maleic acid (144). The bromine is generated in situ from an excess of bromide-bromate solution with the use of acid. Iodide is added to the mixture and is converted to free iodine by the free excess bromine. The free iodine is then titrated with sodium thiosulfate. The addition of sodium bisulfite to maleic acid results in a substituted sodium sulfonate with a corresponding decrease in acidity (145). The acidity decrease is determined by titration with sodium hydroxide to Alizarin Yellow R–Xylene Cyanol FF mixed indicator.

The bromination method applies equally well to fumaric acid. Competitive rates of hydrogenation and bromination are useful for mixtures of the sodium salts of maleic and fumaric acids (146). However, one of the most useful and accurate techniques is that of polarography (147), even for mixtures of the two acids. The preferred conditions for analysis require stringent control of the solvent, temperature, and pH.

Instrumental methods can be used for detection and identification. Table 4 shows different carbonyl-stretching frequencies found in the infrared region for the two acids and maleic anhydride (148,149). Chemical shifts in ppm from the internal standard tetramethylsilane (TMS) are shown for maleic anhydride and two esters (150).

Table 4. IR and NMR Data

Compound	δ, ppm (TMS)[a]	CO stretch, cm^{-1}
maleic acid		1705
fumaric acid		1680
maleic anhydride	7.10	1790
diethyl fumarate	6.83	
diethyl maleate	6.28	

[a] Tetramethylsilane reference.

Specifications for fumaric acid are (151) for a white crystalline powder with a minimum assay of 99% and maximum values for moisture of 0.25%, for iron 3 ppm, and heavy metals 20 ppm. Molten maleic anhydride (18a) has a maximum APHA color of 20, a minimum crystallizing point of 52.5° C, complete and clear solubility in water (4 parts in 10 ml), and a maximum APHA color of 40 after 2 hr of heating at 140°C.

Health and Safety Factors

Fumaric acid is practically nontoxic. It is being used as an acidulant in foods and in pharmaceutical preparations. There are no particular handling problems connected with its use. The Food and Drug Administration has approved the use of fumaric acid and its calcium, magnesium, potassium, and sodium salts "in food at a level not in excess of the amount reasonably required to accomplish their intended effects" (152).

Maleic anhydride is a strong irritant to the skin, eyes, and the mucous membrane of the upper respiratory system. It is so irritating that acute exposure has to be avoided. A worker would voluntarily withdraw from high concentrations of maleic anhydride fumes, if possible. Subacute inhalation leads to severe headache, nosebleed, nausea, and temporary impairment of vision. One case of pulmonary edema after exposure to these fumes has been recorded. There have been no reports of per-

manent pathological changes in exposed workers. Individual workers with a history of bronchial allergies, such as asthma, should not work in areas where maleic anhydride fumes or dust may exist.

If maleic anhydride is left in contact with the skin, painful irritation can result, particularly if the skin is moist, because of the rapid hydrolysis of maleic anhydride to maleic acid in the presence of moisture. Maleic anhydride can cause dermatitis, characterized by the formation of small blisters.

Maleic anhydride is very irritating to the eyes and can cause painful conjunctivitis and possible corneal dullness if not immediately removed.

Oral ingestion may cause death or permanent injury after very short exposure to small quantities (153).

The toxicity of maleic acid is very similar to that of maleic anhydride.

When handling maleic anhydride rubber gloves and chemical safety goggles should be worn. When maleic anhydride dust is present, dust respirators must be worn. In case of maleic anhydride fumes, organic-vapor-cartridge respirators or full-face gas masks, approved by the U.S. Bureau of Mines for organic vapors, should be worn. In normal usage, if the material cannot be handled under an exhaust hood, respirators are mandatory.

Maleic anhydride does not present a severe fire hazard, but it can burn if ignited. Fires can be extinguished with water (fog or spray), carbon dioxide, or dry-powder extinguishers. The autoignition temperature is 470°C.

Uses

The breakdown of maleic anhydride usage in the United States is shown in Table 5 (118). The major application of maleic anhydride is in the formation of resins. The primary reaction in the preparation of maleic resins is esterification. Addition polymerization can take place which leads to three-dimensional molecules and consequently to extremely hard resins. A wide variation in the final properties of a resin end product can be governed by the types of polyhydric alcohols used for esterification, by mixtures of maleic anhydride with other polybasic acids, the use of polymerizable compounds, such as olefins, and by the manner of processing the resin.

Table 5. Uses for Maleic Anhydride

Product	Percent
polyesters	40
alkyd resins and drying oils	16
agricultural chemicals	10
fumaric acid	16
plastics, lubricants, and copolymers	14
miscellaneous and export	4

Polyester resins are made from glycol maleates or fumarates copolymerized with styrene monomer. The resin is rapidly laminated at low temperature and pressure to yield rigid insoluble solids with good dielectric properties and high structural strength. They are used with glass fiber, and other reinforcing materials, to produce large, rigid moldings. Among the products for which these laminating resins and glass fibers are used, are automobile bodies, structural building panels, molded boats,

chemical storage tanks, lightweight pipe, machinery housings, furniture, radar domes, luggage, and bathtubs.

Drying oils, such as linseed, soya, or safflower, can be upgraded by treatment with maleic anhydride and glycerin, or pentaerythritol. Tall oil, which consists of rosin acids and fatty acids plus unsaponifiable matter, forms resins after treatment with maleic anhydride and pentaerythritol. This type of resin is used for general coating applications, particularly in dip coatings for industrial applications and in paper coatings.

Maleic anhydride, when substituted for a part of the phthalic anhydride in alkyd formulations, shortens processing time and develops a harder resin. These phthalic-type alkyd resins are used in baking enamels, plasticizing resins, air-drying enamels, interior flat finishes, automotive finishes, exterior paints, marine paints, and varnishes.

Other maleic alkyds (without phthalic anhydride) can be made using rosins, terpenes, diolefins, or oils. They find application as plasticizers, lacquers, ingredients for printing inks, paints, and varnishes.

Among the agricultural chemicals derived from maleic anhydride are maleic hydrazide, a growth retardant, and Malathion (registered trademark, American Cyanamid Company), an exceptionally effective insecticide. Alkyl maleates are not only insecticides and repellents but are intermediates for the manufacture of fungicides and more specifically acting insecticides (154).

The alkyl esters of maleic and fumaric acids are used in copolymers with polyvinyl acetate to form internally plasticized emulsions which are used as permanently tacky adhesives.

Many commercially important chemicals are easily made from maleic anhydride. These include fumaric acid, succinic acid, aspartic acid, and tartaric acid. When sodium bisulfite is reacted with maleic anhydride, sulfosuccinic acid is formed, which is the basic raw material for the production of wetting agents. Many derivatives of maleic anhydride have important uses (154) in pharmaceuticals, textile finishes, photographic chemicals, surface-active agents, dyestuffs, tanning agents, petroleum additives, rubber chemicals, and synthetic lubricants.

In recent years fumaric acid has gained wide acceptance as a fruit-flavored food acid. Large quantities are now used in the acidulation of fruit-juice drinks, gelatin desserts, pie fillings, jelling aids, refrigerated biscuit doughs, and wines. Usage has increased due to its acceptance by the Food and Drug Adminstration (152). Fumaric acid is nonhygroscopic and is cheaper than citric acid which it is rapidly supplanting.

Bibliography

"Maleic Acid, Fumaric Acid, and Maleic Anhydride" in *ECT* 1st ed., Vol. 8, pp. 680–696, by W. H. Gardner and L. H. Flett, National Aniline Division, Allied Chemical & Dye Corporation.

1. J. Pelouze, *Ann.* **11**, 263 (1834).
2. R. Winckler, *Ann.* **4**, 230 (1832).
3. U.S. Pats. 1,318,631–1,318,633 (1919), J. Weiss and C. Downs (to Barrett Co.).
4. J. Weiss and C. Downs, *Ind. Eng. Chem.* **12**, 228 (1920).
5. T. Flitcroft, H. Skinner and M. Whiting, *Trans. Faraday Soc.* **53**, 784 (1957).
6. K. Schwabe and W. Wagner, *Chem. Ber.* **91**, 686 (1958).
7. H. Skinner and A. Snelson, *Trans. Faraday Soc.* **55**, 404 (1959).
8. C. Beguin and T. Gauman, *Helv. Chim. Acta* **41**, 1376 (1958).
9. S. Mastrangelo, *Anal. Chem.* **29**, 841 (1957).

10. R. Marsh, E. Ubell, and H. Wilcox, *Acta Cryst.* **15**, 35 (1962).
11. C. Davies and V. Malpass, *Trans. Faraday Soc.* **60**, 2075 (1964).
12. R. Wilhoit and D. Shiao, *J. Chem. Eng. Data* **9**, 595 (1964).
13. G. Parks, J. Moseley, and P. Peterson, Jr., *J. Chem. Phys.* **18**, 152 (1950).
14. L. Winstrom and L. Kulp, *Ind. Eng. Chem.* **41**, 2584 (1949).
15. H. Spengler and W. Tamplin, *Anal. Chem.* **24**, 941 (1952).
16. M. Shahat, *Acta Cryst.* **5**, 763 (1952).
17. W. German, A. Vogel, and G. Jeffery, *Phil. Mag.* Ser. 7, **22**, 790 (1936).
18. N. Lange and G. Forker, eds., *Handbook of Chemistry*, 10th ed., McGraw-Hill Book Co., Inc., New York, 1961.
18a. *Monsanto Technical Bulletin No. RE-12*, Monsanto Co., St. Louis, Mo., Sept., 1962.
19. R. Weast, ed., *Handbook of Chemistry and Physics*, 46th ed., The Chemical Rubber Co., Cleveland, 1964–1965.
20. H. Stephen and T. Stephen, eds., *Solubilities of Inorganic and Organic Compounds*, The Macmillan Co., New York, 1963.
21. K. Hojendahl, *J. Phys. Chem.* **28**, 758 (1924).
22. L. Flett and W. Gardner, *Maleic Anhydride Derivatives*, John Wiley & Sons, Inc., New York, 1952.
23. J. Wislicenus, *Ann.* **246**, 93 (1888); W. Schliesser, Ger. Pat. 1,176,126 (1960), to Badische Anilin- u. Soda Fabrik, and Dutch Pat. 94,649 (1960), to Stamicarbon, N.V.
24. W. Perkin, *Ber.* **15**, 1073 (1882).
25. J. Volhard, *Ann.* **268**, 255 (1892).
26. L. Kyrides, *Org. Syn.* **20**, 51 (1940).
27. U.S. Pat. 2,653,168 (1953), S. Spatz (to Allied Chemical & Dye Corp.).
28. U.S. Pat. 3,078,302 (1963), J. Franz and M. Farrar (to Monsanto Co.).
29. Brit. Pat. 928,182 (1963), K. Geddes and R. Maclean (to Distillers Co.).
30. S. Spatz, *J. Org. Chem.* **26**, 4158 (1961).
30a. C. Bischoff and A. Hedenström, *Chem. Ber.* **35**, 4087 (1902).
30b. A. Bader and A. Kontowicz, *J. Am. Chem. Soc.* **75**, 5416 (1953); U.S. Pat. 2,822,378 (1958), A. Bader and A. Kontowicz (to Pittsburgh Plate Glass Co.).
31. H. Boenig, *Unsaturated Polyesters*, American Elsevier Publishing Co., New York, 1964.
32. H. Waddill, J. Milligan, and W. Pepel, *Ind. Eng. Chem. Prod. Res. Develop.* **3** (1), 53 (1964).
33. L. Coleman, *J. Org. Chem.* **24**, 135 (1959).
34. P. Bhatia and W. Roderick, *J. Org. Chem.* **28**, 2018 (1963).
35. Y. Ogata, K. Tsunemitsu, and R. Oda, *Bull. Inst. Phys. Chem. Research (Tokyo), Chem. Ed.* **23**, 281 (1944).
36. Fr. Pat. 1,383,678 (1964), A. Verheyden, S. Westrem, and P. Ochsner (to Lonza, Ltd.); see also Belg. Pat. 550,710 (1957) (to Union Chimique Belge, S.A.), and U.S. Pat. 2,902,512 (1959) (to Union Chimique Belge, S.A.).
37. D. Rittenberg and L. Ponticorvo, *Proc. Natl. Acad. Sci. U.S.* **46**, 822 (1960).
38. Brit. Pat. 933,102 (1964), V. Burnop (to Esso Research & Engineering Co.).
39. *Chemical Safety Data Sheet SD-88*, Manufacturing Chemists' Assoc., Inc., Washington, D.C., Oct., 1962.
40. *Chem. Eng. News*, Feb. 24, 1964, p. 41.
41. G. Baddeley et al., *J. Chem. Soc.* **1952**, 3289; *ibid.*, **1953**, 3969.
42. D. Papa et al., *J. Am. Chem. Soc.* **70**, 3356 (1948).
43. R. Lutz, *Org. Syn.* **20**, 29 (1940).
44. B. Cramer et al., *J. Am. Pharm. Assoc.* **37**, 439 (1948).
45. L. Kamstra, *Proc. S. Dakota Acad. Sci.* **30**, 40 (1951).
46. T. Yoshino and I. Kijima, *J. Soc. Org. Synthet. Chem. Japan* **10**, 338 (1952).
47. F. Zienty, B. Vineyard, and A. Schleppnik, *J. Org. Chem.* **27**, 3140 (1962).
48. B. Dmuchovsky, F. Zienty, and W. Vredenburgh, *J. Org. Chem.* **31**, 865 (1966).
49. B. Dmuchovsky, B. Vineyard, and F. Zienty, *J. Am. Chem. Soc.* **86**, 2874 (1964).
50. R. Hindersinn and R. Ludington, *J. Org. Chem.* **30**, 4020 (1965).
51. R. Miller, J. Bradley, and L. Hamilton, *J. Am. Chem. Soc.* **78**, 5299 (1956).
52. C. Osuch, J. Franz, and F. Zienty, *J. Org. Chem.* **29**, 3721 (1964).
53. R. Dorland and H. Hibbert, *Can. J. Research*, **18B**, 30 (1940).

54. E. Bernatek, P. Groenning, and T. Ledaal, *Acta Chem. Scand.* **18**, 1966 (1964).
55. E. Briner, S. Fliszar, and G. Rosetti, *Helv. Chim. Acta* **47**, 2011 (1964).
56. J. Church and R. Blumberg, *Ind. Eng. Chem.* **43**, 1780 (1951).
57. G. Payne and P. Williams, *J. Org. Chem.* **24**, 54 (1959).
58. M. Miller, *J. Org. Chem.* **28**, 1148 (1963).
59. H. Shechter and H. Barker, *J. Org. Chem.* **21**, 1473 (1956).
60. A. Bader, R. Buckley, F. Leavitt, and M. Szwarc, *J. Amer. Chem. Soc.* **79**, 5621 (1957).
61. D. Stark, *Polymerization of Fumarate Esters and Copolymerization with Olefins*, F. Becker and Co., Wiesbaden, West Germany 1961.
62. J. Lang, W. Pavelich, and H. Clarey, *J. Polymer Sci.* **1**, Part A, 1123 (1963).
63. R. Wiley and D. Parish, *J. Polymer Sci.* **45**, 503 (1960).
64. G. Butler, *J. Polymer Sci.* **48**, 279 (1961).
65. R. Dowbenko and W. Chang, *Polymer Letters* **2**, 469 (1964).
66. U.S. Pat. 2,500,260 (1950), L. Newton (to Union Carbide Corp.).
67. U.S. Pat. 2,494,049 (1950), D. Levin (to Chemical Concentrates Corp.).
68. U.S. Pat. 2,911,359 (1959), W. Stefaniak (to Allied Chemical Corp.).
69. U.S. Pat. 3,141,037 (1964), H. Olenberg, J. Russell, and M. Becker (to Halcon International, Inc.).
70. W. Schiesser, *Angew. Chem.* **74**, 429 (1962).
71. U.S. Pat. 2,764,609 (1956), H. Gamrath (to Monsanto Co.).
72. K. Nozaki, *J. Am. Chem. Soc.* **63**, 2681 (1941).
73. U.S. Pat. 2,414,066 (1947), W. Scott (to Wingfoot Corp.).
74. K. Nozaki and R. Ogg, *J. Am. Chem. Soc.* **63**, 2583 (1941).
75. S. Seltzer, *J. Am. Chem. Soc.* **83**, 1861 (1961).
76. G. Hammond et al., *J. Am. Chem. Soc.* **86**, 3213 (1964).
77. M. Kloetzel, *Org. Reaction* **4**, 1 (1948).
78. E. DeWitt, C. Lester, and G. Ropp, *J. Am. Chem. Soc.* **78**, 2101 (1956).
79. D. Craig, J. Shipman, and R. Fowler, *J. Am. Chem. Soc.* **83**, 2885 (1961).
80. S. Seltzer, *J. Am. Chem. Soc.* **85**, 1360 (1963).
81. J. Berson, R. Reynolds, and W. Jones, *J. Am. Chem. Soc.* **78**, 6049 (1956).
82. J. Sauer, H. Weist, and A. Mielert, *Angew. Chem. Intern. Ed. Engl.* **1**, 268 (1962).
83. K. Takeda, S. Nagakura, and K. Kitahonoki, *Pharm. Bull. (Tokyo)* **1**, 135 (1953).
84. K. Takeda and K. Kitahonoki, *J. Pharm. Soc. Japan* **76**, 869 (1956).
85. R. Cookson and N. Wariyar, *J. Chem. Soc.* **1957**, 327.
86. G. Kondrat'eva, *Khim. Nauka i Prom.* **2**, 666 (1957); (through) *Chem. Abstr.* **52**, 6345 (1958).
87. E. Harris et al., *J. Org. Chem.* **27**, 2705 (1962).
88. H. Batzer and H. Reblin, *Makromol. Chem.* **44**, 179 (1960).
89. J. Stille and L. Plummer, *J. Org. Chem.* **26**, 4026 (1961).
90. R. Hill and H. Barger, *J. Org. Chem.* **30**, 2558 (1965).
91. R. Hill and M. Rabinovitz, *J. Am. Chem. Soc.* **86**, 965 (1964).
92. A. Mustafa et al., *J. Am. Chem. Soc.* **78**, 145 (1956).
93. R. Huisgen, *Angew. Chem. Intern. Ed. Engl.* **2**, 565, 633 (1963).
94. R. Criegee et al., *Chem. Ber.* **98**, 2331 (1965).
95. N. Turro, *Molecular Photochemistry*, W. A. Benjamin, Inc., New York, 1965, p. 194. (However, see also *Ann.* **693**, 20 (1966).)
96. H. Longuet-Higgins and E. Abrahamson, *J. Am. Chem. Soc.* **87**, 2045 (1965); R. Hoffmann and R. Woodward, *J. Am. Chem. Soc.* **87**, 2046 (1965).
97. G. Griffin, A. Vellturo, and K. Furukawa, *J. Am. Chem. Soc.* **83**, 2725 (1961); *Tetrahedron Letters* **3**, 13 (1960).
98. G. Schenck, W. Hartmann, S. Mannsfeld, and W. Metzner, *Chem. Ber.* **95**, 1642 (1962).
99. D. Bryce-Smith and A. Gilbert, *J. Chem. Soc.* **1965**, 918; D. Bryce-Smith and J. Lodge, *J. Chem. Soc.* **1962**, 2675; D. Bryce-Smith and B. Vicery, *Chem. & Ind. (London)* **1961**, 429; *ibid.* **1962**, 2060.
100. E. Grovenstein et al., *J. Am. Chem. Soc.* **83**, 1705 (1961).
101. G. Schenck et al., *Tetrahedron Letters* **1960** (21), 1.
102. D. Bryce-Smith and M. Hems, *Tetrahedron Letters* **1966** (17), 1895.
103. G. Vermont, P. Riccobono, and J. Blake, *J. Am. Chem. Soc.* **87**, 4024 (1965).

104. A. Cox, P. deMayo, and R. Yip, *J. Am. Chem. Soc.* **88**, 1043 (1966); P. deMayo, S. Reid, and R. Yip, *Can. J. Chem.* **42**, 2828 (1964).
105. R. Steinmetz, W. Hartmann, and G. Schenck, *Chem. Ber.* **98**, 3854 (1965).
106. R. Robson, P. Grubb, and J. Barltrop, *J. Chem. Soc.* **1964**, 2153.
107. G. Schenck, W. Hartmann, and R. Steinmetz, *Chem. Ber.* **96**, 498 (1963).
108. R. Criegee et al., *Chem. Ber.* **97**, 2942 (1964).
109. J. Beereboom and M. Schach von Wittenau, *J. Org. Chem.* **30**, 1231 (1965).
110. D. Elad, *Proc. Chem. Soc.* **1962**, 225.
111. S. Huenig and H. Mueller, *Angew. Chem.* **74**, 215 (1962).
112. J. Halpern, J. Harrod, and B. James, *J. Am. Chem. Soc.* **83**, 753 (1961).
113. E. Corey, W. Mock, and D. Pastro, *Tetrahedron Letters* **1961** (11), 347.
114. H. Adkins and G. Krsek, *J. Am. Chem. Soc.* **70**, 383 (1948).
115. M. Baizer and J. Anderson, *J. Org. Chem.* **30**, 3138 (1965).
116. J. Dixon and J. Longfield, in P. H. Emmett, ed., *Catalysis*, Vol. 7, Reinhold Publishing Corp., New York, 1960, Chap. 3.
117. U.S. Pats. 3,156,705–3,156,707 (1964), R. Kerr (to Petro-Tex Chemical Corp.).
118. W. Faith, D. Keyes, and R. Clark, *Industrial Chemicals*, 3rd ed., John Wiley & Sons, Inc., New York, 1965, p. 497.
119. *European Chemical News* **2** (34), 24 (1962).
120. U.S. Pat. 3,106,569 (1963), W. Robinson (to Monsanto Co.).
121. U.S. Pats. 2,625,554 (1953) and 2,674,582 (1954), J. Darby (to Monsanto Chemical Co.).
122. B. Dmuchovsky, M. Freerks, E. Pierron, R. Munch, and F. Zienty, *J. Catalysis* **4**, 291 (1965); see also references cited in this article.
123. U.S. Pat. 2,885,409 (1959), R. Ryder (to American Cyanamid Co.).
124. M. Sittig, "Dibasic Acids and Anhydrides 1966," *Chemical Process Monograph Series 18*, Noyes Development Corp., Park Ridge, N.J., 1966.
125. U.S. Pat. 2,526,689 (1950), W. Rollman (to Standard Oil Development Co.).
126. U.S. Pat. 3,074,969 (1963), R. Kerr et al. (to Pittsburgh Plate Glass Co.).
127. U.S. Pat. 2,954,385 (1960), D. Burney et al. (to Standard Oil Co., Indiana).
128. U.S. Pat. 3,005,831 (1961), J. Dreibelbis (to Pittsburgh Chemical Co.).
129. U.S. Pat. 2,638,481 (1953), J. Nachod (to Hercules Powder Co.).
130. U.S. Pat. 2,863,880 (1958), G. Kohn (to California Spray and Chemical Corp.).
131. U.S. Pat. 2,989,545 (1961), J. Jewett (to American Cyanamid Co.).
132. U.S. Pat. 2,762,449 (1953), M. Sweeney (to United Engineers and Constructors).
133. U.S. Pat. 2,704,296 (1951), E. Dobratz (to Monsanto Chemical Co.).
134. U.S. Pat. 2,393,352 (1946), L. Winstrom (to Allied Chemical & Dye Corp.).
135. U.S. Pat. 3,025,321 (1962), H. Lindahl et al. (to Pure Oil Co.).
136. U.S. Pat. 2,548,687 (1947), S. Spatz (to Allied Chemical & Dye Corp.).
137. U.S. Pat. 2,326,986 (1944), S. Waksman (50% each to Merck & Co. and Chas. Pfizer & Co.).
138. U.S. Tariff Commission, *Synthetic Organic Chemicals, United States Production and Sales*, U.S. Govt. Printing Office, Washington, D.C. (Annual publication. The years covered range from 1950–1965, corresponding to publication dates 1951–1966.)
139. Compilation of B. Thomas, Monsanto Co., private communication to the authors.
140. S. Siggia and J. Hanna, *Anal. Chem.* **23**, 1717 (1951).
141. F. Critchfield and J. Johnson, *Anal. Chem.* **28**, 430 (1956).
142. S. Siggia and N. Floramo, *Anal. Chem.* **25**, 797 (1953).
143. S. Siggia, *Quantitative Organic Analysis via Functional Groups*, 3rd ed., John Wiley & Sons, Inc., New York, 1966, p. 318.
144. H. Lucas and D. Pressman, *Ind. Eng. Chem. Anal. Ed.* **10**, 140 (1938).
145. F. Critchfield and J. Johnson, *Anal. Chem.* **28**, 73 (1956).
146. Reference 143, Chap. 25.
147. P. Elving and I. Rosenthal, *Anal. Chem.* **26**, 1454 (1954).
148. L. Flett, *J. Chem. Soc.* **1957**, 961.
149. R. Barnes, et al., *Infrared Spectroscopy*, Reinhold Publishing Corp., New York, 1944.
150. *NMR Spectra Catalog*, Varian Associates, Palo Alto, Calif., 1962.
151. *Technical Bulletin O/Fl-1*, Monsanto Co., St. Louis, Mo., April, 1966.
152. *Federal Register*, p. 5234 (May 25, 1963).

153. N. Sax, *Dangerous Properties of Industrial Materials*, 2nd ed., Reinhold Publishing Corp., New York, 1963.
154. W. Ashcroft and I. Clifford, *Chem. Prod.* 11 (1961).

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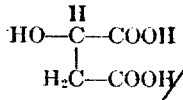
MALIC ACID

Malic acid (hydroxysuccinic acid, hydroxybutanedioic acid, 1-hydroxy-1,2-ethanedicarboxylic acid) is a white or nearly white powdery, granular, or crystalline material. The levorotatory isomer occurs widely distributed in the vegetable kingdom. Malic acid has not enjoyed widespread industrial application to date because of limited availability and high cost. Recent large-scale production facilities for the racemic mixture of malic acid isomers will allow complete exploration of the commercial potential of this acid.

The presence of a hydroxyl group, as well as of two carboxyl groups, results in a highly soluble molecule capable of the reactions usually attributable to these groups.



Malic acid, the principal acid found in apples, is sometimes referred to as "apple acid." The characteristic flavor of malic acid has been used advantageously in the manufacture of apple jams, jellies, candy, and beverage products.

Occurrence

Malic acid occurs widely in biological systems. It is the predominant acid in numerous fruits, where it contributes significantly to the flavor, especially in unripe apples (Table 1). It is present in grapes together with a usually lesser amount of tartaric acid. The change in flavor as some of these fruits ripen is associated with a reduction in malic acid content and a simultaneous increase in sugar. Malic acid occurs in relatively low concentrations thus making the isolation from natural sources expensive and impractical. An ion-exchange process has been published (1) for the

Table 1. Malic Acid in Fruits (3–5)

Fruit	% of total acid	Fruit	% of total acid
apple	97.2	orange pulp	trace
apricot	23.7–69.8	peach	50.0–96.2
banana	53.7–92.3	pear	33.0–86.6
blueberry	6.0	persimmon	100.0
cherry	94.2	pineapple	12.5
cranberry	19.1–23.5	plum	98.5
gooseberry	46.2	quince	100.0
grape (Concord)	60.0	rhubarb	77.0
grapefruit	5.6	strawberry	9.9–11.0
lemon	4.5	watermelon	100.0
orange peel	59.6–80.0		