diimide in 40 ml. of dichloromethane was added dropwise over a 30-min. period. The reaction mixture was stirred at room temperature for 24 hr., followed by removal of the precipitated *N,N'*-dicyclohexylurea by filtration. The filtrate was concentrated by distillation and the residue was dissolved in benzene, and passed through a column (1" × 10") of Florisil in benzene. The product, yellow-orange crystals, m.p. 37–40°, weighed 39 g. (100%) and exhibited a carbonyl absorption at 1790 cm.$^{-1}$ in the infrared spectrum of a melted film.

Anal. Calcd. for $C_{11}H_9O_2N$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.85; H, 5.02; N, 7.54.

N-(o-Chlorophenyl)isomaleimide. To a slurry of 45 g. (0.2 mole) of *N*-(*o*-chlorophenyl)maleamic acid in 1 l. of dichloromethane, a solution of 41.2 g. (0.2 mole) of *N,N'*-dicyclohexylcarbodiimide in 40 ml. of dichloromethane was added dropwise over a 30-min. period. The mixture was stirred at room temperature for 24 hr., followed by filtration of the *N,N'*-dicyclohexylurea and distillation of the solvent under reduced pressure. The residue in benzene was passed through a column of Florisil and the eluates were concentrated to yield 40 g. (97%) of yellow crystals, m.p. 60–66°. Recrystallization of a sample from 1:1 benzene–petroleum ether (b.p. 39–54°) gave an analytical sample, m.p. 65–67°.

Anal. Calcd. for $C_{10}H_6O_2NCl$: C, 57.85; H, 2.91; N, 6.75. Found: C, 58.35; H, 2.73; N, 6.58.

The infrared spectrum of a liquid film showed strong carbonyl absorption at 1800 cm.$^{-1}$

Isomerization of N-n-butylisomaleimide to N-n-butylmaleimide. A solution of 5.0 g. (0.033 mole) of *N*-*n*-butylisomaleimide, 6.06 g. (0.06 mole) of triethylamine, and 3.6 g. (0.06 mole) of acetic acid in 100 ml. of benzene was heated at reflux for 90 min. The solution was cooled, washed with water, dilute sodium hydroxide solution, and again with water. The benzene was removed under reduced pressure and the residue was distilled to yield a clear liquid, b.p. 50–55° (0.5 mm.). Vapor phase chromatographic analysis of this material showed it to be a mixture containing 40% *N*-*n*-butylisomaleimide, 59.4% *N*-*n*-butylmaleimide and 0.6% of an unknown impurity. The recovery was 3.5 g. (70%).

Isomerization of N-phenylisomaleimide to N-phenylmaleimide. A mixture of 5.0 g. (0.029 mole) of *N*-phenylisomaleimide, 1.0 g. (0.012 mole) of anhydrous sodium acetate and 15 ml. of acetic anhydride was heated on the steam bath for 1 hr. After the mixture had cooled to 25°, it was poured into 100 ml. of water causing long, yellow needles to separate. These were collected and dried, 4.5 g. (90%) m.p. 90–91°. A mixture melting point with an authentic sample of *N*-phenylmaleimide was undepressed. When sodium acetate was absent in this reaction, the starting material was recovered.

Isomerization of N,N'-hexamethylenebisisomaleimide to N,N'-hexamethylenebismaleimide. A solution of 4 g. (0.014 mole) of *N,N'*-hexamethylenebisisomaleimide, 1.8 g. (0.03 mole) of acetic acid, and 2.6 g. (0.026 mole) of triethylamine in 200 ml. of dry benzene was heated under reflux for 16 hr., cooled, and washed with water. The benzene was removed under reduced pressure and the residue, 1.4 g. (35%) was recrystallized from isopropyl alcohol, m.p. 136–141°. A mixture melting point with authentic *N,N'*-hexamethylenebismaleimide was undepressed.

Acknowledgment. We are indebted to Miss Olive M. Garty for the vapor phase chromatographic analyses and to Mr. William Birch and Mr. J. T. Commerford for technical assistance.

BOUND BROOK, N. J.

[CONTRIBUTION NO. 191 FROM THE RESEARCH CENTER OF THE UNITED STATES RUBBER COMPANY]

The Chemistry of Maleimide and Its Derivatives.
II. Maleimide and *N*-Methylolmaleimide

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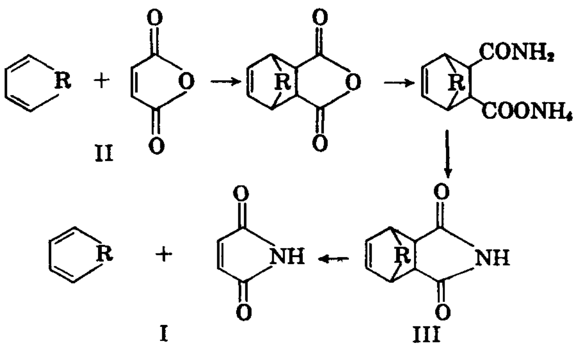
Received March 18, 1960

Maleimide was conveniently synthesized by preparation and pyrolitic decomposition of 3,6-*endo*-methylene-Δ^4-tetrahydrophthalimide. A variety of new *N*-substituted derivatives of maleimide were prepared. The olefinic bonds of maleimide and the derivatives were reactive in vinyl type polymerization under conditions of free radical or anionic initiation.

In an earlier paper,[1] a practical preparation of maleimide (I) by way of *N*-carbamylmaleimide was reported. In this paper, an alternate route for preparation for I and certain aspects of the chemistry of I are presented.

Preparation of I. The sequence of reactions shown in Chart A provides I in yields varying with the substituent R of the diene, II. Selection of cyclopentadiene (II, R = —CH$_2$—) was dictated by such factors as economy, convenience and ease of hydrolysis of the imide, III.

CHART A



Chemistry of I. There are two reactive sites on the maleimide ring—the carboximide function and the double bond. Each exerts an influence upon

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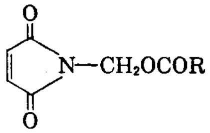
[1] P. O. Tawney, R. H. Snyder, C. E. Bryan, R. P. Conger, F. S. Dovell, R. J. Kelly, and C. H. Stiteler, *J. Org. Chem.*, 25, 56 (1960).

TABLE I

MALEIMIDOMETHYL ESTERS (VI)



Acyl Group	M.P.	B.P.	Yield, %	Method[a]	Nitrogen, % Calcd.	Nitrogen, % Found
Acetyl	91–92°		93	A	8.28	8.12 8.12
Propionyl	43–44°		53	A	7.66	7.60 7.62
n-Butyryl		106–107.5°/ 0.6 mm.	65	A	7.11	6.90 7.06
Crotonyl	60–61°		34	C	7.18	6.93[b]
Benzoyl	120.5–121.0°		66	B	6.06	6.01
Trifluoroacetyl	68.5–69.5°		86	A	6.29	6.27
β-Carboxypropionyl	80.5–82.0°		91	A	6.18	6.31 6.25

[a] A, acid-catalyzed reaction of IV with an acid anhydride; B, reaction of IV with an acylpyridinium halide; C, reaction of IV with mixed anhydride of trifluoroacetic and crotonic acids (see ref. 2). [b] Carbon, calcd.: 55.5; found: 55.0, 55.3; hydrogen, calcd.: 4.61; found: 4.53.

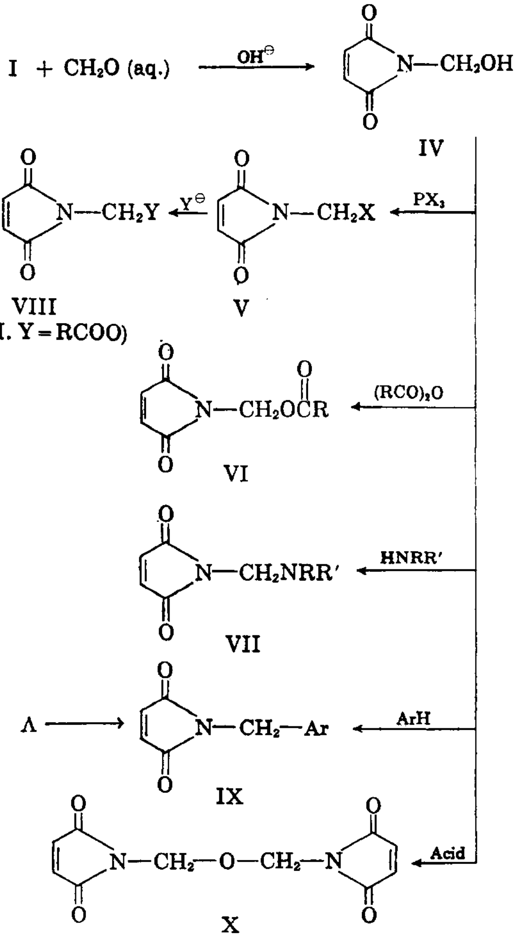
the reactivity of the other, causing I to be somewhat unlike a typical cyclic carboximide or cyclic olefin.

The imide group. Reactions of the carboximide function of I are shown in Chart B. Methylolation of I provided excellent yields of *N*-methylolmaleimide, IV, but the addition of a small amount of base was necessary. Thus, no reaction occurred in a formalin-I solution having a *p*H of about 3, but took place vigorously when the *p*H had been adjusted to about 5 by addition of a small amount of potassium hydroxide solution.

IV was the source of a series of derivatives of maleimide. Esters (Table I) resulted from acid catalyzed reaction with carboxylic acid anhydrides or from reaction with the mixed anhydride of trifluoroacetic acid and a carboxylic acid.[2] An alternate method consisted of reaction of IV with acylpyridinium halides, a variation of the Schotten-Baumann technique which avoided exposure of IV to an alkaline medium in which maleimide polymerizes.

Reaction of IV with phosphorus trichloride produced *N*-chloromethylmaleimide (V. X = Cl) in 80% yield. IV failed to react with concentrated hydrochloric acid, while alcoholic hydrogen chloride merely added hydrogen chloride across the double bond. The halogen of V was apparently no more than moderately reactive, although a complete comparison with other chloromethylimides was impossible due to the sensitivity of the maleimide nucleus to alkaline conditions. In acetone, V reacted with potassium thiocyanate to form maleimidomethyl thiocyanate (VIII. Y = —SCN); in acetic acid solution, V and sodium acetate provided a rather low yield of acetoxymethylmaleimide (VI. R = CH_3). Reaction with acetic acid alone provided the same yield of ester, however, indicat-

CHART B



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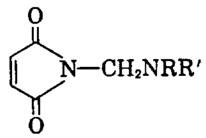
[2] E. J. Bourne, J. E. B. Randle, M. Stacey, J. C. Tatlow, and J. M. Tedder, *J. Am. Chem. Soc.*, 76, 3206 (1954).

TABLE II

ALKYLAMINOMETHYLMALEIMIDES



R	R′	M.P.	B.P.	Yield, %	Method[b]	Nitrogen, % Calcd.	Nitrogen, % Found
C_2H_5—	C_2H_5—		51–55°/0.04 mm.	73	B	15.3	15.2
n-C_4H_9	*n*-C_4H_9		68–69.2°/ 0.02 mm.[a]	74	A	11.7	11.4
				88	B		11.5
—C_5H_{10}—		103–104.5°		40	A	14.4	14.5[e]
				82.5	B		
H	C_6H_5—	127–128.5°		88	C	13.8	13.5[c]
—$C_2H_4OC_2H_4$—		143–145°		62	B	14.3	14.3[d,f]
				65	A		14.3

[a] n_D^{20} 1.4789. [b] A, azeotropic separation of water eliminated from IV and the amine; B, reaction of I with a dialkylaminomethyl ethyl ether; C, reaction of IV with the amine in refluxing dioxane. [c] Mol. wt.: calcd.: 202; found: 192. [d] Mol. wt.: calcd.: 196; found: 188. [e] Carbon, calcd.: 62.0; found: 62.1; hydrogen, calcd.: 7.23; found: 7.04. [f] Carbon, calcd.: 55.2; found, 57.7, 57.8; hydrogen, calcd.: 6.14; found: 6.32, 6.15.

ing that solvolysis may be important in reactions of V in a solvating medium.

Synthesis of a number of other compounds by displacement reactions of V was attempted. Silver nitrite apparently reacted with V but the product was too unstable to isolate. Cyanide ion in water proved too strongly basic, polymerizing the maleimide derivative, while cuprous cyanide would not react under a variety of conditions. In alcoholic hydrogen chloride, V added hydrogen chloride across the double bond, no reaction occurring at the *N*-methylene carbon. Ethoxide ion caused polymerization.

Primary and secondary amines displaced hydroxide from IV, forming the alkylaminomethylmaleimides VII (Table II). The tendency to attack the maleimide ring apparently paralleled the basicity of amines. Thus, aniline reacted solely at the methylene carbon, while piperidine was capable of reacting at both the methylene carbon and the double bond to form *N*-(1-piperidylmethyl)-α-1-piperidyl)succinimide. Piperidine was shown to add to maleimide to form α-(1-piperidyl)succinimide. As it was possible to prepare *N*-(1-piperidylmethyl)maleimide (VII. RR′ = C_5H_{10}) by slow addition of piperidine to a solution of IV with prompt removal of eliminated water from the medium, reaction at the methylene carbon was slightly more facile than reaction at the double bond. The amine derivatives were bright yellow solids or yellow oils, with the exception of the morpholine derivative which was a cream-colored solid. Two items of chemical evidence support the assignment of the maleimide structure to the yellow compounds: (1) they copolymerized with other monomers when initiated by a decomposing free radical source—evidence that the double bond still existed, and (2) the derivatives of secondary amines could be synthesized in high yield by an alternate route[3]—reaction of I with the appropriate dialkylaminomethyl ethyl ether.[4] IV in concentrated sulfuric acid or V (X = Cl), catalyzed by Lewis acids, alkylated benzene, and its derivatives, a reaction displayed by other methylolimides and their derivatives. Another acid-catalyzed reaction of IV was its self-condensation to form bismaleimidomethyl ether (X).

Comparison of the chemistry of I with that of phthalimide is restricted by the sensitivity of the nucleus of the former toward strong bases. A number of reagents, reported in the literature to react smoothly with phthalimide or *N*-methylolphthalimide derivatives, initiate anionic polymerization of maleimide derivatives. Methylolation of phthalimide proceeds rapidly under acid conditions[5] while maleimide reacts slowly or not at all at a pH below 5. Halomethylphthalimides result from reaction of *N*-methylolphthalimide with aqueous hydrohalic[6] acids and solvolyze readily with water or alcohols.[7] *N*-methylolmaleimide does not react with hydrochloric acid to yield *N*-chloromethylmaleimide, nor does the latter form *N*-ethoxymethylmaleimide by reaction with ethyl alcohol. As an explanation, it is suggested that the nitrogen atom of the maleimide nucleus is more electronegative than the nitrogen of phthalimide so that stabilization of a carbonium ion XI is less effective than for XII. This difference should make bond-forming more important in the transition state of displace-

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(3) H. F. Tseou and C. T. Yang, *J. Org. Chem.*, **4**, 123 (1939).

(4) C. M. McLeod and G. M. Robinson, *J. Chem. Soc.*, 119, 1470 (1921).

(5) S. R. Buc, *J. Am. Chem. Soc.*, **69**, 254 (1947).

(6) S. Gabriel, *Ber.*, **41**, 242 (1908).

(7) E. J. Sakellarios, *J. Am. Chem. Soc.*, **70**, 2822 (1948).

TABLE III

POLYMERIZATION[a] OF MALEIMIDE (I)

Comonomer	Monomer Ratio (I:Comonomer) Feed	Monomer Ratio (I:Comonomer) Polymer	Solvent[b]	Initiator[b]	Conversion, %	[η] (Solvent)[b]
Methyl acrylate	1:1	0.7:1	A	C	75	0.15 (A)
Vinyl acetate	1:1	1.3:1	A	C	70	0.09 (A)
Maleic anhydride	1:1	1.5:1	A	C	79	0.12 (B)
Ethyl fumarate	1:1	23.6:1	—	D	35	0.04 (B)
Ethyl maleate	1:1	4.2:1	—	D	5	0.22 (B)

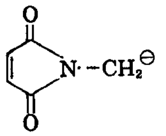
[a] I at 10% concentration in solvent; initiator 2 mole % based on I. [b] A = Dioxane, B = Dimethylformamide, C = Bisazoisobutyronitrile. D = Benzoyl peroxide.

TABLE IV

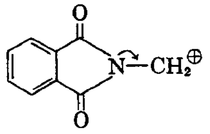
POLYMERIZATION[b] OF MALEIMIDE DERIVATIVES

Maleimide Derivative	Comonomer	Monomer Ratio (Maleimide: Comonomer) Feed	Monomer Ratio (Maleimide: Comonomer) Polymer	Solvent[a]	Initiator[a]	Conversion, %	[η] (Solvent)[a]
IV	Styrene	1:4.9	1:1.4	A	E	47	—
IV	Methyl methacrylate	1:5	1:9	B	E	33	0.7 (C)
IV	Isobutylene	1:9.2	1:1.2	B	E	28	0.52 (A)
IV	Vinyl chloride	1:8	1:6.5	B	E	69	
IV	Isopropylene acetate	1:5	1:1	B	E	19.4	0.33 (C)
IV	Maleic anhydride	1:1.32	3.21:1	B	E	13	0.22 (C)
IV	Ethyl fumarate	1.36:1	5.8:1	B	E	9	0.13 (C)
V, X = Cl	Styrene	1:13	1:2.6	B	E	27	0.60 (C)
V, X = Cl	Acrylonitrile	1:8	1:10	B	D	33	0.43 (C)
VI, R = CH_3	Styrene	1:6.5	1:2.1	B	E	45	0.67 (A)
VI, R = CH_3	Vinyl acetate	1:4.6	1:1.1	B	E	43	0.58 (A)
VI, R = CH_3	Acrylonitrile	1:13	1:19	B	E	62	1.65 (C)
VII, R_1R_2 = C_5H_{10}	Styrene	1:7.5	1:22.2	B	E	1	
VII, R_1 = R_2 = n-C_4H_9	Styrene	1:8.8	1:17	—	D	53	0.20 (C)
VII, R_1 = H, R_2 = C_6H_5	Styrene	1:7.8	1:1.7	B	E	32	
VIII, Y = —SCN	Acrylonitrile	1:12.4	1:10.4	B	E	39	1.67 (C)

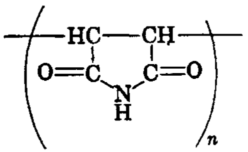
[a] A = Dioxane, B = Acetone, C = Dimethylformamide, D = Azoisobutyronitrile, E = Benzoyl peroxide. [b] Maleimide derivative at 10% concentration in solvent; initiator at 2 mole % based on maleimide derivative.



XI



XII



XIII

ment reactions of methylenemaleimides than of methylenephthalimides. Nucleophilic strength of attacking reagents should thus be more important in reactions with the maleimides than with phthalimides.

The double bond. I and all of the N-substituted maleimides described in this paper were reactive vinyl monomers in free-radical initiated polymerization. The reactivity was displayed in both copolymerization and, unlike maleic anhydride, homopolymerization. In fact, polymerization of I is a very vigorous reaction, yielding a white powder which softens above 400°. It was not possible to demonstrate the presence of aspartic acid among the hydrolysis products of the polymer, indicating that the polymer had a polysuccinimide structure (XIII).

Copolymerization of I and the N-substituted derivatives with various vinyl monomers is presented in Tables III and IV. Only the system I-styrene has been studied sufficiently to allow assignment of monomer reactivity ratios.[8] These ratios have been found to be 0.02 for I and 0.05 for styrene,[9] evidence of a marked tendency to alternate in the copolymer.

Table III presents qualitative data on the reactivity of I with monomers ranging from donor to acceptor types and varying in reactivity. The tendency to alternate is greatest with styrene and least with monomers bearing an electronegative group conjugated with the double bond. The results of

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[8] F. R. Mayo and C. T. Walling, *Chem. Revs.*, 46, 191 (1950).

[9] J. F. Petras, H. C. Tingey, D. E. Cable, unpublished results, these laboratories.

copolymerization of *N*-methylene derivatives of I are presented in Table IV. It may be noted that while IV, V ($X = Cl$), and VI ($R = CH_3$) exhibited a tendency to alternate with styrene, the general activity of the derivatives appears to be less than that of I.

As surprising as the radical-initiated homopolymerization of I was its base-catalyzed polymerization, a reaction which prevented the preparation of many derivatives attainable in the case of other imides. Inoculation of a solution of I with hydroxide or alkoxide ion was followed by an induction period during which the solution gradually developed a red color. Mildly exothermic polymerization then took place. The polymer was red and had a much lower molecular weight than the radical polymer. The color was essentially—but not completely—discharged by stirring in acetic acid, while the radical polymer turned red when suspended in a strongly basic medium. Either polymer in aqueous base slowly dissolved to a colorless solution. Ethyl aconitanilate, which can be considered as a model of an unsaturated group in a polymaleimide molecule similarly is deep red in alkaline medium.[10] As no difference in structure of the two polymers could be demonstrated by examination of hydrolysis products, the anionic polymerization probably proceeds by carbanion attack on olefinic carbon.

Acceptor character. The acceptor[11] character of the maleimide molecule was demonstrated by formation of a yellow 1:1 complex with resorcinol which occurred in an aqueous solution of the components or from a dry melt of the components. The complex had a maximum, congruent melting point at 126–128°. By employing differential spectroscopy, the complex was demonstrated to have a very weak absorption at 329 mμ.

EXPERIMENTAL[12]

Preparation of maleimide. 3,6-*endo*-Methylene-Δ^4-tetrahydrophthalic anhydride (1 kg.) was treated at room temperature with 930 ml. of concd. ammonium hydroxide and 600 ml. of water. After standing several hours in an ice bath, the solid was collected by filtration and the filtrate evaporated to dryness. This residue was combined with the solid from filtration and subjected without further purification to ring closure and pyrolysis.

The apparatus used for pyrolysis consisted of a heated distilling head connected to a 36-inch, 1-inch in diameter Pyrex tube fitted with a concentric thermocouple tube and packed with 4-mesh silica chips. Free volume of this tube was about 230 ml. The tube was heated by a full-length furnace constructed by winding coils of Nichrome wire on a metal pipe. An upper six-inch coil served as a preheater, while the remaining length was covered by the main heater coil. The furnace was lagged with magnesia pipe covering. At the effluent end of the furnace were two 1-l. flasks in series, cooled in ice-water, followed in order by two cold-finger traps cooled in Dry Ice, and a vacuum pump.

One kilogram of the product of reaction of the bicyclic anhydride with ammonium hydroxide was placed in a 2-l. flask and heated by means of a Glas-col mantle until the pot temperature reached 186° and the liquid charge (now the imide) ceased bubbling. The weight of crude imide was 806 g. The flask and mantle were then attached to the cracking apparatus, and the imide was distilled at 3 mm. pressure and 200° pot temperature into the cracking column which had been heated to 405–415°. The rate of distillation into the column averaged 5.56 g. per min.

High boiling products were collected in the ice-cooled receivers, and 243 g. of cyclopentadiene in the Dry Ice traps. The pot residue, presumably polymerized starting material, amounted to 165 g. Maleimide was separated from unchanged starting material by distillation through a 24-inch Vigreux column, yielding 295 g. of product, boiling at 102–105° at 4 mm., and leaving 85 g. of starting material as a higher-boiling residue. The yield of maleimide, based on unrecovered bicyclic imide, was 70%. The crude maleimide melted at 89–91°; one recrystallization from ethyl acetate raised the melting point to 92–93°.[13]

N-Methylolmaleimide. To a suspension of 98 g. (1 mole) of maleimide in 81 ml. of 37% formalin at 30° was added 3 ml. of 5% sodium hydroxide. Within 10 min. all of the maleimide had dissolved and a mildly exothermic reaction had raised the temperature to 35°. Separation of the product began promptly. After 2.5 hr. at room temperature the solution was filtered, yielding 96 g. (75%) of product melting at 99–103°. One recrystallization from ethyl acetate raised the melting point of the material to 104–106°.

Anal. Calcd. for C_5H_5OH: N, 11.05. Found: N, 11.00.

Esterification of IV. *Method A. N-Acetoxymethylmaleimide.* Sulfuric acid (2 drops) was added to a suspension of 10 g. (0.079 mole) of *N*-methylolmaleimide in 9.4 ml. (0.1 mole) of acetic anhydride. When the exothermic reaction had stopped, the solution was cooled and diluted with water, precipitating the ester as a white solid. The yield was 12.3 g. (93%), m.p. 91–92°, unchanged by recrystallization from alcohol.

Anal. Calcd. for $C_7H_2O_4N$: N, 8.28. Found: N, 8.12, 8.12.

Method B. N-Benzoyloxymethylmaleimide. N-Methylolmaleimide (20 g., 0.15 mole) in 30 ml. of hot acetone was added to the suspension formed by mixing 13 ml. of dry pyridine and 19 ml. of benzoyl chloride in 25 ml. of acetone. The temperature rose to 64° and held constant for some time. After cooling, precipitated pyridine hydrochloride was filtered, and the filtrate was diluted with 100 ml. of water. The product (24 g., 66%) separated as a dark oil which solidified quickly. Successive recrystallizations from acetone and aqueous ethanol provided tan crystals melting at 122–123.5°.

Anal. Calcd. for $C_{12}H_9O_4N$: N, 6.06. Found: N, 6.01, 6.02.

Method C. N-Crotonyloxymethylmaleimide. A mixture of 23 g. (0.274 mole) of crotonic acid and 38 ml. (0.274 mole) of trifluoroacetic anhydride was warmed for 10 min. in an oil bath held at 70°. To the resulting solution was added 25 g. (0.2 mole) of *N*-methylolmaleimide. The solid dissolved rapidly as an exothermic reaction set in. After cooling to room temperature, the solution was poured into ice cold bicarbonate solution. The partially solidified ester was taken up in chloroform, dried, and fractionated. There was obtained 13.2 g. (34%) of ester, b.p. 115,117° at less than 0.5 mm., m.p. 60–61°.

Phenylurethane of methylolmaleimide. Phenyl isocyanate (41.7 g., 0.35 mole) was added to a refluxing solution of 50 g. (0.4 mole) of methylolmaleimide in 300 ml. of dry benzene. The solution was refluxed for 1.5 hr. and then left overnight. The benzene was decanted from a precipitated

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[10] C. A. Nau, E. B. Brown, and J. R. Bailey, *J. Am. Chem. Soc.*, **47**, 2599 (1925).

[11] R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

[12] All melting points are uncorrected. Analyses were performed by the Analytical Research Department of the Research Center or by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[13] P. O. Tawney, U. S. Patent **2,524,145**, October 3, 1950.

red oil and on partial evaporation yielded 17.6 g. of the urethane, m.p. 164–167°. Recrystallization from methanol raised the melting point to 167-167.5°. The red oil could not be induced to crystallize and was discarded.

Anal. Calcd. for $C_{12}H_{14}O_4N_2$: C, 58.5; H, 4.07; N, 11.39. Found: C, 58.3; H, 4.32; N, 11.22.

N-Chloromethylmaleimide. Phosphorus trichloride (4.3 g., 0.03 mole) was added to a solution of 10 g. (0.08 mole) of *N*-methylolmaleimide in 50 ml. of acetone in an ice bath. The solution was stirred for a half-hour longer and then concentrated at the aspirator. Water, 50 ml., was added to the partly crystalline residue, precipitating the product. Filtration, followed by thorough washing with ice water, provided 9.2 g. (81%) of white crystals, m.p. 78–79°. Recrystallization from benzene–petroleum ether (b.p. 60–70°) did not change the melting point.

Anal. Calcd. for $C_5H_4O_2NCl$: Cl, 24.4. Found: Cl, 24.44, 24.37.

N-Bromomethylmaleimide, m.p. 82.3–83.3°, was apparently prepared in 52% yield using this technique. However, the compound proved unstable to brief storage and was not analyzed. The preparation was not repeated.

Attempted preparation of N-ethoxymethylmaleimide from IV. Saturated alcoholic hydrogen chloride (30 ml.) and 10 g. of *N*-methylolmaleimide were mixed at room temperature. Solution was complete in 6.25 hr. After standing overnight, the alcohol was evaporated, leaving a solid residue, m.p. 59–70°, insoluble in benzene and petroleum ether and soluble in alcohol and ethyl acetate. Two recrystallizations from ethyl acetate/petroleum ether (b.p. 60–70°) raised the melting point to 75.5–78°. The substance sharply depressed the melting point of *N*-chloromethylmaleimide and gave a positive Beilstein halogen test. Elemental analysis suggested that it was *α*-chloro-*N*-methylolsuccinimide.

Anal. Calcd. for $C_5H_6O_3NCl$: Cl, 21.7. Found: Cl, 21.4.

N-Thiocyanatomethylmaleimide. Potassium thiocyanate (35 g., 0.4 mole) was added to a stirred solution of 50 g. (0.34 mole) of *N*-chloromethylmaleimide in 150 ml. of acetone. A mildly exothermic reaction held the temperature of the resulting suspension to about 40° for over 1 hr. Stirring was continued for an additional hour at room temperature. The solid phase was filtered and extracted twice with hot benzene to yield 19.8 g. of product. The filtrate from the reaction liquors was subjected to two cycles of cooling (ice), filtration, and concentration to yield an additional 21 g. of product. The combined yield of white crystals was 72%, m.p. 106.5–107.5°. Recrystallization from aqueous acetone raised the melting point to 107–108°. The material was insoluble in water and alkanes, soluble in benzene and acetone.

Anal. Calcd. for $C_6H_4O_2N_2S$: N, 16.7; S, 19.0. Found: N, 16.5; S, 19.2.

N-Acetoxymethylmaleimide. 1. A solution of 5 g. (0.034 mole) of *N*-chloromethylmaleimide in 20 ml. of glacial acetic acid was refluxed for 2.75 hr. and then poured into 125 ml. of ice water. The crystals which precipitated melted at 89–91° and did not depress the melting point of ester prepared in esterification method A above. The yield was 2.5 g., 43%.

2. Gentle warming of a mixture of 5 g. (0.034 mole) of *N*-chloromethylmaleimide, 3 g. (0.037 mole) of sodium acetate and 20 ml. of acetic acid caused the solids to dissolve. Precipitation of sodium chloride occurred immediately. The mixture was poured into water and the crystals which precipitated were collected. The yield was about 2 g. The product did not depress the melting point of the ester prepared in method A.

Attempted preparation of N-nitromethylmaleimide. A solution of 14.5 g. (0.1 mole) of *N*-chloromethylmaleimide in 100 ml. of acetonitrile was run into a stirred suspension of 23 g. (0.15 mole) of silver nitrite in 50 ml. of acetonitrile. A mildly exothermic reaction developed, and the reaction temperature was held in the 19–26° range by a cold water bath. Stirring and cooling were continued for 1.5 hr., during which the suspension took on a yellowish color. Evolution of nitrogen oxides could not be detected at this point. The solution was filtered and concentrated at the aspirator leaving a dark residue which decomposed steadily at room temperature with evolution of nitrogen oxides.

Attempted preparation of N-cyanomethylmaleimide. A. *Sodium cyanide.* A warm solution of 10 g. (0.07 mole) of *N*-chloromethylmaleimide in 25 ml. of ethanol was added quickly to 4.3 g. (0.08 mole) of sodium cyanide in 4 ml. of water. An exothermic reaction occurred immediately and deposition of a red, gummy solid resulted. The reaction mass was discarded.

B. *Cuprous cyanide.* A mixture of 1.3 g. (0.01 mole) of *N*-chloromethylmaleimide and 1.9 g. (0.01 mole) of commercial cuprous cyanide was heated on a steam bath for a half hour. Extraction of the reaction mass with hot benzene yielded a solid melting at 77–79°, undepressed on admixture with chloromethylmaleimide.

Similarly, no reaction occurred with freshly prepared cuprous cyanide, even when inoculated by liquors of an allyl bromide–cuprous cyanide reaction.

Ethers. Attempted preparation of N-ethoxymethylmaleimide from V. *N*-Chloromethylmaleimide (10 g., 0.07 mole) and 30 ml. of saturated alcoholic hydrogen chloride were shaken together at room temperature. Solution was complete in 2.25 hr. After standing overnight, the solution was concentrated and diluted with water which precipitated a white solid, m.p. 69–72°. After recrystallization from benzene-ligroin, the product gave a positive Beilstein test. Elemental analysis suggested that this material was *α*-chloro-*N*-chloromethylsuccinimide.

Anal. Calcd. for $C_5H_5O_2NCl_2$: Cl, 39.0. Found: Cl, 38.2.

Preparation of maleimidomethylamines (VII). *Method A. N-Di-n-butylaminomethylmaleimide.* Di-*n*-butylamine (16.8 ml., 0.1 mole) was dripped slowly into a refluxing solution of 12.7 g. (0.1 mole) of *N*-methylolmaleimide in 75 ml. of purified dioxane in a flask equipped with a 20 cm. glass helix-packed column and total-reflux head. Water was removed as its dioxane azeotrope as elimination proceeded, 10 ml. of distillate boiling below 90° being collected. The solution was stripped and distilled. A total of 17.7 g. of yellow oil (74%) was collected in three fractions boiling in the range 66–69.2° at 0.02 mm. The last two fractions had n_D^{20} 1.4789.

This technique provided the corresponding derivatives of aniline, piperidine, and morpholine in 85, 40, and 64% yield, respectively.

Method B. N-(1-Piperidylmethyl)maleimide. Piperidylmethyl ethyl ether[4] (7.2 g., 0.05 mole) was poured over 4.7 g. (0.05 mole) of maleimide, causing a mildly exothermic reaction. The mixture was warmed gently to 80° and allowed to cool. Filtration yielded 8 g. (82.5%) of yellow needles, m.p. 103–104.5°.

This technique provided the corresponding derivatives of di-*n*-butylamine and diethylamine in 88 and 73% yield respectively.

Method C. N-Phenylaminomethylmaleimide. A solution of aniline (7.3 g., 0.08 mole) and *N*-methylolmaleimide (10.0 g., 0.08 mole) in 25 ml. of dry, peroxide-free dioxane was refluxed for 3.75 hr. Cooling and concentrating gave 14 g. (88%) of a yellow solid, m.p. 121–125°. Recrystallization from aqueous acetone gave bright yellow needles, m.p. 127.5–128.5°.

Anal. Calcd. for $C_{11}H_{10}O_2N_2$: N, 13.8; mol. wt., 202. Found: N, 13.5; mol. wt., 192.

N-(1-Piperidylmethyl)-α-(1-piperidyl)succinimide. Piperidene (7.9 ml., 0.08 mole) was poured over 10 g. (0.08 mole) of *N*-methylolmaleimide, causing a vigorous exothermic reaction. The red oil was cooled and diluted with 10 ml. of ethanol and 20 ml. of water, causing deposition of 5.5 g. of white needles. After recrystallization from aqueous ethanol and then from petroleum ether (b.p. 60–70°), the product melted at 123–124°.

Anal. Calcd. for $C_{15}H_{25}O_2N_3$: C, 64.5; H, 8.96; N, 15.1;

neut. equiv. 140. Found: C, 64.7; H, 8.74; N, 15.2, 15.4; neut. equiv. 146, 151.

N-Benzylmaleimide. A solution of 29 g. (0.2 mole) of *N*-chloromethylmaleimide in 90 ml. of dry benzene containing 0.5 g. of zinc chloride was refluxed for 18 hr. The reaction was allowed to cool to room temperature and filtered to remove a small amount of high-melting solid. The filtrate was chilled in ice, depositing 31 g. (83%) of white crystalline solid melting at 65–70° with a slight amount of solid residue. Five grams, recrystallized from a mixture of 15 ml. of benzene and 10 ml. of petroleum ether (b.p. 60–70°) melted at 68–69° (lit. m.p. 67.5°[14]).

Anal. Calcd. for $C_{11}H_9O_2N$: C, 70.6; H, 4.81; N, 7.49. Found: C, 70.4, 70.2; H, 5.10, 5.02; N, 7.49, 7.47.

N-(3-Nitro-4-methylbenzyl)maleimide. *N*-Methylolmaleimide (12.7 g., 0.1 mole) was added to a stirred, ice cold solution of 11.8 ml. (0.1 mole) of *o*-nitrotoluene in 36 ml. of concd. sulfuric acid. Stirring was continued for an hour at ice temperature. The solution was then allowed to warm to room temperature and let stand. The reaction was poured into 400 g. of ice and water where a semisolid mass separated and slowly solidified. This solid was recrystallized from 150 ml. of alcohol yielding 3.1 g. (12%) of material melting at 161–163°. After two successive recrystallizations from benzene, the product melted at 164–165°.

Anal. Calcd. for $C_{12}H_{10}O_4N_2$: C, 58.5; H, 4.06; N, 11.4. Found: C, 58.7, 58.8; H, 4.06, 4.35; N, 11.03.

2,4-Bis(maleimidomethyl)phenol. A solution of 19 g. (0.2 mole) of phenol in 100 ml. of benzene was poured quickly into a stirred solution of 29 g. (0.2 mole) of *N*-chloromethylmaleimide in 100 ml. of benzene. One gram of zinc chloride was added, and the solution was heated to reflux. Hydrogen chloride evolution was initially very brisk and had practically stopped after 1.5 hr. Little change occurred in the original yellow color of the solution during this period, but solid lumps of catalyst became very dark and some brown resin formed. The solution was decanted from the resin and catalyst and concentrated to a greenish syrup. The syrup crystallized when triturated with 20 ml. of ethanol to yield 12.5 g. of crude product. Recrystallization from alcohol yielded pale yellow crystals melting, and apparently polymerizing to a clear gel, at 180.5–182°. The product did not form a colored complex with ferric chloride but was easily soluble in dilute sodium hydroxide.

Anal. Calcd. for $C_{11}H_9O_3N$: C, 65.0; H, 4.43; N, 6.90; for $C_{16}H_{12}O_5N_2$: C, 61.5; H, 3.85; N, 8.97. Found: C, 61.6, 61.3; H, 4.02, 4.10; N, 8.61, 8.49.

Bismaleimidomethyl ether. A solution of 50 g. (0.395 mole) of *N*-methylolmaleimide and 1 g. of *p*-toluenesulfonic acid in 150 ml. of toluene was refluxed for 7 hr. in an apparatus which included a Deane-Stark trap for collecting eliminated water. Only 2.9 ml. of water (theory called for 3.6 ml.) was collected. The hot solution was filtered and allowed to cool overnight. Filtration yielded 35.6 g. of product, m.p. 92–117°. One recrystallization from 500 ml. of ethanol gave 19 g. of material melting at 128–132°, 41% yield. A small sample was recrystallized again for analysis; m.p. 130–131°.

Anal. Calcd. for $C_{10}H_8N_2O_5$: C, 50.9; H, 3.41; N, 11.9; O, 33.9; mol. wt. 236. Found: C, 51.2; H, 3.61; N, 11.6; O, 34.1; mol. wt. 248.

α-(N-Piperidyl)succinimide. Piperidine (8.2 ml., 0.084 mole) was poured into a suspension of 9.7 g. (0.1 mole) of maleimide in 25 ml. of cool water. The temperature of the mixture rose quickly to 50°, and a dark pink color developed. Crystallization occurred on standing overnight at room temperature. Filtration yielded 10.5 g. (68%) of white crystals melting at 141.5–142.5°. The product was soluble in water as well as in aromatic and polar organic solvents. Recrystallization from petroleum ether did not change the melting point.

Anal. Calcd. for $C_9H_{10}O_2N_2$: N, 15.39. Found: N, 15.24, 15.32.

Polymaleimide. (A) *Free radical initiated.* Maleimide (10 g.) and 0.3 g. of benzoyl peroxide were dissolved in 190 g. of chlorobenzene and heated for 2 hr. at 80–90° and then cooled. Petroleum ether (b.p. 60–70°) (800 ml.) was added, and the white polymer (10 g.) was filtered. The material did not soften below 400° and had a dilute solution viscosity of 0.21 in dimethylformamide. It was soluble in dimethylformamide and dimethyl sulfoxide and insoluble in all other pure solvents; however, it was soluble in 3–50% aqueous acetone, aqueous methyl ethyl ketone, and aqueous dioxane and in methanolic acetone or methyl acetate. When suspended in a strongly alkaline non-aqueous medium, the polymer turned deep red, the color being discharged by acidification. In aqueous alkali, the polymer slowly hydrolyzed and dissolved to a colorless solution. A sample was prepared for analysis by 24-hr. extraction with hot acetone.

Anal.[15] Calcd. for $C_4H_3O_2N$: C, 49.5; H, 3.11; N, 14.4. Found: C, 46.7, 46.8; H, 4.56, 4.52; N, 11.5.

(B) *Base-initiated.* Ten grams of maleimide was dissolved in 15 g. of dimethylformamide, and the solution was cooled to 5° by means of an ice bath. Five milliliters of a 10% solution of sodium ethoxide in absolute ethanol was added. A pink color began to develop shortly after addition of the base so that, after 15 min., the solution was deep red. The viscosity of the solution had increased markedly at this point. After 26 hr., the solution was run into 500 ml. of methanol, precipitating 10 g. of a deep red polymer. The color could be nearly discharged by stirring the polymer in glacial acetic acid. The physical properties of this polymer were like those of the radical-initiated polymer, except that the molecular weight was lower—dilute solution viscosity in dimethylformamide, 0.08. A sample was prepared for analysis by 24-hr. extraction with hot acetone.

Anal. Calcd. for $C_4H_3O_2N$: C, 49.5; H, 3.11; N, 14.4. Found: C, 46.3, 45.6; H, 3.92, 3.76; N, 12.27.

Copolymerization of maleimide derivatives. Copolymerization of maleimide and its *N*-substituted derivatives was run in solution in organic solvents, initiated by conventional free radical sources. Details are set forth in Tables III and IV.

Maleimide-resorcinol complex. A solution of 25 g. (0.227 mole) of resorcinol and 15 g. (0.15 mole) of maleimide in 100 ml. of warm water deposited, on cooling, 26 g. of a yellow crystalline product, m.p. 126–128°. Recrystallization from water caused no change in the melting point.

Anal. Calcd. for $C_{10}H_8O_4N$: C, 58.2; H, 3.91; N, 6.79 Found: C, 57.5; H, 4.30; N, 6.66.

The ultraviolet absorption spectrum of the complex was obtained by differential spectroscopy using a Beckman DK-2 spectrophotometer. Solutions of maleimide (5.02 g./l.) and resorcinol (8.02 g./l.) in water were placed in separate 1-cm. cells in the blank beam of the instrument and a solution of maleimide (2.51 g./l.) and resorcinol (4.01 g./l.) in water in a single 2-cm. cell in the sample beam. The spectrum had an absorption maximum at 329 mμ having an optical density of 0.64.

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(15) Close check with the theoretical composition has proved impossible to obtain for polymaleimide due to lack of a means for completely decomposing the polymer.