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Carbamylmaleimides from the Malonamide–Diethyl Oxalate Reaction

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The product formed from malonamide and ethyl oxalate is a salt (I) of 2-hydroxy-3-carbamylmaleimide (IV). An isomeric salt II and a hydrated acid III also have been isolated. Phosphorus oxychloride converts the maleimide IV, the hydrated acid III, or either of the two salts (I, II) to the 2-chloro-3-cyanomaleimide (V). The chlorine in this structure is readily replaceable with amines to give 2-imino derivatives (VI, VIII) and with alcohols to give 2-alkoxy (VII) derivatives. Hydrolysis of the 2-anilino-3-cyanomaleimide forms the hydroxy amide X also obtained from the acid III and aniline. Comparison of the ultraviolet and infrared spectroscopy data for these compounds with data for related compounds confirms the assigned structures. The maleimide structure is confirmed by absorption bands at 1775 cm.$^{-1}$ (carbonyl), 1711 cm.$^{-1}$ (carbonyl), 1640 cm.$^{-1}$ (C=C or ring), and 1350 cm.$^{-1}$ (C–N stretching). The characteristic absorption at 1640 cm.$^{-1}$ even in alkoxy (VII) and piperidino (VIII) types excludes the tautomeric exocyclic C=N structure. The reaction has been extended to the preparation of the known 2-hydroxy-3-phenylmaleimide from phenylmalonamide and ethyl oxalate.

The sodium alkoxide catalyzed reaction of ethyl oxalate with malonamide and its derivatives offers a possible source of either 2-carboxypyrimidines or substituted maleimides. The former reaction represents an adaptation of the ester–malonamide synthesis which is known[1] to give the 2-substituted pyrimidines. The latter reaction has been observed with ethyl oxalate and various amides.[2a,b,c] A study of this reaction in our laboratories has shown that the maleimide is the product formed in the diethyl oxalate–malonamide reaction and we wish to present the data upon which this conclusion is based.

The condensation of ethyl oxalate with malonamide takes place readily using sodium methoxide in absolute methanol with the precipitation of a yellow solid. This solid is slightly soluble in cold water but can be recrystallized from its solution in hot water to give a micro-crystalline, yellow salt designated "salt B." If the solid from the reaction mixture is refluxed with less than sufficient water for complete dissolution, the solid is converted to a mass of yellow needles designated as "salt A." Recrystallization of salt A from water solutions gives salt B. The two salts are isomeric having the structure $C_5H_3O_4N_2Na$. Both give red ferric chloride enol tests and are neutral to litmus. The salt B shows infrared absorption maxima typical of other maleimides for which data are available (see Table I). This absorption data and the chemical evidence to be presented are considered to be sufficient basis for assignment of the maleimide structure I to salt B. The salt A shows in its infrared absorption characteristics somewhat less over-all resemblance to the usual maleimide absorption with strong bands at 1745, 1669, 1538 and 1050 cm.$^{-1}$ and a weak band at 1361 cm.$^{-1}$. The sodium atom probably is oriented in a different manner with respect to the surrounding atoms in the two crystalline forms of the salt. In the absence of X-ray diffraction data the exact position of the atoms cannot be assigned.

The salt A shows in its infrared absorption characteristics somewhat less over-all resemblance to the usual maleimide absorption with strong bands at 1745, 1669, 1538 and 1050 cm.$^{-1}$ and a weak band at 1361 cm.$^{-1}$.

TABLE I

INFRARED SPECTRA OF SUBSTITUTED MALEIMIDES

Substituents 2	3	Absorption bands[a] A	B	C	D
H[b]	H	1802sh	1686	1630m	1340m
OCH_3	CN	1792m	1736s	1639s	1368s
OC_2H_5	CN	1789s	1709vs	1637vs	1344s
[c]	CN	1751m	1695s	1610s	1344s
C_6H_5NH	CN	1776s	1704vs	1631vs	1359s
p-ClC_6H_4NH	CN	1773s	1721s	1650vs	1348s
m-ClC_6H_4-NH	CN	1779m	1704s	1639s	1353s
2,6-$(CH_3)_2$-C_6H_3NH	CN	1773m	1709s	1642s	1351s
Cl	CN	1799*sh*	1721s	1629*m*	1355m
C_6H_5NH	C_6H_5	1764m	1686s	1631s	1364s
OH	C_6H_5	1764m	1698s	1667*m*	1383*s*
CH_3CO_2	C_6H_5	1789s	1727vs	1647*w*	1355s
C_6H_5NH	$CONH_2$	1748*sh*	1721s	1650s	1351s
m-ClC_6H_5-NH	$CONH_2$	1761*sh*	1715s	1661s	1342s
OH	$CONH_2$	1764*sh*	1715s	1634vs	1346*m*
ONa (A)	$CONH_2$	1745*s*	1669*s*	1621s	1361*w*
ONa (B)	$CONH_2$	1776m	1718s	1629s	1346m
Average		1775	1711	1639	1354

[a] In the region A, 1751–1792 cm.$^{-1}$; B, 1686–1736 cm.$^{-1}$; C, 1610–1661 cm.$^{-1}$; D, 1337–1379 cm.$^{-1}$. Additional strong bands occur in most or all of these compounds in the 730–780, 1040–1080, 1450–1550, 3200 regions and for the nitriles at 2270 cm.$^{-1}$; vs. very strong; s, strong; m, medium; w, weak; sh, shoulder; uncertain if italicized. [b] Stadtler spectra No. 2447. [c] Piperidino.

Treatment of either of the salts A or B or the crude reaction mixture with refluxing aqueous hydrochloric acid results in the formation of a solid which separates from the reaction mixture on cooling. This compound is acidic with a pK_a of 2.1 and a neutral equivalent of 193. It gives an intense red ferric chloride enol test and has the empirical composition $C_5H_8N_2O_6$. On vacuum drying at 110° it loses two molecules of water and gives another acidic compound of equivalent acid strength, a neutral equivalent of 158.9, and an empirical formula of $C_5H_4N_2O_4$. Recrystallization from water reconverts this acid to the acid of neutral equivalent 193. Neither acid melts before decomposition at elevated temperatures. These two acids have been assigned structures of the maleimide IV and its hydrate VI. The ultraviolet spectra of the two are identical in alcohol (λ_{max} 234

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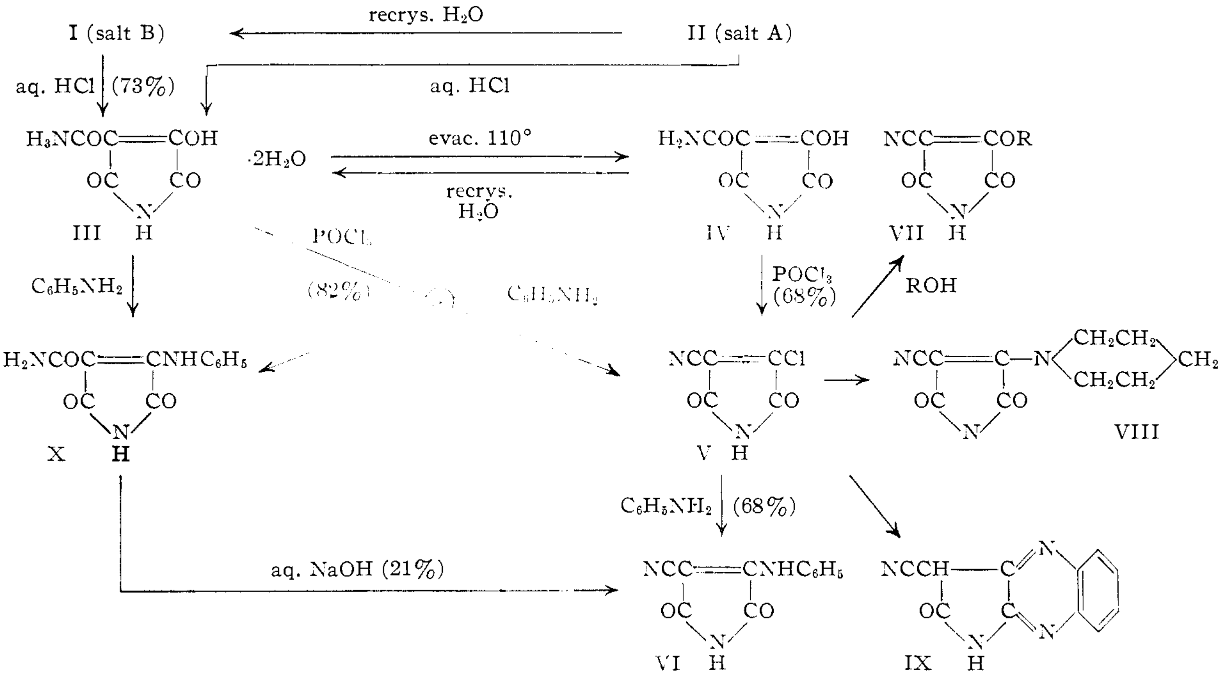
[1] D. J. Brown, *J. Chem. Soc.*, 2312 (1956).

[2] (a) G. S. Skinner and C. B. Miller, THIS JOURNAL, **75**, 977, 6359 (1953); (b) G. S. Skinner and R. E. Ludwig, *ibid.*, **78**, 4656 (1956); (c) W. Wislicenus and W. Sattler, *Ber.*, **24**, 1246 (1891).

mμ, log ε 4.16; 341 mμ, log ε 3.41). The carboxamidomaleimide structure is confirmed by the infrared absorption characteristics. A maleimide pattern (Table I) is observed with carbonyl absorption at 1754 (weak shoulder) and 1706 cm.$^{-1}$, a very strong band at 1631 cm.$^{-1}$ (amide or carbon–carbon double bond), and at 1404 cm.$^{-1}$ (C–N stretching, shifted somewhat). The maleimide structure IV is further confirmed by conversion of the acid to 2-anilino-3-carboxamidomaleimide (X) on reaction with aniline. This imide X has also been obtained by partial hydrolysis of the corresponding nitrile which provides further confirmation for its structure. The infrared spectrum of the hydrate shows a general resemblance to that of the unhydrated acid with somewhat less detail. Both show the same pattern in the 680–800 cm.$^{-1}$ region and are alike in other regions except for a band at 935 cm.$^{-1}$ for the hydrate and a band at 1235 cm.$^{-1}$ for acid neither of which appears in the other.



Both of the sodium salts (I or II) and both of the acids (III or IV) are converted to 2-chloro-3-cyanomaleimide (V) by reaction with phosphorus oxychloride. Yields of 68–82% are obtained. In addition to bands at 1799 (shoulder) and 1721 (carbonyl absorption), 1629 (amide or carbon–carbon double bond) and 1355 cm.$^{-1}$ (C–N stretching) characteristic of the maleimide structure there is a band at 2273 cm.$^{-1}$ confirming the presence of the carbon–nitrogen triple bond linkage. Although it reacts vigorously with water and ammonia, no products were isolated from these reactions. The reaction of aromatic amines, piperidine and aliphatic alcohols gives derivatives (VI, VII, VIII) in which the halogen is replaced. *o*-Phenylenediamine reacts to give a product corresponding in analysis to the quinoxaline derivative IX. Incomplete hydrolysis of the anilino types gives carboxamido derivatives X as previously mentioned, but only oxalic acid, aniline and ammonia were detected after more complete hydrolysis. The infrared absorption characteristics of these alkoxy and substituted amino derivatives also show the characteristic maleimide absorption. The data are summarized in Table I. The strong adsorption in the 1640 cm.$^{-1}$ region previously has been tentatively assigned[2c] to the exocycle C=N in 2-anilino-3-phenylmaleimide and 2-amino-3-phenylmaleimide. Our observation that the absorption band in this region also occurs in 2-alkoxy and 2-piperidino derivatives where no such exocyclic C=N can exist makes it necessary to reassign this band to some other absorption such as the ring carbon–carbon double bond absorption which is found in all of the structures. The adsorption bands at 1775 (carbonyl), 1711 (carbonyl) and at 1350 cm.$^{-1}$ (C–N stretching) are characteristic of this class of compounds.

The infrared data are summarized in Table I for all of the compounds to which we have assigned maleimide structures. In addition to the tabulated data there are several bands which are in accord with other recognized structural features such as those in the 3200 (O–H, N–H region) and the 2270 cm.$^{-1}$ (C≡N region). There are also unassigned strong absorption bands which occur with some regularity at 730–780, 1040–1080 and 1450–1550 cm.$^{-1}$. The characteristic features of the maleimide structure occur in the carbonyl region. Three bands appear with reasonable uniformity at 1775, 1711 and 1639 cm.$^{-1}$. These bands can be assigned to two carbonyl stretching frequencies and a carbon–carbon double bond stretching or ring vibration, respectively. The enolic hydroxyl and imino hydrogen adsorption maxima cannot be distinguished with certainty using the potassium bromide pellet technique. The compounds are insoluble in chlorinated solvents. The 1711 cm.$^{-1}$ band is shifted to as high as 1736 cm.$^{-1}$ and the 1640 cm.$^{-1}$ band almost always appears in the maleimides. Absorption in these two regions does not, by itself, provide conclusive elimination of the alternative oxazolidinedione structure.[3]

The possibility that these compounds exist in an isomeric oxazolidinedione structure is eliminated by their preparation with base rather than acid catalysis, their chemical properties and their infrared absorption characteristics. The oxazolidinediones apparently are formed only from oxalyl chloride and amides and not from base-catalyzed condensations.[2c] The oxazolidinediones are easily cleaved by alkali and are non-enolic. The absorption in the carbonyl region of the infrared occurs at 1780, 1750 and 1660 cm.$^{-1}$ for the oxazolidinediones,[3] whereas in the maleimides the absorption in this region usually is characterized by three bands at 1775, 1711 and 1639 cm.$^{-1}$.

The ultraviolet absorption data for several compounds obtained during this study are summarized in Table II. It has been reported previously that N-isobutylmaleimide[4] and 2-methyl-3-ethylmaleimide[5] absorb at 295 mμ (log ϵ 2.84) and 294 mμ (log ϵ 2.64) with a hypsochromic shift in non-polar solvents and an indication of a second maximum present below 220 mμ. The latter band has been moved into the ultraviolet in the substituted maleimides we have obtained. The band is fairly constant as to location and intensity. The weaker band in the 300–400 mμ region is subject to substitution effects. The greatest shift toward longer wave length as shown by the 3-phenyl derivatives and the greatest increase in intensity is shown by the 2-anilino derivatives; the 2-methoxy-3-cyano derivative shows the least effect. 2-Hydroxy-3-carbamylmaleimide shows the solvent shift absorbing at 350 mμ in water and 341 mμ in methanol.

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA OF SUBSTITUTED MALEIMIDES

Substituents 2	Substituents 3	Solvent[a]	Maxima[b]	
OCH_3	CN	M	235(4.03)	304(3.11)
OH	$CONH_2$	W	235(4.36)	350(3.45)
OH	$CONH_2$[c]			
OH	$CONH_2$	M	234(4.16)	341(3.41)
OH	C_6H_5	M	233(4.14)	400(3.44)
NHC_6H_5	C_6H_5	M	244(4.25)	397(3.76)
NHC_6H_5	CN	M	237(4.19)	368(3.76)

[a] W, water; M, methanol. [b] Stated as λ_{max} with log ϵ in parentheses. [c] Hydrated form.

Phenylmalonamide also reacts readily with ethyl oxalate using sodium methoxide in methanol as a solvent. The product formed in this reaction is 2-hydroxy-3-phenylmaleimide and is identical with the product previously obtained from phenylacetamide and diethyl oxalate.[2a] The cyclization to the imide takes place with the elimination of one of the carboxamido groups. Conversion to previously described 2-acetoxy and 2-anilino derivatives has been carried out. The 2-hydroxy-3-phenylmaleimides and their derivatives have infrared and ultraviolet absorption characteristics similar to those of the 3-cyano and 3-carboxamido analogs. The data are included in Tables I and II.

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Experimental[6]

Reaction of Malonamide with Diethyl Oxalate.—A suspension of 20.4 g. (0.20 mole) of finely divided malonamide in a solution of 7.9 g. (0.34 mole) of sodium in 400 ml. of dry methanol was stirred vigorously while 35.0 g. (0.24 mole) of diethyl oxalate was added. The mixture was stirred for two hours at room temperature to complete the formation of a bright yellow crystalline mass. These crystals were collected, washed with methanol, and dried to give 39.0 g. of crude reaction mixture containing unreacted malonamide and sodium salts.

Sodium Salt A (II).—Ten grams of the yellow salt mixture was refluxed with 80 ml. of distilled water for 30 minutes. The solid was converted to a mass of fine needles during this time. These were filtered from the hot solution and dried to give 5.6 g. of salt A. The recrystallization was repeated using 40 ml. of water. The salt is neutral to litmus and gives a red ferric chloride test.

Anal. Calcd. for $C_5H_3O_4N_2Na$: N, 15.73; Na, 12.92. Found: N, 15.55; Na, 12.83.

Sodium Salt B (I).—The filtrates from the recrystallization of salt A deposited 2.4 g. of light yellow needles on cooling. It is differentiated from salt A on the basis of its infrared spectrum. If the original reaction product is dissolved in hot water, salt B separates on cooling. Also if salt A is dissolved in hot water, salt B separates on cooling. The salt is neutral and gives a red ferric chloride test.

Anal. Calcd. for $C_5H_3O_4N_2Na$: N, 15.73; Na, 12.92. Found: N, 15.90; Na, 12.74.

2-Hydroxy-3-carbamylmaleimide Dihydrate (III).—This hydrated acid can be prepared by acidification of an aqueous suspension of either salt A or B or the crude reaction mixture. A suspension of 39 g. of the crude reaction mixture in 400 ml. of water was heated to boiling and acidified with 35 ml. of concd. hydrochloric acid. The solid dissolved and on cooling 28.0 g. (73% based on the malonamide used) of the acid separated as pale yellow needles. The acid after recrystallization from water lost water on heating and decomposed at 230° with the evolution of carbon dioxide. The half-neutralization point gave a pK_a value of 2.1. The acid gives a strong red ferric chloride test and is slightly soluble in cold water and in methanol.

Anal. Calcd. for $C_5H_4N_2O_4 \cdot 2H_2O$: C, 31.25; H, 4.20; N, 14.58; neut. equiv., 192.1. Found: C, 31.26; H, 4.28; N, 14.50; neut. equiv., 193.2.

Saturated (cold) aqueous solutions of acidic 2,4-dinitrophenylhydrazone and of the hydrate acid were mixed and allowed to stand. The precipitated solid was collected, washed with water, and vacuum dried at 80°, m.p. 233–234°. The analysis indicates loss of 2 moles of water in addition to that lost in hydrazone formation.

Anal. Calcd. for $C_{11}H_8N_6O_7$: N, 25.00. Found: N, 24.60.

2-Hydroxy-3-carbamylmaleimide (IV).—A weighed quantity (0.2751 g.) of 2-hydroxy-3-carbamylmaleimide dihydrate (III) was dried for 1.5 hours to constant weight at 100° under 2 mm. vacuum. The yield of product was 0.2239 g., corresponding to a loss of 1.985 moles of water per mole of compound. The product gives a red ferric chloride test and the half-neutralization point gives a pK_a of 2.4. Recrystallization from water converts this product to the dihydrate III. If heated rapidly, the compound melts and decomposes at about 230°.

Anal. Calcd. for $C_5H_4N_2O_4$: C, 38.47; H, 2.58; N, 17.95; neut. equiv., 156.1. Found: C, 38.43; H, 2.67; N, 17.97; neut. equiv., 158.9.

2-Chloro-3-cyanomaleimide.—One gram (0.0052 mole) of

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(3) J. C. Sheehan and E. J. Corey, THIS JOURNAL, **74**, 360 (1952).

(4) W. R. Roderick, *ibid.*, **79**, 1710 (1957).

(5) H. M. Muir and A. Neuberger, *Biochem. J.* (*London*), **45**, 163 (1949).

(6) Analyses by Micro Tech Laboratories, Skokie, Ill.

2-hydroxy-3-carbamylmaleimide dihydrate (III) was refluxed in 10 ml. of phosphorus oxychloride for 30 minutes. The residue obtained on removing the excess phosphorous oxychloride under vacuum was extracted three times with 30-ml. portions of boiling benzene. The extracts were concentrated to 40 ml. and chilled to precipitate 0.66 g. (82.5%) of crude product. Recrystallization from benzene gave white needles, m.p. 187–189°, which decompose slowly in moist air or quickly in warm water. The same product is obtained in 68% yield from salt B (I), in 59% yield from salt A (II) and in similar yield from 2-hydroxy-3-carbamylmaleimide (IV).

Anal. Calcd. for $C_5HN_2O_2Cl$: C, 38.37; H, 0.64; N, 17.91. Found: C, 38.40; H, 0.79; N, 17.60.

2-Anilino-3-cyanomaleimide (VI).—Five grams (0.031 mole) of 2-chloro-3-cyanomaleimide was dissolved in a solution of 6 g. (0.077 mole) of aniline in 20 ml. of cold methanol. The reaction mixture is refluxed for five minutes and diluted with 50 ml. of water. On cooling, 4.6 g. (68%) of the product separated in mica-like crystals, m.p. 228–230°. Recrystallization from methanol gave plates, m.p. 228–229°.

Anal. Calcd. for $C_{11}H_7N_3O_2$: N, 19.71. Found: N, 19.74.

2-(*m*-Chloroanilino)-3-cyanomaleimide was prepared in 77% yield by the procedure given for the anilino analog. Recrystallization from methanol gave yellow needles, m.p. 209–210°.

Anal. Calcd. for $C_{11}H_6N_3O_2Cl$: N, 16.97. Found: N, 16.88.

2-(*p*-Chloroanilino)-3-cyanomaleimide was prepared in 63% yield by the procedure given for the anilino analog. Recrystallization from methanol–water gave yellow needles, m.p. 259–260°.

Anal. Calcd. for $C_{11}H_6N_3O_2Cl$: N, 16.97. Found: N, 17.00.

2-(2′,6′-Dimethylanilino)-3-cyanomaleimide was prepared in 40% yield by the procedure given for the anilino analog. The crude material was contaminated with a dark red, unidentified impurity which precipitated from the reaction mixture on adding water. Evaporation of the solution decanted from this impurity gave a solid which was recrystallized from methanol–water to give yellow needles, m.p. 250–251°.

Anal. Calcd. for $C_{13}H_{11}N_3O_2$: N, 17.42. Found: N, 17.63.

2,3-Dihydro-2-keto(1H)pyrrolo[2,3-b]quinoxaline-3-carbonitrile (IX) was prepared from *o*-phenylenediamine in 78% yield by the procedure given for the aniline reaction. Recrystallization from methanol–dimethylformamide gave yellow crystals, m.p. over 360°. The compound is insoluble in ordinary solvents, slightly soluble in boiling pyridine, and very soluble in dimethylformamide or dilute sodium hydroxide.

Anal. Calcd. for $C_{11}H_6N_4O$: N, 26.65. Found: N, 26.35.

2-Piperidino-3-cyanomaleimide (VIII) was prepared in 63% yield from piperidine and 2-chloro-3-cyanomaleimide using dioxane as a solvent. The precipitated crude solid was recrystallized from methanol–water to give yellow needles, m.p. 209–210°.

Anal. Calcd. for $C_{11}H_{10}N_3O_2$: N, 20.48. Found: N, 20.30.

2-Methoxy-3-cyanomaleimide (VII, R = CH_3).—One gram (0.0064 mole) of 2-chloro-3-cyanomaleimide was refluxed for five minutes with 5 ml. of absolute methanol. Evaporation to dryness left a solid mass which on recrystallization from ethyl acetate–petroleum ether gave 0.69 g. (71%) of the product as white crystals, m.p. 190–191°.

Anal. Calcd. for $C_6H_4N_2O_3$: N, 18.42. Found: N, 18.14.

2-Ethoxy-3-cyanomaleimide (VII, R = C_2H_5) was prepared in 57% yield by the procedure given for the methoxy analog. Recrystallization from ethyl acetate–petroleum ether gave the pure product, m.p. 136–137.5°.

Anal. Calcd. for $C_7H_6N_2O_3$: N, 16.86. Found: N, 17.11.

2-Anilino-3-carbamylmaleimide (X). (a) **From 2-Anilino-3-cyanomaleimide.**—One gram (0.04 mole) of 2-anilino-3-cyanomaleimide was refluxed with 20 ml. of 2 *N* potassium hydroxide for 15 minutes. Acidification of the cooled mixture gave the crude product. Recrystallization from dioxane gave 0.23 g. (21%) of the product, which decomposes without melting at 300°. If this hydrolysis is prolonged, aniline, identified as its tribromo derivative, is found in the distillate and oxalic acid dihydrate (m.p. 98–100°) is formed on acidification of the reaction mixture.

Anal. Calcd. for $C_{11}H_9N_3O_3$: C, 57.14; H, 3.92; N, 18.18. Found: C, 57.07; H, 3.93; N, 18.25.

(b) **From the Hydrate Acid.**—A mixture of 2.7 g. (0.014 mole) of the acid and 50 ml. of aniline was refluxed in a flask with a water separator until solution resulted. This required about one hour. On cooling, 2.2 g. of crude product precipitated. This was triturated with cold 2 *N* potassium hydroxide, filtered, and the filtrate acidified to give 0.8 g. (24.8%) of the product having an infrared spectrum identical with that of 2-anilino-3-carbamylmaleimide prepared as described in the preceding paragraph. The base-insoluble fraction was identified as oxanilide, m.p. 150–151°, by comparison of its infrared spectrum and melting point with those of an authentic specimen.

2-(*m*-Chloroanilino)-3-carbamylmaleimide was prepared in 27% yield from the corresponding cyano derivative on refluxing with 2 *N* potassium hydroxide following the procedure given above. Recrystallization of the crude product from dioxane–water gave yellow needles, m.p. 273–275°.

Anal. Calcd. for $C_{11}H_8N_3O_3Cl$: N, 15.82. Found: N, 15.65.

2-Hydroxy-3-phenylmaleimide from Phenylmalonamide.—A mixture prepared by adding 10.2 g. (0.07 mole) of diethyl oxalate to a solution of 12 g. (0.067 mole) of phenylmalonamide and 4.4 g. (0.15 mole) of sodium in 100 ml. of dry methanol was stirred for two hours at room temperature. The soids were separated by filtration. The filtrate was concentrated on a steam-bath and acidified to deposit 7.2 g. (57%) of the product as yellow needles, m.p. 217.5–219°, reported[2a] m.p. 216–218°. The product has a neutral equivalent of 187.6 (calcd. 189.2) and a pK_a (from the half-neutralization point) of 3.4. Basic hydrolysis gives phenylacetamide, m.p. 157°, and phenylacetic acid.

2-Acetoxy-3-phenylmaleimide was prepared in 90% yield from the hydroxy derivative and acetyl chloride as previously described,[7] m.p. 133–135° (methanol), reported 134–135°.

2-Anilino-3-phenylmaleimide was prepared in 80% yield by refluxing the hydroxy derivative with aniline. The recrystallized product melted at 179–180°, reported[2a] m.p. 179–180°.

Infrared spectra were obtained using a Baird double beam recording infrared spectrometer with sodium chloride optics. The materials were examined as potassium bromide pellets using the technique previously described.[8]

Ultraviolet spectra were obtained using distilled water or spectral grade solvents with a Beckman DU spectrophotometer and 1-cm. quartz cells.

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[7] J. Volhard and F. Henke, *Ann.*, **282**, 78 (1894).

[8] D. H. Anderson and N. B. Woodall, *Anal. Chem.*, **25**, 1906 (1953).