ice-bath and 78.1 g. (0.494 mole) of diethyl malonate was added dropwise. The addition required one hour. After the addition was completed, the ice-bath was removed and the mixture was stirred at 25–35° until no more heat was evolved. The reaction mixture was hydrolyzed by pouring it onto crushed ice, and the lower layer was dried and distilled; yield of diethyl nitromalonate,[9] 45.5 g. (61.1%), b.p. 97–103° (1 mm.), n^{21}D 1.4273.

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(9) David I. Weishlat and Douglas A. Lyttle (to Upjohn Co.), U. S. Patent 2,644,838, July 7, 1953.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE R. B. WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

Maleic Hydrazide. I. Reactions with Selected Electrophilic Reagents[1]

BY HENRY FEUER AND HARRY RUBINSTEIN[2]

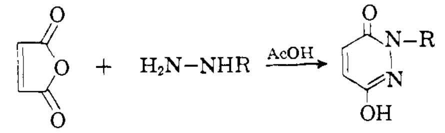
RECEIVED APRIL 14, 1958

It has been established that the reaction of maleic hydrazide with benzenesulfonyl chloride or with acetic anhydride leads to O-substituted maleic hydrazides, 3-(1H-6-pyridazinonyl) benzenesulfonate (I) and 3-(1H-6-pyridazinonyl) acetate (II). Treatment of 1-benzenesulfonyl-2-(3-carboxyacryloyl)-hydrazine (III) and 1-acetyl-2-(3-carboxyacryloyl)-hydrazine (IV), respectively, with glacial acetic acid gives the N-substituted compounds, 2-benzenesulfonyl-6-hydroxy-3(2H)-pyridazinone (V) and 2-acetyl-6-hydroxy-3(2H)-pyridazinone (VI) which are distinctly different from I and II with regard to infrared spectra and acidity characteristics. The five-membered ring isomer of V, N-benzenesulfonylaminomaleimide (VIIa) is obtained by refluxing III with thionyl chloride; VIIa is converted in basic or acidic medium as well as in dry xylene to the six-membered compound V, and the latter, on further treatment with base, undergoes ring opening and is reconverted to III.

The alkylation reactions of maleic hydrazide have received much attention, and the structures of the alkylated products are well established for the N- and O-methylated compounds.[3,4] This, however, is not so for the acylated derivatives of maleic hydrazide.

A patent for the acylation of maleic hydrazide[5] states that it is not known whether these acylated derivatives are N- or O-substituted. Stefanye and Howard[6] have reported the benzoylation of maleic hydrazide with benzoyl chloride and claimed that this reaction gave the O-derivative. Their proof that O-substitution had occurred was based on the ease of formation and hydrolysis of the product. O-Derivatives of phthalyl hydrazide have been reported to hydrolyze very readily.[7]

Maleic hydrazide was found to react with benzenesulfonyl chloride[8] and with acetic anhydride[5,8] to give products which could be either the N- or O-substituted derivatives. In order to establish the course of substitution that had taken place in these and in similar reactions, an unambiguous synthesis of N- or O-substituted derivatives was undertaken. Two possible reaction schemes were considered. The first was the reaction of 6-chloro-3-pyridazinone with silver or sodium acetate to form the O-derivative; the second was the preparation of the N-substituted hydrazides, benzenesulfonyl hydrazide (VIIIa) and acetyl hydrazide (VIIIb) followed by their reactions with maleic anhydride to give the N-substituted maleic hydrazides, 2-benzenesulfonyl-6-hydroxy-3(2H)-pyridazinone (V) and 2-acetyl-6-hydroxy-3(2H)-pyridazinone (VI).

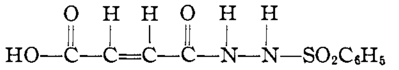


VIIIa, R = $SO_2C_6H_5$ V, R = $SO_2C_6H_5$

b, R = $COCH_3$ VI, R = $COCH_3$

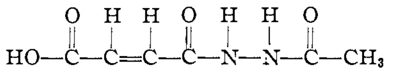
When the first scheme was attempted, no reaction took place; the failure can be ascribed to the inertness of the halogen in 6-chloro-3-pyridazinone. A somewhat similar observation has been made by Druey[4] in the case of 3,6-dichloropyridazine.

The second reaction scheme then was attempted by treating VIIIa and VIIIb with maleic anhydride in glacial acetic acid. This reaction when carried out at room temperature gave materials which were identified by their elemental analyses, acidity characteristics and infrared data, as 1-benzenesulfonyl-2-(3-carboxyacryloyl)-hydrazine (III) and 1-acetyl-2-(3-carboxyacryloyl)-hydrazine (IV), respectively. On titration with base, these compounds behaved like dibasic acids, III exhibiting pK_a values of 3.5 and 8.1 and IV of about 3.15 and 10.8.[9] Examination of the infrared spectra disclosed absorption maxima for the carbonyl group at 5.92μ for III and at 5.94μ for IV. These maxima indicate the presence of a conjugated carboxylic acid.[10]



$$HO-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-\overset{H}{\overset{|}{N}}-SO_2C_6H_5$$

III



$$HO-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-CH_3$$

IV

By refluxing compounds III and IV in glacial acetic acid, products were obtained the elemental analyses of which were compatible with V and VI. Compound V also formed when III was heated in

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(1) (a) From the Ph.D. thesis of Harry Rubinstein, Purdue University, 1958; (b) presented before the Division of Organic Chemistry at the San Francisco Meeting of the American Chemical Society, April, 1958.

(2) Purdue Research Foundation Fellow 1956–1957.

(3) K. Eichenberger, A. Staehelin and J. Druey, *Helv. Chim. Acta*, **37**, 837 (1954).

(4) J. Druey, Kd. Meier and K. Eichenberger, *ibid.*, **37**, 121 (1954).

(5) J. W. Zukel and W. D. Harris, U. S. Patent 2,614,917 (Oct. 21, 1952); *C. A.*, **47**, 1889h (1953).

(6) D. Stefanye and W. L. Howard, *J. Org. Chem.*, **19**, 115 (1954).

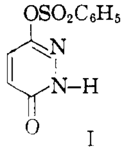
(7) F. M. Rowe and A. T. Peters, *J. Chem. Soc.*, 1331 (1933).

(8) H. Rubinstein, Master's Thesis, Purdue University, February, 1956.

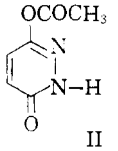
(9) We are very grateful to Dr. H. Boaz of Eli Lilly and Co. for carrying out this titration.

(10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 140.

xylene at 120°. Compounds V and VI differed in their melting points and infrared spectra from the reaction product of maleic hydrazide with benzenesulfonyl chloride and acetic anhydride, respectively, indicating that the latter reaction probably led to the O-substituted compounds

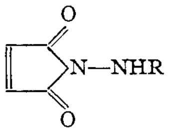


I



II

I and II. The possibility, however, that the substituted N-aminomaleimides, N-benzenesulfonylaminomaleimide (VIIa) and N-acetylaminomaleimide (VIIb), had formed from III and IV had to be considered,



VIIa, R = $SO_2C_6H_5$
VIIb, R = $COCH_3$

When compound III was refluxed with thionyl chloride rather than acetic acid, a new compound was obtained, the molecular formula of which was the same as that of compounds I and V. However, its infrared spectrum and melting point were distinctly different from these two compounds and it was postulated that this new compound corresponded to structure VIIa.

The problem resolved itself then into establishing the structure of each of the three isomers I, V and VIIa.

Assignment of Structure Based on Infrared Data.—The infrared carbonyl asborption maxima (see Table I) of I, V and VIIa were examined and revealed bands at 6.03, 5.80 and 5.58μ, respectively. Since it is well established that five-membered ring carbonyl compounds absorb at shorter wave lengths than six-membered ring carbonyls,[11,12] the assignment of the five-membered ring structure was given to compound VIIa (C=O group at 5.58μ), which resulted from the reaction of thionyl chloride and III.

TABLE I

CARBONYL STRETCHING VIBRATIONS OF CYCLIC HYDRAZIDE AND RELATED COMPOUNDS[a]

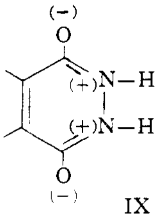
Compound	Cm.$^{-1}$
3,6-Pyridazinedione	1656[b]
Perhydro-3,6-pyridazinedione (XIV)	1664
3-(1H-6-Pyridazinonyl) acetate (I)	1658
2-Benzenesulfonyl-6-hydroxy-3(2H)-pyridazinone (V)	1724
N-Benzenesulfonylaminomaleimide (VIIa)	1792
Bis-maleimide (XI)	1789
Perhydro-1,4,6,9-tetraketopyridazo[1,2-a]-pyridazine (XIII)	1718[a]
1-Benzenesulfonyl-2-(3-carboxyacryloyl)-hydrazine (III)	1684
1-Acetyl-2-(3-carboxyacryloyl)-hydrazine (IV)	1689

[a] All spectra were obtained in a Nujol mull. [b] Denotes a broad peak.

It has been established that, although the carbonyl stretching vibration in amides is shifted to longer wave lengths than in ketones, sulfonamides do not cause such shifts.[13] This being the case, and assuming that both V and I exist as the monoenol, the carbonyl stretching vibration of V would be expected at a shorter wave length than that of I. The compound having the carbonyl absorption maximum at 5.80μ therefore was assigned structure V which is in agreement with its mode of preparation. The remaining material had to be I which shows very little difference in its carbonyl absorption maximum from that of maleic hydrazide.

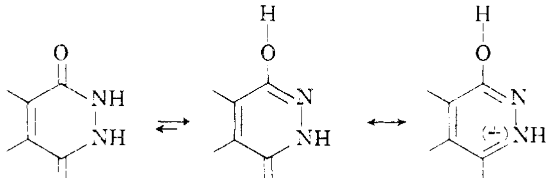
Assignment of Structure Based on Acidities and Reactions with Base and Acid.—Maleic hydrazide is a fairly strong acid having a pK_a value of about 5.5[8] (5.65).[14] This would not normally be expected from a cyclic lactam structure. This strong pK_a value and the fact that it does not appear to have an olefinic double bond has been interpreted to mean that maleic hydrazide and certain of its derivatives have aromatic character.[3,8,15]

Hunter has postulated[16] that a proton transfer between N- and O- does not actually occur in amides, lactams and related compounds; instead a phenomenon termed "mesohydric tautomerism," is thought to occur which involves only the electron pair of the nitrogen. Arndt and co-workers[15] have pointed out that this type of "tautomerization" is not possible in maleic hydrazide since it would involve a structure IX with two adjacent



IX

positive charges. Because of this, the aromatization of maleic hydrazide has been depicted as[8,17]



This sequence can account for the lability of one proton and hence the acidity of maleic hydrazide.

If the foregoing assumptions are correct both the N- and O-derivatives of maleic hydrazide should show a tendency to aromatize as the formulas show. It is apparent that the N-derivatives of maleic hydrazide require a tautomeric change in order to become aromatic without violating the adjacent charge rule. The O-derivatives, however, can aro-

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[11] Reference 10, p. 114.

[12] R. N. Jones and C. Sandorfy, Weissberger "Technique of Organic Chemistry," Vol. 9, Interscience Publishers, Inc., New York, N. Y., 1956, p. 458.

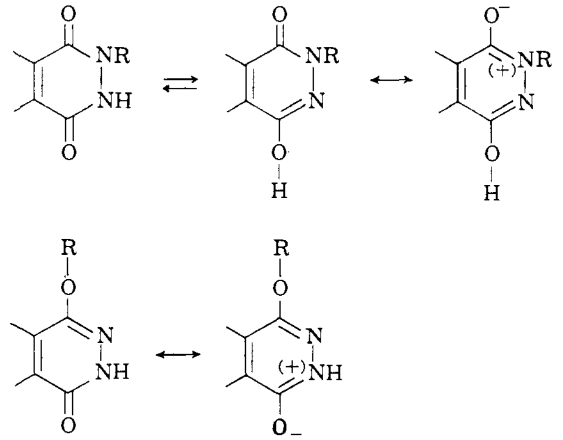
[13] Reference 10, p. 299.

[14] D. M. Miller and R. W. White, *Can. J. Chem.*, **34**, 1510 (1956).

[15] F. Arndt, L. Loewe and L. Ergener, *Rev. Faculté Sci. Univ. Istanbul*, **13a**, 103 (1948).

[16] L. Hunter, *J. Chem. Soc.*, 806 (1945).

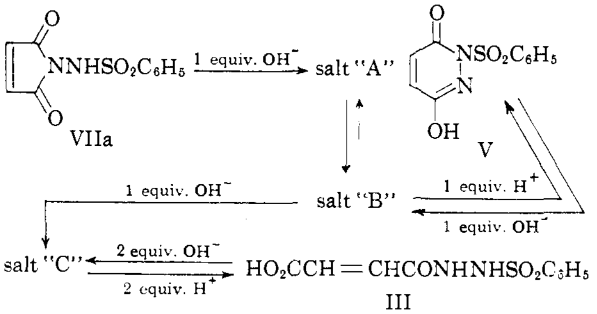
[17] H. Hellman and I. Löschmann, *Chem. Ber.*, **89**, 594 (1956).



matize without the transfer or loss of a proton. This implies that the O-derivatives of maleic hydrazide would be neutral or of the same order of acidity as lactams whereas the N-derivatives would be expected to be fairly strong acids.

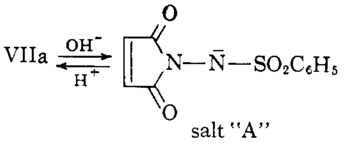
These expectations were borne out by titration of the various maleic hydrazide derivatives. Compounds V and VI were found to be acidic having pK_a values from 7 to 7.5. The O-derivatives I and II proved to be neutral or very weakly acid and were hydrolyzed upon heating with base.

A careful study of the reactions of compounds III, V and VIIa, with base disclosed the transformations

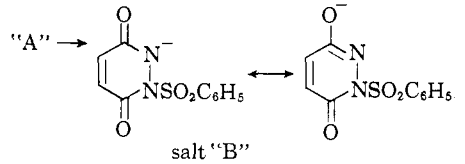


The products were identified after reacidification, on the basis of infrared analyses and mixed melting point determinations. Salt "A" gave mostly V, salt "B" gave only V and salt "C" gave only III on reacidification.

The following equations may illustrate the mechanism of the transformation of VIIa to V and of V to III.

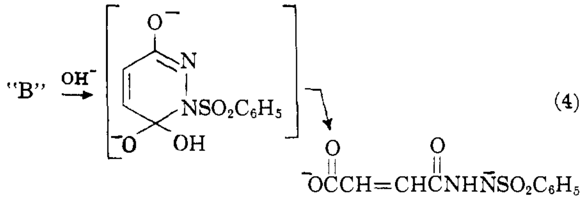

(1)

salt "A"


(2)

salt "B"

$$\text{"B"} \underset{OH^-}{\overset{H^+}{\rightleftarrows}} \text{V} \qquad (3)$$


(4)

salt "C"

$$\text{"C"} \underset{OH^-}{\overset{H^+}{\rightleftarrows}} \text{III} \qquad (5)$$

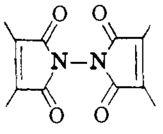
Steps 1, 2 and 3 take place when VIIa is treated with one equivalent of base, followed by reacidification. Step 2 involves an equilibrium between the salt of a five- and a six-membered ring, which as expected is shifted in favor of the resonance-stabilized six-membered ring. The ring-opening reaction probably occurs by an attack of the second equivalent of base (step 4) on the carbonyl carbon.

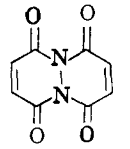
Supporting evidence for the proposition that the six-membered ring hydrazide V is more stable than the five-membered ring maleimide VIIa was found by the transformation of VIIa to V in refluxing acetic acid or in *dry xylene* at 120°.

On the basis of their infrared spectra, acidity characteristics and reactions with base and acid, the structures of 3-(1H-6-pyridazinonyl) benzenesulfonate (I), 3-(1H-6-pyridazinonyl) acetate (II), 2-benzenesulfonyl-6-hydroxy-3(2H)-pyridazinone (V), 2-acetyl-6-hydroxy-3(2H)-pyridazinone (VI) and N-benzenesulfonylaminomaleimide (VIIa) are thus well established.

The reaction of III with thionyl chloride to give a five-membered ring seemed to be quite interesting and novel. It was, therefore, studied with related structures. Several reactions were carried out with 1-acetyl-2-(3-carboxyacryloyl)-hydrazine (IV), but all attempts gave only gummy materials which could not be purified.

When 1,2-bis-(3-carboxyacryloyl)-hydrazine (X), $(HO_2CCH{=}CHCONH)_2$, was treated with thionyl chloride, a halogen-free, neutral compound was obtained, the elemental analysis of which corresponded to bis-dimaleimide (XI) or bicyclic dimaleichydrazide (XII).


XI


XII

The infrared spectrum of this compound showed a maximum for the carbonyl stretching vibration at 5.59μ, which is in close agreement with the five-membered ring structure VIIa. A compound of structure XII would be expected to exhibit the carbonyl absorption maximum at a longer wave length, since it has been found that its saturated analog, bicyclic disuccinhydrazide[18] (XIII), absorbs at 5.82μ, and since it is well established that α,β-unsaturation shifts the carbonyl absorption to longer wave lengths. In agreement with this, it

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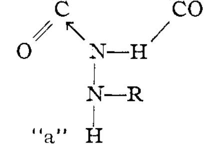
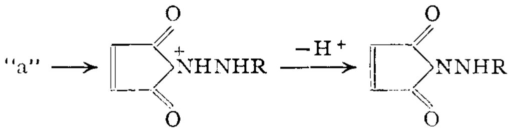
(18) H. Feuer, G. B. Bachman and E. H. White, THIS JOURNAL, 73, 4716 (1951).

was found that maleic hydrazide absorbs at a longer wave length than cyclic succinhydrazide (XIV)[18] (see Table I). Thus from consideration of the infrared data structure XII can be eliminated as a possibility and structure XI is assigned to the reaction product which resulted from the treatment of X with thionyl chloride.

A temperature effect does not seem to be responsible for the exclusive formation of the five-membered cyclic hydrazides from the substituted maleic acid hydrazines on refluxing with thionyl chloride. For, III was recovered unchanged when heated in dry xylene at the same temperature (75°). A mechanism as pictured below might be considered in the formation of maleimides. It involves an intramolecular attack of the hydrazine nitrogen on the acid chloride (or its precursor). This step is essentially irreversible and once the less stable five-membered maleimide is formed, it cannot revert to the resonance-stabilized six-membered maleic hydrazide.



(I)



(II)

The formation of the six-membered maleic hydrazides from the substituted maleic acid hydrazines might involve a simple dehydration reaction. However, the possibility that a five-membered ring compound is an intermediate cannot be ruled out completely since it can undergo a thermal transformation to a six-membered maleic hydrazide in glacial acetic acid or dry xylene at 120°.

Experimental

3-(1H-6-Pyridazinonyl) Benzenesulfonate (I).[8]—Five grams of maleic hydrazide and 30 ml. of benzenesulfonyl chloride were heated gently on a hot-plate until a slightly yellow solution formed. An equal volume of water was added with stirring and the mixture placed on ice overnight and filtered. This gave 5.5 g. of slightly yellow material, which was **3-(1H-6-pyridazonyl) benzenesulfonate monohydrate**, m.p. 134–135°.

Anal. Calcd. for $C_{10}H_8O_4N_2S.H_2O$: C, 44.50; H, 3.75; N, 10.65. Found: C, 44.79; H, 4.07; N, 10.89.

The monohydrate was dried for five days over phosphorus pentoxide and refluxing toluene to give **3-(1H-6-pyridazonyl) benzenesulfonate**, m.p. 144°.

Anal. Calcd. for $C_{10}H_8O_4N_2S$: C, 47.6; H, 3.10; N, 11.10. Found: C, 47.87; H, 3.56; N, 11.37.

3-(1H-6-Pyridazinonyl) Acetate (II).[5,8]—Two grams of maleic hydrazide was refluxed with 50 ml. of acetic anhydride for four hours. The resulting solution was evaporated to dryness on a steam-bath. The product was recrystallized by dissolving it in absolute ethanol and reprecipitating it by the addition of hexane. This gave 2.04 g. (74% yield) of II, m.p. 122–123°.

Anal. Calcd. for $C_6H_6O_3N_2$: C, 46.75; H, 3.89; N, 18.18. Found: C, 46.93; H, 3.90; N, 18.29.

1-Acetyl-2-(3-carboxyacryloyl)-hydrazine (IV).—A three-necked 300-ml. flask was fitted with a stirrer, condenser and a solid addition device consisting of a wide rubber tube, a pinch clamp and an erlenmeyer flask. Into this flask was placed 9.8 g. of maleic anhydride dissolved in 150 ml. of glacial acetic acid. Then 7.4 g. of acetyl hydrazide[19] was dropped in with stirring. The total addition took 10 minutes and when all the acetyl hydrazide had been added the solution had almost turned solid. The solid was filtered and dried to a constant weight of 17 g. (98% yield). This material gave a positive ferric chloride test and had a melting point of 170–171° dec. Recrystallization twice from ethanol gave IV, m.p. 172° dec.

Anal. Calcd. for $C_6H_8N_2O_4$: C, 41.8; H, 4.65; N, 16.28; neut. equiv., 172. Found: C, 41.92; H, 4.42; N, 16.47; neut. equiv., 176.

1-Benzenesulfonyl-2-(3-carboxyacryloyl)-hydrazine (III).—Twenty grams of benzenesulfonyl hydrazide[20] slowly was added to 11.4 g. of maleic anhydride dissolved in 200 ml. of acetic acid. After stirring the solution for 10 minutes, it was filtered giving 30 g. (95% yield) of white III. It was recrystallized from water or from ethanol and had a m.p. 157–158° dec. from both solvents.

Anal. Calcd. for $C_{10}H_{10}O_5N_2S$: C, 44.50; H, 3.70; N, 10.38; neut. equiv., 135, 270. Found: C, 44.39; H, 3.78; N, 10.47; neut. equiv., 132, 280.

2-Benzenesulfonyl-6-hydroxy-3(2H)-**pyridazinone** (V). (a) **With Benzenesulfonyl Hydrazide.**—In a three-necked 300-ml. flask was placed 8.5 g. of maleic anhydride (0.087 mole) dissolved in 150 ml. of acetic acid. Fifteen grams (0.088 mole) of benzenesulfonyl hydrazide was added over a 30-minute interval with stirring and gentle refluxing. The reaction mixture was refluxed for an additional two hours. Upon cooling compound V was obtained, which after drying weighed 19 g. (86% yield), m.p. 195–210° dec. Recrystallization from isopropyl alcohol raised the m.p. to 212° dec.

Anal. Calcd. for $C_{10}H_8N_2SO_4$: C, 47.6; H, 3.18; N, 11.11; neut. equiv., 252. Found: C, 47.42; H, 3.21; N, 11.05; neut. equiv., 252.

(b) **With 1-Benzenesulfonyl-2-(3-carboxyacryloyl)-hydrazine** (III).[21] Five grams of III was heated with stirring in 45 ml. of dry xylene at 120° for 24 hours. Cooling and filtration gave 3.6 g. of a yellowish material and evaporation of the filtrate gave an additional 0.7 g. Their infrared spectra were identical with that of V, and a mixed melting point determination after recrystallization from isopropyl alcohol, with an authentic sample of V, showed no depression.

2-Acetyl-6-hydroxy-3(2H)-**pyridazinone** (VI).—Five grams of 1-acetyl-2-(3-carboxyacryloyl)-hydrazine was refluxed in glacial acetic acid for two hours. Most of the acetic acid was then removed *in vacuo* and the remaining slurry was placed on ice and filtered while frozen giving 3.7 g. (82% yield) of VI, m.p. 160–162° dec. after recrystallization from benzene or chloroform.

Anal. Calcd. for $C_6H_6N_2O_3$: C, 46.70; H, 3.89; N, 18.2; neut. equiv., 154. Found: C, 46.88; H, 4.08; N, 18.07; neut. equiv., 159.

N-Benzenesulfonylaminomaleimide (VIIa).—Forty ml. of thionyl chloride and 3.88 g. of 1-benzenesulfonyl-2-(3-carboxyacryloyl)-hydrazine were refluxed for three hours in a 100-ml. flask. Upon cooling, 2.43 g. of material was obtained. Evaporation of the thionyl chloride gave an additional 1.18 g. of VIIa (98% total yield), m.p. 157–159° after recrystallization twice from chloroform using Norite.

Anal. Calcd. for $C_{10}H_8N_2O_4S$: C, 47.61; H, 3.17; N, 11.11; neut. equiv., 252. Found: C, 47.42; H, 3.47; N, 11.40; neut. equiv., 252.

Conversion of N-Benzenesulfonylaminomaleimide (VIIa) **to 2-Benzenesulfonyl-6-hydroxy-3**(2H)-**pyridazinone** (V). (a) **With Base.**—N-Benzenesulfonylaminomaleimide (1.37 g., 5.5 mmoles) was suspended in 20 ml. of water and 0.22 g. (5.5 mmoles) of sodium hydroxide in 20 ml. of water was added. The mixture was stirred until a clear slightly greenish solution resulted. This was treated slowly with 10% hydrochloric acid until it had a *p*H of about six. The solution was frozen and filtered giving 0.2 g. of 2-benzenesul-

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(19) Th. Curtius and T. S. Hoffman, *J. prakt. Chem.*, [2] **53**, 513 (1896).

(20) Th. Curtius and F. Lorenzen, *ibid.*, [2] **58**, 166 (1898).

(21) We are indebted to John Asunskis, Purdue University, for carrying out this experiment.

fonyl-6-hydroxy-3(2H)pyridazinone (V) as shown by its infrared spectrum and melting point. The filtrate was then partially frozen and treated again with 10% hydrochloric acid until it had a *p*H of about two. The mixture was filtered giving 0.51 g. of a yellowish material, m.p. 120–130° dec. The filtrate was next treated with about 2 ml. of concentrated hydrochloric acid and frozen overnight giving 0.4 g. of a white product m.p. 150–160° dec. The infrared spectrum of this material indicated that it was a mixture of V and 1-benzenesulfonyl-2-(3-carboxyacryloyl)-hydrazine (III). On recrystallization from isopropyl alcohol, III, which was less soluble, was separated from V and the identity of these materials again was established by infrared analysis.

The above yellow material was recrystallized from isopropyl alcohol and gave a small amount of a yellow polymer after standing on ice for several hours. Upon concentrating the alcohol solution a solid was obtained which was identified as V by its infrared spectrum and melting point.

(b) **With Anhydrous Acetic Acid.**—Four grams of VIIa was heated at 120° in anhydrous acetic acid for 25 hours. Several successive freezings of the solution gave 1.45 g., and evaporation to dryness gave an additional 0.5 g. of material. It was identified as V by infrared analysis and by mixed melting point determinations with an authentic sample of V which gave no depressions.

(c) **With Dry Xylene.**[21]—Four grams of VIIa was heated in 45 ml. of dry xylene at 120° for 25 hours. Cooling gave 2.0 g. of brownish material (m.p. 180–190° dec.) and evaporation of the filtrate gave an additional 0.3 g. These materials were identified as V, as described in (b).

Reaction of 2-Benzenesulfonyl-6-hydroxy-3(2H)-pyridazinone (V) with Base.—(a) **Using One Equivalent of Base.**—Two grams (0.079 mole) of V was treated with 0.32 g. of sodium hydroxide (0.08 mole) in a 125-ml. erlenmeyer flask containing 30 ml. of water. The mixture was heated for one hour on a water-bath and then neutralized with concd. hydrochloric acid and frozen. This gave 0.83 g. of material m.p. 189–191° dec. Part of this material was recrystallized from water and gave a m.p. of 206° dec. A mixed melting point determination with an authentic sample of V which had been recrystallized from water, m.p. 206° dec., showed no depression. By evaporation of the rest of the reaction mixture to dryness a small amount of oil was obtained which when treated with isopropyl alcohol gave sodium chloride and more of the starting material.

(b) **Using Two Equivalents of Base.**—In this experiment 2.53 g. (0.1 mole) of V was placed into a 100-ml. beaker and 0.85 g. of sodium hydroxide (0.21 mole) in 30 ml. of water was added. The material dissolved giving a wine colored (red) solution. This was stirred and acidified slowly with 15% hydrochloric acid until it was strongly acidic. Upon standing for one hour, 1.6 g. of a granular precipitate, m.p. 155–160° dec., separated from the solution. By refreezing and acidifying, an additional 0.73 g. of the above material was obtained. This material was identified as 1-benzenesulfonyl-2-(3-carboxyacryloyl)-hydrazine (III) by a mixed melting point determination and infrared analysis.

1,2-Bis-(3-carboxyacryloyl)-hydrazine (X).—A solution of 5.95 g. (0.1 mole) of 85% hydrazine hydrate in 25 ml. of glacial acetic acid was prepared by adding slowly with stirring the cooled acid to the hydrazine which was surrounded by ice. The resulting solution then was added with stirring over a 10-minute interval to a solution of 20 g. (0.2 mole) of maleic anhydride in 100 ml. of glacial acetic acid keeping the temperature below 30°. The resulting mixture then was allowed to stand at about 30° for three hours and filtered. The product, which was obtained in 96% yields, was recrystallized twice from ethanol giving yellow crystals which melted at 185–187° dec. (lit.[22] val. 185–187°).

Bis-maleimide (XI).—Two grams of 1,2-bis-(3-carboxyacryloyl)-hydrazine was heated for 7 hours with 30 ml. of freshly distilled thionyl chloride (b.p. 75.5–76°; Coleman, Mathieson and Bell), in a 50-ml. flask equipped with a condenser and drying tube. The solution was then cooled in Dry Ice, filtered through a sintered glass filter and the resulting precipitate was dried *in vacuo*. This procedure gave 1.47 g. (87% yield) of which after recrystallization from purified dioxane gave yellow green crystals, m.p. 259–260° dec.

Anal. Calcd. for $C_8H_4N_2O_4$: C, 50.00; H, 2.04; N, 14.58. Found: C, 49.70; H, 2.40; N, 14.61.

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[22] H. Feuer, E. H. White and J. E. Wyman, This Journal, **80**, 3790 (1958).

LAFAYETTE, IND.

[CONTRIBUTION FROM THE R. B. WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

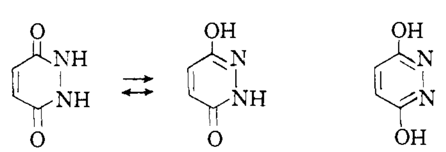
The Chemistry of Maleic Hydrazide. II.[1] The Course of the Michael-type Addition[2]

BY HENRY FEUER AND RONALD HARMETZ

RECEIVED APRIL 14, 1958

Maleic hydrazide adds readily in the presence of base to compounds with activated double bonds, such as methyl vinyl ketone, acrylonitrile, methyl acrylate and dimethyl itaconate, to give high yields of monoaddition products. A structure determination is presented which proves that these reactions lead to N-substituted maleic hydrazides.

Maleic hydrazide (I) has been reported[3-6] to exist in one or more of the following tautomeric forms and to undergo a number of reactions with substitution on oxygen or nitrogen. Thus methylation of I with diazomethane gave a mixture of 6-methoxy-3(2H)-pyridazinone and 2-methyl-6-methoxy-3(2H)-pyridazinone,[3] and Hellmann[7] reported that compound I underwent Mannich-type reactions to yield N-substituted products. Also it has been established[1] recently that acylation reactions lead exclusively to esters of I.



I

When compound I was treated with methyl vinyl ketone, methyl acrylate, acrylonitrile and dimethyl itaconate in the presence of catalytic amounts of base, the monoaddition products 2-(3′-oxobutyl)-6-hydroxy-3(2H)-pyridazinone (II), 2-(2′-carbomethoxyethyl)-6-hydroxy-3(2H)-pyridazinone (III), 2-(2′-cyanoethyl)-6-hydroxy-

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[1] Paper I, This Journal, **80**, 5873 (1958).

[2] (a) From the Ph.D. thesis of Ronald Harmetz; (b) presented before the Division of Organic Chemistry at the New York City Meeting of the American Chemical Society, September, 1957.

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[4] J. Druey, K. D. Meier and K. Eichenberger, *Helv. Chim. Acta*, **37**, 121 (1954).

[5] R. H. Mizzoni and P. E. Spoerri, This Journal, **73**, 1873 (1951).

[6] D. M. Miller and R. W. White, *Can. J. Chem.*, **34**, 1510 (1956).

[7] H. Hellmann and I. Löschmann, *Angew. Chem.*, **67**, 110 (1955); *Chem. Ber.*, **89**, 594 (1956).