Anal. Calcd for $C_{29}H_{20}N_5O_5$: C, 66.02; H, 5.54; N, 13.28. Found: C, 65.80: H, 5.53; N, 13.19.

Registry No.—**5**, 31446-92-1; **5** free base, 31446-93-2; **7** (R = Ph), 29985-00-0; **7** (R = Me), 31489-84-6; **8**, 31446-95-4; **8** perchlorate, 31446-96-5; **8** picrate, 31446-97-6; **9**, 31446-98-7; **9** picrate, 31446-99-8; **9** (5-acetyl), 31382-26-0; **10**, 31382-27-1; **13**, 19611-52-0; **14**, 31382-29-3.

Reactions of 3-Carboxyacryloylhydrazines and the Formation of Maleimides, Isomaleimides, and Pyridazinones

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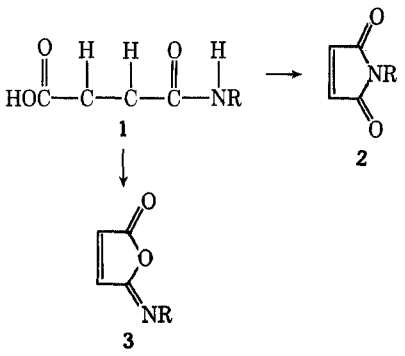
Some of the previous structure assignments for the reaction products arising from ring closure reactions of 3-carboxyacryloylhydrazines are in error. Criteria are presented for distinguishing between 3-carboxyacryloylhydrazines, isomaleimides, maleimides, and pyridazinones.

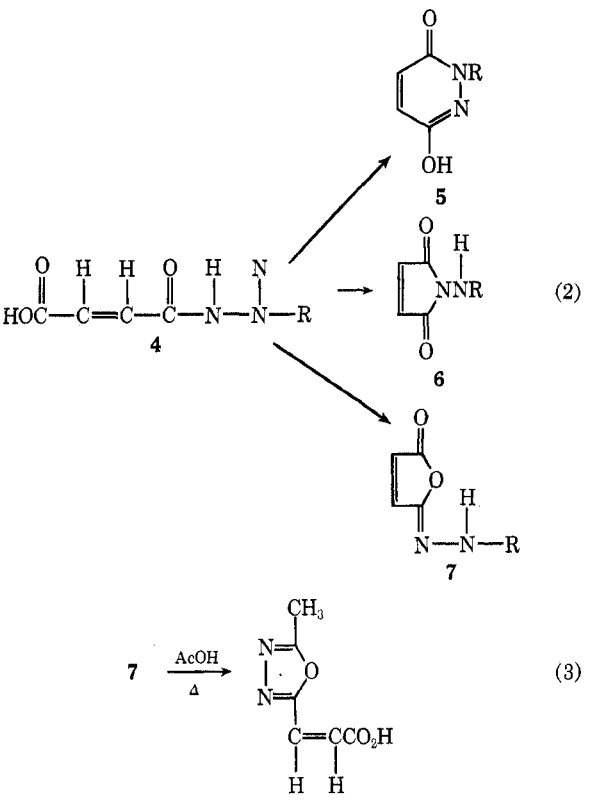
Recently, there has been a great deal of interest in the formation of N-substituted maleamic acid derivatives **1** and in their conversion to maleimides **2** and isomaleimides **3** upon dehydration[1-12] (eq 1).



(1)

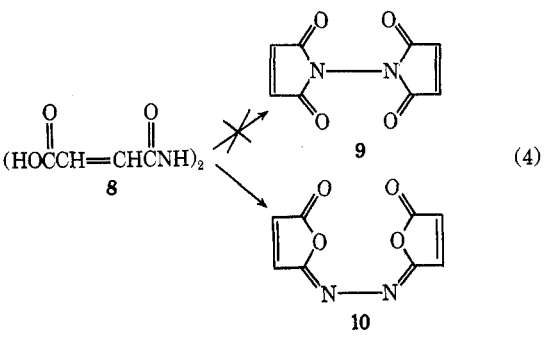
With substituted β-acryloylhydrazides **4** an additional ring closure to pyridazinones **5** may take place (eq 2). It also has been shown that **7** (R = $COCH_3$) rearranges in boiling acetic acid to a 1,3,4-oxadiazole[13-15] (eq 3).

Feuer and Rubinstein[1] suggested that the dehydration of substituted 3-carboxyacrylolylhydrazines **4** in thionyl chloride led to the corresponding substituted maleimides **6**. These structure assignments were based upon infrared absorption of the amide carbonyl group and elemental analysis. They also reported the formation of the bismaleimide **9** as the product of the dehydration of 1,2-bis(3-carboxyacryloyl)hydrazine (**8**) (eq 4).



(2)

(3)



(4)

Subsequently, Feuer and Asunskis[2] prepared what were thought to be various substituted aminomalei-

(1) H. Feuer and H. Rubinstein, *J. Amer. Chem. Soc.*, **80**, 5873 (1958).
(2) H. Feuer and J. Asunskis, *J. Org. Chem.*, **27**, 4684 (1962).
(3) W. R. Roderick and P. L. Bhatia, *ibid.*, **28**, 2018 (1963).
(4) R. J. Cotter, C. K. Sauers, and J. M. Whelan, *ibid.*, **26**, 10 (1961).
(5) A. E. Kretov, N. E. Kyl'chitskaya, and A. F. Mal'new, *J. Gen. Chem. USSR*, **31**, 2415 (1961).
(6) D. Y. Curtin and L. I. Miller, *Tetrahedron Lett.*, 1869 (1965).
(7) E. Hedaya, R. L. Hinman, and S. Theodoropulos, *J. Org. Chem.*, **31**, 1311 (1966).
(8) E. Hedaya, R. L. Hinman, and S. Theodoropulos, *ibid.*, **31**, 1317 (1966).
(9) M. L. Ernst and G. L. Schmir, *J. Amer. Chem. Soc.*, **88**, 5001 (1966).
(10) W. R. Roderick, *J. Org. Chem.*, **29**, 745 (1964).
(11) C. K. Sauers, *ibid.*, **34**, 2275 (1969).
(12) C. K. Sauers, *Tetrahedron Lett.*, 1149 (1970).
(13) A. Le Berre, J. Godin, and R. Garreau, *C. R. Acad. Sci., Ser. C*, **265**, 570 (1967).
(14) J. Godin and A. Le Berre, *Bull. Soc. Chim. Fr.*, **10**, 4210 (1968).
(15) M. Dormoy, J. Godin, and A. Le Berre, *ibid.*, **10**, 4222 (1968).

mides in order to study the effect of the substituent on their transformation to the supposed pyridazinones **5**. These workers, however, did not consider that they might be dealing with isomaleimide–maleimide or isomaleimide–pyridazinone interconversions.

More recently Hedaya and coworkers[7,8] showed that the reaction product of **8** with thionyl chloride was the biisomaleimide **10**. They also reported that 1-acetyl-2-(3-carboxyacryloyl)hydrazine reacted with acetic anhydride at room temperature to give the isomaleimide **7** (R = $COCH_3$). These results were confirmed by Le Berre and coworkers.[13] Both groups used the appearance of a typical AB pattern in the nmr spectrum to rule out the malemide structure. However, there has been disagreement between these investigators regarding the fate of **7** in acetic acid. LeBerre reported that **7** (R = $COCH_3$) was converted to an oxadiazole (eq 3), whereas Hedaya suggested that **7** was transformed to **5**.

In other recent studies Baloniak[16,17] reacted various nitrophenylhydrazine derivatives with acid solutions and reported the formation of **6** and their isomerization to **5**. These results seem anomalous when considered along with the work of Hedaya and LeBerre and the related work with maleamic acids.[3-7,10-13,18]

This work deals with a reexamination of the reaction of maleic anhydride with substituted hydrazines and of the cyclization reactions of 3-carboxyacryloylhydrazines in order to resolve the discrepancies in the literature.

Results

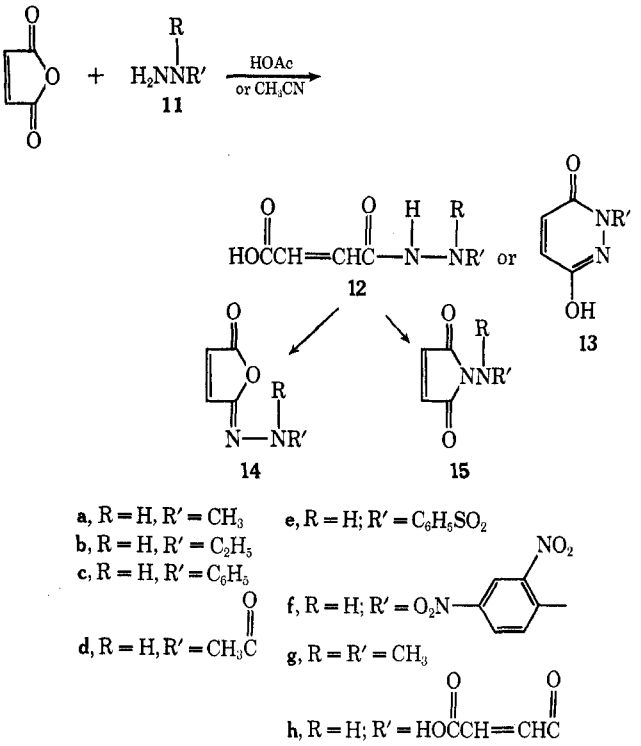
The nature of the group substituted on hydrazine and on the 3-carboxyacryloylhydrazines resulting from the reaction of hydrazines **11** with maleic anhydride plays an important part in the formation of five- or six-membered ring compounds. Electron-donating groups give the pyridazinones **13a,b** directly by the reaction of maleic anhydride with the substituted hydrazines **11a,b** (Scheme I). More neutral or electron-attracting groups give the substituted 3-carboxyacryloylhydrazines **12c–h**.

The reaction of β-acryloylhydrazines **12d–f** carrying electron-withdrawing substituents with dehydrating agents such as acetic anhydride or thionyl chloride leads to the formation of the isomaleimides **14d–f**. On the other hand, a mixture consisting of isomaleimide **14g** and maleimide **15g** was obtained with the 1,1-dimethyl compound **12g** and only polymeric material with the phenyl derivative **12c**.

The course of the reaction of **12** in acid solutions such as acetic acid again depends upon the substituent group present. In the case of electron-donating groups six-membered ring formation occurs (**12c** gives **13c**), whereas with electron-withdrawing groups maleimide formation takes place (**12d–f** gives **15d–f**). Maleimide formation also takes place when *N,N*-dimethyl-3-carboxyacryloylhydrazine (**12g**) is reacted in acid solutions.

Proof of Structure of 3-Carboxyacryloylhydrazines 12.—As shown in Table I the infrared spectra of **12** exhibit carbonyl absorption in the 1710–1695-cm^{-1} region indicating the presence of an α-β-unsaturated system.[19] The nmr spectra of **12** showed vinyl proton peaks at δ 6.3–6.5. Surprisingly, compounds **12d–f,h** having strongly electron-withdrawing groups exhibited a single peak for the vinyl protons, indicating a balanced electronic effect. The phenyl and the *N,N*-dimethyl compounds gave a typical AB pattern where the outer transitions were quite weak, indicating a small difference in chemical shift as would be expected from this type of system.

Scheme I



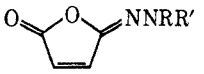
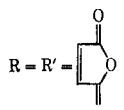
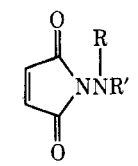
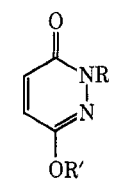
Proof of Structure of Isomaleimides 14.—The infrared spectra of isomaleimides show a strong and characteristic carbonyl absorption peak in the 1778–1790-cm^{-1} region[7], absorption in the C=N region at 1600–1650[3,7] cm^{-1}, and strong N–H absorption at 3140–3500 cm^{-1}. The nmr data (Table I) show the presence of nonequivalent vinyl protons. The acetyl derivative **14d** exhibits a typical AB pattern consistent with the reports of Hedaya[7] and LeBerre.[13] The dimethyl compound **14g** and biisomaleimide **14h** give a similar pattern. In the case of the benzenesulfonyl and 2,4-dinitrophenyl derivatives **14e** and **14f**, only half of the quartet peaks were found in dimethyl sulfoxide solution; the other half were masked by the aromatic protons. In both cases the use of chloroform as the solvent shifted the vinyl proton peaks sufficiently to confirm the presence of a quartet. The isomaleimide vinyl protons had coupling constants J = 5.5–6.0 cps.[11]

Proof of Structure of Maleimides 15.—The infrared spectra of the maleimides show a broad carbonyl absorption at 1705–1715 cm^{-1} which is characteristic of imides.[4,7,14] The carbonyl absorption of six-membered ring pyridazines is found at lower frequencies (Table I). Thus, previously reported pyridazinones[1,2,7] are most probably maleimides. The nmr spectra show conclusively that the maleimide structure is correct since

(16) S. Baloniak, *Rocz. Chem.*, **41**, 1143 (1967).
(17) S. Baloniak, *ibid.*, **42**, 1231 (1968).
(18) These transformations are currently being investigated by Mr. Michael Parnarouskis.
(19) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, p 168.

TABLE I

SPECTRAL PROPERTIES OF 3-ACRYLOYLHYDRAZINES, ISOMALEIMIDES, MALEIMIDES, AND PYRIDAZINONES

R	R′	Registry no.	Ir, cm^{-1},[a] CO stretch	Nmr[b-d] Olefinic protons, δ	*J*, Hz	Aromatic protons, δ	Substituent protons, δ
			3-Acryloylhydrazines				
H	C_6H_5	31413-85-1	1695 (s)	6.95 d, 6.34 d	10	7.45–6.75 m	
H	CH_3CO	17789-76-3	1688 (s)	6.50 s			1.97 s ($COCH_3$, 2.9 H)
H	$C_6H_5SO_2$	31413-87-3	1688 (s)	6.36 s		8.1–7.7 m	
H	$2,4\text{-}(NO_2)_2C_6H_3$	31413-88-4	1710 (s)	6.55 s		10.12–7.42 m	
H_3C	CH_3	10191-43-2	1700 (m)	6.40, 6.37			2.64 s [$N(CH_3)_2$, 6.1 H]
H	$HO_2CCH{=}CHCO$	5343-00-0	1679 (br)	6.52 s			
			Isomaleimides 				
H	CH_3CO	6903-87-3	1778	7.79 d, 6.79 d	5.5		1.98 s ($COCH_3$, 3 H)
H	$C_6H_5SO_2$	30986-27-7	1790	7.70 d, 6.79 d	5.5	7.9–7.4 m	
				7.08 d, 6.23 d	5.5[e]	8.2–7.2 m	
H	$2,4\text{-}(NO_2)_2C_6H_3$	31413-91-9	1785	7.95 d, 6.97 d	6	9.0–7.8 m	
				7.52 d, 6.58 d	6[f]	9.2–7.9 m	
H_3C	CH_3	31413-92-0	1783	7.14 d, 6.07 d	5.5[g]		3.20 s [$N(CH_3)_2$, 6 H]
R = R′ = 		6990-21-2	1790	8.01 d, 7.12 d	6[h]		
			Maleimides 				
H	CH_3CO	20311-07-3	1715	7.08 s			1.89 s ($COCH_3$, 3 H)
H	$C_6H_5SO_2$	30986-29-9	1715	6.86 s		7.8–7.3 m	
H	$2,4\text{-}(NO_2)_2C_6H_3$	20970-35-8	1715	7.30 s		8.90–7.35 m	
CH_3	CH_3	10270-11-8	1705	6.62 s			2.87 s [$N(CH_3)_2$, 6.1 H]
			Pyridazinones 				
H	H	10071-13-3	1660	7.02 s			
CH_3	H	10071-37-1	1660	7.20 d, 7.04 d	10		3.57 s (CH_3, 3.2 H)
C_2H_5	H	31414-00-3	1664	7.36 d, 7.19 d	10		4.08 q (CH_2, 2 H), 1.32 t (CH_3, 3 H)
C_6H_5	H	1698-54-0	1650	7.10 d, 7.0 d	10	7.68–7.25 m	
C_2H_5	CH_3CO	31414-01-4	1660	7.28 d, 6.92 d	10		3.99 q (CH_2, 2 H), 2.15 s ($COCH_3$, 3 H), 1.09 t (CH_3, 2 H)

[a] Run as a Nujol mull. [b] Parts per million. [c] All spectra were run in DMSO-d_6 unless indicated otherwise. [d] d = doublet, m = multiplet, q = quartet, s = singlet, t = triplet. [e] Run in $CDCl_3$ at 66°. [f] Run in $CDCl_3$ at room temperature. [g] Run in CCl_4; data were obtained from a mixture of maleimide and isomaleimide by cancelling out maleimide values. [h] Run in DMSO-d_6 at 100°.

only a single peak is found in the vinyl region. Ferric chloride tests on all the maleimides were negative.

Proof of Structure of 6-Hydroxy-3(2*H*)-pyridazinones 13.—The carbonyl stretching frequency for the pyridazinones **13a–c** appears in the 1650–1670-cm^{-1} region (Table I). These data do not agree with those tabulated previously.[1,7] The previous data reported absorptions at 1740–1710 cm^{-1} which are typical for maleimides and are at a much higher frequency than would be expected for the amide carbonyl in six-membered rings.[20]

The nmr spectra of these compounds exhibit a typical AB pattern for the vinyl protons and show coupling constants J = 9.5–10 cps. The 1,2-dihydro-3(2*H*)-pyridazinone exhibits a singlet in the vinyl region because of the equivalency of the protons due to rapid tautomerization.[21] All pyridazinones were acidic and their molecular weight could be determined by potentiometric titration. They gave a positive ferric chloride test typical for phenols and enols. Further proof of structure for the pyridazinones was the reaction of these compounds with acetic anhydride to give the corresponding acetoxy derivatives.

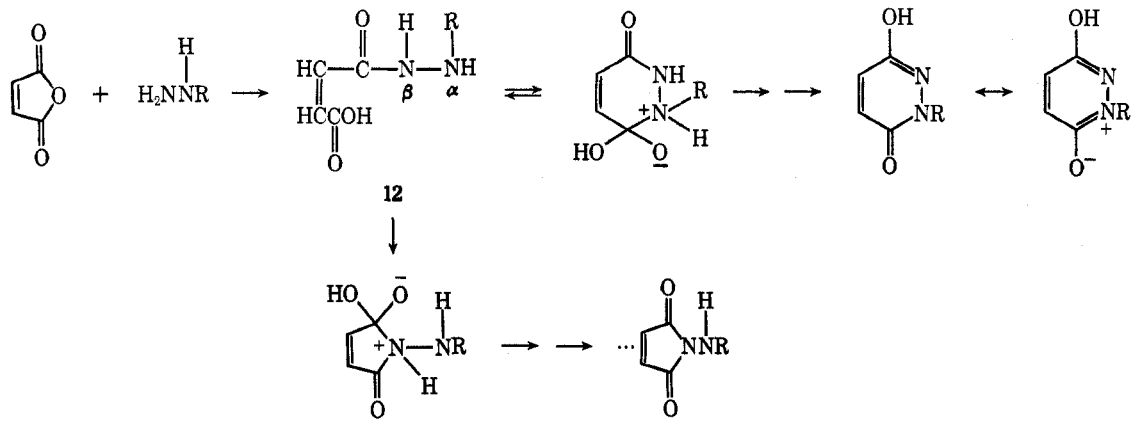
Discussion

The reaction of maleic anhydride and hydrazine in acetic acid or acetonitrile leads to the formation of β-

(20) See ref 19, p 213.

(21) A. R. Katritzky and A. T. Waring, *J. Chem. Soc.*, 1523 (1964).

SCHEME II



acryloylhydrazines **12** or pyridazinones **13** depending upon the electronic (or perhaps steric) environment of the nitrogen atom. This is not too surprising since the two structures may be considered as ring–chain tautomers[22] and the equilibrium between the pair in each case would be expected to depend upon the nucleophilicity of the α nitrogen atom (Scheme II). In the case of neutral or electron-withdrawing substituents the open chain tautomer is favored.

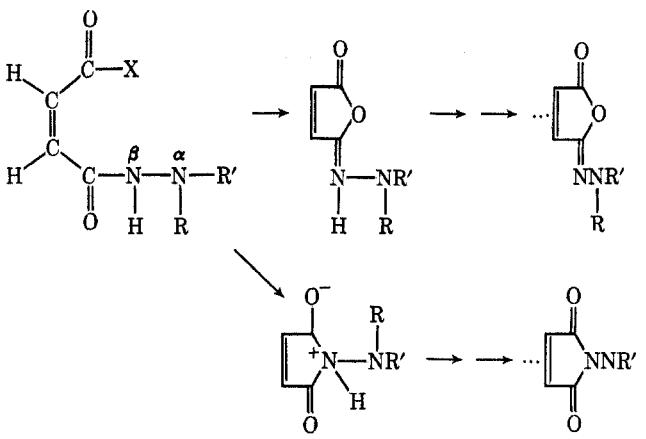
The reaction of **12** in acid solutions upon heating involves conditions which probably favor the ring tautomer by driving the equilibrium to completion *via* subsequent dehydration steps. This reaction leads to five- or six-membered ring formation depending upon the nucleophilicity of the α or β nitrogen atom (Scheme II). It has been suggested that such a reaction gives the thermodynamically favored reaction product[8,23] and hence the more stable five- or six-membered ring. In the case of electron-donating groups this would most likely be the resonance-stabilized pyridazinone ring, whereas with electron-withdrawing groups the maleimides might be expected to be more stable.

The reaction of β-acryloylhydrazines and related compounds with dehydrating agents, *i.e.*, acetic anhydride,[1,2,11] thionyl chloride,[1,2,7] and trifluoroacetic anhydride,[7,10] probably occurs with intermediate mixed anhydride formation as has been suggested for previously described dehydrations.[8,11,24]

Under these conditions the competition which takes place involves an attack by the β nitrogen on the carbonyl oxygen of the amide on the mixed anhydride carbonyl carbon atom (Scheme III). Attack by oxygen is favored and the reaction proceeds with the formation of the kinetically favored isomaleimide ring.[4,11] The substituent group on the α nitrogen again plays a role in the reaction since with the *N*,*N*-dimethyl derivative **12g** a mixture consisting of the isomaleimide and maleimide was obtained. This result was unexpected since Sauers in her study[11] has shown that in the case of *N*-arylmaleamic acids the ratio of maleimide to isomaleimide increased with decreasing electron density on the benzene ring. It may be that the influence of the nitrogen substituent in hydrazines plays a markedly different role from that of directly substituted maleamic acids.

(22) P. R. Jones, *Chem. Rev.*, **63**, 461 (1963).
(23) H. Rubinstein, Ph.D. Dissertation, Purdue University, 1958, p 24.
(24) R. Paul and A. S. Kende, *J. Amer. Chem. Soc.*, **86**, 4162 (1964); D. V. Kashelikar and C. Ressler, *ibid.*, **86**, 2467 (1964).

SCHEME III



X = CH_3CO_2, CF_3CO_2, OSOCl

Experimental Section

All infrared spectra were obtained on a Beckman IR-10 spectrometer using Nujol mulls. The nmr spectra were obtained on Varian A-60 and Perkin-Elmer R-20 spectrometers. The data are shown in Table I. Melting points are corrected.

Preparation of Hydrazines 11.—All hydrazines were prepared by known methods or purchased commercially. The following hydrazines were prepared by the methods indicated in the literature or by slight variations of these methods: methylhydrazine,[25,26] ethylhydrazine,[25,27] acetic acid hydrazide,[28] benzenesulfonic acid hydrazide.[29]

Preparation of 3-Carboxyacryloylhydrazines 12.—These compounds were prepared by the methods indicated in the literature (All compounds were purified after preparation and gave neutralization equivalents indicating better than 98% purity. The maleic anhydride was recrystallized from chloroform before use.): 1-phenyl-2-(3-carboxyacryloyl)hydrazine,[30] 1-(2,4-dinitrophenyl)-2-(3-carboxyacryloyl)hydrazine,[2] 1-acetyl-2-(3-carboxyacryloyl)hydrazine,[1] 1-benzenesulfonyl-2-(3-carboxyacryloyl)hydrazine,[1] 1,1-dimethyl-2-(3-carboxyacryloyl)hydrazine,[30] 1,2-bis(3-carboxyacryloyl)hydrazine.[1]

Preparation of Isomaleimides 14.—The isomaleimides were prepared by the methods indicated in the literature except as noted (The methods used were those described by the authors for the preparation of maleimides. Thionyl chloride and acetic anhydride were distilled before use.): *N*-acetylaminoisomaleimide,[2] *N*-benzenesulfonylaminoisomaleimide,[2] 1-(2,4-dinitrophenyl)aminoisomaleimide,[2] *N*,*N*′-biisomaleimide.[1]

(25) H. H. Watt, "Organic Syntheses," Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1943, p 395.
(26) A. Graefe, U. S. Patent 2,962,532 (1960).
(27) A. N. Kost and R. S. Sagetullin, *Zh. Obshch. Khim.*, **33**, 867 (1963).
(28) T. Curtius and T. F. Hoffman, *J. Prakt. Chem.*, [2] **53**, 513 (1896).
(29) T. Curtius and F. Lorenzen, *ibid.*, **58**, 166 (1898).
(30) K. Eichenberger, *et al.*, *Helv. Chim. Acta*, **37**, 837 (1954).

1,1-Dimethylaminoisomaleimide (14g) and N,N-Dimethylaminomaleimide (15g).—*N,N*-Dimethyl-2-(3-carboxyacryloyl)-hydrazine (5.0 g) was slowly added to 120 ml of acetic anhydride, the mixture was stirred under anhydrous conditions for 48 hr, and the solvent was removed *in vacuo*. The residue was extracted with four 25-ml portions of petroleum ether (bp 30–60°) and the combined ether extracts were concentrated to about 25 ml giving yellow crystals. Recrystallization from petroleum ether gave 2.12 g of a product, mp 58–59°. The nmr data (Table I) showed this to be a mixture of maleimide and isomaleimide in the ratio of 2:1.

Anal. Calcd for $C_6H_5N_2O_2$: C, 51.43; H, 5.71; N, 20.00. Found: C, 51.15; H, 5.75; N, 19.91.

A mixture of the maleimide and isomaleimide (0.80 g) was refluxed for 2 hr in glacial acetic acid. Work-up of the resulting solution gave pure maleimide (0.66 g).[31]

Preparation of Maleimides 15.—The maleimides were prepared by the methods described for the preparation of the pyridazinones:[1,2] *N*-acetylaminomaleimide,[1,8] *N*-benzenesulfonylaminomaleimide,[2] and *N*-(2,4-dinitrophenyl)aminomaleimide.[2]

***N,N*-Dimethylaminomaleimide (15g).**—Glacial acetic acid (100 ml) was added to 5.0 g of *N,N*-dimethyl-2-(3-carboxyacryloyl)hydrazine. The mixture was refluxed for 2 hr during which time the color changed from light green to light red. The resulting solution was concentrated *in vacuo* and the remaining oil was extracted with four 10-ml portions of petroleum ether (bp 30–60°). The combined ether extracts were concentrated and gave yellow crystals which after recrystallization from petroleum ether gave 1.6 g of a yellow powder, mp 83–84°.

Anal. Calcd for $C_6H_5N_2O_2$: C, 51.43; H, 5.71; N, 20.00. Found: C, 51.28; H, 5.83; N, 20.14.

2-Ethyl-6-hydroxy-3(2*H*)-pyridazinone (13b).—Glacial acetic acid (150 ml) and maleic anhydride (7.9 g) were mixed and 4.3 g of ethylhydrazine was added dropwise over 5 min while stirring and keeping the temperature below 30°. The solution turned light green and then yellow during the addition. Stirring for 15 min, concentrating *in vacuo*, and recrystallizing the resulting solid from 95% ethanol gave 3.0 g of **13b**, mp 143.5–145°.

Anal. Calcd for $C_6H_8N_2O_2$: C, 51.43; H, 5.71; N, 20.00; neut equiv, 140. Found: C, 51.72; H, 5.91; N, 20.25; neut equiv, 138.8.

2-Ethyl-6-acetoxy-3(2*H*)-pyridazinone.—The pyridazinone **13b** (0.3 g) was added to 25 ml of acetic anhydride and refluxed for 1 hr, and the solvent was removed *in vacuo*. The residue was recrystallized from hexane giving 0.3 g of product, mp 76–77°.

Anal. Calcd for $C_8H_{10}N_2O_3$: C, 52.74; H, 5.49; N, 15.38. Found: C, 52.89; H, 5.60; N, 15.33.

2-Methyl-6-hydroxy-3(2*H*)-pyridazinone (13a).—Following a similar procedure as described for the preparation of **13b** gave **13a**, mp 215–216° (lit.[30] mp 210–211°). Acetonitrile was also found to be a suitable solvent for the reaction.

Anal. Calcd for $C_5H_6N_2O_2$: C, 47.63; H, 4.80; N, 22.22. Found: C, 47.56; H, 4.68; N, 22.46.

2-Methyl-6-acetoxy-3(2*H*)-pyridazinone melted at 90.5–92.0° (benzene).

Anal. Calcd for $C_7H_8N_2O_3$: C, 50.00; H, 4.80; N, 16.66. Found: C, 49.91; H, 4.76; N, 16.48.

2-Phenyl-6-hydroxy-3(2*H*)-pyridazinone (13c).—The procedure similar to that described for **13b** gave 2.3 g of **13c**, mp 262–263° (lit.[32] mp 259–260°).

(31) We are indebted to Mr. Michael Parnarouskis of Lowell Technological Institute for providing this data in response to the suggestion of one of the referees.

Registry No.—2-Methyl-6-acetoxy-3(2*H*)-pyridazinone, 31443-72-8.

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Studies in Nonpyridinoid Aza-Aromatic Systems. II. Reactions of the Anions of Benzo[*b*][1]pyrindine and Its 1,2-Dihydro Derivative[1]

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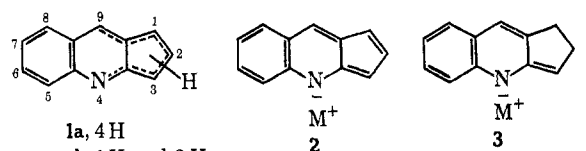
The reactivities of the anions of benzo[*b*][1]pyrindine (**1**) and of its 1,2-dihydro derivative **4** toward electrophilic reagents, such as methyl iodide, 9-fluorenone, and benzophenone, were investigated. The azulene-like, delocalized anion **2** underwent only C-methylation at C_1 and C_3 in almost equal proportions; the 1,2-dihydro anion **3** underwent exclusive methylation at C_3. Both anions reacted with benzophenone in a reversible fashion at C_3 and probably also at the nitrogen center to form a labile aminocarbinolate. The behavior of **2** is in accord with the chemical behavior expected of a nitrogen isostere of an azulene. Access to derivatives of the benzo[*b*][1]pyrindine system, starting from **4**, was gained by the synthesis of 3-methylene derivatives of **4**, followed either by a dehydrogenation with DDQ to yield a fulvene **13** or by base-promoted hydrogen transfer to provide a pyrindine **28**. Finally, abortive and partially successful attempts to dehydrogenate 1,2-dihydro anion **3** did uncover an apparently general, alternative approach to 3-methylene derivatives of **4**.

The previous study of the synthesis and tautomeric character of benzo[*b*][1]pyrindine (cyclopenta[*b*]quinoline)[1] was prompted by an interest in the aromatic character of the 4H tautomer **1a**. Being a nitrogen isostere of 5,6-benzazulene, **1a** might be expected[2] to undergo electrophilic attack in the five-membered ring and nucleophilic attack in the six-membered nitrogen ring. The latter ring would be a six-π-electron counterpart of the azulene's cyclohepta ring. Since less than 1% of this 4H tautomer is present in benzo[*b*][1]pyrindine, it seemed appropriate to convert the mixture of 1H, 3H, and 4H benzo[*b*][1]pyrindines into their common anion **2** and to examine its chemical behavior toward certain electrophiles. Furthermore, a parallel consideration of its 1,2-dihydro derivative **3** merited



1a, 4 H
b, 1 H and 3 H

2

3

attention, in order to compare the chemical responses of a derivative with disrupted conjugation. At the same

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