The Dehydration of *N*-Benzyloxy and *N*-Hydroxymaleamic Acid and the Isomerization of *N*-Benzyloxyisomaleimide

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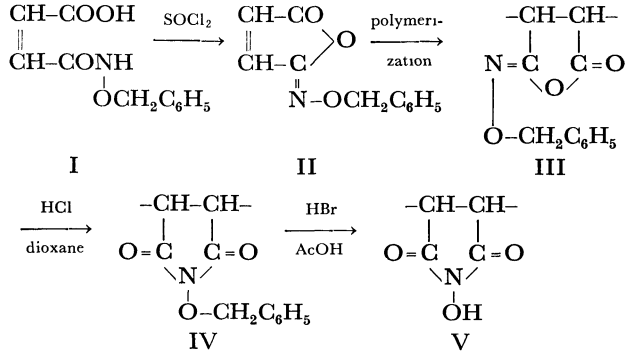
The dehydration of *N*-benzyloxy and *N*-hydroxymaleamic acids and the isomerization of *N*-benzyloxyisomaleimide were carried out under various conditions to obtain *N*-benzyloxyisomaleimide, *N*-hydroxyisomaleimide, and *N*-benzyloxymaleimide. *N*-substituents, such as benzyloxy, hydroxy, and acetoxy groups, depress the reactivity of nitrogen electronically and facilitate the formation of isomaleimides in the dehydration of *N*-substituted maleamic acids. The thermal isomerization of *N*-benzyloxyisomaleimide to the maleimide has been successful only in *N*,*N*-dimethylformamide. Further the conversion of isomaleimide to maleimide was performed *via* the addition of hydrogen bromide to isomaleimide followed by isomerization and dehydrobromination.

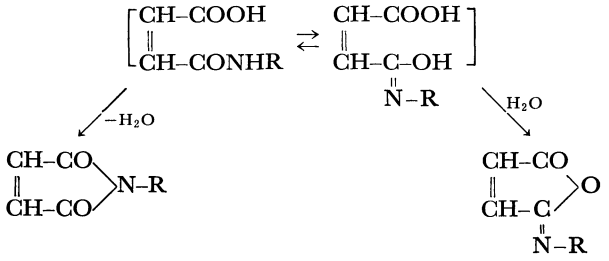
In peptide syntheses, *N*-hydroxysuccinimide has been frequently used as a convenient component for activation of carboxyl group of amino acids. In our early works, we reported the preparation of polymer (*e.g.* V) having the *N*-hydroxyimide structure in the chain and the activation of carboxylic acid group by use of such polymers.[1,2] During the course of these works, it was found[2] that the dehydrocyclization product of *N*-benzyloxymaleamic acid (I) with thionyl chloride was not the expected *N*-benzyloxymaleimide but *N*-benzyloxyisomaleimide (II), and that *N*-benzyloxy- (IV) or *N*-hydroxysuccinimide (V) structure was obtained by successive isomerization and hydrolysis of polymer (III). In this paper, we wish to report



the result of the further investigation on cyclization reactions of *N*-benzyloxy- and *N*-hydroxymaleamic acids with various dehydrating agents and also on the possibility of direct isomerization of *N*-benzyloxyisomaleimide to *N*-benzyloxymaleimide.

Results and Discussion

The Dehydration of N-*Benzyloxymaleamic Acid.* The dehydration of *N*-substituted amic acids, especially *N*-substituted maleamic and phthalamic acids, produces the corresponding imides[3–5] or isoimides[5–9] depending on the nature of amic acids and the reaction condition employed. One would postulate that *N*-substituted maleamic acid would be in equilibria with the tautomer of iminohydrine structure which is strongly stabilized by conjugation with the double bond and that the iminohydrine tautomer will produce the corresponding isoimide by treatment with dehydrating agents under certain condition as shown in Scheme 1.[8]



Scheme 1

Cotter[6] and Roderick[7] investigated on the reagents used for the dehydration of amic acids and classified the reagents which employed most commonly to effect the dehydration of amic acids to imides and isoimides. The effect of *N*-substituents in amic acids on the direction of the dehydration, however, has not been investigated systematically.

Ames reported[10] the formation of *N*-benzyloxymaleimide by treating *N*-benzyloxymaleamic acid (I) with thionyl chloride. We reported that the product obtained by Ames's procedure was *N*-benzyloxyisomaleimide (II).[2] In this paper, the action of phosphorus pentoxide, dicyclohexylcarbodiimide

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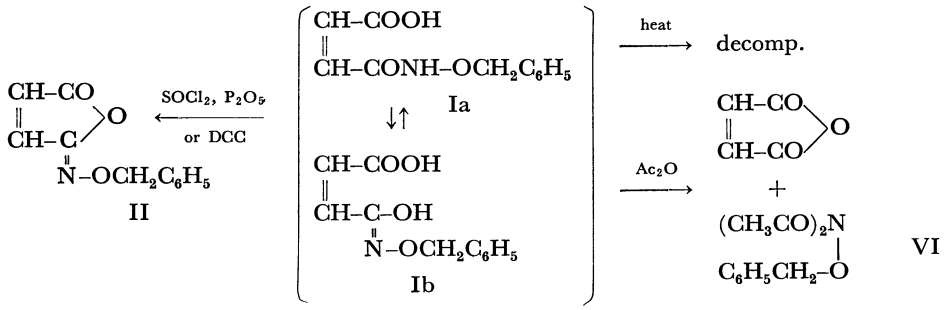


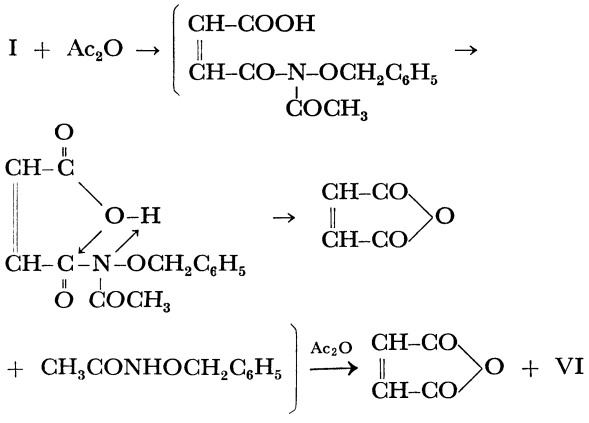
Sheme 2

TABLE 1. THE ISOMERIZATION OF *N*-BENZYLOXYISOMALEIMIDE (II)[a] TO THE CORRESPONDING IMIDE (XIII)

No.	Solvent[b] (10 ml)	Catalyst (g)	Reaction temp. (°C)	Reaction time (hr)	Yield of XIII (recovered II) (%)
1	DMSO[e]		170~180	4	(60)
2	NB[f]	—	150~160	10	(90)
3	—	—	140~150	4	(61)
4	DMF[g]	—	reflux	10	40
5	AAn[h]	CH_3COONa (0.4)	reflux	10	(60)
6	DMF	Pyridine (1.0)	100	6	(90)
7	NB	Quinoline (0.5)	150~160	10	(72)
8	Dioxane	CF_3COOH (0.3)	reflux	20	(88)
9	Dioxane	$BF_3 \cdot OEt_2$ (0.3)	reflux	10	(78)
10	CH_3COOH	HBr (2.0)	r. t.	5	85[c]
11	Dioxane	I_2 (0.1)	reflux	5	(75)
12	Dioxane	TsOH (0.2)	reflux	5	28[d]

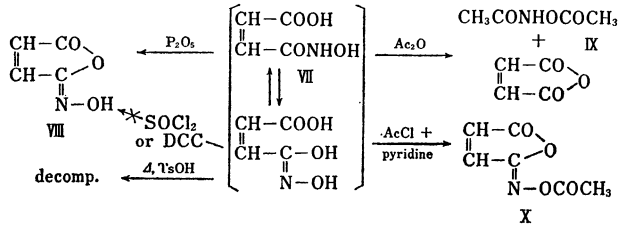
a) One gram of II was used for the reaction in every case. b) In the case of No. 5, 20 ml of the solvent was used. c) The product was α-bromo-*N*-benzyloxysuccimide(XV). d) The product was the mixture of II and XIII which was identified by IR spectrum. e) DMSO; dimethylsulfoxide. f) NB; nitrobenzene. g) DMF; *N*,*N*-dimethylformamide. h) AAn; acetic anhydride.

(DCC), acetic anhydride as well as thionyl chloride will be reported. Treatment of I with these dehydrating agents produced various compounds as shown in Scheme 2. The dehydration was carried out with thionyl chloride in benzene, phosphorus pentoxide in *N*,*N*-dimethylformamide(DMF) and DCC in DMF or dioxane. In every cases, the product was only the isoimide (II) in about 70% yield. The compound (I) decomposed at about 145°C and so the thermal dehydration failed to produce the imide. Treatment of I with acetic anhydride at room temperature gave maleic anhydride and *N*,*N*-diacetyl-*O*-benzylhydroxylamine (VI) probably due to the following way (Scheme 3).



Scheme 3

The Dehydration of N-*Hydroxymaleamic Acid.* We attempted the dehydration of *N*-hydroxymaleamic acid (VII) with phosphorus pentoxide, thionyl chloride, acetic anhydride, *p*-toluenesulfonic acid (TsOH), DCC and acetyl chloride-in-pyridine. These results are shown in Scheme 4. Ivanov *et al.*[4] reported that they obtained *N*-hydroxymaleimide by treatment of VII with phosphorus pentoxide. However, *N*-



Scheme 4

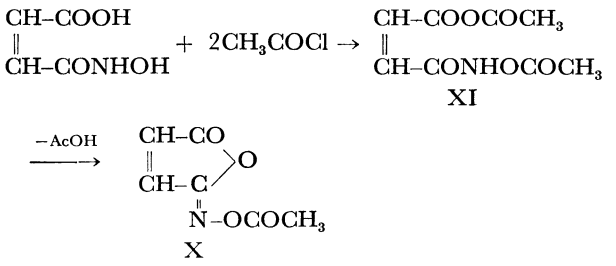
hydroxyisomaleimide(VIII) was obtained instead of the corresponding maleimide by the dehydration of VII with phosphorus pentoxide as shown in Scheme 4. Using thionyl chloride and DCC as dehydrating agents, neither *N*-hydroxymaleimide nor *N*-hydroxyisomaleimide was obtained. The compound(VII) decomposed at *ca.* 130°C and the thermal dehydration failed. The compound (VII) decomposed at 100°C by treatment with TsOH. The reaction of VII with acetic anhydride yielded *N*,*O*-diacetylhydroxyamine (IX) and maleic anhydride. With excess acetyl chloride

TABLE 2. PHYSICAL AND SPECTRAL DATA OF II, VIII, X, AND XIII

Compd.	Formula	Mp (°C)	Anal. (Calcd) % C	H	N	IR data[a] (cm^{-1})
II	$C_{11}H_9O_3N$	80~80.5	64.93 (65.02)	4.60 (4.46)	6.91 (6.89)	1795 (C=O) (s) 1630 (C=N) (m)
VIII	$C_4H_3O_3N$	145 (dec.)	42.81 (42.49)	2.45 (2.67)	12.49 (12.39)	1770 (C=O) (s) 1700 (?) (s) 164~20 (C=N) (s)
X	$C_6H_5O_4N$	115~116.5	46.06 (46.46)	3.02 (3.25)	9.02 (9.03)	1786 (C=O) (s) 1662 (C=N) (m) 1808 (C=O of =N-OCOCH$_3$) (s)
XIII	$C_{11}H_9O_3N$	89~90.5	64.45 (65.02)	4.13 (4.46)	6.86 (6.89)	1730 10 (C=O) (s)

a) Absorption intensity is expressed; s=strong, m=medium

in pyridine, VII gave *N*-acetoxyisomaleimide (X) probably through XI as shown in Scheme 5. Struc-



Scheme 5

tural evidences (IR and NMR spectra) of these compounds are shown in Tables 2 and 3.

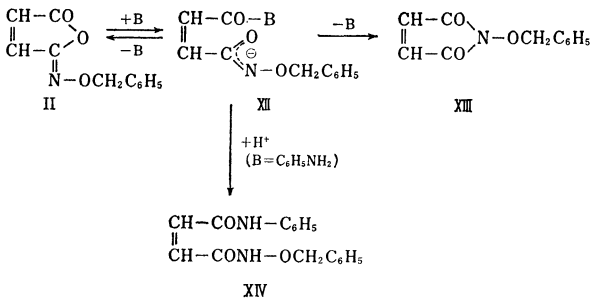
TABLE 3. NMR DATA[a] OF II, VIII, X, XIII, AND XVI

Compd.	Chemical shift (δ)	Multiplicity[b] (J, Hz)	Number of protons	Assignment
II[c]	5.13	S	2	Methylenic H
	6.30	D (9)	1	Olefinic H_b[d]
	7.20	D (9)	1	Olefinic H_a[d]
	7.28	S	5	Aromatic H
VIII	5.62	D (8)	1	Olefinic H_b
	7.66	D (8)	1	Olefinic H_a
X	2.24	S	3	$OCOCH_3$
	6.61	D (6)	1	Olefinic H_b
	7.55	D (6)	1	Olefinic H_a
XIII	5.06	S	2	Methylenic
	6.53	S	2	Olefinic H
XVI[17]	7.36	M	5	Aromatic H
	2.32	S	3	$OCOCH_3$
	6.75	S	2	Olefinic H

a) NMR spectra were measured in deuteriochloroform solution.
b) S=singlet, D=doublet, M=multiplet.
c) Carbon tetrachloride was used for the solvent.
d) H_a and H_b are indicated in XVII.

The Isomerization of N-*Benzyloxyisomaleimide (II) to the Corresponding Maleimide (XIII).* Isomerization of many cyclic isoimides to imides can be found in the literatures.[6-8,11-14] This reaction proceeds by basic or acidic catalyst and also thermally. For example, *N*-arylisomaleimide,[6,14] *N*-methoxyisophthalimide[11] and *N*-phenylisophthalimide[12] isomerize to the corresponding imides in the presence of sodium acetate in acetic anhydride, hydrogen bromide in nitromethane and thermally in chlorobenzene, respectively.

We carried out the attempted isomerization of *N*-benzyloxyisomaleimide (II) to *N*-benzyloxymaleimide (XIII) under certain conditions. The results are shown in Table 1. The thermal isomerization of II to XIII did not occur in dimethylsulfoxide (DMSO), nitrobenzene or by heating without solvent (Nos. 1—3). In DMF, however, II isomerized to XIII in a 40% yield when refluxed for ten hours (No. 4). In this case, basic impurities in DMF might act as an acyl group transfer agent by attacking the carbonyl group to give the intermediate (XII) as shown in Scheme 6. To confirm this, sodium acetate, pyridine, and quinoline were used as basic components, but the isomerization of II to XIII did not occur (Nos. 5—7). On the other hand, the isoimide (II) reacted with aniline in DMF at 100°C to give the ring opening product (XIV) in a 91% yield. In these reactions, it is most plausible

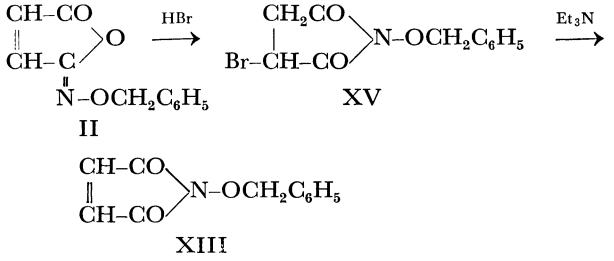


Scheme 6

11) L. A. Carpino, *J. Amer. Chem. Soc.*, **79**, 98 (1957).
12) A. E. Kretov, N. E. Kyl'Chitskaya, and A. J. Mal'nev, *Zh. Obshch. Khim.*, **31**, 2415 (1961).
13) D. Y. Curtin and L. L. Miller, *J. Amer. Chem. Soc.*, **89**, 637 (1967).
14) C. K. Sauers, *J. Org. Chem.*, **34**, 2275 (1969).

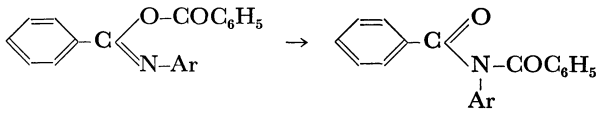
that the base attacks first the carbonyl group to form the intermediate (XII) from which the starting isomaleimide (II), maleimide (XIII) or the ring opening product (XIV) is produced according to the kinds of bases. Trifluoroacetic acid and boron trifluoride etherate were uneffective on the isomerization of II to XIII (Nos. 8 and 9).

On the other hand, *N*-substituted saturated amic acids are known to produce only the corresponding imides. Therefore the use of the compound which can add to double bond and easily leave to regenerate double bond is thought to be an alternate method to obtain intended compound (XIII). In order to verify this expectation, the reaction of II with hydrogen bromide was carried out in acetic acid at room temperature. As expected, the reaction yielded α-bromo-*N*-benzyloxysuccinimide (XV). (No. 10, Table 1) as shown in Scheme 7. The compound (XV) was easily dehydrobrominated with base to give XIII. Iodine and TsOH, which are known as effective catalysts for the isomerization of maleic acid derivatives, were not effective on the isomerization of II to XIII.



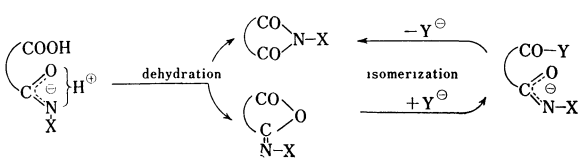
Scheme 7

Curtin and Miller[14] indicated that the electron-withdrawing substituents on Ar ring retarded the O→N migration of benzoyl group (*i.e.* ρ in Hammett rule was negative) in the following example. On



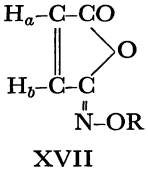
the other hand, Yamada *et al.*[5] examined the dehydrocyclization of *N*-β- or *N*-γ-hydroxypropylmaleamic acid with acetic acid and suggested the formation of maleimide or isomaleimide depended on the steric factor in the intermediates. These works and our results lead to the following conclusion.

The electron-withdrawing substituents such as hydroxy, acetoxy, and benzyloxy reduced the nucleophilic reactivity of nitrogen in *N*-substituted maleamic acids resulting the formation of isomaleimides in either the dehydration or the isomerization process shown below. Isomaleimide obtained by the dehydrocyclization of maleamic acid was isomerized to maleimide by heating in DMF, while the reason of effectiveness of DMF was not enough explained. Further, an indirect method was indicated to obtain maleimide in which the double bond of isomaleimide was saturated once with HBr to facilitate the isomerization.



Proof of Structure of N-*Substituted Isoimides and Imides.* Proof of the structures of II, VIII, X, and XIII were derived from the elemental analyses, IR and NMR spectra. Physical properties and spectral evidence were summarized in Tables 2 and 3. To compare with X, *N*-acetoxymaleimide (XVI)[16] was put in Table 3. Isomaleimides generally have two sharp bands in the infrared at *ca.* 1780 (strong) and 1670 (medium) cm^{-1}. These absorptions can be associated with the anhydride-like carbonyl and the >C=N– bonds present in the isomaleimide ring.[8] In contrast, maleimides have characteristic broad carbonyl bands in the infrared with maxima near 1720 cm^{-1}.[8] Infrared data of the compounds II, X, and XIII agree with these infrared data. The compound (VIII) have three bands of almost the same intensity at 1770, 1700, and 1630 cm^{-1}. We could not assign the band at 1700 cm^{-1}. In comparison with X, *N*-acetoxymaleimide have three bands at 1813 (strong, acetoxy carbonyl), 1780 (medium, imide), and 1741 (strong, imide) cm^{-1}.

The NMR spectra of isoimides show two doublets due to unsymmetrical nature of olefinic hydrogen. In contrast, maleimides have only one singlet due to symmetrical nature of olefinic hydrogen. The NMR data of the compounds II, VIII, and X show two doublets due to H_a and H_b which are shown in XVII. On the other hand, those of the compounds XIII and XVI show only one singlet due to symmetrical nature of olefinic hydrogen.



Experimental

All melting and boiling points are uncorrected. Infrared spectra were measured as potassium bromide disks or in liquid state using a Hitachi Infrared Photometer Model EPI-S2. NMR spectra were obtained with a Japan Electron Optics C-100 spectrometer in deuteriochloroform solution with tetramethylsilane as an internal standard. All solvents used for reactions were purified by usual methods.

Dehydration of N-*Benzyloxymaleamic Acid (I). Treatment of I with Thionyl Chloride*: According to Ames's procedure, the amic acid (I) was treated with thionyl chloride in benzene at refluxing temperature followed by working up of the reaction mixture to give the isoimide (II). Recrystallization from *n*-hexane gave colorless needles, mp 80—80.5°C (lit,[10] mp 80—81°C). Yield 72%.

Treatment of I with Phosphorus Pentoxide: Phosphorus pentoxide (1.7 g) was suspended in 10 m*l* of DMF. The amic acid (I), 2.2 g, was dissolved in 10 m*l* of DMF and the latter was combined with the suspension of P_2O_5 with cooling in

16) M. Narita, T. Teramoto, and M. Okawara, This Bulletin, **44** (1971), in press.

ice-cold water. After the exothermal reaction ended, the mixture was kept for 6 hr at room temperature and was poured into 100 m*l* of water. The precipitate was collected on filter and washed with water to give 1.4 g of the product (II), mp 73—76°C. Recrystallization from *n*-hexane gave colorless needles, mp 80—80.5°C.

Treatment of I with Dicyclohexylcarbodiimide: The amic acid (I), 1.0 g, was added to a solution of 1.1 g of dicyclohexylcarbodiimide in 10 m*l* of DMF. The reaction mixture was kept for 5 hr at room temperature. Dicyclohexylurea began to precipitate immediately. It was filtered off and the filtrate was poured into 100 m*l* of water to give precipitates which was collected by filtration and washed with water. The product was recrystallized from *n*-hexane, yield 0.73 g, mp 79—80.5°C. The same reaction was carried out in 10 m*l* of dioxane instead of DMF, yield 0.7 g, II, mp 79—80.5°C.

Treatment of I with Acetic Anhydride: The amic acid (I), 5.0 g, was suspended in 20 m*l* of acetic anhydride. It took 20 hr at room temperature till all the compounds dissolved in acetic anhydride. At the end of this time, acetic anhydride was distilled off under reduced pressure. The residue was dissolved in *n*-hexane and cooled. The product (VI) crystallized and was collected by filtration with suction, yield 0.23 g, mp 98—101°C. Repeated recrystallization of the product from *n*-hexane afforded needles of *N,N*-diacetyl-*O*-benzylhydroxylamine, mp 101—102°C (lit,[10] mp 101—102°C). The filtrate was distilled under reduced pressure to give three fractions. Fraction I, bp 63—65°C/3.5 mmHg (1.35 g), was maleic anhydride, fraction II, bp 120—5°C/0.4 mmHg (0.93 g), was the product (VI) and fraction III, bp 125—135°C/0.4 mmHg (1.96 g), was a mixture of VI and undefined product. These products were identified by IR spectra.

Dehydration of N-*Hydroxymaleamic Acid (VII). Treatment of VII with Phosphorus Pentoxide*: Phosphorus pentoxide, 6.0 g, was suspended in 7 m*l* of DMF and a solution of 2.6 g of the amic acid in 8 m*l* of DMF was mixed with it and the mixture was cooled in ice-cold water. When the heat ceased to evolve from the reaction mixture, it was kept for 5 hr at room temperature and poured into 80 m*l* of water. The solution was kept in a refrigerator for several days until the crystals appeared. Yield 0.24 g, mp 145°C (dec.). Further recrystallization from benzene-ethanol furnished pure *N*-hydroxyisomaleimide, mp 148°C (dec.).

Treatment of VII with Acetic Anhydride: The amic acid (VII), 5.0 g, was suspended in 20 m*l* of acetic anhydride. It took 20 hr at room temperature till all the compounds dissolved in acetic anhydride. At the end of this time, acetic anhydride was distilled off under reduced pressure. The residue was dissolved in 40 m*l* of hot benzene and cooled. The product, *N,O*-diacetylhydroxylamine (IX), crystallized and was collected by filtration with suction, yield 1.4 g, mp 86—90°C. Repeated recrystallisation of the product from benzene furnished colorless needles, mp 88.5—90°C (lit,[15] mp 91°C). IR (KBr disks): 3350, 3150 cm^{-1} (NH), 1795 cm^{-1} (–CO–O–N), 1655 cm^{-1} (–CO–NH–).

Found: C, 41.23; H, 6.14; N, 11.93%. Calcd for $C_4H_7NO_3$: C, 41.02; H, 6.03; N, 11.96%.

The filtrate (benzene solution) was distilled under reduced pressure to give maleic anhydride, bp 91—93°C/16 mmHg, (4.25 g). Maleic anhydride was identified by infrared spectrum. The pot residue was found to be *N,O*-diacetylhydroxylamine (0.65 g).

Treatment of VII with Acetyl Chloride and Pyridine: The amic acid (VII), 6.5 g, and 10 g of pyridine was dissolved in 50 m*l* of DMF. To this solution, a solution of 10 g of acetyl chloride in 50 m*l* of DMF was added with stirring under cooling with ice-cold water to maintain the temperature below 20°C. After the exothermal reaction ended, the mixture was kept for 6 hr at room temperature. DMF was distilled off under reduced pressure and the viscous residue was poured into 200 m*l* of water to give a precipitate, which was collected and washed with water, yield 2.9 g, mp 99—114°C. Recrystalization from carbon tetrachloride gave *N*-acetoxyisomaleimide, mp 115—116.5°C.

Isomerization of N-*Benzyloxyisomaleimide (II) to the Corresponding Imide (XIII).* Nos. 1—4 (see Table 1). The isoimide (II), 1.0 g, was dissolved in 10 m*l* of the solvent and the reaction was continued under the conditions described in Table 1. The solvent was distilled off under a reduced pressure and the residue was recrystallized from *n*-hexane. The respective products were characterized by mixed melting point with authentic sample and IR spectra. In the case of No. 4, the product was *N*-benzyloxymaleimide (XIII).

Nos. 5—9, No. 11, and No. 12 (see Table 1). The reaction was carried out under the condition shown in Table 1. After the reaction was over, the mixture was poured into 100 m*l* of water and the precipitate was collected and washed with water. The precipitates were recrystallized from *n*-hexane. The product was identified by mixed melting point with authentic sample and IR spectrum.

Reaction of N-*Benzyloxyisomaleimide (II) with Hydrogen Bromide and Dehydrobromination of the Product (XV).* No. 10 (see Table 1). The isoimide (II) was dissolved in 10 m*l* of 20% hydrogen bromide in acetic acid. The reaction mixture was kept for 5 hr at room temperature and then poured into 70 m*l* of water. The precipitate was collected and washed with ethanol, yield 1.2 g, mp 73—91°C. Repeated recrystallizations, from ethanol gave colorless needles, α-bromo-*N*-benzyloxysuccinimide (XV), mp 96—96.5°C. The product has characteristic bands at 3100—3050 cm^{-1}, 1500 cm^{-1} ($-C_6H_5$) and 1797 (weak), 1740 cm^{-1} (strong) (imide).

Found: C, 47.27; H, 3.43; N, 5.03; Br, 28.45%. Calcd for $C_{11}H_{10}NO_3Br$: C, 46.51; H, 3.55; N, 4.93; Br, 28.10%.

The imide (XV) (1.5 g) was suspended in 8 m*l* of triethylamine and allowed to stand for 3 hr at room temperature and poured into 80 m*l* of water. The precipitate was filtered off and washed with water to give 0.44 g of *N*-benzyloxymaleimide (XIII), yield 41%, mp 78—90°C. It was recrystallized from *n*-hexane to give light yellow crystals, mp 89.5—91°C.

Reaction of N-*Benzyloxyisomaleimide (II) with Aniline.* The isoimide (II), 1.02 g, was combined with 1.0 g of aniline in 10 m*l* of DMF and heated for 6 hr at 100°C. The mixture was cooled and poured into 50 m*l* of water to give precipitates, which were collected and washed with water to give 1.35 g of the product (XIV). The product was recrystallized from ethanol, mp 139.5—140.5°C. It has characteristic bands at 3320 cm^{-1} (NH), 1660, 1620 cm^{-1} (CO) and 1545 cm^{-1} (NH).

Found: C, 69.76; H, 5.72; N, 9.45%. Calcd for $C_{17}H_{16}N_2O_3$: C, 68.90; H, 5.44; N, 9.45%.

15) O. Exner and M. Horák, *Collect. Czech. Chem. Commun.*, **24**, 2992 (1959).