TABLE I

	HO	LU	ΔE	Phase	λ_{max}, nm
(a) No H bond	0.579	−0.021	0.600	Vapor[a]	540
(b) Intramolecular H bond	0.640	0.000	0.640		
(c) Intramolecular H bond	0.564	0.026	0.538	$CHCl_3$	604
				Ethanol	610
(d) H-bonded dimer	0.612 (a_u)	0.011 (b_g^*)	0.601 ($a_u \rightarrow b_g^*$)	Crystal	560
	0.516 (b_g)	−0.013 (a_u^*)	0.529 ($b_g \rightarrow a_u^*$)		668

[a] Reference 10.

bonding decreases in the order ethanol, $CHCl_3$, and CCl_4 as reflected by the absorption maxima in these solvents. At the same time, intermolecular hydrogen bonding, case c, is indicated to decrease the energy of the lowest transition. In practice, it may not be possible to distinguish between a and b, and case a quite likely represents a hypothetical situation. It is thought that case d resembles the situation in the crystalline solid state. In the dimer, which belongs to point group C_{2h},[11] the HOMO and LUMO of the monomer are each split into dimer orbitals of a_u or b_g symmetry. The allowed[11] electronic transitions are then $a_u \rightarrow b_g^*$ and $b_g \rightarrow a_u^*$ which, as indicated in Table I, are predicted to appear at lower energies than those of the free molecule, in agreement with experimental findings. Similarly, the lower transition energy in the situation involving intermolecular hydrogen bonding is also in agreement with experiment.

The general features of the hydrogen-bonding models for the amorphous state of indigo were confirmed by infrared spectroscopy. Thus, the crystalline state is completely H bonded, as seen by the dominance of an NH bonded frequency at 3285 cm^{-1}. The infrared spectrum of the amorphous state is characterized by both free NH (3378 cm^{-1}) and bonded NH (3285 cm^{-1}) transitions. Also the carbonyl region[4] indicates that free C=O sites are in greater abundance in the amorphous state than in the crystalline phase. Therefore it is not surprising that the λ_{max} of the lowest π-π^* transition in amorphous indigo (640 nm) lies at higher energy than the crystal (668 nm). The amorphous form, most likely, represents a disordered array of the H-bonded situations shown in Figure 2.

It is pertinent to note that similar changes in spectral features do not occur where the NH moiety in indigo is replaced by O, S, or Se. In addition, indigoid molecules with bulky substituents on the 4, 5, and/or 7 positions do not show hydrogen-bonding shifts between solution and solid phases,[4] since the sterically hindering groups prevent the interaction of CO and NH groups on neighboring molecules. For example, 5,5′,7,7′-tetrabromoindigo in either $CHCl_3$ or the solid state shows no discernible difference between the peak maxima in the visible region.[4] The electronic absorption properties supported by the simple MO model do, however, clearly demonstrate that dramatic spectral differences are to be expected between the spectra of crystalline and amorphous dyes when strong H-bonding forces are the dominant intermolecular interaction.

Registry No.—Indigo, 482-89-3.

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(10) M. Klessinger and M. Lüttke, *Chem. Ber.*, **99**, 2136 (1966).

(11) F. A. Cotton, "Chemical Applications of Group Theory," Interscience, New York, N. Y., 1963.

Reactions of N-Substituted Maleamic Acids with Thionyl Chloride and Chloroacetyl Chloride

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N-Substituted maleamic acids are dehydrated to either the corresponding maleimide or the maleisoimide, depending on the dehydration conditions and the nature of the substituent.[1] When powerful dehydrating agents such as trifluoroacetic anhydride, *N,N′*-dicyclohexylcarbodiimide, or ethyl chloroformate are allowed to react with maleamic acids in the presence of triethylamine, maleisoimides are formed as the main products. Other dehydrating agents yield the corresponding imides or mixtures of imides and maleisoimides.[2] Recently N-substituted maleisoimides have been prepared using mild dehydrating agents, such as acetyl chloride, or even weak dehydrating agents, such as acetic anhydride, under controlled conditions.[1a,b] In this report the effects of thionyl chloride and chloroacetyl chloride on N-substituted maleamic acids will be presented.

The behavior of thionyl chloride toward N-substituted maleamic acids depends on the nature of the substituent and also on the temperature. A few reports have been published regarding the effects of thionyl chloride on N-substituted maleamic acids. Feuer and Rubenstein[3] reported the preparation of *N*-benzenesulfonylaminomaleimide and bismaleimide by refluxing the corresponding maleamic acids with thionyl chloride. The bismaleimide was found recently to have the bismaleisoimide structure.[4] Others[5] have utilized boiling thionyl chloride for the prepara-

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(1) (a) T. M. Pyriadi and H. J. Harwood, *J. Org. Chem.*, **36**, 821 (1971); (b) T. M. Pyriadi, Ph.D. Thesis, The University of Akron, Akron, Ohio, 1970.

(2) R. J. Cotter, C. K. Sauers, and J. M. Whelan, *J. Org. Chem.*, **26**, 10 (1961).

(3) H. Feuer and H. Rubinstein, *J. Amer. Chem. Soc.*, **80**, 5873 (1958).

(4) H. Feuer, *J. Org. Chem.*, **36**, 3372 (1971).

(5) W. R. Roderick and P. L. Bhatia, *ibid.*, **28**, 2018 (1963), and references cited therein.

TABLE I

PRODUCTS FROM THE REACTION OF THIONYL CHLORIDE WITH N-SUBSTITUTED MALEAMIC ACIDS AT DIFFERENT CONDITIONS

NR	Temp, °C	Mol of $SOCl_2$	Mol of Et_3N	Time, min	Product	Yield, %
Phenyl	−20	1	1	30	*N*-Phenylmaleimide	9
Phenyl	0–5	1	2	17	α-Chloro-*N*-(phenyl)succinimide	26
Phenyl	25	1	2	40	α-Chloro-*N*-(phenyl)succinimide	40
Phenyl	40	Excess[a]	0	10	α-Chloro-*N*-(phenyl)succinimide	50
Phenyl	78	Excess[a]	0	30	α-Chloro-*N*-(phenyl)succinimide	57
Propyl	−20	1	1	40	*N*-Propylmaleimide	3
Propyl	78	Excess[a]	0	10	*N*-Propylmaleimide	6
Ethyl	25	1	1	45	*N*-Ethylmaleimide	16
p-Methoxyphenyl	−20	1	1	30	*N*-(*p*-Methoxyphenyl)maleimide	4
p-Methoxyphenyl	78	Excess[a]	0	40	*N*-(*p*-Methoxyphenyl)maleimide and α-chloro-*N*-(*p*-methoxyphenyl)succinimide in the ratio 1:6	62
p-Nitrophenyl	25	1	2	40	α-Chloro-*N*-(*p*-nitrophenyl)succinimide	8
p-Nitrophenyl	78	Excess[a]	0	45	α-Chloro-*N*-(*p*-nitrophenyl)succinimide	85

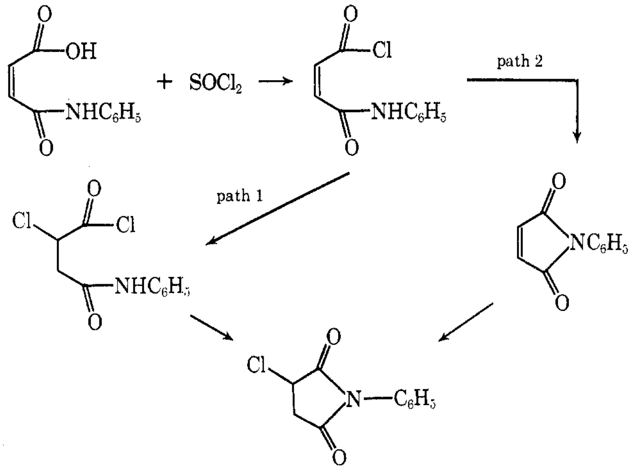
[a] The maleamic acid was refluxed in excess thionyl chloride; otherwise methylene chloride was used as a solvent.

tion of maleimides. On the other hand, Kretov and Kul'chitskaya[6] reported the preparation of several *N*-arylimides of chorosuccinic acid by allowing thionyl chloride to react with *N*-arylmaleamic acids at temperatures ranging from 12 to 78°. These reactions and related ones have been studied here at temperatures from −25 to 78° with and without triethylamine as a catalyst.

The reaction of *N*-phenylmaleamic acid with thionyl chloride in methylene chloride in the presence of 1 or 2 equiv of triethylamine at 0–5° yielded only α-chloro-*N*-phenylsuccinimide. When the reaction was conducted at −20°, *N*-phenylmaleimide was the sole product. Excess thionyl chloride alone reacted with *N*-phenylmaleamic acid at room temperature, 40°, and at reflux, yielding always α-chloro-*N*-phenylsuccinimide.

It seems possible that the chlorosuccinimide arose from the addition of hydrogen chloride, formed in the reaction, to either *N*-phenylmaleimide or an intermediate product, perhaps *N*-phenylmaleamoyl chloride, as shown in Scheme I.

SCHEME I



In another experiment, *N*-phenylmaleimide in methylene chloride solution was mixed with thionyl chloride, and 1 equiv of water was added to the mixture; no α-chloro-*N*-phenylsuccinimide could be detected in the mixture. This result was confirmed by another experiment in which moist hydrogen chloride was passed through a solution of *N*-phenylmaleimide in acetic acid, using the precedure of Roderick;[7] but no addition of hydrogen chloride to the maleimide was observed. The procedure was repeated using *N*-(*p*-methoxyphenyl)maleamic acid, and a 12% yield of α-chloro-*N*-(*p*-methoxyphenyl)succinimide was obtained. The conclusion here is that addition of hydrogen chloride must be mostly to the *N*-phenylmaleamoyl chloride or to the maleamic acid in Scheme I.

When *N*-(*p*-methoxyphenyl)maleamic acid was refluxed with thionyl chloride, a mixture of *N*-(*p*-methoxyphenyl)maleimide and α-chloro-*N*-(*p*-methoxyphenyl)succinimide was formed. This result is in contrast to the report of Kretov and Kul'chitskaya,[6] where they have reported the preparation of α-chloro-*N*-(*p*-anisyl)succinimide by treating thionyl chloride with *N*-(*p*-anisyl)maleamic acid. The general results of Kretov's report, however, agree with the findings here, in that their reported yields of α-chloro-*N*-arylsuccinimides are relatively higher for compounds having electron-accepting groups on the nitrogen [the highest yield reported is for α-chloro-*N*-(*p*-nitrophenyl)succinimide, 84%, while the yield of the corresponding *N*-(*m*-nitrophenyl) derivative is 79%].

When *N*-ethyl- and *N*-propylmaleamic acids were allowed to react with thionyl chloride in the presence of triethylamine at −20 or 25°, the products were *N*-ethylmaleimide and *N*-propylmaleimide, respectively. The last product was also obtained when *N*-propylmaleamic acid was refluxed with thionyl chloride.

On the other hand, when *N*-(*p*-nitrophenyl)maleamic acid was dehydrated with thionyl chloride at room temperature in the presence of excess triethylamine, the product was only α-chloro-*N*-(*p*-nitrophenyl)succinimide. The results of these experiments are listed in Table I.

Therefore, it seems that the products of the dehydration of N-substituted maleamic acids with thionyl chloride are highly dependent on the nature of the substituent. Generally, electron-releasing substituents favor the formation of the maleimide, while electron-accepting substituents tend to favor the formation of α-chloro N-substituted succinimides. This conclusion is in accord with the results obtained in

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(6) A. E. Kretov and N. E. Kul'chitskaya, *J. Gen. Chem. USSR*, **26**, 221 (1956).

(7) W. R. Roderick, *J. Org. Chem.*, **79**, 1710 (1957).

the reactions of 1,2-bis(3-carboxyacryloyl)hydrazine and 1-benzenesulfenyl-2-(3-carboxyacryloyl)hydrazine with boiling thionyl chloride.[3] The result is also in accord with the preparation of *N*-phenyl, *N*-(*p*-nitrophenyl), and *N*-(*m*-nitrophenyl) derivatives of α-chlorosuccinimide.[6]

Generally, the addition of hydrogen chloride to N-substituted maleimides is expected to be slower than addition to the corresponding maleamoyl chlorides suggested in Scheme I. However, substituents on the nitrogen of the maleimide would have a great effect on the rate of addition of hydrogen chloride. Such an effect would be opposite to the conclusions mentioned above regarding the addition to N-substituted maleamoyl chloride (Scheme I).

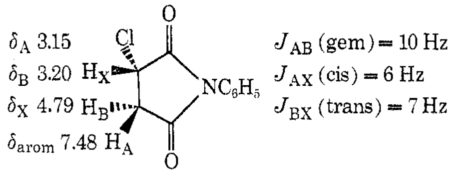
It appears that thionyl chloride may form N-substituted maleisoimides provided that the products are highly stabilized. The bismaleisoimide, prepared by Feuer,[4] seems to be the first maleisoimide reported from the dehydration of maleamic acids with thionyl chloride.

Chloroacetyl chloride reacted with *N*-phenylmaleamic acid in the presence of 1 molar equiv of triethylamine at 0–5°, forming *N*-phenylmaleisoimide in 54% yield.[8] When 2 molar equiv of triethylamine was employed, the product was only *N*-phenylmaleimide, no isoimide being detected in the infrared spectrum of the compound. These results are in agreement with previously suggested mechanism.[1a]

Experimental Section

Preparation of Maleamic Acids.—The procedures used here were similar to those in a previous work.[1a]

Reaction of *N*-Phenylmaleamic Acid with Thionyl Chloride in Presence or Absence of Triethylamine.—To a solution of 0.025 mol of *N*-phenylmaleamic acid in 100 ml of methylene chloride, 0.025 mol of triethylamine was added. The mixture was cooled in an ice bath to 0.5°. Thionyl chloride (0.025 mol) was added dropwise during 5 min, after which stirring was continued for 10 min. A violent reaction and fuming was observed at the beginning and an orange solution formed. The mixture was filtered from a small amount of triethylamine hydrochloride and the filtrate was stirred with excess dilute sodium bicarbonate solution for 50 min. The methylene chloride layer was then washed with water and dried with anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The orange-yellow solid that remained was recrystallized from boiling water to obtain 0.2 g (26%) of α-chloro-*N*-phenylsuccinimide, mp 118–119°. Ir (CCl_4) showed C=O absorption at 1728 cm^{-1} and no absorption was observed around 1650 cm^{-1}, indicating the absence of a carbon–carbon double bond. The nmr spectrum showed an ABX-type pattern as follows.[9]



Using excess triethylamine in this reaction resulted in a 40% yield of α-chloro-*N*-phenylsuccinimide when the reaction was conducted at 25°. When *N*-phenylmaleamic acid was allowed to react with excess thionyl chloride at 40°, the yield was 50%. The optimum yield (57%) was obtained when the last mixture was refluxed for 0.5 hr. When the amic acid and 1 equiv of thionyl chloride were allowed to react at −20° (Dry Ice–acetone bath), the product was *N*-phenylmaleimide (9.5% yield), mp 88° (lit.[10] mp 89–89.8°).

Reaction of Thionyl Chloride with *N*-Phenylmaleimide in Presence of Water.—In a three-necked flask *N*-phenylmaleimide[10] (0.01 mol) and thionyl chloride (0.01 mol) in 40 ml of methylene chloride were stirred and warmed to about 30°. Water (0.01 mol) was then added drop by drop. A violent reaction occurred in the beginning and hydrogen chloride was evolved, but without any change in the color of the solution. The solution was washed with water and dried with anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The residue was unchanged *N*-phenylmaleimide, mp 88–89°.

Separation of *N*-(*p*-Methoxyphenyl)maleimide from α-Chloro-*N*-(*p*-methoxyphenyl)succinimide.—The solid yellow product left from refluxing thionyl chloride with *N*-(*p*-methoxyphenyl)-maleamic acid was dissolved in alcohol by heating, filtered, and cooled. A white precipitate was obtained by filtration. When the filtrate was evaporated, yellow crystals of *N*-(*p*-methoxyphenyl)maleimide were obtained, mp 148° (lit. mp 148–149°).[7] This last compound showed the presence of chlorine on sodium fusion, while the corresponding imide did not.

Anal. Calcd for $C_{11}H_{10}O_3NCl$: C, 55.12; H, 4.21; N, 5.84. Found: C, 55.27; H, 4.03; N, 5.64. *Anal.* Calcd for $C_{11}H_9O_3N$: C, 65.02; H, 4.43; N, 6.89. Found: C, 65.11; H, 4.42; N, 6.77.

Registry No.—Thionyl chloride, 7719-09-7; chloroacetyl chloride, 79-04-9; *N*-phenylmaleamic acid, 555-59-9; *N*-propylmaleamic acid, 36342-07-1; *N*-ethylmaleamic acid, 4166-67-0; *N*-(*p*-methoxyphenyl)maleamic acid, 24870-10-8; *N*-(*p*-nitrophenyl)maleamic acid, 36342-10-6; 2-chloro-*N*-phenylsuccinimide, 36342-11-7; *N*-phenylmaleimide, 941-69-5; *N*-(*p*-methoxyphenyl)maleimide, 1081-17-0; 2-chloro-*N*-(*p*-methoxyphenyl)succinimide, 36342-13-9.

Acknowledgment.—The author is grateful to the College of Pharmacy, University of Baghdad, for providing space, reagents, and equipment.

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(8) For experimental procedure see ref 1a.

(9) The coupling constants were calculated according to A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969.

(10) *Org. Syn.*, **41**, 94 (1961).

The Bromination of Perdeuterionaphthalene[1]

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Aromatic bromination is known to proceed by the two-step sequence shown.

$$ArH + Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArHBr^+ + Br^-$$

$$ArHBr^+ \xrightarrow{k_2} ArBr + H^+$$

If the first step is rate controlling ($k_2 \gg k_{-1}$), the observed rate constant varies with bromide ion concentration according to the equation $k_{obsd} = k_1K/(K + Br^-)$ (eq 1), where K is the dissociation constant of the tribromide ion and k_1 the true rate constant of bromination by free, uncomplexed bromine.[3] If the second step is partially or completely rate determining, a different dependence on bromide ion is obtained.[4,5] In

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(1) Kinetics of Aromatic Halogenation. XIII.

(2) Taken from the M. A. Thesis of Albert Ehrlich, Bryn Mawr College, 1969.

(3) E. Berliner and M. C. Beckett, *J. Amer. Chem. Soc.*, **79**, 1425 (1957).

(4) E. Berliner, J. B. Kim, and M. Link, *J. Org. Chem.*, **33**, 1160 (1968).

(5) B. T. Baliga and A. N. Bourns, *Can. J. Chem.*, **44**, 363, 379 (1966).