At the end of the reaction time, the contents were cooled to 110° and 30 ml. of chloroform was added. The dark brown-maroon solution was chromatographed directly on Florisil[19] (elution with acetone–hexane, 1:1) to give the colorless products as the only identifiable materials.

In all cases a substantial amount of red-brown polymer was produced, and quantities of the hydroxylamines and vinylpyridines were recovered in the early fractions of the distillations.

2-[2-(1-Pyrrolidinyl)ethyl]pyridine N-Oxide Dihydrochloride (II· 2HCl).—A solution of 7.9 g. (0.045 mole) of 2-(2-pyrrolidinylethyl)pyridine and 5.4 g. of 30% hydrogen peroxide (0.0475 mole) in 30 ml. of absolute ethanol was allowed to stand at room temperature with occasional swirling for 4 days. Platinum-on-charcoal (5%) was added to decompose any residual peroxide. After filtration, the filtrate was evaporated under reduced pressure to give an uncrystallizable yellow oil. This material was treated with ethereal hydrogen chloride in the usual manner and the precipitated white solid was filtered and dried to afford 6.8 g. (57.1%) of II dihydrochloride, m.p. 165–166°. Three recrystallizations of the salt from ethanol–ether (Darco G-60) gave pure N-oxide dihydrochloride as pale yellow blades m.p. 166–167.5°.

Anal. Calcd. for $C_{11}H_{18}Cl_2N_2O$: C, 49.82; H, 6.84; N, 10.57; equiv. wt. 133. Found: C, 49.74; H, 6.95; N, 10.38; equiv. wt. 133.

λ_{max}^{EtOH} 238sh (2,950), 243 (3,050), 254.5 (3,250), 261 (3,600), 268 (3,000), 277sh (1,150), 285sh (957), and 295sh mμ (432).

The free N-oxide was prepared by dissolving the dihydrochloride in ethanol and slowly adding two equivalents of a dilute ethanolic sodium hydroxide solution. The precipitated sodium chloride was filtered and the filtrate was concentrated to give a yellow oil.

Pyrolysis of II.—A 3.0-g. sample of II was placed in an oil bath at 180° under reduced pressure. A colorless liquid soon began to distil, b.p. 43–64° (13 mm.), 1.60 g. Raising of the bath temperature to 230° afforded no additional material; a dark red-brown polymer remained in the heel of the distilling flask. Vapor phase chromatography of the distillate[14] indicated that it was a two-component system. 2-Vinylpyridine and N-hydroxypyrrolidine had the same retention times as the constituents of the distillate.

Polynuclear Heterocycles. II. Addition Reactions of Benzophenazines

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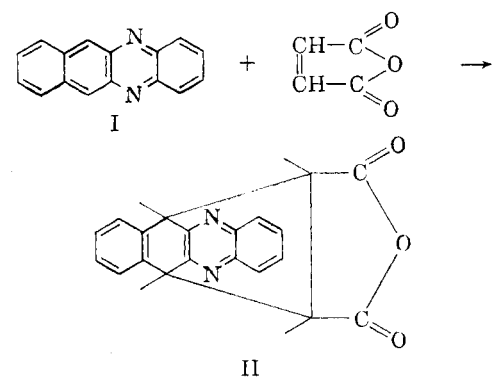
Benzo[*a*]-, benzo[*b*]-, dibenzo[*a,i*]-, and dibenzo[*h,i*]phenazine are utilized as diene components under typical Diels-Alder conditions, and structures are assigned to the adducts formed with maleic anhydride, diethyl maleate, benzoquinone, and dimethyl acetylenedicarboxylate. The reaction between these phenazine derivatives and nucleophilic agents such as benzenesulfinic acid, aromatic amines, and mercaptans is described, and the structure of the products was determined by the use of substituted phenazine derivatives. Spectral data, as they relate to the assignment of structures, are discussed.

Numerous attempts to use the double bond system of an aromatic nucleus as a diene component have been described in the literature. Attempts to add maleic anhydride to phenanthrene, chrysene, or pyrene were unsuccessful.[1]

Anthracene, its homologs and its derivatives, as well as numerous benzo derivatives of anthracene, such as naphthacene, add maleic anhydride readily across the *meso* positions.[1]

As a continuation of our studies[2] in the azanaphthacene series, we investigated the reaction of maleic anhydride with benzo[*b*]phenazine (I), which is structurally analogous to naphthacene.

These components react readily in an inert solvent to give benzo[*b*]phenazine-6,11-*endo*succinic anhydride (II).[3] The latter structure is preferred to the alternative structures in which the maleic



I II

anhydride has added either across the 1,4-positions or across the nitrogen atoms for the following reasons: A. The parent compound phenazine, which has essentially the same bond structure as I and differs only in the absence of the fused benzo group, does not add maleic anhydride.[4] B. If addition of maleic anhydride had occurred across the nitrogen atoms, the ultraviolet absorption spectrum of the adduct should be similar to that of the dihydrophenazines, whereas it is quite different. This point

(1) "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 485, summarizes the work in this field.

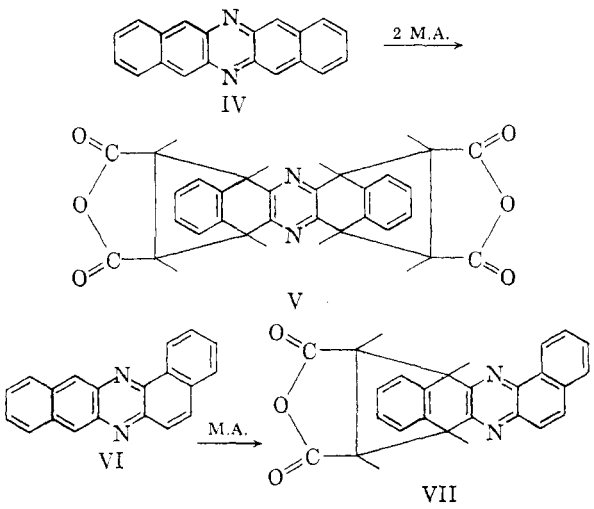
(2) J. A. VanAllan, G. A. Reynolds, and R. E. Adel, *J. Org. Chem.*, **27**, 1659 (1962).

(3) According to the rules suggested by the International Union of Pure and Applied Chemistry, *J. Am. Chem. Soc.*, **82**, 5545 (1960), the generic name of II is 6,11-dihydro-6,11-ethano-5,12-diazanaphthacene-13,14-dicarboxylic anhydride; IIa is diethyl 6,11-dihydro-6,11-ethano-5,12-diazanaphthacene-13,14-dicarboxylate; IIb is 6,11,13,14,-15,18-hexahydro-15,16-dioxo-5,11-diaza-13,14-benzenonaphthacene. For convenience and brevity, we have used the additive name.

(4) M. Lora Tomayo, R. Perez Ossaris, and M. Sanz Burati, *Anales real. soc. españ. fis. y quím.* (Madrid), **50B**, 865 (1954); *Chem. Abstr.*, **50**, 361 (1956).

will be discussed later. Diethyl maleate, benzoquinone, and dimethyl acetylenedicarboxylate react with I to give diethyl benzo[*b*]phenazine-6,11-*endo*succinate (IIa),[3] benzo[*b*]phenazine-6,11-*endo*-dihydrobenzoquinone (IIb),[3] and dimethyl benzo-[*b*]phenazine-6,11-*endo*maleate (IIc), respectively, demonstrating that the reaction is a typical Diels-Alder reaction.

Since the extension of the Diels-Alder reaction to heterocyclic systems of this type is new, it was of interest to examine its scope. Accordingly, benzo-[*a*]phenazine (III) was prepared and found to be completely unreactive toward maleic anhydride. On the other hand, dibenzo[*b,i*]phenazine (IV) reacts with two moles of maleic anhydride to give the adduct V. Dibenzo[*a,i*]phenazine (VI), which may be considered to be a composite of I and III, adds maleic anhydride and dimethylacetylene dicarboxylate to give VII and dibenzo[*a,i*]phenazine-8,13-*endo*succinate (VIIa), respectively.



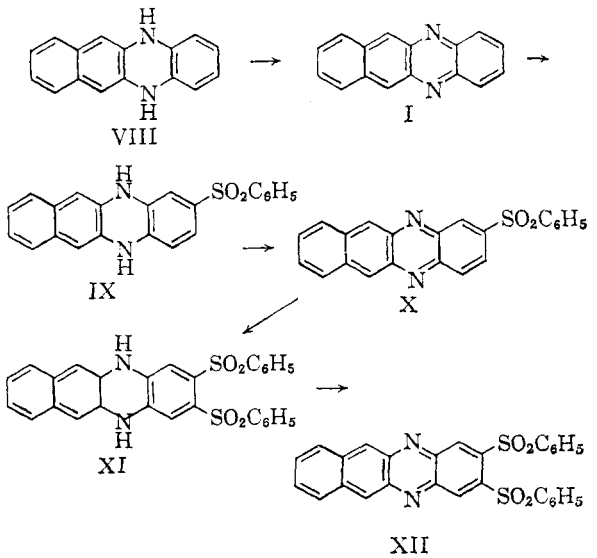
The infrared spectra of the maleic anhydride adducts show the presence of an anhydride group.[5] It is known that pentacene and benzo[*a*]anthracene add dienophiles across the *meso* positions. It is assumed, by analogy, that addition has taken place across the *meso* position in this heterocyclic series. The ultraviolet spectra confirm this assignment, as will be discussed later.

In contrast to the carbocyclic series, which requires the presence of at least two linear fused rings,[6] the analogs of this series require at least four linear fused rings for the addition of a dienophile to take place. Attempts to add maleic anhydride to 2,3-diphenyl-6,7-benzoquinoxaline, which has three linear fused rings, were unsuccessful.

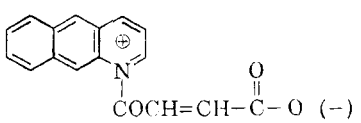
Having thus established the reactivity of the *meso* positions of benzo[*b*]phenazine, we turned our attention to the addition reactions of the quinoid type system of I.

In 1896, Hinsberg[7] observed that phenazine and benzenesulfinic acid reacted to form 2-phenylsulfonylphenazine; the yield was poor, because the intermediate phenylsulfonyldihydrophenazine underwent disproportionation. The product was thought to be a 2-derivative, since phenazine is structurally analogous to an orthoquinone. Bradley and Hannon[8] confirmed the 2-orientation but considered that its formation by quinone-type addition was unlikely. A nitrogen-to-carbon migration of the sulfonyl group, such as occurs in azobenzene, appeared to them to be more probable, following 5:10 addition of the sulfinic acid to the azine nucleus. They have further demonstrated that 2-phenylsulfonylphenazine adds a second phenylsulfonyl group in a similar manner to give 2,7-bis(phenylsulfonyl)phenazine. Their reluctance to accept the quinoid addition mechanism is based on the failure of other nucleophilic reagents such as aniline to add to phenazine. Because we have added other nucleophilic reagents to I, and for other reasons detailed later, we believe that the rearrangement mechanism is open to question.

Since 5,12-dihydrobenzo[*b*]phenazine (VIII) and its derivatives are much more stable[9] than 5,10-dihydrophenazine, they are free from the complications mentioned previously. Thus, I readily adds benzenesulfinic acid to give 2-phenylsulfonyl-5,12-dihydrobenzo[*b*]phenazine (IX) which, after oxidation to X, adds a second mole of benzenesulfinic



(5) *Cf.*, 1-azaanthracene which, with maleic anhydride, gives an adduct of structure



Y. Etienne, *Ann. chim.* [12], **1**, 33 (1946).

(6) J. G. Martin, *Chem. Rev.*, **61**, 537 (1961).

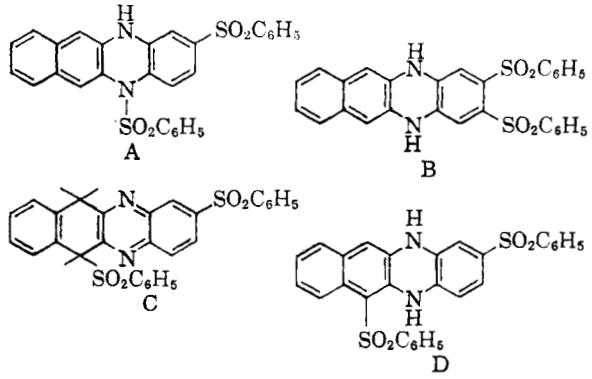
(7) O. Hinsberg and A. Himmelschein, *Ber.*, **29**, 2020 (1896).

(8) W. Bradley and J. Hannon, *Chem. Ind.*, 540 (1959).

(9) G. M. Badger, R. S. Pearce, and R. Pettit, *J. Chem. Soc.*, 3199 (1951).

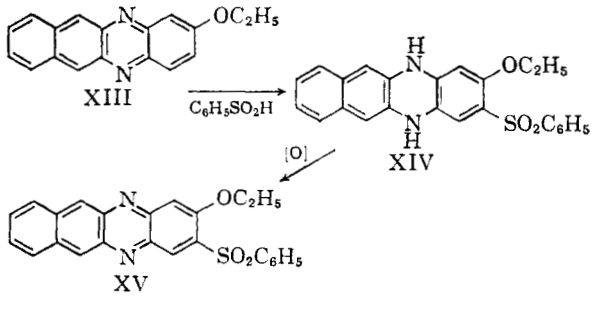
acid to give 2,3-bis(phenylsulfonyl)-5,12-dihydrobenzo[*b*]phenazine (XI).

Examination of the ultraviolet absorption spectrum of XI leaves little doubt that the adduct is a dihydrophenazine. The more probable modes of addition of the second phenylsulfonyl group are shown in structures A, B, C, and D.



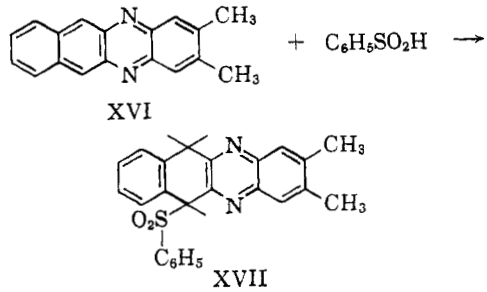
Since XI may be oxidized to 2,x-diphenylsulfonylbenzo[*b*]phenazine (XII), structure A may be excluded, provided no rearrangement has occurred during the oxidation. The spectrum of adduct C would resemble that of the maleic anhydride addition product (II). The spectrum of XI is quite different, which eliminates C from consideration. Structure D would result from the 6,11-addition of benzenesulfinic acid to IX, followed by rearrangement of the hydrogen atoms. This possibility is rejected because there is no precedent for this type of addition in the analogous carbocyclic series (*i.e.*, naphthacene). Structure B is therefore the preferred structure for XI.

2-Ethoxybenzo[*b*]phenazine (XIII), which contains an electron-donating group, reacts with benzenesulfinic acid to give 2-ethoxy-3-phenylsulfonyl-5,11-dihydrobenzo[*b*]phenazine (XIV). Oxidation of XIV gives 2-ethoxy-3-phenylsulfonylbenzo[*b*]-phenazine (XV). These structures are assigned because of the similarity of their ultraviolet absorption spectra to those of X and XI.



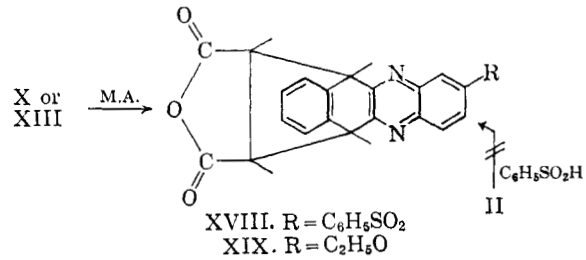
These limited data suggest that the addition of benzenesulfinic acid to the benzo[*b*]phenazine nucleus is not greatly influenced by the presence of electron-withdrawing groups ($C_6H_5SO_2^-$) or by electron-donating groups ($C_2H_5O^-$).

In 2,3-dimethylbenzo[*b*]phenazine (XVI), the 2,3-positions, at which addition of the benzenesulfinic acid is presumed to occur, are blocked. However, an adduct is obtained with these components which is assumed to be 6,11-dihydro-2,3-dimethyl-6-phenylsulfonylbenzo[*b*]phenazine (XVII), since its ultraviolet absorption spectrum resembles very closely that of II.



The evidence presented suggests that nucleophilic reagents preferentially add at the 2,3-positions if these positions are not substituted; if they are, addition occurs at the 6- or 11-position. In symmetrical molecules the latter positions are equivalent.

Maleic anhydride reacts readily with 2-phenylsulfonylbenzo[*b*]phenazine (X) and the 3-ethoxy derivative (XIII) to give the adducts XVIII and XIX, respectively, indicating that the 6,11-positions in these compounds still retain their reactivity. Benzo[*b*]phenazine-6,11-*endo*succinic anhydride (II) does not add benzenesulfinic acid. The orthoquinoid structure in II is apparently seriously disturbed, as shown by the profound differences between the ultraviolet spectrum of II and that of the benzo[*b*]phenazines.



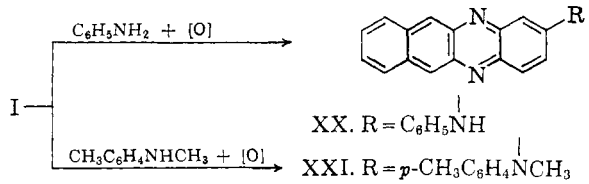
Benzo[*a*]phenazine (III) does not react with benzenesulfinic acid while dibenzo[*b*,*i*]phenazine (IV) appears to add one mole of benzenesulfinic acid. However, because of the difficulty in preparing pure IV and the insolubility of the adduct, an analytically pure product could not be prepared.

Dibenzo[*a*,*i*]phenazine (VI), which adds maleic anhydride readily, is completely inert toward benzenesulfinic acid. This behavior is almost certainly related to the fine structure of IV (*cf.* discussion of ultraviolet spectra), but the relation is not clear.

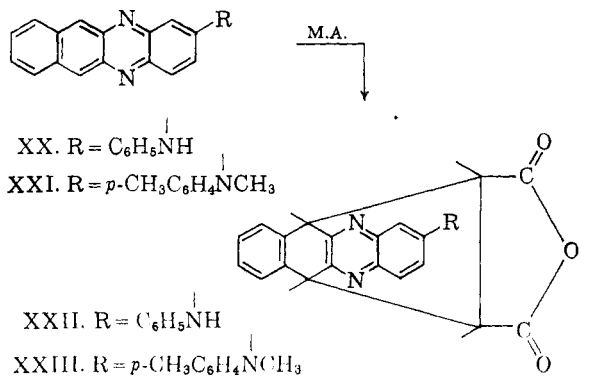
Other nucleophilic reagents, such as aniline[10] and N-methyl-*p*-toluidine, also react with benzo[*b*]-

(10) O. Hinsberg, *Ann.*, **319**, 257 (1901).

phenazine (I) to give 2-anilinobenzo[*b*]phenazine (XX) and 2-(N-methyl-*p*-toluidino)-benzo[*b*]-phenazine (XXI), respectively. The substituent groups are assigned the 2-position by analogy with the substitution of phenazine which adds benzenesulfinic acid in the 2-position.



The ultraviolet spectra of XX and XXI are very similar to the spectrum of I, indicating the presence of the phenazine system, rather than the dihydrophenazine system. Presumably, air oxidizes the initial adduct. The addition of maleic anhydride to XX and XXI to give 2-anilino-6,11-*endo*succinic anhydride benzo[*b*]phenazine (XXII) and 2-(N-methyltoluidino)-6,11-*endo*succinic anhydride benzo[*b*]phenazine (XXIII), respectively, confirms the presence of the azine system in XX and XXI, since 5,12-dihydrobenzo[*b*]phenazine and its derivatives do not add dienophiles.



Quite surprisingly, 2,3-dimethylbenzo[*b*]phenazine adds one mole of aniline. The initial addition product apparently undergoes aerial oxidation to give 2,3-dimethyl-6-anilinobenzo[*b*]phenazine (XXIV), since its ultraviolet absorption spectrum is typical of the benzo[*b*]phenazine series.

Attempts to add the nucleophilic reagents, mercaptoacetic acid, mercaptosuccinic acid, and *o*-mercaptobenzoic acid, to I gave 5,12-dihydrobenzo-[*b*]phenazine (VIII) as the only identifiable material.

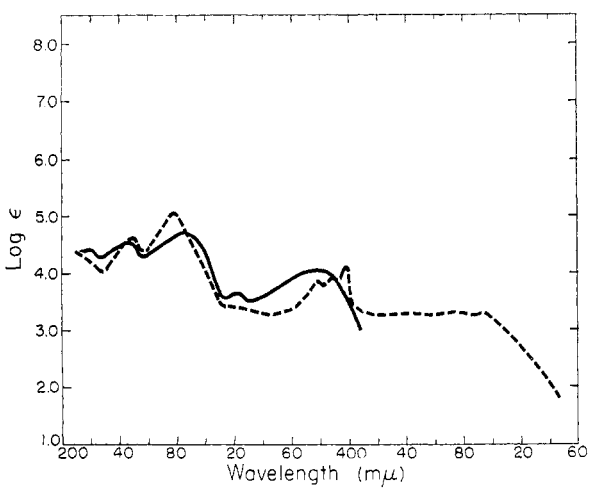


Fig. 1.—Benzo[*b*]phenazine - - -; N,N′-bis(β-cyanoethyl)-benzo[*b*]phenazine ——.

Discussion of Ultraviolet Spectra

In the following discussion, the ultraviolet spectra of the key compounds are compared and contrasted. This seemed necessary to enable the absorption spectra of the azacarbons to be used for structural determinations.

The azacarbons discussed here show three main regions of absorption (groups I, II, III) in the ultraviolet or in the visible region. The origin and nature of these bands in related materials are discussed in detail by Badger.[11]

The spectra of benzo[*b*]phenazine and its derivatives differ from those of the corresponding 5,12-dihydro derivatives in the following respects: (a) The band at about 400 μ has considerable fine structure in the phenazine derivatives, whereas the dihydro derivatives have a single broad band in this region. (b) The phenazines have considerable absorption in the visible region, but the dihydro derivatives have little, if any, absorption in the visible (Fig. 1).

The adduct of benzo[*b*]phenazine with maleic anhydride (II) has a distinctly different ultraviolet absorption spectrum from that of either benzo[*b*]-phenazine or of its 5,12-dihydro derivative. The spectrum of this adduct shows a maximum at 238 μ and at 318 μ. It is because of this difference that a structure in which the maleic anhydride has undergone a transannular addition across the nitrogen atoms is excluded. If such an addition occurred, the spectrum of the adduct would resemble the spectra of the 5,12-dihydrobenzo[*b*]phenazine series.

Moreover, the spectrum of the adduct (II) would be expected to resemble that of 2,3-dimethylquinoxaline, whereas, in fact, it is quite different (Fig. 2). The adduct with dibenzo[*a*,*i*]phenazine (VII) (Fig. 3) again has a spectrum greatly different from that of the parent azacarbon, but its absorption closely approximates that of 5-azaphenanthrene (Badger, ref. 11, p. 533). Clar[12] has observed a corresponding phenomenon in the linear and angular carbocyclic series. He has ascribed this abnormality to the asymmetry of the naphthalene residue in the linear hydrocarbons. There is little doubt that an analogous situation exists in the linear and angular phenazine series.

(11) G. M. Badger, "The Chemistry of Heterocyclic Compounds," Vol. 12, Interscience Publishers Inc., New York, N. Y., 1958, p. 551.
(12) E. Clar, *Ber.*, **65**, 503 (1932).

TABLE I
ANALYTICAL DATA

No.	M.p., °C.	Solvent of crystallization[a]	Solvent of Empirical Formula	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N	Lit. ref. or method of preparation
I	233	C								Ref. 10
II	394	C	$C_{20}H_{12}O_3N_2$	73.2	3.7	8.5	73.2	3.6	8.5	A
IIa	178	T + L	$C_{24}H_{22}O_4N_2$	71.5	5.0	7.0	71.7	5.2	6.8	A
IIb	>400	THF	$C_{22}H_{14}O_2N_2$	78.6	3.6	8.3	78.2	3.6	8.8	A
IIc	190	CH_3CN	$C_{22}H_{16}O_4N_2$	71.1	4.3	7.5	71.1	4.1	7.8	A
III	142									Ref. 13, 14
IV	*ca.* 340	THF/CH_3OH	$C_{20}H_{12}N_2$	85.7	4.3	10.0	85.8	4.6	8.9	D
V	>390	T	$C_{28}H_{16}O_6N_2$	70.6	3.7	6.1	70.4	3.4	5.9	A
VI	247	T								Ref. 10, D
VII	295	C	$C_{24}H_{14}O_3N_2$	76.4	3.7	7.4	76.1	3.6	7.2	A
VIIa	225	CH_3CN + A	$C_{26}H_{18}O_4N_2$	74.0	4.3	6.6	74.4	4.4	6.5	A
VIII	>400									Ref. 10
IX	290	C	$C_{22}H_{16}O_2N_2S$	71.1	4.3	7.5	71.2	4.6	7.3	[b]
X	268	C	$C_{22}H_{14}O_2N_2S$	71.3	3.8	7.6	71.6	4.1	7.2	D
XI	221	T	$C_{28}H_{20}O_4N_2S$	65.5	3.9	5.5	65.0	3.9	5.4	B
XII	>340	T	$C_{28}H_{18}O_4N_2S$	65.8	3.5	5.5	65.6	4.0	5.3	D
XIII	167	C	$C_{18}H_{14}ON_2$	78.8	5.2	10.2	78.8	5.5	10.3	D
XIV	*ca.* 205	T	$C_{24}H_{20}O_3N_2S$	69.3	4.8	6.7	69.0	4.5	6.3	B
XV	>260	T	$C_{24}H_{18}O_3N_2S$	69.6	4.3	6.7	69.0	4.7	6.7	D
XVI	273	C	$C_{18}H_{14}N_2$	83.7	5.5	10.8	83.6	5.6	10.9	D
XVII	>400	DMS	$C_{24}H_{20}O_2N_2S$	72.0	5.0	7.0	70.8	4.8	8.1	[c]
XVIII	285	T	$C_{26}H_{16}O_5N_2S$	66.8	3.4	6.0	66.2	3.6	5.9	A
XIX	211	C	$C_{22}H_{16}O_4N_2$	70.0	4.2	7.5	70.8	4.7	7.6	A
XX	*ca.* 290	DMF + A	$C_{22}H_{15}N_3$	82.1	4.7	13.0	82.5	5.1	12.9	C[d]
XXI	>365	DMF + A	$C_{24}H_{19}N_3$	82.5	5.4	12.0	82.1	5.2	12.0	C
XXII	326	THF	$C_{26}H_{17}O_3N_3$	74.5	4.1	10.0	73.9	3.9	9.5	A
XXIII	360	C	$C_{28}H_{21}O_3N_3$	75.0	4.7	9.4	75.0	4.7	8.5	A

[a] Abbreviations for solvents: C = cyclohexanone; T = trichlorobenzene; DMF = dimethylformamide; A = alcohol; T + L = toluene–ligroin; DMS = dimethyl sulfoxide; THF = tetrahydrofuran. [b] Hinsberg[10] mentions this compound but gives no physical properties. [c] We are not able to obtain an analytically pure product. [d] Hinsberg[10] describes an adduct presumed to be this, but its melting point of 155° is different from ours.

TABLE II
ULTRAVIOLET ABSORPTION SPECTRAL DATA

Substituent	I λ(mμ)	I ε	II λ(mμ)	II ε	III λ(mμ)	III ε	λ(mμ)	ε	λ(mμ)	ε
Benzo[*b*]phenazines										
None	248	4.65	288	4.96	398	4.13	466	3.32	494	3.27
					405	3.34				
2,3-Dimethyl	255	4.60	290	5.00	382	3.75	466	3.98	498	3.20
					392	3.85				
					406	4.01				
2-Phenylsulfonyl	248	4.79	295	5.12	385	3.30			498	2.48
					406	3.15				
2-Anilino	248	4.65	288	4.96	398	4.13	466	3.34	494	3.00
2,3-Diphenylsulfonyl	254	4.42	295	4.78	400	4.04	526	3.36	640	3.08
2-Ethoxy	262	4.62	288	5.01	388	4.02	474	3.58		
					389	4.10	506	3.45		
					405	4.15				
5,12-Dihydrobenzo[*b*]phenazines										
2-Phenylsulfonyl	250	4.30	298	4.77	408	3.95				
3-Phenylsulfonyl-2-C_2H_5O	260	4.78	292	4.99	420	4.36				
2,3-Diphenylsulfonyl	248	4.44	292	4.74	402	4.23				
N,N-Bis(β-cyanoethyl)	215	4.43								
	247	4.52	288	4.77	380	4.09				

The ultraviolet absorption data for benzo[*b*]-phenazine and some of its derivatives are contained in Tables II and III. The solvent in all cases is acetonitrile, except where indicated.

Experimental

The adducts of maleic anhydride and the phenazines were all prepared in a similar manner, which is illustrated by the following general procedure. The analytical results are collected in Table I.

Method A.—A mixture of the phenazine (0.01 mole) and the dienophile (0.02 mole) in 40 ml. of trichlorobenzene was refluxed until the red color of the phenazine had disappeared, *i.e.*, about 1.5–2 hr. The mixture was cooled, and the product was collected by filtration and crystallized from a suit-

(13) O. Hinsberg, *Ann.*, **237**, 327 (1887).
(14) F. Kehrmann and C. Mermod, *Helv. Chim. Acta*, **10**, 64 (1927).

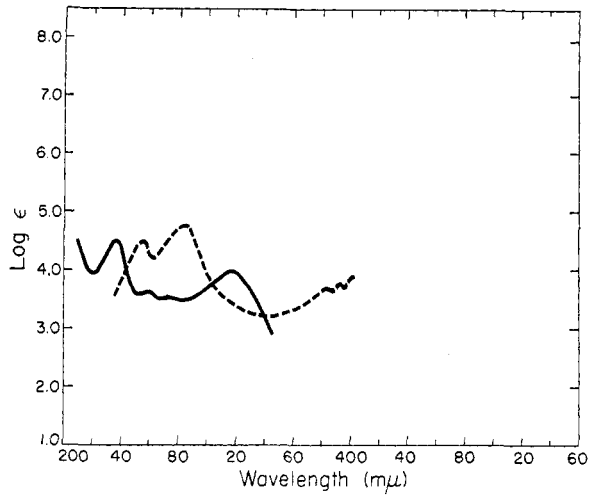


Fig. 2.—2,3-Dimethylquinoxaline ---· in dioxane; 6,11-*endo*succinic anhydride benzo[*b*]phenazine——.

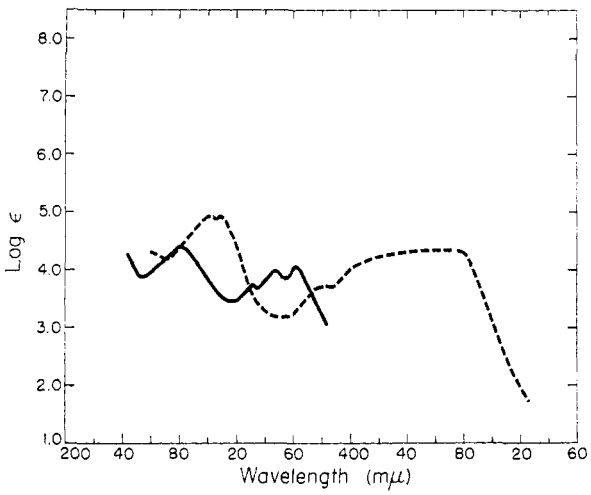


Fig. 3.—Dibenzo[*a,i*]phenazine ---, in dimethyformamide; 8,13-*endo*succinic anhydride dibenzo[*a,i*]phenazine ——, in dioxane.

TABLE III

SPECTRAL DATA FOR THE DIELS-ALDER ADDUCTS OF BENZO[*b*]PHENAZINE AND OF DIBENZO[*a,i*]PHENAZINE

Compound No.	λ(mμ)	log ε	λ(mμ)	log ε	λ(mμ)	log ε
II	238	4.51			318	4.00
IIc	245	4.43	279	4.18	318	4.04
					332	3.99
					468	2.30
					500	2.20
VII			282	4.43	332	3.75
					348	4.02
					365	4.10
VIIa	225	4.67	289	4.43	332	3.75
					348	4.02
					365	4.10

able solvent, giving a yield of purified product of the order of 80 to 90%.

Method B. Benzenesulfinic Acid Added to Phenazines.—A solution of 0.1 mole of the phenazine and 0.11 mole of benzenesulfinic acid sodium salt in 200 ml. of acetic acid was refluxed until the bright red solution had turned yellow, *i.e.*, about 0.5–1 hr. The reaction mixture was cooled, and the product was collected by filtration and purified by crystallization; yield, 84–89%.

Method C. Addition of Arylamines to Benzo[*b*]phenazine.—A mixture of benzo[*b*]phenazine[10] (2 g.) and an equal weight of the arylamine in 15 ml. of acetic acid was heated on the steam bath for 1 hr. After the mixture had cooled, the product was collected and crystallized from dimethylformamide and alcohol; yield, 60–70%.

Benzo[*b*]phenazine-6,11-*endo*diethylsuccinate (IIa).—A solution of 5 g. of I in 25 ml. of diethyl maleate was refluxed for 3 hr. Ligroin was added to the cold solution. The product separated and was crystallized from toluene–ligroin; yield, 4.3 g.

Method D. Oxidation of Dihydrophenazines to Phenazines.—The dihydrophenazine was dissolved in a minimum amount of warm pyridine and added to an equal weight of cupric acetate dihydrate dissolved in warm pyridine. The combined solutions were warmed on the steam bath while air was passed in for 0.5 hr. The reaction mixture was cooled and then flooded with methanol. The solid was isolated by filtration, washed well with water, then methanol, and dried. The product was then recrystallized from the appropriate solvent.

The Synthesis of 2-Substituted Imino-3-amino-4-thiazolidones

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Although 4-substituted thiosemicarbazides react with ethyl monochloroacetate or other derivatives of monochloroacetic acid to produce 1,3,4,-thiadiazine derivatives, their reaction in presence of sodium acetate furnishes 2-substituted imino-3-amino-4-thiazolidones. This structure was established by different reactions and chemical transformation to the known 2-phenylimino-4-thiazolidone.

The known reactions of monochloroacetic acid or its derivatives with thiosemicarbazide, 4-substituted thiosemicarbazides or thiosemicarbazones follow two different paths. 1,3,4-Thiadiazine derivatives were obtained from 4-methyl- or 4-ethylthiosemicarbazide and monochloroacetic acid[1] in the presence of sodium acetate or with ethyl monochloroacetate[2] and some other substituted thiosemicarbazides. A compound of this type was claimed to be obtained when treating thiosemicarbazide with

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