washed with water and recrystallized from a small quantity of water. For analysis the crystals were dried at 1–2 mm. and 50–60° for one hour (Table V).

Natural Antimycic Acid Methyl Ester-methyl Ether.—Seventy-five mg. of natural antimycic acid was suspended in 1 ml. of methanol and to this mixture diazomethane solution was added until the color of the latter remained. The solution was set aside for one hour and the excess of diazomethane and the solvent then removed under reduced pressure. The product was recrystallized from ethyl acetate to give a yield of 26 mg. (31%) of m.p. 155–156°.[2]

Acknowledgment.—We wish to acknowledge gratefully the help given us by the Tanabe Pharmaceutical Co. (Osaka, Japan).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF DELAWARE]

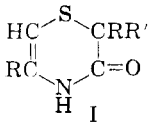
Some Derivatives of 2,3-Dihydro-4H-1,4-thiazin-3-one and 1,4-Thiazane

BY GLENN S. SKINNER, JAMES S. ELMSLIE AND JAMES D. GABBERT

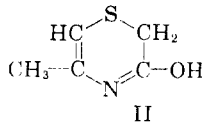
RECEIVED DECEMBER 16, 1958

A series of dialkylmercaptoacetamides has been prepared and condensed with α-halocarbonyl compounds to give intermediate cyclic keto alcohols which were dehydrated to 2,2-dialkyl-2,3-dihydro-4*H*-1,4-thiazin-3-ones. Some of these in turn were oxidized to the sulfone and, in case of hydrogen at position 5, also to the epoxide.

Dialkylmercaptoacetic acids and amides previously have been condensed with an α-haloacetamide to give the corresponding amide acid and the diamide,[1] both of which were converted to thiomorpholinediones. In the present work the dialkylmercaptoacetamides were condensed with α-chloroacetaldehyde and α-haloketones to form the



I



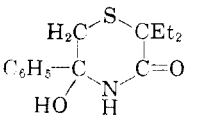
II

corresponding 2,3-dihydro-4*H*-1,4-thiazin-3-ones (I). These compounds are not known, but a monoalkyl derivative believed to have the lactim structure has been reported (II).[2]

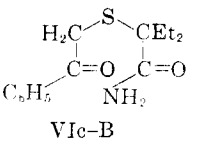
Only the dialkylmercaptoacetamide resulting from the alkaline hydrolysis of a 5,5-dialkyl-2-iminothioaolidone was used (Fig. 1) in the preparation of I. The mercaptoamide was therefore separated from the mercapto acid before use. The yield of the thioazolidone from the interaction of thiourea and the acid bromide was improved by lowering the temperature and extending the period of reaction. Hydrolysis of the thiazolidone with 5% sodium hydroxide for a shorter time (8–30 hours) gave better conversion to the mercaptoamide. When the hydrolysis of IIIa was continued for less than 16 hours, a third product was isolated which was identified as 5,5-diethyl-2,4-thiazolidinedione by comparing it with an authentic sample prepared by the acid hydrolysis of IIIa.[3,4]

When Clemmensen and Heitman[5] hydrolyzed IIIa with barium hydroxide, they obtained an oil and a solid which they believed to be X and VII, respectively (Table I). The solid was crystallized from water (m.p. 147°). Pennington and coworkers,[6] who prepared VII by another method, reported it to be a low melting solid which they did not purify. They postulated that Clemmensen and Heitman had obtained the disulfide of diethylmercaptoacetamide. We have prepared this disulfide by air oxidation of VII and have found it to melt at 159–160°.

Several of the products from the condensation of VII, VIII and IX with chloroacetaldehyde, chloroacetone and phenacyl bromide were oils. During the distillation of these oils water was evolved indicating that the compounds of general formula I were formed by the dehydration of corresponding intermediates. In every condensation using pure VII a solid product precipitated from the reaction mixture. The reaction of VII with chloroacetaldehyde and chloroacetone, respectively, gave intermediates which were unstable at room temperature. The first lost one mole of water on standing in a desiccator over calcium chloride to yield Ia (Table II). The second yielded Ib upon standing at room temperature in a closed vial. The intermediate VIc from phenacyl bromide was stable at room temperature. However, it lost one mole of water to give Ic when refluxed in ethanol. The compound VIc has the empirical formula $C_{14}H_{19}NO_2S$ and could conceivably be VIc-A or VIc-B.



VIc-A



VIc-B

The infrared spectra of both VIa and VIc showed OH bands at 2.8 and 2.9 μ, respectively, which were absent in the dehydrated products Ia and Ic. Also, the spectra of VIa and VIc showed carbonyl bands at 6.1 and 6.0 μ respectively, which were still present in Ia and Ic (see Table III). In an attempt to prepare the *p*-nitrobenzoyl derivative of VIc the only product which could be iso-

(1) G. S. Skinner and J. B. Bicking, THIS JOURNAL, **76**, 2776 (1954).

(2) H. Sokol and J. J. Ritter, *ibid.*, **70**, 3517 (1948).

(3) W. J. Doran and H. A. Shonle, *J. Org. Chem.*, **3**, 193 (1938).

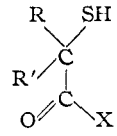
(4) H. Erlenmeyer and H. von Meyerberg, *Helv. Chim. Acta*, **20**, 1388 (1937).

(5) E. Clemmensen and A. H. C. Heitman, *Am. Chem. J.*, **40**, 280 (1908).

(6) F. C. Pennington, W. D. Cellmer, W. M. McLamore, V. V. Bogert and I. A. Solomans, THIS JOURNAL, **75**, 109 (1953)

TABLE I

DISUBSTITUTED MERCAPTOACETIC ACIDS AND AMIDES

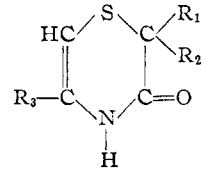


	X	R	R'	B.p., °C. (mm.)	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
VII	NH_2	C_2H_5	C_2H_5	109 (1.05)	9.52	9.45		
VIII	NH_2	C_2H_5	n-C_4H_9	103 (0.4)	7.99	7.86	15.91	15.51
IX	NH_2	C_2H_5	C_6H_5	M.p. 72°	7.16	7.15		
X	OH	C_2H_5	C_2H_5	86.0 (0.5)[a]			21.63	21.52
XI	OH	C_2H_5	n-C_4H_9	103 (0.5)			18.09	17.92

[a] M.p. 37–37.5°.

TABLE II

2,2-DISUBSTITUTED- AND 2,2,5-TRISUBSTITUTED-2,3-DIHYDRO-4*H*-1,4-THIAZIN-3-ONES



	R_1	R_2	R_3	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
Ia	C_2H_5	C_2H_5	H	52.5–53	8.18	8.17[a]
Ib	C_2H_5	C_2H_5	CH_3	65–66	7.76	7.76
Ic	C_2H_5	C_2H_5	C_6H_5	153.5–154	5.66	5.55[b]
Id	C_2H_5	n-C_4H_9	H	118[e]	7.03	6.93
Ie	C_2H_5	n-C_4H_9	CH_3	130[f]	6.56	6.45
If	C_2H_5	n-C_4H_9	C_6H_5	71–72	5.09	5.06
Ig	C_2H_5	C_6H_5	H	145	6.39	6.38
Ih	C_2H_5	C_6H_5	CH_3	118	6.00	6.00[c]
Ii	C_2H_5	C_6H_5	C_6H_5	137	4.74	4.75[d]

[a] Calcd.: C, 56.10; H, 7.65. Found: C, 56.35; H, 7.73. [b] Calcd.: C, 67.98; H, 6.93. Found: C, 67.25; H, 6.51. [c] Calcd. S, 13.74. Found: S, 13.61. [d] Calcd. C, 73.19; H, 5.80. Found: C, 74.03; H, 5.88. [e] B.p. at 3.0 mm. [f] B.p. at 3.5 mm.

lated was the dehydration product Ic; VIa gave negative Tollens and phenylhydrazine tests. These facts, together with the ease of dehydration, indicate very strongly that the intermediates of type VI are cyclic alcohols and not acycylic aldehydes or ketones.

The dehydration products I are assigned the indicated structure for the following reasons. Their infrared spectra show an NH band at 3.1 μ, a carbonyl band at 6.0–6.1 μ and a band at 3.2–3.25 μ for the CH in a double bond (Table III). Also an N-methyl derivative of Ib was prepared by an adaptation of the method of Loudon and Ogg.[7] The product had the composition expected for 2,2-diethyl-4,5-dimethyl-2,3-dihydro-1,4-thiazin-3-one (Ij) and the NH band was now missing from its infrared spectrum.

The 2,3-dihydro-4*H*-1,4-thiazin-3-ones Ia, Ib and Ic were oxidized with peracetic acid[8]; Ib and Ic gave the corresponding sulfones XII and XIII but Ia gave a sulfone-epoxide XIV (Table IV).

Acknowledgments.—The authors are grateful to the Laboratories of Merck, Sharp and Dohme, West Point, Penna., for financial aid to J. S. Elmslie and J. D. Gabbert and for the analyses. We also thank Dr. H. C. Beachell for aid in the interpretation of the infrared spectra.

(7) J. C. Loudon and J. Ogg, *J. Chem. Soc.*, 739 (1955).
(8) A. Pomerantz and R. Connor, THIS JOURNAL, **61**, 3386 (1939).

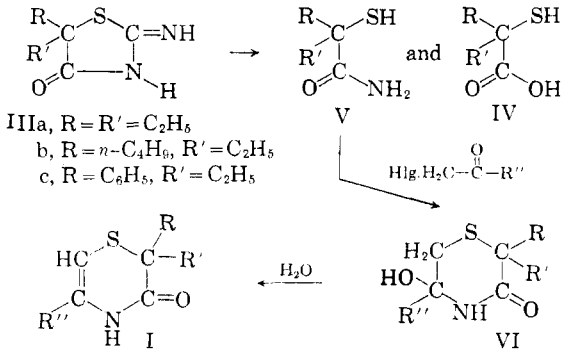
TABLE III

CHARACTERISTIC INFRARED BANDS OF THE 2,2,5-TRISUBSTITUTED-2,3-DIHYDRO-1,4-THIAZIN-3-ONES AND THEIR DERIVATIVES

Compound	Wave lengths, microns OH	NH	CH in >C=C<	>C=O	>SO_2	Epoxide
Ia		3.10	3.20	6.1		
Ib		3.10	3.25	6.1		
Ic		3.10	3.25	6.1		
Id		3.10	3.25	6.0		
If		3.10	3.25	6.0		
Ig		3.10	3.25	6.0		
Ih		3.10	3.25	6.0		
Ii		3.10	3.20	6.0		
Ij			3.25	6.1		
XII		3.10	3.20	5.9	7.5	
					9.0	
XIII		3.05	3.25	5.9	7.5	
					8.95	
XIV		3.10		5.9	7.5	8.0
					8.9	12.1 (*cis*)
VIa	2.8	3.10		6.1		
VIc	2.9	3.10		6.1		

Experimental

5,5-Disubstituted-2-imino-4-thiazolidones.—The 5,5-disubstituted-2-imino-4-thiazolidones were prepared by adding the corresponding α-bromoacetyl bromide to a solution



IIIa, R = R' = C_2H_5
b, R = n-C_4H_9, R' = C_2H_5
c, R = C_6H_5, R' = C_2H_5

Ia, R = R' = C_2H_5, R'' = H, BIa
b, R = R' = C_2H_5, R'' = CH_3, VIb
c, R = R' = C_2H_5, R'' = C_6H_5, VIc

Fig. 1.—Synthesis of 2,2,5-trisubstituted-2,3-dihydro-4*H*-1,4-thiazine-3-ones.

of thiourea in refluxing acetic acid. The yield of IIIa (Fig. 1) was raised from 77 to 84% by lowering the temperature of the stirred reaction mixture to 90° and heating for 7 hours instead of 3 hours.

Basic Hydrolysis of 5,5-Disubstituted-2-imino-4-thiazolidones.—The solutions of the thiazolidones in aqueous

TABLE IV

THE OXIDATION PRODUCTS OF 2,2-DIETHYL-5-SUBSTITUTED-2,3-DIHYDRO-4*H*-1,4-THIAZIN-3-ONES

	Structure	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
XII	Sulfone of Ib	128–128.5	49.75	50.05	6.96	6.93	6.45	6.42
XIII	Sulfone of Ic	189–189.5	60.19	60.24	6.14	6.15	5.02	5.00
XIV	Sulfone-epoxide of Ia	143.5–144	43.81	43.85	5.98	6.08	6.39	6.37

sodium hydroxide were heated under reflux in a stainless steel flask as detailed below.

Thiazolidone	M.p., °C.	NaOH soln. equivs. (%)	Time, hr.	Yield, % of amide	Yield, % of acid
IIIa	232–233	4 (5)	30	58	39
IIIb	203	3 (10)	24	41	17
IIIc	211–213	3 (5)	8	46	43

Two methods were used for separating the products. Method A: The hydrolysate was cooled in ice and acidified with concentrated hydrochloric acid. The viscous smelly oil was separated by extraction with ether. The ether layer was then extracted with dilute hydrochloric acid to remove any unreacted thiazolidone which was recovered by neutralizing with ammonium hydroxide. The ether layer was then extracted with several portions of a saturated solution of sodium bicarbonate until all acidic material was removed. The disubstituted mercaptoacetamides were recovered by removing the ether under diminished pressure and distilling the residue in the two cases VII and VIII and filtration of the solid in case IX (Table I). In the distillation of VII and VIII, a second, higher boiling portion was obtained. In the case of the former the product solidified in the side arm and was recrystallized from carbon tetrachloride, m.p. 77.5–78°. A melting point of a mixture of this solid and 5,5-diethyl-2,4-thiazolidinedione, prepared by the acid hydrolysis of IIIa, was 77.5–78°. The sodium bicarbonate layer was cooled in ice, acidified with concentrated hydrochloric acid and extracted with ether. Distillation of the ether and then the residue afforded the disubstituted mercaptoacetic acid. The product from IIIc could not be purified by distillation since it decomposed when heated.

Method B: The acidified hydrolysate was stirred with an excess of sodium bicarbonate until all reaction ceased. The mixture was extracted continuously with ether. Removal of the ether under diminished pressure and distillation yielded the mercaptoamide, the thiazolidinedione and the thiazolidone as a residue. The sodium bicarbonate layer was cooled, acidified and extracted continuously with ether. The acid was obtained by distillation. Method A was used in separating the products IIIb and IIIc and method B for IIIa.

Basic Hydrolysis of 5,5-Diethyl-2,4-thiazolidinedione.—This compound (16.4 g., 0.095 mole) was dissolved in 40 cc. (0.4 mole) of 5% sodium hydroxide and the mixture was refluxed for 16 hours. The hydrolysate was worked up by method A; yield of mercaptoamide, 4.7 g. (34%); yield of unreacted thiazolidinedione, 3.3 g. (20%); yield of mercapto acid, 5.4 g. (38%).

Oxidation of Diethylmercaptoacetamide to the Disulfide.—Diethylmercaptoacetamide was dissolved in boiling water and allowed to cool to room temperature. As air was passed over this solution, long colorless crystals of the disulfide precipitated. Recrystalilzation from methanol–water afforded the pure product, m.p. 159–160°. *Anal.* Calcd. for $C_{12}H_{24}N_2O_2S_2$: C, 49.28; H, 8.26; N, 9.58. Found: C, 49.40; H, 8.01; N, 9.58.

2,2,5-Trisubstituted-2,3-dihydro-4H-1,4-thiazin-3-ones.—In a typical experiment, 17.5 g. (0.10 mole) of butylethylmercaptoacetamide was dissolved in 0.10 mole of a 10% aqueous sodium hydroxide solution in a 100-cc. flask. To this cooled, stirred solution was added 9.2 g. (0.10 mole) of chloroacetone during a 10-minute period. After stirring for one hour, the oil which separated was taken up in ether, the ether removed, and the oil distilled; yield 19.8 g. (98.3%), b.p. 136–140° (4 mm.). Redistillation afforded pure Ie, $n^{25}D$ 1.5219, d^{25}_4 1.0517. Id was produced similarly, yield 42.8%, $n^{21}D$ 1.5297, d^{21}_4 1.0793; likewise, If, 63.6%; Ig, 67.9%; Ih, 80%; Ii, 91.5%.

2,2-Diethyl-1,4-thiazan-3-on-5-ol (VIa) and 2,2-Diethyl-2,3-dihydro-4H-1,4-thiazin-3-one (Ia).—To 44 cc. (0.11 mole) of ice-cold 10% sodium hydroxide in a 100-cc. r.b. flask was added 12.5 g. (0.085 mole) of VII. A 40% solution of chloroacetaldehyde (20.8 g., 0.11 mole) was added dropwise to this cooled, stirred solution during 20 minutes. After stirring for 2 hours, the white solid which had formed was filtered and washed with water. A portion of this solid (VIa) was dissolved in cold methanol and water was added dropwise until the solid precipitated, m.p. 77–78°. A weighed portion of VIa, placed in a vacuum desiccator over $CaCl_2$, required 10 days to reach constant weight. One equivalent of water was lost affording a quantitative yield of Ia. The yield of Ia based on the amount of mercaptoamide used was 64%.

2,2-Diethyl-5-methyl-1,4-thiazan-3-on-5-ol (VIb) and 2,2-Diethyl-5-methyl-2,3-dihydro-4H-1,4-thiazin-3-one (Ib) were prepared similarly; VIb was recrystallized from chloroform–petroleum ether, m.p. 76.5–77.5°. The compound lost water on standing at room temperature to produce Ib. Recrystallization from methanol–water produced pure Ib; yield 88% (based on mercaptoamide used).

2,2-Diethyl-5-phenyl-1,4-thiazan-3-on-5-ol (VIc) and 2,2-Diethyl-5-phenyl-2,3-dihydro-4H-1,4-thiazin-3-one (Ic).—The same procedure was used as above except that the reaction mixture was allowed to warm to room temperature. The solid was collected and recrystallized from chloroform–petroleum ether (1:1) producing pure (VIc), m.p. 105–106°.

Anal. Calcd. for $C_{14}H_{19}NO_2S$: C, 63.36; H, 7.22; N, 5.28. Found: C, 63.22; H, 7.15; N, 5.24.

A second crop of solid was Ic. Recrystallization from ethanol produced pure Ic. The combined yield of VIc and Ic was 66%. Refluxing VIc in absolute ethanol for 2 days produced a 95% yield of Ic.

2,2-Diethyl-4,5-dimethyl-2,3-dihydro-1,4-thiazin-3-one (Ij).—Methyl iodide (2.2 g., 0.015 mole) was added rapidly to a stirred, refluxing suspension of powdered KOH (1.25 g., 0.025 mole) in 35 cc. of acetone containing 1.85 g. (0.010 mole) of Ib. After refluxing for 20 minutes the mixture was cooled, the solid was separated by decantation and washed thoroughly with acetone. The acetone washings were combined with the supernatant liquid and the acetone was removed under diminished pressure. The residual oil was distilled producing Ij, b.p. 105° (0.22 mm.), yield 1.65 g. (83%), $n^{25}D$ 1.5265, d^{25}_4 1.0723.

Anal. Calcd. for $C_{10}H_{17}NOS$: C, 60.26; H, 8.60; N, 7.03; S, 16.08. Found: C, 60.64; H, 8.74; N, 6.83; S, 15.70.

2,2-Diethyl-5-methyl-2,3-dihydro-4H-1,4-thiazin-3-one 1,1-Dioxide (XII).—To a solution of 3.7 g. (0.020 mole) of Ib in 20 cc. of a 1:1 mixture of acetic acid and acetic anhydride, cooled in an ice-salt-bath was added dropwise 6 cc. of 30–35% hydrogen peroxide. The mixture was allowed to warm up to room temperature slowly and stood for 5 days. Manganese dioxide was added until all reaction ceased, and the mixture was filtered. The solvent was removed from the filtrate under diminished pressure (50° at 25 mm.). The residual oil was washed repeatedly with hot water, and the washings cooled to produce 2.9 g. of white solid (XII), m.p. 124–125°. The filtrate was added to the washed residue, the solvent was removed and the entire process was repeated producing 0.5 g. of product; total yield, 3.4 g. (78%). Recrystallization from ethanol afforded pure XII (Table IV).

2,2-Diethyl-5-phenyl-2,3-dihydro-4H-1,4-thiazin-3-one 1,1-Dioxide (XIII).—The same procedure as above was employed except that the relatively pure product (XIII) precipitated from the reaction mixture, m.p. 187–188°, yield 89%. Recrystallization from isopropyl alcohol gave the pure product.

2,2-Diethyl-5,6-epoxy-2,3,5,6-tetrahydro-4H-1,4-thiazin-3-one 1,1-dioxide[9] **(XIV)** was prepared by the same method used for the preparation of XII. When most of the solvent was removed and the solution was cooled the product precipitated, m.p. 130–135°, yield 38%. Repeated recrystallization from isopropyl alcohol produced pure XIV.

(9) This compound will be indexed in "Chemical Abstracts" under the name of 3,3,-diethyl-8-oxa-2-thia-5-azabicyclo[4·1·0]heptan-4-one 2,2-dioxide.

NEWARK, DELAWARE

[CONTRIBUTION FROM THE QUARTERMASTER RESEARCH & ENGINEERING CENTER]

The Structure of Indanthrone

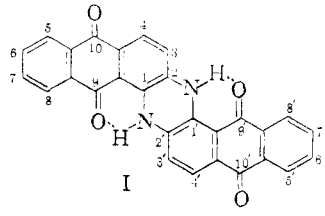
BY JULIUS WEINSTEIN AND CHARLES MERRITT, JR.

RECEIVED DECEMBER 1, 1958

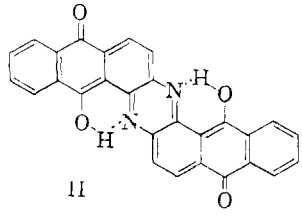
Studies of spectra of indanthrone and related compounds in the ultraviolet, visible and infrared regions of the spectrum have led to the conclusion that indanthrone in the solid state and in inert solvents exists primarily in a keto form. This conclusion is based on the following evidence: (1) The presence of an N–H stretching band in the infrared spectrum of indanthrone and N-methylindanthrone at 3.16 μ; (2) indanthrone, N-methylindanthrone and N,N′-dimethylindanthrone all have approximately the same integrated absorbancy index for the carbonyl stretching absorption band at about 6.0 μ; (3) nearly identical spectra are observed for indanthrone and its N-methyl substituted derivatives in both the ultraviolet and visible regions of the spectrum.

Introduction

The structure of indenthrone, N,N′-dihydro-1,2:2′,1′-anthraquinoneazine (I), has been a subject of controversy for many years. In a recent



I



II

paper Wyman[1] has proposed an enol structure II based substantially on the interpretation of infrared spectra. The argument presented is based on a failure to observe an N–H stretching band in the 3 μ region. This argument, however, is weakened considerably by the fact that an hydroxyl stretching band expected to be shown in the same region by the enol structure was also not observed. A second feature of the argument is the assignment of the 6.3 μ band for indanthrone to C=N, but this also appears doubtful.

Recently, Durie and Shannon[2] have questioned Wyman's interpretation of the spectra for the same reasons. They, however, were also unable to observe either an O–H or an N–H band in the 3 μ region. Moreover, their argument in favor of the keto structure is unfortunately based on an interpretation of bands in the 6 μ region which were incorrectly tabulated by Wyman for N-methylindanthrone and N,N′-dimethylindanthrone.

Since the keto structure I and the enol structure II involve a change in the electronic configurations of the molecule, the visible and ultraviolet regions of the spectrum might yield more decisive information. Accordingly, it seemed desirable to re-examine the infrared spectra and to investigate the visible and ultraviolet spectra of indanthrone and its N-methyl derivatives.

Experimental

Indanthrone and 3,3′-dichloroindanthrone were obtained through the courtesy of Mr. P. Kronowitt of Ciba States Ltd. The sample of indanthrone was purified by repeated recrystallization from 1,2,4-trichlorobenzene. N-Methylindanthrone and N,N′-dimethylindanthrone were prepared according to the procedure of Bradley and Leete.[3] The methylated derivatives were characterized by analysis for carbon, hydrogen and nitrogen and by comparing their visible spectra in pyridine solutions with the spectra reported by Bradley and Leete. The amino anthraquinones, 6-chloroindanthrone and 3,3′-dibromoindanthrone were kindly provided by Dr. O. Stallman of the du Pont Co. The anthraquinoneazines were prepared by oxidation of the appropriate indanthrone with nitric acid, according to Scholl's procedure.[4] The infrared spectra of indanthrone and its N-methyl derivatives were obtained in the 3 and 6 μ regions by means of a Beckman IR-3 spectrophotometer equipped with LiF and NaCl optics as required. Samples were prepared as mulls in a perfluorocarbon oil and their transmittancy measured against the oil as a reference.

Samples for the quantitative study of the intensity of the carbonyl absorption bands were ground and dispersed in the mull by means of a "wiggle bug" in order to achieve a fine particle size and uniform distribution. Transmittancy values were measured in 1-mm. cells. The integrated absorbancy indices were calculated by the approximation method of Ramsay.[5] The Naperian logarithm of the reciprocal of the recorded transmittance ratio was divided by the product of concentration in moles per liter and cell thickness in centimeters. This quotient multiplied by the half intensity band width (*i.e.*, effective slit width) in reciprocal centimeters gives the approximate integrated molar absorbancy index.

Spectra of indanthrone, its N-methyl derivatives and the amino anthraquinones in the visible region were obtained in 1,2,4-trichlorobenzene as a solvent. The spectra in the ultraviolet region were obtained on dyed cellophane films. Spectra in the ultraviolet were also measured in dimethylformamide as a solvent, but intense general absorption by the solvent at wave lengths shorter than 270 mμ obscures the shorter wave length portions of the spectra. All measure-

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