collected. Fractions 8 to 10 contained a small amount of starting material, whereas fractions 11 to 14 contained the product. The melting points of the material in fractions 12, 13, and 14 were 75–76, 78, and 74–76°, respectively. Recrystallization from chloroform, to which isooctane was added, yielded 2.96 g. (18.5 mmoles, 67%) of the nitrile XII, m.p. 78–80°. Sublimation at 60–70° under high vacuum increased the melting point to 79.5–80.5°, λ_{max} 287 mμ (ϵ 8.5 × 10^3) and 244 mμ (ϵ 7.8 × 10^3).

Anal. Calcd. for $C_8H_4N_2S$: C, 59.98; H, 2.52; N, 17.49; S, 20.02. Found: C, 59.90; H, 2.57; N, 17.49; S, 20.09.

B. **Deshydroxyluciferin (XIV).**—DL-Cysteine was prepared by the reduction of cystine (0.26 g., 1.08 mmoles) as described above; it was dissolved in 25 ml. of water and then adjusted to pH 7.5. Methanol (25 ml.) and then a solution of 2-cyanobenzothiazole (0.37 g., 2.31 mmoles) in 25 ml. of methanol was added. The mixture was allowed to stand for 85 min. during which time the ultraviolet absorption shifted from 288 to 292 mμ. Water was added (40 ml.) and the methanol was evaporated *in vacuo*. The pH of the resulting solution was adjusted to about 9 by addition of 10% sodium hydroxide, and the mixture was extracted with ethyl acetate (150 ml.). The aqueous solution was filtered and acidified with hydrochloric acid to pH 1. The whitish precipitate was collected, washed with water, and dried *in vacuo* at 65°. There was obtained 0.50 g. (1.92 mmoles, 89%) of 2-(2'-benzothiazolyl)-Δ^2-thiazoline-4-carboxylic acid (XIV), m.p. 164–166°. For analysis, this material was recrystallized from methanol, m.p. 166–167°. See Table I for the ultraviolet absorption.

Anal. Calcd. for $C_{11}H_8N_2O_2S_2$: C, 49.98; H, 3.05; N, 10.60; S, 24.26. Found: C, 50.40; H, 3.10; N, 10.43; S, 24.17.

2-(4'-Pyridyl)-Δ^2-thiazoline-4-carboxylic Acid (XV).—Cysteine was prepared by the reduction of DL-cystine (0.73 g., 3.35 mmoles) as described above; it was dissolved in 20 ml. of water and adjusted to a pH of about 8. Methanol (20 ml.) was then added, followed by a solution of 4-cyanopyridine (0.57 g., 4.06 mmoles) in 20 ml. of methanol. The mixture was allowed to react overnight. Most of the methanol was removed *in vacuo*, water was added (80 ml.), the pH was adjusted to 8.5, and the mixture was extracted with ethyl acetate (250 ml.). The aqueous phase was filtered, the dissolved ethyl acetate was removed in a stream of nitrogen, and the pH was lowered to about 2 by the addition of hydrochloric acid. The precipitate was collected, washed with water, and dried *in vacuo* to give 0.74 g. (3.55 mmoles, 58.5%) of 2-(4'-pyridyl)-Δ^2-thiazoline-4-carboxylic acid (XV), m.p. 177–179° dec. For analysis, the compound was crystallized from methanol under nitrogen in dim light, m.p. 178–179.5° dec. At a slower rate of heating, the melting point was observed at 173–174° dec. (lit.[5] m.p. 174–175°). See Table I for the ultraviolet absorption.

Anal. Calcd. for $C_9H_8N_2O_2S$: C, 51.91; H, 3.87; N, 13.45; S, 15.40. Found: C, 52.07, 51.88; H, 3.99, 3.95; N, 13.49, 13.45; S, 15.44, 15.49.

Acknowledgment.—We thank the National Institutes of Health for its support of this work and Miss Laurie Kayser for the tests with luciferase.

Spectroscopic Studies on Dyes. V. Derivatives of *cis*-Indigo[1]

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A comparison of the visible spectrum of N,N'-oxalylindigo with the spectra of the photochemically produced *cis* isomers of N,N'-diacetylindigo and N,N'-bis(trifluoroacetyl)indigo suggests a noncoplanar *cis* configuration for all three molecules. This was further substantiated by a study of the carbonyl stretching frequencies in the infrared region. The formation of oxalylindigo from indigo and oxalyl chloride was studied in benzene and chlorobenzene solutions, using spectrophotometric techniques. The results indicate a two-step mechanism with *trans*-N-(chlorooxalyl)indigo as the intermediate. By a similar technique the alkaline hydrolysis of oxalylindigo in aqueous dimethylformamide was found to proceed in two steps involving the stepwise hydrolysis of the two amide linkages. Owing to the slowness of the second step it was possible to determine the visible spectrum of the intermediate anion and to assign a *trans* configuration to it in view of the long wave length (571 mμ) of the absorption maximum. (Heller had previously observed a blue intermediate in this reaction which he attributed to *cis*-indigo.)

Although the structure of indigo has long been known and it is recognized that the molecule possesses a *trans* configuration,[3,4] derivatives of *cis*-indigo have been reported in the literature[5] and the existence of *cis*-indigo has also been postulated.[6] In view of our current understanding of the *cis–trans* isomerization of conjugated compounds, it is considered highly unlikely that the unstable *cis* isomer could exist at ambient temperatures (except, possibly for a few microseconds).[4,7] Recent theoretical and spectroscopic studies aimed at a better understanding of the indigo chromophore system[8] are also in accord with this conclusion.

This investigation was undertaken with the objective of clarifying the structure of N,N'-oxalylindigo, which had been variously reported as having a *trans*[6] and a *cis*[4] configuration. Since in the first part of this work we concluded that this compound exists in the *cis* configuration (it is, indeed, the only derivative of *cis*-indigo that can be made directly from indigo!), it was considered desirable to study the mechanism of its formation. In addition, some of the evidence reported by Heller[6] for the formation of "*cis*-indigo" during the alkaline hydrolysis of oxalylindigo was re-examined.

Experimental

Absorption spectra for the substituted indigos are shown in Figures 1–3. Figure 4 shows the spatial arrangement of the carbonyl groups in a *cis*-indigo.

N,N'-Diacetylindigo was prepared by the method of Liebermann and Dickhuth.[9]

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[1] (a) Presented before the Organic Chemistry Division at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964; (b) This research was supported by the U. S. Army Research Office (Durham).

[2] To whom all correspondence should be sent: U. S. Army Research Office, Box CM, Duke Station, Durham, N. C.

[3] T. Posner, *Ber.*, **B59**, 1799 (1926).

[4] W. R. Brode, E. G. Pearson, and G. M. Wyman, *J. Am. Chem. Soc.*, **76**, 1034 (1954).

[5] (a) R. Pummerer and F. Meininger, *Ann.*, **590**, 173 (1954); P. Friedländer and L. Sander, *Ber.*, **B57**, 637 (1924).

[6] G. Heller, *ibid.*, **B77**, 163 (1944).

[7] (a) G. M. Wyman, *Chem. Rev.*, **55**, 625 (1955); (b) E. Fischer and Y. Frei, *J. Chem. Phys.*, **27**, 808 (1957); (c) G. Gabor and E. Fischer, *J. Phys. Chem.*, **66**, 2478 (1962).

[8] (a) W. Lüttke and M. Klessinger, *Chem. Ber.*, **97**, 2342 (1964); (b) M. Klessinger and W. Lüttke, *Tetrahedron*, **19**, 315 (1963).

[9] C. Liebermann and F. Dickhuth, *Ber.*, **24**, 4131 (1891).

N,N′-Bis(trifluoroacetyl)indigo was synthesized in the following manner. Indigo powder (2 g.; this was provided through the courtesy of Du Pont), which had been purified by vatting followed by oxidation, was refluxed in 25 ml. of trifluoroacetic anhydride for 13 hr. The product was filtered off, rinsed with ether, and recrystallized from benzene; yield, 1 g. The product was found to contain 27% indigo[10] (determined by measurement of its absorption at 625 mμ in benzene).

Anal. Calcd. for a mixture of 27% indigo and 73% N,N′-bis(trifluoroacetyl)indigo: C, 58.42; H, 2.31; F, 18.55; N, 7.31. Found: C, 58.16; H, 2.57; F, 18.65; N, 7.12.

Oxalylindigo was prepared by the following modification of the Friedländer and Sander[5b] method. Indigo powder (2 g., purified by vatting followed by oxidation) was stirred for 30 min. in 30 ml. of nitrobenzene at 120°. Oxalyl chloride (3 ml.) was added through a dropping funnel and the solution was allowed to cool with continued stirring over a 12-hr. period. The reaction mixture was then diluted with 30 ml. of benzene and the product was removed by filtration. The crystals were washed with a 1:1 ethanol–ether mixture and recrystallized from nitrobenzene; yield, 1.2 g.

Anal. Calcd.: C, 68.35; H, 2.54; N, 8.85. Found: C, 68.30; H, 2.68; N, 8.83.

It was found that the formation of oxalylindigo could also be studied spectrophotometrically in the following manner. To a dilute solution of indigo in benzene contained in a 2.5-cm. absorption cell 1 drop of oxalyl chloride was added. After shaking the solution for a few seconds its visible spectrum was recorded periodically; these spectra are shown in Figure 5. (The same reaction was also carried out in chlorobenzene solution.)

Hydrolysis of Oxalylindigo.—A solution of approximately 10^{-5} *M* concentration was made up in 25% aqueous dimethylformamide in a 5-cm. absorption cell. The solution was cooled to 4° and 2 drops of 1% aqueous NaOH was added. The solution was thoroughly shaken and its visible spectrum was recorded periodically during 1.75 hr. The observed spectra are shown in Figures 6 and 7.

Absorption Spectra.—The spectral absorption curves were determined by means of a Cary Model 14 recording spectrophotometer, using matched quartz absorption cells. Measurements were made at 20°, except where otherwise indicated. The infrared spectra were determined by means of a Perkin-Elmer Model 21 spectrometer equipped with rock-salt optics. All spectra were measured against the solvent as the reference. Spectroscopic-grade solvents were used for all measurements.

Photochemical *cis–trans* Isomerization.—The dye solution (contained in the appropriate absorption cells) was irradiated with filtered radiation from a 100-w. microscope illuminator (Model #735) made by the American Optical Co. Heating of the solution was minimized by blowing a stream of compressed air onto the cell.

Discussion of Results

Configuration of Oxalylindigo.—While the facile formation of oxalylindigo from indigo and oxalyl chloride has long been known,[5b] its geometrical configuration has not been conclusively established to date. Noting the similarity of its absorption spectrum to that of an irradiated solution of N,N′-diacetylindigo, Brode assumed that it possessed a *cis* configuration.[4] However, Heller observed that the compound could also be obtained by the action of oxalyl chloride on N,N′-diacetylindigo (which was known to have a *trans* structure); hence, he assigned it a *trans* configuration.[6]

In the present work the photochemical *trans* → *cis* isomerization of N,N′-diacetylindigo and of N,N′-bis(trifluoroacetyl)indigo were re-examined in carbon tetrachloride solution, since it was found that in this solvent (with the aid of suitable filters, see Table I) it was possible to convert most of each dye to the unstable *cis* form (*cf.* Figures 1 and 2). From these curves it was possible to calculate the approximate spectral absorption curves for the *cis* isomers by the

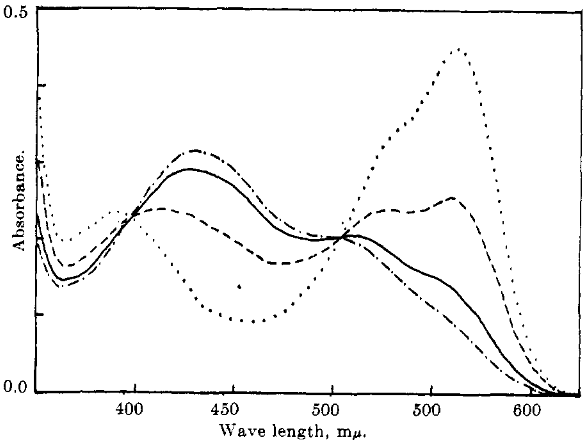

Figure 1.—Spectral absorption curves for N,N′-diacetylindigo in CCl_4: concentration, 1.71 × 10^{-5} *M*; cell length, 5.0 cm.; ......, irradiated with blue light (λ 350–510 mμ) for 5 min.; – – – –, irradiated with white light for 5 min.; ———, irradiated with yellow light (λ >495 mμ) for 5 min.; –·–·–, irradiated with orange light (λ >520 mμ) for 5 min.

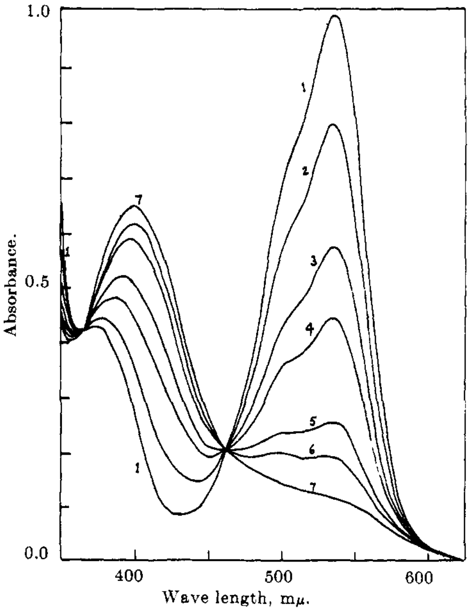

Figure 2.—Spectral absorption curves for N,N′-bis(trifluoroacetyl)indigo in CCl_4: concentration, 6.14 × 10^{-5} *M*; cell length, 2.5 cm.; see Table I for the irradiation times and Corning filter numbers used.

Table I

Irradiation Times and Filters Used for the Spectra of N,N′-Bis(trifluoroacetyl)indigo Given in Figure 2

Curve	Corning filter no.	Time, min.	λ range, mμ
1	Freshly prepared solution		
2	3-68	5	>525
3	3-68	10	
4	5-60[a]	10	350-495
5	3-69	10	>510
6	3-69	15	
7	3-69	20	

[a] Solution 7 was irradiated in this manner in order to demonstrate the reversibility of the reaction.

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(10) N,N′-Bis(trifluoroacetyl)indigo was found to be relatively unstable; it decomposed into indigo on standing at room temperature. However; since N,N′-bis(trifluoroacetyl)indigo is much more soluble than indigo, it was possible to obtain freshly prepared solutions of the trifluoroacetyl derivative substantially free of indigo for qualitative spectroscopic and photochemical measurements. Moreover, since indigo absorbs at considerably longer wave lengths and does not show phototropism, its presence did not cause any interference.

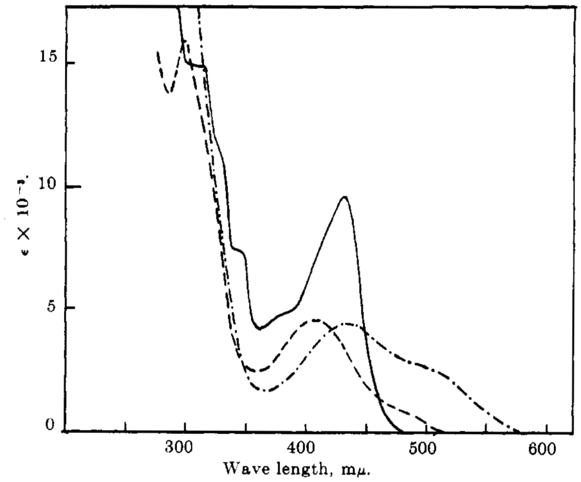


Figure 3.—Spectral absorption curves for (a) oxalylindigo (———); (b) *cis*-N,N′-diacetylindigo (·—·—·—); and (c) *cis*-N,N′-bis(trifluoroacetyl)indigo (– – – –). Solvents: a, $CHCl_3$; b and c, CCl_4.

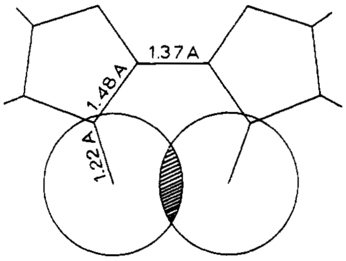
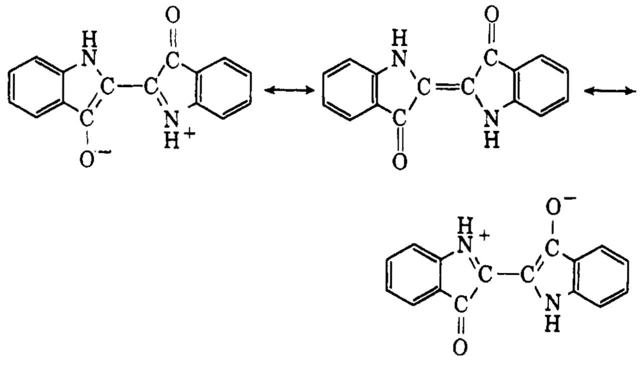


Figure 4.—Diagram of the spatial arrangement of the carbonyl groups in a *cis*-indigo. Bond distances and angles are drawn to scale on the basis of crystallographic data on *trans*-indigo [E. A. Gribova, G. S. Zhdanov, and G. A. Golder, *Kristallografiya*, **1**, 53 (1956)]. The circles show the van der Waals radii (1.40 Å.) of the carbonyl oxygen atoms.

method described earlier by one of us.[11] The calculated curves are shown in Figure 3, along with the absorption curve for oxalylindigo. From the similarity between the absorption curve of oxalylindigo and the curves for *cis*-N,N′-diacetylindigo and *cis*-N,N′-bis(trifluoroacetyl)indigo the conclusion is inescapable that oxalylindigo possesses a *cis* configuration. At the same time the extreme hypsochromic shift brought about by the *trans* → *cis* isomerization of the N,N′-diacylindigos suggests a considerable weakening of the indigo chromophore system in the *cis* derivatives.

Although during the last 40 years a variety of resonance structures have been proposed to explain the deep color of indigo dyes,[12] recent spectroscopic[8a,11] and theoretical[8b] studies have conclusively demonstrated that the resonance forms



(first proposed by Arndt and Eistert)[13] are of greatest importance in the ground state of the molecule. In N-acylated indigos the normal amide-type resonance[14] $(>\mathrm{N{-}\overset{|}{C}{=}O} \rightleftharpoons >\mathrm{N^{+}{=}\overset{|}{C}{-}\ O^{-}})$ would be expected to be superimposed upon the indigo resonance. Since the acyl carbonyl groups are in competition with the dye carbonyl groups for the electrons of the nitrogen atoms, this type of substitution would be expected to weaken the indigo resonance and cause the hypsochromic shift observed when the spectra of the *trans*-N,N′-diacyl derivatives are compared with that of indigo (*cf.* Table II). Nonetheless it is clear from these data that the indigo resonance still predominates and, in fact, the spectra of these *trans* derivatives are quite similar to that of *trans*-thioindigo (*cf.* ref. 4), whose sulfur atoms are less effective electron donors than the nitrogens are in indigo.

TABLE II

ABSORPTION FREQUENCIES OF INDIGO DERIVATIVES IN THE VISIBLE AND INFRARED REGIONS

	Cm.⁻¹		
Substituent	Visible band (× 10⁻²)	Dye carbonyl	Acyl carbonyl
None	166[a,b]	1616, 1631[c]	. . .
trans-Thio	183[a,d]	1656[a]	. . .
trans-N,N′-Diacetyl	179[e]	1689[e]	1710[e]
trans-N,N′-Bis(trifluoroacetyl)	187[e]	1700[e]	1742[e]
cis-Thio	204[a,d]	1702[a]	. . .
cis-N,N′-Diacetyl	232[e]	1736[e]	1710[e]
cis-N,N′-Bis(trifluoroacetyl)	247[e]	1745[e,f]	1742[e]
Oxalyl	233[a]	1742[a]	1710, 1720[a,g]

[a] In chloroform. [b] Ref. 4. [c] Solid, in KBr (ref. 17). [d] Ref. 11. [e] In carbon tetrachloride. [f] Assignment only approximate, owing to interference with acyl carbonyl band. [g] Symmetrical and antisymmetrical stretching frequencies, expected of *cis*-oxalyl derivatives [*cf.* B. Milligan, E. Spinner, and J. M. Swan, *J. Chem. Soc.*, 1919 (1961)].

The situation appears to be drastically different in the *cis*-N,N′-diacyl derivatives, including oxalylindigo. In these compounds there is considerable hindrance to coplanarity due to the overlap of the two carbonyl oxygen atoms of the parent dye molecule (*cf.* Figure 4) compounded by the electrostatic repulsion between these strongly polar groups, much in the same way as has been reported for thioindigo.[15] Owing to the noncoplanarity of these *cis* isomers the indigo-type resonance will be further diminished (since it involves the central bond), while the amide resonance remains relatively unaffected. The observed extensive shift to short wave lengths (which is approximately twice as large as for thioindigo dyes) suggests that in these

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(11) G. M. Wyman and W. R. Brode, *J. Am. Chem. Soc.*, **73**, 1487 (1951).

(12) For a review, *cf.* ref. 8a.

(13) F. Arndt and B. Eistert, "Tautomerie und Mesomerie," F. Enke, Stuttgart, 1938, p. 173.

(14) *Cf.* R. N. Jones and C. Sandorfy in "Technique of Organic Chemistry," A. Weissberger, Ed., Vol. IX, Interscience Publishers, Inc., New York, N. Y., 1956, p. 476.

(15) D. A. Rogers, J. D. Margerum, and G. M. Wyman, *J. Am. Chem. Soc.*, **79**, 2464 (1957).

cis isomers the latter is making a substantial contribution to the ground state.[16]

These conclusions were further confirmed by a study of the carbonyl stretching bands of these compounds in the infrared region (*cf.* Table II). An increase in this frequency during the *trans* → *cis* isomerization of certain thioindigo dyes has previously been reported,[17] suggesting increased double-bond character for the carbonyl group, presumably as a result of less indigo resonance. The indigoid carbonyl frequencies in the *cis*-N,N′-diacylindigos occur at still higher frequencies; in fact, at such high frequencies as to suggest ring strain and practically no conjugation with the central double bond.[18] Thus the spectroscopic evidence (based on both electronic and vibrational spectra) indicates that oxalylindigo as well as the unstable isomers of the two N,N′-diacylindigos exist in a noncoplanar *cis* configuration that involves an appreciable twisting of one-half of the molecule about the central double bond.

Formation of Oxalylindigo.—Since oxalylindigo is the only derivative of *cis*-indigo that is readily formed from indigo, it was decided to study its formation spectrophotometrically in the hope of arriving at a better understanding of this reaction that involves a *trans* → *cis* transformation. The absorption curves in Figure 5 describe the progress of the reaction between oxalyl chloride and indigo at 20° in benzene solution. (The reaction was also found to follow a similar course in chlorobenzene solution.) It is clear from these curves that the reaction proceeds through a colored intermediate (λ_{max} 578 mμ). Moreover, it is apparent from the absorption curves in Figure 5 that during the first stage of the reaction (0 → 1) indigo is rapidly and essentially completely converted to this intermediate and that conversion of the intermediate to oxalylindigo (1 → 4) takes place at an appreciably slower rate. (Had this not been the case, there would not have been an isosbestic point common to curves 1–4.)

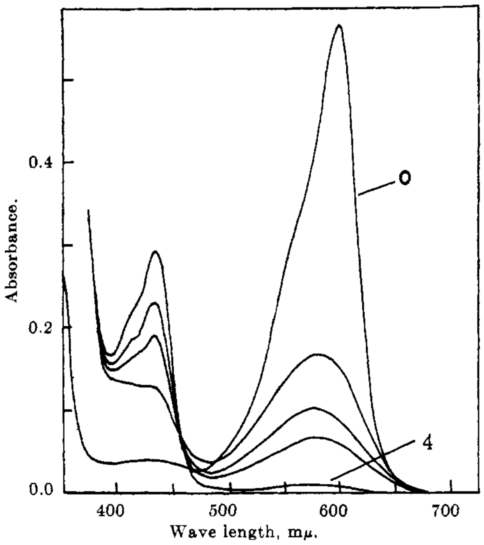


Figure 5.—Spectral absorption curves observed during the reaction of indigo with oxalyl chloride in benzene: curve 0, indigo; curve 4, oxalylindigo; reaction time (0 → 4), 20 min.

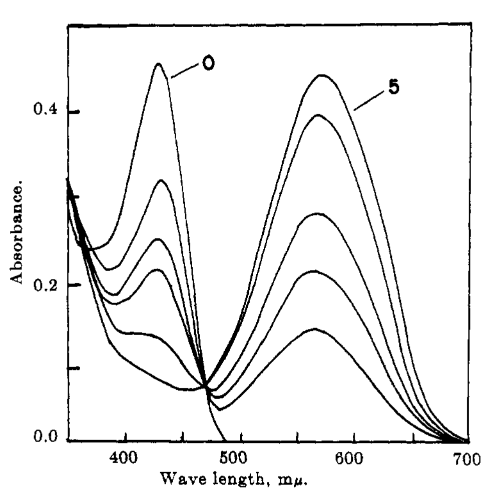
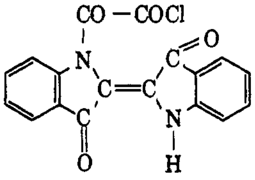
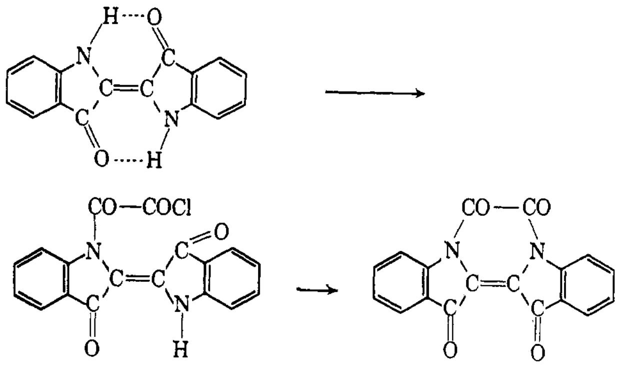


Figure 6.—Spectral absorption curves observed during the first stage of the alkaline hydrolysis of oxalylindigo: solvent, 25% aqueous dimethylformamide; temperature, 4°; reaction time (0 → 5), 25 min.



The intermediate very probably has the structure shown below for the following reasons. (1) λ_{max} is at such a long wave length as to preclude a *cis* configuration. (2) *trans*-N,N′-Bis(chlorooxalyl)indigo is excluded as the intermediate since it would be expected to have its first absorption band at a shorter wave length than that of *trans*-N,N′-diacetylindigo (561 mμ), owing to the electron-withdrawing effect of the ClCO–CO group. (If the electronegativity of this group is comparable with that of CF_3CO group, the absorption band should be near 536.5 mμ).[19] (3) Assuming that *trans*-N,N′-bis(chlorooxalyl)indigo would have λ_{max} 545–550 mμ, the λ_{max} observed for the intermediate is just about where it would be expected, *i.e.*, somewhat less than halfway between that of indigo and the disubstituted derivative. On the basis of this structure for the intermediate, the following mechanism is suggested for this reaction which involves ring closure of the *trans* intermediate to the



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[16] It was pointed out by one of the referees that the proximity of the indoxyl oxygens in the *cis* isomers will limit the extent of their polarization, thus causing the observed strong shifts to shorter wave lengths. While this effect is undoubtedly a contributing factor, it is not a sufficient explanation in itself, since the hypsochromic shifts are far more extensive in the N,N′-diacylindigos than those observed for thioindigo dyes (*cf.* ref. 11).

[17] J. Weinstein and G. M. Wyman, *J. Am. Chem. Soc.*, **78**, 2387 (1956).

[18] Ref. 14, pp. 484–485.

[19] It would have been desirable to obtain the absorption spectra of some N-monacyl derivatives of indigo for comparison. Unfortunately such compounds have never been reported and our attempts at synthesizing N-acetylindigo and N-trifluoroacetylindigo also failed.

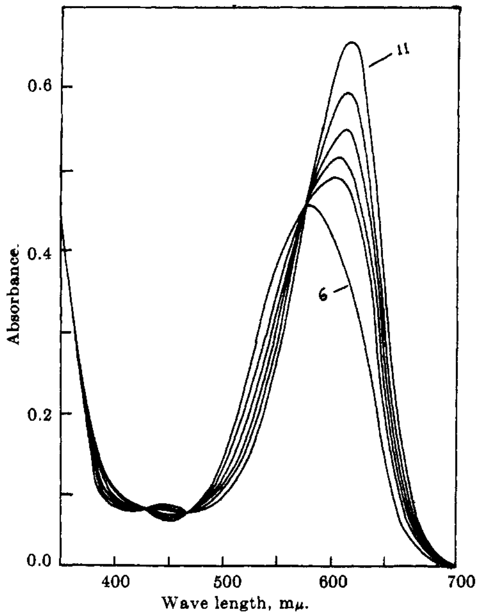
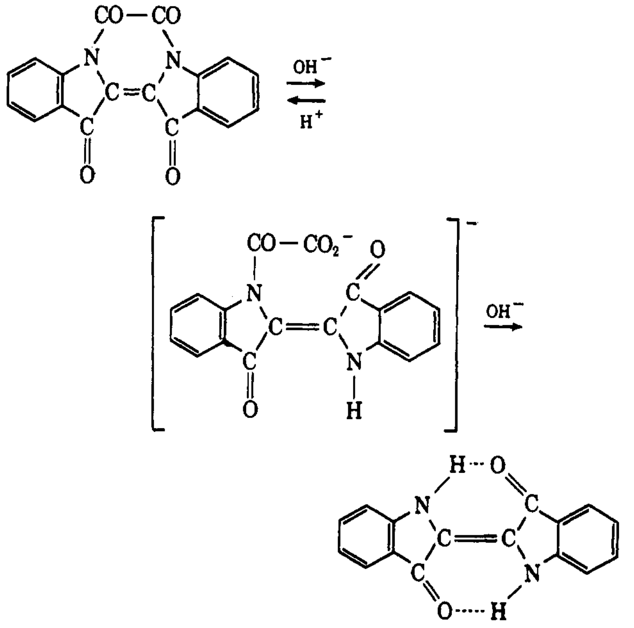


Figure 7.—Spectral absorption curves observed during the second stage of the alkaline hydrolysis of oxalylindigo: conditions identical with Figure 6; reaction time (6 → 11), 80 min.

cis derivative. The preferential stabilization of the *trans* structure in indigo dyes has been attributed to the formation of a hydrogen bond between C═O and NH that is normally only possible in the *trans* configuration.[4] However, in N-monoacylated derivatives of indigo, such as the intermediate postulated for this reaction, hydrogen bonding is possible in *both* the *trans* and *cis* configurations, resulting in six- and seven-membered hydrogen-bonded rings, respectively. Consequently, one might expect that the energy difference between the two configurations in the intermediate would be considerably less than it is for indigo. While this suggests that these conditions are more favorable for the formation of *cis* derivatives than is the case in other reactions (*e.g.*, alkylation), the exact nature of the observed *trans* → *cis* transformation remains to be elucidated.[20]

Hydrolysis of Oxalylindigo.—The results of a spectrophotometric study of the alkaline hydrolysis of oxalylindigo in aqueous dimethylformamide at 4° are shown in Figures 6 and 7. The absorption curves confirm Heller's visual observation to the effect that a blue intermediate (λ_{max} 571 mμ) is formed during the hydrolysis "with a color that is not so deep as that of indigo."[6] However, it can be shown that, when oxalylindigo is hydrolyzed in a mixture of benzene and aqueous NaOH, the blue color is found in the aqueous layer; consequently the colored species is most probably the anion formed by the attack of a hydroxide ion on the substrate and not *cis*-indigo, as had been postulated by Heller. Moreover, acidification of the solution containing this intermediate (curve 5 in Figure 6) results in partial re-formation of oxalylindigo, thus providing further confirmation of the following mechanism for the reaction. This mechanism is also



consistent with what is known today of the mechanism of base-catalyzed hydrolysis reactions, since there is every reason to expect that the second step (attack by OH^- on the carbonyl group which has an electron-rich carboxylate anion attached to it) would take place at a much slower rate than the original attack on the carbonyl group of the oxalylindigo molecule. It is clear from Figures 6 and 7 that the first step occurs at a much faster rate than the second and that it is essentially complete before any appreciable amount of indigo is formed.

The *trans* configuration is assigned to this intermediate mainly on the basis of its absorption spectrum. Although *cis*-indigo is not known, by analogy with the thioindigo dyes[11] its first absorption band would be expected to occur at a wave length shorter than 550 mμ. Consequently it is difficult to envisage a derivative of *cis*-indigo that would have its first absorption band at such a long wave length as the intermediate in this reaction. Thus it appears that in this reaction *cis* → *trans* isomerization about the double bond is essentially simultaneous with nucleophilic attack on the first carbonyl group.

Acknowledgment.—The authors are greatly indebted to Professor W. Luettke for having made available to them the manuscript of reference 8a.

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(20) A possible route for the *trans* → *cis* transformation, involving the following tautomeric form, was suggested by one of the referees.