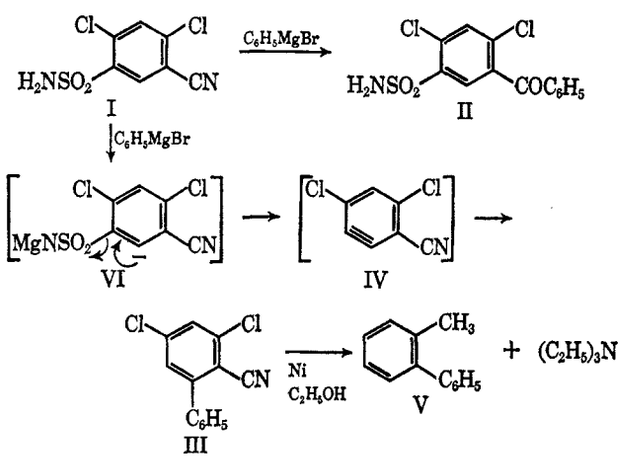
nickel desulfurizations of chlorosulfamylanthranilic acids.[2]

The loss of nitrogen could be rationalized by reduction of the nitrile to the primary amine followed by alkylation by ethanol and debenzylation all catalyzed by the Raney nickel.[3] This explanation is supported by isolation of triethylamine hydrochloride from this reaction.

The *cine* substitution found in the replacement reaction implicates the benzyne IV as an intermediate. The hydrogen on the phenyl flanked by the sulfamyl and cyano groups should be quite acidic, so the formation of the anion VI seems plausible. This could be converted into IV by loss of $MgNSO_2^-$. The addition of the phenyl *ortho* to the cyano seems contrary to the generalization that the reaction proceeds to place the negative charge adjacent to the most strongly electron-withdrawing group.[4] It is possible that phenylmagnesium bromide is complexed to the cyano group, and this directs phenylation to the adjacent carbon.



Experimental Section[5]

Reaction of Phenylmagnesium Bromide and 2,4-Dichloro-5-sulfamylbenzonitrile.—Phenylmagnesium bromide was prepared by the reaction of 12.16 g (0.5 g-atom) of magnesium and 78.5 g (0.5 mol) of bromobenzene in 225 ml of tetrahydrofuran. After addition of 25 g (0.1 mol) of 2,4-dichloro-5-sulfamylbenzonitrile dissolved in 100 ml of tetrahydrofuran the reaction mixture was stirred at 25° for 30 min and refluxed for 90 min. After chilling, ice–water (350 ml) and 12 *N* sulfuric acid (200 ml) were added and the resulting solution was extracted with ether. The ether was extracted with 10% sodium hydroxide and the organic phase was concentrated to give 15 g (60%) of **3,5-dichloro-2-biphenylcarbonitrile** (III). Recrystallization from an ethanol–water mixture gave white crystals, mp 149–150°.

Anal. Calcd for $C_{13}H_7Cl_2N$: C, 62.92; H, 2.84; N, 5.64. Found: C, 63.01; H, 3.04; N, 5.33.

Acidification of the basic ether extract with hydrochloric acid gave 4.0 g (12%) of **2,4-dichloro-5-sulfamylbenzophenone** (II). This was dissolved in dilute sodium hydroxide, treated with charcoal, and reprecipitated by addition of acid. Recrystallization from an ethyl acetate–hexane mixture gave white crystals, mp 200–201°.

Anal. Calcd for $C_{13}H_9Cl_2NO_3S$: C, 47.29; H, 2.75; N, 4.24. Found: C, 47.56; H, 2.73; N, 4.28.

Dehalogenation of 3,5-Dichloro-2-biphenylcarbonitrile.—A mixture of 500 mg of 3,5-dichloro-2-biphenylcarbonitrile and a teaspoon of activated Raney nickel in 60 ml of ethanol was refluxed for 2.5 hr. The nickel was then removed by filtration and the volatile solvents were evaporated under vacuum. Addition of ether to the oily residue caused the separation of a white solid which was collected by filtration and identified by its nmr and infrared spectra as triethylamine hydrochloride. Evaporation of the ether gave an oil which on thin-layer chromatography (silica gel G, $CHCl_3$ development) showed a major spot (at highest R_f) and three traces. Chromatography on silica gel developing with chloroform gave four drops of the major product free of contamination. This was distilled in a small alembic (pot temperature 110°, 15 mm) to give a few drops of a colorless oil. The infrared and nmr spectra were identical with those of authentic 2-methylbiphenyl and very different than that of 3-methylbiphenyl.

Anal. Calcd for $C_{13}H_{12}$: C, 92.81; H, 7.20. Found: C, 92.93, 92.69; H, 7.27, 7.18.

Registry No.—Benzyne, 462-80-6; II, 16355-12-7; III, 16355-13-8; V, 643-58-3.

(2) J. Weinstock and N. C. F. Yim, unpublished results.

(3) For precedents for the last two steps, see G. R. Pettit and E. E. van Tamelin, *Org. Reactions*, **12**, 356 (1961).

(4) J. F. Bunnett, *J. Chem. Educ.*, **38**, 278 (1961).

(5) We wish to thank Miss M. Carroll and her staff for microanalytical data and Mr. R. J. Warren for nmr spectral data. Infrared spectra were determined on a Perkin-Elmer Infracord spectrometer and nmr spectra were obtained on a Varian A-60 spectrometer.

The Chemistry of 3-Oxo-2-phenylindolenine[1]

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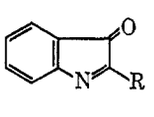
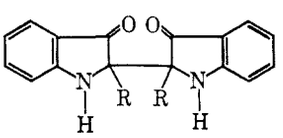
Received November 21, 1967

Recently Hassner and Haddadin[2] have shown that 17-keto steroids react with *o*-nitrobenzaldehyde to produce an exocyclic unsaturated indoxyl, which was postulated to have arisen from a 3-oxoindolenine of type **1a**, by a tautomeric shift. Little is known about endocyclic unsaturated indoxyls **1**. Although several workers have claimed to have isolated 3-oxoindolenines, these structures have either been shown to be erroneous, *e.g.*, the compounds are dimers of type **2**, or are subject to debate in the literature.[3-7]



1a, R = C_6H_5
b, Ia·HCl



2a, R = CH_3
b, R = C_6H_5

We decided to investigate the chemistry of 3-oxoindolenines and chose the 2-phenyl derivative because it could not undergo isomerization to an exocyclic unsaturated isomer. 3-Oxo-2-phenylindolenine (**1a**) was first described by Baeyer as an unstable red solid melting at 102°.[8] This compound was reported to readily react with base or acid and to dimerize on heating in benzene. That such endocyclic unsaturated indoxyls might be unstable and isomerize to an exocyclic unsaturated indoxyl or dimerize is not surprising; they contain a

(1) Stereochemistry. XXXIV. Nitro Compounds. VII. For paper XXXIII, see F. Fowler and A. Hassner, *J. Amer. Chem. Soc.*, **80**, 2875 (1968).

(2) A. Hassner, M. J. Haddadin, and P. Catsoulacos, *J. Org. Chem.*, **31**, 1363 (1966).

(3) O. Neunhoeffer and G. Lehman, *Chem. Ber.*, **94**, 2960 (1961).

(4) A. Hassner and M. Haddadin, *J. Org. Chem.*, **28**, 224 (1963).

(5) D. A. Jones, Ph.D. Thesis, University of Minnesota, Minneapolis, Minn., 1961 discussed several reactions in which 3-oxoindolenines have been postulated as intermediates but in no case have they been isolated.

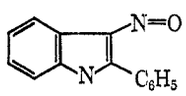
(6) R. K. Callow and E. Hope, *J. Chem. Soc.*, 1191 (1929).

(7) R. Pummerer, *Chem. Ber.*, **44**, 338, 810 (1911).

(8) A. Baeyer, *ibid.*, **45**, 2157 (1912); L. Kalb and J. Bayer, *ibid.*, **45**, 2150 (1912).

strained five-membered ring and resemble the heretofore unknown cyclopentadienone.

The method employed by Baeyer[8] in the synthesis of **1** involved the reaction of 2-phenylindole with sodium nitrite in acetic acid. The identity of the product has aroused considerable controversy.[9-11] Two structures were put forth, a nitroso compound **3** and an isonitroso compound **4a**. We feel that on the basis of spectral evidence neither of these structures are acceptable.



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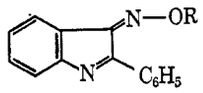
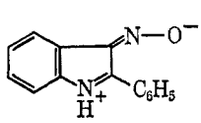


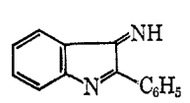
4a, R = H
b, R = Ac

Our product prepared by Baeyer's method, *i.e.*, sodium nitrite in acetic acid, corresponds in every way to that reported by other workers.[8,10,11] However, its infrared spectrum indicated the presence of a salt at 2300–2700 cm^{-1}, and, unlike a true oxime, there was no OH or C=N absorption and no N=O absorption. The compound yields an acetylated product **4b** which is identical with that reported by Campbell and Cooper.[11] The fact that the same product was obtained regardless of whether the synthesis was carried out under acidic or basic conditions and that salt formation occurred even on treatment of a 2-phenylindole with amyl nitrite in ether in the absence of catalyst leads us to the conclusion that the compound is a zwitterion **5**. This salt is unaltered by acid or base. A molecular weight determination indicates a monomer.

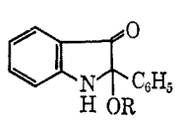
Attempts to continue with Baeyer's procedure, that is, to reduce the oxime **5** to an amine with zinc in acetic acid led to intractable tars even when the reaction was run under a nitrogen blanket. We finally obtained the desired 3-amino-2-phenylindole by carrying out the reduction with sodium dithionite ($Na_2S_4O_4$) in alcohol. The amine was highly unstable, turning from tan to green a few minutes after isolation, and was immediately oxidized with lead tetraacetate to the imine **6**. The latter was hydrolyzed to **1b**, the hydrochloride of oxoindolenine **1a**.



5



6



7a, R = H
b, R = CH_3

Neutralization and work-up of **1b** yielded two indoxyls, the 3-oxo-2-phenylindolenine (**1a**) in 25% overall yield and 2-hydroxy-2-phenylindoxyl (**7a**) in 10% yield. That the final product is indeed **1a** and not a dimer was established by the melting point correspondence to that found by Baeyer, who obtained a correct elemental analysis of **1a** the molecular weight determination in carbon tetrachloride [210 (calcd 207)] and the uv spectrum—250, 265, and 433 mμ (ε 37,200, 42,700, and 4680)—which fits the spectrum expected for such a system, by comparison with spectra of indoxyl derivatives. The long wave length maximum at 433 mμ is nearly the same for the isatogen **8** (438 mμ, ε 1120) as for **1a** in keeping with similar trends in pyridine and pyridine N-oxide. On the other hand, the bathochromic shift in the lower wavelength maximum from 265 to 290 mμ going from **1a** to its N-oxide **8** is probably attributable to the N→O auxochrome in the latter. Conjugated indoxyls absorb at a higher wavelength (455 mμ)[2] whereas simple indoxyls, *i.e.*, **2** and **7** absorb at 400 mμ.

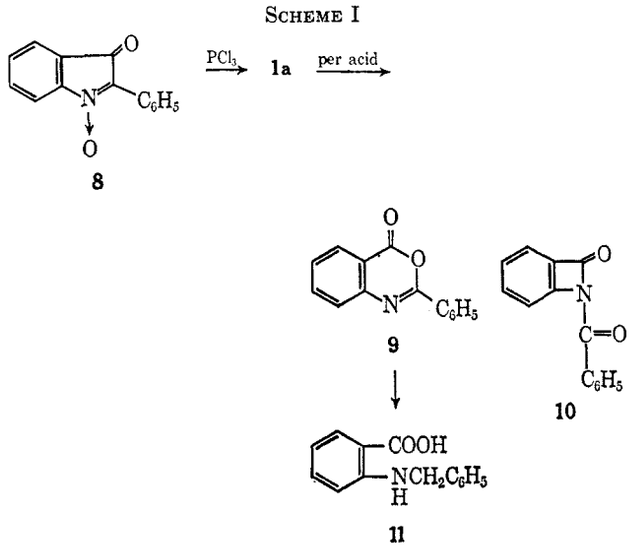
The second product obtained from the neutralization of **1b** is presumed to be 2-hydroxy-2-phenylindoxyl (**7a**). This conclusion is based upon the following data: the infrared spectrum of **7a** indicates OH and NH absorption and its ultraviolet spectrum shows typical indoxyl absorption at 400 mμ. Alcohol **7a** also results on addition of water to **1a**. It is possible to acetylate **7a** as inferred by the disappearance of the OH and appearance of acetoxy C=O absorption in the infrared. Since neither product could be purified, further analysis did not seem feasible.

3-Oxo-2-phenylindolenine (**1a**) was stable to air oxidation and did not appear to undergo dimerization to **2b** in benzene as previously reported.[8] On treatment with base it formed intractable tars, with water it gave **7a**, and with alcohol it formed a heat-sensitive 2-methoxy derivative **7b** that was converted reversibly into **1a**.

The similarity in structure between 2-phenylisatogen (**8**) and 3-oxo-2-phenylindolenine **1a** suggested the possibility of interconversion of these two compounds. Several deoxygenating agents were tried in an attempt to convert the isatogen into the corresponding oxoindolenine. Finally phosphorous trichloride was found successful but the yield of **1a** was poor.

We then attempted the conversion of the oxoindolenine **1a** into isatogen **8** (see Scheme I). It was expected that, like pyridine, the indolenine when treated with per acid would yield the N-oxide. This was not the case. With *m*-chloroperbenzoic acid, an isomer of **8** was obtained which corresponded in every way to that obtained by Jones from 3-acetoxy-2-phenylindole with per acid.[5] Jones assigned structure **9** to the product, based upon the work of Zentmyer and Wagner.[12] The latter authors dismissed structure **10** on the basis of

SCHEME I



8

9

10

11

(9) E. Fischer, *Chem. Ber.*, **21**, 1073 (1888).
(10) A. Angeli and F. Angelico, *Gazz. Chim. Ital.*, **30**, 268 (1900).
(11) N. Campbell and R. Cooper, *J. Chem. Soc.*, 1208 (1935).
(12) D. Zentmyer and E. Wagner, *J. Org. Chem.*, **14**, 967 (1949).

strain in the four-membered ring.[13] We were able to unequivocally confirm[14] the assigned benzoxazine structure **9** by sodium borohydride reduction to N-benzylanthranilic acid (**11**). It is not possible to tell yet if per acids undergo reaction with **1a** on the carbonyl to yield **9** by a Baeyer–Villiger rearrangement, or by attack on the C=N either through an oxaziridine or *via* a peroxy compound.

Experimental Section[15]

3-Oximino-2-phenylindole(5). A. Using Sodium Nitrite in Acetic Acid.—A solution of 4.036 g of 2-phenylindole[16] in 90 ml glacial acetic acid was heated on a steam bath in order to obtain complete solution. Excess sodium nitrite (1.5 g) was slowly added to the dark green solution. A yellow-green precipitate quickly formed. The mixture was allowed to stand for 1 hr and then was diluted with water (200 ml), and the solid was filtered and dried. The product was redissolved in hot concentrated sodium hydroxide, and any residue was filtered off. The purified yellow-orange compound was precipitated by the addition of glacial acetic acid. The yield of dried oxime was 3.824 g (82%): mp 272–274° dec (lit.[10] mp 272–273° dec); ir, 2750–2300 (multiplet), 1838, 1517, 757, 746, 714, and 667 cm^{-1}; uv, λ_{max} (95% C_2H_5OH), 386 mμ (ε 3160), 330 (3800), 264 (35,500), 230 (12,000); molecular weight in pyridine, 236 (calcd 222).

B. Using Sodium Ethoxide and Amyl Nitrite.—Product **5** was obtained in 81% yield from a reaction of 2-phenylindole with isoamyl nitrite and sodium ethoxide in ethanol at 0°, following work-up with boric acid.

C. Using Amyl Nitrite in Ether Without a Catalyst.—The reaction was carried out with 3.96 g of 2-phenylindole in 60 ml of anhydrous ether, and 2.4 ml of isoamyl nitrite. After 2 hr at 25° a small amount of precipitate began to form from the yellowish solutions. After 26 hr, the product was filtered off and dried. The yield of **5** was 2.84 g, mp 276–277° dec, no purification was necessary. The product was identical in every way with **5** as prepared above.

Acetylation of Oxime 5.—Oxime **5** (753 mg) was acetylated by refluxing overnight in 15 ml of acetic anhydride and 9 ml of pyridine. The product was dissolved in acetone, and the resulting solution was filtered and then evaporated to dryness. The resulting red gum was crystallized from ethanol. The yield was 600 mg: mp 116° (lit.[11] mp 117°); ir, 1785 (C=O), triplet at 1178, 1165, and 1153 (oxime acetate), 1000, 918 cm^{-1}.

3-Imino-2-phenylindolenine (6).—To a solution of 86.9 g of **5** in 300 ml of ethanol and 500 ml of 2 *N* sodium hydroxide was added slowly an excess (16.7 g) of sodium dithionite ($Na_2S_2O_4$). The mixture was heated on the steam bath until the solution turned a light yellow color. The resulting product was filtered off, washed with 150 ml of water and 5 ml of ethanol, and then dried for 10 min under vacuum. The yield of 3-amino-2-phenylindole was 82%, mp 174–176° (lit.[10] mp 180°). The amine (20.4 g) in 100 ml of anhydrous benzene was oxidized with 150 g of activated lead dioxide by heating for 15 min and the imine **6** was obtained from benzene in 81% yield: mp 112–115° (lit.[8] mp 114°); ir, 1639, 1605, 1600, 1520, 766, 748, 685 cm^{-1}.

3-Oxo-2-phenylindolenine (1a).—A slurry, prepared from 6.90 g of imine **6** in concentrated hydrochloric acid was filtered under suction and the product 3-oxo-2-phenylindolenine hydrochloride (**1b**) was dried under vacuum over sodium carbonate; the ir spectrum showed absorptions at 2650–2550 (multiplet), 1730 (C=O), 1625, 1575, 768, 720, and 674 cm^{-1}.

The compound was placed in benzene, and the mixture was concentrated to drive off any excess hydrochloric acid. Excess calcium carbonate was added, and the mixture was heated briefly on the steam bath and then filtered. The residue was washed with hot benzene and the filtrates were combined and then evaporated down to a small volume, whereupon petroleum ether (20–40°) was added. Immediately upon addition of petroleum ether an unstable yellow product (**7a**) precipitated and was filtered off; uv maxima in carbon tetrachloride were at 407 mμ (ε 2630), 265 (46,800), and 250 (ε 24,600).

The filtrate from **7a** was concentrated until red crystals began to form. The solution was cooled and allowed to stand overnight. The red crystalline material was collected and dried and then recrystallized from ether to give 4.62 g of **1a**: mp 102° (lit.[8] mp 102°); mol wt 209.3 (calcd 207); uv, λ_{max} (CCl_4), 433 mμ (ε 4680), 270 (40,070) sh, 265 (42,700), 250 (37,200); ir, 1739 (C=O) and 1608 cm^{-1}.

2-Methoxy-2-phenylindoxyl (7b).—A solution of 445 mg of 3-oxo-2-phenylindolenine (**1a**) in 100 ml of absolute methanol was refluxed 2 hr and then evaporated to dryness under vacuum at room temperature. Recrystallization of the product from ether–petroleum ether afforded a mixture of indolenine **1a** and the methoxy compound **7b**, mp 104–107°. This product could not be further purified.

The above procedure was repeated with 422 mg of material. This time the product was recrystallized from methanol by first concentrating the solution, then by keeping the solution at −10°, and constantly scratching the flask with a glass rod until brilliant yellow crystals began to form. After crystallization began, the flask was allowed to sit for 2 hr at −10°, then the yellow crystals of **7b** were filtered off. The yield was 400 mg: mp 87°; mol wt 226 (calcd 239); uv, λ_{max} (CCl_4), 405 mμ (ε 4790), 265 (50,100), 250 (37,200); ir, 3436, 1703, 1626, 762, 753, 717, 701 (sh), 664 cm^{-1}.

Anal. Calcd for $C_{15}H_{13}O_2N$: C, 75.34; H, 5.47. Found: C, 75.18; H, 5.42.

If the methoxy compound **7b** was heated in methanol and the solution was concentrated, the product obtained was a mixture of indolenine **1a** (predominantly) and indoxyl **7b**.

2-Phenylisatogen (8).—A modification of the procedure by Krohnke and Meyer-Delius[17] was employed. A solution of 4 g of *o*-nitrostilbene–pyridinium bromide (mp 253–255°)[17] in 200 ml of 50% aqueous acetic acid, was placed in white porcelain dishes and kept in the sunlight. The solution slowly turned orange and finally red-orange crystals were deposited. The product was recrystallized from methanol: 2.13 g; mp 188–189° (lit.[5] mp 189–190°); uv, λ_{max} (CCl_4), 438 mμ (ε 1120), 290 (35,500), 285 (34,700); ir, 1720 (C=O), 1709, 1385 cm^{-1} (ArN—O).

Deoxygenation of 2-Phenylisatogen (8) to 1a.—To a solution of 2 g of 2-phenylisatogen in 20 ml of chloroform was added 1.7 g of phosphorous trichloride (excess) at 0° for 1 hr. The solution was allowed to remain at room temperature for 30 hr and was then evaporated to dryness under vacuum. To the residue (a greenish-yellow oil) was added 2.5 ml of concentrated hydrochloric acid. The resulting slurry was filtered and the solid was dried. The solid mass was placed in benzene and then concentrated from 150 to 35 ml. To this solution excess calcium carbonate was added, and then the mixture was boiled for 15 min. The suspension was filtered, and the residue was washed with hot benzene. The filtrates were combined and concentrated. Petroleum ether was then added and the resulting yellow green tar was filtered off. The solution was further concentrated until red amorphous material began to precipitate. Three recrystallizations from ether yielded 65 mg of a product melting at 101–102°. The infrared and ultraviolet spectra were identical with those of 3-oxo-2-phenylindolenine (**1a**). A mixture melting point experiment with authentic **1a** showed no depression.

Attempts to deoxygenate **8** with triethyl phosphite in benzene at 0° led to tarry material. Refluxing of **8** with triphenylphosphine in benzene or methylene chloride led to recovery of starting material.

Oxidation of 3-Oxo-2-phenylindolenine (1a) to 9.—To a solution of 433 mg of **1a** in 25 ml of chloroform was added 685 mg of *m*-chloroperbenzoic acid (85% pure). The red solution which turned pale yellow after 15 min was kept at room tempera-

(13) There are several recent reports of the possible intermediacy of benzazetidones in reactions: G. Ege, *Angew. Chem. Intern. Ed. Engl.*, **4**, 699 (1965); E. M. Burgess and G. Milne, *Tetrahedron Lett.*, 93 (1966); R. K. Smalley, H. Suschitzky, and E. M. Tarner, *ibid.*, 3465 (1966).

(14) J. L. Pinkus recently found confirmatory evidence for structure **9** from mass spectra data. He also isolated **9** from peracid oxidation of **1a**. We are grateful to Professor Pinkus, University of Pittsburgh, Pittsburgh, Pa., for communicating these results to us prior to publication.

(15) All melting points were taken on a Fisher–Johns melting point apparatus, and are uncorrected. Infrared spectra were determined in the solid phase (KBr) using a Perkin-Elmer Infrared 21 spectrophotometer. Ultraviolet spectra were measured on a Cary Model XIV instrument. Molecular weights were determined in carbon tetrachloride, unless otherwise noted, using a Mechrolab Vapor osmometer, Model 301A.

(16) V. Sadovskaya, N. Grineva, and V. Ufimstov, *J. Gen. Chem. USSR*, **33**, 545 (1963).

(17) F. Kröhnke and M. Meyer-Delius, *Chem. Ber.*, **84**, 932 (1951).

ture overnight. The solution was poured through a column of neutral alumina and then evaporated on the rotovac. The resulting material was crystallized from methanol affording yellowish needles of 9: 316 mg (70.6%); mp 122.5° (lit.[5] mp 124°). The infrared spectrum indicated the presence of a carbonyl at 1764 cm^{-1}.

Anal. Calcd for $C_{14}H_9O_2N$: C, 75.34; H, 4.08. Found: C, 74.55; H, 4.04.

Hydrolysis of 120 mg of 9 in 15 ml of boiling 5% sodium hydroxide gave 105 mg of N-benzoylanthranilic acid, mp 181–181.5° (lit.[12] mp 182°).

Sodium Borohydride Reduction of 9 to 11.—To a solution of 300 mg of 9 in absolute ethanol was added 210 mg of sodium borohydride (excess), and the reaction mixture was allowed to sit 4 hr. The solution was evaporated to dryness in a vacuum, and the residue was extracted with hot chloroform. The chloroform solution was concentrated and cooled to yield brownish white crystals. After two recrystallizations from chloroform, 275 mg (90%) of 11, mp 175°, was obtained (ir, 1661 (C=O), 1245, and 1235 cm^{-1}) identical in every respect with authentic N-benzylanthranilic acid.[13]

Registry No.—1a, 2989-63-1; 7b, 16355-10-5; 9 1022-46-4.

Acknowledgment.—This investigation was supported by Public Health Service Grant CA-04474 from the National Cancer Institute.

(18) G. Lockemann and H. Rein, *Chem. Ber.*, **80**, 485 (1947).

Dichloro(O,O′-1,4-dioxane)zinc(II)

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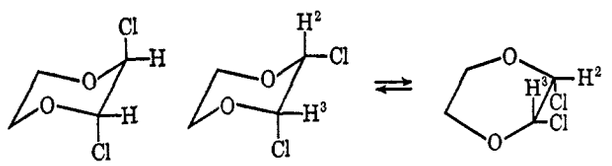
Received December 26, 1967

The reaction between 1,4-dioxane and chlorine produces a mixture of isomers of 2,3-dichloro-1,4-dioxane,[2] mp 30° (*trans*) and 51° (*cis*).[3,4] The *trans* isomer exists in a diaxial chair conformation [I (C_{aa})] while the *cis* isomer exists in an axial–equatorial chair conformation which is continuously inverting [II (C_{ae}), II (C_{ea})].[5–7]



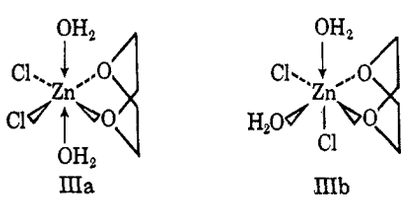
I(C_{aa}) II(C_{ae}) II(C_{ea})

Because *cis*- and *trans*-2,3-dichloro-1,4-dioxane constitute a valuable heterocyclic system with which to study axial/equatorial stereospecificity thresholds with respect to alkoxy substituents, it was desirable to develop a specific method for the synthesis of each isomer.

Preparation of pure I poses no problem since it is lower boiling and more thermodynamically stable than II. Preparation and isolation of pure II is more difficult owing to its ease of interconversion to I. The only method of preparing pure II reported in the literature[5] is low temperature (below 90°) chlorination of dioxane with subsequent vapor–liquid chromatographic separation of the two isomers.

The only catalyst reported used in the chlorination of 1,4-dioxane is $SnCl_2$.[8] The presence of $SnCl_2$ increased the 2,3-dichloro product yield by 28%; no product isomer distribution was reported. It was decided to try other metal chlorides (Lewis acids) but with electron configurations about the metal ion different from the $3d^{10}4s^2$ structure of Sn^{+2}, preferably those with vacant 4s orbitals. An added restriction was the solubility of the metal chlorides in dioxane. The metal chlorides most readily available and which meet these requirements are $ZnCl_2$, $CuCl_2$, $FeCl_3$, and $AlCl_3$. Zinc chloride, the first catalyst to be tried, selectively catalyzed the formation of II without detectable amounts of I. An investigation was then made of the structure of the zinc chloride–dioxane complex initially formed which apparently is the stereospecific catalyst for the formation of *cis*-2,3-dichloro-1,4-dioxane.

A white zinc chloride–dioxane complex has been reported as being polymeric units of ($ZnCl_2$–dioxane)$_n$ formed at ambient temperature with the dioxane ring in the chair conformation.[9,10] The infrared spectrum of the yellow zinc chloride–dioxane complex obtained in the present study shows an increased number of absorption frequencies in the regions 2950–2870, 1960–1480, 1440–1375, and 1325–1280 cm.$^{-1}$ as compared with the dioxane chair absorption frequencies. This suggests that the complexed dioxane ring exists in a boat conformation.[9] An absorption at 620 cm^{-1}, indicative of oxygen–zinc bonds, also supports the dioxane boat structure with zinc chelation as the stabilizing force for the less stable boat conformation.[11] The very pronounced hygroscopic property of the complex is considered as d-orbital participation which expands the coordination number of zinc from four to six, using the $4d_{z^2}$ and $4d_{x^2-y^2}$ orbitals.



IIIa IIIb

Although the nmr spectrum resolution of the complex in aqueous solution was insufficient to discern structure IIIa from IIIb, the respective absorption peak area ratios are sufficiently accurate to exclude the possibility of a second dioxane ring participation.

It is concluded that the structure of the zinc chloride–dioxane complex which catalyzes the stereospecific

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