The reaction mixture was dissolved in ice-water, extracted with ether and the aqueous phase acidified with cold concentrated hydrochloric acid. The oily enolic product was extracted with ether–methylene chloride, the extract dried and concentrated. The solid residue was crystallized from ether; 6.2 g. of material, m.p. 130–134°, was obtained. The analytical sample, white needles from acetone, melted at 137–138°.

Anal. Calcd. for $C_{18}H_{15}O_4N$: C, 69.89; H, 4.88; N, 4.52. Found: C, 70.00; H, 4.94; N, 4.62.

Oxindole-3-propionic Acid (XIb) from Benzyl β-Isatylidene-β-hydroxypropionate (VIIIb).—Three and nine-hundredths grams (0.01 mole) of benzyl β-isatylidene-β-hydroxypropionate (VIIIb) was shaken with 2 g. of 10% palladium-on-charcoal catalyst in 100 ml. of glacial acetic acid containing 1 ml. of concd. sulfuric acid in an atmosphere of hydrogen until three moles of hydrogen had been absorbed. The catalyst was then removed by filtration and the filtrate concentrated *in vacuo* to a heavy sirup. Upon the addition of 20 ml. of water, the product solidified and was collected by filtration. An 82% yield of crystals, 1.65 g., m.p. 163–165°, was obtained. The product gave no depression with the Kendall acid.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE RESERCH LABORATORIES OF THE GLIDDEN COMPANY, SOYA PRODUCTS DIVISION]

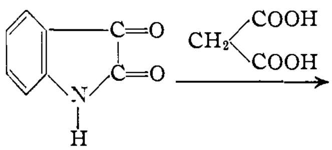
Studies in the Indole Series. XIV. Oxindole-3-acetic Acid

BY PERCY L. JULIAN, HELEN C. PRINTY, ROGER KETCHAM AND ROBERT DOONE

RECEIVED APRIL 24, 1953

The synthesis of oxindole-3-acetic acid has been achieved for the first time. All previous attempts to isolate this substance involved vigorous hydrolysis procedures which resulted in the formation of 2-oxo-1,2,3,4-tetrahydroquinoline-4-carboxylic acid. The present successful synthesis had its origin in the observation that acetaminoacrylic acid, in its tautomeric imino modification, condenses smoothly with oxindole in the absence of hydroxyl ions to produce stable α-isatylidene-α-methylacetic acid. Its reduction product, α-oxindolylmethylacetic acid, is likewise stable and is converted into the corresponding quinolonecarboxylic acid only on vigorous hydrolysis. Following this observation it was, therefore, not surprising that we successfully achieved the synthesis of oxindole-3-acetic acid by reduction of the condensation product of oxindole with dibenzyl oxalate.

Oxindole-3-acetic acid (IV) has enjoyed a long history in the literature but has, up to the present, eluded all attempts at its synthesis. Even its precursor in certain condensation reactions, namely, isatylideneacetic acid (II), has likewise never been secured. Thus Borsche and Jacobs[1] condensed isatin (I) with malonic acid in acetic acid solution and obtained 2-oxo-1,2-dihydroquinoline-4-carboxylic acid (III) instead of the expected isatylideneacetic acid (II).



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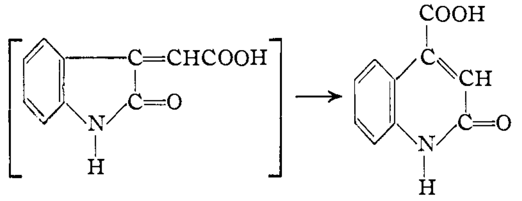
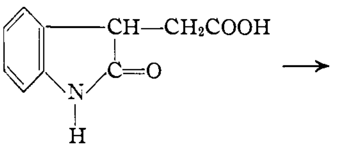


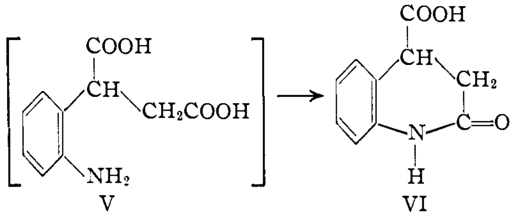
II III

Aeschlimann[2] demonstrated that the constitution III was to be assigned to the acid of Borsche and Jacobs and further that the condensation I → III took place even in the absence of solvents at 200°, followed by recrystallization of the products from non-aqueous solvents to avoid the possibility of isomerization during purification. Such a result would indicate that isatylideneacetic acid (II) is an extremely labile substance and hardly capable of existence.

Gränacher and Mahal[3] reported the preparation of "oxindole-3-acetic acid" by reduction of "oxindole-3-α-thiolacetic acid," which was obtained by alkaline hydrolysis of 3-rhodanylideneoxindole. Aeschlimann,[2] however, showed that their product was not oxindole-3-acetic acid (IV), but instead 2-oxo-1,2,3,4-tetrahydroquinoline-4-carboxylic acid (VI), formed by hydrolytic rupture of the oxindole ring to produce *o*-aminophenylsuccinic acid (V), which, in its turn, underwent ring closure to produce VI. Indeed, Aeschlimann was so impressed with this comparative instability of the oxindole as over against the quinolone ring structure that he even proposed the constitution X for oxindole-3-aldehyde (VII), prepared first by Friedlander and Kielbasinski[4] by alkaline hydrolysis of Thioindigo Scarlet R. His conclusion was based upon the observation that oxindole-3-aldehyde (3-formyloxindole) (VII) is a relatively strong acid and behaved more like indolecarboxylic acid (X) than like an aldehyde. Accordingly, he represented the mechanism of its transformation, during the hydrolysis of Thioindigo Scarlet R, in a manner indicated by formulas VII → X. It is true indeed that oxindole-



IV



V VI

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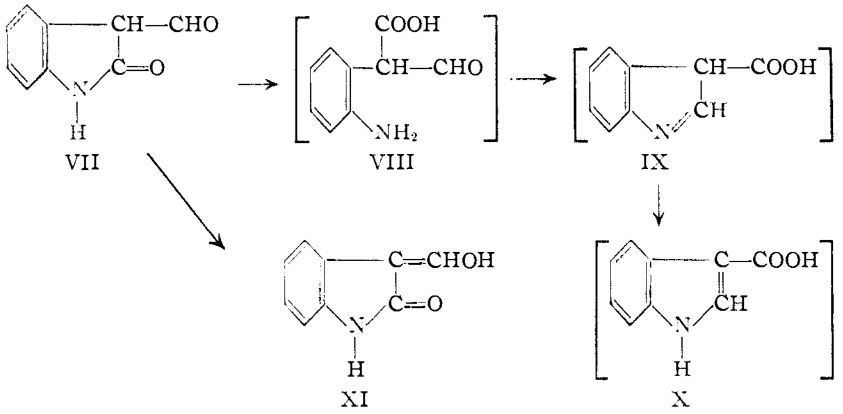
[1] W. Borsche and W. Jacobs, *Ber.*, **47**, 354 (1914).

[2] J. A. Aeschlimann, *J. Chem. Soc.*, 2902 (1926).

[3] Ch. Gränacher and A. Mahal, *Helv. Chim. Acta*, **6**, 467 (1923).

[4] P. Friedlander and S. Kielbasinski, *Ber.*, **44**, 3098 (1911).



3-aldehyde (VII), like most acyloxindoles, is a relatively strong acid, dissolving readily in sodium bicarbonate solutions.[5] This is, however, to be attributed to its existence as a stable enol XI which Behringer and Weissauer[6] aptly designated as a vinylog of a true carboxylic acid. This conception of these 3-acyl compounds, supported by their isatin-like ultraviolet spectra, has necessitated a reexamination of the chemistry of these "3-acyloxindoles," the results of which will be the subject of a later communication.

Gränacher and Kouniniotis[7] later confirmed Aeschlimann's findings that their "oxindoleacetic acid" actually had the structure VI. They likewise showed that the "oxindole-3-acetic acid" patented by Schering,[8] and prepared by reduction of the condensation product of isatin and malonic acid, is actually 2-oxo-1,2,3,4-tetrahydroquinoline-4-carboxylic acid (VI).

Hill and Henze[9] and later Hill, Schultz and Lindwall[10] attempted the preparation of oxindole-3-aminoacetic acid by condensation of hydantoin with isatin, followed by reduction and hydrolysis. Their compound was the quinolonecarboxylic acid (III), which, on reduction, gave VI. Thus their amino acid had suffered, under the vigorous hydrolysis, rupture of the ring, deaminization, and renewed ring closure to III.

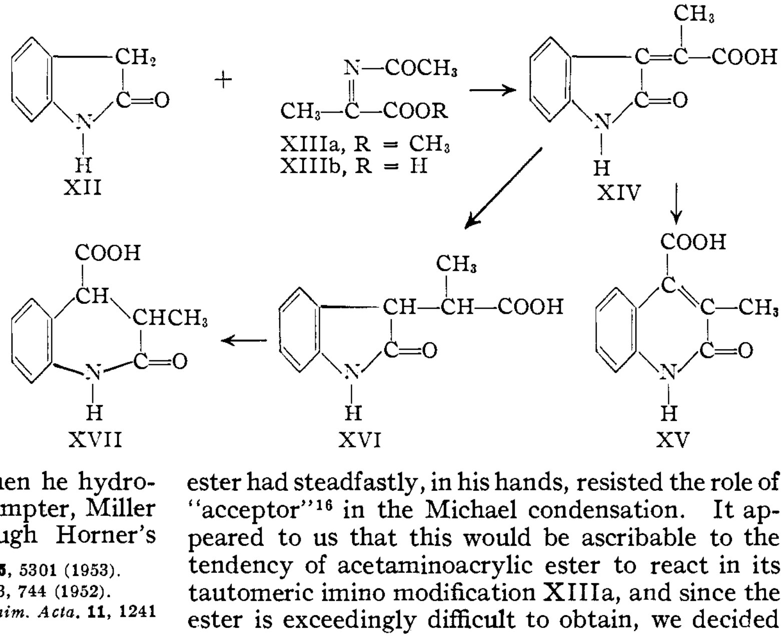
Zrike and Lindwall[11] likewise showed that instead of securing oxindole-3-acetic acid from the hydrolysis product of oxindole-3-malonitrile, they obtained the quinolonecarboxylic acid (VI).

Horner[12] thought that he had prepared oxindole-3-acetic acid (IV) when he hydrolyzed ethyl oxindole-3-acetate, but Sumpter, Miller and Hendrick[13] showed that although Horner's ethyl oxindole-3-acetate had the correct structure, his acid was actually again the quinolonecarboxylic acid (VI). Thus the many and varied attempts to secure oxindole-3-acetic acid have all ended in obtaining 2-oxo-1,2,3,4-tetrahydroquinoline-4-carboxylic acid (VI).

Julian, Pikl and Boggess[14] formulated their product derived from the hydrolysis of 1,3-dimethyloxindole-3-acetonitrile as an oxindoleacetic acid. Sumpter[15] later noted the work of Julian, Pikl and Boggess[14] and stated that "in view of the non-existence of 'oxindoleacetic acid' . . ., it seems entirely possible that Julian's (acid) has been incorrectly formulated and that the compound may be the quinoline derivative."

This statement of Sumpter is undoubtedly correct and underscores the implication rather generally accepted that oxindoleacetic acids cannot exist as such. Our long experience with oxindoles led us to feel, however, that only because of the vigorous hydrolysis attendant upon all previous attempts to prepare an oxindoleacetic acid had such efforts shattered. A fortuitous circumstance in connection with another investigation demonstrated this quite clearly.

Among our early efforts to prepare oxytryptophan from oxindole, we had planned a Michael condensation between the latter and acetaminoacrylic ester. In a chance discussion of these plans with Professor Roger Adams, he informed us that acetaminoacrylic ester had steadfastly, in his hands, resisted the role of "acceptor"[16] in the Michael condensation. It appeared to us that this would be ascribable to the tendency of acetaminoacrylic ester to react in its tautomeric imino modification XIIIa, and since the ester is exceedingly difficult to obtain, we decided to study the condensation between oxindole and the acid itself XIIIb under conditions similar to those employed in the Michael condensation.



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(5) P. L. Julian and H. Printy, This Journal, **75**, 5301 (1953).

(6) H. Behringer and H. Weissauer, *Ber.*, **85**, 743, 744 (1952).

(7) Ch. Gränacher and Ch. Kouniniotis, *Helv. Chim. Acta*, **11**, 1241 (1928).

(8) German Patent 431,510.

(9) A. J. Hill and H. R. Henze, This Journal, **46**, 2806 (1924).

(10) A. J. Hill, A. S. Schultz and H. G. Lindwall, *ibid.*, **52**, 769 (1930).

(11) E. Zrike and H. G. Lindwall, This Journal, **58**, 49 (1936).

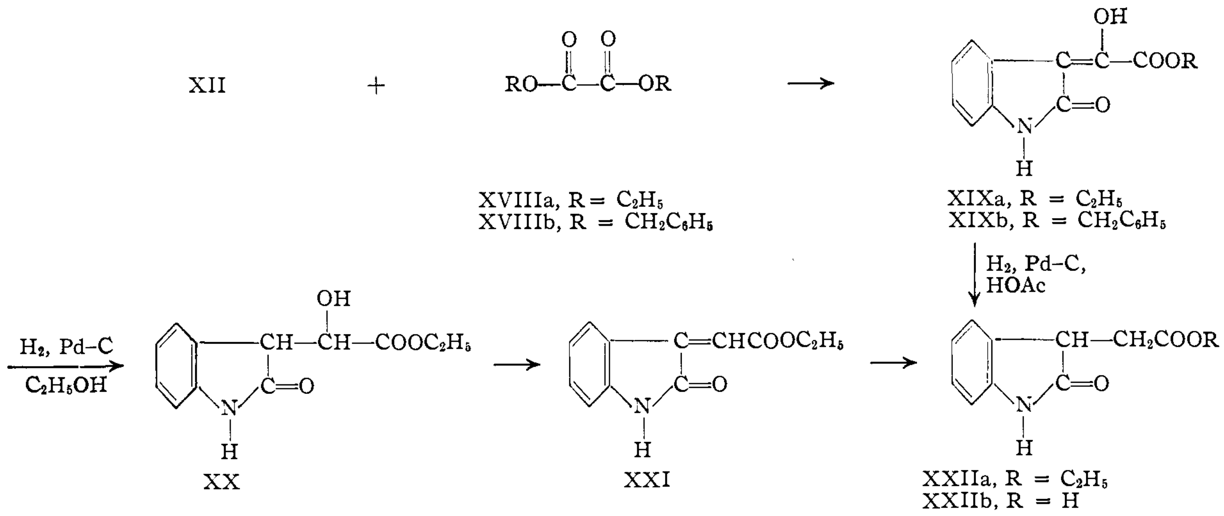
(12) L. Horner, *Ann.*, **548**, 117 (1941).

(13) W. C. Sumpter, M. Miller and L. N. Hendrick, This Journal, **67**, 1037 (1945).

(14) P. L. Julian, J. Pikl and D. Boggess, *ibid.*, **56**, 1797 (1934).

(15) W. C. Sumpter, *Chem. Revs.*, **37**, 443 (1945).

(16) R. Connor and W. R. McClellan, *J. Org. Chem.*, **3**, 570 (1939).



Somewhat to our surprise, we secured an almost quantitative yield of the stable isatylidenemethylacetic acid (XIV), and thus for the first time had prepared an isatylideneacetic acid. Its structure was evidenced by the strong similarity between its ultraviolet absorption spectrum and that of isatin. Its spectrum is, however, quite different from that of the corresponding quinolone-4-carboxylic acid (XV) (Fig. 1). Mild ozonization of its methyl ester yielded isatin. It was moreover catalytically reduced in the presence of palladium-on-charcoal to oxindole-3-methylacetic acid (XVI). The isatylideneacetic acid (XIV) was converted on hydrolysis to the quinolonecarboxylic acid (XV), and likewise the oxindolemethylacetic acid (XVI) was similarly converted on acid hydrolysis to the quinolonecarboxylic acid (XVII). Thus an oxindoleacetic acid had been prepared for the first time, and it owed its existence to the absence of any appreciable hydroxyl ion concentration in the system involved in its preparation. As further proof of its constitution, it was prepared, although in poorer yield, by the condensation of oxindole with pyruvic acid instead of with acetaminoacrylic acid. The difference in yield is indicative of the fortunate absence of water in the first mode of preparation.

These observations led us, therefore, to restudy the condensation between oxindole (XII) and diethyl oxalate (XVIIIa), a type of reaction studied earlier by Julian, Pikl and Wantz[17] and later investigated by Horner,[12] wherein Horner obtained what we now know to be the stable enol XIXa. Horner successfully reduced XIXa with zinc dust and acetic acid to oxindoleacetic ester (XXIIa), the constitution of which was verified by Sumpter, Miller and Hendrick.[13] We have found that XIXa is definitely an isatylidene derivative and that, on catalytic reduction in the presence of palladium-on-carbon in alcoholic solution, reduction stopped at the consumption of one mole of hydrogen, and there could be isolated the oxindole-3-hydroxyacetic ester (XX). The latter, on taking up in glacial acetic acid in the presence of a small quantity of sulfuric acid, suffered dehydration to the isatylideneacetic ester (XXI), which, in turn, was smoothly catalytically reduced in the presence of palladium-on-charcoal to oxindoleacetic ester (XXIIa).

On substituting dibenzyl oxalate (XVIIIb) for diethyl oxalate in the condensation, the reaction proceeded equally as smoothly to yield the stable enol XIXb, which, on catalytic reduction in glacial acetic acid–sulfuric acid solution, yielded the long-sought-for oxindole-3-acetic acid (XXIIb).

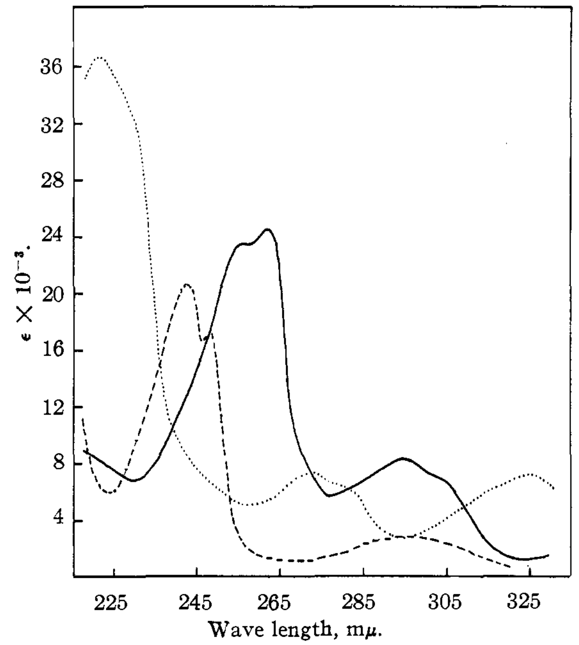


Fig. 1.—Ultraviolet absorption spectra in methanol of isatylidenemethylacetic acid, ——; isatin, - - -; and 2-oxo-3-methyl-1,2-dihydroquinoline-4-carboxylic acid, ...

Acknowledgment.—The authors are indebted to Dr. Edwin W. Meyer and Mr. Francis A. Taylor for technical assistance.

Experimental[18]

Isatylidenemethylacetic Acid (XIV). A. From Oxindole and Acetaminoacrylic Acid.—Six and nine-tenths grams of sodium was dissolved in 300 ml. of absolute ethanol, and 13.3 g. of oxindole (XII) was dissolved in this solution. α-

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[17] P. L. Julian, J. Pikl and F. E. Wantz, THIS JOURNAL, 57, 2026 (1935).

[18] Analyses are by Micro-Tech Laboratories, Skokie, Illinois.

Acetaminoacrylic acid,[19] 12.9 g., was added and the solution refluxed for six hours under nitrogen. During this period, fine yellow crystals of sodium salt came out. These were filtered, washed with absolute ethanol and ether and dried. The maximum yield, 21.8 g. (97%), was obtained only after six hours of refluxing.

The free acid was obtained from 15.6 g. of sodium salt by dissolving the salt in 100 ml. of glacial acetic acid, and diluting the warm solution with 200 ml. of 5% hydrochloric acid. A first crop of 10.1 g., m.p. 199°, was obtained. A second crop of 1.4 g. of material melting at 198° was obtained by neutralizing the mother liquor with 10% sodium hydroxide, concentrating and reacidifying it.

The acid crystallized from ethanol–ethyl acetate in orange prisms, m.p. 203° dec.

Anal. Calcd. for $C_{11}H_9O_3N$: C, 65.01; H, 4.46; N, 6.89. Found: C, 65.10; H, 4.47; N, 7.20.

B. **From Oxindole and Pyruvic Acid.**—When 6.65 g. of oxindole was refluxed for six hours under nitrogen with 4.4 g. of distilled pyruvic acid and a solution prepared from 3.45 g. of sodium in 150 ml. of absolute ethanol, 9.87 g. (87%) of yellow sodium salt was obtained. This was hydrolyzed to the free acid in the manner previously described, and 5.72 g. of orange acid, m.p. 191–196°, was obtained. This gave no depression when melted with the product described in A.

Methyl Isatylidenemethylacetate.—A suspension of 10.1 g. of isatylidenemethylacetic acid (XIV), 7 ml. of distilled thionyl chloride and a drop of pyridine in 40 ml. of absolute ether was stirred at room temperature for one hour. The suspension was chilled to 0° and 10 ml. of anhydrous methanol added with stirring. The reaction was kept at 0° for two hours, then was filtered and the methyl ester washed with ether, 50% methanol and water. The yield of material of melting point 167–170° was 7.25 g. Several recrystallizations from methanol resulted in yellow prisms, m.p. 178–180°.

Anal. Calcd. for $C_{12}H_{11}O_3N$: C, 66.34; H, 5.10; N, 6.44. Found: C, 66.04; H, 5.18; N, 6.40.

Ozonization of 2.17 g. of this ester in 230 ml. of chloroform at −15° afforded 1.1 g. of isatin, m.p. 197–200°.

Oxindole-3-methylacetic Acid (XVI).—When 2.76 g. of XIV in 100 ml. of methanol was shaken with 0.28 g. of 10% palladium-on-charcoal catalyst, at one atmosphere, one molar equivalent of hydrogen was absorbed very rapidly. The catalyst was filtered and the filtrate concentrated to a volume of 20 ml. Upon the addition of 10 ml. of water, 1.78 g. of material, m.p. 162–163°, was obtained. A second crop of 0.92 g. melted at 152–157°. Recrystallization from ether–petroleum ether (b.p. 35–65°) resulted in white prisms, m.p. 163–164°.

Anal. Calcd. for $C_{11}H_{11}O_3N$: C, 64.37; H, 5.40; N, 6.82. Found: C, 64.62; H, 5.47; N, 6.71.

When methyl isatylidenemethylacetate was reduced in the same manner, the saturated methyl ester was formed. This crystallized very slowly from ether–petroleum ether (b.p. 35–65°) in fine white prisms, m.p. 81–82°.

Anal. Calcd. for $C_{12}H_{13}O_3N$: C, 65.73; H, 5.97; N, 6.38. Found: C, 65.57; H, 6.05; N, 6.38.

2-Oxo-3-methyl-1,2-dihydroquinoline-4-carboxylic Acid (XV).—Two hundred and eighty milligrams of isatylidenemethylacetic acid (XIV) was refluxed for 17 hours with 36 ml. of 6% hydrochloric acid. The solution, after concentration and chilling, deposited 200 mg. of white needles, m.p. 295–305°. Crystallization from water raised the melting point to 315–317°. This product gave no depression when melted with a sample of 2-oxo-3-methyl-1,2-dihydroquinoline-4-carboxylic acid (m.p. 315–317°) prepared from 1-propionylisatin by the method of Meyer.[20]

The alkaline isomerization of XIV led to the same product but in very poor yield.

The acid XV, upon reduction with sodium amalgam as described by Aeschlimann,[2] afforded a white product, m.p. 212–214°; this was identical with 2-oxo-3-methyl-1,2,3,4-tetrahydroquinoline-4-carboxylic acid (XVII) obtained from the acid rearrangement of oxindole-3-methylacetic acid (XVI).

Ethyl Oxindole-3-hydroxyacetate (XX).—Ethyl isatylidenehydroxyacetate (ethyl oxindole-3-glyoxylate) (XIXa) was prepared as described by Horner.[12] The enol XIXa, 4.66 g., was dissolved in 100 ml. of ethanol and reduced with 5 g. of 10% palladium-on-charcoal catalyst.[21] The reduction proceeded rapidly with the absorption of one molar equivalent of hydrogen. The product, which had crystallized during the reaction, was redissolved with 150 ml. of methylene chloride; the solution was filtered and concentrated *in vacuo* to obtain a crop of white material, 2.35 g., m.p. 194–195°. Several recrystallizations from acetone–benzene afforded white needles, m.p. 183–184° dec.

Anal. Calcd. for $C_{12}H_{13}O_4N$: C, 61.26; H, 5.57; N, 5.95. Found: C, 61.62; H, 5.70; N, 6.03.

From the hydrogenation mother liquor, 1.58 g. of orange material, m.p. 156–165°, was obtained. This was shown to be impure ethyl isatylideneacetate (XXI).

Ethyl Isatylideneacetate (XXI).—A 0.5-g. sample of ethyl oxindole-3-hydroxyacetate (XX) was dissolved in 10 ml. of glacial acetic acid containing a drop of concentrated sulfuric acid and the solution kept at 25° for 15 hours. The solution was diluted with water, and the yellow precipitate collected by filtration. The crude material, 0.4 g., m.p. 165–167°, crystallized from acetone as orange needles, m.p 169–170°.

Anal. Calcd. for $C_{12}H_{11}O_3N$: C, 66.34; H, 5.10; N, 6.44. Found: C, 66.24; H, 5.41; N, 6.57.

Rearrangement to **2-oxo-1,2-dihydroquinoline-4-carboxylic acid (III)** was effected by refluxing 0.3 g. of the ester (XXI) with 37 ml. of 6% hydrochloric acid for one hour. The product obtained melted at 340°, lit. m.p. 343°.

Ethyl Oxindole-3-acetate (XXIIa) A.—A solution of 2.17 g. of ethyl isatylideneacetate (XXI) in 50 ml. of ethanol was hydrogenated in the presence of 1 g. of palladium-on-charcoal catalyst until one molar equivalent of hydrogen was absorbed. The reaction was then filtered, the solvent removed *in vacuo*, and the residue crystallized from ether. One and six-tenths grams (72%) of ethyl oxindole-3-acetate (XXIIa), m.p. 94–96°, lit. m.p. 95°,[12,13] was obtained.

B.—Four and sixty-six hundredths grams of ethyl isatylidenehydroxyacetate (XIXa) was hydrogenated in 200 ml. of glacial acetic acid containing 1 ml. of concentrated sulfuric acid and 5 g. of 10% palladium-on-charcoal catalyst. The reduction stopped after two molar equivalents of hydrogen was absorbed; the reaction mixture was filtered onto 4 g. of sodium acetate, and the solvent removed *in vacuo*. The residue was extracted with ether and water, the ethereal portion dried and concentrated to a low volume. Upon the addition of petroleum ether, a first crop of 2.63 g., m.p. 94–98°, was obtained. The mother liquor yielded an additional 1.18 g. of material, m.p. 88–93° (87%).

When 0.3 g. of XXIIa was rearranged with hydrochloric acid,[13] 0.2 g. of **2-oxo-1,2,3,4-tetrahydroquinoline-4-carboxylic acid (VI)**, m.p. 218°, was obtained.

Benzyl Isatylidenehydroxyacetate (XIXb).—When the condensation of dibenzyl oxalate with oxindole was attempted in ethanol using sodium ethoxide, the product obtained, in 85% yield, was ethyl isatylidenehydroxyacetate (XIXa). However, the desired product was obtained by adding a solution of 6.65 g. of oxindole and 20 g. of dibenzyl oxalate[22] in 100 ml. of dry benzene to 1.5 g. of powdered sodium in 50 ml. of benzene. The reaction mixture was stirred for three hours under nitrogen while a precipitate slowly formed. The mixture was diluted with ice-water, extracted with ether and the aqueous portion acidified with cold concentrated hydrochloric acid. The resulting yellow precipitate was collected, washed with water and dried. The material, 10 g., m.p. 204–206°, was recrystallized from acetone. The purified material was obtained as deep yellow needles, m.p. 205–206° dec.

Anal. Calcd. for $C_{17}H_{13}O_4N$: C, 69.14; H, 4.43; N, 4.74. Found: C, 68.71; H, 4.24; N, 5.11.

Oxindole-3-acetic Acid (XXIIb).—A solution containing 7.85 g. of benzyl isatylidenehydroxyacetate (XIXb) in 200 ml. of glacial acetic acid and 0.5 ml. of concentrated sulfuric acid was shaken with 4 g. of 10% palladium-on-charcoal catalyst under 3–4 atmospheres of hydrogen until three molar equivalents was absorbed. The reaction was then filtered onto 4 g. of sodium acetate and the solvent removed *in vacuo* with mild heating. The residual sirup was shaken

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(19) M. Bergman and K. Grafe, *Z. physiol. Chem.*, **187**, 187 (1930).

(20) H. Meyer, *Monatsh.*, **26**, 1323 (1905).

(21) Obtained from The American Platinum Works, Newark, N. J.

(22) R. Adams and L. F. Weeks, This Journal, **38**, 2514 (1916).

with 300 ml. of ether and 150 ml. of water, the ethereal layer was dried over sodium sulfate, concentrated and crystallization induced by the addition of petroleum ether (b.p. 35–65°). The acid (XXIIb), 2.88 g., m.p. 126–146°, after softening at 105°, appeared to be solvated.

An additional 0.73 g. of acid, m.p. 125–135°, softening at 105°, was obtained from the aqueous phase by continuous extraction with ether. The yield of acid was 70%.

The acid crystallized from acetone–benzene in fine white needles which softened at 142° and melted clear at 147°.

Anal. Calcd. for $C_{10}H_9O_3N$: C, 62.82; H, 4.74; N, 7.32. Found: C, 63.03; H, 4.89; N, 6.98.

That XXIIb is not immediately rearranged to 2-oxo-1,2,3,4-tetrahydroquinoline-4-carboxylic acid (VI) is indicated by the fact that only the acetic acid (XXIIb) was recovered from an aqueous solution at *p*H 1 after being kept at 30° for 15 hours. However, refluxing XXIIIb for 30 minutes in 6% hydrochloric acid effected rearrangement to VI, m.p. 218°.

CHICAGO, ILL.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY COLLEGE, CORK, IRELAND]

Polynitrogen Systems from Hydrazinocarbonic Acids. I. Diformazans[1]

BY F. L. SCOTT,[1a] D. A. O'SULLIVAN AND J. REILLY

RECEIVED MARCH 17, 1953

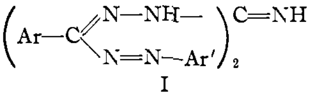
The formation of iminotricarbaundecaztetraenes from dialdehydic diaminoguanidines and the oxidation of the resulting formazans have been discussed. Here, the main points of interest are the ready symmetrical fission of the new diformazan system on oxidation, and the specificity of its mode of formation. A number of additional new formazan systems derived from tetrazolyl- and quinolylhydrazones as starting substances are described. The preparation of some new guanazyls is given, chiefly as a comparison with the other couplings.

Coupling of an aldehydic hydrazone (R—CH=$N^{\alpha}\cdot NH^{\beta}R'$) with an electrophilic[2] diazonium cation (Dn^+) may result in one of three possible modes of attack: (i) reaction of Dn^+ with the β-nitrogen atom—with tetrazene formation[3]; (ii) reaction of the electrophile with R or R'[4]; or (iii) by reaction of the Dn^+ with the methine carbon to yield a formazan.[5]

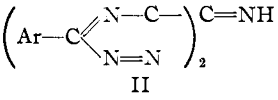
Competitive reaction occurs, the center of highest electron density having the greatest likelihood of combination with Dn^+. To enhance the possibility of formazan formation (the process of interest, in the present work), the nucleophilicity of the other possible reaction centers must be diminished. R is already deactivated by conjugation with the methine unsaturation, and, in the present experiments where R was always aromatic, it was occasionally further deactivated by nitrosubstitution. If R' were aromatic it would be activated by its bonding to the (unprotonized) β-nitrogen atom. To eliminate this possibility, in the present series, only hydrazones were examined where R' was both aliphatic and electrophilic. This last quality in this radical also diminished the possibility of tetrazene formation. Thus attention was confined to aryl aldehydic derivatives of the hydrazinocarbonic acid class.

The coupling reactions of the guanylhydrazones, previously[6] investigated, were in accord with these expectations—formazans or "guanazyls" being formed very readily. This present communication extends the investigation to some diaminoguanidine derivatives and demonstrates the analogy with the monoaminoguanidine compounds. Despite this, however, aldehydic acylhydrazones do not, in general, afford formazans.[7]

In addition to determining the relative coupling efficiency of dialdehydic diaminoguanidines, with the synthesis of a new formazan system, the 6-imino-1,3,9,11-tetraaryl-3,6,9-tricarbaundecaz-1,3,8,10-tetraene (I), the present experiments were designed to provide a new tetrazole type—the bis-(5-aryl-2′-tetrazolyl)-formimine (II) class. The formation of the congeners of the iminotricarbaundecaztetraenes proved specific, and a qualitative comparison system was developed. The standard reference substances were benzaldehyde phenylhydrazone and benzaldehyde guanylhydrazone. Comparison was also made with the derivatives of the heterocyclic hydrazines, 5-hydrazinotetrazole and 2-quinolylhydrazine.



I



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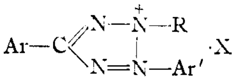

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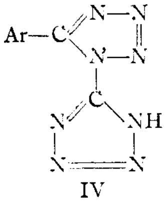
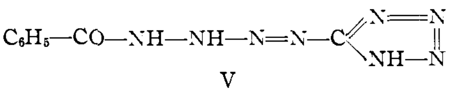


IV



V

The phenyldiazonium ion reacted readily with benzaldiaminoguanidine and with benzal-2-quinolylhydrazine, in line with the ready reaction of this

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(1) Previous preliminary notes on this topic from this laboratory have been: F. L. Scott, D. A. O'Sullivan and J. Reilly, *J. Chem. Soc.*, 3508 (1951); *Chem. and Ind.*, 782 (1952).

(1a) Chemistry Department, University of California, Los Angeles, 24, Calif.

(2) C. R. Hauser and D. S. Breslow, THIS JOURNAL, **63**, 418 (1941).

(3) (a) Busch (and co-workers) postulate that tetrazene coupling is a preliminary to formazan formation. See for example M. Busch and H. Pfeiffer, *Ber.*, **59**, 1162 (1926); M. Busch and R. Schmidt, *ibid.*, **63B**, 1950 (1930); *J. prakt. Chem.*, (II), **131**, 182 (1931); compare (b) K. A. Hofmann and H. Hock, *Ber.*, **44**, 2946 (1911).

(4) I. Hauser, D. Jerchel and R. Kuhn. *Chem. Ber.*, **84**, 651 (1951). Compare also W. E. Bachmann and R. A. Hoffmann, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 224.

(5) H. von Pechmann, *Ber.*, **27**, 1690 (1894).

(6) E. Wedekind, *Ber.*, **30**, 444 (1897).

(7) *Vide* F. L. Scott, M. Ruszkiewicz and J. Reilly (forthcoming publication).