titrated for percarbonate; none was found. Another portion, 2.59 g., was diluted with 50 cc. of methanol, and the precipitated polystyrene was washed with methanol and dried to constant weight in vacuum at 60°, 0.841 g. 78% polymerization, $\eta_{sp}/c_g = 0.103$. A small quantity of hydroquinone was added to the remainder of the solution which was then distilled, about 5 cc. being collected, boiling 130–135°. The distillate was treated with 0.2 g. of phenyl isocyanate, leading to isopropyl N-phenylcarbamate, 0.086 g., 5.4% yield, melting point and mixed melting point, 83–86°. The second 100-cc. portion was distilled similarly. This distillate was treated with 0.4 g. of 2,4-dinitrophenylhydrazine and 10 cc. of 95% ethanol and worked up for acetone dinitrophenylhydrazone. No more than a trace of impure material, melting 110–120° was obtained.

A portion (42.8 g.) of reaction product, from which the low boiling material had been distilled, was added to a sodium myristylate–myristyl alcohol–ethylbenzene solution as described in the preceding section. The solution was boiled, becoming quite dark; about 20 cc. of distillate was collected, the residue was boiled for one-half hour, and 20 cc. more of distillate was taken. The combined distillates were treated with 1.2 g. of phenyl isocyanate, leading to isopropyl N-phenylcarbamate, m. p. 83–85°, mixed melting point 84–87°, 0.66 g., 68% recovery.

Another portion of the polymerization product, 19.3 g., was treated with excess methanol; the liquid was decanted and the precipitated polystyrene was dissolved in benzene and reprecipitated with methanol. The combined supernatant liquids were evaporated in vacuum at room temperature, leaving a small oily residue. This residue was treated with sodium myristylate as described above and worked up for isopropyl N-phenylcarbamate. None was found. The reprecipitated polystyrene was dried to constant weight in vacuum at room temperature, dissolved in 50 cc. of ethylbenzene, added to sodium myristylate–myristyl alcohol in ethylbenzene and worked up for isopropyl N-phenylcarbamate; this product was obtained, m. p. and mixed 81–84°, 0.14 g., 32% yield. Some high melting material contaminated the product, presumably diphenylurea.

Summary

The decomposition of diisopropyl peroxydicarbonate at 54° in styrene–benzene, in ethylbenzene, and in styrene–ethylbenzene appears to be largely a first order reaction accompanied by a reaction of higher order; the rate in styrene–benzene at 54° is equivalent to that of benzoyl peroxide at 82°. Its efficiency in initiating the polymerization of styrene at 54° is similar to that of benzoyl peroxide.

The decomposition in ethylbenzene leads to high yields of carbon dioxide and isopropyl alcohol. In the presence of styrene these products are formed in quite low yields, the alkyl carbonate radicals adding to styrene monomer more rapidly than they may lose carbon dioxide, despite their formal derivation from the unstable alkyl carbonic acid. Isopropyl alcohol may be removed from the polystyrene by saponification.

The effects of quinone and two hydroquinones on these reactions are discussed.

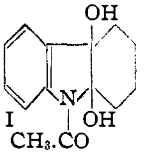
CAMBRIDGE, MASS. RECEIVED MARCH 15, 1949

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

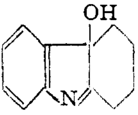
The Structure of the So-called 11-Hydroxytetrahydrocarbazolenine[1]

BY BERNHARD WITKOP*

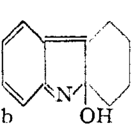
In 1923, Perkin and Plant[2] noticed a "curious and unexpected result" when they treated 9-acetyl-10,11-dihydroxyhexahydrocarbazole (I) with hot aqueous alcoholic potassium hydroxide. They



I



IIa



IIb

obtained an orange substance, $C_{12}H_{13}NO$ (II), m. p. 79°, to which they ascribed the structure of an 11-hydroxytetrahydrocarbazolenine (IIa), or, less likely, that of the isomeric hydroxy derivative (IIb). In this paper we show that the correct structure of this colored transformation product is that of a spiro-[cyclopentane-1,2'-ψ-indoxyl] (II). Table I summarizes the reactions and further transformations carried out with compound (II).

Compound (I) was obtained either according to Perkin and Plant[2] by the action of nitric acid on N-acetyltetrahydrocarbazole or by a second unambiguous method to be published later. The transformation product (II), m. p. 79°, see Table I, after distillation in high vacuum, had a pure yellow color with no shade of orange or red. Its absorption spectrum[3] (Fig. 1) shows a characteristic maximum at 400 mμ, whereas the colorless acetyl compound (IV) has its peak of absorption at 340 mμ. Perkin and Plant[2] considered this acetyl compound to be an O-acetyl derivative. The infrared spectra (Fig. 2 and Table II) show clearly that what they assumed to be (II), has a free NH-band (2.9 μ) which is lacking in the case of the acetyl compound (IV). Another important band in the infrared absorption spectrum shows up at 5.85 μ, and is typical of a carbonyl function in a five membered ring (*cf.* oxindole, Table II). The formation of a dinitrophenylhydrazone from the yellow transformation product confirmed this suggestion. The reduction of the "hydroxytetrahydrocarbazolenine" with lithium aluminum hydride furnished two products: a solid colorless compound (V) $C_{12}H_{15}NO$, m. p. 146°, and a liquid colorless base (VI), $C_{12}H_{15}N$. V on dehydrogena-

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* Harvard University Faculty 1948–.

[1] This investigation was supported by a grant-in-aid from Research Corporation, New York.

[2] Perkin and Plant, *J. Chem. Soc.*, **123**, 676 (1923).

[3] I am indebted to Dr. E. R. Blout, Polaroid Corporation, Cambridge, for kindly making arrangements for measuring the ultraviolet spectra.

TABLE I

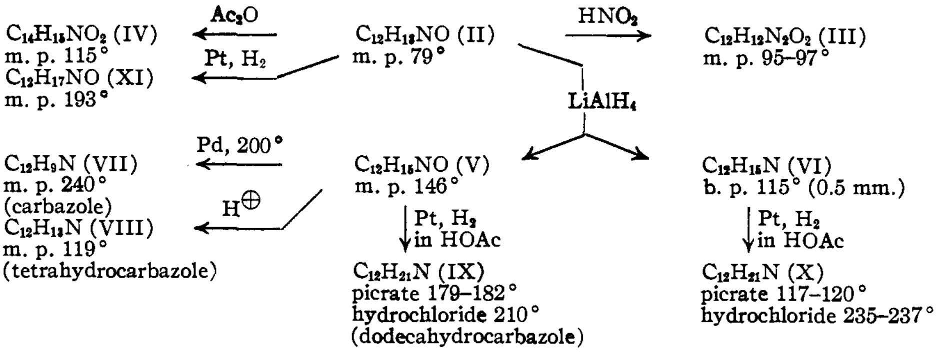

TABLE II

THE MAJOR INFRARED ABSORPTION BANDS IN μ OF SOME COMPOUNDS DISCUSSED

No.	Compound	NH	OH	CH (aliphatic)	CO		Aromatic and "finger print" region	
1	9-Acetyl-10,11-dihydroxyhexahydrocarbazole (I)[a]	..	2.86 2.98	3.4	6.05	..	6.72	7.14
2	Spiro-[cyclopentane-1,2′-ψ-indoxyl] (II)	2.88	..	3.4	5.88	6.16[c]	6.70 6.77	7.53
3	Spiro-[cyclopentane-1,2′-N-nitroso-ψ-indoxyl] (III)	..	..	3.4	5.80	6.18	6.9	8.7
4	Spiro-[cyclopentane-1,2′-N-acetyl-ψ-indoxyl] (IV)	..	(2.8)	3.4	5.80 6.00	6.17	6.8	7.23
5	Spiro-[cyclopentane-1,2′-dihydroindoxyl] (V)[b]	2.90	2.75	3.39	..	6.17	6.71 6.78	7.18
6	Tetrahydrocarbazole (VIII) (from V and authentic)	2.90	..	3.4	..	..	6.80	7.51
7	Spiro-[cyclopentane-1,2′-dihydroindole] (VI)	2.96	..	3.45	..	6.18	6.72 6.81	
8	*cis*-Hexahydrocarbazole	2.95	..	3.4	..	6.18	6.72 6.81	
9	Carbazole (VII) (from V and authentic)	2.90	..	..	..	6.19	6.84	7.54
10	7′,8′,9′,10′-Tetrahydro-[spirocyclopentane-1,2′-ψ-indoxyl] (XI)	2.93	..	3.45	6.02	6.28		7.35
11	Oxindole	2.93	3.18	(3.38)	5.88	6.17	6.78	7.19

[a] All compounds are measured in approximately 3% chloroform solution. [b] The spectrum of this compound in carbon disulfide solution shows 2 new bands at 3.09 and 8.18 not present in chloroform. [c] This very sharp and characteristic band has considerable diagnostic value. Diphenylamine has a similar strong band at 6.23, indoles have none.

tion with palladium, yielded carbazole (VII), on hydrogenation with Adams catalyst in glacial acetic acid gave IX, $C_{12}H_{21}N$, a strong base. This base was identical with dodecahydrocarbazole (presumably the *cis–cis* isomer) prepared by catalytic hydrogenation of *cis*-hexahydrocarbazole. Dodecahydrocarbazole has been previously obtained by electrolytic reduction of octahydrocarbazole[4] and by catalytic reduction (copper chromite) of carbazole.[5]

The most interesting reaction of V was noticed when its picrate was prepared: appearing first in a light-yellow form, it changed to dark red within a few hours at room temperature, within a few seconds at 80°. The rearranged picrate was identical with tetrahydrocarbazole picrate. In the same way, compound (V) itself is instantly converted into tetrahydrocarbazole in contact with a trace of acid, even acetic acid.

The oxygen-free base VI, an isomer of hexahydrocarbazole, is neither identical nor isomorphous with the *cis*- and *trans*-hexahydrocarbazoles nor a mixture thereof, though the physical constants of these substances (Table III) and their infrared spectra (Table II) do not differ much. The base, $C_{12}H_{21}N$ (X), obtained on perhydrogenation, proved definitely different from the isomeric dodecahydrocarbazole IX (Table I).

Finally compound II was hydrogenated in glacial acetic acid and PtO_2 to give a colorless tetrahydro derivative (XI), $C_{12}H_{17}NO$ (m. p. *193*°) in which the characteristic grouping $-\mathrm{NH}-\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}-\mathrm{CO}-$, suggested by all the experimental and spectral evidence, was still intact (*cf.* Table II).

TABLE III

	Free base	Picrate	Benzoyl
$C_{12}H_{15}N$ (VI), °C.	B. p. 115 (0.5 mm.)	148	110–112
cis-Hexahydrocarbazole, °C.	M. p. 99	166	106
trans-Hexahydrocarbazole, °C.	M. p. 127	179	133

The unambiguous synthesis of authentic 11-

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(4) Perkin and Plant, *J. Chem. Soc.*, **125**, 1503 (1924).

(5) Adkins and Coonradt, THIS JOURNAL, **63**, 1563 (1941).

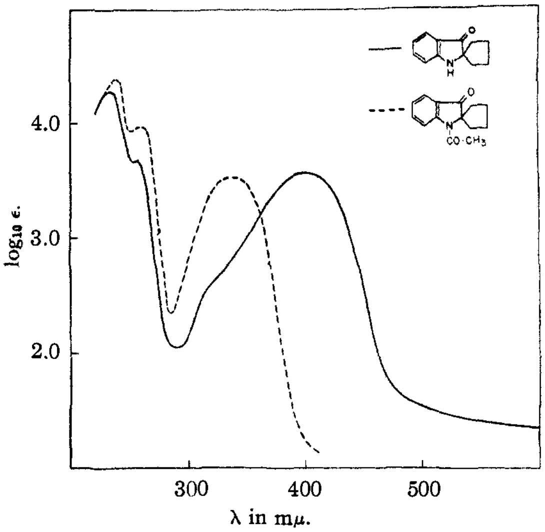
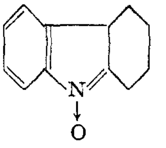
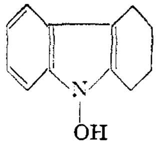


Fig. 1.—Ultraviolet absorption spectra of spiro-[cyclopentane-1,2'-pseudoindoxyl] (II), and of its N-acetyl derivative (IV) in ethanol.

hydroxytetrahydrocarbazolenine was then undertaken to shed some light on the situation. The principle employed, *viz.*, action of hydrogen peroxide on the Grignard derivative of tetrahydrocarbazole, was apparently first used by Oddo[6] and in the indole series by Ingraffia.[7] The exploratory investigation of the reaction showed the surprising result that some of the so-called "11-hydroxytetrahydrocarbazolenine" (II) could be isolated besides much unreacted starting material and unstable colored products of a nature undetermined as yet. For a moment, this result led to the consideration and consequent rejection of a nitrone-like structure (XII), which would probably mainly exist as (XIII).[8,9]



XII



XIII

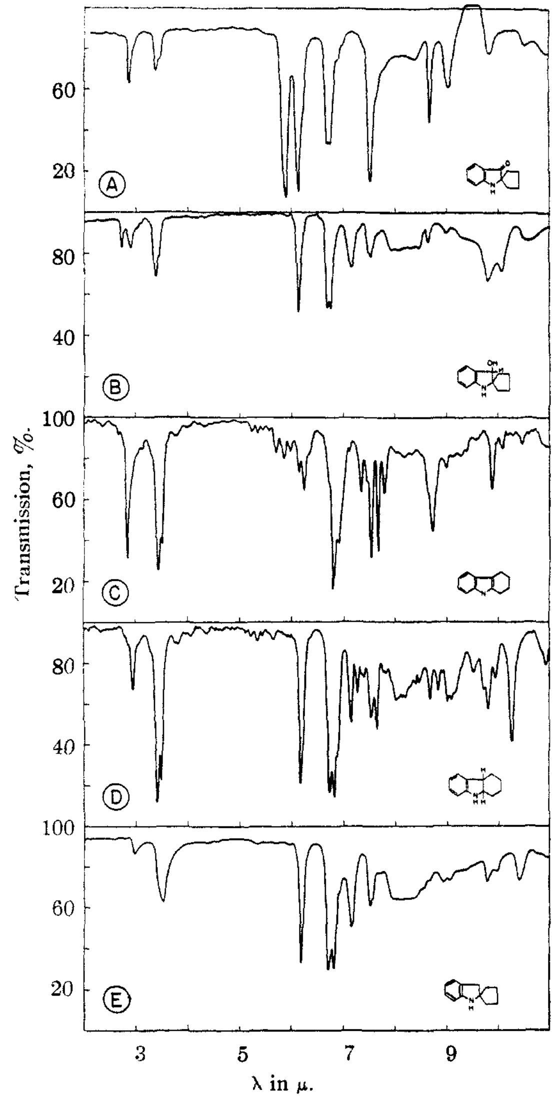


Fig. 2.—Infrared absorption spectra (in chloroform).

At this point mention must be made of another observation by Perkin and Plant,[2] *viz.*, the rearrangement of I under the influence of acetic anhydride or elevated temperature yielding a colorless compound $C_{14}H_{15}NO_2$, m. p. 104°, formulated by them as IV following a suggestion of Sir Robert Robinson, who pointed out that the loss of water, characteristic of this transformation, might indicate a pinacol type of rearrangement resulting in either XIV or IV, of which Perkin and Plant selected the latter, since they could not effect ring opening by the action of alkali. The experimental and spectral evidence presented in this investigation, leaves no doubt that the yellow transformation product (II) is nothing else than the desacetyl derivative of IV. Dr. R. B. Woodward modified Robinson's suggestion and kindly pointed out that I in acid solution would be more likely to form an intermediate carbonium structure (XVI), rearranging to (XIV) (R = CH_3CO),

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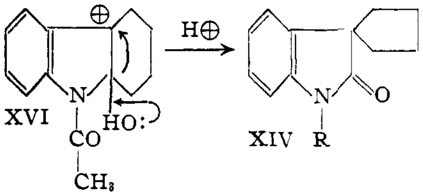
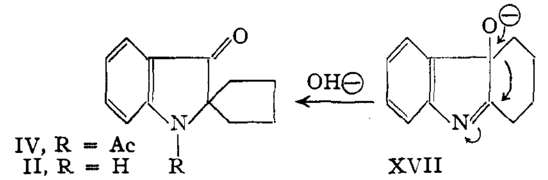
[6] Oddo and Binaghi, *Gazz. chim. ital.*, **51**, II, 343 (1921).

[7] Ingraffia, *ibid.*, **63**, 175 (1933).

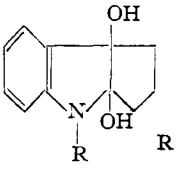
[8] Ingraffia's yellow compounds (ref. 8), resulting from the action of hydrogen peroxide on indolyl magnesium derivatives and formulated as N-hydroxyindoles, may have to be reinvestigated and should not be quoted as analogs in this connection. Another yellow hydroxy indole, arising from the action of concentrated sulfuric acid on benzoin oxime, was formulated as 2-phenylindoxyl by E. Fischer and Hütz, *Ber.*, **28**, 585 (1895), and was shown to be 1-hydroxyphenylindole by Angeli, *Atti Reali Accad. Linc.*, [5] **13**, 255 (1904).

[9] The general course of the reaction of indolyl magnesium compounds with alkyl halides or related derivatives results almost exclusively in the formation of β-substituted derivatives, *cf.* Oddo, "Grignard's Traité de Chimie Organique," Vol. **19**, pp. 295, 356, Paris, 1942. A similar 9,11-relation in tetrahydrocarbazole is only shown in the reaction with alkyl halides at elevated temperature [Plancher, *Atti Reali Accad. Linc.*, [5] **9**, I 221 (1900); *Gazz. chim. ital.*, **59**, 340 (1929)], but not in Grignard reactions using ether or tetrahydrofuran as solvents (unpublished experiments).





whereas base might well produce the intermediate anion (XVII), rearranging to II. The change in the latter case is analogous to a benzilic acid type of rearrangement.



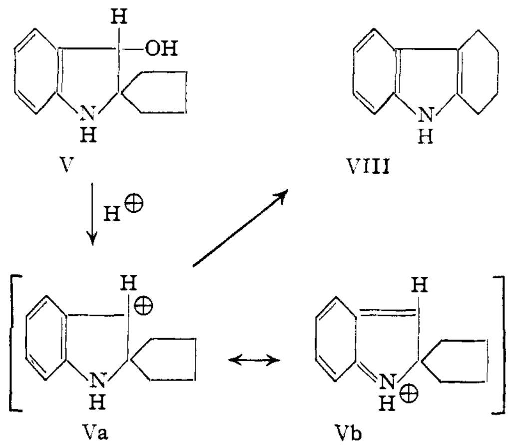
XVIII R = H or Ac

It is now clear why the analogous 9,10-dihydroxytetrahydropentindole (XVIII)[10] can be boiled with alcoholic potassium hydroxide without rearrangement, since constriction to a four-membered ring cannot occur.

Thus, the formation of (II) in the reaction of tetrahydrocarbazolyl magnesium iodide with hydrogen peroxide becomes clear. The intermediate 11-hydroxytetrahydrocarbazolenine rearranges under the action of excess Grignard base in the same way as it does in the treatment of I with alcoholic alkali.

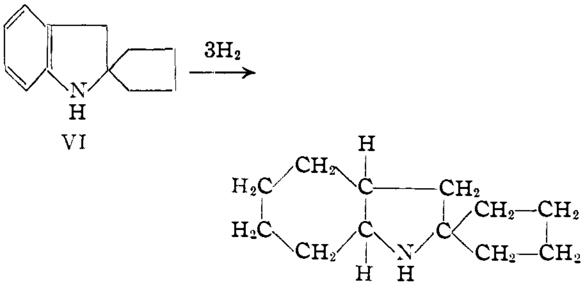
The changes presented in Table I can now be formulated without difficulty. Like indoxyl itself, spiro-[cyclopentane-1,2′-*pseudo*indoxyl] (II)[11] is somewhat soluble in water, possesses a striking fluorescence,[12] is easily nitrosated to III, acetylated to IV,[13] yet lacks the faculty of autoxidation.[14]

V is clearly expressed by the structure of a spiro-[cyclopentane-1,2′-dihydroindoxyl]. The action of acid produces an *o*-aminobenzylcarbonium ion (Va ←→ Vb), which can easily undergo a Wagner–Meerwein shift to tetrahydrocarbazole (VIII). That even dilute acetic acid is capable of bringing about this rearrangement is a remarkable fact, but well compatible with the structure proposed. It



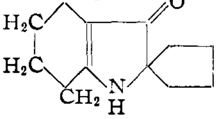
becomes now understandable that dodecahydrocarbazole is formed on hydrogenation in glacial acetic acid, or, likewise, that carbazole is the result of dehydrogenation.

The base (VI) isomeric with hexahydrocarbazole, is spiro-[cyclopentane-1,2′-dihydroindole], its perhydrogenation product is expressed by (X) (formulated as *cis*).

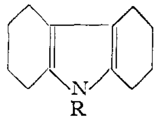


X

Finally, catalytic hydrogenation of II leads to a bz-tetrahydro product (XI), in the same way as the



XI



XIX

hydrogenation of carbazole[15] sometimes results in the formation of a pyrrole structure (XIX) known to be very inert to further hydrogenation.

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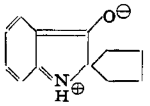
(10) Plant and Tomlinson, *J. Chem. Soc.*, 298 (1933).

(11) Name and numbering comply with "The Ring Index," New York, 1940, Structure Number 1419. Other possible names are ψ-indoxylspirocyclopentane (used by Perkin and Plant[2]) or 6-aza-7,8-benz-spiro[4,4]nonanone-9.

(12) If one likes to use Mumm's suggestions on the phenomenon of fluorescence, *Ber.*, **72**, 29 (1939), the contribution of the polar resonance structure (IIc) may be a reason for the fluorescence of II.



IIc

(13) Baeyer, *ibid.*, **16**, 2190 (1883); Vorländer and Drescher, *ibid.*, **34**, 1857 (1901).

(14) A suitable compound for comparison would be 2,2-dimethyl-ψ-indoxyl which cannot be the structure of the colorless alkali fusion product of anilinoisobutyric acid obtained by Bucherer and Grollé, *ibid.*, **39**, 992 (1906), listed as such by "Beilstein," **21**, 295 and accepted by Plant and Facet, *J. Chem. Soc.*, **127**, 2037 (1925). The latter tried to synthesize compound II by the use of a similar reaction.

(15) v. Braun and Ritter, *Ber.*, **55**, 3792 (1922); **58**, **389**, 2156 (1925); Plant, *J. Chem. Soc.*, 1595 (1930); *cf.* Campbell and Barclay, *Chem. Revs.*, **40**, 359 (1947).

Experimental[16]

9-Acetyltetrahydrocarbazole.—The acetylation of tetrahydrocarbazole[17,18,19] gave better yields than the copper powder method or the action of acetyl chloride on the Grignard compound of tetrahydrocarbazole, when the potassium salt of tetrahydrocarbazole reacted with acetyl chloride in the following manner: potassium chips were heated in toluene in an atmosphere of nitrogen under vigorous stirring until the metal was finely distributed throughout the solvent. To this hot suspension a solution containing the equivalent amount of tetrahydrocarbazole was added slowly. When all the potassium was used up, the solution was cooled and acetyl chloride was added dropwise and very slowly. From the resulting reaction mixture the toluene was removed *in vacuo*. The residue was leached out repeatedly with hot chloroform, leaving the potassium chloride behind. The chloroform extracts were evaporated *in vacuo* and the residual tetrahydrocarbazol after distillation at 0.2 mm. (120°, bath) was obtained in the form of colorless crystals m. p. 78°, in a yield averaging 50 to 75%.

9-Acetyl-10,11-dihydroxyhexahydrocarbazole (I).—When 16.5 g. of N-acetyltetrahydrocarbazole was nitrated in glacial acetic acid following the procedure of Perkin and Plant the weight of the mixture of the crystalline nitrated and hydroxylated products separating spontaneously averaged 12–13 g. in three separate runs. Boiling alcohol, applied in three consecutive portions of 200 cc., left only 1.3 g. of 12 g. of the above mixture undissolved. From this alcoholic solution, after two hours of undisturbed standing at room temperature, 2.3 g. of 5-nitro-9-acetyltetrahydrocarbazole deposited in yellow needles. The mother liquor on standing for twenty hours in the ice-box yielded 6.8 g. of a mixture consisting mainly of the colorless plates of the dihydroxy compound. By careful repeated extraction of this crude product with small portions of acetone it was possible to get the accompanying nitro product into solution.[20] The residual colorless crystals (5.5 g.) melted at 204° and were pure dihydroxy compound as the comparison with an analytically pure sample obtained from N-acetyltetrahydrocarbazole by a more direct method and in better yield clearly showed.

Spiro-[cyclopentane-1,2′-pseudoindoxyl] (II), "**11-Hydroxytetrahydrocarbazolenine.**"—This compound was obtained by warming the above dihydroxy compound with alcoholic aqueous alkali according to Perkin and Plant. The crude product, obtained in about 90% yield of the theoretical in the form of a yellow-red mass started distilling at 70° (below the melting point) and 10^{-5} mm. using a small molecular still. The honey-yellow distillate solidified in magnificent rosettes, m. p. 77–79°.

Anal. Calcd. for $C_{12}H_{13}NO$: C, 77.0; H, 6.95. Found: C, 76.91; H, 7.15.

Fluorescence.—The most beautiful blue fluorescence is produced when a trace of the material is dropped into 10 cc. of the ether. The fluorescence in more concentrated solutions of acetone or methanol is strikingly green and disappears on the addition of ferric chloride solution, mineral acids or potassium hydroxide.

Influence of Acid.—When 20 mg. of the non-basic material was dissolved in 1 cc. of concentrated sulfuric acid and left for ten hours at room temperature no steam distillable reaction product could be obtained either in acidic or in alkaline medium. In another experiment, 100 mg. of the compound which is itself steam volatile only to a very small extent, gave no volatile product when subjected to steam distillation in the presence of 5 cc. of 2 *N* sulfuric acid.

2,4-Dinitrophenylhydrazone: The 2,4-dinitrophenylhydrazone of II was prepared in glacial acetic acid solution containing a few drops of water. The fine yellow needles melted at 183–185°.

Anal. Calcd. for $C_{18}H_{17}N_5O_4$: N, 19.5. Found: N, 18.8.

Picrate.—The picrate, prepared in petroleum ether solution and recrystallized from benzene–petroleum ether, appeared as red rods, m. p. 159–161°.

Anal. Calcd. for $C_{18}H_{16}N_4O_8$: N, 13.46. Found: N, 13.65.

Spiro-[cyclopentane-1,2′-N-nitroso-ψ-indoxyl] (III).—The pseudoindoxyl compound (II) was dissolved in methanol and a solution of the necessary amount of sodium nitrite in the same volume of water was added. When a cloudiness appeared at this point, more methanol was added. When 2 *N* hydrochloric acid was added dropwise at 0°, crystallization soon started. The crystals, short glistening almost colorless needles, were collected and washed with little ice-cold methanol. Recrystallized from a little methanol they formed faintly yellow leaflets, m. p. 95–97°. The solution of the nitrosamine showed no trace of fluorescence.

Anal. Calcd. for $C_{12}H_{12}N_2O_2$: C, 66.66; H, 5.55; N, 13.21. Found: C, 66.28; H, 5.71; N, 13.08.

Libermann Test.—When two drops of concentrated sulfuric acid was added to a mixture of 1 mg. of nitrosamine and 2 mg. of phenol a blue color arose that turned to red on the addition of water and changed to a beautiful blue on the addition of alkali.

Spiro-[cyclopentane-1,2′-ψ-N-acetylindoxyl] (IV).—From 150 mg. of II, 130 mg. of crude acetyl product was obtained following the procedure of Perkin and Plant. On recrystallization from 15 cc. of petroleum ether colorless cubes separated, m. p. 115°. The solution of the acetyl product in organic solvents showed neither color nor fluorescence. The infrared absorption spectrum (see Table II) showed no NH-band.

Anal. Calcd. for $C_{14}H_{15}NO_2$: C, 73.79; H, 6.61. Found: C, 73.99; H, 6.73.

Reduction with Lithium Aluminum Hydride

A. Spiro-[cyclopentane-1,2′-dihydroindoxyl] (V).—The yellow and strongly fluorescent solution of 570 mg. of II in 30 cc. of absolute ether was added in the course of ten minutes to a solution of excess lithium aluminum hydride (120 mg.) in 30 cc. of absolute ether. The instantaneous reduction was accompanied by evolution of heat and by loss of color and fluorescence. After all the ketone had been added the reaction mixture was kept refluxing for another five minutes. After careful decomposition of the reaction mixture with ice and water the ethereal layer was dried and evaporated. The crystalline residue weighed 550 mg. and had a characteristic aromatic odor. On recrystallization from benzene–petroleum ether soft silky colored and odorless needles separated, m. p. 146°. Together with a second crop from mother liquors 270 mg. of pure crystals was obtained.

Anal. Calcd. for $C_{12}H_{15}NO$: C, 76.19; H, 7.93. Found: C, 76.46; H, 7.93.

Ferric Chloride Test.—One drop of an aqueous solution of ferric chloride (5%) produced a distinct red color when added to a solution of 4 mg. of V dissolved in methanol-water or in absolute methanol. In chloroform solution the coloration produced was red-brown. The color deepening to blood-red within thirty seconds, stayed for a couple of minutes, fading then to yellow and forming a light brown precipitate. No ferric chloride test was given when the reduction product had come into contact with dilute acid before.

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(16) All melting points are corrected. I am indebted to Mr. S. Nagy (Microchemical Laboratories, Massachusetts Institute of Technology) for the careful execution of the analyses reported.

(17) Perkin and Plant, *J. Chem. Soc.*, **119**, 1831 (1921).

(18) Rogers and Corson, This Journal, **69**, 2910 (1947).

(19) Gaseous ketene, prepared according to Hurd, *J. Org. Chem.*, **5**, 121 (1941), fails to acetylate tetrahydrocarbazole when bubbled in excess through an ethereal solution, which is in accordance with its behavior toward diphenylamine, *cf.* Staudinger, "Die Ketene Stuttgart, 1912, p. 35.

(20) The dihydroxy compound did not react with acetone to give an isopropylidene derivative when left with an excess of absolute acetone in the presence of anhydrous copper sulfate for ten days at room temperature.

A solution of 2 mg. of V in 3 cc. of concentrated sulfuric acid, either technical or containing a trace of nitric acid, turned yellow after ten minutes, green after thirty minutes, and finally deep blue-green after one hour and later.

Ehrlich Reaction.—Emerald green on warming, fading on cooling, reappearing on warming, etc.; yellow-brown on the addition of sodium nitrite.

Picrate.—A solution of V in ether, on the addition of ethereal picric acid, deposited yellow needles after standing for a short time. The crystals could be collected and washed with ether.

Conversion into Tetrahydrocarbazole Picrate.—The above picrate changed from light yellow to a dark brown-red in the course of a few hours at room temperature *in the desiccator*, or within a few seconds at 80 to 90°. This rearranged red picrate melted at 143° unaffected by admixture of authentic tetrahydrocarbazole picrate.

Anal. Calcd. for $C_{12}H_{13}N \cdot C_6H_3N_3O_7$: C, 54.00; H, 4.03. Found: C, 53.90; H, 4.26.

Rearrangement of Spiro-[cyclopentane-1,2′-dihydroindoxyl] (V) into Tetrahydrocarbazole.—When 20 mg. of V was dissolved in 4 cc. of 2 *N* hydrochloric acid, the solution soon became cloudy on warming and deposited colorless glistening platelets, not soluble in hot water or mineral acid. The collected and washed crystals showed a sharp melting point at 120°. The ferric chloride test was negative. The same product was obtained by the action of glacial or dilute acetic acid on V. It was not possible to crystallize the O-acetyl product resulting from V in ethereal solution with excess ketene.

Anal. Calcd. for $C_{12}H_{13}N$: C, 84.21; H, 7.60. Found: C, 84.57; H, 7.40.

B. **Spiro-[cyclopentane-1,2′-dihydroindole] (VI).**—The mother liquors from the preparation of V, freed from petroleum ether and benzene, constituted a yellow oil (240 mg.) of a strong aromatic odor reminiscent of diphenyl. Using the customary device for micro steam distillations the product came over with the first 100 cc. of condensate, forming colorless oily drops on the aqueous surface. The water was saturated with ammonium chloride and exhaustively extracted with ether. The dried ethereal extract left 180 mg. of an oily weak amine which distilled at 115° (bath) and 0.5 mm., forming a colorless liquid.

Anal. Calcd. for $C_{12}H_{15}N$: C, 83.18; H, 8.73. Found: C, 83.45; H, 9.02.

One drop of the amine in 5 drops of methanol reacted with one drop of aqueous 5% ferric chloride solution to give the colors red-green-yellow within three seconds; finally a light brown precipitate was formed. The compound did not contain an aromatic amino group since attempted diazotization and coupling with an alkaline solution of β-naphthol produced no colors.

Hydrochloride.—The hydrochloride crystallized from ether or 2 *N* hydrochloric acid as transparent prisms, m. p. 170–173°.

Anal. Calcd. for $C_{12}H_{15}N \cdot HCl$: C, 68.71; H, 7.69. Found: C, 68.61; H, 7.83.

Picrate.—The picrate crystallized from petroleum ether (not from ether) or from water as long, soft yellow needles, m. p. 148°, differing from *cis*-hexahydrocarbazole picrate which melted at 164° (red melt). The mixture melting point of the two picrates was 132–140°.

Anal. Calcd. for $C_{12}H_{15}N \cdot C_6H_3N_3O_7$: C, 53.73; H, 4.51. Found: C, 53.35; H, 4.67.

Spiro-[cyclopentane-1,2′-N-benzoyldihydroindole].—Three drops of the free amine dissolved in 2 cc. of absolute ether reacted with three drops of benzoyl chloride under distinct warming. Soon the hydrochloride crystallized which was collected and washed with ether. The combined ethereal mother liquors were washed with dilute base, then dilute acid and finally with water. The dried ethereal solution on slow evaporation left beautiful crystals melting at 110–112°.

Anal. Calcd. for $C_{19}H_{19}NO$: C, 82.29; H, 6.91. Found: C, 81.78; H, 7.00.

A solution of 1 mg. of the compound in concentrated sulfuric acid containing a trace of nitric acid appeared first yellow and changed to deep green in the course of one-half hour.

Catalytic Dehydrogenation of Spiro-[cyclopentane-1,2′-dihydroindoxyl] (V).—An intimate mixture of 80 mg. of (V) and 50 mg. of palladium black was heated to 200° (oil-bath) in the course of ten minutes. About 4 cc. of gas was given off at 150°. At the same temperature the formation of water was observed. The semimicro sublimation of the reaction mixture at 0.2 mm. and 120–140° yielded a slightly yellow sublimate, which became colorless on extraction with warm petroleum ether (b. p. 20–40°). The remaining crystals were finally washed with ice-cold ether and showed then a melting point of 240° (clear melt) unaffected by admixture of pure *carbazole*. Likewise, the infrared absorption spectrum was identical with that of authentic carbazole (Table II).

Carbazole Picrate.—The picrate crystallized from benzene-petroleum ether as red, silky needles, m. p. 184–186°. Carbazole picrate is reported to melt at 182° (uncor.).

Anal. Calcd. for $C_{12}H_9N \cdot C_6H_3N_3O_7$: C, 54.54; H, 3.07. Found: C, 54.24; H, 3.32.

The final mother liquors from the preparation of the pure carbazol consisted of a semi-solid crystalline mass giving a very strong blue color reaction with concentrated sulfuric acid containing a trace of nitric acid. This color reaction was indistinguishable from that of diphenylamine.

Catalytic Hydrogenations

Dodecahydrocarbazole Picrate from Spiro-[cyclopentane-1,2′-dihydroindoxyl] (V).—When 100 mg. of V (m. p. 146°) was hydrogenated in 5 cc. of glacial acetic acid in the presence of 50 mg. of platinum oxide, about 3 moles of hydrogen were taken up in the course of thirty minutes. The hydrogenation was then stopped. After filtration and dilution with water, ether extracted some weakly basic material, possibly chiefly starting material. On adding strong alkali to the acid solution and extraction with ether, one obtained an oil of definite amine smell and of strongly basic reaction. From aqueous solution the picrate crystallized immediately in yellow needles which had to be washed repeatedly with small volumes of ice-cold methanol in order to get rid of a bluish-green coloration; m. p. 175–177°. The mixture of synthetic dodecahydrocarbazole picrate (m. p. 179–182°, *vide infra*) and the above picrate melted at 177–180°.

Anal. Calcd. for $C_{12}H_{21}N \cdot C_6H_3N_3O_7$: C, 52.94; H, 5.92. Found: C, 53.10; H, 6.12.

Dodecahydrocarbazole from Hexahydrocarbazole.—Five hundred mg. of *cis*-hexahydrocarbazole (m. p. 97°) dissolved in 10 cc. of glacial acetic acid in the presence of 500 mg. of platinum oxide took up 213 cc. of hydrogen (calcd. for 3 moles 200 cc.) within ninety minutes. The amine, isolated in the usual fashion, was a colorless oil (450 mg.). The picrate crystallized immediately in fine yellow needles melting, after recrystallization from a little methanol, at 179–182°.

Anal. Calcd. for $C_{12}H_{21}N \cdot C_6H_3N_3O_7$: C, 52.94; H, 5.92. Found: C, 53.00; H, 5.66.

Hydrochloride.—The picrate was converted into the hydrochloride with the help of hydrochloric acid and ether. Micro sublimation of this hydrochloride from slide to slide at 180° yielded snow flake crystals, m. p. 210°.

***cis*-Perhydrospiro-[cyclopentane-1,2′-dihydroindole] (X).**—When 200 mg. of liquid spiro-[cyclopentane-1,2′-dihydroindole] (VI) and 50 mg. of platinum oxide was hydrogenated simultaneously in 10 cc. of glacial acetic acid, 32.5 cc. of hydrogen (deducted 10 cc. for the reduction of the catalyst) was taken up in the course of forty minutes. The basic constituents were then isolated in the usual way and converted into the hydrochloride, which melted between 150–180° and resisted further purification. After reconversion into the free base, further hydrogenation in the presence of 100 mg. of platinum oxide led to the uptake of 58 cc. of hydrogen (deducted 25 cc. for the catalyst) within seventy minutes, totaling an uptake of 80 cc. or almost 3 millimoles of hydrogen. The amine was isolated in the usual way. From the solution of the amine in absolute ether dried hydrogen chloride precipitated the crystalline colorless hydrochloride, m. p. 235-237°.

Anal. Calcd. for $C_{12}H_{21}N{\cdot}HCl$: C, 66.82; H, 9.83. Found: C, 67.00; H, 10.05.

Picrate.—From the solution of the hydrochloride in water aqueous picric acid produced the picrate which after some standing and scratching formed light yellow little cubes, m. p. 112-114°. The picrate is exceedingly soluble in methanol and has to be recrystallized from aqueous methanol, m. p. 117-120° (yellow clear melt).

Anal. Calcd. for $C_{18}H_{24}N_4O_7$: C, 52.94; H. 5.92. Found: C, 52.68; H, 5.85.

7′,8′,9′,10′-Tetrahydrospiro-[cyclopentane-1,2′-ψ-indoxyl] (XI).—A solution of 300 mg. of II in 5 cc. of glacial acetic acid was added to a suspension of platinum from 100 mg. of platinum oxide in 5 cc. of the same solvent. The hydrogen uptake for four half-hour periods was: 45, 33, 15.5, 7.5 cc. The total consumption after two hours amounted to 100.3 cc. or the equivalent of 2.5 moles of hydrogen. The solution by this time had lost its colors and fluorescence. After filtration and dilution with water, it was extracted with ether. The basic constituents were then extracted from the ether solution with several portions of 2 *N* hydrochloric acid. The residual ether did not contain any appreciable amount of material. The acid extracts were basified and extracted with ether. The dried ethereal extracts left 220 mg. of colorless crystalline material. On recrystallization from benzene-petroleum ether one obtained colorless rectangular prisms, showing a transformation into rhomboid crystals between 150-170° (micro hot-stage), melting at 193° without decomposition.

Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.39; H, 8.97. Found: C, 75.0; H, 9.06.

Picrate.—The picrate, prepared from ethereal solution, crystallized directly in yellow lissom needles, m. p. 169-171° (sintering 164°). The salt is appreciably soluble in warm water.

Anal. Calcd. for $C_{18}H_{20}N_4O_8$: N, 13.33. Found: N, 13.33.

"Synthetic" Spiro-[cyclopentane-1,2′-pseudoindoxyl][21] **(II).**—To an ethereal solution of ethylmagnesium iodide, prepared from 4.2 g. of magnesium and 27.3 g. of ethyl iodide, was added dropwise a benzene solution of 25 g. of tetrahydrocarbazole. When the reaction had subsided, the mixture was refluxed for an hour. The mixture was then chilled in a salt-ice-bath, and 20 cc. of 30% hydrogen peroxide added dropwise. The reaction was very vigorous. After the addition of all the hydrogen peroxide the mixture was left in the ice-bath for an hour and then kept in the refrigerator overnight. The reaction mixture was then poured onto crushed ice in 2 *N* hydrochloric acid. The resultant mixture was extracted with ether. The combined ether extracts were dried and filtered through a column containing approximately 100 g. of aluminum oxide. Using four portions of 200 cc. of ether to elute the column, four fractions were obtained, of which the first weighed 8.5 g. and had a strong fluorescence, and the second fraction 8.8 g. These two fractions were combined and rechromatographed in benzene solution, using consecutive portions of 25 cc. of benzene-petroleum ether 1:4 for elution. The following fractions were obtained

Fraction	1	2	3	4	5-9
Weight	6.5 g.	3.6 g.	0.4. g.	0.2 g.	0.1 g.

All fractions yielded yellow solutions with strong blue fluorescence in ether and green fluorescence in alcohol or acetone. They all darkened on standing and exposure to light and air and lost their easy solubility in benzene to a considerable extent. The infrared spectra taken of fractions 1 to 4 showed that fraction 1 consisted mainly of tetrahydrocarbazole. The spectrum of fraction 2 showed clearly the presence of the two bands, 5.87 and 6.14 μ characteristic of (II). Fraction 2 was distilled in high vacuum, and the yellow solid distillate going over between 80-100° at 0.01 mm. was crystallized from benzene-petroleum ether, yielding yellow crystals, m. p. 75°.

Anal. Calcd. for $C_{12}H_{13}NO$: C, 77.0; H, 6.95. Found: C, 77.17; H, 6.94.

The infrared spectrum was practically identical with that of II prepared from I (Table II).

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Summary

The rearrangement of 9-acetyl-10,11-dihydroxyhexahydrocarbazole under the action of alkali is shown to lead to spiro-[cyclopentane-1,2′-ψ-indoxyl]. The attempted synthesis of the intermediate 11-hydroxytetrahydrocarbazolenine, *viz.* the reaction of tetrahydrocarbazolyl magnesium iodide with 30% hydrogen peroxide leads to the same product. A number of interesting transformations of this compound are described in this investigation.

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[21] This experiment was carried out with the assistance of Mr. J. B. Patrick.