Anal. Calcd. for $C_{26}H_{34}O_6N_2.0.5H_2O$: C, 67.6; H, 7.2; N, 6.1. Found: C, 67.5; H, 7.7; N, 5.9.

This salt was dissolved in dilute (1:4) hydrochloric acid (20 ml.) and continuously extracted with ether for 8 hr. Removal of the ether gave a colorless oil (0.096 g.) which was dried over solid sodium hydroxide *in vacuo* for 16 hr., $[\alpha]^{16.5}D$ +14.5° (water, *c* 1.93).

Anal. Calcd. for $C_7H_{10}O_4$: equiv., 158. Found: neut. equiv., 162.

The *p*-bromophenacyl derivative prepared in the usual way after recrystallization once from benzene-light petroleum and twice from alcohol gave colorless needles radiating from a center, m.p. 105–106°, undepressed when admixed with the derivative from the natural carboxylactone.

Anal. Calcd. for $C_{15}H_{15}O_5Br$: C, 50.7; H, 4.3; Br, 22.5. Found: C, 50.7; H, 4.4; Br, 22.8.

ADELAIDE, SOUTH AUSTRALIA
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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

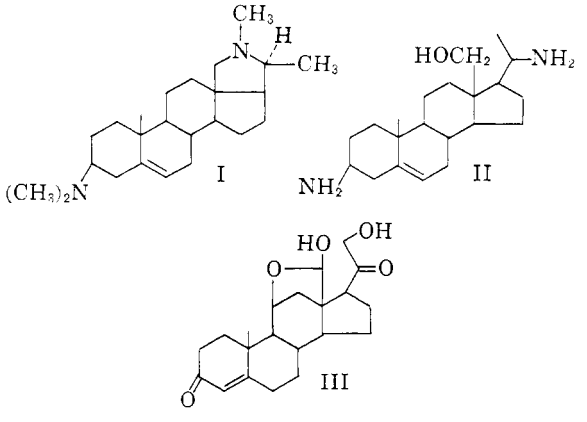
The Synthesis of Dihydroconessine[1]

BY E. J. COREY[2a] AND W. R. HERTLER[2b]

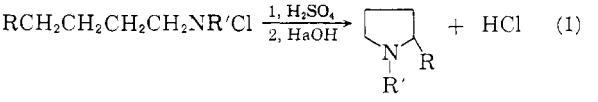
RECEIVED MARCH 20, 1959

Dihydroconessine has been synthesized from 3β-acetoxybisnorcholenic acid. Introduction of the amino function at C_{18} was effected by the free radical chain decomposition of 3β-dimethylamino-20α-methylchloroaminoallopregnane (Hofmann–Löffler–Freytag reaction), which offers a general method for the selective functionalization of the C_{18} angular methyl group of steroids.

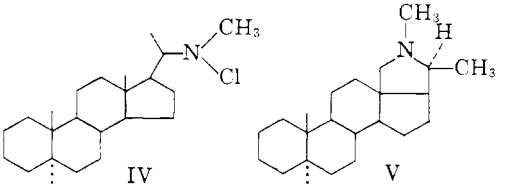
The structural feature which imparts special interest to the *Holarrhena* steroid-alkaloid conessine (I) is the presence of functionality at the C_{18} angular methyl group, a feature shared with the related alkaloid holarrhimine[3] (II) and the important steroid hormone aldosterone (III). The synthesis of such structures poses a unique problem, functionalization of an angular methyl group which cannot be activated by standard procedures, for which the extensive steroid literature provides little assistance.



Attempts to synthesize aldosterone from steroid precursors lacking substitution at C_{18} by cleavage and reclosure of ring D[4] have led to products lacking the appropriate stereochemistry, and previous to this work the preparation of C_{18}-substituted steroids with normal configurations has been limited to arduous total synthesis as exemplified by the recent work on aldosterone.[5] A different approach to the problem appeared to be the use of reactions capable of transforming unactivated angular methyl groups selectively because of favorable proximity, and in this connection the free-radical chain decomposition of a C_{20}-N-chloroamine (Hofmann–Löffler–Freytag reaction)[6] seemed especially attractive. This reaction, which generally results in the transformation of an aliphatic chloroamine to a pyrrolidine[7] as shown in equation 1, should in the case of a steroidal N-chloro-20-amine result in the formation of a C_{18}–C_{20} imine bridge as is found in conessine. This paper describes the synthesis of dihydroconessine (XVII) using the Hofmann–Löffler–Freytag reaction as the key step.



Jeger, Arigoni and co-workers[8] in a preliminary communication have described a similar synthesis of the previously unknown conanine (V) from 20α-methylchloroaminoallopregnane (IV). Jeger[9] also



(1) Described in a preliminary communication, THIS JOURNAL, **80**, 2903 (1958).

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(3) See L. Labler, V. Cerny and F. Sorm, *Coll. Czech. Chem. Comm.*, **20**, 1484 (1955), for the elegant interrelation of conessine and holarrhimine.

(4) D. H. R. Barton, A. Da S. Campos-Neves and A. I. Scott, *J. Chem. Soc.*, 2698 (1957).

(5) (a) J. Schmidlin, G. Anner, J. R. Billeter and A. Wettstein, *Experientia*, **11**, 365 (1955); (b) E. Vischer, J. Schmidlin and A. Wettstein, *ibid.*, **12**, 50 (1956); W. S. Johnson, J. C. Collins, R. Pappo and M. B. Rubin, THIS JOURNAL, **80**, 2585 (1958).

(6) (a) A. W. Hofmann, *Ber.*, **16**, 558 (1883); (b) K. Löffler and C. Freytag, *ibid.*, **42**, 3427 (1909).

(7) See, however, S. Wawzonek and P. J. Thelen, THIS JOURNAL, **72**, 2118 (1950), and S. Wawzonek, M. F. Nelson and P. J. Thelen, *ibid.*, **73**, 2806 (1951).

(8) P. Buchschacher, J. Kalvoda, D. Arigoni and O. Jeger, *ibid.*, **80**, 2905 (1958).

(9) F. Greuter, J. Kalvoda and O. Jeger, *Proc. Chem. Soc.*, 349 (1958).

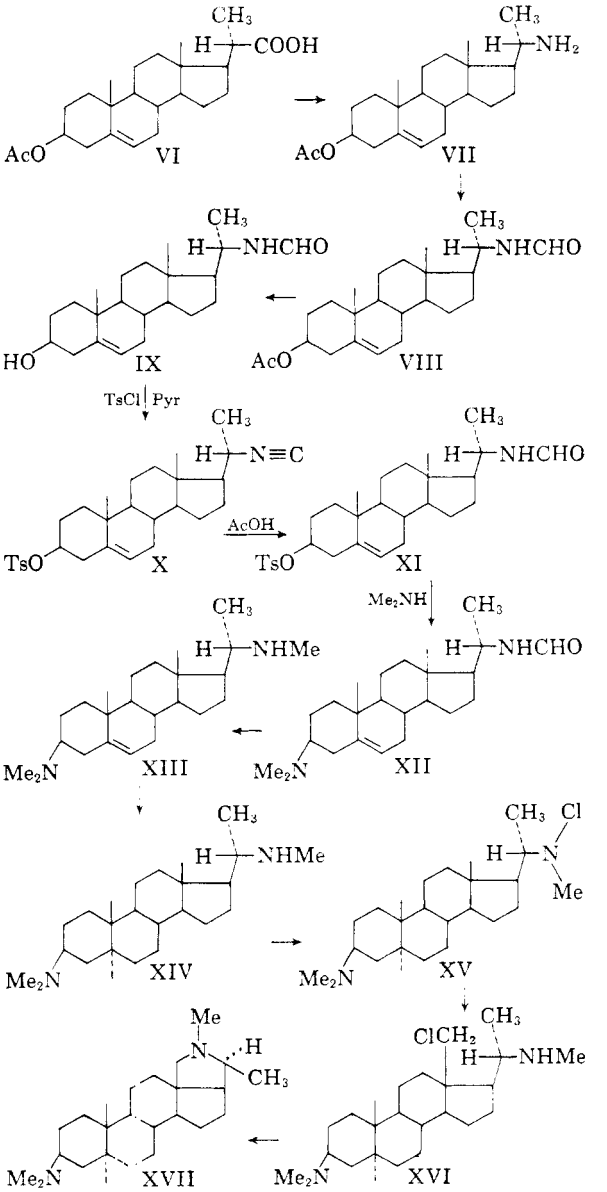
has shown recently that the decomposition of 21-diazoallopregnan-20-one leads to the formation of a methylene bridge between C_{18} and C_{20}, representing a second direct synthetic approach to C_{18}-substituted steroids.

The correct gross structure of conessine was first proposed in 1952 by Haworth,[10] who later obtained conclusive evidence for the position of the double bond.[11] The position of the heterocyclic ring was proved by McNiven[12] and Tschesche.[13] Sorm, *et al.*, have shown that the methylimino bridge is attached at C_{20} in the α-configuration by converting holarrhimine (which has the same configuration at C_{20} as does conessine)[8] to 3β,-20α-bis-(dimethylamino)-allopregnane,[14] which, in turn, was related to 3β-acetoxybisnorallocholanic acid.[15]

Since the configuration at C_{20} of conessine was established as α, the precursor used for the synthesis was a 20α-aminosteroid, 3β-acetoxy-20α-aminopregnene-5 (VII), prepared according to Julian[16] from 3β-acetoxybisnorcholenic acid (VI) *via* the acid chloride, the acid azide and the 20α-isocyanate. The route envisioned from this point was first to protect the C_{20}-amino group by formylation, and then to replace the 3β-acetate with a 3β-dimethylamino group *via* a 3β-*p*-toluenesulfonate.

The amine VII on treatment with refluxing formic acid–acetic anhydride gave 3β-acetoxy-20α-formamidopregnene-5 (VIII). This acetate was readily saponified with potassium carbonate in methanol to give 3β-hydroxy-20α-formamidopregnene-5 (IX). Treatment of the formamido alcohol IX with *p*-toluenesulfonyl chloride in pyridine did *not* give the expected 3β-*p*-toluenesulfonoxy-20α-formamidopregnene-5 (XI). Instead, *p*-toluenesulfonyl chloride–pyridine removed the elements of water from the formamido group to produce an isonitrile. The excess sulfonyl chloride then esterified the 3β-hydroxyl group. This unexpected dehydration appeared to take place relatively rapidly, for treatment of the formamido alcohol IX with just one equivalent of *p*-toluenesulfonyl chloride gave rise to an isonitrile containing almost no sulfonic ester. A brief study was made of the generality of this new procedure for preparing isonitriles from formamides, and the results have been reported elsewhere,[17] as have been related studies with phosphorus oxychloride–pyridine.[18] The intervention of isonitrile was nullified easily, however, since treatment of the crude 3β-*p*-toluenesulfonoxy-20α-isocyanopregnene-5 (X) with a mixture of acetic acid and ether caused hydration of the isonitrile giving the desired 3β-*p*-toluenesulfonoxy-20α-formamidopregnene-5 (XI).

The conditions of choice for the dimethylaminolysis of the *p*-toluenesulfonate XI had to be such that ionization to the 3,5-cyclosteroid cation through homoallylic participation be maximized, for the desired 3β-amine could arise only from reaction of this cation and dimethylamine. Extensive experimentation with cholesterol derivatives carried out by Dr. D. N. Jones in these laboratories indicated that dimethylamine–dimethylformamide was the most satisfactory reagent. Under these conditions a mixture of amines was obtained from XI from which 3β-dimethylamino-20α-formamidopregnene-5 (XII) was isolated in poor yield by column chromatography. Reduction of the amino formamide XII with lithium aluminum hydride gave 3β-dimethylamino-20α-methylaminopregnene-5 (XIII).



(10) R. D. Haworth, J. McKenna, R. G. Powell and G. H. Whitfield, *Chemistry & Industry*, 215 (1952).

(11) (a) R. D. Haworth, J. McKenna and G. H. Whitfield, *J. Chem. Soc.*, 1102 (1953); (b) R. D. Haworth, L. H. C. Lunts and J. McKenna, *ibid.*, 3749 (1956); (c) R. D. Haworth and J. McKenna, *Chemistry & Industry*, 1510 (1957); (d) R. D. Haworth and M. Michael, *J. Chem. Soc.*, 4973 (1957).

(12) N. L. McNiven, *Chemistry & Industry*, 1296 (1957).

(13) R. Tschesche and A. C. Roy, *Chem. Ber.*, **89**, 1288 (1956).

(14) (a) L. Labler, V. Cerny and F. Sorm, *Chemistry & Industry*, 1119 (1955); (b) V. Cerny and F. Sorm, *Coll. Czech. Chem. Comm.*, **20**, 1473 (1955); *Chem. Listy*, **49**, 909 (1955).

(15) V. Cerny, L. Labler and F. Sorm, *Coll. Czech. Chem. Comm.*, **22**, 76 (1957); *Chem. Listy*, **50**, 1126 (1956).

(16) P. L. Julian, E. W. Meyer and H. C. Printy, THIS JOURNAL, **70**, 887 (1948).

(17) W. R. Hertler and E. J. Corey, *J. Org. Chem.*, **23**, 1221 (1958).

(18) I. Ugi and R. Meyr, *Angew. Chem.*, **70**, 702 (1958).

At this point an attempt was made to transform the diamine XIII to conessine *via* the N-chloro derivative by irradiation with ultraviolet light in sulfuric acid solution. However, extensive decomposition occurred, and no pure product could be isolated, probably because of the presence of the Δ^5-double bond. Indeed, Siddiqui[19] has shown that sulfuric acid causes migration and oxidation of the double bond of conessine. In order to avoid difficulties introduced by the presence of the double bond, 3β-dimethylamino-20α-methylaminopregnene-5 was hydrogenated to give 3β-dimethylamino-20α-methylaminoallopregnane (XIV), which on treatment with N-chlorosuccinimide[20] gave the corresponding N-chloro derivative XV. Irradiation of a sulfuric acid solution of the 3β-dimethylamino-20α-methylchloroaminoallopregnane with ultraviolet light either in the presence or absence of dibutylchloroamine carrier produced dihydroconessine (XVII) in good yield. The synthetic dihydroconessine thus prepared was found to be identical with an authentic sample of dihydroconessine prepared by hydrogenation of conessine with respect to melting point, mixture melting point, and infrared spectrum. Evidence for the presence of some 18-chloro intermediate XVI was obtained during the isolation of dihydroconessine from chloroamine irradiation. When the crude ether-soluble, basic product was warmed, an ether-insoluble amine salt was formed, clearly due to the cyclization of XVI to dihydroconessine hydrochloride. A more general study of the intermediacy of structures of the type XVI in the Hofmann–Löffler–Freytag reaction will be published separately.

Experimental[21]

3β-Hydroxy-20α-formamidopregnene-5 (IX).—3β-Acetoxy-20α-formamidopregnene-5 was prepared from acetoxybisnorcholenic acid by a method described earlier.[17] Saponification of the ester was carried out as follows: 3β-acetoxy-20α-formamidopregnene-5 (37.6 g., 97 mmoles) was added to a slurry of 31.5 g. of potassium carbonate in 550 ml. of methanol containing a few ml. of water. After boiling briefly on a steam-bath, the mixture was stirred at room temperature for 3.5 hours, and then was poured into 1.5 liters of water. The basic solution was made slightly acidic by careful addition of hydrochloric acid. The amorphous solid material was filtered and the filter cake dried by heating to 100° at 0.1 mm. pressure. Crystallization from acetone–hexane gave 33.5 g. (100%) of 3β-hydroxy-20α-formamidopregnene-5, m.p. 230–233° dec. Further crystallization from acetone–hexane gave microcrystals, m.p. 229–230° dec., $[\alpha]^{24}D$ −70.4° (methanol, *c* 1).

Anal. Calcd. for $C_{22}H_{35}O_2N$: C, 76.47; H, 10.21; N, 4.06. Found: C, 76.31; H, 10.08; N, 4.32.

3β-*p*-Toluenesulfonoxy-20α-formamidopregnene-5 (XI).—3β-Hydroxy-20α-formamidopregnene-5 (70 g., 0.202 mole) was covered with 400 ml. of dry pyridine and cooled in an ice-bath for 20 minutes. Then 116 g. of *p*-toluenesulfonyl chloride was added, and cooling in the ice-bath was continued until heat was no longer evolved. The solution was stored for 23 hours at +5° and for 5 hours at room temperature, cooled, treated with several pieces of chipped ice, and poured into a mixture of ice and hydrochloric acid. The products were extracted with methylene chloride. The methylene chloride solution was washed with water and dried over sodium sulfate. Removal of solvent *in vacuo* gave a dark gummy residue which consisted of a mixture of 20α-formamide and 20α-isocyanide. The residue was dissolved in a mixture of 200 ml. of ether and 200 ml. of glacial acetic acid and let stand for two hours at room temperature. The solution was diluted with 400 ml. of methylene chloride and washed twice with cold water and once with cold 10% sodium bicarbonate solution. After drying over sodium sulfate, the solution was boiled for 10 minutes with Darco, filtered, and concentrated *in vacuo*. The residue was recrystallized from ethyl acetate–hexane to give 74.2 g. (74%) of light tan 3β-*p*-toluenesulfonoxy-20α-formamidopregnene-5, m.p. 128–131°. Repeated crystallization from ethyl acetate–hexane gave colorless microcrystals, m.p. 132–133°, $[\alpha]^{27}D$ −47.4° (chloroform, *c* 1).

Anal. Calcd. for $C_{29}H_{41}NSO_4$: C, 69.70; H, 8.27. Found: C, 69.92; H, 8.32.

3β-Dimethylamino-20α-formamidopregnene-5 (XII).—3β-*p*-Toluenesulfonoxy-20α-formamidopregnene-5 (74 g., 0.148 mole) was dissolved in 400 ml. of dry dimethylformamide in a flask protected from atmospheric moisture. Dry gaseous dimethylamine was bubbled through the solution with heating at 80° for 18 hours. The solution was cooled, poured into ice-water, and extracted twice with methylene chloride. The combined methylene chloride extracts were washed five times with water, dried over sodium sulfate, and concentrated *in vacuo* to a dark gum. The residue was dissolved in benzene and treated with hydrogen chloride. The resulting precipitate (45 g.) was filtered and thoroughly washed with benzene. The remaining solid was treated with ethanol and ammonium hydroxide solution and extracted into benzene. The benzene solution was dried over sodium sulfate, boiled with Darco, filtered, and concentrated to a solid foam (30.7 g.) of which 20 g. was dissolved in a small amount of benzene and placed on a column of 2 kg. of neutral Woelm aluminum oxide. Two-liter fractions were collected. Fractions 11–59 (15:1 benzene–ether) consisted of oily material (13.5553 g.) from which no pure compound could be isolated. The infrared spectra of these fractions had a weak band at 1315 cm.$^{-1}$ which probably indicates the presence of some 3,5-cyclo-6β-dimethylamino compound. Fractions 60–81 (15:1 benzene–ether and 4:1 benzene–ether) consisted of 6.4283 g. of solid material which was converted to the hydrochloride, washed with warm tetrahydrofuran, and reconverted to the free base. Repetition of this procedure gave 1.805 g. (5%) of 3β-dimethylamino-20α-formamidopregnene-5 which on crystallization from acetone–hexane gave prisms, m.p. 226–230° dec., $[\alpha]^{27}D$ −52° (chloroform, *c* 1.25).

Anal. Calcd. for $C_{24}H_{40}N_2O$: C, 77.36; H, 10.82; N, 7.52. Found: C, 77.31; H, 10.90; N, 7.23.

3β-Dimethylamino-20α-methylaminopregnene-5 (XIII).—3β-Dimethylamino-20α-formamidopregnene-5 (1.435 g., 3.85 mmoles) was dissolved in 100 ml. of dry tetrahydrofuran, and to this was added 1.0 g. of lithium aluminum hydride. The resulting slurry was stirred at reflux for 36 hours. Then water was added with stirring, and the precipitated salts were filtered off and thoroughly washed with ether. The combined filtrate and washings was dried over magnesium sulfate. The drying agent was removed by filtration, and dry hydrogen chloride was passed into the filtrate. The amine hydrochloride was filtered, washed with ether, and dissolved in water. The aqueous solution was made strongly alkaline with sodium hydroxide and extracted with ether-benzene. The organic layer was dried over sodium sulfate and concentrated *in vacuo*. The white residue was recrystallized from acetone–water to give 1.107 g. (80%) of 3β-dimethylamino-20α-methylaminopregnene-5 as flat needles, m.p. 119.5–122.5°. Further recrystallization from acetone gave flat needles, m.p. 123–124.5°, $[\alpha]^{27}D$ −37° (chloroform, *c* 1.3).

Anal. Calcd. for $C_{24}H_{42}N_2$: C, 80.38; H, 11.81; N, 7.81. Found: C, 80.23; H, 11.84; N, 7.78.

Attempted Preparation of Conessine.—3β-Dimethylamino-20α-methylaminopregnene-5 (65.1 mg., 0.1815 mmole) was treated with 3 ml. of dry ether and 26.7 mg. (0.2 mmole) of N-chlorosuccinimide. The slurry was swirled occasionally and after 0.5 hour was diluted with ether–pentane, washed three times with water, dried over sodium sulfate, and concentrated *in vacuo* to 66 mg. of white N-chloro-3β-dimethylamino-20α-methylaminopregnene-5. The N-chloro compound was dissolved in 20 ml. of 90% sulfuric acid at 0° with the development of a dark red color. After the addition

(19) (a) S. Siddiqui, *Proc. Indian Acad. Sci.*, **2A**, 426 (1935); (b) S. Siddiqui and V. Sharma, *ibid.*, **6A**, 191 (1937).

(20) H. Ruschig and J. Schmidt-Thome, U. S. Patent 2,697,107 (1954).

(21) All melting points are corrected.

of 1 ml. of dibutylchloroamine, the solution was irradiated at 0° in a quartz test-tube with a mercury arc lamp under a stream of nitrogen for 2.5 hours. The dark solution was poured over ice, made alkaline with sodium hydroxide, and concentrated somewhat by warming *in vacuo*. The basic solution was extracted twice with ether. The ether extract was dried over sodium sulfate and concentrated to 69.8 mg. of black solid which was refluxed with dilute ethanolic potassium hydroxide for 5 minutes. The alcoholic solution was diluted with water and extracted with ether. Removal of the ether *in vacuo* gave 37.4 mg. of dark oil which was chromatographed on 4 g. of Woelm neutral alumina. The 15.7 mg. of yellow oil which was obtained on elution with 3:1 benzene–ether failed to yield a pure compound.

3β-Dimethylamino-20α-methylaminoallopregnane (XIV).—Platinum oxide (300 mg.) was hydrogenated in 15 ml. of acetic acid, and to the pre-reduced catalyst was added a solution of 600 mg. (1.672 mmoles) of 3β-dimethylamino-20α-methylaminopregnane-5 in 15 ml. of glacial acetic acid containing 4 drops of water. The theoretical quantity of hydrogen was taken up in 4.5 hours, and the solution was filtered, poured over ice, and made basic with sodium hydroxide. The product was extracted into ether, and the ethereal solution was dried over sodium sulfate. Removal of the ether *in vacuo* gave 552.7 mg. (92%) of crystalline 3β-dimethylamino-20α-methylaminoallopregnane. Crystallization from aqueous acetone gave plates, m.p. 103.5–104.5°, $[\alpha]^{27}D$ +27.5° (chloroform, *c* 0.95).

Anal. Calcd. for $C_{24}H_{44}N_2$: C, 79.93; H, 12.30; N, 7.77. Found: C, 79.23; H, 12.06; N, 7.80.

Dihydroconessine (XVII). A. With Dibutylchloroamine Carrier.—3β-Dimethylamino-20α-methylaminoallopregnane (103.7 mg., 0.2875 mmole) and 40.8 mg. (0.305 mmole) of N-chlorosuccinimide were covered with 4 ml. of dry ether and swirled occasionally. After one-half hour the solution was diluted with a little ether–pentane, washed three times with water, dried over sodium sulfate, and concentrated *in vacuo* to 107.5 mg. of white N-chloro-3β-dimethylamino-20α-methylaminoallopregnane. The chloroamine was dissolved in 10 ml. of 90% sulfuric acid at 0°. To the resulting orange-yellow solution was added 100 mg. of dibutylchloroamine. The solution was irradiated in a quartz test-tube at 0° with a mercury arc lamp under a stream of nitrogen. After 70 minutes, the solution was poured over ice and made alkaline with sodium hydroxide while keeping the temperature close to 0° by addition of ice. The product was extracted into ether, and the ether solution was washed with sodium chloride solution, dried over sodium sulfate, concentrated *in vacuo*, and heated at about 80° to remove N-butylpyrrolidine. The residue (84.4 mg.) appeared to be an amine salt—it was insoluble in ether and gave a Beilstein test for halogen. The residue was dissolved in methanol, and ammonium hydroxide solution was added. The product was extracted with ether–pentane. After drying over potassium carbonate the solvent was removed, and the oily residue (70 mg.) was chromatographed on 7 g. of Woelm neutral alumina (activity grade 1). Elution with 3:1 benzene–ether gave 57.4 mg. (56% based on starting diamine) of semi-crystalline material which crystallized readily from aqueous acetone as flat needles, m.p. 100.5–101°, mixture m.p. with dihydroconessine (m.p. 99–100°) 99.5–100.5°, mixture m.p. with 3β-dimethylamino-20α-methylaminoallopregnane (m.p. 103.5–104.5°) 72.5–86° (lit.[22] m.p. 105–105.5° for dihydroconessine); $[\alpha]^{26}D$ +53.5° (chloroform, *c* 0.8) (lit.[3] $[\alpha]D$ +51.8°). The infrared spectrum of the synthetic dihydroconessine was identical in all respects with that of dihydroconessine prepared by hydrogenation of conessine.

B. Without Carrier.—N-Chloro-3β-dimethylamino-20α-methylaminoallopregnane (90 mg., 0.228 mmole) was dissolved in 10 ml. of 90% sulfuric acid at 0°. The resulting solution was irradiated in a quartz test-tube at 0° with a mercury arc lamp under a stream of nitrogen. After 70 minutes the solution was poured over ice, made alkaline with sodium hydroxide, and extracted with ether. The ether was evaporated, and the residue was refluxed with 10 ml. of ethanol containing 1 g. of potassium hydroxide for 0.5 hour. The solution was diluted with water and extracted with ether. The ether solution was dried over sodium sulfate and concentrated *in vacuo* to a slightly yellow semi-solid (80.3 mg.) which was chromatographed on 7.5 g. of Woelm neutral alumina. Elution with 2:1 benzene–ether gave 64.4 mg. of oil (79%) which crystallized from aqueous acetone as flat needles, m.p. 101.5–102.5°, mixture m.p. with authentic dihydroconessine, 100.5–102°.

(22) E. Späth and O. Hromatka, *Ber.*, **63**, 126 (1930).

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

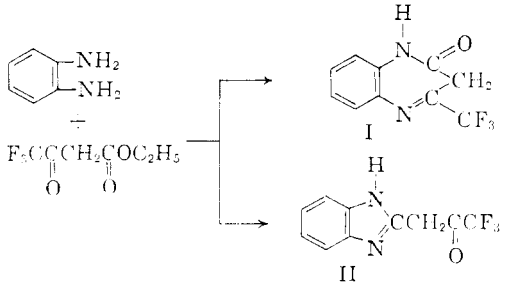
A Study of the Condensation of Ethyl γ,γ,γ-Trifluoroacetoacetate with *o*-Phenylenediamine[1]

BY FRANCES BAIRD WIGTON AND MADELEINE M. JOULLIÉ[2]

RECEIVED FEBRUARY 28, 1959

The reactions of *o*-phenylenediamine with γ,γ,γ-trifluoroacetoacetate has been studied under various conditions. The structure and nature of the products formed was investigated by both chemical and physical methods.

Earlier investigators have studied the condensation of ethyl acetoacetate with *o*-phenylenediamine under several conditions.[3] A number of products were reported, but their identity was not completely established in all cases. The present study is concerned with the condensation of ethyl γ,γ,γ-trifluoroacetoacetate and *o*-phenylenediamine. The primary objectives of this work were to establish the nature of the products formed as well as to observe the effects of the fluorine atoms on the reaction and on the reaction products. Theoretically, the reaction between these two compounds could lead to the formation of either one or both of two cyclic products, namely, 4-(trifluoromethyl)-1*H*-1,5-benzodiazepin-2(3*H*)-one (I) and 3-(2-benzimidazolyl)-1,1,1-trifluoro-2-propanone (II). The condensation was carried out under



(1) Presented before the Division of Organic Chemistry at the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959.

(2) To whom all inquiries should be addressed.

(3) (a) O. Hinsberg and P. Koller, *Ber.*, **29**, 1500 (1896); (b) S. Coffey, J. Thompson and F. Wilson, *J. Chem. Soc.*, 856 (1936); (c) L. Monti, *Gazz. chim. ital.*, **70**, 648 (1940); (d) W. Sexton, *J. Chem. Soc.*, 303 (1942).