$$\overset{13}{\text{—CH=CH—}}\overset{11}{\text{CH=CH—CH}_2\text{—CH}_2\text{—}} \quad (2)$$

$$\text{—CH}_2\text{—CH}_2\text{—}\overset{11}{\text{CH=CH—}}\overset{9}{\text{CH=CH—}} \quad (3)$$

that result from either a 1,6-addition or hydrogenation of end double bond only (1) would produce 11-octadecenoic acid on the characteristic 1,4-addition to a conjugated diene. It is postulated that a 1,6-addition to the conjugated diene system is then the main course of hydrogenation.

In the selective hydrogenation of a poly-unsaturated compound, the addition occurs in a progressive or stepwise manner. The hydrogenation of methyl β-eleostearate would be selective in this respect if no monoethenoid compound were produced before all of the conjugated triene had been converted into the two diene structures. The analysis shows, however, that hydrogenation to a monoethenoid compound did occur before all of the triene system had disappeared. It has been shown that when 23% of the original ester had been reduced, the percentages of triene and diene total 100, and it can be concluded that no monoethenoid compound had been produced to this point of hydrogenation. When 40% of the ester had been hydrogenated, the percentages of remaining triene and diene produced did not total 100 and it is therefore concluded that some monoethenoic and saturated material were formed.

The solvent hydrogenation of methyl β-eleostearate has been shown to be fairly selective in the manner of addition of hydrogen, occurring predominantly by a 1,6-addition. It is non-selective however, in the respect that it does not occur in a stepwise manner.

Summary

Data on the solvent hydrogenation of methyl β-eleostearate are reported. *trans*-11,12-Octadecenoic acid (vaccenic) was isolated from the products of hydrogenation and its structure and configuration confirmed.

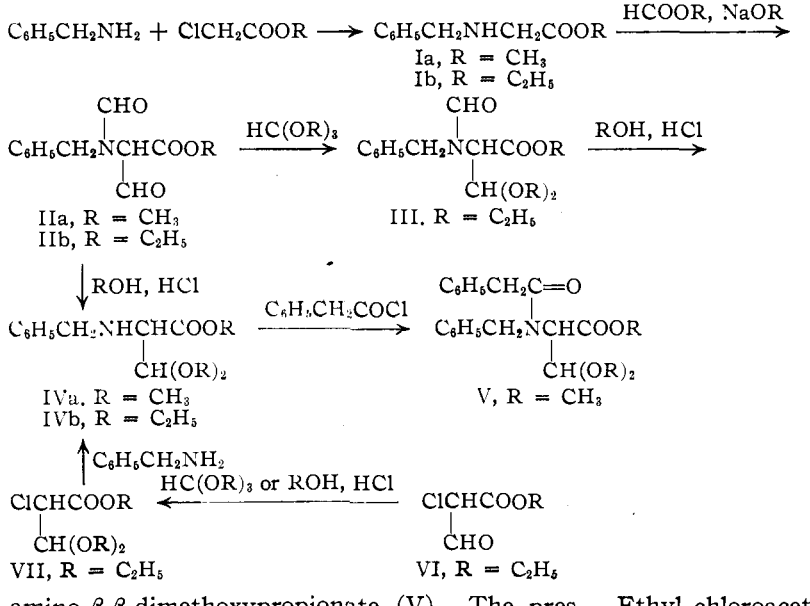
PITTSBURGH, PA. RECEIVED JULY 2, 1949

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF WINTHROP CHEMICAL COMPANY, INC.]

The Preparation of Some α-Benzylamino-β,β-dialkoxypropionic Acid Derivatives

BY JOHN A. KING[1] AND FREEMAN H. MCMILLAN[1]

As an intermediate in the synthesis of substances possibly related to penicillin it was desirable to use methyl α-(N-phenacetyl)-benzyl-amino-β,β-dimethoxypropionate (V). The present paper reports the preparation of this material.



Because they were more readily available, the ethyl esters (b series of compounds) were used throughout the exploratory experiments; after suitable reaction conditions had been found the corresponding methyl esters (a series of compounds) were prepared.

Benzylamine and ethyl chloroacetate condensed in benzene solution to give ethyl benzylaminoacetate (Ib). Treatment of this with ethyl formate and sodium ethoxide gave ethyl α,N - diformylbenzylaminoacetate (IIb). This was first acetalified to ethyl α-(N-formyl)-benzylamino-β,β-diethoxypropionate (III) by a modification of Claisen's[1a] orthoformate method and (III) was then converted to ethyl α-benzylamino - β,β - diethoxypropionate (IVb) with ethanolic hydrogen chloride by Fischer's[2] method.

Compound IVb was also prepared by another method. Ethyl chloroacetate was formylated by a modification of the method of Wislicenus[3] to yield

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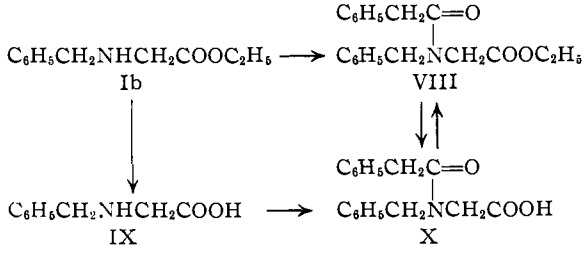
(1a) Claisen, *Ber.*, **40**, 3903 (1907).

(2) Fischer and Giebe, *ibid.*, **31**, 545 (1898).

(3) Wislicenus, *ibid.*, **43**, 3528 (1910).

ethyl formylchloroacetate (VI). VI was converted to its acetal, ethyl α-chloro-β,β,-diethoxypropionate (VII), by Fischer's method, but a better yield was obtained by Claisen's orthoformate procedure. Benzylamine and (VII) condensed in benzene solution to give (IVb).

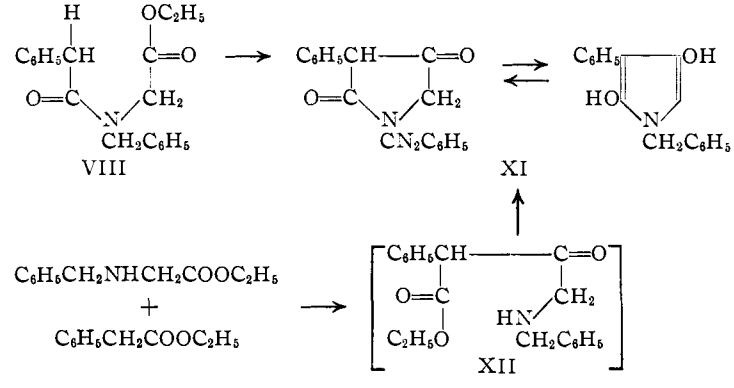
Ethyl benzylaminoacetate (Ib) was treated with phenacetyl chloride to give ethyl (N-phenacetyl)-benzylaminoacetate (VIII). The ester linkage of VIII was selectively hydrolyzed to give



(N-phenacetyl)-benzylaminoacetic acid (X), which was reconverted to the ester VIII by the method of Freudenberg and Jakob.[4] The same acid X was prepared by saponification of ethyl benzylaminoacetate to benzylaminoacetic acid (IX) followed by acylation with phenacetyl chloride.

Benzylamine and methyl chloroacetate condensed to give methyl benzylaminoacetate (Ia). This was formylated to give methyl α,N-diformylbenzylaminoacetate (IIa), which was converted by methanolic hydrogen chloride to methyl α-benzylamino-β,β-dimethoxypropionate (IVa) in an over-all yield of 17%. However, if neither of the intermediates (Ia) or (IIa) was isolated, the dimethoxy ester (IVa) was obtained in 36% over-all yield from methyl chloroacetate. (IVa) was converted, on acylation with phenacetyl chloride, into methyl α-(N-phenacetyl)-benzylamino-β,β-dimethoxypropionate (V).

It was originally planned to convert (VIII) to its α-formyl derivative, $C_6H_5CH_2N(COCH_2C_6H_5)CH(CHO)COOC_2H_5$, which could then be acetalified by either of the previously used methods However, when (VIII) was treated with ethyl formate and sodium ethoxide, under conditions which converted (I) to (II), the product isolated in 79% yield had the empirical formula $C_{17}H_{15}NO_2$, in which two carbon atoms had been lost instead of one gained. When the reactants were added in the reverse order the same product was obtained in 92% yield. This high-melting crystalline solid was base-soluble to give a crystalline sodium salt, acidification of which regenerated the original substance. Its empirical formulas was incompatible with a dicarboxylic acid or an enolizable keto acid and left as the only alternative a dicarbonyl compound in which at least one of the carbonyl groups could be strongly enolic; and in order to correspond to the empirical formula, this compound must be cyclic. Comparison of the empirical formulas of the cyclic dicarbonyl compound and of (VIII) revealed that the only difference was C_2H_5OH; presumably the carbethoxy group had reacted intramolecularly to eliminate a molecule of ethanol. Of the three methylene groups present in (VIII) only two are sterically capable of reaction with the carbethoxy group: ring closure between the carbethoxy and the methylene attached to the nitrogen would give a four-membered ring in which neither oxygen could be strongly enolic; ring closure between the carbethoxy and the methylene of the phenacetyl group would produce 1-benzyl-3-phenyl-2,4-pyrrolidinedione (1-benzyl-3-phenyl-2,4-dihydroxypyrrole) (XI) in which the keto groups are practically phenolic. Thus, it seemed very probable that the material $C_{17}H_{15}NO_2$ was (XI). This was confirmed by an independent synthesis of the material by a method which itself served as a proof of structure.



Although ethyl formate[5] and ethyl oxalate,[6] which cannot condense with themselves or be acylated, condense with ethyl phenylacetate in the presence of sodium ethoxide to give good yields of the respective acylated esters, simple aliphatic esters cannot be satisfactorily used for the acylation of ethyl phenylacetate. For example, ethyl α-phenylacetoacetate must be prepared from the nitrile via the iminochloride,[7] instead of by acylation of ethyl phenylacetate with the ethyl acetate. In spite of the prognosis of a poor yield of the desired product, ethyl phenylacetate was acylated with ethyl benzylaminoacetate to produce ethyl α-phenyl-β-keto-γ-benzylaminobutyrate (XII) which was cyclized in the reaction mixture to give a 5% yield of the same pyrrole derivative (XI) as had been obtained previously. Because of its amphoteric nature and probable instability to more than gentle treatment, no effort was made to isolate the intermediate amino-

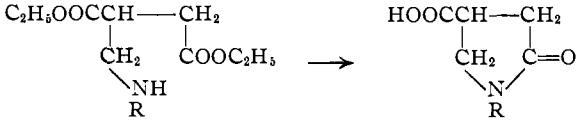
(1) Freudenberg and Jakob, *Ber.*, **74**, 1001 (1941).

(5) Wislicenus, *ibid.*, **20**, 2930 (1887).

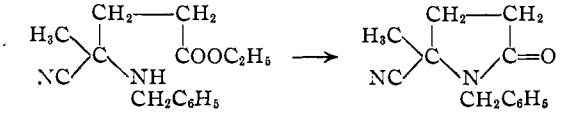
(6) Wislicenus, *ibid.*, **20**, 589 (1887); **27**, 1091 (1894); Levene and Meyer, "Organic Syntheses," Coll. Vol. II, 1943, p. 288.

(7) Beckli, *Ber.*, **31**, 3160 (1898).

ketoester (XII). Its facile conversion to (XI) finds close analogy in Anschütz and Reuter's[8]



alkaline cyclization of various ethyl α-(arylaminomethyl)-succinates to 1-aryl-4-carboxypyrrolidones (pseudo-itaconilic acids) and even closer analogy in Kuhling and Frank's[9] conversion of ethyl γ-cyano-γ-benzylaminovalerate to 1-benzyl-5-methyl-5-cyano-2-pyrrolidone.



It is believed that the cyclization of (VIII) to (XI) is the first instance of the use of an intramolecular Claisen, or Dieckmann, reaction for the preparation of a pyrrole derivative.

Experimental[10,11]

Ethyl Benzylaminoacetate, Ib.—Ethyl chloroacetate (244 g., 2.0 moles), benzylamine (428 g., 4.0 moles) and benzene (2 liters) were stirred under reflux. The benzylamine hydrochloride was removed by filtration at the end of three and five hours of refluxing. The filtrate was concentrated to 500 cc. and again filtered. The final filtrate was fractionally distilled to give 267.5 g. (69% yield) of product, b. p. 150–152° (12 mm.). Mason and Winder[12] prepared the substance in unspecified yield in ethanol solution and reported the b. p. 160–165° (10–20 mm.), and Mannich and Kuphal[13] used no solvent to obtain an unspecified yield of product b. p. 153–154° (18 mm.). If the refluxing is carried out for an unnecessarily long time or if the distillation is carried out at too high pressure there will be a considerable pot-residue of 1,4-dibenzyl-2,5-diketopiperazine,[12,13] m. p. 168–170°, with a much lower yield of desired product.

Ethyl α,N-Diformylbenzylaminoacetate, IIb.—To a vigorously stirred mixture of ethyl benzylaminoacetate (193 g., 1.00 mole) and ethyl formate (370 g., 5.00 moles) maintained at 0 ± 5° there was added during one hour a finely divided suspension of sodium ethoxide (68 g., 1.00 mole) in benzene (400 cc.). The mixture was stirred two and one-half hours after the addition was complete and was then refrigerated twenty hours. The clear solution was extracted twice with water, the combined aqueous extract was washed once with benzene, then the aqueous layer was acidified (hydrochloric acid) with chilling. The resultant heavy oil was extracted with ethyl acetate and removal of the solvent from the extract left 197.5 g. (79.5% yield) of red oil. A small sample for analysis was dissolved in aqueous potassium carbonate, the solution was extracted with ether (extract discarded), filtered and acidified. The precipitated oil soon crystallized, was powdered and then washed several times with distilled water. The product melted at 86–89°.

Anal. Calcd. for $C_{13}H_{15}NO_4$: C, 62.65; H, 6.02. Found: C, 62.96; H, 5.72.

Ethyl α-Benzylamino-β,β-diethoxypropionate, IVb.—A mixture of ethyl α,N-diformylbenzylaminoacetate (50.0 g., 0.20 mole), ethyl orthoformate (30.0 g., 0.20 mole) and powdered ammonium chloride (1.0 g.) was refluxed (oil bath) with a thermometer in the liquid until the liquid temperature fell to 78.5°. The cooled mixture was dissolved in chloroform and washed with sodium carbonate solution until the washings were colorless. After a final wash with water the solvent was removed to leave 31.0 g. (50% yield, crude) of ethyl α-(N-formyl)-benzylamino-β,β-diethoxypropionate (III) as a moderately viscous brown oil which was not purified further.

Sixteen and one-tenth grams (0.05 mole) of this crude formyl acetal was dissolved in 100 cc. of 35% ethanolic hydrogen chloride and allowed to stand sixteen hours at room temperature. The solvent was removed *in vacuo* and the residue was dissolved in a mixture of chloroform and aqueous sodium carbonate. The chloroform layer was washed with water, dried, and the solvent removed to leave 10.3 g. (71% yield, crude) of red oil which decomposed badly on distillation; b. p. 170–185° (6 mm.).

Anal. Calcd. for $C_{16}H_{25}NO_4$: C, 65.09; H, 8.47. Found: C, 64.92; H, 7.71.

Ethyl Formylchloroacetate, VI.—This was prepared essentially by the method of Wislicenus,[3] except that sodium ethoxide in dry ether was used as the condensing agent instead of potassium ethoxide in alcohol–ether. It was obtained in 78% yield.

Ethyl α-Chloro-β,β-diethoxypropionate, VII.—This was prepared from (VI) by the method of Fischer,[2] using ethanolic hydrogen chloride at 0°, in 40% yield, and by the method of Claisen[1] in 82% yield. It boiled at 105–110° (9 mm.). Wohl and Schweitzer[14] reported the b. p. as 116–117° (11 mm.).[15]

Condensation of Benzylamine and VII.—VII (26.9 g., 0.12 mole) and benzylamine (26.0 g., 0.243 mole) were stirred under reflux for three hours in dry benzene (200 cc.). The mixture was concentrated and filtered, then the filtrate was fractionally distilled to give 10 g. (28% yield) of ethyl α-benzylamino-β,β-diethoxypropionate (IVb), b. p. 180–185° (6 mm.). The yield could not be improved by omitting the solvent and using a higher temperature, either in a flask or in an autoclave. When the N-potassium salt of benzylamine and the chloroester were heated in xylene, none of the desired product was obtained.

Ethyl (N-Phenacetyl)-benzylaminoacetate, VIII.—Phenacetyl chloride (154 g., 1.00 mole) was dropped into an emulsified mixture (Hershberg stirrer) of ethyl benzylaminoacetate (193 g., 1.00 mole), potassium carbonate (152 g., 1.10 mole) and water (500 cc.) maintained at 0°. The mixture was stirred fifteen minutes after the addition was complete, benzene (500 cc.) was added and the mixture was stirred another fifteen minutes. The benzene was separated and washed with dilute acid and then with water; the solution was dried, the solvent was removed, and the residue was distilled to give 290 g. (93% yield) of product, b. p. 210° (1–2 mm.); $n^{25}D$ 1.5500.

Anal. Calcd. for $C_{19}H_{21}NO_3$: N, 4.50. Found: N, 4.77.

(N-Phenacetyl)-benzylaminoacetic Acid, X.—A. VIII (10.0 g.) was warmed on the steam cone with 100 cc. of 10% caustic soda until solution was complete, and then chilled. At this point the sodium salt of the acid crystallized as pearly platelets; the mixture was diluted with cold water to complete solution (about 600 cc. total volume), filtered, extracted with benzene (extract discarded) and acidified. The acidic solution was then extracted with benzene and the acid crystallized from the extract; the product weighed 7.4 g. (81% yield) and melted at 104–106°.

(8) Anschütz and Reuter, *Ann.*, **254**, 146 (1889).

(9) Kuhling and Frank, *Ber.*, **42**, 3954 (1909); see also Weber, *Ber.*, **40**, 4044 (1907), for other examples.

(10) All melting points and boiling points are uncorrected.

(11) Microanalyses are by Misses P. Curran and A. Rainey of these laboratories.

(12) Mason and Winder, *J. Chem. Soc.*, **65**, 187 (1894).

(13) Mannich and Kuphal, *Ber.*, **45**, 314 (1912).

(14) Wohl and Schweitzer, *ibid.*, **40**, 96 (1907).

(15) After this work was completed Oroshnik and Spoerri, THIS JOURNAL, **67**, 721 (1945), described the preparation of this material by the alcoholic hydrogen chloride and the ethyl orthoformate methods in 62 and 37% yield, respectively. Their product boiled at 113–115° (15 mm.).

Anal. Calcd. for $C_{17}H_{17}NO_3$: N, 4.94. Found: N, 5.03.

B. Ethyl benzylaminoacetate (36.6 g., 0.20 mole) was warmed on the steam cone with 200 cc. of 10% caustic soda until solution was complete. The solution was chilled and extracted with ether (extract discarded). To the chilled and stirred solution there was added dropwise phenacetyl chloride (31.0 g., 0.20 mole); after an additional thirty minutes of stirring the solution was extracted with benzene (extract discarded), acidified with hydrochloric acid and again extracted with benzene. This extract was washed with water and then with aqueous potassium carbonate. The carbonate wash was extracted once with ether (ether discarded) and then acidified. The resultant pale yellow oil crystallized from benzene in large prisms. The product weighed 30.7 g. (54% yield) and melted at 104–105°; when this acid was mixed with a sample (m. p. 104–106°) prepared by method A the mixture melted at 104–106°.

Esterification of X to VIII.—X (10.0 g.) was placed in a flask with ethanol (100 cc.) and acetyl chloride (4 cc.) and the mixture was refluxed on the steam cone for one hour and then allowed to stand twenty-four hours at room temperature. The solvent was removed, the residue was taken into benzene, the solution was washed with aqueous potassium carbonate and the solvent was removed to leave the ester (VIII) (10.1 g., 92% yield); $n^{25}D$ 1.5513.

Methyl Benzylaminoacetate, Ia.—Methyl chloroacetate (216 g., 2.00 moles), benzylamine (428 g., 4.00 moles) and benzene (2 liters) were stirred under reflux for five hours and then filtered. The benzene was removed from the filtrate by vacuum distillation and the residue was refrigerated overnight. The mixture was again filtered and the filtrate was fractionally distilled to give 175 g. (49% yield) of product, b. p. 130–132° (6 mm.).

Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.04; H, 7.26; N, 7.82. Found: C, 66.59; H, 7.57; N, 7.83.

Methyl α,N-Diformylbenzylaminoacetate, IIa.—This was prepared in essentially the same manner as (IIb), but using methyl benzylaminoacetate (179 g., 1.00 mole), and methyl formate (300 g., 5.00 moles) maintained at −10 to −5° to which there was added sodium methoxide (54 g., 1.00 mole) in dry benzene (400 cc.). The white crystalline product weighed 186 g. (79% yield) and melted at 112°. It could be recrystallized from aqueous methanol but the m. p. was not changed.

Anal. Calcd. for $C_{12}H_{13}NO_4$: C, 61.28; H, 5.53; N, 5.96. Found: C, 61.01; H, 5.53; N, 5.82.

Methyl α-Benzylamino-β,β-dimethoxypropionate, IVa.—A. IIa (77.0 g., 0.35 mole) was dissolved in 500 cc. of 10% dry methanolic hydrogen chloride and allowed to stand overnight at room temperature. The solution was taken to dryness under vacuum; there was added 500 cc. of saturated aqueous potassium carbonate and 500 cc. of benzene and the mixture stirred until no more solid remained. The benzene was separated and fractionally distilled to give 39 g. (44% yield) of product, b. p. 110° (0.10 mm.), which was a pale yellow oil.

Anal. Calcd. for $C_{13}H_{19}NO_4$: N, 5.53. Found: N, 6.06.

B. Methyl chloroacetate (108 g., 1.00 mole) and benzylamine (214 g., 2.00 moles) were dissolved in benzene (500 cc.) and the mixture was stirred under reflux two and one-half hours. The mixture was chilled and filtered, all the benzene was removed under vacuum and the mixture was again filtered. To this filtrate there was added methyl formate (300 g., 5.0 moles) and the mixture was stirred at 0° as a suspension of sodium methoxide (54 g., 1.00 mole) in benzene (800 cc.) was added during one hour. The mixture was stirred three hours after the addition was completed and was then refrigerated overnight. Water (400 cc.) was added, the aqueous layer was separated and acidified. The acidic mixture was extracted with benzene and the solvent was removed under vacuum from the extract. The residue was dissolved in 600 cc. of saturated methanolic hydrogen chloride and allowed to stand sixteen hours at room temperature. The solvent was removed under vacuum, and the residue was stirred with 600 cc. of 40% potassium carbonate solution until there was no further reaction. The mixture was then extracted with benzene, from which there was obtained on fractional distillation 90.0 g. (36% over-all yield) of methyl α-benzylamino-β,β-dimethoxypropionate, b. p. 118° (0.4 mm.).

Methyl α-(N-Phenacetyl)-benzylamino-β,β-dimethoxypropionate, V.—To an emulsified mixture (Hershberg stirrer) of methyl α-benzylamino-β,β-dimethoxypropionate (34.3 g., 0.135 mole), sodium carbonate (20 g., 0.189 mole) and water (200 cc.) there was added dropwise phenacetyl chloride (21.6 g., 0.140 mole). The mixture was stirred four hours after the addition was complete and was then extracted with benzene. The extract was washed, dried, and the solvent was removed to leave 46.2 g. (92.4% yield) of viscous yellow oil which could not be crystallized or distilled.

Anal. Calcd. for $C_{21}H_{25}NO_5$: N, 3.77. Found: N, 4.11.

1-Benzyl-3-phenyl-2,4-pyrrolidinedione, XI.—A. To a vigorously stirred and chilled mixture of ethyl (N-phenacetyl)-benzylaminoacetate (62.2 g., 0.20 mole) and ethyl formate (74 g., 1.00 mole) there was added a suspension of sodium ethoxide (13.6 g., 0.20 mole) in benzene (200 cc.) during one hour. The mixture was stirred two hours after the addition was complete and was then refrigerated overnight. The mixture was extracted with water (500 cc.), the aqueous layer was separated, filtered and then acidified to give a white solid which weighed 42.0 g. (79% yield) and melted at 202–204°. A sample for analysis was recrystallized four times from ethanol and then melted at 209°.

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 77.00; H, 5.66; N, 5.28. Found: C, 76.78; H, 5.67; N, 5.26.

The same material was obtained, in 92% yield, by reverse addition of the reactants. Ethyl formate (8.0 g., 0.108 mole) was dropped into a stirred and chilled suspension of sodium ethoxide (6.8 g., 0.10 mole) in ether (100 cc.). This mixture was stirred one hour, then ethyl (N-phenacetyl)-benzylaminoacetate (31.1 g., 0.10 mole) was dropped in and the mixture was stirred three hours as it was allowed to warm up to room temperature. The mixture was then extracted with water (100 cc.), acidification of the extract giving 24.5 g. of product that melted at 205–206° after one recrystallization from ethanol.

The material was soluble in cold dilute sodium hydroxide to give a sodium salt which was much less soluble in concentrated base. When the material was dissolved in hot dilute base, 35% caustic added to incipient cloudiness, and the solution allowed to cool slowly, the salt crystallized in long filaments. This sodium salt dissolved in its own water of crystallization at about 90° but no satisfactory analysis could be obtained because of the ease with which the hydrate lost water and because of the hygroscopicity of the material after it was thoroughly dried.

When this sodium salt was dissolved in water and the solution was acidified, the original material, m. p. 205–206°, was regenerated.

B. To a hot solution of sodium ethoxide, prepared from 2.3 g. (0.10 mole) of sodium and 50 cc. of ethanol, there was added ethyl benzylaminoacetate (19.3 g., 0.10 mole) followed by ethyl phenylacetate (16.4 g., 0.10 mole). The mixture was then stirred three hours during which it was allowed to cool to room temperature. After dilution with ether (100 cc.) the mixture was extracted with water (150 cc.). Acidification of the aqueous extract gave 1.51 g. (5% yield) of product which, after recrystallization from ethanol, melted at 205–206° alone or when mixed with the same material prepared by method A.

Summary

Ethyl α-benzylamino-β,β-diethoxypropionate has been prepared by two methods. Methyl α-benzylamino-β,β-dimethoxypropionate has been

prepared and converted into methyl α-(N-phenacetyl) - benzylamino - β,β - dimethoxypropionate. Some of the reactions of these substances and of the intermediates from which they were prepared have been studied.

RENSSELAER, NEW YORK RECEIVED APRIL 16, 1949

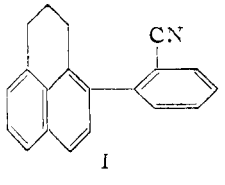
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

A Study of Isomerization in the Methylperinaphthene Series

BY V. BOEKELHEIDE AND CLIFFORD E. LARRABEE[1]

Perinaphthene and its derivatives exhibit some unusual properties and the explanation has been advanced that, because of the symmetry of the molecule, the corresponding ions and radicals have a relatively high degree of stabilization due to resonance.[2] One implication of the resonance concept is that all of the monosubstituted perinaphthenes having the same substituent variously placed at the 1-, 3-, 4-, 6-, 7- or 9- positions should, on conversion to the corresponding anion followed by acidification, yield the same product or the same mixture of products. For the purpose of testing this idea a study of the preparation and isomerization of some methylperinaphthenes has been made.

That symmetry might be an important factor in influencing the behavior of perinaphthene and its derivatives was first suggested by Klyne and Robinson,[3] who proposed that perinaphthene derivatives, when prepared, would be found to be tautomeric. Although they were unsuccessful in preparing 1-methylperinaphthene, they thought that it should exist as a mixture of six forms corresponding to the six positions possible for the "extra" hydrogen on the nucleus. Evidence that perinaphthene derivatives may be readily isomerized was first obtained by Fieser and Gates,[4] who found that the reaction product of *o*-chlorophenylmagnesium bromide and perinaphthanone, when subjected to dehydration, hydrogenation and treatment with cyanide, gave two products, I and II. Presumably the intermediate perinaphthene derivative isomerized to a mixture.



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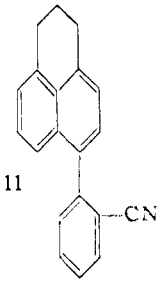
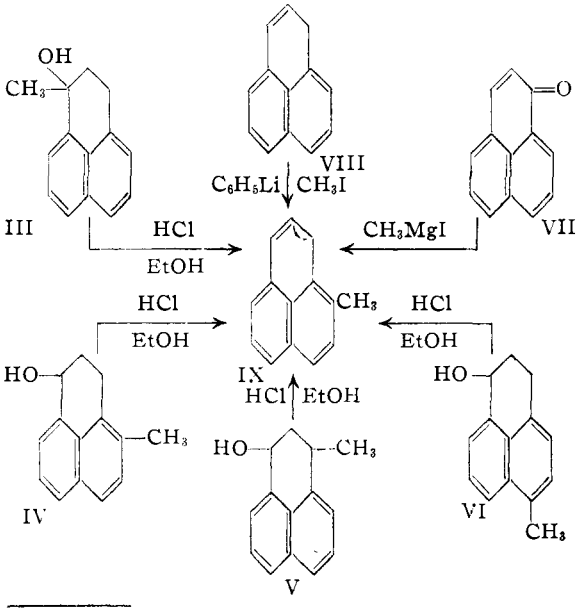


However, since the intermediate perinaphthene derivative was not isolated and since the results can also be interpreted on the basis that the Grignard addition occurred in both a 1,4- and 1,6- fashion,[5] isomerization was not established.

For the investigation of isomerization in the methylperinaphthene series, it seemed desirable to try to prepare several different methylperinaphthenes in order to determine whether interconversion would occur. Of the methods available for preparing perinaphthene derivatives, the most feasible appeared to be dehydration of the appropriate carbinol. This method was used by Fieser and Newton[6] for converting the tertiary alcohol, 7-methylperinaphthanol-7, to a methylperinaphthene, and it has been used recently for preparing perinaphthene in good yield.[2] Therefore the various alcohols shown by formulas III, IV, V and VI were prepared for use in the dehydration step.

The preparation of III and IV has been previously described.[3,6] In the preparation of V, 9-methylperinaphthanone-7 was obtained from α-naphthyl methyl ketone by the successive steps of Reformatsky addition of ethyl bromoacetate, dehydration, hydrolysis, hydrogenation and cy-



(1) Beaunit Mills Fellow, 1948–1949; present address: General Aniline and Film Corp., Easton, Pennsylvania.

(2) See the accompanying paper, THIS JOURNAL, **72**, 1245 (1950).

(3) Klyne and Robinson, *J. Chem. Soc.*, 1991 (1938).

(4) Fieser and Gates, THIS JOURNAL, **62**, 2335 (1940).

(5) For examples of 1,4-Grignard additions in this series, see Koelsch and Anthes, *J. Org. Chem.*, **6**, 558 (1941), and Koelsch and Rosenwald, THIS JOURNAL, **59**, 2166 (1937).

(6) Fieser and Newton, *ibid.*, **64**, 917 (1942).