Dehydration of N-(β-Hydroxypropyl)-carbazole (IV).—In a typical experiment, 29 cc. of dry benzene, 29 g. of phosphorus pentoxide and 0.2 g. of *p-t*-butylcatechol were heated to refluxing in a 125-cc., 3-necked flask, equipped with condenser, stirrer and dropping funnel. Five and eight-tenths grams (0.022 mole) of (IV) in 27 cc. of dry benzene was added over a period of fifteen minutes. After fifteen minutes more of refluxing, the contents of the flask were diluted with a large volume of water and neutralized with sodium carbonate. The solid was filtered, washed and air-dried. The product contained no monomer, but 4 g. (88% yield) of a solid which was precipitated as a white powder from its benzene solution with methyl alcohol. This powder had a softening point of 180°. Viscosity measurements at several concentrations indicate that this material is a polymer having a molecular weight between 20,000 and 40,000.

Summary

A method is described for preparing N-vinylcarbazole and the polymer of N-propenylcarbazole. The synthesis and properties are given for N-(β-hydroxyethyl)-carbazole and N-(β-hydroxypropyl)-carbazole and several esters of each.

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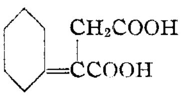
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

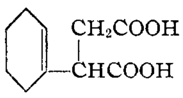
The Stobbe Condensation with Cyclohexanone

BY WILLIAM S. JOHNSON, CHESTER E. DAVIS,[1] RICHARD H. HUNT AND GILBERT STORK[2]

The first report of this condensation was made in 1941 by Robinson and Seijo[3] who used equimolar quantities of cyclohexanone, dimethyl succinate and sodium methoxide. The product (yield unspecified) gave on hydrolysis an acid melting at 186–187° which was presumed by them to be cyclohexylidenesuccinic acid, I.[4] A product also presumed to have this structure had been previously reported by Ingold, Seeley and Thorpe[5] as melting at 175°, the evidence for the position of the double bond being based on the odor of the oxidation product.[6] More recently Alder, Pascher and Schmitz[7] described the sodium ethoxide-catalyzed Stobbe condensation of cyclohexanone with diethyl succinate. The crude saponified product was obtained in "over 40%" yield and on purification gave a dibasic acid melting at 146°, also presumed to be cyclohexylidenesuccinic acid, I. An acid of the same description has since been similarly prepared in 37% yield (after a reaction period of more than two weeks) by Swain, Todd and Waring[8] who suggested that the 146° acid was not I, but cyclohexenylsuccinic acid, II. That this conclusion was correct is demonstrated below.



I



II

The probable nature of the other products is also elucidated.

The modified procedure for the Stobbe condensation involving the use of potassium *t*-butoxide[9] was employed with striking success, the distilled half-ester III being obtained in 84% yield after a reaction period of only ten minutes. Saponification of the half-ester with barium hydroxide gave a mixture from which two pure acids were isolated, one melting at 179–180° with evolution of gas and the other at 145–146° without decomposition. According to Stobbe's generalization[10] that all itaconic acids melt around 170–185° with elimination of water (anhydride formation) and that alkylidene pyrotartaric acids melt around 140–155° with very slow decomposition it would be concluded that the 180° acid is I and the 146° acid II. The opposite conclusion is reached, however, on the basis of the generalizations regarding the behavior of such acids with acetyl chloride at room temperature, since the lower melting acid reacted more rapidly than the 180° acid.

The structures of the two acids were shown by oxidation with cold alkaline permanganate: the 180° acid gave cyclohexanone isolated in 28% yield as the semicarbazone, while the 146° acid under identical reaction conditions gave no detectable cyclohexanone. The former therefore is undoubtedly cyclohexylidenesuccinic acid, I, and the latter the 3-carbon tautomer II. When the half-ester was similarly oxidized no cyclohexanone could be detected and the position of the double bond is therefore formulated in the endocyclic position (formula III). Although exclusion from the liquid half-ester of all traces of the isomeric cyclohexylidene derivative could not be established by the oxidation tests, the appreciable quantities of the derivative obtained on saponification of the

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[3] Robinson and Seijo, *J. Chem. Soc.*, 582 (1941).

[4] Robinson and Seijo (ref. 3) state that, "All the substances mentioned in this section afforded cyclohexanone on oxidation with alkaline permanganate." This observation is not incompatible with the premise set forth in the present communication that their material was actually the paraconic acid IV.

[5] Ingold, Seeley and Thorpe, *ibid.*, 853 (1923).

[6] The authors (ref. 5) state that "It instantly decolorizes cold alkaline permanganate, and gives an odour of *cyclo*hexane . . ." (undoubtedly they meant cyclohexanone).

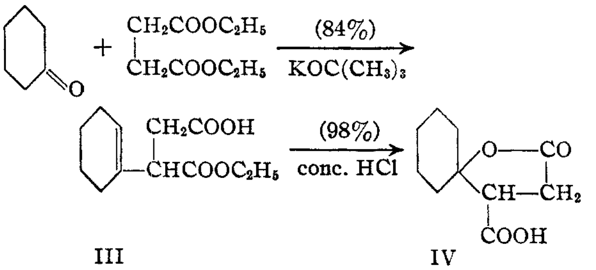
[7] Alder, Pascher and Schmitz, *Ber.*, **76B**, 27 (1943).

[8] Swain, Todd and Waring, *J. Chem. Soc.*, 548 (1944).

[9] (a) Johnson, Petersen and Schneider, THIS JOURNAL, **69**, 74 (1947); (b) Johnson, Goldman and Schneider, *ibid.*, **67**, 1357 (1945); (c) Johnson, Johnson and Petersen, *ibid.*, **67**, 1360 (1945); (d) Johnson and Petersen, *ibid.*, **67**, 1366 (1945).

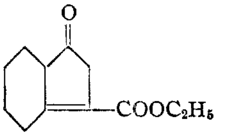
[10] Stobbe, *Ann.*, **308**, 67 (1899).

half-ester seem attributable to a partial isomerization of the bond from the endo- to the exo-cyclic position by a base-catalyzed tautomerism.[11]

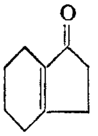


III IV

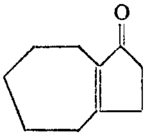
The half-ester III was treated with hydrobromic and acetic acid in an effort to effect decarbethoxylation as in other series,[9] but no carbon dioxide was evolved even on prolonged heating.[12] The product of this treatment was a crystalline acid melting at 186–187° (yield 98%), which proved to be isomeric with the dicarboxylic acids I and II described above. That it was γ,γ-pentamethyleneparaconic acid IV was shown by the neutral equivalent and by its reaction with diazomethane to give a neutral, *mono*-methyl ester. The melting point of this derivative (76–76.5°) is in agreement with that (73.5–74.5°) reported for a substance isolated by Robinson and Seijo[3] from the reaction betwen cyclohexanone and dimethyl succinate and then presumed to be the paraconic ester. For the preparation of the paraconic acid IV it was found expedient simply to warm the half-ester III with concentrated hydrochloric acid which effected practically quantitative conversion. This behavior suggests that the product of Robinson and Seijo, m. p. 186–187°, which was prepared by hydrolysis with concentrated hydrochloric acid was likewise the paraconic acid IV instead of cyclohexylidenesuccinic acid.[13] Isolation of the same acid (melting at 187°) by the English workers from alkaline hydrolyses seems attributable to the presence in their reaction mixture of methyl pentamethyleneparaconate which we have found readily convertible to the paraconic acid upon saponification. The intermediary hydroxy acid is evidently quite easily lactonized in aqueous solution as it is liberated from the salt.



V



VI



VII

Some preliminary studies were made on the cyclization of the half-ester III according to methods already developed for the synthesis of hydrindone derivatives.[9c,d] When III was heated with zinc chloride, acetic anhydride and acetic acid, followed by hydrochloric and acetic acid to hydrolyze the intermediary keto ester V, 4,5,6,7-tetrahydro-1-indanone VI was produced˙ The best conditions have not yet been ascertained for this reaction which, nevertheless, serves to extend the scope of the general synthetic scheme. It is noteworthy that Plattner and Büchi[14] have recently applied our synthetic scheme to cycloheptanone for the synthesis of the bicyclic ketone VII which they employed in a new azulene synthesis.

Experimental[15]

β-Carbethoxy-β-cyclohexenylpropionic Acid (III).—To a refluxing solution of 5.6 g. of potassium in 100 ml. of dry *t*-butyl alcohol was added (atmosphere of nitrogen) a mixture of 11.9 g. of cyclohexanone (Eastman Kodak grade, redistilled) and 30.1 g. of diethyl succinate, followed by 10 ml. of *t*-butyl alcohol to complete the transfer of reagents. After refluxing for ten minutes (atmosphere of nitrogen), the mixture was cooled in an ice-bath and acidified with a freezing mixture of 20 ml. of concentrated hydrochloric acid and 20 g. of ice. Most of the *t*-butyl alcohol was removed at reduced pressure, and the residue was extracted with ether. The ether layer was extracted thoroughly with saturated sodium bicarbonate solution. Acidification of the aqueous extracts with dilute hydrochloric acid liberated the half-ester which was taken up in ether, washed with saturated sodium chloride solution and dried over anhydrous sodium sulfate. Evaporation of the ether, and distillation of the residue gave 23.1 g. (84% yield) of colorless viscous oil, b. p. 150–155° (0.5 mm.). Redistillation gave material boiling at 154–156° (0.5–0.6 mm.), $n^{25}\text{D}$ 1.4830.

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.69; H, 7.87.

With longer reaction periods, the yields were lower: after twenty-five minutes, 78%; after one hour, 60%.

Saponification of β-Carbethoxy-β-cyclohexenylpropionic Acid.—The above half-ester (5.18 g.) was heated with a solution of 9.5 g. of barium hydroxide octahydrate in 80 ml. of water for seven hours on the steam-bath. After cooling the mixture was carefully acidified with hydrochloric acid and the colorless precipitate of dibasic acids separated by filtration. A small amount of additional dibasic acid was isolated from the filtrate by saturation with sodium chloride and extraction with ether.

The dried solid dibasic acid mixture was treated with 100 ml. of acetyl chloride at room temperature for one and one-half hours. The solvent was evaporated under reduced pressure, and the residue was taken up in ether and extracted with saturated sodium bicarbonate solution. Acidification of the aqueous extracts gave 1.25 g. of material melting at 137–149°. Recrystallization from water gave 1.07 g. of very crude **cyclohexylidenesuccinic acid** (I), m. p. 150–156° (dec.). Repeated recrystallization from the same solvent eventually gave fine colorless needles, m. p. 179–180° (dec.) with slight previous softening.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.58; H, 6.85.

The anhydride which remained in the ether solution after extraction with bicarbonate (see above) was isolated as an oil upon evaporation of the ether. It was hydrolyzed by heating on the steam-bath with 100 ml. of saturated sodium bicarbonate solution for eight hours. After

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[11] *Cf.* the isomerization of cyclohexeneacetic acid to cyclohexylideneacetic acid, Linstead, *J. Chem. Soc.*, 362 (1927).

[12] Decarboxylation can be effected easily by pyrolysis of the paraconic acid (IV) giving a mixture of lactone and unsaturated acids. The exact nature of these products and the mechanism of the reaction will be the subject of a future communication.

[13] Robinson and Seijo obtained a neutral equivalent of 96 which is in agreement with requirements for a dibasic acid rather than IV, but, possibly, had added excess alkali and back-titrated, in which event a second equivalent of alkali would have been consumed in the hydrolysis of the lactonic to the hydroxy dibasic acid.

[14] Plattner and Büchi, *Helv. Chim. Acta*, **29**, 1608 (1946).

[15] All melting points are corrected.

acidification, the dibasic acid was isolated by ether extraction; yield 3.05 g. of material melting at 140–147°. (The total yield of crude dibasic acid from half-ester, thus was 4.30 g. or 95%.) Recrystallization from water gave 2.83 g. of **cyclohexenylsuccinic acid (II)**, m. p. 140–146°. It was difficult to obtain this material pure, but by repeated recrystallization from the same solvent it was eventually obtained as colorless prisms melting at 145–146° with slight previous softening. Further recrystallization did not raise the m. p.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.58; H, 7.34.

Experiments with the pure dibasic acids described above showed that (a) with acetyl chloride at room temperature the 146° acid was almost completely converted to the anhydride after one and one-half hours, while under the same conditions about 70% of the 180° acid was recovered unchanged; (b) both of the acids were converted into γ,γ-pentamethyleneparaconic acid by the action of concentrated hydrochloric acid as described below for the preparation of this substance from the half-esters.

Oxidation Experiments.—A solution of 0.319 g. of potassium permanganate in 18 ml. of water was added slowly over a period of one and one-half hours to a well stirred and cooled (ice-bath) solution of 0.200 g. of cyclohexylidenesuccinic acid, m. p. 179–180° (dec.), and 0.213 g. of potassium carbonate in 10 ml. of water. After the addition was complete the mixture was distilled until 5 ml. of distillate was collected. This was treated with 0.100 g. each of semicarbazide hydrochloride and sodium acetate, whereupon colorless crystals of cyclohexanone semicarbazone separated immediately; yield 0.043 g. or 28%; m. p. 164–165.5° either alone or when mixed with an authentic specimen of the derivative. A control experiment was carried out by distilling a suspension of 0.0365 g. of cyclohexanone in 25 ml. of water and treating the first 5 ml. of distillate as described above. The yield of semicarbazone, m. p. 164–165.5°, was 0.0270 g. or 47%. According to this factor it is calculated that the actual yield of cyclohexanone in the oxidation experiment was approximately 59%.

When the 146° acid II and the half-ester III were treated by exactly the same oxidation procedure as described above not a trace of semicarbazone was detected.

γ,γ-Pentamethyleneparaconic Acid (IV).—A mixture of 12.93 g. of once distilled β-carbethoxy-β-cyclohexenylpropionic acid and 140 ml. of concentrated hydrochloric acid was heated on the steam-bath for about fifteen minutes. The light brown solution was allowed to stand at room temperature overnight, and then chilled. The crude grayish crystalline paraconic acid was separated by filtration and washed with water; yield 6.92 g., m. p. 170–176°. Evaporation of the filtrate and washings to about 30–40 ml. and cooling gave an additional 4.21 g. of colorless material, m. p. 185–186.5°, making the total yield 11.13 g. or 98%. Recrystallization of the crude material from benzene–alcohol gave colorless prisms, m. p. 186–187° without decomposition.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12; neut. equiv., 198. Found: C, 60.57; H, 7.02; neut. equiv., 199.

For the preparation of the paraconic acid IV it was unnecessary to distil the half-ester. Thus the crude oily acidic fraction obtained from a Stobbe condensation with 12.2 g. of cyclohexanone was treated as described above with 250 ml. of concentrated hydrochloric acid. Solution was complete after heating on the steam-bath for thirty minutes. The yield of colorless recrystallized paraconic acid, m. p. 185–186°, was 18.0 g. or 73% over-all from cyclohexanone.

The paraconic acid is also formed from the half-ester with hydrobromic acid, hydrobromic–acetic acid, and hydrochloric–acetic acid.

Methyl γ,γ-pentamethyleneparaconate was prepared in quantitative yield by the action of diazomethane in ether solution on the paraconic acid described above. After two recrystallizations from petroleum ether (b. p. 60–68°) followed by recrystallization from dilute alcohol it was obtained as fine colorless needles, m. p. 76–76.5°.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.48; H, 7.97.

Saponification of 1.45 g. of the methyl ester with 3.5 g. of potassium hydroxide in 30 ml. of water was complete after three hours of refluxing. After filtering and cooling, the mixture was acidified with dilute sulfuric acid to give 1.22 g. (90%) of colorless paraconic acid, m. p. 186–187° without decomposition.

4,5,6,7-Tetrahydro-1-indanone.—A mixture of 4.90 g. of the half-ester III, 1.0 g. of fused zinc chloride dissolved in 50 ml. of acetic acid and 100 ml. of acetic anhydride was refluxed for nine hours. After cooling slightly the excess anhydride was decomposed by the cautious addition of 50 ml. of water; then 25 ml. of concentrated hydrochloric acid was added and refluxing continued for one hour to decarbethoxylate the keto ester V. The solution was cooled, made strongly alkaline, and steam distilled until the distillate failed to give a positive test with 2,4-dinitrophenylhydrazine reagent (prepared from 0.25 g. of 2,4-dinitrophenylhydrazine dissolved in 50 ml. of concentrated hydrochloric acid and diluted with 200 ml. of water). The distillate was treated with 2.5 g. of semicarbazide hydrochloride and 2.5 g. of sodium acetate and heated on the steam-bath for twenty-five minutes. On concentrating and cooling a total of 0.291 g. of tan semicarbazone was obtained, m. p. 242–243° dec. (introduced in bath at 235°). Recrystallization from dilute alcohol gave pale yellow prisms, m. p. 242.5–243° dec. (introduced at 237°) (reported,[16] 243°).

The 2,4-dinitrophenylhydrazone was prepared directly from 0.154 g. of the semicarbazone and 0.145 g. of 2,4-dinitrophenylhydrazine in 10 ml. of alcohol. Upon addition of 4 drops of concentrated hydrochloric acid to the refluxing suspension, the mixture became homogeneous momentarily and then the deep red derivative separated from the hot solution. On cooling there was obtained 0.223 g. of material melting at 235–238°. Recrystallization from alcohol–ethyl acetate gave red needles, m. p. 238.5–239.5°.

Anal. Calcd. for $C_{15}H_{16}O_4N_4$: C, 56.95; H, 5.10. Found: C, 57.10; H, 4.96.

Summary

The condensation of cyclohexanone with diethyl succinate in the presence of potassium *t*-butoxide gives β-carbethoxy-β-cyclohexenylpropionic acid in 84% yield. Alkaline hydrolysis affords a mixture of the tautomeric cyclohexenylsuccinic and cyclohexylidenesuccinic acids, the structures of which were shown by oxidative degradation. These substances are readily lactonized by strong mineral acid to give γ,γ-pentamethyleneparaconic acid which is also obtained in 98% yield directly from the half-ester by acid hydrolysis. The proof of structure of these substances has cleared up some discrepancies in the previous literature.

Cyclization of β-carbethoxy-β-cyclohexenylpropionic acid according to previous procedures has led to a new synthesis of 4,5,6,7-tetrahydro-1-indanone.

Madison, Wisconsin Received May 1, 1948

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[16] Nenitzescu and Przemetzky, *Ber.*, **74B**, 676 (1941).