While the optimum temperature for liquid hydrocarbon synthesis depended most upon the history and age of the catalyst, and upon whether or not the catalyst was supported, maximum liquid hydrocarbon yields were usually obtained near 225° which is at least 30° above that generally found best for Fischer–Tropsch synthesis.[18] This appears consistent with the participation of the endothermic water gas shift.

The values of the apparent activation energy for the over-all, or total reaction, found in the present work to lie between 20.3 and 25.3 with an average of 23.1 kcal., compare closely with the values of 23.8 and 26.4 kcal.[10] found for the synthesis from carbon monoxide on a cobalt–thoria–magnesia–kieselguhr catalyst. This indicates that a similar rate controlling mechanism, which is clearly not diffusion, may be involved in both syntheses.

The authors are tentatively inclined to attribute the much smaller oil yields produced in the hydrogenation of carbon dioxide, in comparison with carbon monoxide, to limitations imposed by the water gas equilibrium.

Acknowledgment.—The authors are indebted to Mr. R. N. R. Mulford for several analyses on the liquid hydrocarbons synthesized.

Summary

The present work comprised a study of several types of copper-activated, cobalt catalysts for the synthesis of higher hydrocarbons from carbon dioxide and hydrogen at atmospheric pressure, and in a temperature range from 175 to 300°.

Catalysts containing no alkali produced no liquid hydrocarbons or only traces, but did yield small amounts of liquid hydrocarbons after a suitable poisoning. Alkalizing with potassium carbonate or phosphate was necessary in order to produce catalysts active for liquid hydrocarbon synthesis, and it appears that the alkali can act as a selective poison for methane-forming catalyst centers.

Small additions of cerium oxides to the alkalized catalysts were very effective in increasing synthesis life and catalyst stability.

Although an alkalized, ceria-containing catalyst supported on a natural kieselguhr produced only methane, when a flux-calcined kieselguhr was substituted as a support, a catalyst was obtained which synthesized nearly as much liquid hydrocarbons as unsupported catalysts of about the same composition.

The optimum synthesis temperature was near 225°, but depended on catalyst composition and activity. Raising synthesis temperature some 25 to 100° for several hours produced a selective poisoning of catalyst hydrogenation centers, which caused a marked increase in liquid hydrocarbon formation upon resumption of synthesis at the initial temperature.

While the carbon monoxide theoretically available from the water gas reaction (assuming no complicating reactions) is in all cases ample to account for all of the higher hydrocarbons formed, it is entirely inadequate to account also for the amounts of methane formed. The maximum liquid hydrocarbon yield obtained was 95 ml. per cubic meter of carbon dioxide passed, and was accompanied by 360 liters of gaseous hydrocarbons.

The apparent activation energy for the over-all synthesis was found to be 23.1 kcal.

RECEIVED JUNE 24, 1949

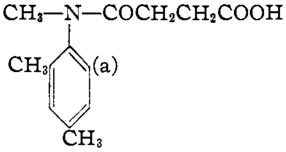
[18] Hall and Smith, *J. Soc. Chem. Ind. (London)*, **65**, 128 (1946).

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

Restricted Rotation in Aryl Amines. XI. Influence of Groups Decreasing the Basicity of the Nitrogen Atom

BY ROGER ADAMS AND JOSEPH R. GORDON[1]

In a recent paper,[2] a comparison of various groups in the 6-position upon the stability of the optically active forms of compounds of type I was discussed. It was found that the methyl and methoxyl groups had the relative effectiveness on stability expected from the previously reported work on optically active biphenyl derivatives. The molecules, however, in which the bromine, iodine and nitro groups were present were much less stable than anticipated. This anomalous behavior was ascribed to the tendency for an increased double bond character of the carbon–nitrogen bond in the derivatives of amines of decreased basicity. The tendency for double bond formation will aid in forcing the substituents on the amino nitrogen into a coplanar configuration with the ring.



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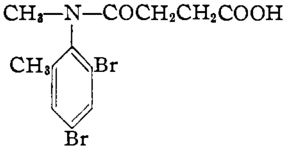

II

(a) = Br, I, NO_2, CH_3, OCH_3

This hypothesis was supported by a comparison of the stability of the bromo derivative (I) with the dibromo-*o*-toluidine derivative (II). The

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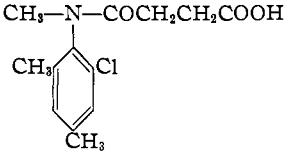
[1] An abstract of a thesis submitted by Joseph R. Gordon to the Graduate College of the University of Illinois, 1949, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

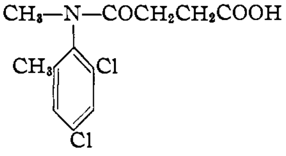
[2] Adams and Sundholm, THIS JOURNAL, **70**, 2667 (1948).

optically active form of the latter had a half-life in boiling butanol of 1.1 hr. as compared with 3.1 hr. for the former. Similarly, the analogous derivative of 1-amino-2-methylnaphthalene (half-life 5.7 hr.) was more stable than that of the 1-amino-2-methyl-4-chloronaphthalene (half-life 4.1 hr.).[3] In this pair the chlorine atom cannot effect the hindrance of rotation except by inducing electronic changes since the *ortho* groups to the nitrogen are the same in both molecules.

Another pair of compounds has now been synthesized and the half-lives of their optically active forms compared. They are represented by formulas III and IV. The half-life of III in boiling butanol was thirty-four minutes. Compound IV, however, was completely racemized in thirty minutes in the same solvent. In boiling methyl acetate, the racemization of III showed a half-life of about sixty-three hours while the half-life of IV averaged about eighteen hours. The chlorine derivatives were less stable than the corresponding bromine derivatives. This decrease in stability of the chlorine over the bromine analogs is greater than would be anticipated if size of substituent were the only factor. Since chlorine is more electronegative than bromine, it decreases the basicity of the amine more than does bromine. Basicity of the amine, therefore, probably has more influence upon the optical stability of these compounds than relative size of the groups.



III



IV

The synthesis of the monochloro compound III was first attempted by chlorination with sodium hypochlorite of N-succinyl-1-methylamino-2,4-dimethylbenzene. It was discovered, however, that chlorination was taking place in the 5- rather than the 6-position[4] which was also observed in the nitration of this compound.[2] The synthesis of the 6-derivative was effected by chlorination of 1-acetamido-2,4-dimethylbenzene, followed by hydrolysis, methylation and succinylation. Chlorination of 1-acetamido-2-methylbenzene yielded 1-acetamido-2-methyl-4,6-dichlorobenzene, which was then hydrolyzed, methylated and succinylated.

Experimental

1-Acetamido-2,4-dimethylbenzene.—To a solution of 83 ml. of concentrated hydrochloric acid in 750 ml. of water was added 121 g. of 1-amino-2,4-dimethylbenzene. The mixture was heated to 50° and 122 g. of acetic anhydride was added with vigorous stirring. A solution of 164 g. of crystalline sodium acetate in 400 ml. of water was immediately added. After cooling in ice, white crystals were collected which were recrystallized from ethanol, m. p. 127–127.5°. The yield was 134 g. (84%).

1-Acetamido-2,4-dimethyl-6-chlorobenzene.—Chlorine was passed through a solution of 130 g. of 1-acetamido-2,4-dimethylbenzene and 1 g. of ferric chloride in 300 ml. of glacial acetic acid until 56.7 g. was taken up. The mixture was poured into 3 l. of water and the product collected on a filter. It was recrystallized from ethanol. It formed white crystals, m. p. 197–198°. The yield was 149 g. (95%). This compound was identical with that obtained by Orton and King[5] by chlorination with acetylchloroamino-2,4-dichlorobenzene. They reported m. p. 196.5–197.5°.

1-Amino-2,4-dimethyl-6-chlorobenzene.—A suspension of 149 g. of 1-acetamido-2,4-dimethyl-6-chlorobenzene in 500 ml. of 15% hydrochloric acid was refluxed for fifteen hours. The mixture was cooled and neutralized with aqueous ammonia. The product separated as an oil. It was collected and steam-distilled until the distillate became clear. The distillate was extracted with ether and the ether extract dried over potassium hydroxide, the ether evaporated and the product distilled *in vacuo*; b. p. 85–88° (2 mm.). The product was further purified by recrystallizing from ethanol. It formed white crystals, m. p. 39–40°. The yield was 30 g. (25%). Orton and King[5] report m. p. 37–38°. Roper, Thompson and Cohen[6] report m. p. 39–40°.

1-Methylamino-2,4-dimethyl-6-chlorobenzene.—A mixture of 29.5 g. of 1-amino-2,4-dimethyl-6-chlorobenzene, 100 ml. of water and 48 g. of dimethyl sulfate was stirred for one hour after the solution became homogeneous. The temperature was maintained between 50–60° by means of a steam-bath. The solution was then cooled, acidified with 35 ml. of concentrated hydrochloric acid, cooled below 10° and then a solution of 13 g. of sodium nitrite in 75 ml. of water was added dropwise with stirring, keeping the temperature between 5–10°. Stirring was continued for thirty minutes after addition of the sodium nitrite. The cold solution was extracted with ether, the ether extract washed with 5% aqueous sodium hydroxide and then with water. The ether was removed by passing a current of air over the surface of the solution.

The nitrosamine was reduced by adding it carefully in portions to a solution of 135 g. of stannous chloride dihydrate in 132 ml. of concentrated hydrochloric acid which was first heated to 40°. Cooling was necessary to keep the temperature under 60°. After standing overnight, the mixture was cooled in ice, and made strongly alkaline by addition of a solution of 176 g. of sodium hydroxide in 250 ml. of water. The mixture was steam-distilled until the distillate came over clear. The distillate was extracted with ether and dried over potassium hydroxide. After the ether was evaporated, the oil was distilled *in vacuo*, b. p. 78–80° (1.4 mm.); $n^{20}{}_D$ 1.5500; $d^{20}{}_4$ 1.0724; M_D calcd. 49.6, found, 50.1. The yield was 12.0 g. (35%).

Anal. Calcd. for $C_9H_{12}NCl$: C, 63.68; H, 7.13. Found: C, 63.98; H, 7.15.

Picrate of 1-Methylamino-2,4-dimethyl-6-chlorobenzene.—A solution of 1 g. of 1-methylamino-2,4-dimethyl-6-chlorobenzene in 15 ml. of ethanol was added to 15 ml. of a saturated ethanol solution of picric acid. The mixture was heated to boiling and then allowed to cool slowly. This produced yellow crystals which were recrystallized from ethanol, m. p. 162–163° (cor.).

Anal. Calcd. for $C_9H_{12}NCl \cdot C_6H_3N_3O_7$: C, 45.19; H, 3.79. Found: C, 45.23; H, 3.95.

N-Succinyl-1-methylamino-2,4-dimethyl-6-chlorobenzene.—To a solution of 8.46 g. of 1-methylamino-2,4-dimethyl-6-chlorobenzene in 75 ml. of dry benzene was added 7.5 g. of succinic anhydride and a drop of 85% phosphoric acid. The solution was refluxed for eight hours. It was then cooled, diluted with 75 ml. of ether and extracted thoroughly with 5% aqueous potassium hydroxide. The alkaline extract was washed with ether and

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(3) Adams and Albert, THIS JOURNAL, **64**, 1475 (1942).

(4) This chlorination was carried out by N. K. Sundholm.

(5) Orton and King, *J. Chem. Soc.*, **99**, 1188 (1911).

(6) Roper, Thompson and Cohen, *ibid.*, **85**, 377 (1904).

acidified with 1:2 hydrochloric acid. The product separated as an oil which easily crystallized on cooling in ice. It was recrystallized from a mixture of benzene and petroleum ether (b. p. 30–60°). It formed white crystals, m. p. 137–137.5° (cor.). The yield was 10.2 g. (74%).

Anal. Calcd. for $C_{13}H_{16}NO_3Cl$: C, 57.89; H, 5.98. Found: C, 57.96; H, 5.96.

N-Succinyl-1-methylamino-2,4-dimethyl-5-chlorobenzene.[4]—To a solution of 5.2 g. of sodium hydroxide in 35 ml. of distilled water was added 5 ml. of a dilute aqueous solution of mercuric chloride. After addition of 40 g. of ice, the weight of the flask and contents was recorded. Keeping the temperature of the solution below 5°, chlorine was bubbled in at a fast rate until the yellow color of the mercuric oxide disappeared. The addition of the chlorine was then stopped and the flask weighed again. The increase in weight was 6.0 g. A portion of 64 ml. of this solution which contained 4.8 g. of chlorine was diluted to 150 ml. and added dropwise over three-quarters of an hour to 15 g. of N-succinyl-1-methylamino-2,4-dimethylbenzene[2] dissolved in 200 ml. of glacial acetic acid. The temperature was kept near 20° during the addition. After the addition of the sodium hypochlorite, the mixture was stirred for twenty minutes. The mixture was then diluted to 600 ml. with water and concentrated aqueous ammonia added with stirring and cooling at such a rate that the temperature did not rise above 25°. When the solution was alkaline to litmus, the addition of ammonia was stopped, the solution was cooled to 10°, and concentrated hydrochloric acid was added until the precipitation of the organic acid was complete. The mixture was then allowed to stand for one hour in ice, the acid filtered off, and then dried. It was recrystallized from benzene. It formed white crystals, m. p. 158° (cor.). The yield was 4.3 g. (25%).

Anal. Calcd. for $C_{13}H_{16}NO_3Cl$: C, 57.89; H, 5.98. Found: C, 58.08; H, 5.62.

Resolution of N-Succinyl-1-methylamino-2,4-dimethyl-6-chlorobenzene.—A solution of 6.68 g. of N-succinyl-1-methylamino-2,4-dimethyl-6-chlorobenzene and 7.21 g. of cinchonidine in 200 ml. of a mixture of 9:1 ethyl acetate and methanol by volume was filtered and placed in a refrigerator overnight. No crystals formed. The solution was evaporated to 175 ml. by passing a current of air over its surface. After cooling overnight in the same manner, 5.35 g. of a salt had crystallized. These crystals were collected and the filtrate evaporated with a current of air to 125 ml. The solution was replaced in the refrigerator overnight and a second crop of 4.47 g. of crystals was collected. Succeeding fractions were collected as shown in the following table. The specific rotation readings were taken by making 0.10 g. of each crop up to 20 ml. with absolute ethanol. A one-decimeter tube was used.

Crop	Wt., g.	α_D at 29°	$[\alpha]^{29}D$	Vol. in ml.
I	5.35	−0.315	−63	175
II	4.47	− .332	−67	125
III	0.91	− .344	−69	75
IV	0.245	− .331	−66	40
V	1.78	− .333	−67	20
VI	0.67			0

Of fraction I, 5.25 g. was recrystallized from 75 ml. of the ethyl acetate and methanol mixture. The results were

Crop	Wt., g.	$\alpha^{29}D$	$[\alpha]^{29}D$	Vol. in ml.
A	3.40	−0.309	−61.8	75
B	0.70	− .313	−62.6	40
C	0.46	− .316	−63.2	20
D	0.51			0

Crops A and B had sufficiently similar rotations and were therefore taken as the pure less-soluble salt (*l*B*d*A). It formed white, feathery crystals, m. p. 166–167° (cor.).

Rotation. 0.10 g. made up to 20 ml. with absolute ethanol at 29° gave α_D −0.309°; *l*, 1; $[\alpha]^{29}D$ −61.8°.

It has been found by experience that the alkaloidal salts of many acids are difficult to obtain in a strictly pure state so that the analyses will conform exactly to the theoretical. Since the acids have been analyzed before and after salt formation, the exact composition of the salts is irrelevant.

Anal. Calcd. for $C_{13}H_{16}NO_3Cl \cdot C_{19}H_{22}N_2O$: C, 68.02; H, 6.78. Found: C, 67.11; H, 6.99.

***d*- and *l*-N-Succinyl-1-methylamino-2,4-dimethyl-6-chlorobenzene.**—A mixture of 4.0 g. of the less-soluble salt, crops A and B, and 50 ml. of 1:1 hydrochloric acid at 0° was stirred in an ice water mixture for ten minutes. The salt was seen to decompose and form an oil, which crystallized on stirring. The suspension was filtered and the crystals returned to the flask. After repeating three times the treatment with hydrochloric acid, the suspension of crystals in acid was placed in a refrigerator overnight. The process was repeated until the filtrate gave a negative test with Mayer's reagent.[7] The crystals were then washed with water until the filtrate gave a negative test with silver nitrate. The residue was dried in a vacuum desiccator over phosphorus pentoxide. The *d*-acid was recrystallized from benzene and petroleum ether (b. p. 30–60°). It formed white crystals, m. p. 137.5–138.5° (cor.). The yield was 1.02 g.

Rotation. 0.0625 g. made up to 2.0 ml. with absolute ethanol at 31° gave α_D +0.408°; *l*, 1; $[\alpha]^{31}D$ +13°.

Anal. Calcd. for $C_{13}H_{16}NO_3Cl$: C, 57.86; H, 5.98. Found: C, 57.97; H, 6.04.

The crude crops IV and V, 1.99 g. from the original crystallization of mixed salts, were combined and decomposed with 1:1 hydrochloric acid as described above. The *l*-acid was recrystallized from benzene and petroleum ether (b. p. 30–60°). It formed white crystals, m. p. 137.5–138°. The yield was 0.29 g.

Rotation. 0.0615 g. made up to 2.0 ml. with absolute ethanol at 31° gave α_D −0.409°; *l*, 1; $[\alpha]^{31}D$ −13°.

Racemization of *d*-N-Succinyl-1-methylamino-2,4-dimethyl-6-chlorobenzene.—The racemization was carried out using a 50-ml. flask connected to a reflux condenser by means of a ground glass joint. The sample was placed in a 20-ml. volumetric flask which was then filled to the mark with the solvent used. After thorough mixing the solution was transferred to a two-decimeter tube. The rotation was taken and the entire solution transferred to the flask. The flask was heated without reflux until the volume was approximately 15 ml. Heating was continued with reflux for an appropriate interval. The flask was then cooled in an ice-bath to the same temperature as before heating, and the contents transferred to the volumetric flask which was then filled to the mark. After observing the rotation, the entire cycle was repeated.

With *n*-butanol as a solvent, 0.23 g. of *d*-acid was thus racemized. The average rate constant was 1.05×10^{-2} min.$^{-1}$; half-life period, 33 min. ± 3 min. A check racemization in *n*-butanol gave a rate constant of 1.02×10^{-2} min.$^{-1}$; half-life period, 34 min. ± 4 min.

A solution of 0.22 g. of the *d*-acid was made up to 20 ml. of methyl acetate and racemized in the above manner. The average rate constant was 5.46×10^{-3} hr.$^{-1}$; half-life period, 63 hr. ± 20 hr.

1-Acetamido-2-methylbenzene.—The procedure was identical with that used for the acetylation of 1-amino-2,4-dimethylbenzene. From 107 g. of *o*-toluidine a white crystalline product was obtained which was recrystallized from ethanol. It formed white crystals, m. p. 109–110°. The yield was 135 g. (91%). Alt[8] reports m. p. 110°.

1-Acetamido-2-methyl-4,6-dichlorobenzene.—Direct chlorination in acid solution as previously described was again used. From 75 g. of the 1-acetamido-2-methylbenzene and 35.5 g. of chlorine 97 g. (89%) of the chlorinated product resulted which was recrystallized from ethanol.

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(7) Stephenson, "Some Microchemical Tests for Alkaloids," J. P. Lippincott, Philadelphia, Pa., 1921, p. 8.

(8) Alt, *Ann.*, **252**, 319 (1889).

It formed white crystals, m. p. 184–186°. Claus and Stapelberg[9] report m. p. 186°.

1-Amino-2-methyl-4,6-dichlorobenzene.—The hydrolysis of 1-acetamido-2-methyl-4,6-dichlorobenzene was carried out in 15% hydrochloric acid solution as previously detailed. The crude product obtained from the steam-distillation was dried over potassium hydroxide and distilled *in vacuo*, b. p. 109–110° (3 mm.). The distillate was then recrystallized from ethanol. From 97 g. of the amide, 22 g. of the primary amine (28%) was obtained as white crystals, m. p. 59°. Chattaway and Orton[10] report m. p. 59–60°.

1-Methylamino-2-methyl-4,6-dichlorobenzene.—The methylation of the primary amine was carried out under conditions similar to those for the preparation of the monochloro derivative. From 22 g. of primary amine, a yield of 8.5 g. (36%) was obtained; colorless liquid, b. p. 94–95° (1.5 mm.), n^{20}_D 1.5236, d^{20}_4 1.1528; M_D calcd. 49.8, found, 50.2.

Anal. Calcd. for $C_8H_9NCl_2$: C, 50.55; H, 4.77; N, 7.37. Found: C, 50.83; H, 4.99; N, 7.39.

N-Succinyl-1-methylamino-2-methyl-4,6-dichlorobenzene.—To a solution of 7.5 g. of 1-methylamino-2-methyl-4,6-dichlorobenzene in 75 ml. of dry benzene was added 5.9 g. of succinic anhydride and one drop of 85% phosphoric acid. The solution was refluxed for six hours and then worked up as previously described. The oily product crystallized on stirring. It was recrystallized from benzene and petroleum ether (b. p. 30–60°) and formed white crystals, m. p. 156–157°. The yield was 5.2 g. (46%).

Anal. Calcd. for $C_{12}H_{13}NO_3Cl_2$: C, 49.65; H, 4.48. Found: C, 50.08; H, 4.50.

Resolution of N-Succinyl-1-methylamino-2-methyl-4,6-dichlorobenzene.—A solution of 3.60 g. of N-succinyl-1-methylamino-2-methyl-4,6-dichlorobenzene and 3.64 g. of cinchonidine in 60 ml. of a mixture of 9:1 ethyl acetate and methanol by volume was filtered and placed in a refrigerator overnight. Crystals weighing 2.70 g. were collected. The mother liquor was taken down by means of a current of air and replaced in the refrigerator. Succeeding fractions were obtained as shown in the following table. The specific rotation readings were taken by making 0.10 g. of the salt up to 20 ml. with absolute ethanol and observing in a one-decimeter tube.

Crop	Wt., g.	α_D at 31°	$[\alpha]^{31}_D$	Vol. in ml.
I	2.70	−0.318	−64	60
II	1.57	− .316	−63	40
III	1.30	− .326	−65	20
IV	0.33	− .327	−65	5
V	0.50			0

Crop I, containing 37% of the total amount present, was recrystallized from a 9:1 ethyl acetate and methanol mixture. The following results were obtained.

Crop	Wt., g.	α_D 31°	$[\alpha]^{31}_D$	Vol. in ml.
A	0.97	−0.330	−66	30
B	1.40	− .331	−66	10
C	0.21			0

Crops A and B, having identical rotations, were accepted as the pure less-soluble salt (*l*B*l*A). It formed white, feathery crystals, m. p. 160° (cor.).

Rotation. 0.10 g. made up to 20 ml. with absolute ethanol at 31° gave α_D −0.330; *l*, 1; $[\alpha]^{31}_D$ −66.2°.

Anal. Calcd. for $C_{12}H_{13}NO_3Cl_2 \cdot C_{19}H_{11}N_2O$: C, 63.69; H, 6.01. Found: C, 62.97; H, 6.26.

***d*- and *l*-N-Succinyl-1-methylamino-2-methyl-4,6-dichlorobenzene.**—The pure less-soluble salt, crops A and B, weighing 2.25 g., was decomposed in the usual way with 1:1 hydrochloric acid with the following improvement. After the decomposed salt turned from an oil to a crystalline mass, it was transferred to a sintered glass funnel. All washings were carried out in the funnel without removing the crystals. When the filtrate had given a negative Mayer's test and a negative chloride ion test, it was dried in a vacuum over phosphorus pentoxide. It formed white crystals, m. p. 157–158° (cor.). The yield was 1.03 g.

Rotation. 0.1110 g. made up to 2.0 ml. with absolute ethanol at 31° gave α_D −0.193°; *l*, 1; $[\alpha]^{31}_D$ −3°.

Anal. Calcd. for $C_{12}H_{13}NO_3Cl_2$: C, 49.65; H, 4.48. Found: C, 49.23; H, 4.91.

The more-soluble salt, crops III and IV, 1.43 g., which was decomposed in the usual manner produced white crystals, m. p. 157–158°. The yield was 0.54 g.

Rotation. 0.1140 g. made up to 2.0 ml. with absolute ethanol at 31° gave α_D +0.196°; *l*, 1; $[\alpha]^{31}_D$ +3°.

Racemization of 1-N-Succinyl-1-methylamino-2-methyl-4,6-dichlorobenzene.—In a test run the *l*-acid was completely racemized in thirty minutes in boiling *n*-butanol.

A solution of 0.465 g. of the *l*-acid in 20 ml. of methyl acetate was racemized in the usual way. The average rate constant was 2.01 × 10^{-2} hr.$^{-1}$; half-life period, 17 hr. ± 4 hr. A check racemization in methyl acetate resulted in an average rate constant of 1.78 × 10^{-2} hr.$^{-1}$; half-life period, 19 hr. ± 4 hr.

Summary

1. N-Succinyl-1-methylamino-2,4-dimethyl-6-chlorobenzene and N-succinyl-1-methylamino-2-methyl-4,6-dichlorobenzene have been prepared, resolved and the half-lives of the optically active forms determined.

2. The half-life of the monochloro compound was thirty-four minutes in boiling butanol and sixty-three hours in boiling methyl acetate. The dichloro compound racemized completely in thirty minutes in boiling butanol and had a half-life of eighteen hours in boiling methyl acetate.

3. Thus, further evidence is presented to substantiate the fact that the basicity of the amine has an important influence upon the optical stability of hindered amines with electronegative substituents.

Urbana, Illinois Received September 30, 1949

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(9) Claus and Stapelberg, *Ann.*, **274**, 292 (1893).

(10) Chattaway and Orton, *J. Chem. Soc.*, **77**, 791 (1900).