potassium hydroxide in aqueous dioxane can be used successfully.

Certain aromatic *N*-chloroimines yield amides by a Beckmann rearrangement.[7] We were unsuccessful in attempts to obtain ϵ-caprolactam by treatment of *N*-chlorocyclohexanimine with such reagents as sulfuric acid, boron trifluoride, stannic chloride, and antimony pentachloride. Only cyclohexanone was isolated from the complexes after hydrolysis.

We have found that 2-aminocyclohexanone hydrochloride[3a] can be readily converted to 2-aminocyclohexanone oxime hydrochloride. A Beckmann rearrangement of this oxime should give either 2-oxo-7-aminohexamethylenimine or 2-oxo-3-aminohexamethylenimine. The latter could presumably be hydrolyzed to lysine. Paper chromatographic analysis of the products of an attempted Beckmann rearrangement of the oxime showed no ninhydrin-positive compounds, indicating that 2-oxo-7-aminohexamethylenimine was probably formed and was hydrolyzed to the *gem*-diamino derivative which would be expected to lose ammonia and be hydrolyzed to adipaldehydic acid. The presence of ammonia was noted during addition of base to the acid treated oxime. This direction of ring opening parallels the results of McLaren and Ungnade with 2-alkylcyclohexanone oximes.[8]

EXPERIMENTAL

Preparation of N-chloroimines. (a) *Triethylamine method.* To a solution of triethylamine in a solvent such as dry hexane or benzene was added an equimolar amount of the *N,N*-dichloroamine. The solution was stirred at room temperature for a short time and then at reflux temperature for 1–3 hr. The amine salt was filtered off and the filtrate was distilled at reduced pressure.

(b) *Potassium hydroxide method.* To a solution of potassium hydroxide in aqueous dioxane (0.1 mole per 120 cc. of water and 200 cc. of dioxane) was added an equimolar amount of the *N,N*-dichloroamine with vigorous stirring, maintaining the temperature below 35° during the addition and during a subsequent 15–30 min. reaction period. The solution was saturated with ammonium chloride and extracted thoroughly with ether. The combined extracts were dried and distilled from a water bath at reduced pressure.

N-Chlorocyclohexanimine. This compound was prepared in 52% yields by method (a) and 30% yields by method (b). It had b.p. 33–35°/1 mm., n_D^{25} 1.5053.

Anal. Calcd. for $C_6H_{10}ClN$: C, 54.76; H, 7.66; Cl, 26.95. Found: C, 54.09; H, 7.45; Cl, 26.42.

Its infrared absorption spectrum was consistent with an *N*-chloroimine structure and it could be hydrolyzed to cyclohexanone, identified as its 2,4-dinitrophenylhydrazone.

N-Chloroisopropylidenimine. This compound was prepared in 40% yields by method (a). It had b.p. 54–55°/100 mm.

Anal. Calcd. for C_3H_6ClN: C, 39.46; H, 6.61; Cl, 38.74; N, 15.31. Found: C, 39.59; H, 6.82; Cl, 38.41; N, 15.41.

Hydrolysis with dilute acid gave acetone, identified as its 2,4-dinitrophenylhydrazone.

2-Aminocyclohexanone oxime hydrochloride. 2-Aminocyclohexanone hydrochloride[3a] (9 g., 0.06 mole) in 15 cc. of water was added to 4.9 g. (0.07 mole) of hydroxylamine hydrochloride and 3.2 g. (0.03 mole) of sodium carbonate in 10 cc. of water. The solution was warmed on the steam bath 1.5 hr., cooled in ice, and filtered. The filtrate was concentrated and filtered again. The total solids were dissolved in methanol, treated with activated charcoal and filtered. Ether was added to the filtrate to precipitate the 2-aminocyclohexanone oxime hydrochloride, 7.1 g. A second crop of crystals was obtained by concentrating the mother liquor and adding ether. Total yield 7.9 g., 80%. An analytical sample was obtained by recrystallization from methanol-ether mixtures. It melted at 225° dec. Its infrared spectrum was consistent with an oxime structure.

Anal. Calcd. for $C_6H_{13}ClN_2O$: C, 43.75; H, 7.95; N, 17.01. Found: C, 43.94; H, 7.96; N, 17.16.

Beckmann rearrangement of 2-aminocyclohexanone oxime hydrochloride. One gram of the oxime was dissolved in 1 cc. of sulfuric acid containing one drop of water. After hydrogen chloride evolution ceased, the solution was heated to 120° for 2 min., cooled, diluted with 9 cc. of water, let stand several hours. Lysine hydrochloride (0.1 g.) was treated in the same way, as a control. The solutions were treated with saturated barium hydroxide solution at 80° to *p*H 10 ("pHydrion" test paper) and centrifuged. The *p*H was adjusted to 5 with dilute sulfuric acid and the solutions were chromatographed on Whatman No. 1 filter paper with a phenol solvent.[9] The chromatograms were dried, sprayed with ninhydrin solution, and developed in an oven at 35° for 1 hr. A well defined spot appeared for the lysine control but no spot appeared for the oxime rearrangement product.

In another experiment after the oxime had been heated with acid and diluted with water, cold potassium hydroxide solution was added until the solution was strongly basic. Ammonia was evolved as evidenced by its odor and reaction with moist indicator paper held above the solution.

RESEARCH AND ENGINEERING DIVISION
MONSANTO CHEMICAL CO.
DAYTON 7, OHIO

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[6] *N*-Chlorocyclohexanimine was subsequently prepared independently by W. S. Knowles and G. Alt, *J. Org. Chem.*, **25**, 2047 (1960), and shown to be an intermediate in the transformation of *N,N*-dichlorocyclohexylamine to 2-aminocyclohexanone.

[7] W. Theilacker and H. Mohl, *Ann. der Chem.*, **563**, 99 (1949).

[8] A. D. McLaren and H. E. Ungnade, *J. Org. Chem.*, **10**, 29 (1945).

[9] R. J. Block, R. Le Strange, and G. Zweig, *Paper Chromatography*, N. Y. Academic Press, 1952, p. 53.

The Identity of Nottbohm's "C_6H_6O" with Sorbanilide

MORDECAI B. RUBIN AND M. F. HOOVER

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In 1916 Nottbohm[1] reported a synthesis of dienoic acids by the sequence illustrated. The intermediate anilide dianilium sulfonates (II. a,b,c) were obtained in good yield as crystalline solids. Refluxing these with hydrochloric acid followed by refluxing with concentrated sodium hydroxide solution and acidification afforded the dienoic acids in good yield. However, if IIa or IIb were refluxed with concentrated sodium hydroxide

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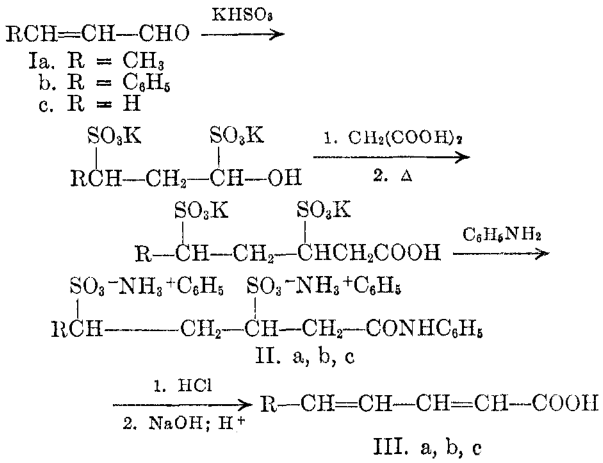
[1] O. Nottbohm, *Ann.*, **412**, 49 (1916).

omitting the hydrochloric acid treatment, crystalline solids were obtained upon dilution with water. Thus, for example, crotonaldehyde (Ia) led to the formation of a substance, m.p. 155–156°, which gave negative qualitative tests for sulfur and nitrogen and possessed an elementary analysis corresponding to the empirical formula C_6H_6O.



$$\mathrm{RCH{=}CH{-}CHO} \xrightarrow{\mathrm{KHSO_3}}$$

Ia. $R = CH_3$
b. $R = C_6H_5$
c. $R = H$

$$\mathrm{R\overset{SO_3K}{\overset{|}{C}}H{-}CH_2{-}\overset{SO_3K}{\overset{|}{C}}H{-}OH} \xrightarrow[2.\ \Delta]{1.\ \mathrm{CH_2(COOH)_2}} \mathrm{R{-}\overset{SO_3K}{\overset{|}{C}}H{-}CH_2{-}\overset{SO_3K}{\overset{|}{C}}HCH_2COOH} \xrightarrow{\mathrm{C_6H_5NH_2}}$$

$$\mathrm{R\overset{SO_3{}^-NH_3{}^+C_6H_5}{\overset{|}{C}}H{-}CH_2{-}\overset{SO_3{}^-NH_3{}^+C_6H_5}{\overset{|}{C}}H{-}CH_2{-}CONHC_6H_5}$$

II. a, b, c

$$\xrightarrow[2.\ \mathrm{NaOH;\ H^+}]{1.\ \mathrm{HCl}} \mathrm{R{-}CH{=}CH{-}CH{=}CH{-}COOH}$$

III. a, b, c

We have repeated this series of reactions starting with crotonaldehyde and obtained a substance with the same melting point and elementary analysis which gave at best doubtful qualitative tests for nitrogen. In view of (1) the difficulty of accommodating a transformation of IIa to $(C_6H_6O)_n$, (2) the similarity of the melting point with that reported for sorbanilide,[2] and (3) the very similar elemental analysis of C_6H_6O and sorbanilide ($C_{12}H_{13}NO$), we were led to compare the two substances in spite of the dubious tests for nitrogen. Mixture melting point and infrared spectral comparison with an authentic sample of sorbanilide[2] proved the identity of the two substances.

The explanation for the formation of sorbanilide presumably lies in the relative rates of elimination *vs.* amide hydrolysis and the fortuitous choice of reaction time by Nottbohm. Essentially all the material not converted to sorbanilide by refluxing IIa with sodium hydroxide solution was obtained as sorbic acid by acidification of the alkaline filtrate. Attempts to characterize the product formed from IIa with hydrochloric acid were not successful.

Nottbohm also reported formation of a substance, m.p. 188°, C_9H_8O, from cinnammaldehyde (Ib). This appears likely to be the unreported anilide of 5 - phenyl - 2,4 - pentadienoic acid. (*Anal.* Calcd. for $C_{17}H_{15}ON$: C, 81.9; H, 6.1; reported by Nottbohm[1]; C, 81.8, 81.7; H, 6.2, 6.1.)

CARNEGIE INSTITUTE OF TECHNOLOGY
SCHENLEY PARK
PITTSBURGH 13, PA.

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(2) O. Doebner and A. Wolf, *Ber.*, 34, 2221 (1901) report m.p. 154–156° for sorbanilide.

The Metalation of Diphenylferrocenylcarbinol[1]

ROBERT A. BENKESER, WALTER P. FITZGERALD, AND MARVIN S. MELZER

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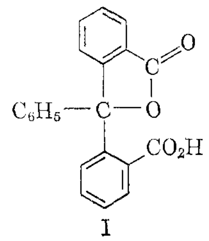
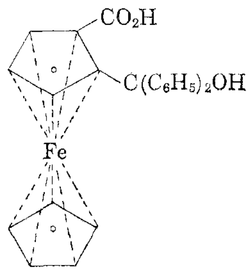
It is known that triphenylcarbinol can be metalated with *n*-butyllithium and then carbonated to form the lactone of triphenylcarbinol-2,2′-dicarboxylic acid[2] (I).

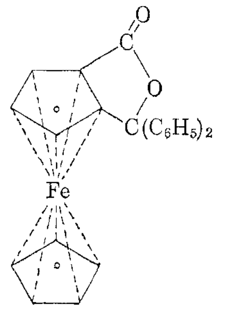


I

We are hereby reporting that a somewhat analogous reaction occurs with diphenylferrocenylcarbinol. Treatment of the latter compound with *n*-butyllithium, followed by carbonation with Dry Ice produced 2-carboxydiphenylferrocenylcarbinol (II) in 73% yield. When II was heated or treated with acid it readily converted to the lactone of 2-carboxydiphenylferrocenylcarbinol (III).



II



III

The structure of II was clearly indicated by its acidic nature and infrared spectrum which showed a strong carboxyl band at 5.95 μ and bands at 9 and 10 μ indicating an unsubstituted C_5 ferrocene ring. The ready conversion of II to III places the carboxyl group at the 2- rather than 3- position relative to the alcohol function.

The structure of III was clearly indicated by its elemental analysis, molecular weight and infrared spectrum. The latter showed unambiguous five-

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(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF 49(638)-297. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) (a) H. Gilman, G. E. Brown, F. J. Webb, and S. M Spatz, *J. Am. Chem. Soc.*, 62, 977 (1940); (b) H. Gilman and G. E. Brown, *J. Am. Chem. Soc.*, 62, 3208 (1940).