Anal. Calcd. for $C_{21}H_{32}Cl_2N_2$: N, 7.30. Found: N, 6.91.

4,4-Diphenyl-1-methylpiperidine (VI).—A mixture of 11 g. of 3,3-diphenyl-N,N,N′,N′-tetramethyl-1,5-pentanediamine dihydrochloride and 6 g. of 3,3-diphenyl-N,N,N′,N′-tetramethyl-1,5-pentanediamine was heated at 290–310° for 20 minutes. When the evolution of trimethylamine had ceased, the glassy solid was dissolved in water, the aqueous solution made basic with dilute sodium hydroxide solution and the oil extracted with ether. The ether extracts were dried, concentrated and the residue distilled; yield 6.3 g., b.p. 168–174° (2 mm.). After one recrystallization from petroleum ether, the solid melted over a range of 63–70°. The methiodide melted at 302–303° after one recrystallization from methanol–ether and did not depress the melting point of a sample of 4,4-diphenyl-1,1-dimethylpiperidinium iodide (m.p. 302–303°) prepared from IV.

1,5-Diethoxy-3,3-diphenylpentane (XI).—To a solution of potassium amide (10 g. of potassium) in 500 ml. of liquid ammonia, there was added 55.8 g. (0.23 mole) of II. After the reaction mixture had been stirred for 0.5 hour, 37 g. (0.24 mole) of β-bromoethyl ethyl ether was added and the mixture was stirred at room temperature until all of the ammonia had evaporated. The residue was decomposed with water, the oil extracted with ether and the ether extracts concentrated. The residue was dissolved in ethanol and upon dilution with water, a white solid crystallized; yield 53 g. (74.5%), m.p. 58–59°.

Anal. Calcd. for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.88; H, 8.50.

1,5-Diacetoxy-3,3-diphenylpentane (XIII).—A solution of 30 g. (0.096 mole) of XI and 250 ml. of glacial acetic acid containing 100 g. of anhydrous hydrogen bromide was refluxed for 48 hours. The acetic acid was removed *in vacuo*, the residual oil dissolved in ether and the ether layer washed with a cold 5% sodium bicarbonate solution. The ether extracts were dried over sodium sulfate, filtered, concentrated and the residue distilled; yield 17.7 g. (54%), b.p. 180–197° (1 mm.). The viscous oil solidified and after three recrystallizations from petroleum ether melted at 73–74°.

Anal. Calcd. for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 74.11; H, 6.68.

1,5-Dihydroxy-3,3-diphenylpentane (XIV).—A solution of 21 g. (0.062 mole) of XIII, 100 ml. of 50% sodium hydroxide and 150 ml. of 95% ethanol was refluxed for 20 hours. The ethanol was distilled off, the reaction mixture poured on ice and the solid filtered. After several recrystallizations from benzene–petroleum ether the white solid (12 g., 76%) melted at 108–109°.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.67; H, 7.86. Found: C, 79.28; H, 8.19.

Attempted Preparation of 1,5-Dichloro-3,3-diphenylpentane.—To a cold (0°) stirred solution of 10 g. (0.039 mole) of XIV in 150 ml. of dry pyridine, there was added slowly 15 g. of thionyl chloride. A precipitate formed and the mixture was stirred for two hours in an ice-bath and for an additional two hours at room temperature. The reaction mixture was poured on ice, acidified and a gum was obtained. The latter slowly crystallized and consisted chiefly of unreacted XIV (m.p. 105–109°). The experiment was repeated using dimethylaniline instead of pyridine, but only a tarry residue was obtained.

4,4-Diphenyltetrahydropyran (XII).—A solution of 15.5 g. (0.05 mole) of 1,5-diethoxy-3,3-diphenylpentane, 150 ml. of 48% hydrobromic acid and 75 ml. of glacial acetic acid was refluxed for 22 hours. The reaction mixture was cooled, poured on ice, the oil extracted with benzene, and the benzene extracts concentrated. The residual solid was crystallized from ethanol; yield 6 g. (51%), m.p. 85–86°.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.69; H, 7.61. Found: C, 85.55; H, 7.36.

N,N-Bis-(3,3-diphenylpropyl)-benzylamine.—To a solution of potassium amide (13.1 g. of potassium) in 800 ml. of liquid ammonia, there was added slowly 28 g. (0.168 mole) of diphenylmethane. The deep-red reaction mixture was stirred for one hour, followed by the addition of 39 g. (0.168 mole) of N,N-bis-(β-chloroethyl)-benzylamine.[6] After the addition of 500 ml. of anhydrous ether, the reaction mixture was allowed to stir overnight and was then decomposed with water. The ether layer was separated, dried, concentrated and distillation of the oil resulted in decomposition. The residue, when triturated with petroleum ether, gave 24 g. (58%) of a tan solid which melted at 102–103°, after three recrystallizations from ethanol.

Anal. Calcd. for $C_{37}H_{37}N$: N, 2.82. Found: N, 2.99.

Acknowledgment.—The authors wish to express their appreciation to Mr. Edwin Conner and his staff for the microanalyses reported in this paper.

BLOOMFIELD, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA]

The Hydrolysis of Some Cyanocinnamic Acids

BY HENRY RAPOPORT, ARTHUR R. WILLIAMS, ORVILLE G. LOWE AND WILLIAM W. SPOONCER

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The hydrolysis of 2-(2′-cyanophenyl)-cinnamic acid (I) has been shown to proceed through β-amino-β-[2-(2′-carboxyphenyl)]-phenylpropionic acid (IV) as the major path. The very slow elimination of ammonia from the latter compound is responsible for the slow ammonia evolution during the hydrolysis of I to 2-(2′-carboxyphenyl)-cinnamic acid (V).

During the course of work on the synthesis of dibenzocycloheptadiene,[1] conversion of 2-(2′-cyanophenyl)-cinnamic acid (I) to 2-(2′-carboxyphenyl)-cinnamic acid (V) was a projected step. It was finally accomplished by hydrolysis with potassium hydroxide in ethylene glycol at 200° for 48 hours. However, when boiling aqueous potassium hydroxide was used, conditions which had been eminently successful in hydrolyzing other nitriles in the synthetic sequence, only 50% of the theoretical quantity of ammonia had been evolved by the end of a two-week period. This unexpected result has been investigated, and the reaction path and intermediates have been found to provide a reasonable explanation for the extremely slow ammonia evolution.

A comparison of the rate of ammonia evolution from 2-(2′-cyanophenyl)-cinnamic acid (I) and a number of model compounds was sought first in order to indicate possibly the cause of this very slow hydrolysis of I. The compounds prepared and subjected to hydrolysis were *p*-cyanobenzoic acid and 2-(2′-cyanophenyl)-benzoic acid, to explore possible steric and electronic effects, and *p*-cyanocinnamic acid, to test the rather remote chance that ammonia, as liberated, was adding to the α,β-unsaturated acid portion. The hydrolyses were all carried out with boiling 1 *N* aqueous potassium

(1) H. Rapoport and A. R. Williams, THIS JOURNAL, **71**, 1774 (1949).

hydroxide in a stainless steel flask, using a nitrogen stream to remove continuously the liberated ammonia, and the results are shown in Fig. 1. There is a striking difference between the three model compounds,[2] from all of which over 90% of the theoretical amount of ammonia was evolved in 50 hours, and 2-(2′-cyanophenyl)-cinnamic acid, from which only 27% was realized.

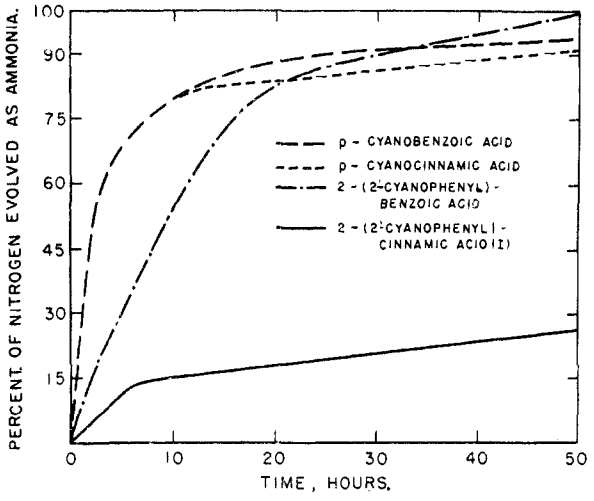


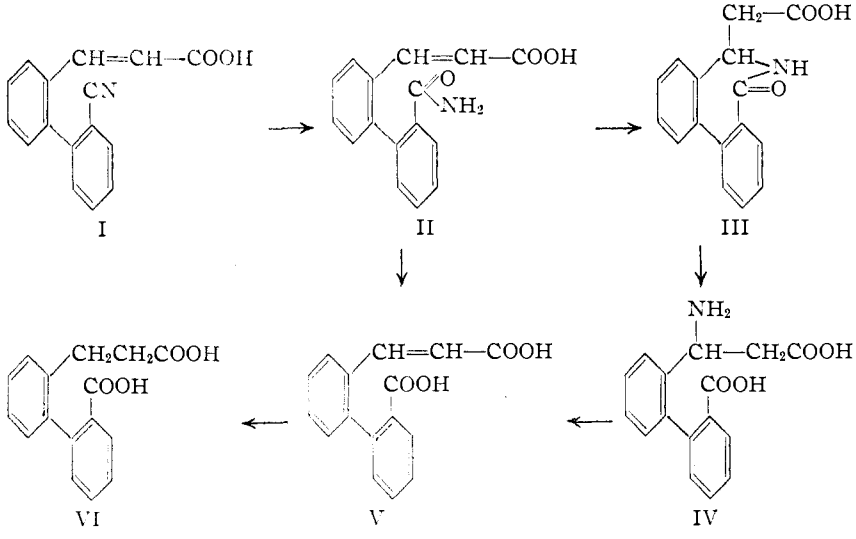
Fig. 1.—Evolution of ammonia from *p*-cyanobenzoic acid, *p*-cyanocinnamic acid, 2-(2′-cyanophenyl)-benzoic acid and 2-(2′-cyanophenyl)-cinnamic acid on heating under reflux in 1 *N* potassium hydroxide.

Since the cause for this extremely slow ammonia evolution appeared to be unique for 2-(2′-cyanophenyl)-cinnamic acid, an examination of its hydrolysis intermediates was undertaken. A sample of I was hydrolyzed until 30% of the theoretical ammonia had been evolved, and the hydrolysate was then hydrogenated. Hydrogen absorption indicated only 32% of the material still retained the olefinic double bond, and from the hydrogenated hydrolysate a 29% yield of β-[2-(2′-carboxyphenyl)]-phenylpropionic acid (VI) was isolated. This very close agreement among ammonia evolution (30%), hydrogen absorption (32%), and amount of VI isolated (29%) showed that that portion of starting cinnamic acid (I) which had not lost its nitrogen as ammonia now existed as saturated material, and the portion from which ammonia had been evolved existed as V in solution prior to hydrogenation.

As a working hypothesis, the path shown in the formula diagram was postulated to explain these observations. The first step is visualized as a rapid hydrolysis of I to the amide II, which then cyclizes by addition to the acrylic acid residue to give the lactam III, although a portion of amide II is being concurrently hydrolyzed to V and thus accounts for the initial rapid ammonia evolution of about 10%. Loss of ammonia now proceeds slowly by hydrolysis of the lactam III to amino acid IV, and the latter, a β-amino acid, slowly loses ammonia forming V. Either III → IV or IV → V might be the slowest step of the sequence.

This hypothesis seemed amenable to proof through isolation of the various postulated intermediates, which was then undertaken. An hydrolysis of I was allowed to proceed to 28% of ammonia evolution and from the hydrolysate the following compounds were obtained: carboxycinnamic acid V (26% yield); acid lactam III (22%), and amino acid IV, as its N-2,4-dinitrophenyl derivative (31%). The total yield (79%) and nature of the isolated products strongly supported the intermediates in the diagram as being the only ones involved in the hydrolysis. However, the existence of the acid lactam III in the hydrolysate to the extent actually found (22%) was open to question since it might have been formed from the amino acid IV during the isolation process.

To avoid this difficulty and differentiate acid lactam III from amino acid IV directly in the hydrolysate, recourse was made to the analysis of aliquots for total nitrogen (Dumas) and primary amino nitrogen (Van Slyke). In an experiment examined after 11% ammonia evolution, all the nitrogen remaining in the hydrolysate (theory, 89%; found, 85%) was as primary amino nitrogen (87%). The same was true for an hydrolysis analyzed after 41% ammonia evolution; the nitrogen remaining in the hydrolysate (theory, 59%; found, 59%) was all as primary amino nitrogen (59%). These data prove the presence of acid lactam III in the hydrolysate to the extent previously found (22%) was an artifact that arose during the isolation.



In the light of these observations, the hydrolysis of 2-(2′-cyanophenyl)-cinnamic acid (I) is best explained as proceeding to amide II, some of which is converted directly to diacid V, while the major portion forms acid lactam III. This in turn is hy-

(2) Similar results were obtained with β-[2-(2′-cyanophenyl)]-phenylpropionic acid.

drolyzed to amino acid IV. Reactions I → II, II → V, II → III, and III → IV are very rapid in comparison with the slow loss of ammonia from the amino acid IV to give the final product, diacid V.[3]

Experimental[4]

2-(2′-Cyanophenyl)-benzoic Acid.—Beckmann rearrangement of phenanthrenequinonemonoxime as previously described[1] gave 2-(2′-cyanophenyl)-benzoic acid, m.p. 170–172°.

2-(2′-Cyanophenyl)-cinnamic Acid (I).—The cinnamic acid, prepared as described[1] from the benzoic acid by conversion to acid chloride, Rosenmund reduction and condensation with malonic acid, melted at 224–225°.

***p*-Cyanobenzoic Acid.**—*p*-Cyanobenzoic acid was prepared from *p*-aminobenzoic acid using the method of Valby and Lucas[5] and melted at 220–221° (reported[5] m.p. 218.5–219°).

***p*-Cyanobenzaldehyde.**—A mixture of 10 g. (0.068 mole) of *p*-cyanobenzoic acid and 25 ml. of thionyl chloride was heated under reflux for one hour. Most of the thionyl chloride was distilled, then two separate 80-ml. portions of benzene were added and distilled. The residue was then distilled at reduced pressure and 9.7 g. (0.059 mole, 87%) of ***p*-cyanobenzoyl chloride**, b.p. 112–115° (4 mm.), was obtained. This material was reduced by the general procedure[6] using 2.7 g. of 5% palladium-on-barium sulfate, 0.13 ml. of sulfur–quinoline poison and 50 ml. of xylene. Hydrogen chloride evolution ceased after 94% of theory had been evolved in 2.5 hours, and the mixture was filtered through filter aid. Two portions of 20% sodium bisulfite solution (250 and 125 ml.) were used to extract the xylene, and the combined bisulfite solutions were washed with ether, treated with sodium carbonate until *p*H 8, and extracted thoroughly with five 200-ml. portions of benzene. After washing, drying and distilling the benzene, 4.8 g., 63%, of *p*-cyanobenzaldehyde was obtained as a crystalline residue, m.p. 95° with preliminary softening (reported m.p. 100°,[7] 95–96°[8]).

***p*-Cyanocinnamic Acid.**—A mixture of 4.8 g. (0.037 mole) of *p*-cyanobenzaldehyde, 5.7 g. (0.055 mole) of malonic acid, 30 ml. of dry pyridine and 0.6 ml. of piperidine was heated for one-half hour at 80°, two hours at 100° and boiled for one-half hour. It was then poured into 250 ml. of 3 *N* hydrochloric acid and the precipitated *p*-cyanocinnamic acid was removed by filtration and crystallized from ethanol; yield 5.3 g., 83%, m.p. 254–256° (reported m.p. 248–249°,[7] 254°[9]).

Standard Hydrolysis Procedure.—The hydrolyses were carried out in a 100 ml. cylindrical stainless steel flask with an efficient condenser and a nitrogen sweep. After adding approximately 1.25 millimoles of cyano acid and 25 ml. of 1.0 *N* potassium hydroxide, the solution was heated under reflux (bath temperature, 125°) and the evolved ammonia, continuously removed by the nitrogen sweep, was titrated[10] with 0.03 *N* hydrochloric acid.

Hydrolysis of 2-(2′-Cyanophenyl)-cinnamic Acid (I) **and Examination of Hydrolysis Products. A. By Hydrogenation.**—A solution of 5.0 g. (20 millimoles) of 2-(2′-cyanophenyl)-cinnamic acid (I) in 100 ml. of 1 *N* potassium hydroxide was heated under reflux in a steel flask, the evolved ammonia being removed with a nitrogen stream and titrated as described above. When the ammonia evolution had reached 6 millimoles (30%), the cooled solution was hydrogenated using 0.5 g. of 5% palladium-on-carbon as catalyst. Within 30 minutes, 6.4 millimoles (32%) of hydrogen was absorbed and absorption ceased completely. The solution was filtered, acidified, extracted with benzene, and the benzene extracts washed with carbonate solution. The yield of β-[2-(2′-carboxyphenyl)]-phenylpropionic (VI) obtained upon acidification of the carbonate washings was 1.57 g., 5.8 millimoles, 29%, m.p. 170–173° (reported[1] m.p. 171–173°).

B. By Isolation of Intermediates.—Hydrolysis of 3.6 g. (14.5 millimoles) of the cyanocinnamic acid (I) with 25 ml. of 2 *N* potassium hydroxide was carried out as above and discontinued after 4 millimoles, 28%, of ammonia had been evolved. Dilution of the solution to 600 ml. and acidification with 35 ml. of 2 *N* hydrochloric acid gave a precipitate which crystallized from methanol–water to yield 1.0 g. (3.7 millimoles, 26%) of 2-(2′-carboxyphenyl)-cinnamic acid (V), m.p. 224–225° (reported[1] m.p. 230–231°). The aqueous filtrate was neutralized with 10 ml. of 2 *N* potassium hydroxide and concentrated to 300 ml. under reduced pressure (water-pump), whereupon 350 mg. (1.3 millimoles, 9%) of the **acid lactam** (III) precipitated as a white powder, purified further by crystallization from water, m.p. 242–244°.

Anal. Calcd. for $C_{16}H_{13}O_3N$: C, 71.9; H, 4.9; N, 5.2; equiv. wt., 267. Found: C, 72.4; H, 5.0; N, 5.2; equiv. wt., 268.

The methyl ester of the lactam was prepared in the usual manner from methanol and sulfuric acid using a 5-hr. reflux period and was crystallized from methanol, m.p. 193–194°.

Anal. Calcd. for $C_{17}H_{15}O_3N$: C, 72.6; H, 5.4; N, 5.0; OCH_3, 11.0. Found: C, 72.4; H, 5.5; N, 5.2; OCH_3, 11.1.

The filtrate resulting after removal of the acid lactam was concentrated to 100 ml., acidified with 5 ml. of 2 *N* hydrochloric acid, and extracted with two 50-ml. portions of *n*-butyl alcohol. After washing the combined extract with two 50-ml. portions of water and concentrating to dryness with an air stream on the steam-bath, a residue was obtained which was crystallized from 300 ml. of water to give an additional 500 mg. (1.9 millimoles, 13%) of acid lactam (III). The aqueous mother liquors were concentrated to 20 ml., 2.1 g. of sodium bicarbonate and 1.5 g. of 2,4-dinitrobromobenzene in 20 ml. of ethanol was added, and the mixture was heated under reflux for four hours. Evaporation of the ethanol on the steam-bath, dilution with water to 100 ml., filtration from a small amount of insoluble material, and acidification with 12 *N* hydrochloric acid yielded 1.95 g. of the yellow **N-2,4-dinitrophenyl derivative of β-amino-β-[2-(2′-carboxyphenyl)]-phenylpropionic acid (IV)** which was crystallized from 20 ml. of methanol, m.p. 199–201°. When the combined aqueous layer and washings from the butanol extraction were evaporated to 6 ml. and treated with 2,4-dinitrobromobenzene as above, an additional 90 mg. of the amino acid was isolated as the N-2,4-dinitrophenyl derivative, bringing the total yield to 2.04 g., 4.5 millimoles, 31%.

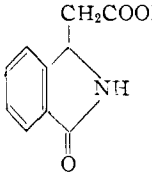
Anal. Calcd. for $C_{22}H_{17}O_8N_3$: C, 58.5; H, 3.8; N, 9.3; equiv. wt., 226. Found: C, 58.4; H, 3.7; N, 9.1; equiv. wt., 227.

The dimethyl ester of the N-2,4-dinitrophenyl derivative of the amino acid (IV) was prepared with methanol and sulfuric acid using a 3-hour reflux period, and was purified from methanol, m.p. 133–134°.

Anal. Calcd. for $C_{24}H_{21}O_8N_3$: C, 60.1; H, 4.4; N, 8.8; OCH_3, 13.0. Found: C, 60.2; H, 4.2; N, 9.1; OCH_3, 13.1.

C. By Primary Amino Group Analysis.—A 210-mg. (0.84 millimole) sample of the cyanocinnamic acid was hydrolyzed by the same procedure as used above in the standard hydrolysis determinations. After 0.09 millimole of the original nitrogen present had been evolved as ammonia, aliquots of the remaining solution were analyzed for total nitrogen (Dumas) and primary amino nitrogen (Van Slyke).[11]

(3) The same path undoubtedly obtains for the hydrolysis of *o*-cyanocinnamic acid, where we have found 12% ammonia evolution from the *cis*-acid and 9% from the *trans* in 100 hours. In these cases, the five-membered lactam ring in the intermediate 3-carboxymethylphthalimidine, is much more stable than the seven-membered ring in the lactam III, and hence was the only product isolated from short hydrolysis (10% sodium hydroxide for three hours) by F. M. Rowe, A. S. Haigh and A. T. Peters [*J. Chem. Soc.*, 1098 (1936)]. Extended times, or better, higher temperature would very likely yield *o*-carboxycinnamic acid.



(4) All melting points are corrected, and those above 200° were taken in evacuated capillaries; microanalyses were performed by the Microchemical Laboratory, University of California.

(5) E. P. Valby and H. J. Lucas, THIS JOURNAL, **51**, 2718 (1929).

(6) E. B. Hershberg and J. Cason, *Org. Syntheses*, **21**, 84 (1941).

(7) N. Moses, *Ber.*, **33**, 2623 (1900).

(8) H. B. Hass and M. L. Bender, THIS JOURNAL, **71**, 1767 (1949).

(9) C. W. Shoppee, *J. Chem. Soc.*, 968 (1930).

(10) T. S. Ma and G. Zuazaga, *Ind. Eng. Chem., Anal. Ed.*, **14**, 280 (1942).

(11) F. Pregl and J. Grant, "Quantitative Organic Microanalysis," The Blakiston Company, Philadelphia, Pa., 1946, p. 142.

The solution was found to contain 0.71 millimole of total nitrogen and 0.73 millimole of primary amino nitrogen. Thus, of the original nitrogen, 11% was evolved as ammonia, and all that remained in the hydrolysate (85%) was as primary amino nitrogen (87%).

A second sample of 200 mg. (0.80 millimole) of the cyanocinnamic acid (I) was treated in the same way. After 0.33 millimole, 41%, of the original nitrogen had been evolved as ammonia, the hydrolysate contained 0.47 millimole, 59%, total nitrogen and 0.47 millimole, 59%, primary amino nitrogen. The acid lactam (III) gave no primary amino nitrogen with the analytical procedure used.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, SHARP AND DOHME, INC.]

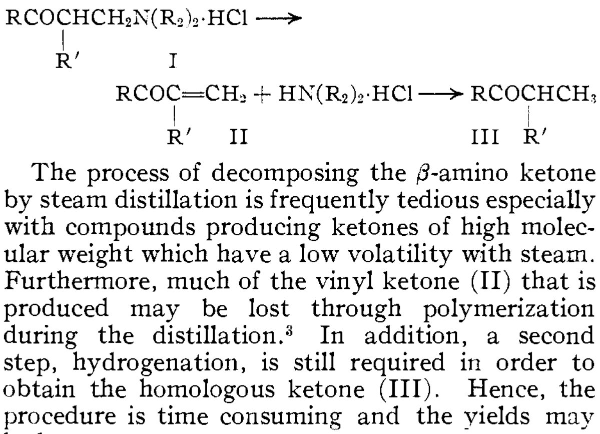
A Convenient Deamination of β-Dialkylamino Ketones

BY EVERETT M. SCHULTZ AND JOHN B. BICKING

RECEIVED OCTOBER 24, 1952

It has been found that β-*t*-amino ketone hydrochlorides of the type prepared by the Mannich reaction are deaminated by hydrogen over Raney nickel. The products are an amine and a ketone having the same carbon skeleton as the Mannich base.

As is well known, the hydrochloride of a Mannich base (I) may be decomposed into an unsaturated ketone (II) and an amine by steam distillation or dry distillation.[1,3] The reduction of the unsaturated ketone so obtained leads to the next higher homolog (III) of the ketone used in the Mannich reaction.[2,3] This procedure may be used in synthesis to lengthen the carbon chain of a ketone.[2] It is also useful to prove the structures of Mannich bases since from the structure of the homologous ketone, which usually is readily determined, the structure of the Mannich base can be deduced easily.



The process of decomposing the β-amino ketone by steam distillation is frequently tedious especially with compounds producing ketones of high molecular weight which have a low volatility with steam. Furthermore, much of the vinyl ketone (II) that is produced may be lost through polymerization during the distillation.[3] In addition, a second step, hydrogenation, is still required in order to obtain the homologous ketone (III). Hence, the procedure is time consuming and the yields may be low.

A simple, one-step method of degradation that provides a good yield of the homologous ketone (III) from a Mannich base has been found in this Laboratory. In this process, a solution or suspension of the hydrochloride of the amino ketone in absolute alcohol is submitted to hydrogenolysis over Raney nickel at a pressure of 60–100 atmospheres and a temperature of 80°. One mole of hydrogen per mole of amino ketone is absorbed at a moderate rate and then the consumption of hydrogen ceases. Of course, if the Mannich base contains an olefinic double bond (*e.g.*, M, Table I), additional hydrogen is required. The other product of the reaction, in addition to the homologous ketone (III), is the hydrochloride of the secondary amine used in the preparation of the Mannich base. The reaction mixture when freed of catalyst occasionally was colorless but usually was green due to dissolved nickel compounds. In any event, the color was removed readily in the subsequent purification. The ketones obtained were colorless, possessed very sharp boiling points and yielded derivatives that reached a maximum melting point after one recrystallization. Hence, the products were apparently very pure.

TABLE I

MANNICH BASES (I)

No.	Formula			
A[13]	$C_6H_5CHCOCH_3$ / $CH_2N(CH_3)_2\cdot HCl$			
	$C_6H_5C(R)(R_1)COCH(R_2)CH_2Am\cdot HCl$			
	R	R_1	R_2	Am
B	H	Methyl	H	Dimethylamino
C	H	Ethyl	H	Dimethylamino
D	H	*n*-Propyl	H	Dimethylamino
E	H	*n*-Propyl	H	1-Piperidyl
F	H	Isopropyl	H	Dimethylamino
G	H	Benzyl	H	Dimethylamino
H	H	Phenyl	H	Dimethylamino
I	H	Phenyl	Methyl	Dimethylamino
J	Benzyl	Phenyl	H	Dimethylamino
	$RCOCH_2CH_2Am\cdot HCl$			
	R			Am
K	Phenyl			Dimethylamino[1]
L	*m*-Hydroxyphenyl			Dimethylamino
M	Styryl			Diethylamino[12]
N	*p*-Methoxyphenyl			Dimethylamino[3]

Fourteen Mannich bases having a variety of structures (Table I) were submitted to the degradation and in all cases deamination occurred and a good yield of the homologous ketone (III) was obtained. The age of the Raney nickel catalyst employed or the use of catalyst from different preparations did not influence the result of the reaction. Therefore, the procedure appears to have general application.

The amino ketones used in this work are listed in Table I. The homologous ketones derived

(1) C. Mannich and G. Heilner, *Ber.*, **55**, 356 (1922).

(2) F. F. Blicke, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 322.

(3) C. Mannich and D. Lammering, *Ber.*, **55**, 3510 (1922).