ammonium polysulfide. The tube was heated electrically five hours at 165–170°, cooled and opened. The contents were washed into a beaker with concentrated ammonia and evaporated to dryness. The residue was leached with 20 ml. of boiling water and again evaporated to dryness. This residue was again leached with 5 ml. of boiling water and a third evaporation to dryness was made. After this final evaporation the beaker was allowed to stand on the steam-bath and the amide gradually sublimed on the walls of the container. Crystals were removed batchwise and collected. The product obtained in this manner had a satisfactory melting point.

By this technique there was obtained 120 mg. of *n*-butyramide, m.p. 116° (yield 10%), and 300 mg. of *n*-valeramide, m.p. 108° (yield 25%). This is the first reported production of *n*-butyramide from methyl ethyl ketone by the Willgerodt reaction and the product showed no melting point depression when mixed with an authentic sample of *n*-butyramide. The 25% yield of *n*-valeramide compares well with a yield of 31% previously reported.[3]

The reaction mixture from methyl amyl ketone was evaporated to dryness, then leached with 20 ml. of boiling water. After evaporation to half the volume, then cooling, the *n*-heptanamide crystallized. When recrystallized from hot water, it melted at 95–96°. The yield was 30% as compared with a previously reported 38%.[3]

Analytical Procedure.—The method of wet combustion of organic samples containing C-14 followed the technique of Steele and Sfortunato.[16]

When a relatively volatile liquid, *e.g.*, methyl ethyl ketone was assayed, the arm of the combustion tube containing the sample was chilled with liquid nitrogen during the evacuation process.

The technique involved in the Hofmann degradation of the aliphatic amides was the same as that described in a previous paper for phenylacetamide,[17] except that the molar proportions of amide, bromine and barium hydroxide, were changed from 1:2:3 to 1:1.1:3, to give a better yield of aliphatic amine. Propylamine was obtained in 60% yield and was combusted as the hydrochloride (m.p. 156°). Butylamine was obtained in about the same yield and was also oxidized as the hydrochloride (m.p. 193°). Hexylamine hydrochloride (70% yield) melted at 215°. The yields of carbon dioxide in the degradations of the aliphatic amides varied from 70–75%.

The definition of specific activity (Table I) is again[17] the number of counts per minute above background per square centimeter of an "infinitely thick" layer of barium carbonate. In a combustion, the number of counts is multiplied by the number of carbon atoms in the compound to correct for dilution by non-tagged carbon atoms, as was explained previously.

Acknowledgment.—Our thanks are expressed to Dr. R. W. Dodson for making available the facilities of the Chemistry Department at the Brookhaven National Laboratory.

UPTON, L. I., N. Y.

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[16] R. Steel and T. Sfortunato, "Techniques in the Use of C-14," Brookhaven National Laboratory Publication BNL-T-6, 1949.

[17] E. V. Brown, E. Cerwonka and R. C. Anderson, THIS JOURNAL **73**, 3735 (1951).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF FORDHAM UNIVERSITY AND BROOKHAVEN NATIONAL LABORATORY]

Studies in the Mechanism of the Willgerodt Reaction. III. Nature of the Labile Intermediate[1]

BY EDWARD CERWONKA,[2] R. CHRISTIAN ANDERSON[3] AND ELLIS V. BROWN

RECEIVED JULY 23, 1952

The nature of the labile intermediate participating in the Willgerodt reaction with phenyl *n*-butyl ketone has been investigated using deuterium as a tracer. δ-Phenylvaleramide, the reaction product from this ketone, was found to have retained only 5% of the deuterium which had originally replaced hydrogen on the beta carbon of the alkyl side chain. This evidence is interpreted as indicating that an unsaturated intermediate has been formed during the course of the Willgerodt reaction.

In the first paper[4] of this series experimental evidence was presented to show that no rearrangement of the carbon skeleton of acetophenone takes place in the Willgerodt reaction, either in the formation of phenylacetamide or of the ammonium phenylacetate by-product.

Once it had been established that the structure of the carbon skeleton of the starting compound remained unchanged during the course of the Willgerodt reaction, interest was focused on the possible manner by which the oxygen function could migrate to its terminal position on the alkyl chain. If the migration were stepwise, as was the feeling of most investigators, compounds intermediate between the starting ketone and final amide might exist as such and could be isolated. Due possibly to their extreme reactivity under the reaction conditions, these compounds have not yet been obtained.

Failing in the isolation of intermediates, the approach of several workers in this field has been to introduce possible intermediates into the reaction, instead of the usual starting compound, and to study the results. From the behavior of such "manufactured" intermediates deductions as to the mechanism of migration of the functional group have been made by Carmack and DeTar[5] and McMillan and King.[6]

Carmack and DeTar noted that unsaturated hydrocarbons, acetylenic or olefinic, give products of the same nature as ketones. Consequently, these authors believe that there must be one fundamental mechanism involving the preliminary formation of a labile intermediate which has an unsaturated C–C bond in the side chain.[5b] That this unsaturated carbon bond is largely acetylenic in character is suggested further by the relatively good yields of product obtained from straight chain ketones as compared with those obtained from the isomeric branched-chain compounds. Obviously, there can be no triply bonded intermediate in the case of the branched-chain ketone without loss of a carbon atom or chain at the point of branching.

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[1] Research carried out under the auspices of the U. S. Atomic Energy Commission.

[2] A.E.C. Predoctoral Fellow, 1949–1951.

[3] Brookhaven National Laboratory.

[4] E. V. Brown, E. Cerwonka and R. C. Anderson, THIS JOURNAL, **73**, 3735 (1951).

[5] (a) M. Carmack and D. F. DeTar, *ibid.*, **68**, 2029 (1946); (b) M. Carmack and M. A. Spielman, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, chap. 2.

[6] (a) J. A. King and F. H. McMillan, THIS JOURNAL, **68**, 632 (1946); (b) F. H. McMillan and J. A. King, *ibid.*, **70**, 4143 (1948).

The unsaturated C–C bond is pictured as being originally located adjacent to the carbonyl group of the ketone through enolization of the α-hydrogen. A shift of this bond in the direction of the terminal carbon is effected by virtue of the successive addition, elimination and re-addition of the elements of an unsymmetrical reagent. As to whether this reagent is specifically ammonia, amine, hydrogen sulfide or water, Carmack and DeTar are noncommittal. When the terminal carbon is reached, an irreversible oxidation by the action of sulfur produces a thioamide. If the Kindler modification is employed the thioamide is the product obtained and, in the standard Willgerodt procedure, the thioamide is converted to a carbonamide by the action of hot aqueous ammonia.[7]

McMillan and King also believe that an unsaturated, labile intermediate plays an important role in the mechanism of the Willgerodt reaction. They, however, are of the opinion[6a] that this intermediate is olefinic in nature and imply that an acetylenic starting compound is reduced to an olefin as a preliminary step. The main feature of the McMillan–King mechanism rests in its employment of hydrogen sulfide as the specific unsymmetrical reagent that brings about migration of the olefinic bond to a terminal position. Once this position is reached, the thioamide and carbonamide are successively formed.

A few experiments suggest that nitrogen could be one of the elements of the reagent which King and McMillan consider to be hydrogen sulfide. Kindler, for example, obtained thioamides by heating ketimines with sulfur.[8] Stanek was able to effect the Willgerodt transformation by heating oximes, hydrazones, phenylhydrazones and azines with sulfur.[9] A variety of opinions exists therefore both as to the constitution of the transforming reagent and as to the degree of unsaturation of the labile intermediate. In this paper we are concerned with the second of these questions.

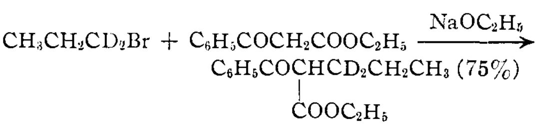
In a study of the nature of the labile intermediate of the Willgerodt reaction, we have not attempted to isolate a specific unsaturated compound but to find evidence of its existence using deuterium as a tracer. The principle may be made clear by its application to a hypothetical experiment involving the compounds just discussed, the consequences of deuterium exchange being neglected for the time being. If the Willgerodt reaction is carried out on phenyl ethyl ketone-α-d_2, $C_6H_5COCD_2CH_3$, in a protium medium, the product β-phenyl propionamide would be isolated as expected.[5a] Intermediates involved in forming this amide are the isomers, $C_6H_5CH{=}CDCH_3$ and $C_6H_5CH_2CD{=}CH_2$, according to the McMillan–King mechanism. Consequently 50% of the deuterium originally present on the ketone is present in the final product, $C_6H_5CH_2CHDCONH_2$. By the Carmack–DeTar argument this ketone proceeds by way of $C_6H_5C{\equiv}CCH_3$ and $C_6H_5CH_2C{\equiv}CH$ to form $C_6H_5CH_2CH_2CONH_2$, with loss of all the original deuterium to the excess reaction components.

Choice of Compound.—Unfortunately phenyl ethyl ketone-α-d_2 would be unsuitable for this experiment, since numerous studies in the literature[10–12] have shown that an enolic deuterium atom exchanges rapidly with hydrogen of the solvent as the result of an ionic equilibrium. One next considers the possibility of a Willgerodt reaction using phenyl propyl ketone-β-d_2, $C_6H_5COCH_2CD_2CH_3$, in which the deuterium is no longer alpha to the carbonyl group. In the product γ-phenylbutyramide, however, deuterium, if present, would be located alpha to the amide carbonyl ($C_6H_5CH_2CH_2CD_2CONH_2$) and exchange is again facilitated. Consequently, one is led to the choice of phenyl n-butyl ketone-β-d_2, $C_6H_5COCH_2CD_2CH_2CH_3$, in which molecule the deuterium is protected from exchange by its β-position. Deuterium, in this case, should also be protected from exchange if present in the Willgerodt transformation product, $C_6H_5CH_2CH_2CD_2CH_2CONH_2$.

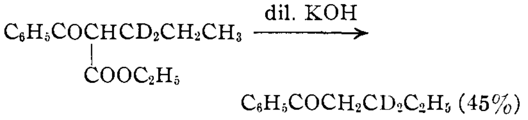
Method of Synthesis.—Phenyl n-butyl ketone was synthesized according to the series of reactions represented by equations (1) through (4). Actual yields obtained are shown in parentheses to the right of each equation.

$$(CH_3CH_2CO)_2O \xrightarrow{LiAlD_4} CH_3CH_2CD_2OH\ (40\%) \qquad (1)$$

$$CH_3CH_2CD_2OH \xrightarrow{PBr_3} CH_3CH_2CD_2Br\ (47\%) \qquad (2)$$



$$CH_3CH_2CD_2Br + C_6H_5COCH_2COOC_2H_5 \xrightarrow{NaOC_2H_5} C_6H_5CO\underset{\overset{|}{COOC_2H_5}}{CH}CD_2CH_2CH_3\ (75\%) \qquad (3)$$



$$C_6H_5CO\underset{\overset{|}{COOC_2H_5}}{CH}CD_2CH_2CH_3 \xrightarrow{\text{dil. KOH}} C_6H_5COCH_2CD_2C_2H_5\ (45\%) \qquad (4)$$

$$C_6H_5COCH_2CD_2C_2H_5 \xrightarrow[H_2O]{(NH_4)_2SS_x} C_6H_5CH_2CH_2C(?)_2CH_2CONH_2\ (5\%) \qquad (5)$$

It was expected that the reduction of propionic anhydride to propanol would show an over-all addition of two deuterium atoms to the carbonyl function[13] yielding theoretically the product $CH_3CH_2CD_2OH$. In this connection it is appropriate to mention that Westheimer and co-workers[14] have recently reported the preparation of deuterated ethanol, CH_3CD_2OH, by the reduction of phenyl acetate with lithium aluminum deuteride. Their product showed the expected two deuterium atoms per molecule.

The Willgerodt reaction was performed with the deuterated ketone according to the last of the above equations. Samples of alcohol, ketone and amide were assayed for deuterium using a procedure that included (1) combustion of the compound to deuterated water, (2) conversion of the heavy

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[7] A. Bernthsen, *Ann.*, **184**, 297 (1877).

[8] K. Kindler, *ibid.*, **431**, 193, 222 (1923).

[9] J. Stanek, *Collection Czechoslov. Chem. Communs.*, **12**, 671 (1947).

[10] S. K. Hsu, C. K. Ingold and C. L. Wilson, *J. Chem. Soc.*, 78 (1938).

[11] W. K. Walters and K. F. Bonhoeffer, *Z. physik. Chem.*, **A182**, 265 (1938).

[12] K. F. Bonhoeffer, *Trans. Faraday Soc.*, **34**, 242 (1938).

[13] (a) R. V. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 1197 (1947); (b) F. H. Hochstein, *ibid.*, **71**, 305 (1949).

[14] F. H. Westheimer, *et al.*, *ibid.*, **73**, 2403 (1951).

water sample to ethane by the action of diethylzinc, and (3) the assay of the ethane sample in a mass spectrometer. Data obtained are listed in Table I. The calculated figure of 1.88 atoms deuterium per molecule takes cognizance of the fact that the lithium aluminum deuteride had an isotopic purity of 94%.

TABLE I

Compound	Atoms deuterium per molecule	
	Expected	Found
$CH_3CH_2CD_2OH$	1.88	1.75, 1.78
$C_6H_5COCH_2CD_2CH_2CH_3$	1.88	1.78, 1.67
$C_6H_5CH_2CH_2C(?)_2CH_2CONH_2$	?	0.11, 0.08

Discussion

Application of the Carmack–DeTar mechanism to the Willgerodt reaction with phenyl *n*-butyl ketone-β-d_2 leads one to write the unsaturated intermediates, $C_6H_5CH_2C{\equiv}CC_2H_5$ and $C_6H_5CH_2CH_2C{\equiv}CCH_3$ which would give rise to the nondeuterated amide, $C_6H_5CH_2CH_2CH_2CH_2CONH_2$.

The King–McMillan scheme would include the olefinic compound $C_6H_5CH_2CH{=}CDC_2H_5$ (I), wherein half the deuterium originally present on the beta carbon is retained. If this structure adds H_2S in a non-Markownikoff manner the mercaptan, $C_6H_5CH_2CH_2CDSHC_2H_5$, results. This may eliminate H_2S to yield the olefin, $C_6H_5CH_2CH_2CD{=}CHCH_3$ (II), and subsequently an amide, $C_6H_5CH_2CH_2CDHCH_2CONH_2$, with an assay of about one deuterium atom per molecule.

If, on the other hand, structure (I) adds H_2S in a Markownikoff manner we obtain the mercaptan, $C_6H_5CH_2CHSHCDHC_2H_5$. Re-elimination of H_2S from the β,γ-position gives an olefin similar to (I) in which one-quarter of the ketone deuterium content is retained. Successive addition and elimination of H_2S at the β,γ-position will further reduce the deuterium assay of the mercaptan, which must eventually be transformed to an olefin such as (II) before an amide product is obtained. The expected assay of this amide may be 0.25, 0.125, 0.0625, etc., deuterium atom per molecule, depending on the number of additions and re-eliminations of H_2S at the β,γ-position.

If, as a third possibility, the labile intermediate participating in the transformation of phenyl *n*-butyl ketone-β-d_2 to δ-phenylvaleramide were saturated, we would expect an amide with a deuterium assay equal to that of the original ketone.

The data of Table I show that about 5% of the deuterium content of the ketone was retained by the amide. This result excludes the possibility of a saturated intermediate and can be more easily fitted into the Carmack–DeTar picture of the reaction mechanism by virtue of its shorter path as compared with the King–McMillan scheme. Since it is known that phenyl isobutyl ketone gives α-methyl-γ-phenylbutyramide[5a,6a] without loss of carbon, a completely acetylenic intermediate would not seem likely unless separate mechanisms are operating for straight and branched chain compounds.

It should be noted that another mechanism may be postulated in the future which might interpret the result of this experiment in a different manner.

Experimental

Preparation of *n*-Propanol-1-d_2 ($CH_3CH_2CD_2OH$).—Anhydrous propyl alcohol was required for conversion to the bromide. In view of the proximity of the boiling points of propyl alcohol and water, it was decided to use a synthesis which excluded water completely. This method was adapted from a synthesis of anhydrous methanol by Nystrom, Yanko and Brown.[15]

Distillation of reagents and solvents was carried out before beginning the preparation. Propionic anhydride and monobutyl carbitol were distilled *in vacuo*. Diethyl carbitol, 1500 ml., was distilled first from sodium, then from lithium aluminum hydride. When the distillation of diethyl carbitol was carried out at 4 mm., the stillhead temperature was 38°. At temperatures above 60° ether-splitting is said to occur by the action of both sodium and lithium aluminum hydride.[16]

Lithium aluminum deuteride (8.913 g., 0.212 mole) was converted into a fine slurry in one liter of anhydrous diethyl carbitol. To the suspension was added dropwise with stirring, 26.0 g. (0.20 mole) of propionic anhydride dissolved in an equal volume of anhydrous diethyl carbitol. The temperature was maintained below 50°, stirring was continued about six hours and the mixture was allowed to stand for an hour. At this time 240 g. of monobutyl carbitol was run into the reaction mixture. This effected the decomposition of excess hydride and the liberation of propanol by alcoholysis. The propyl alcohol was distilled over at a head temperature of 26° at 8 mm. pressure. When the temperature reached 42° only diethyl carbitol was being obtained. The distillate was collected in a trap chilled with liquid nitrogen. It was then fractionated and the yield of pure propanol-1-d_2, boiling range 96.0–97.5°, was 9.90 g., 40% based on propionic anhydride.

Preparation of *n*-Propyl Bromide-1-d_2 ($CH_3CH_2CD_2Br$).—This synthesis was patterned after one given in "Organic Syntheses"[17] for the preparation of isobutyl bromide from isobutyl alcohol. From 8.6 g. of anhydrous propanol-1-d_2 there was obtained 8.2 g. of *n*-propyl bromide-1-d_2 (47% yield).

Preparation of Phenyl *n*-Butyl Ketone-β-d_2 ($C_6H_5COCH_2CD_2C_2H_5$).—The method used was a modification of the procedure of Perkin and Calman.[18] Sodium (1.6 g., 0.070 mole) was added to 80 ml. of absolute ethanol. When all the sodium had dissolved, the flask was cooled to 0° and 13.73 g. (0.072 mole) of ethyl benzoylacetate was added with shaking. The mixture was allowed to stand an hour in the cold whereupon 8.2 g. (0.066 mole) of *n*-propyl bromide-1-d_2 was added and the mixture was refluxed for a period of four hours.

After the excess alcohol had been distilled, the oily residue was cooled, washed with water several times to remove sodium bromide and traces of alkali, dried with anhydrous sodium sulfate and distilled under reduced pressure. The product was collected over a boiling range of 113–119° at 2 mm. pressure. The mixture of ethyl α-benzoylvalerate-β-d_2 and unreacted ethyl benzoylacetate weighed about 13 g. Separation of the esters was not attempted as it was easier to fractionate the ketonic products of decarboxylation obtained in the next step.

The crude esters were added to an alcoholic potash solution prepared by dissolving 4.5 g. of potassium hydroxide in 120 ml. of ethanol and 60 ml. of water, the mixture was heated on the steam-bath six hours and, after cooling, the oily ketone layer was separated, dried and fractionally distilled under reduced pressure.

Acetophenone, resulting from decarboxylation of unreacted benzoylacetic ester, was distilled at 72–75°, while deuterated valerophenone, the desired product, distilled at 104–106°. The yield of pure product was 3.4 g., a yield of 33% based on *n*-propyl bromide.

The Willgerodt Reaction with Phenyl *n*-Butyl Ketone-β-d_2.—The reaction had previously been reported by Carmack

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[15] R. F. Nystrom, W. H. Yanko and W. G. Brown, THIS JOURNAL, **70**, 441 (1948).

[16] W. G. Brown, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, chap. 10.

[17] C. R. Noller, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 358–359.

[18] W. H. Perkin and A. Calman, *J. Chem. Soc., Trans.*, **49**, 160 (1886).

and DeTar to give δ-phenylvaleramide in 29% yield.[19] In an 8-inch Pyrex ignition tube were sealed 3.0 g. of sulfur, 1.0 g. of phenyl *n*-butyl ketone-*β*-d_2, 3.0 ml. of pyridine, 2.0 ml. of ammonium polysulfide and 5 ml. of 15 *M* ammonium hydroxide. The tube was heated five hours at 165–170°, cooled, and the contents washed into a beaker using concentrated ammonia. The mixture was evaporated to dryness on the steam-bath, the residue was ground and leached with 20 ml. of boiling water. Evaporation and subsequent recrystallization from hot water yielded 55 mg. of δ-phenylvaleramide, m.p. 104–105°.

Combustion of the Compounds.—The technique involved is fully described in a paper by Anderson, Delabarre and Bothner-By.[20]

Samples of the organic compounds, weighing between 5 and 10 milligrams, were combusted in oxygen at one atmosphere. The resultant gases were bled into a vacuum system where the water was condensed in a Dry Ice–acetone trap and the carbon dioxide in a liquid nitrogen trap, the oxygen carrier being pumped away. The water trap was designed to give a small internal surface area. The amount of carbon dioxide was determined manometrically, to ensure that complete combustion had taken place. To eliminate troublesome exchange of deuterated water with adsorbed water, three consecutive combustions were run, and the third water sample used in the conversion to ethane.

Conversion of Heavy Water to Ethane.—A detailed description of the apparatus and technique involved in the conversion of deuterated water to ethane is given by Friedman and Irsa.[21]

The synthesis of diethylzinc followed a method described in "Organic Syntheses" in which ethyl iodide and a copper-zinc couple were the starting materials.[22] The product was fractionated at ordinary pressure in a nitrogen atmosphere. It was transferred to a reservoir bulb on the vacuum manifold described by Friedman and Irsa[21] which permitted removal of the nitrogen and storage of the reagent *in vacuo*.

The procedure afforded quantitative conversion of a sample of deuterated water to pure ethane which was removed from the vacuum line in a gas sample bulb. The joint of this bulb fitted the mass spectrometer by means of which the deuterium assay was obtainable.

Mass Spectrometric Assay of Ethane.—The ethane was analyzed in a Consolidated–Nier model 21-201 mass spectrometer using the superposition method of analysis. The atom per cent. deuterium was calculated by this method from the relative ion intensities of the mass 30 and mass 31 peaks in the observed spectra. By multiplying the atom per cent. deuterium by the number of hydrogen atoms in the molecule one obtains the number of atoms of deuterium per molecule of organic compound.

Samples of the alcohol, ketone and amide, were combusted in duplicate. The deuterated water from each combustion was then converted to ethane. To aid in the calibration of the spectrometer a sample of "light" or distilled water, as well as a sample of "heavy" water (99.8% D_2O) was converted to ethane. From the atom per cent. deuterium in each sample the data presented in the table were obtained.

Acknowledgments.—We are indebted to several members of the Chemistry Department of Brookhaven National Laboratory: Dr. R. W. Dodson for making available the laboratory facilities, Dr. Aksel A. Bothner-By for valuable suggestions in the work, especially for the method of synthesis of the deuterated ketone, Miss Yvette Delabarre for the microcombustions of the deuterated compounds, and to Dr. Lewis Friedman and Mr. A. P. Irsa for the mass spectrometric assays.

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[19] D. F. DeTar and M. Carmack, THIS JOURNAL, **68**, 2025 (1946).

[20] R. C. Anderson, Y. Delabarre and A. A. Bothner-By, *Anal. Chem.*, **24**, 1298 (1952).

[21] L. Friedman and A. P. Irsa, *ibid.*, **24**, 876 (1952).

[22] Reference 17, pp. 184–187.

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

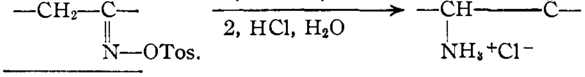
The Problem of the Unsaturated Three-membered Ring Containing Nitrogen

BY DONALD J. CRAM AND MELVIN J. HATCH

RECEIVED MARCH 26, 1952

The structure of the unstable intermediate isolated in the application of the Neber rearrangement to the 2,4-dinitrophenylacetoneoxime system has been further investigated. The structural evidence, both old and new, is most simply rationalized on the basis of formula (A). The ring has been opened at "a" by catalytic hydrogenation to give in the presence of acetic anhydride an acylated vinylamine, and in the absence of acylating reagent and in the presence of water, 2,4-dinitrophenylacetone. The double bond at "b" was reduced with lithium aluminum hydride to give an ethylenimine. These results coupled with the observation of Neber that the double bond at "b" undergoes solvolytic cleavage to give aminoketals or aminoketones suggest that the intermediate is an unsaturated three-membered heterocyclic ring. The position assigned to the double bond in the ring is supported by spectral data.

Although the synthesis of α-aminoketones from oximetosylates through the use of the Neber rearrangement was discovered over 25 years ago,[1a] this novel reaction has received little more than passing attention since the discoverer completed his original series of investigations.[1d] While attempting to determine the course of the rearrangement, in two cases Neber[1c,1d] succeeded in isolating unstable intermediates whose assigned structures (IIIA and IIIB) he considered to provide a satisfactory justification for the gross mechanism of the general reaction. The presumed substance, 2-(2,4-dinitrophenyl)-3-methyl-2-azirine (IIIA) was well characterized through analyses and molecular weight determinations. However, the suggestion that the unstable intermediates contain an azacyclopropene ring (azirine ring system)[2] warrants critical examination.[3]



$$\underset{\underset{\text{N—OTos.}}{\|}}{\text{—CH}_2\text{—C—}} \xrightarrow[\text{2, HCl, H}_2\text{O}]{\text{1, NaOEt, EtOH}} \underset{\underset{\text{NH}_3{}^+\text{Cl}^-}{|}}{\text{—CH}}\text{———}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—}$$

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[1] (a) P. W. Neber and A. Friedolsheim, *Ann.*, **449**, 109 (1926); (b) P. W. Neber, A. Burgard and W. Thier, *ibid.*, **526**, 277 (1936); (c) P. W. Neber and A. Burgard, *ibid.*, **493**, 281 (1932); (d) P. W. Neber and G. Huh, *ibid.*, **515**, 283 (1935).

[2] A. M. Patterson and L. T. Capell, "Ring Index," Reinhold Publishing Corp., New York, N. Y., 1940, p. 3.

[3] The widely recognized instability of ethylenimines [for references, see Elderfield, "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 61] coupled with the strain associated with three-membered rings containing double bonds [see M. J. Schlatter, THIS JOURNAL, **63**, 1734 (1941)] indicate that structures IIIA and IIIB should be accepted with reserve.