solid mixture. Resublimation of this material gave benzoic acid m.p. 115–120° which, after recrystallization from water, melted at 120–122° alone or when mixed with an authentic sample, and phthalic anhydride, m.p. 125–132°, the identity of which was also established by a mixture melting point and by comparison of infrared spectra.

Final confirmation of the structure of the hydrocarbon[7] was obtained by comparison of it with 2-phenylnaphthalene.

Identification of fraction 3 as 5,6,7,8-tetrahydro-2-aceto-naphthone. Small portions of a solution containing iodine (10 g.) and potassium iodide (20 g.) in water (100 ml.) were added to a mixture of 1.0 g. of fraction 3, (b.p. 151–153°, n_D^{25} 1.5517), described above, 5 ml. of 10% sodium hydroxide, and 20 ml. of dioxane, until a permanent color appeared. The mixture was diluted with water to 150 ml. The iodoform was separated by filtration and the filtrate was treated with two 20-ml. portions of ether. The aqueous solution was acidified to pH 2 with concentrated hydrochloric acid. After the excess free iodine had been reduced by the addition of sodium bisulfite, the product was separated from the solution by extraction with three 50-ml. portions of ether. The residue, after removal of the ether by distillation, was dissolved in 50 ml. of 10% aqueous sodium bicarbonate. The crude acid was collected after acidification of the basic solution with hydrochloric acid. Purification of the acid proved to be difficult. However, it was found that after the acid had been sublimed at 125°/0.5 mm., it could be recrystallized from petroleum ether B to give colorless

(7) A similar conclusion regarding the structure of this hydrocarbon was obtained by G. Maier, *Ber.*, **90**, 2949 (1957).

crystals melting at 151–152.5°. 5,6,7,8-Tetrahydro-2-naphthoic acid has been reported to melt at 153°.[4]

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.98; H, 6.87; neut. equiv. 176. Found: C, 75.30; H, 6.87; neut. equiv. 178.0, 178.7.

A mixture of 1.0 g. of this ketone, 5 ml. of 10% aqueous sodium hydroxide, 5.0 g. of potassium permanganate, and 75 ml. of water, was heated at the reflux temperature and stirred vigorously for 30 min. An additional 5.0 g. of permanganate was added during the next hour. After an additional 3 hr. of heating and stirring, the solution was acidified and sufficient sodium sulfite was added to reduce the manganese dioxide. The product was extracted with several portions of ether. After the ether had been removed by distillation, the product was recrystallized from a carbon tetrachloride–petroleum ether B mixture to give a colorless acid, m.p. 195–202° (dec.), neut. equiv. 71.7, which did not depress the melting point of benzene-1,2,4-tricarboxylic acid[5] but only depressed the melting point of benzene-1,2,3-tricarboxylic acid by 1°. Positive identification of this acid was attained by conversion to the anhydride by sublimation at 210°/1 mm. The product obtained did not depress the melting point of benzene-1,2,4-tricarboxylic acid anhydride, m.p. 165–167°.

Acetophenone. A sample of fraction 1, on treatment with 2,4-dinitrophenylhydrazine reagent, gave a 2,4-dinitrophenylhydrazone, m.p. 240–245° which did not depress the melting point of an authentic sample of benzophenone-2,4-dinitrophenylhydrazone, m.p. 243–246°.

Treatment of 0.5 g. of fraction 1 with sodium hypoiodite yielded 0.2 g. of an acid, m.p. 120–122°. A mixture of this acid and benzoic acid melted at 120–122°.

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Pyrolysis of Esters. XIII. Pyrolysis of Amides[1,2]

WILLIAM J. BAILEY AND CHARLES N. BIRD[3]

Amides have been shown to pyrolyze in a manner very similar to that of esters but at a higher temperature. Pyrolysis of *N*-(2-acetoxyethyl)-*N*-ethylacetamide produced cleavage at both the ester and the amide linkages to form *N*-ethylacetamide and vinyl acetate as well as acetic acid and *N*-vinyl-*N*-ethylacetamide. Cleavage of *N*-(1,3-dimethylbutyl)acetamide occurred at 590° to produce acetamide plus impure 4-methyl-1-pentene. Cleavage of the corresponding *N*-methyl dialkylated derivative occurred at 570° to produce *N*-methylacetamide plus a mixture of 4-methyl-1-pentene and 4-methyl-2-pentene. Similarly, cleavage of *N*-(1,3-dimethylbutyl)acetanilide occurred at 510° to produce a 91% yield of acetanilide and a 72% yield of a mixture of the two possible olefins. Pyrolysis of the *tert*-alkylamide, *N*-(1,1,3,3-tetramethylbutyl)-acetamide also occurred at 510° to produce acetamide and a mixture of two olefins.

It was shown in this laboratory that the pyrolysis of esters was an excellent method for the synthesis of strained dienes, such as 1,2-dimethylene-4-cyclohexene,[4] provided that charring was eliminated. Since the pyrolysis usually follows the Hofmann rule in direction of elimination, many interesting monomers and olefins can be prepared by this procedure.[5] Although the pyrolysis of esters

has been widely used, very little information is available concerning the pyrolysis of the nitrogen analogs, the amides. Primary amides are known to dehydrate when they are heated to produce good yields of the corresponding nitriles and, under slightly more vigorous conditions, to produce the corresponding imide plus ammonia and the carboxylic acid.[6] None of these reactions is, however,

(1) Previous paper in this series, *J. Org. Chem.*, **22**, 1189 (1957).

(2) Presented before the Division of Organic Chemistry at the 132nd National Meeting of the American Chemical Society, New York, N. Y., September 1957.
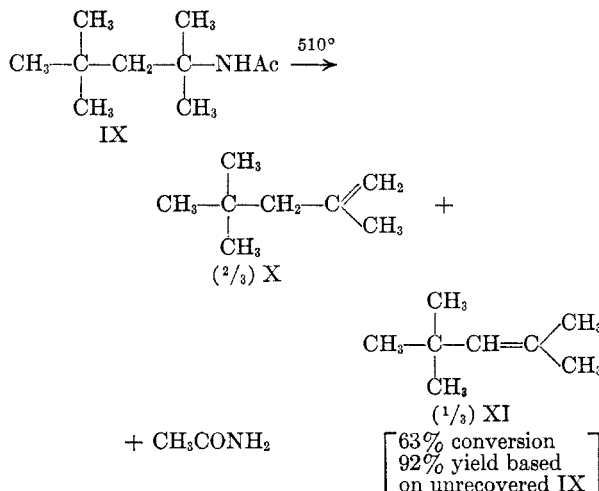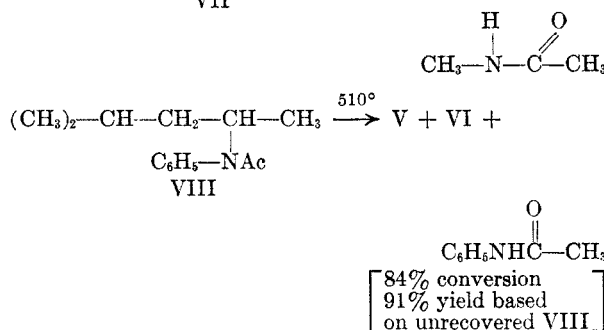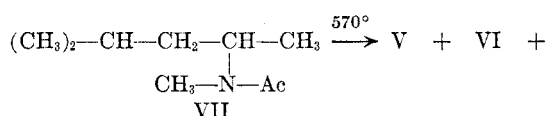
(3) Office of Naval Research Fellow, 1951–55.

(4) W. J. Bailey and J. Rosenberg, *J. Am. Chem. Soc.*, **77**, 73 (1955).

(5) (a) W. J. Bailey and C. King, *J. Am. Chem. Soc.*, **77**, 75 (1955); (b) W. J. Bailey, J. J. Hewitt, and C. King, *J. Am. Chem. Soc.*, **77**, 357 (1955); (c) W. J. Bailey, J. J. Hewitt, and F. A. Naylor, *J. Org. Chem.*, **22**, 1076 (1957).

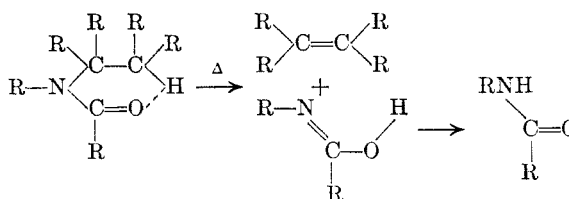(6) (a) R. S. Boehner and C. E. Andrews, *J. Am. Chem. Soc.*, **38**, 2503 (1916); (b) R. S. Boehner and A. L. Ward, *J. Am. Chem. Soc.*, **38**, 2505 (1916); (c) D. Davidson and M. Karten, *J. Am. Chem. Soc.*, **78**, 1066 (1956).

analogous to the decomposition of an ester to an olefin and an acid. An analogous reaction is possible only with an N-alkylamide.

Patents have been issued[7,8] covering the synthesis of N-vinylamides by the pyrolysis of acetates of the corresponding amides and cyclic imides. Hexaacetylstreptamine[9] has been pyrolyzed to a mixture of 2,4-diacetimidophenol and 5-acetamido-2-methylbenzoxazole. Burns, Jones, and Ritchie[10] pyrolyzed N-acetyl-α-acetoxyisobutyramide to methacrylonitrile and Hagemeyer[11] pyrolyzed α-acetoxypropionamide to acrylonitrile.

$$CH_3-\overset{\overset{O}{\|}}{C}-O-CH=CH_2 + H\underset{\underset{Et}{|}}{N}-\overset{\overset{O}{\|}}{C}-CH_3 \underset{41\%}{\overset{490°}{\longleftarrow}}$$

III

$$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-\underset{\underset{Et}{|}}{N}-\overset{\overset{O}{\|}}{C}-CH_3 \underset{57\%}{\overset{465°}{\longrightarrow}}$$

I

$$CH_2=CH-\underset{\underset{Et}{|}}{N}-\overset{\overset{O}{\|}}{C}-CH_3 + HOAc$$

II

$$(CH_3)_2-CH-CH_2-\underset{\underset{NHAc}{|}}{CH}-CH_3 \overset{590°}{\longrightarrow}$$

IV

$$(CH_3)_2-CH-CH_2-CH=CH_2 +$$

V

$$(CH_3)_2-CH-CH=CH-CH_3$$

VI

$$+ CH_3CONH_2 \qquad \begin{bmatrix} 50\% \text{ conversion} \\ 68\% \text{ yield based} \\ \text{on unrecovered IV} \end{bmatrix}$$

$$(CH_3)_2-CH-CH_2-\underset{\underset{\underset{VII}{CH_3-N-Ac}}{|}}{CH}-CH_3 \overset{570°}{\longrightarrow} V + VI +$$

$$CH_3-\underset{\underset{H}{|}}{N}-\overset{\overset{O}{/\!/}}{C}-CH_3$$

$$(CH_3)_2-CH-CH_2-\underset{\underset{\underset{VIII}{C_6H_5-NAc}}{|}}{CH}-CH_3 \overset{510°}{\longrightarrow} V + VI +$$

$$C_6H_5NH\overset{\overset{O}{\|}}{C}-CH_3 \qquad \begin{bmatrix} 84\% \text{ conversion} \\ 91\% \text{ yield based} \\ \text{on unrecovered VIII} \end{bmatrix}$$

(7) W. E. Hanford and H. B. Stevenson, U. S. Patent 2,231,905 (1941).

(8) W. H. Coover and J. B. Dickey, U. S. Patent 2,585,-230 (1952).

(9) R. L. Peck, C. E. Hoffnine, Jr., E. W. Peel, R. P. Graber, F. W. Holly, R. Mozingo, and K. Folkers, J. Am. Chem. Soc., 68, 776 (1946).

(10) R. Burns, D. T. Jones, and P. D. Ritchie, J. Chem. Soc., 714 (1935).

(11) H. Hagemeyer, U. S. Patent 2,417,748 (1947).

$$\underset{IX}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-NHAc} \overset{510°}{\longrightarrow}$$

$$\underset{(^2/_3) X}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-C\overset{\nearrow CH_2}{\searrow CH_3}} +$$

$$\underset{(^1/_3) XI}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH=C\overset{\nearrow CH_3}{\searrow CH_3}}$$

$$+ CH_3CONH_2 \qquad \begin{bmatrix} 63\% \text{ conversion} \\ 92\% \text{ yield based} \\ \text{on unrecovered IX} \end{bmatrix}$$

For these reasons a series of N-substituted amides were prepared and pyrolyzed. The primary purpose of this study was to determine the relative ease of the pyrolysis of an amide compared to an ester under the controlled conditions developed in this laboratory. It was hoped that this information would shed some light on the exact mechanisms of the pyrolyses of amides and esters, which are believed to proceed through a transient six-membered intermediate. Although Hanford and Stevenson[7]

$$R-N\overset{\overset{R}{|}\overset{R}{|}}{\underset{\underset{R}{|}\overset{\overset{R}{|}}{}}{\overset{C-C}{\underset{C=O}{}}\overset{R}{\underset{H}{}}} \overset{\Delta}{\longrightarrow} \overset{R}{R}\!\!>\!\!C=C\!\!<\!\!\overset{R}{R} + R-N\overset{H}{\underset{\underset{R}{|}}{\overset{}{}}}\overset{C-O}{} \longrightarrow \overset{RNH}{\underset{R}{}}\!\!>\!\!C=O$$

had studied the pyrolysis of N-(β-acetoxyethyl)-amides, this problem was reinvestigated under a wider range of conditions. N-(2-Acetoxyethyl)-N-ethylacetamide (I) was prepared by the acetylation of N-ethylethanolamine in a 92% yield. Pyrolysis of this ester-amide I at 465° under conditions that produced very little, if any, charring liberated 63% of the theoretical amount of acetic acid. At the same time a 35% conversion (or 57% yield, based on unrecovered starting material) to N-vinyl-N-ethylacetamide (II) was realized. The structure of II was indicated by analysis and absorption of 1 mole of hydrogen upon catalytic hydrogenation. In contrast to the N-methyl and N-phenyl derivatives, II gave a solid polymer of low molecular weight, softening point 122°, when it was treated with boron trifluoride etherate at room temperature; however, the analysis of this polymer was invariably several per cent higher in carbon then expected from pure poly-N-vinyl-N-ethylacetamide.

In an effort to increase the conversion, the N-(2-acetoxyethyl)-N-ethylacetamide was pyrolyzed under more vigorous conditions at 490°. A rather surprising result was observed in this experiment. In addition to the expected N-vinyl-N-ethylacet-

amide (II), a 25% yield of vinyl acetate plus a 41% yield of N-ethylacetamide (III) were produced. The N-ethylacetamide (III) had the correct analysis and was converted to the known solid hydrochloride. Apparently under these more vigorous conditions the elimination reaction is not as selective, producing a variety of products. It does illustrate that an amide derived from a secondary amine can compete with an ester group (probably by a cyclic six-membered ring) in a thermal decomposition. Several other possible products, such as those resulting from the abstraction of a β-hydrogen on the ethyl group, probably were formed but they were not isolated.

Further study of other N-alkylamides was undertaken. Since a series of esters of methylisobutylcarbinol had been studied in order to determine their relative ease of pyrolysis,[12] it appeared that amides related to this series would afford the information necessary to compare the ease of pyrolysis of amides with that of esters.

For this reason N-(1,3-dimethylbutyl)acetamide (IV) was prepared from methyl isobutyl ketoxime by catalytic reduction, followed by acetylation. Pyrolysis of IV at 590° produced a 50% conversion to acetamide and a 13% conversion to a mixture of olefins.

Although there was surprisingly little charring at this high temperature, 15% of the material was lost as noncondensable gases during pyrolysis. Since 25% of the starting amide IV was recovered unchanged, the yield of acetamide, based on unrecovered IV, was 67% and the yield of the olefins was only 18%. The infrared absorption spectrum of the mixture of olefins plus refractive index data indicated that the mixture consisted of 4-methyl-1-pentene (V) plus both the cis- and trans-4-methyl-2-pentene (VI). Thus it appeared that the pyrolysis of an amide of a primary amine requires a temperature more than 100° higher than that of the corresponding ester.

It was of interest to determine the effect of replacing the hydrogen on the nitrogen with an alkyl or an aryl group. The secondary amine, N-(1,3-dimethylbutyl)-N-methylamine, was prepared in a 91% yield by the reductive alkylation of methylamine with methyl isobutyl ketone in the presence of a copper-chromite catalyst. Acetylation of this amine with acetic anhydride produced the desired N-(1,3-dimethylbutyl)-N-methylacetamide (VII) in an 87% yield. Pyrolysis of VII at 570° was accompanied by a small amount of charring, and 13% of the material was lost as noncondensable gases. Distillation of the pyrolyzate yielded a 27% conversion to a mixture of olefins and a 44% recovery of crude starting amide VII. Unfortunately, the boiling point of N-methylacetamide was so close to that of VII that quantitative recovery of the amides

was not accomplished. Infrared measurements as well as refractive index data on the mixture of olefins from the pyrolyzate indicated that the mixture consisted of 4-methyl-1-pentene (V) and 4-methyl-2-pentene (VI) in nearly equal amounts.

An aryl-substituted amide, N-(1,3-dimethylbutyl)acetanilide (VIII), was prepared in three steps from methyl isobutyl ketone in an over-all yield of 84%. Azeotropic distillation of the water formed by the reaction of aniline and methyl isobutyl ketone in the presence of zinc chloride gave a 90% yield of N-1,3-dimethylbutylideneaniline. Hydrogenation of the anil in the presence of a copper-chromite catalyst gave a 95% yield of the corresponding amine, which was acetylated in a 98% yield to give the desired N-(1,3-dimethylbutyl)-acetanilide (VIII). Pyrolysis of the solid VIII at 510° proceeded very smoothly with little or no charring. Distillation of the pyrolyzate gave a 67% conversion to a mixture of olefins and an 84% conversion to acetanilide. Since 8% of the starting amide VIII also was recovered, the yield of the acetanilide, based on unrecovered VIII, was 91% and the yield of the olefin mixture was 72%. Infrared measurements as well as refractive index data indicated that the mixture of olefins consisted of nearly equal amounts of 4-methyl-1-pentene (V) and 4-methyl-2-pentene (VI).

Since it was shown that tertiary esters decompose at a temperature at least 50° below the decomposition temperature of similar secondary esters,[5b] an amide derived from a primary amine attached to a tertiary carbon atom was studied. When N-(1,1,3,3-tetramethylbutyl)acetamide (IX) was pyrolyzed at 510°, very little charring occurred. Distillation of the pyrolyzate gave a 41% conversion to a mixture of olefins and a 63% conversion to acetamide. This formation of acetamide appears to be in marked contrast with the work of Ritter and Kalish[13a] who obtained acetonitrile, water, and diisobutylene by the liquid phase pyrolysis of IX. Cook, et al.,[13b] also obtained acetonitrile from the treatment of a series of N-substituted acetamides with phosphorus pentoxide. Since 32% of the starting amide IX was recovered unchanged, the yield of acetamide, based on unrecovered IX, was 92% and the yield of olefins was 60%. Infrared measurements plus refractive index data indicated that the olefin mixture consisted of approximately two thirds of 2,4,4-trimethyl-1-pentene (X) and one third of 2,4,4-trimethyl-2-pentene (XI).

It is extremely interesting that two of the classes of amides studied, the N-tert-alkylamide IX and the N-alkylanilide VIII, pyrolyzed as conveniently as many esters. The reaction is clean-cut enough in many cases to be of value for the synthesis of

(12) W. J. Bailey and J. J. Hewitt, J. Org. Chem., 21, 43 (1956).

(13) (a) J. J. Ritter and J. Kalish, J. Am. Chem. Soc., 70, 4048 (1948); (b) J. W. Cook, G. T. Dickson, D. Ellis, and J. D. Loudon, J. Chem. Soc., 1078 (1949).

olefins. In any event, these pyrolyses should be useful for the degradation of N-substituted amines and should compete successfully with the Hofmann exhaustive methylation procedure[14a] or the decomposition of the corresponding amine oxide.[14b] Certainly many of the amides are easier to prepare than the key intermediate in the other two degradative methods.

It can be concluded that amides probably decompose by a cyclic process similar to that proposed for esters although additional work is needed to prove this point.[15] The amides derived from primary amines on this basis would be expected to be more stable than the corresponding esters, since the formation of the enol of an amide requires more energy than the formation of the corresponding carboxylic acid. This effect is partially compensated by the fact that a carbon-nitrogen bond is weaker than a carbon-oxygen bond.[16] The introduction of a substituent on the nitrogen of the amide would be expected to increase the steric strain in the starting amide. Furthermore, any group that would stabilize the enol form might be expected to aid the pyrolysis. Finally, the fact that the N-tert-alkylamides decompose at a lower temperature than do the other related amides indicates the similarity between ester and amide pyrolyses.

It should be noted that amides are not as selective in the direction of elimination as originally reported for esters.[5] However, more recent work in this laboratory has shown that the pyrolysis of methylisobutylcarbinyl acetate at 500°, in contrast to earlier work, actually gave a mixture of olefins consisting of 45% 4-methyl-1-pentene (V), 11% cis-4-methyl-2-pentene and 44% trans-4-methyl-2-pentene (VI). Thus the composition of olefins from the pyrolysis of the amides agrees at least qualitatively with that from the ester pyrolysis.

Although the yields of the amides from all the pyrolyses are in general quite high, the yields of the olefinic products are reasonably high only for the pyrolyses conducted at the lower temperatures. The low yield of the olefins at the high temperatures can be easily rationalized. Recent work, which will be reported separately, has shown that olefins containing a gamma hydrogen are thermally unstable and presumably decompose by a cyclic mechanism. For example, 4-methyl-1-pentene (V) cleaves at 595° to give, as the major product, propylene in a 72% yield. Even more surprising is the fact that 2,4,4-trimethyl-1-pentene (X) will cleave at temperatures as low as 500° into two molecules of isobutylene.

The extension of this study to other amides, including cyclic amides, will be reported separately.

N-(2-Acetoxyethyl)-N-ethylacetamide (I). To 775 g. of acetic anhydride heated under reflux was added dropwise 178 g. (2.0 moles) of N-ethylethanolamine. After the mixture had been heated under reflux for 12 hr., the excess acetic anhydride and acetic acid were removed under reduced pressure, and the residue was fractionated through a 12-inch Vigreux column to yield 318 g. (92%) of N-(2-acetoxyethyl)-N-ethylacetamide (I), b.p. 84.2° (0.55 mm.), n_D^{25} 1.4500, d_{25}^4 1.0502.

Anal. Calcd. for $C_8H_{15}O_3N$: C, 55.47; H, 8.73; N, 8.08. Found: C, 55.68; H, 8.44; N, 8.10.

Pyrolysis of N-(2-acetoxyethyl)-N-ethylacetamide (I). *A. Formation of N-vinyl-N-ethylacetamide* (II) *at 465°*. At a rate of 1 g. per minute, 118 g. (0.68 mole) of N-(2-acetoxyethyl)-N-ethylacetamide (I) was dropped through a vertical Vycor tube packed with glass helices and externally heated at 465° as previously described.[12] A stream of oxygen-free nitrogen was introduced at the top of the tube throughout the pyrolysis. The pyrolyzate was condensed in a 6-inch spiral condenser and collected in a side-inlet flask cooled in a Dry Ice–chloroform bath. The pyrolyzate was distilled through a 12-inch, helix-packed column to produce 60 g. of an azeotrope [11% acetic acid and 89% N-vinyl-N-ethylacetamide (II)], b.p. 39.6° (3.7 mm.); 83° (40 mm.), a forerun of acetic acid, and 45 g. of recovered starting material. (Titration of aliquot portions of the pyrolyzate indicated that 63% of the theoretical amount of acetic acid had been liberated.) The azeotrope was dissolved in chloroform and this solution was extracted several times with a 25% potassium carbonate solution. The aqueous extracts were re-extracted with chloroform and the combined chloroform solutions were dried over anhydrous potassium carbonate. The solvent was removed under reduced pressure, and the residue was fractionated through a 6-inch, helix-packed column to yield 26.5 g. (35%) of N-vinyl-N-ethylacetamide (II), b.p. 63.2° (14 mm.), n_D^{25} 1.4732. The yield of II, based on unrecovered starting material, was 57%.

Anal. Calcd. for $C_6H_{11}NO$: C, 63.68; H, 9.80; N, 12.38. Found: C, 64.16; H, 9.64; N, 12.64.

Hydrogenation of 0.92 g. (0.0081 mole) of II in the presence of 0.1 g. of platinum oxide catalyst resulted in the absorption of 201 ml. (99%) of hydrogen in 30 min. at 24°. The vinylamide II also rapidly decolorized a solution of bromine in carbon tetrachloride.

B. Formation of vinyl acetate and N-ethylacetamide (III) *at 490°*. By the use of the same procedure described above, 70 g. (0.404 mole) of N-(2-acetoxyethyl)-N-ethylacetamide (I) was dropped through the pyrolysis tube at 490° over a period of 1 hr. The pyrolyzate was crudely fractionated through an 8-inch Vigreux column to remove all the material boiling below 126° (28 mm.). These fractions were refractionated through the same column to yield 8.7 g. (25%) of impure vinyl acetate, b.p. 75–77°, n_D^{25} 1.3720–1.3729 [reported[18] b.p. 71–72° (728 mm.)]. (Eastman Kodak vinyl acetate had n_D^{25} 1.3915.)

Continued fractionation of the low boiling fraction through the same column produced 14.3 g. (41%) of N-

(14) (a) A. W. Hofmann, *Ber.*, **14**, 494, 659 (1881); (b) A. C. Cope, T. T. Foster, and P. H. Towle, *J. Am. Chem. Soc.*, **71**, 3929 (1949).

(15) C. D. Hurd and F. H. Blunck, *J. Am. Chem. Soc.*, **60**, 2419 (1938).

(16) L. Pauling, *Nature of the Chemical Bond*, 2nd ed., Cornell University Press, Ithaca, N. Y., 1948, p. 53.

(18) A. Skrabal and A. Zahorka, *Monatsh.*, **48**, 459 (1927).

ethylacetamide (III), b.p. 48° (0.37 mm.), b.p. 206.5–207.5° (763 mm.), n_D^{25} 1.4306 (reported[19] b.p. 206°).

Anal. Calcd. for C_4H_9NO: C, 55.14; H, 10.41. Found: C, 55.41; H, 10.09.

This material did not decolorize a solution of bromine in carbon tetrachloride. Dry hydrogen chloride was bubbled through 4 to 5 drops of the liquid N-ethylacetamide (III) to produce a hygroscopic crystalline mass of N-ethylacetamide hydrochloride, m.p. 76–77.5° (measured in a stoppered test tube on a bulk sample) (reported[20] m.p. "about" 60°).

Pyrolysis of N-(1,3-dimethylbutyl)acetamide (IV). N-1,3-Dimethylbutylamine was prepared by the catalytic hydrogenation of methyl isobutyl ketoxime (Ames Laboratories, Inc., South Norwalk, Conn.) according to the method of Smith and Adkins.[21] Acetylation of the resulting amine with acetic anhydride, followed by fractionation of the reaction mixture through a 17-inch, helix-packed column, produced an 86% yield of N-(1,3-dimethylbutyl)acetamide (IV),[22] b.p. 71° (0.4 mm.), n_D^{25} 1.4380 [reported[21] b.p. 94–95° (1 mm.), n_D^{25} 1.4378].

At the rate of 1 g. per minute, 59 g. (0.412 mole) of N-(1,3-dimethylbutyl)acetamide (IV) was dropped through a vertical Vycor tube which was heated externally at 590° as described previously. Dry, oxygen-free nitrogen was passed through the tube at a rate of 60 bubbles per minute. The pyrolysis receiver was transferred directly to a distillation column and the material boiling below 75° (16 mm.) was removed quite rapidly to yield 10.82 g. of crude distillate. This material was refractionated through a 6-inch, helix-packed column to yield 4.7 g. of a low-boiling forerun, b.p. 25–46°, and 4.97 g. (14.3%) of a mixture of 4-methyl-1-pentene (V), and 4-methyl-2-pentene (VI), b.p. 46.5–50.0° (730 mm.), n_D^{25} 1.3800–1.3834 (reported[23] for V, b.p. 53.6–53.9°, n_D^{20} 1.3825; reported[24] for the isomeric 4-methyl-2-pentene (VI), b.p. 58.6–59.0°, n_D^{25} 1.3869).

The infrared absorption spectrum of the olefin obtained from the pyrolysis was compared with the spectra reported for 4-methyl-1-pentene (V),[25a] cis-4-methyl-2-pentene,[25b] and trans-4-methyl-2-pentene[25c] (VI). These data indicated that the olefin mixture was largely 4-methyl-1-pentene (V) but that both cis- and trans-4-methyl-2-pentene (VI) were present in substantial amounts.

The higher-boiling residues from the two distillations were fractionated through a 6-inch, helix-packed column to yield 15.0 g. (26% recovery) of unchanged N-(1,3-dimethylbutyl)acetamide (IV) and 12.1 g. (50%) of impure acetamide, b.p. 96–110°. Two recrystallizations of this acetamide from a 1:10 methanol-ether mixture produced pure material, m.p. 81.2–82.0° (reported[26] m.p. 82–83°). A mixed melting point determination of this sample with an authentic sample of acetamide showed no depression.

At 570° pyrolysis of IV gave a 20% yield of olefin and a 30% yield of acetamide.

N-(1,3-Dimethylbutyl)-N-methylamine. To a hydrogenation vessel which had been cooled to −22° were added 212 g. (2.12 moles) of methyl isobutyl ketone, 306 g. of absolute ethanol, 15.3 g. of copper-chromium oxide catalyst, and 103 ml. (2.5 moles) of anhydrous methylamine. At 180° and 170

atmospheres pressure the theoretical amount of hydrogen was absorbed. The catalyst was removed by filtration and the filtrate was fractionated through an 18-inch, helix-packed column to yield 221 g. (91%) of N-(1,3-dimethylbutyl)-N-methylamine, b.p. 62–63° (89 mm.), n_D^{25} 1.4080.

Anal. Calcd. for $C_7H_{17}N$: C, 73.04; H, 14.78. Found: C, 73.52; H, 14.46.

N-(1,3-Dimethylbutyl)-N-methylacetamide (VII). To a heated mixture of 215 g. (2.1 moles) of acetic anhydride and 126 g. (2.1 moles) of glacial acetic acid was added dropwise over a period of 1.5 hr., 121.5 g. (1.05 moles) of N-(1,3-dimethylbutyl)-N-methylamine. After the mixture had been heated at 100–110° for an additional 2 hr., the excess acetic anhydride was hydrolyzed with 35 ml. of water. After the excess acetic acid was removed by distillation under reduced pressure, the residue was dissolved in 750 ml. of ether. This solution was washed successively with three 100-ml. portions of 0.05N hydrochloric acid, three 100-ml. portions of a 15% sodium carbonate solution, and two 100-ml. portions of water. After the ether solution had been dried over magnesium sulfate, it was distilled through an 18-inch, helix-packed column to yield 144 g. (87%) of crude amide, b.p. 72.5° (2.4 mm.). Recrystallization from n-pentane at −22° produced 136 g. of pure liquid N-(1,3-dimethylbutyl)-N-methylacetamide (VII), n_D^{25} 1.4430.

Anal. Calcd. for $C_9H_{19}NO$: C, 68.74; H, 12.18, N, 8.91. Found: C, 68.97, H, 11.88, N, 9.16.

Pyrolysis of N-(1,3-dimethylbutyl)-N-methylacetamide (VII). At the rate of 1.2 g. per minute, 52.4 g. (0.33 mole) of N-(1,3-dimethylbutyl)-N-methylacetamide (VII) was dropped through the standard pyrolysis apparatus at 570°. The pyrolyzate (45.3 g.) was then flash-distilled under reduced pressure to yield 12.8 g. of crude olefin, b.p. 25–75° (100 mm.), n_D^{25} 1.3856. Refractionation of the crude olefin fraction through a 6-inch, helix-packed column produced 7.7 g. (27%) of a mixture of 4-methyl-2-pentene (VI) and 4-methyl-1-pentene (V), b.p. 48–58°, n_D^{25} 1.3853–1.3869. The infrared absorption spectrum indicated that there was slightly more than 50% of the isomeric 4-methyl-2-pentenes (VI) in the mixture.

The higher boiling residue from the pyrolyzate was fractionated through the same column to yield 23.3 g. of a mixture of the starting amide and N-methylacetamide, b.p. 63.6–72.2° (2.5 mm.), n_D^{25} 1.4364–1.4434 [reported[27] for N-methylacetamide, b.p. 140.5° (90 mm.), n_D^{25} 1.4301). No convenient method of quantitative separation of the N-methylacetamide and the starting amide VII was found.

Pyrolysis of N-(1,3-dimethylbutyl)-N-methylacetamide (VII) at 555° produced a 21% yield of a mixture of olefins, b.p. 46–57°, n_D^{25} 1.3840–1.3858.

N-(1,3-Dimethylbutylidene)aniline. In a 1-l., three-necked flask, fitted with a Dean-Stark trap, a condenser, and a drying tube, were placed 93 g. (1.0 mole) of freshly distilled aniline, 100 g. (1.0 mole) of methyl isobutyl ketone, 300 ml. of dry toluene, and 0.7 g. of pulverized anhydrous zinc chloride. After the mixture had been heated under reflux for 29 hr. and 16.7 ml. (92%) of water had been collected, the zinc chloride was removed by filtration. The solvent was removed by rapid distillation under reduced pressure, and the residue was distilled through an 18-inch, helix-packed column to yield 158 g. (90%) of N-(1,3-dimethylbutylidene)-aniline, b.p. 65° (0.9 mm.), n_D^{25} 1.5106 [reported[28] b.p. 107° (11 mm.) and no yield].

Anal. Calcd. for $C_{12}H_{17}N$: C, 82.23; H, 9.78. Found: C, 82.17; H, 9.54.

N-(1,3-Dimethylbutyl)aniline. In a 300-ml. hydrogenation vessel were placed 72 g. (0.41 mole) of N-(1,3-dimethylbutyl-idene) aniline, 72 ml. of absolute alcohol, and 3.6 g. of copper-chromium oxide catalyst and the contents were shaken at

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(20) A. W. Titherly, *J. Chem. Soc.*, 391 (1901).

(21) M. E. Smith and H. Adkins, *J. Am. Chem. Soc.*, **60**, 657 (1938).

(22) The authors are indebted to Dr. Robert Barclay, Jr., for the preparation of this compound.

(23) C. G. Schmitt and C. E. Boord, *J. Am. Chem. Soc.*, **54**, 754 (1932).

(24) S. P. Mulliken, R. L. Wakeman, and H. T. Gerry, *J. Am. Chem. Soc.*, **57**, 1605 (1935).

(25) (a) American Petroleum Institute Research Project 44, *Infrared Spectral Data*, Carnegie Institute of Technology, Serial No. 710; (b) Serial No. 929; (c) Serial No. 931.

(26) E. C. Wagner, *J. Chem. Educ.*, **7**, 1135 (1930).

(27) C. Naegli, L. Gruntuch, and P. Lendorff, *Helv. Chim. Acta*, **12**, 255 (1929).

(28) I. G. Farbind. A.-G., French Patent **838,434** (1939) [*Chem. Abstr.*, **33**, 7817 (1939)].

150° with hydrogen at 160 atmospheres pressure. After the theoretical amount of hydrogen had been absorbed, the contents of the bomb were filtered and the solvent was removed from the filtrate by distillation under reduced pressure. The residue was fractionated through a 24-inch, helix-packed column to yield 69.2 g. (95%) of N-(1,3-dimethylbutyl)-aniline, b.p. 60.5° (0.4 mm.), n_D^{25} 1.5165 (reported[29] in "rather mediocre yields" but with no physical constants).

Anal. Calcd. for $C_{12}H_{19}N$: C, 81.30; H, 10.80. Found: C, 81.29; H, 10.56.

N-(1,3-Dimethylbutyl)acetanilide (VIII). To a mixture of 114 ml. of glacial acetic acid and 188 ml. (2.0 moles) of acetic anhydride heated under reflux in a 1-l., three-necked flask, equipped with a magnetic stirrer, a condenser, and a dropping funnel, was added dropwise over 30 min. 177.3 g. (1.0 mole) of N-(1,3-dimethylbutyl)aniline. After the mixture had been heated under reflux for an additional hour, the excess acetic anhydride and acetic acid were removed by distillation under reduced pressure. The residue was dissolved in 500 ml. of ether and the solution was extracted successively with two 50-ml. portions of $0.05N$ hydrochloric acid, three 50-ml. portions of 15% sodium carbonate solution, and two 50-ml. portions of water. After the ether solution had been dried over magnesium sulfate, the ether was removed by distillation. The residue was recrystallized twice from petroleum ether (30–60°) to produce 214.2 g. (98%) of N-(1,3-dimethylbutyl)acetanilide (VIII), m.p. 49.1–50.0° (reported[29] m.p. 67° for the acetylated product from the reductive alkylation of aniline with isopropyl alcohol or methylisobutylcarbinol but with no yield or analysis).

Anal. Calcd. for $C_{14}H_{21}NO$: C, 76.66; H, 9.65. Found: C, 76.92; H, 9.85.

Pyrolysis of N-(1,3-dimethylbutyl)acetanilide (VIII). At the rate of 1.2 g. per minute, 54.5 g. (0.25 mole) of molten N-(1,3-dimethylbutyl)acetanilide (VIII) was added dropwise from a heated dropping funnel to the pyrolysis tube at 510°. The pyrolyzate (52.7 g.) was collected in a cooled side-inlet flask connected directly to the pyrolysis tube. The low boiling products of the pyrolysis were removed under reduced pressure while the pyrolyzate was maintained at 75°. The crude olefin fraction was refractionated through a 6-inch, helix-packed column to yield 14 g. (67%) of a mixture of 4-methyl-1-pentene (V) and 4-methyl-2-pentene (VI), b.p. 47–58°, n_D^{25} 1.3839–1.3852. The infrared absorption spectrum indicated that this mixture was composed of nearly equal parts of the 4-methyl-1-pentene (V) and 4-methyl-2-pentene (VI).

The solid residue from the pyrolyzate was crushed and extracted for 5.5 hr. with petroleum ether (30–60°) in a Soxhlet extractor. The insoluble material in the cup plus a few crystals in the petroleum ether extract were dried to yield 28.2 g. (84%) of nearly pure acetanilide, m.p. 111–113°. A mixed melting point determination with an authentic sample of acetanilide showed no depression.

The solvent was removed from the petroleum ether solution from the Soxhlet extractor by evaporation, and the residue was recrystallized from petroleum ether to yield 4.1 g. (7.5% recovery) of the starting anilide VIII, m.p. 46–48°. The yield of the olefin mixture, based on unrecovered

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(29) A. Guyot and M. Fournier, *Bull. soc. chim.*, [4], 47, 203 (1930).

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starting material, was 72% and that of the acetanilide was, therefore, 91%.

N-(1,1,3,3-tetramethylbutyl)acetamide (IX). To a hot mixture of 120 g. (2.0 moles) of glacial acetic acid and 204 g. (2.0 moles) of acetic anhydride was added 129 g. (1.0 mole) of 1,1,3,3-tetramethylbutylamine[30] over a period of 2 hr. After the mixture had been heated at 90–95° for an additional hour, the excess acetic anhydride and acetic acid were removed by distillation under reduced pressure. The residue was suspended in 1.5 l. of ether and the mixture was cooled. The precipitate was removed by filtration and dried in a vacuum desiccator to yield 164 g. (96%) of slightly impure amide. Recrystallization of this material from petroleum ether (60–80°) yielded white needles of pure N-(1,1,3,3-tetramethylbutyl)acetamide (IX), m.p. 99.5–100° (reported[31] m.p. 98–99°, with no yield).

Pyrolysis of N-(1,1,3,3-tetramethylbutyl)acetamide (IX). At the rate of 0.8 g. per minute, 56.3 g. (0.33 mole) of molten N-(1,1,3,3-tetramethylbutyl)acetamide (IX) was dropped from a heated dropping funnel (130°) through the pyrolysis tube at 510°. The pyrolyzate (55 g.) was condensed in a steam-heated coil condenser and collected in a side-inlet flask cooled in ice. The volatile fraction was removed by distillation under reduced pressure by heating the pyrolyzate at 80°. Fractionation of this low-boiling material through a 6-inch, helix-packed column gave 5.8 g. of a forerun and 13.4 g. (35%) of a mixture of 2,4,4-trimethyl-1-pentene (X) and 2,4,4-trimethyl-2-pentene (XI), b.p. 52–56° (130–140 mm.), n_D^{25} 1.4071–1.4116 [reported[32] for X, b.p. 101° (760 mm.), n_D^{20} 1.4082, and for XI, b.p. 104.5° (760 mm.), n_D^{20} 1.4158]. Comparison of the infrared absorption spectrum of this mixture with those of 2,4,4-trimethyl-1-pentene (X)[33a] and 2,4,4-trimethyl-2-pentene (XI)[33b] indicated that the mixture consisted of about two thirds of the 1-isomer X and one third of the 2-isomer XI.

After the solid residue from the pyrolyzate plus 50 ml. of water were heated for several minutes on the steam bath, the resulting mixture was cooled in ice. The insoluble material was removed by filtration to yield 17.8 g. (32% recovery) of the starting amide, m.p. 99–100°. Water was removed from the filtrate by distillation under reduced pressure to yield 12.2 g. (63%) of impure acetamide, m.p. 71–77°. Two recrystallizations of this crude material from a 1:10 methanol-ether mixture gave nearly pure acetamide, m.p. 80–81°. A mixed melting point determination with an authentic sample of acetamide showed no depression.

The yield of olefins, based on unrecovered starting material, was, therefore, 53%, and the yield of acetamide was 92%.

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(30) The authors are indebted to the Rohm & Haas Co. for a generous supply of this amine.

(31) F. C. Whitmore, C. D. Wilson, J. V. Capinjola, C. O. Tongberg, G. H. Fleming, R. V. McGrew, and J. N. Crosby, *J. Am. Chem. Soc.*, 63, 2035 (1941).

(32) C. O. Tongberg, J. D. Pickens, M. R. Fenske, and F. C. Whitmore, *J. Am. Chem. Soc.*, 54, 3706 (1932).

(33) (a) American Petroleum Institute Research Project 44, *Infrared Spectral Data*, Carnegie Institute of Technology, Pittsburgh, Pa., Serial No. 725; (b) Serial No. 825.