pressure while any other nitroamine would be capable only of intermolecular hydrogen bonding.

Experiment showed that sublimation was effective in separating the isomers at 120° without decomposition. When a gentle current of air was drawn through the sublimation tube, separation time was reduced to four to six hours. Since temperatures higher than are obtainable in steam distillation are used and the product is obtained nearly pure and dry, sublimation furnishes a more rapid and elegant method for the separation of aminonitropyridines. The apparatus for this work has been described.[4]

Table I summarizes the information obtained on total yield and percentage of each isomer obtained from the nitration of 2-aminopyridine, 2-amino-3-methylpyridine, 2-amino-4-methylpyridine, 2-amino-5-methylpyridine and 2-amino-6-methylpyridine. The nitration and separation of isomers was carried out as described in the Experimental portion of the paper. No claim of originality in the nitration procedure is made, the aim being to combine what proved to be the most useful steps in already published work.[1-3,5-7] In this way, a general method of syntheses for compounds of this type has been devised.

TABLE I

NITROAMINES PREPARED

Starting pyridine	Isomeric nitro product	M.p., °C.	Yield, % Individual	Yield, % Total
2-Amino	3-Nitro	163–164	20.0	
	5-Nitro	188	63.1	83.1
2-Amino-3-methyl	5-Nitro	255	90.0	90.0
2-Amino-4-methyl	3-Nitro	134–136	22.3	
	5-Nitro	220	47.3	69.6
2-Amino-5-methyl	3-Nitro	190	33.5	33.5
2-Amino-6-methyl	3-Nitro	141	24.2	
	5-Nitro	187	46.4	70.6

Experimental

Nitration Procedure.—As indicated, this method was used for 2-aminopyridine and all the 2-aminopicolines. 2-Aminopyridine (25.3 g., 0.27 mole) was dissolved cautiously in 50 ml. of concd. sulfuric acid (d. 1.84). Vigorous stirring and cooling were used to keep the temperature below 20°. To this solution, cooled to 5–10°, was added dropwise 40 ml. of a 1:1 mixture of concd. sulfuric acid (d. 1.84) and concd. nitric acid (d. 1.42). During this addition, solution temperature was maintained below 20°.

If the intermediate pyridylnitramine was desired, the solution was poured over ice at this point and the pyridylnitramine (m.p. 185–189° dec.) collected.

If the nitroamines were desired, the solution was warmed cautiously. At 35–40°, the exothermic rearrangement of the nitramine to nitroamines caused a sudden increase in temperature. When this initial rise had subsided, the solution was held at 50° for four hours to complete the rearrangement.

The solution was then poured over ice and neutralized with concd. ammonia (250 ml., d. 0.90). The precipitate of 2-amino-3-nitropyridine and 2-amino-5-nitropyridine was collected by suction filtration and dried in a vacuum oven at 70°.

Sublimation.—The apparatus used and its operation has been described.[4] A charge of 20–60 g. can be handled. Six hours is generally sufficient for complete separation.

When the separation is complete, the residual isomer can be recrystallized from dilute alcohol and the sublimed isomer washed out of the condensing tube with acetone and the acetone evaporated to give a pure crystalline product.

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[4] L. N. Pino and W. S. Zehrung, *J. Chem. Education*, **31**, 476 (1954).

[5] G. R. Lappin and F. B. Slezak, THIS JOURNAL, **72**, 2806 (1950).

[6] O. Seide, *J. Russ. Phys. Chem. Soc.*, **50**, 534 (1920); *C. A.*, **18**, 1497 (1924).

[7] O. Seide, *Ber.*, **57B**, 791, 1802 (1924).

Hydroxymethylene Ketones. IV. Orientation in the Condensation of Methyl *n*-Hexyl Ketone with Methyl Formate

BY E. EARL ROYALS AND E. R. COVINGTON[1]

RECEIVED NOVEMBER 17, 1954

In continuation of our investigations concerning the condensation of unsymmetrical ketones with formic esters,[2] it was decided to determine the manner in which methyl *n*-hexyl ketone condenses with methyl formate.

We have shown in the present work that methyl *n*-hexyl ketone condenses with methyl formate in ether solution in the presence of sodium methoxide at *both* the methyl and the methylene units to give the isomeric hydroxymethylene ketones I and II.[3] The presence of both I and II in the condensation product was shown by ultimate conversion of I to α-*n*-amylcrotonaldehyde (IX) and II to α-nonenaldehyde (X) by the reaction sequence of Chart 1. The mixed sodium salts of the hydroxymethylene ketones I and II were treated with methanolic hydrogen chloride according to the procedure of Royals and Brannock[4] to give a reaction product probably consisting of the isomeric β-ketoacetals III and V and the methoxymethylene ketone IV. Reduction of the mixture with lithium aluminum hydride followed by treatment of the resulting mixture (probably containing VI, VII and VIII) with aqueous sulfuric acid gave a mixture of α-*n*-amylcrotonaldehyde (IX) and α-nonenaldehyde (X). The aldehyde mixture was separated by fractional distillation into three fractions constituting 40, 12 and 48% of the distilled aldehydes. The lower boiling fraction was identified as α-*n*-amylcrotonaldehyde by the preparation of the semicarbazone, m.p. 169°, which showed no m.p. depression on admixture with an authentic sample, m.p. 170°. The higher boiling fraction was identified as α-nonenaldehyde by the preparation of a semicarbazone, m.p. 163°, which showed no depression on admixture with an authentic sample, m.p. 164–165°. A mixture of the semicarbazones from the lower and higher boiling fractions showed m.p. 137–150°.

The formation of α-*n*-amylcrotonaldehyde in appreciable amounts from the above reaction sequence was rather unexpected. Despite the above evidence from m.p.'s of semicarbazones, it seemed de-

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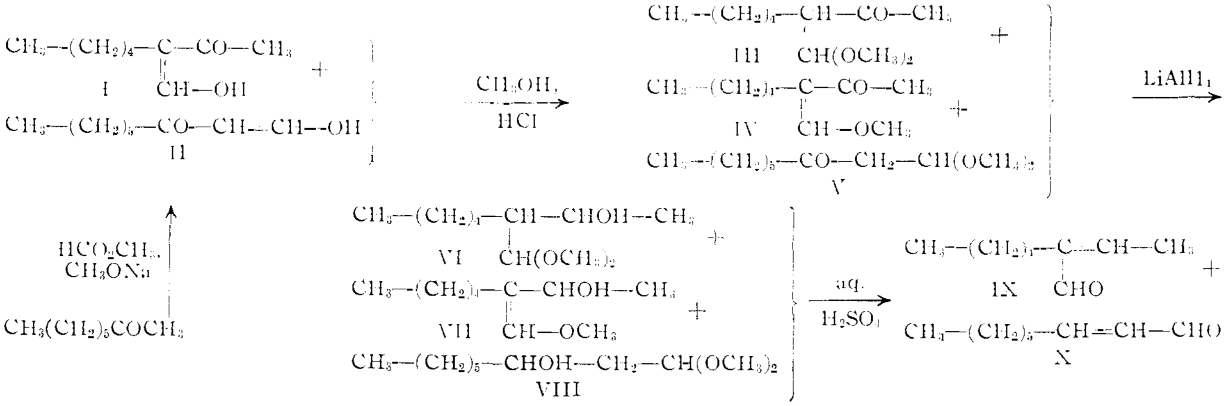
[1] Abstracted from a thesis presented by E. R. Covington to the Graduate Faculty of Emory University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1954.

[2] See Papers I, II and III, E. E. Royals and K. C. Brannock, THIS JOURNAL, **76**, 3041 (1954), for previous work in this field.

[3] It is known that the results of condensations between esters and ketones are dependent upon the experimental conditions, the nature of the ester, and the type of basic catalyst used. See, for example, R. P. Mariella, *ibid.*, **69**, 2670 (1947); R. Levine, J. A. Conroy, J. T. Adams and C. R. Hauser, *ibid.*, **67**, 1512 (1945).

[4] E. E. Royals and K. C. Brannock, *ibid.*, **75**, 2050 (1953).

Chart I



sirable to obtain further evidence regarding the structures of the two aldehydes obtained. The higher boiling aldehyde fraction was hydrogenated over platinum black to *n*-nonyl alcohol whose 1-naphthylurethan, m.p. 61–62°, gave no m.p. depression on admixture with an authentic specimen. The lower boiling aldehyde fraction, tentatively identified[5] as α-*n*-amylcrotonaldehyde, on hydrogenation over platinum black gave 2-ethylheptanol, m.p. of 1-naphthylurethan 41.5°. Since 2-ethylheptanol has not previously been reported in the literature, it was necessary to synthesize this material by an unequivocal method. α-Ethyl-heptanoic acid (not previously reported) was prepared by the malonic ester method in 55% over-all yield from diethyl malonate. Lithium aluminum hydride reduction of α-ethylheptanoic acid gave 2-ethylheptanol in 75% yield. The alcohol gave a 1-naphthylurethan, m.p. 43–44°, which failed to depress the m.p. of the 1-naphthylurethan of the reduction product of the lower boiling aldehyde fraction.

It is obvious from these results that distinct limitations are placed on the synthesis of pure α,β-unsaturated aldehydes by reaction sequences of the type illustrated in Chart 1 because of the occurrence of both methyl and methylene condensation in the first step. Another possible limitation is that in the second step of the synthetic sequence hydroxymethylene ketones resulting from methylene condensation give mixtures of β-ketoacetals and methoxymethylene ketones.[2] It seemed desirable to determine whether such a mixture may be successfully used without separation for the preparation of pure α,β-unsaturated aldehydes in the aliphatic series.[6] Diethyl ketone was chosen for the test case, since only methylene condensation with methyl formate is possible, and it is known[2] that the condensation product is a mixture of β-ketoacetal and methoxymethylene ketone. Lithium aluminum hydride reduction of this mixture and subsequent hydrolysis and dehydration of the product gave pure 1-methyl-2-ethylacrolein in 54% yield from the mixed condensation product.

Experimental[7]

Condensation of Methyl Formate with Methyl *n*-Hexyl Ketone.—Methyl formate, 40 g. (0.67 mole), was condensed with 70 g. (0.55 mole) of methyl *n*-hexyl ketone in the presence of 27 g. (0.5 mole) of sodium methoxide in 300 ml. of dry ether according to the procedure of Royals and Brannock.[4] The reaction mixture was stirred for 2.3 hours after which time the ether was removed under the vacuum from a water aspirator. Methanol, 96 g. (3 moles), was added to the residual sodium salts, the mixture was cooled to 0°, and a solution of 28 g. (0.78 mole) of hydrogen chloride in 50 g. (1.56 moles) of methanol was added. The reaction mixture was allowed to stand for 1.3 hours, then worked up as described by Royals and Brannock. The product isolated, 41.2 g. (44% yield based on observed saponification equivalent), showed b.p. 100–112° (3 mm.), $n^{25}\text{D}$ 1.4350, sapon. equiv., 187. The calculated saponification equivalent for the β-ketoacetal (III or V) is 202, while that for the methoxymethylene ketone (IV) is 170. Hence, the product consisted of 53% β-ketoacetal and 47% methoxymethylene ketone.

Preparation of a Mixture of α-Nonenaldehyde and α-Amylcrotonaldehyde.—The mixture of β-ketoacetals and methoxymethylene ketone described above was reduced with lithium aluminum hydride and the resulting crude product was hydrolyzed and dehydrated with aqueous sulfuric acid essentially according to the directions of Seifert and Schinz.[6] The products from four small runs utilizing a total of 65 g. of the β-ketoacetal and methoxymethylene ketone mixture were combined to give 28.5 g. (58% yield) of a crude mixture of α-nonenaldehyde and α-*n*-amylcrotonaldehyde. This mixture was fractionally distilled through a Todd column with monel spiral packing in an atmosphere of nitrogen to give: (A) 7.3 g., b.p. 69–74° (6.5 mm.), $n^{31}\text{D}$ 1.4431–1.4463; (B) 2.2 g., b.p. 74–82° (6.5 mm.); (C) 8.8 g., b.p. 82–83° (6.5 mm.), $n^{31}\text{D}$ 1.4490.

Fraction (A) was identified as α-*n*-amylcrotonaldehyde by formation of a semicarbazone, m.p. 169°. A sample of α-*n*-amylcrotonaldehyde was prepared by condensation of acetaldehyde with *n*-heptaldehyde according to the procedure of Zaar.[5] This material showed b.p. 67° (4.5 mm.), $n^{31}\text{D}$ 1.4489, and gave a semicarbazone, m.p. 170°, which did not depress the m.p. of the semicarbazone of fraction (A).

Hydrogenation of 6.6 g. of fraction (A) in 25 ml. of ethanol over 0.1 g. of platinum black in a Parr low pressure hydrogenation apparatus gave 3.5 g. of an alcohol, b.p. 65–73° (3 mm.), $n^{27}\text{D}$ 1.4310, m.p. of 1-naphthylurethan 41.5°. The m.p. of a mixture of this 1-naphthylurethan with that of an authentic sample of the 1-naphthylurethan of 2-ethylheptanol (prepared as described below, m.p. 43–44°) was 41.5–43.5°.

Fraction (C) was identified as α-nonenaldehyde by formation of a semicarbazone, the m.p. of which (163°) was not depressed by an authentic sample of α-nonenaldehyde semicarbazone (m.p. 164–165°). The authentic sample of α-nonenaldehyde was prepared by the method of Scanlan and Swern.[8]

Hydrogenation of 7 g. of fraction (C) in 25 ml. of ethanol over 0.1 g. of platinum black gave 4.8 g. of *n*-nonyl alcohol.

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(5) B. Zaar, *Ber. Schimmel and Co. Akt. Ges.*, 311 (1929); *C. A.*, **24**, 2107 (1930), has reported the preparation on α-*n*-amylcrotonaldehyde by condensation of acetaldehyde with *n*-heptaldehyde; no conclusive structure proof was offered.

(6) P. Seifert and H. Schinz, *Helv. Chim. Acta*, **34**, 728 (1951), have successfully reduced certain alkoxymethylene ketones in the alicyclic series with lithium aluminum hydride to the corresponding carbinols, but the reaction has not been investigated in the acyclic series.

(7) All reported m.p.'s are uncorrected.

(8) J. T. Scanlan and D. Swern, This Journal, **62**, 2309 (1948).

b.p. 72–76° (3 mm.), $n^{27}\mathrm{D}$ 1.4301, m.p. of 1-naphthylurethan 61–62° (reported[9] m.p. 65.5°).

The 1-naphthylurethan of an authentic sample of *n*-nonyl alcohol, m.p. 61°, did not depress the m.p. of our 1-naphthylurethan.

Synthesis of α-Ethylheptanoic Acid.—Alkylation of diethyl malonate first with *n*-amyl bromide, then with ethyl bromide by standard procedures[10] gave diethyl ethyl-*n*-amylmalonate, b.p. 129–134° (7.5 mm.), $n^{24}\mathrm{D}$ 1.4292 (reported[11] b.p. 136.5° (10 mm.), $n^{25}\mathrm{D}$ 1.4259) in 54% over-all yield.

Diethyl ethyl-*n*-amylmalonate, 69.5 g. (0.27 mole), was refluxed for six hours in a solution of 112 g. of potassium hydroxide in 830 ml. of ethyl alcohol. The solution was then cooled, 250 ml. of water was added, and the alcohol was removed by distillation. The basic aqueous layer was extracted with ether, then acidified with hydrochloric acid; crude ethyl-*n*-amylmalonic acid separated on cooling in an ice-bath and stirring. The crude acid was collected by filtration, and the mother liquor was twice extracted with 100-ml. portions of ether. The ether extracts were combined, the crude acid dissolved therein, and the solution was dried over anhydrous sodium sulfate. After removal of ether, the crude acid was decarboxylated by heating at 180–185° until evolution of carbon dioxide ceased. The residual product was distilled from a simple distillation flask to give 34 g. (80% yield) of crude α-ethylheptanoic acid, b.p. 110–114° (3.5 mm.), $n^{23}\mathrm{D}$ 1.4240. Another similar run gave 73.5% yield. Fractional distillation of 34 g. of crude material gave 23.3 g. (68.5%) of pure α-ethylheptanoic acid, b.p. 121–122° (6 mm.), $n^{27}\mathrm{D}$ 1.4255. *Anal.* Calcd. for $C_9H_{18}O_2$: C, 68.31; H, 11.46; neut. equiv., 158.2. Found: C, 68.80; H, 11.48; neut. equiv., 158.1.

Synthesis of 2-Ethylheptanol.—A solution of 15.8 g. (0.1 mole) of α-ethylheptanoic acid in 150 ml. of ether was added dropwise to a solution of 6.2 g. (0.16 mole) of lithium aluminum hydride in 200 ml. of ether at such rate as to maintain gentle reflux. After addition was complete the mixture was refluxed for an additional hour, then cooled in ice and the excess lithium aluminum hydride decomposed by the dropwise addition of 25 ml. of water. The mixture was treated with 250 ml. of 10% sulfuric acid. The aqueous layer was separated, saturated with sodium chloride, and thrice extracted with 100-ml. portions of ether. The original ether layer and the ether extracts were combined, washed with sodium carbonate solution, then with water, and dried over anhydrous sodium sulfate. The ether was removed by distillation, and the residue was fractionally distilled through the Todd column to give 9.8 g. (68% yield) of 2-ethylheptanol, b.p. 92° (5 mm.), $n^{23}\mathrm{D}$ 1.4330. *Anal.* Calcd. for $C_9H_{20}O$: C, 74.93; H, 13.98. Found: C, 74.54; H, 13.67. The alcohol gave a 1-naphthylurethan, m.p. 43–44° after two crystallizations from petroleum ether.

Synthesis of 1-Methyl-2-ethylacrolein.—Diethyl ketone, 50 g. (0.58 mole), was condensed with 45 g. (0.75 mole) of methyl formate in the presence of 27 g. (0.5 mole) of sodium methoxide and the resulting sodium salt of the hydroxymethylene ketone was treated with methanolic hydrogen chloride according to the procedure of Royals and Brannock.[4] The reaction product (a mixture of the β-ketoacetal and methoxymethylene ketone) showed b.p. 53–58° (3.5 mm.), $n^{25}\mathrm{D}$ 1.4260 and was obtained in 62% yield. This mixture was reduced with lithium aluminum hydride at −10° and the reduction product was hydrolyzed and dehydrated essentially as described by Seifert and Schinz.[6] The product was fractionally distilled through the Todd column to give 12.9 g. (54%) of 1-methyl-2-ethylacrolein, b.p. 77–78.5° (100 mm.), $n^{28}\mathrm{D}$ 1.4390–1.4440, m.p. of 2,4-dinitrophenylhydrazone 158° (reported m.p. 159°[12] and 161°[13]), m.p. of semicarbazone 205° (reported[17] m.p. 207°).

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(9) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 842 (1934).

(10) R. Adams and R. M. Kamm in H. Gilman and A. H. Blatt, "Organic Syntheses," 2nd Ed., Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 250.

(11) A. W. Dox and E. G. Jones, THIS JOURNAL, **50**, 2033 (1928); H. A. Shonle, A. K. Ketlch and E. E. Swanson, *ibid.*, **52**, 2440 (1930); P. Karrer, B. Shibata, A. Wattstein and L. Jacubowicz, *Helv. Chim. Acta*, **13**, 1292 (1930).

(12) C. F. H. Allen, THIS JOURNAL, **52**, 2955 (1930).

(13) M. M. Backes, *Compt. rend.*, **196**, 277 (1933).

Nitrolysis of 1,3–6,8-Diendomethylene-1,3,6,8-tetrazacyclodecane

BY R. J. J. SIMKINS AND GEORGE F WRIGHT

RECEIVED NOVEMBER 4, 1954

In view of the successful nitrolysis of hexamethylenetetramine and related compounds[1] as well as 1,3-dicyclohexylimidazolidine[2] it seemed possible that conditions could be found wherein 1,3–6,8-diendomethylene-1,3,6,8-tetrazacyclodecane (I),[3] could be nitrolyzed to 1,3,6,8-tetranitro-1,3,6,8-tetrazacyclodecane (X). However we have been unsuccessful in the attempt to synthesize this compound, which might be expected to exhibit unusual explosive properties. Instead we have found that the nitrolysis of I takes quite a different course.

In contrast to hexamethylenetetramine, 1,3–6,8-diendomethylene-1,3,6,8-tetrazacyclodecane (I) is not a stable compound.[4] The yield from 1,2-diaminoethane and formaldehyde is lower than that of hexamethylenetetramine from ammonia and formaldehyde and the purity of I is not so high. A solution of I in acetic acid is unstable, and the dinitrate decomposes within an hour, whereas hexamethylenetetramine dinitrate is permanently stable. Under these circumstances it might be expected that the methods of hexamethylenetetramine nitrolysis would not be applicable to diendomethylenetetrazacyclodecane I. Indeed when I is treated with ammonium nitrate and nitric acid in acetic anhydride at 65° it seems to decompose, since 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX, II) is the only product which has been isolated.

When hexamethylenetetramine is treated at 25° with nitric acid and acetic anhydride alone nitrolysis occurs smoothly to give a good yield of 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane and bisacetoxymethylnitramide. Under these conditions a relatively small yield of impure 1,6-diacetoxy-2,5-dinitro-2,5-diazahexane (IV), is obtained from diendomethylenetetrazacyclodecane I. However a good yield of relatively pure IV is obtained when acetyl chloride is included in the system. Indeed the yield approaches the 2:1 ratio expected if nitrolytic scission has occurred at two symmetrically disposed methylene–amine linkages in the diendomethylenetetrazacyclodecane.

Although IV has been identified previously[5] by synthesis from 1,2-dinitraminoethane (III) and formalin, it has now been characterized further by conversion to the unstable nitroxy analog V, which in turn has been transformed to 1,6-dimethoxy-2,5-dinitro-2,5-diazahexane VI by known methods.[5]

Although we have not yet succeded in the preparation of tetranitrotetrazacyclodecane (X), certain controlled solvolyses can be caused to alter the nitrolysis of diendomethylenetetrazacyclodecane I. If nitric acid is added to an ethanolic solution of I, the precipitate which first forms (the mono- and/or dinitrate) redissolves when more nitric acid is added

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(2) J. L. Boivin and G. F. Wright, *Can. J. Research*, **28**, 213 (1950).

(3) C. A. Bischoff, *Ber.*, **31**, 3248 (1898).

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(5) G. S. Myers and G. F. Wright, *Can. J. Research* **27B**, 489 (1949).