chilled 40% aqueous dimethylamine. After the addition was complete the solution was heated until the excess dimethylamine had been distilled off. The oily product was separated hot, dried, and when the product was thermally stable, distilled.

Preparation of alkyl tetraethylphosphorodiamidate by reaction of the phosphorodiamidic chloride with the sodium alcoholate. A solution of 4 moles diethylamine in chloroform was slowly added to a solution of one mole of phosphoryl chloride (or thiophosphoryl chloride) in dry chloroform at 0°. The solution was stirred 2 hr. at room temperature and then heated to distill out most of the chloroform. A large volume of petroleum ether was then added and the precipitated amine salt was filtered. The solvent was then removed and the phosphorodiamidic chloride was distilled.

The sodium alcoholate was prepared by reaction of sodium sand with the alcohol in toluene. To the dispersion of the sodium alcoholate in toluene was slowly added the phosphorodiamidic chloride. The mixture was warmed for several hours, then filtered. The organic layer was washed with water, dried, and distilled. Thermally unstable compounds were treated with a decolorizing carbon, and last traces of solvent were removed by mild heating in vacuum.

o-Cresyl tetraethylphosphorodiamidate (XVIII). *o*-Cresol (1.5 moles) was added to 3.25 moles phosphoryl chloride containing 1 g. anhydrous magnesium chloride and maintained at 90°, and then refluxed overnight. The excess chloride was distilled off and the *o*-cresyl phosphorodichloridate distilled, b.p. 110° (7 mm.), n_D^{30} 1.5170–80 (51% conversion). When the magnesium chloride was not present, the conversion dropped to 33%.

The reaction with diethylamine was carried out in a manner similar to that already described.

Bis(pentachlorophenyl) dibutylphosphoroamidate (XXII). One hundred grams (0.376 mole) pentachlorophenol in warm chlorobenzene was added to 111 g. (0.724 mole) $POC._3$ at 70°. Refluxing for 2 hr. gave only a small quantity of evolved HCl, so the solution was cooled to 100° and 29.7 g. (0.376 mole) pyridine was added, causing formation of a heavy precipitate of amine hydrochloride. The mixture was stirred at 100° for 1 hr., cooled, and filtered. The filtrate was concentrated *in vacuo* leaving 130 g. of a brown oil which soon crystallized. This bis(pentachlorophenyl)phosphorochloridate was taken up in toluene and added to 185 g. cold dibutylamine. The solution was refluxed 3 days and cooled, and the amine salt was filtered. Volatile materials were removed in vacuum leaving a semi-crystalline brown oil which was treated with ligroin and filtered. The precipitate was recrystallized from benzene, 33 g., m.p. 144–145°, white solid, soluble in most organic solvents.

Tetraethyl benzenephosphonic diamide (XXI). Benzenephosphonic dichloride (Victor Chemical Co.) was treated with diethylamine in the same manner that was employed with the amides already described.

Diethyl diethylphosphoroamidate (XX). Diethylphosphorochloridate (Victor Chemical Co.) was reacted with 2 moles diethylamine in the manner previously described.

Polymeric material from ethyl phosphorodichloridate and p-phenylenediamine. Four grams of *p*-phenylenediamine (Eastman Technical, purple crystals) were dissolved in a solution of chloroform containing 20 cc. pyridine. Ethyl phosphorodichloridate (6.1 g.) was slowly added. The reaction was quite exothermic. No attempt was made to prevent contact with air. The thick purple precipitate was filtered and washed with petroleum ether, dried, triturated with water, then with acetone, and then dried in vacuum at 110°. The resulting hard solid was powdered, giving beautiful purple crystals (under microscope), insoluble in acetone, dimethyl formamide, and other organic solvents. On heating it turns white at 190°, starts melting at 235°, and chars at 320°. It is readily decomposed by acids and bases.

Anal. Calcd. for $C_8H_{11}N_2O_2P$: C, 48.5, H, 5.6, N, 14.1. Found, C, 45.4, H, 5.2, N, 12.5. Mol. wt. 1250 (approx.) determined cryoscopically in acetic acid.

Solubility of acetylene in various phosphoramidates. A weighed amount of phosphoramidates was saturated with acetylene and the gain in weight was determined. III absorbed 8% of its own weight, IV and XIII absorbed nothing. By comparison hexamethylphosphoramide absorbed 14% of its weight.

PHILADELPHIA 18, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Pyrolysis of Esters. XII. Ketone Cleavage of Acetoacetic Esters by Pyrolysis[1,2]

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The pyrolysis of acetoacetic esters is shown to be an excellent procedure for the ketone cleavage. For example, in the pyrolysis of ethyl α-isopropylacetoacetate at 525° the ester portion decomposes to give ethylene and the resulting acetoacetic acid almost simultaneously loses carbon dioxide to give an 82% yield of methyl isobutyl ketone, more than double the yield obtained by conventional basic hydrolysis. In many cases the saving of time and material as well as adaptability to large quantities recommend the pyrolysis of acetoacetic ester rather than hydrolysis. The ketone cleavage by pyrolysis is particularly advantageous if the acetoacetic ester contains a branched group or if the resulting ketone has a moderately high solubility in water.

Previous work[1,4–6] in this laboratory has shown that the pyrolysis of esters is an excellent method for the preparation of strained or sensitive olefins provided that charring is eliminated. Since the products from the pyrolysis of an ester are an olefin and an acid, it seemed logical that this reaction would be useful also in the synthesis of acids and

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[1] Previous paper in this series, *J. Org. Chem.*, 22, 1076 (1957).

[2] Presented in part before the Division of Organic Chemistry at the 126th National Meeting of the AMERICAN CHEMICAL SOCIETY, New York, N. Y., September 1954.

[3] Office of Naval Research Fellow, 1950–52; Union Carbide Fellow, 1952–53; Du Pont Fellow, 1953–54.

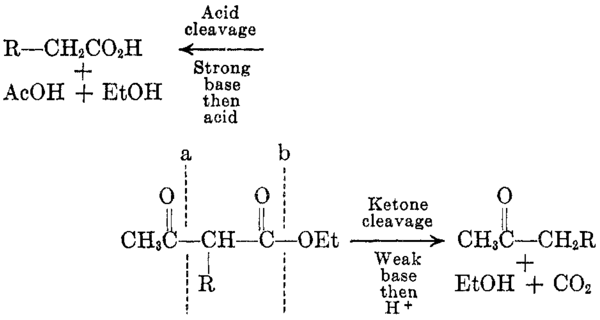
[4] W. J. Bailey and W. A. Klein, *J. Am. Chem. Soc.*, **79**, 3124 (1957).

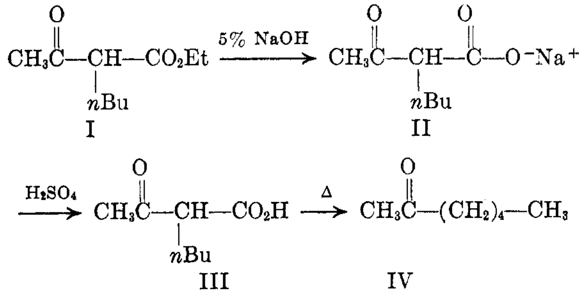
[5] W. J. Bailey and J. Economy, *J. Am. Chem. Soc.*, **77**, 1133 (1955).

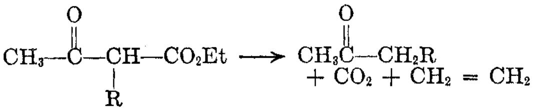
[6] W. J. Bailey and J. Rosenberg, *J. Am. Chem. Soc.*, **77**, 73 (1955).

their derivatives. In a previous paper[7] it was shown that pyrolysis had many advantages over hydrolysis in the conversion of an ethyl ester of a fatty acid to the corresponding acid. This method was particularly useful in the preparation of water-soluble or sterically hindered acids. For example, diethyl glutarate was pyrolyzed to give a 97% yield of glutaric acid and ethyl 1,3,5-trimethylbenzoate was converted to the hindered acid in a 91% yield.

From a search for other examples of the utility of the pyrolysis reaction for the preparation of products from the acid portion it appeared that the ketone cleavage of acetoacetic esters would be an attractive field. Pyrolysis appeared to have an advantage over the basic hydrolysis of the ester group to obtain the ketone cleavage since base can cleave the acetoacetic ester in two ways. In addition to attack of the base at the ester group (cleavage point *b*) to give the ketone, attack at the ketone group (cleavage point *a*) can take place to give the acid cleavage by a reverse Claisen condensation. Strong base tends to favor acid cleavage while weak base tends to favor ketone cleavage. Steric hindrance and electronegative groups in the α-position also tend to favor acid cleavage. It seemed possible, therefore, that pyrolysis of the acetoacetic ester would promote cleavage only at the ester portion to give a high yield of the ketone cleavage product.





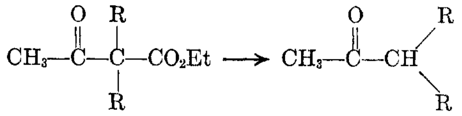


$\text{I. R} = n\text{-Butyl} \xrightarrow{71\%\text{ at }525°} \text{IV. R} = n\text{-Butyl}$

$\text{V. R} = \text{Isopropyl} \xrightarrow{82\%\text{ at }525°} \text{VI. R} = \text{Isopropyl}$

$\text{VII. R} = \text{Cyclohexyl} \xrightarrow{79\%\text{ at }525°} \text{VIII. R} = \text{Cyclohexyl}$

$\text{IX. R} = \text{Allyl} \xrightarrow{63\%\text{ at }540°} \text{X. R} = \text{Allyl}$



$\text{XI. R} = \text{Ethyl} \xrightarrow{50\%\text{ at }500°} \text{XII. R} = \text{Ethyl}$

$\text{XIII. R} = n\text{-Butyl} \xrightarrow{56\%\text{ at }490°} \text{XIV. R} = n\text{-Butyl}$

Several acetoacetic esters have been pyrolyzed according to the literature but none by the same procedure or conditions that are reported in this paper. Kimel and Cope[8] pyrolyzed a series of substituted allyl acetoacetates and obtained the corresponding substituted allyl acetones. In this case the allyl group migrated to the α-carbon atom by means of a cyclic mechanism similar to that of the Claisen rearrangement and the resulting acetoacetic acid immediately lost carbon dioxide. Ethyl acetoacetate has been pyrolyzed in the liquid phase but the only product isolated under these conditions was dehydroacetic acid in an 86% yield.[9]

The ester chosen for the initial pyrolysis studies was ethyl *n*-butylacetoacetate (I), since this ester gives a high yield by conventional ketone cleavage and was selected as an example for *Organic Syntheses*.[10] The reported yield of the methyl *n*-amyl ketone (IV) from acetoacetic ester was 52 to 61% or, calculated from the alkylated ester I, was 74 to 86%. It was thought that, if the pyrolysis could produce the ketone IV in any comparable yield, it would represent a large improvement since the experimental procedure for the hydrolysis method is long and tedious and cannot be conveniently adapted to the preparation of large quantities. For example, by the *Organic Syntheses* method for the preparation of 300–350 g. of IV, a 12-l. flask and 5 l. of a 5% sodium hydroxide solution are initially used. The ketone IV is isolated and purified by four separate steam distillations followed by extraction with a saturated calcium chloride solution.

For these reasons, ethyl *n*-butylacetoacetate (I) was dropped through a standard pyrolysis tube[11] packed with Pyrex helices and externally heated at 525°. Care was taken to minimize charring by the introduction of a slow stream of oxygen-free nitrogen. Under these conditions the ester portion of the molecule decomposed by a cyclic six-membered ring mechanism to produce ethylene and the acetoacetic acid III which immediately decomposed under these same conditions by another cyclic six-

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[7] W. J. Bailey and W. N. Turek, *J. Am. Oil Chemist's Soc.*, **33**, 317 (1956).

[8] W. Kimel and A. C. Cope, *J. Am. Chem. Soc.*, **65**, 1992 (1943).

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[10] J. R. Johnson and F. D. Hager, *Org. Syntheses*, **Coll. Vol. I**, 2nd ed., 351 (1941).

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membered ring mechanism to produce carbon dioxide and the desired ketone IV. The pyrolysate was fractionated without further treatment to produce a 59% conversion to the methyl *n*-amyl ketone (IV) and a 17% recovery of the starting acetoacetic ester I. The yield of the ketone IV, based on unrecovered I, was 71%.

The ketone cleavage by pyrolysis of I appears to have several advantages over the conventional basic hydrolysis: (1) the procedure has been shortened from several steps to only one step; (2) the isolation of the final product has been simplified since the two by-products, ethylene and carbon dioxide, escape as a gas; (3) no additional reagents are required; and (4) the quantities can be conveniently increased to prepare large amounts of the ketone. Thus, this saving of both time and material plus the fact that the yields by these two methods are almost comparable recommend the pyrolysis method.

Of course many substituted acetoacetic esters give much poorer yields on basic ketone cleavage than does the *n*-butyl derivative I.[10,12] This is particularly true if the substituent is branched. Apparently the added strain accelerates the acid cleavage at the expense of the ketone cleavage. For example, ethyl isopropylacetoacetate (V) produces only a 36% yield of the corresponding ketone VI by conventional hydrolysis. The lower yield in this case can partly be attributed to the higher water solubility of VI. It appeared, therefore, that the cleavage of V would make an excellent test of the usefulness of the pyrolysis method of ketone cleavage.

When the isopropylacetoacetic ester V was pyrolyzed at 525° under the same conditions indicated for I, a 71% conversion to methyl isobutyl ketone (VI) was realized. Since a 13% recovery of the starting ester V also was obtained, the yield of VI, based on unrecovered material, was 82%. In this particular case, in addition to the advantages listed above, the pyrolytic procedure produces more than double the yield obtained by the conventional hydrolysis procedure.

In order to show that the ketone cleavage by pyrolysis is a general reaction, several other acetoacetic esters were studied. Ethyl α-cyclohexylacetoacetate (VII) on pyrolysis at 525° gave a 72% conversion to cyclohexylacetone (VIII) plus a 9% recovery of VII. The yield of VIII, based on unrecovered VII, was, therefore, 79%. This yield compares very favorably with the 55% yield obtained by Adams, Abramovitch, and Hauser[13] for the basic hydrolysis of VII and with the 60% yield obtained by Darzens and Rost[14] from the reaction of methylmagnesium bromide on α-cyclohexylacetyl chloride.

At 540° ethyl α-allylacetoacetate (IX) gave a 54% conversion to allylacetone (X) and at 510° a 50% conversion. At the lower temperature a 20% recovery of the starting ester was obtained so that the yield of X, based on unrecovered IX, was 63%. At either temperature it was not possible to eliminate charring completely. Although the yield of allylacetone (X) from the pyrolysis of IX is better than the 31% reported by Kimel and Cope[8] for the pyrolysis of allyl acetoacetate or the 35% obtained by conventional hydrolysis of IX,[15] it is less than the 85% reported by Schechter, Green, and La Forge[16] for a 4-day hydrolysis of IX at 0°.

It was hoped that the pyrolysis of disubstituted acetoacetic esters, which very often give poor yields of the corresponding ketones on hydrolysis, would give clean-cut results. However, a substantial amount of charring and decomposition always occurred so that the yields of ketones were lowered to approximately the same range as those from hydrolysis. Thus, pyrolysis of ethyl α,α-diethylacetoacetate (XI) at 500° gave a 33% conversion to 3-ethyl-2-pentanone (XII). Since only a 35% recovery of starting material XI was obtained, the yield of XII, based on unrecovered material, was 50%. Renfrow and Renfrow[12] reported a 45% yield of the ketone XII by basic hydrolysis.

Similarly, pyrolysis of ethyl α,α-di-*n*-butylacetoacetate (XIII) at 490° gave a 33% conversion to 3-butyl-2-heptanone (XIV) and a 41% recovery of starting material. The yield of XIV, based on unrecovered material, was, therefore, 56%. A pyrolysis at 535° increased the conversion to 45% but did not increase the yield. The reported yield for basic hydrolysis was 64%.[12]

One may conclude that, because of the saving of time and material as well as the adaptability to large quantities of material, the ketone cleavage of acetoacetic esters by pyrolysis is preferable to the conventional basic hydrolysis in many cases. It is particularly useful if the desired ketone is fairly water soluble or the starting ester contains a branched substituent.

The extension of this pyrolytic method to the production of other acids and their derivatives will be reported separately.

EXPERIMENTAL[17]

Pyrolysis of ethyl α-n-butylacetoacetate (I). Ethyl α-*n*-butylacetoacetate (I), b.p. 108–110° (14 mm.), n_D^{25} 1.4263

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[12] W. B. Renfrow and A. Renfrow, *J. Am. Chem. Soc.*, **68**, 1901 (1946).

[13] J. T. Adams, B. Abramovitch, and C. R. Hauser, *J. Am. Chem. Soc.*, **65**, 552 (1943).

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[15] H. Hibbert and J. A. Timm, *J. Am. Chem. Soc.*, **45**, 2438 (1923).

[16] M. S. Schechter, N. Green, and F. B. La Forge, *J. Am. Chem. Soc.*, **71**, 3165 (1949).

[17] The authors are indebted to Dr. Mary H. Aldridge and Miss Kathryn Gerdeman for the microanalyses. All melting points are corrected.

[reported b.p. 109–112° (15 mm.),[12] n_{D}^{20} 1.4283[18]], was prepared in an 80% yield by the method of Renfrow and Renfrow[12] by the use of potassium *tert*-butoxide as the condensing agent and *n*-butyl bromide as the alkylating agent. At the rate of 0.6 g. per minute, 202 g. (1.075 moles) of the acetoacetic ester I was added dropwise to a Vycor combustion tube packed with $^1/_8$-in. Pyrex helices and externally heated at 525°, as described previously.[11] Charring was minimized by the introduction of a slow stream of oxygen-free nitrogen at the top of the column. The pyrolysate was condensed in a 6-in. spiral condenser and collected in a side-arm flask cooled in a Dry-Ice bath. (In preliminary runs to determine the proper temperature for the pyrolysis the noncondensable gases were conducted through an Ascarite tube, and the extent of pyrolysis was determined from the amount of absorbed carbon dioxide.) The pyrolysate, without any further treatment, was fractionally distilled through an 8-in., helix-packed column to yield 72.1 g. (59%) of methyl *n*-amyl ketone (IV), b.p. 79° (70 mm.), n_{D}^{25} 1.4065 [reported[19] b.p. 151° (760 mm.), n_{D}^{20} 1.4086], and 33.2 g. (17% recovery) of the starting ester I. The yield of IV, based on unrecovered I, was 71%.

The methyl *n*-amyl ketone (IV) was further characterized by conversion to its semicarbazone, m.p. 125° (reported[19] m.p. 125°).

Pyrolysis of ethyl α-isopropylacetoacetate (V). Ethyl α-isopropylacetoacetate (V), b.p. 99.5–102° (26 mm.), n_{D}^{25} 1.4216 [reported b.p. 96–98° (20 mm.),[20] n_{D}^{20} 1.4240[21]], was prepared in a 70% yield by the method of Hauser[20] by the alkylation of acetoacetic ester with isopropyl alcohol, except that the time of the addition of the boron trifluoride was increased to 6 hr. and larger quantities were used. By use of the same procedure and apparatus described above, 203 g. (1.18 moles) of V was added dropwise to the pyrolysis tube heated at 525° at the rate of 0.6 g. per minute. Fractional distillation of the pyrolysate through an 8-inch, helix-packed column produced 83.4 g. (71%) of methyl isobutyl ketone (VI), b.p. 114–115°, n_{D}^{25} 1.3949 (reported[22] b.p. 114–120°, $n_{\mathrm{D}}^{23.5}$ 1.3952[23]), and 26.4 g. (13% recovery) of the starting ester V. The yield of VI, based on unrecovered V, was, therefore, 82%.

The methyl isobutyl ketone was further characterized by conversion to its semicarbazone, m.p. 134° (reported[23] m.p. 132–133°).

Pyrolysis of ethyl α-cyclohexylacetoacetate (VII). Ethyl α-cyclohexylacetoacetate (VII), b.p. 146–148° (21 mm.), n_{D}^{25} 1.4570 [reported[13] b.p. 146–148° (20 mm.)], was prepared in a 32% yield by the alkylation of acetoacetic ester with cyclohexanol.[13] At the rate of 0.5 g. per minute, 98.5 g. (0.465 mole) of VII was pyrolyzed at 525° in the same pyrolysis apparatus described above. Fractional distillation of the pyrolysate through an 8-in., helix-packed column produced 46.4 g. (72%) of cyclohexylacetone (VIII), b.p. 87–88° (19 mm.), n_{D}^{5} 1.4499 [reported[14] b.p. 83–85° (13 mm.)], and 8.8 g. (9% recovery) of starting ester VII (slightly contaminated with a high refracting impurity). The yield of VIII, based on unrecovered VII, was 79%.

The cyclohexylacetone also was converted to its semicarbazone, m.p. 166–167° (reported[13] m.p. 166°).

Pyrolysis of ethyl α-allylacetoacetate (IX). Commercial ethyl α-allylacetoacetate (IX) (Benzol Products Co.) was fractionated to yield reasonably pure IX, b.p. 89.5–90° (9 mm.), n_{D}^{25} 1.4370 [reported[16] b.p. 96–97° (14 mm.), n_{D}^{26} 1.4365]. At 540°, 52 g. (0.306 mole) of IX was pyrolyzed over a period of 90 min., as described above. Fractionation of the pyrolysate produced 16 g. (54%) of allylacetone (X), b.p. 76–77° (125–130 mm.), n_{D}^{25} 1.4195 (reported[8] b.p. 127–128°, n_{D}^{25} 1.4174). From a second pyrolysis at 510° of 70 g. (0.41 mole) of IX in 110 min. were obtained 19.7 g. (50%) of allylacetone (X), b.p. 72° (105–110 mm.), n_{D}^{25} 1.4195, and 14 g. (20% recovery) of starting material. In the latter pyrolysis the yield of X, based on unrecovered IX, was 63%.

The allylacetone was further characterized by conversion to its 2,4-dinitrophenylhydrazone, m.p. 107–108° (reported[8] m.p. 107–108°).

Pyrolysis of ethyl α,α-diethylacetoacetate (XI). By a modification of the procedure of Renfrow,[22] 144 g. (0.88 mole) of ethyl acetoacetate was alkylated with ethyl bromide. If the alkylation was carried out in two steps without purification of the intermediate ethyl α-ethylacetoacetate, mixtures of products were eliminated and 90 g. (55%) of ethyl α,α-diethylacetoacetate (XI), b.p. 90–92° (9 mm.), n_{D}^{25} 1.4311 [reported[22] b.p. 96–99° (13–14 mm.)], was obtained. After 77 g. (0.413 mole) of XI had been pyrolyzed at 500° over a period of 2.25 hr. under the same conditions described above, the pyrolysate was fractionally distilled through an 8-in., helix-packed column to yield 15.3 g. (33%) of 3-ethyl-2-pentanone (XII), b.p. 134–139°, n_{D}^{25} 1.4078 (reported[22] b.p. 135–139°), and 27 g. (35% recovery) of the starting ester XI. The yield of XII, based on unrecovered XI, was, therefore, 50%.

Pyrolysis of ethyl α,α-di-n-butylacetoacetate (XIII). Ethyl α,α-di-*n*-butylacetoacetate (XIII) was prepared by the method of Renfrow and Renfrow[12] with the exception that the reaction mixture was heated at 80° for 5 hr. after the addition of the butyl bromide to insure complete reaction with the fivefold increase in the quantities of reagents. Thus, alkylation of 186 g. (1 mole) of acetoacetate with *n*-butyl bromide in the presence of potassium *tert*-butoxide gave 162 g. (67%) of ethyl α,α-di-*n*-butylacetoacetate (XIII), b.p. 146–147° (20 mm.), n_{D}^{25} 1.4373 [reported[12] b.p. 146–149° (18 mm.)]. Pyrolysis of 70.1 g. (0.29 mole) of XIII over a period of 1.5 hr. at 490° through the apparatus described, followed by fractionation through an 8-in., helix-packed column, gave 16 g. (33%) of 3-butyl-2-heptanone (XIV), b.p. 85–88° (8 mm.), n_{D}^{25} 1.4270 [reported[22] b.p. 104–107° (12 mm.)], and 28.8 g. (41% recovery) of the starting ester XIII. The yield of XIV in this case, based on unrecovered XIII, was 56%.

A second pyrolysis of 69.5 g. (0.29 mole) of XIII over a period of 1.5 hr. at 535° produced 20.3 g. (45%) of XIV, b.p. 86–89° (10 mm.), n_{D}^{25} 1.4269.

The 3-butyl-2-heptanone (XIV) was further characterized by conversion to its semicarbazone, m.p. 108–109° (reported[22] m.p. 109°).

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