run, the ester was reduced in an enamel-lined pot fitted with reflux condenser, dropping funnel and an efficient stirring device. The yield was 41–47% of fractionated phenylethyl alcohol distilling at 116–118° under 25 mm. pressure. Phenylacetic acid was recovered from the liquors, giving a total recovery of 82–85%. The phenylethyl alcohol was purified by treatment with calcium chloride as described by Hesse and Zeitschel.[10]

Recently a paper in an Italian journal[11] has described a modification of this Bouveault and Blanc reduction of ethyl phenylacetate to phenylethyl alcohol. The new method employs calcium shavings as well as sodium in the reduction, and it is claimed that a yield of 65% of the alcohol is obtained and also phenylacetic acid recovered.

Summary

Benzyl cyanide may be obtained in a yield of 76% from benzyl chloride and sodium cyanide mixture. Stirring is an important factor in the yield. Phenylacetamide may be recovered from the extraction wash-waters.

Ethyl phenylacetate may be prepared in a yield of 72% from benzyl cyanide or from phenylacetamide by a single-step hydrolysis and esterification with sulfuric acid and alcohol.

The ester on reduction with sodium and absolute alcohol in the presence of toluene as a diluent gives phenylethyl alcohol in a yield of 47%. Unreduced phenylacetic acid may be recovered and re-employed for the preparation of the ester. The efficiency of this step is 85%.

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NOTE

The Ketenic Decomposition of Ketones; Acetylacetone, Diacetyl and Pinacolin.—Three ketones, acetone, methylethyl ketone and diethyl ketone, have thus far been subjected to pyrogenic decomposition. All have been found to decompose into gaseous products giving either ketene or methyl ketene[1] in various yields. The decompositions of three other ketones, acetylacetone, pinacolin and diacetyl have been studied in the present investigation.

Acetylacetone is unusually interesting, inasmuch as there are three possible ways by which decomposition to ketenes might occur.

$$CH_3COCH_2COCH_3 \longrightarrow CH_2{=}C{=}O + CH_4 + O{=}C{=}CH_3 \qquad (1)$$
$$CH_3COCH_2COCH_3 \longrightarrow CH_3{-}CO{-}CH{=}C{=}O + CH_4 \qquad (2)$$
$$CH_3COCH_2COCH_3 \longrightarrow CH_4 + O{=}C{=}C{=}C{=}O + CH_4 \qquad (3)$$

It is apparent that with the elimination of methane, either ketene, acetyl ketene, or carbon suboxide are possible residues. The reaction products of these three substances with aniline, namely, acetanilide, aceto-acetani-

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[10] Ref. 4 a. The calcium chloride addition compound is washed with petroleum ether, then decomposed with water and the alcohol regained by extraction with ether.

[11] Lewinsohn, *Riv. ital. ess. profum.*, **4**, 102 (1922); *Abstr. Chem. ind.*, **9**, 553 (1923); *C. A.*, **17**, 2031 (1923).

[1] Hurd and Cochran, This Journal, **45**, 515 (1923). Hurd and Kocour, *ibid.*, **45**, 2167 (1923). Hurd, *ibid.*, **45**, 3095 (1923).

lide and malonanilide are compounds with sufficiently variant properties so that the identification of any or all of them would be a simple matter. Acetanilide alone, of the three, was found. This indicates that ketene alone is formed. It even eliminates the possibility of a transient existence of carbon suboxide, because this compound is known to be quite stable at high temperatures. It is prepared in good yields by pyrogenic methods.[2] Concerning acetyl ketene, admittedly, little is known of its behavior at high temperatures, but there is no reason to assume its formation in this reaction. If ketene and methane are the two fundamental products of decomposition, Reaction 1 indicates that the central carbon atom of acetylacetone is the one which is expelled as methane.

Acetylacetone was an interesting compound to study for another reason. When acetone is pyrogenically decomposed, ketene and methane are known to be the products of decomposition. It has usually been considered, and correctly so as will be proved, that the methane molecule came from one acetone molecule. It is not inconceivable, however, for some of the methane molecules to have come from the interaction of two acetone molecules. If so, acetylacetone would be the intermediate product:

$$CH_3CO{-}CH_3 + H{-}CH_2COCH_3 \longrightarrow CH_3COCH_2COCH_3 + CH_4 \qquad (4)$$

Acetylacetone has never been observed in this reaction. In fact, no appreciable amounts of material boiling higher than acetone are ever encountered. This would indicate one of two things. Either acetylacetone is not formed as an intermediate product, or if formed it is decomposed at once. Were the latter view correct, acetylacetone should give even better yields of ketene than acetone itself, and none of it should escape decomposition. Such was not found to be the case. Following the pyrogenic decomposition, a considerable quantity of acetylacetone was recovered unchanged. The yield of ketene, although considerable, was much less than would have been obtained similarly with acetone. Thus, it seems established that acetone is decomposed almost exclusively into simpler compounds by the influence of heat, there being no evidence to support the intermediate existence of the more complex acetylacetone. Contrariwise, the evidence seems to point to the fact that acetone may be an intermediate product when acetylacetone is decomposed. Ketene would be the other product.

$$CH_3COCH_2COCH_3 \longrightarrow CH_2{=}C{=}O + CH_3COCH_3 \qquad (5)$$

A low-boiling liquid, presumably acetone, was isolated in this reaction.

The percentage yield of ketene is based upon Reaction 1 and not upon Reaction 5, for two reasons. First, the quantity of low-boiling material in the condensate (acetone) was slight. Second, at 700°, the yield of ketene from acetylacetone dropped to a small value. Since this is the

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[2] Ott and Schmidt, *Ber.*, **55B**, 2126 (1922).

optimum temperature[3] for the production of ketene from acetone, it is illogical to assume that acetone is a major product of the reaction.

Pinacolin, the second ketone in this series, contains a $CH_3—CO—$ group, as does acetone. Differing from acetone, however, the tertiary carbon to which the group is linked makes it impossible for methane to be eliminated as a primary decomposition product. Pinacolin is an interesting ketone, therefore, to study from the standpoint of ketene fission. Both ketene and dimethyl ketene appear to be possible, although improbable, products of decomposition: $(CH_3)_3CCOCH_3 \longrightarrow (CH_3)_3CH + O{=}C{=}CH_2$; or, $(CH_3)_3CCOCH_3 \longrightarrow (CH_3)_2C{=}C{=}O + CH_3—CH_3$.

Experimentally, the pinacolin was destructively decomposed into gaseous products, but no dimethyl ketene was found, and less than 2% of ketene was noted. Ketene may have been formed in accordance with the first equation. It must be kept in mind, however, that dimethyl ketene may have been formed and decomposed, by a secondary reaction, to ketene. A very similar occurrence was noted in the formation of both methyl ketene and ketene by the pyrogenic decomposition of diethyl ketone. The former only[4] is explicable as a primary decomposition product. However, the case of pinacolin differs, since no dimethyl ketene was observed; with diethyl ketone, some methyl ketene was apparent.

From this work with pinacolin, it can be inferred that no ketone with the carbonyl group attached to a tertiary carbon will prove suitable for ketene production. This immediately eliminates the aromatic ketones, such, for example, as acetophenone.

The last ketone to be investigated was diacetyl. There has been recorded no previous work with α-diketones upon which to base an analogy. The two conceivable plans by which ketene elimination could take place are: $CH_3COCOCH_3 \longrightarrow CH_2{=}C{=}O + CO + CH_4$, and $CH_3COCOCH_3 \longrightarrow 2CH_2{=}C{=}O + H_2$. The yields of ketene formed in this decomposition are based upon the first equation, inasmuch as it seems more plausible. If acetone is regarded as an intermediate product, the yield of ketene should be less than from acetone itself. Such was the experimental observation.

Experiments.—The acetylacetone and the pinacolin were of good quality. They were both redistilled before use. The diacetyl was impure. Its boiling point range was from 80° to 120°. It was fractionated, and the portion which boiled below 92° was employed. It was a clear, yellow liquid.

The apparatus was the same as that used by the authors[3] in the determination of the optimum conditions for the preparation of ketene from acetone. Ketene was estimated by its reaction with aniline. Acetanilide was found to precipitate from pure aniline in a less objectionable manner than from an ethereal solution of aniline. A minor difference in the apparatus was the substitution of a salt-bath[2] for the boiling water-bath. The temperature of the bath was maintained about 25–40° warmer than the boiling point of the ketone in question.

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[3] Hurd and Tallyn, This Journal, **47**, 1427 (1925).

[4] Hurd, *ibid.*, **45**, 3096 (1923).

The temperature limits for ketene production from acetylacetone[5] in yields above 10% are 610° and 650°. The maximum yield of 16.7% was obtained at 635°, in which experiment the diketone was introduced at a rate of 2–2.5 cc. per minute. At 585° and at 700° the yields were less than 5%. In the various runs, between one-tenth and four-tenths of the original volume of acetylacetone suffered decomposition into gaseous products. The condensate was largely acetylacetone, but in addition it contained small amounts of lower- and of higher-boiling material. There was a tendency, both with acetylacetone and to a less extent with pinacolin, for much material to condense in the end of the combustion tube before reaching the condenser. This difficulty was eliminated by heating that portion of the tube gently with a free flame.

With pinacolin, the first two runs at 605° and at 665° gave such insignificant yields of ketene that the acetanilide was not worked up in either case. It was introduced at the rate of 3 cc. per minute. At these temperatures, more than two-thirds of the pinacolin was recovered. At 705°, most of the pinacolin was decomposed into gaseous products when it was introduced at 1 cc. per minute. The yield of ketene was between 1.5 and 2%.

With diacetyl, yields of ketene which ranged bewteen 10.8 and 14.5% were produced at 605–625°. This is considerably below the temperature (700°) found to be best for ketene production from acetone, but about the same as that from acetylacetone. At more elevated temperatures, the yield dropped considerably. For example, at 675° the yield was observed to be 3.3%.

The similarity of the decomposition of these two diketones, one alpha and one beta, is quite marked. There was no evidence that other ketenes than ketene itself were formed in these pyrogenic reactions.

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NEW BOOKS

Les Actualités de Chimie Contemporaine. (**Current Chemistry.**) Published under the direction of A. HALLER, Professor of the Faculty of Sciences, at the University of Paris. Vol. III. By A. ORÉKOFF, P. PASCAL, FRÉDÉRIC SWARTS, CH. COURTOT, G. DUPONT and R. LOCQUIN. Librairie Octave Doin, 8, place de l'Odéon, 1925. 326 pp. 14 figs. 12 × 19 cm. Price, unbound, 12 francs.

This book, the third volume of a series, presents six essays by the authors above mentioned upon these respective subjects: The Theory of Variable Affinity; Diamagnetism and Chemical Constitution; The Significance of Atomic Constants; The Chemistry of Indene; Different Turpentine Oils; The Dialkyl Ethinyl Carbinols.

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The second volume (1924) presented articles upon micro-analysis, atomic structure, molecular refraction and dispersion, anthraquinone, mydriatics and myatics and optical rotation.

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[5] Some preliminary work on the pyrogenic decomposition of acetylacetone was performed by Mr. S. J. Wayo.