sequent removal of the ether was crystallized from cyclohexane to give 10 g. or a 66.5% yield of ester which melted at 89°.

Anal. Calcd. for $C_{20}H_{17}O_2N$: N, 4.62. Found: N, 4.78.

A 3-g. sample of the methyl N,N-diphenyl-*p*-aminobenzoate was hydrolyzed (in accordance with the conditions described above with the *m*-ester), and gave a quantitative yield of **N,N-diphenyl-*p*-aminobenzoic acid** which melted at 202° after crystallization from acetic acid.

Anal. Calcd. for $C_{19}H_{15}O_2N$: N, 4.84. Found: N, 4.85 and 4.82.

Methyl N-Phenyl-*p*-aminobenzoate.—A mixture of 75 g. (0.3 mole) of iodobenzene, 7.5 g. (0.05 mole) of methyl *p*-aminobenzoate, 13.8 g. of anhydrous potassium carbonate, 0.5 g. of potassium iodide, 1 g. of copper bronze, and 40 cc. of nitrobenzene was heated at 200° for six hours. After removal of the nitrobenzene and the excess of iodobenzene by steam distillation, the oil obtained from the ether extract of the residue was crystallized from methanol to give 3 g. or 27% of the ester melting at 115°.

Anal. Calcd. for $C_{14}H_{13}O_2N$: N, 6.17. Found: N, 6.20.

One gram of the ester was hydrolyzed (under conditions previously described with the diphenylamino esters) to give a quantitative yield of **N-phenyl-*p*-aminobenzoic acid** which melted at 156° after crystallization from acetic acid or ethanol.

Anal. Calcd. for $C_{13}H_{11}O_2N$: N, 6.57. Found: N, 6.64.

Metalation of Diphenylmethylcarbinol.—An ether solution of 19.8 g. (0.1 mole) of diphenylmethylcarbinol and three equivalents of *n*-butyllithium was refluxed with stirring for forty-eight hours and then carbonated by solid carbon dioxide. From the acidic product was isolated 8.62 g. of oily crystals melting between 160–200°. Two crystallizations from ethanol gave 4.7 g. or 17.3% of the **lactone of diphenylmethylcarbinol-2,2′-dicarboxylic acid** melting at 211–212°.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.6; H, 4.47. Found: C, 71.4 and 71.7; H, 4.39 and 4.37.

Metalation of Triphenylcarbinol.—Metalation of triphenylcarbinol, in essential accordance with earlier directions[1] but with 4 molecular equivalents of *n*-butyllithium, gave a 57.7% yield of the lactone of triphenylcarbinol-2,2′-dicarboxylic acid, in addition to a 32% recovery of triphenylcarbinol.

Summary

Metalation of triphenylamine by *n*-butyllithium involves the meta position, and not the ortho position as was the case with an earlier series of representative nitrogen compounds. N,N-Diphenyl-*m*-aminobenzoic acid prepared for identification of the reaction product is readily synthesized from diphenylamine and methyl *m*-iodobenzoate (followed by hydrolysis), whereas the use of the corresponding *m*-iodobenzoic acid is unsatisfactory.

Metalation of diphenylmethylcarbinol, followed by carbonation, gives the lactone of diphenylmethylcarbinol-2,2′-dicarboxylic acid.

Ames, Iowa Received July 31, 1940

[Contribution from the Laboratories of the Shell Development Company]

The Catalyzed Cleavage of Diacetone Alcohol and Other Ketols and Unsaturated Ketones[1]

By S. H. McAllister, Wm. A. Bailey, Jr., and C. M. Bouton

In the course of an investigation of the chemical properties of ketols, a series of experiments was made on the catalytic vapor phase reactions of diacetone alcohol. It was found that a solid phosphoric acid type catalyst caused the cleavage of the diacetone alcohol to acetic acid and isobutylene, and since no previous work had been reported on this cleavage at the time the subject was being studied, the reaction was subjected to a rather thorough investigation which was extended to include analogous reactions of other ketols and unsaturated ketones.

Experimental

General Procedure.—The experimental work was carried out in a gas-fired catalytic furnace using a 32 × $^3/_4$″ stainless steel catalyst tube. The catalyst in the form of 6–8 mesh particles occupied the center 42 cc. of the tube, the rest being packed with glass balls. Fresh catalyst was used for each experiment. The temperature gradient through the tube was measured by means of a sliding thermocouple; the reaction temperature was arbitrarily taken as the average temperature over the catalyst bed. Typical temperature profiles are shown in Fig. 1.

The ketol or unsaturated ketone was fed by means of nitrogen pressure directly to the furnace. The products were cooled to room temperature to remove the normally liquid material, the gases were scrubbed with water to remove acids, acetone, or ketene which might be carried over, and the isobutylene or propylene was collected in carbon dioxide-cooled receivers. Permanent gases were metered, but no significant amounts were obtained.

The silica-phosphoric acid catalyst used in the earlier experiments was Universal Oil Products Company commercial olefin polymerization catalyst. It contained 60.4% total phosphorus as phosphorus pentoxide and 25%

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[1] Presented at the Baltimore meeting of the American Chemical Society. April, 1939.

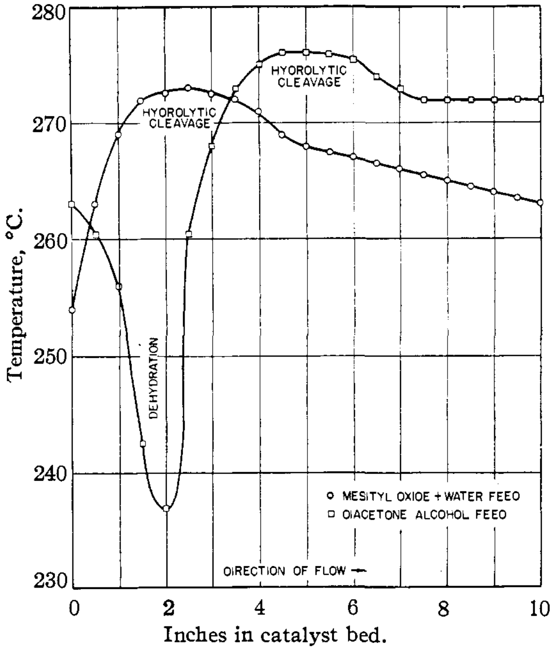

Fig. 1.—Temperature gradient over catalyst bed in vapor-phase cleavage.

free phosphoric acid (H_3PO_4) (titratable in ice water). The catalyst was later modified by treating with water to reduce its polymerization activity. After drying for fifteen hours at 110° the modified catalyst contained 57.0% total phosphorus as phosphorus pentoxide and 5% free phosphoric acid. The effect of this treatment on the activity of the catalyst is shown in Table I.

TABLE I

REACTIONS OF DIACETONE ALCOHOL IN THE VAPOR PHASE; EFFECT OF CATALYSTS

Catalyst volume, 42 cc.

Reactor packed with	Silica phosphoric acid	Modified silica-phosphoric acid
Average temperature, °C.	265	265
Feed rate, vol. of liquid feed/vol. of catalyst/hr.	1.4	1.4
Feed, grams	164.7	156.5
Product, g.	163.0	155.0
Product, mole per cent. converted to		
Isobutylene	75.0	84.5
Diisobutylene	2.8	0.2
Polyisobutylene (as diisobutylene)	3.7	..
Acetic acid	84.5	84.5
Acetone	6.7	9.6
Mesityl oxide	9.2	5.2

Reaction of Diacetone Alcohol.—The diacetone alcohol used (obtained from Shell Chemical Company) was redistilled at reduced pressure, the fraction boiling in the range 67–69° (19 mm.) being taken for the experimental work (d^{20}_4 0.9378, n^{20}_D 1.4213).

The products from the cleavage were analyzed as follows: samples were taken of the liquid products and of the contents of the water scrubber which was used to absorb the acetic acid or ketene carried over and these were titrated for acetic acid. In general, less than 5% of the total acid was obtained in the scrubber. The liquid products and water in the scrubber were combined and fractionally distilled in a glass column corresponding to about 6 theoretical plates. The dissolved isobutylene was collected in a carbon dioxide-cooled receiver and weighed. The fraction boiling between 55 and 80° was analyzed for acetone by the method of Bryant and Smith,[2] the results being expressed as carbonyl values. Any diisobutylene or hydrocarbon present in this intermediate fraction was isolated by treating a sample with an excess of sodium bisulfite and centrifuging in a Babcock bottle. The next fraction, boiling above 80°, contained the mesityl oxide and water azeotrope (boiling point 91.8°, 65% mesityl oxide by weight). The amount of mesityl oxide found was corrected for the small amount of acetic acid present as determined by titration. The residue consisted of acetic acid and any higher boiling ketones formed in the reaction. In several instances the acid was dehydrated with benzene and obtained as glacial acid.

The isobutylene collected in the carbon dioxide-cooled receivers was of over 98% purity as determined by absorption in 65% sulfuric acid.

Using the modified cleavage catalyst a series of experiments were made to determine the effect of varying the temperature and feed rate in the range of 225–300°. The results of this study are shown in Fig. 2.

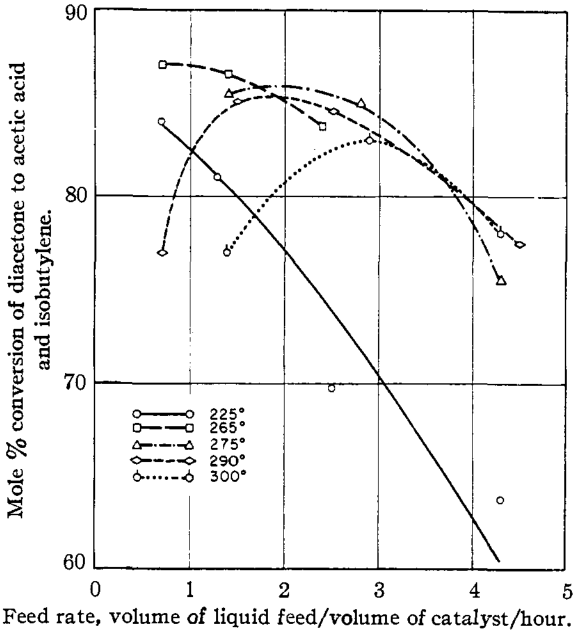

Fig. 2.

Reaction of Mesityl Oxide.—The mesityl oxide used was prepared by the dehydration of the diacetone alcohol with sodium acid sulfate at 90–100°, and was redistilled through an efficient column. The portion used for the experiments distilled at 128.4–129.7° (d^{20}_4 0.8541 and n^{20}_D 1.4445).

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(2) Bryant and Smith, THIS JOURNAL, 57, 57 (1935).

The products were analyzed by the procedure described above. No attempt was made to isolate the ketene formed; its formation was evident however from the fact that in contrast to the diacetone alcohol experiment essentially all of the acetic acid was found in the water scrubbers and not in the liquid product trap, hence the acid was produced by reaction of ketene and water in the scrubbers. Over 90% of the product collected in the primary receiver was mesityl oxide, boiling range 128–130°. With mesityl oxide feeds the catalyst rapidly lost its activity due to the formation of a tarry resin on the surface. Thus the conversion varied throughout a run. For example, in one run at 300° at a liquid feed rate of 0.9 volume per volume of catalyst space per hour the conversion to ketene (recovered as acetic acid) and isobutylene was 36% during the first hour, 13% during the next four hours, and 10% during the last two hours. The average yield was about 40% based on the mesityl oxide consumed.

In order to study reaction mechanism experiments were also made in which water was added to the feed. The product resembled the diacetone cleavage product (see Table II).

Reaction of 4-Hydroxy-2-pentanone.—4-Hydroxy-2-pentanone was made by condensation of acetone with acetaldehyde at 10° using solid lime as catalyst. The crude ketol, after filtration to remove lime, was fractionally distilled. The fraction selected boiled at 174–177° (d^{20}_4 0.9679 and n^{20}_D 1.4299).

In a typical experiment, 176 g. of the ketol was passed over the cleavage catalyst at 265° with a liquid feed rate of 1.4 volumes per volume of catalyst per hour, a sample of the product in the primary receiver was titrated for acidity, and the balance was distilled. Small amounts of acetaldehyde and acetone were recovered, as well as 73 g. of 2-penten-4-one (after drying its azeotrope with water over anhydrous sodium sulfate, b. p. 121–122°).

Of the product collected in the carbon dioxide-cooled trap, 3% was soluble in potassium hydroxide solution (probably acetaldehyde) and 95% was soluble in 98% sulfuric acid but insoluble in 65% acid (propylene).

The catalyst was covered with a resinous material at the end of the run. About 45% of the hydroxy ketone was converted apparently to acetic acid and propylene, 5% to acetone and acetaldehyde, and most of the balance was dehydrated to 2-penten-4-one.

Reaction of 3-Hydroxy-2-butanone.—The 3-hydroxy-2-butanone used was prepared from 3-chloro-2-butanone by hydrolysis with aqueous sodium carbonate at 90–100°. The ketol was recovered from the aqueous product by ether extraction and was distilled. The material boiling at 142–144° (d^{20}_4 1.0117 and n^{20}_D 1.4190) was selected for experimental purposes.

A total of 127.5 g. of the ketol was passed over the catalyst at 265° at a liquid feed rate of 1.6 volumes per volume of catalyst per hour. Titration of the product showed 4% conversion to acid, as acetic acid, and 25% of unreacted ketol was recovered by distillation. Approximately 1300 cc. of an olefinic gas boiling below −70° also was obtained. The principal reaction was apparently dehydration to methyl vinyl ketone, a part of which resinified on the catalyst.

Reaction of C_8-Ketol.—The C_8-ketol was made by condensation of methyl ethyl ketone in the presence of soda lime at 10° using the apparatus described by McAllister and Bullard[3] and maintaining the kettle temperature at 110°. The fraction used boiled at 77–78° at 5–6 mm. (d^{20}_4 0.9277 and n^{20}_D 1.4358); its carbonyl value was 0.691 mole per 100 g.

A total of 89 g. of C_8-ketol was passed over the modified catalyst at 260°, using a liquid feed rate of 1.1 volumes per volume of catalyst per hour. All the product was recovered in the primary receiver. Upon distillation, two hydrocarbon fractions were obtained, one of 9 g. boiling at 31–34°[4] (bromine number,[5] after redistillation, of 232 g. per 100 g. indicating C_5H_{10}) and the other boiling at 68–71°.[6] The second fraction contained some methyl ethyl ketone which was removed by treatment with sodium bisulfite, and the bromine number of the 2.5 g. remaining hydrocarbon was 187 g. per 100 g., indicating C_6H_{12}. Both the hydrocarbons dissolved readily in 65% sulfuric acid and are probably tertiary olefins. The presence of acetic acid in the product was demonstrated by the fact that the fraction boiling between 108 and 140° contained 1.47 equivalents of acid per 100 g. Ten grams of propionic acid, b. p. 141°, 95% by titration, was recovered as well as 49 g. of C_8-unsaturated ketone, boiling range 165–167°.

Thus approximately one-fourth of the C_8-ketol was cleaved to acids and olefins, about 7% was converted to methyl ethyl ketone, and the balance was dehydrated to C_8-unsaturated ketone.

Reaction of C_8-Unsaturated Ketone.—The C_8-unsaturated ketone was obtained by dehydration of C_8-ketol with sodium acid sulfate at 90–100°; after redistillation it boiled in the range 165 to 168° (d^{20}_4 0.8552 and n^{20}_D 1.4517). Its molecular weight in benzene was 126 and its carbonyl value was 0.792 mole per 100 g.

Seventy grams of C_8-unsaturated ketone was cleaved on modified catalyst at 305°, with a liquid feed rate of 1.1 volumes per volume of catalyst per hour. The product from the furnace was quenched in a small amount of water, to avoid dimerization of methylketene by immediately converting it to propionic acid. Products were analyzed as described for C_8-ketol cleavage products. An amylene (14 g.) and a hexylene (4 g.) were recovered, as well as 14 g. of propionic acid. Evidence for the presence of acetic acid again was found, and 36 g. of the C_8-ketone was recovered unchanged.

Hydrolytic Cleavage of a C_8-Unsaturated Ketone.—270 Grams of a C_8-unsaturated ketone, obtained as by-product in the preparation of C_7 ketone from acetone and methyl ethyl ketone (see below) and having a boiling range of 165–169° after two distillations, was passed over modified catalyst at 265° with a liquid feed rate of 1.6 volumes per volume of catalyst per hour, and at the same time 53 g. of water was passed over the catalyst. In this

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[3] McAllister and Bullard, U. S. Patent 2,130,592 (September 20, 1938).

[4] 2-Methyl-1-butene boils at 31.05° (Sherrill and Walter, This Journal, **58**, 742 (1936)).

[5] An adaptation of the method of Rosenmund, *Z. angew. Chem.*, **27**, 58–59 (1920), in which several determinations are made with varying excess quantities of the pyridine sulfate dibromide, a graph of bromine supplied against bromine consumed is plotted, and an extrapolated value is determined, for which all the bromine supplied is consumed.

[6] The pure high-boiling isomer of 3-methyl-2-butene boils at 70.2–70.5° (van Risseghem, *Bull. soc. chim. Belg.*, **47**, 47 (1938)).

case no hexylene or acetic acid was obtained, but 120 g. of propionic acid, b. p. 140–142°, and 114 g. of an amylene boiling at 30–36° were recovered, as well as 70 g. of C_8-unsaturated ketone, b. p. 165–169°.

A sample of C_7-unsaturated ketone was also cleaved on the catalyst, but in this case the products were not completely identified. The ketone was prepared by condensation of acetone with methyl ethyl ketone at 10° in the presence of soda lime, dehydration of the mixture of ketols with sodium hydrogen sulfate at 90–100°, and fractional distillation of the product. Its boiling range was 147–149° (d^{20}_4 0.8545 and n^{20}_D 1.4447) and its carbonyl value was 0.880 mole per 100 g.

Discussion

The reactions of diacetone alcohol and mesityl oxide were studied most extensively. The results for diacetone (Table I and Fig. 2) show that by using the modified phosphoric acid catalyst polymerization of the isobutylene to diisobutylene is suppressed and excellent yields of acetic acid and isobutylene can be obtained. Furthermore, the catalyst remains active with diacetone alcohol for more than fifty hours. At high feed rates and low temperature, the conversion per pass to acetic acid and isobutylene is somewhat lowered due to the fact that a portion of the diacetone is not cleaved under these conditions, while at the highest temperatures and with low feed rates the conversion per pass is also lowered due to the increased reversion of the diacetone alcohol to acetone as the result of the extended time of contact with the hot metallic surfaces before the diacetone alcohol reaches the catalyst.

While very good yields of acetic acid and isobutylene were obtained starting with diacetone alcohol, it was doubtful whether the reaction proceeded directly to these products in a single step. It was quite possible that the first reaction to occur is dehydration of diacetone to mesityl oxide, followed either by a hydrolytic cleavage of the mesityl oxide or, alternatively, cleavage of the mesityl oxide to ketene and isobutylene and subsequent hydration of the ketene. In order to test the first step of this hypothetical mechanism, mesityl oxide and water, in approximately stoichiometrical proportions, were passed over a sample of the cleavage catalyst under conditions comparable to those employed when using diacetone alcohol. Comparative results are shown in Table II, Expts. 1 and 2. Since the conversion of mesityl oxide and water to acetic acid and isobutylene is even greater than that of diacetone alcohol, it would appear that the first step in the catalyzed cleavage of diacetone alcohol is dehydration to mesityl oxide.

TABLE II

CATALYZED CLEAVAGE OF DIACETONE ALCOHOL REACTION MECHANISM

Catalyst volume, 42 cc.; untreated silica-phosphoric acid catalyst; average temperature, 265°.

Run	1	2	3
Feed, moles			
Diacetone alcohol	1.45	0	0
Mesityl oxide	0	1.52	2.31
Water	0	1.65	3.78
Feed rate			
Vols. of liquid feed/vol. of catalyst/hr.	1.43	1.51	4.83
Moles (of diacetone alcohol or mesityl oxide)/hr.	0.48	0.48	1.38
Product, moles			
Acetic acid	1.21	1.37	2.19
Isobutylene	1.05[a]	1.27[a]	2.08
Diisobutylene	0.022	...	0.046
Mesityl oxide	.12	0.12	.055
Acetone	.17	.03	.02
Recovery of products, mole % of feed			
Acetic acid	84	90	95
Isobutylene	72[a]	84[a]	90
Diisobutylene	3.0	...	4.0
Mesityl oxide	8.3	7.9	2.4
Acetone	5.9	1.0	0.5
Materials balance			
Weight %	98	99	98

[a] Catalyst was dark at end of run, probably due to formation of isobutylene polymers.

Experiments with no water in the feed demonstrated that mesityl oxide is cleaved to some extent, forming ketene and isobutylene[7]

$$(CH_3)_2C{=}CHCOCH_3 \longrightarrow (CH_3)_2C{=}CH_2 + CH_2{=}C{=}O$$

but this reaction was initially much slower than the cleavage of diacetone alcohol, and most of the mesityl oxide was recovered unchanged.

A comparison was then made of the cleavage of mesityl oxide in the presence of an excess of water and with an approximately equivalent amount of water. The results are shown in Table II, Expts. 2 and 3. It will be seen that a very large increase in reaction rate was caused by an increase in concentration of water in the reaction mixture. This is presumptive evidence that hydrolytic cleavage of the mesityl oxide

$$(CH_3)_2C{=}CHCOCH_3 + H_2O \longrightarrow CH_3COOH + (CH_3)_2C{=}CH_2$$

predominates over direct cleavage to ketene

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(7) McAllister and Bailey, U. S. Patent 2,143,489 (Jan. 10, 1939).

and isobutylene followed by hydration of the ketene.[8,9]

Sufficiently accurate data are not available for the precise calculation of the heats of the several reactions, but the dehydration appears to be endothermic and the hydrolytic cleavage of the mesityl oxide to be an exothermic reaction. These conclusions were arrived at by comparison of the temperature gradients over the catalyst bed (taken under comparable conditions) for cleavage of diacetone alcohol and for hydrolytic cleavage of mesityl oxide, as shown in Fig. 1.

A series of other ketols and unsaturated ketones was also cleaved on the catalyst to form organic acids or ketenes (recovered as acids) and olefins. The compounds worked with include 3-hydroxy-2-butanone, 4-hydroxy-2-pentanone, and C_8-ketol and C_8-unsaturated ketones from methyl ethyl ketone. The cleavage reaction therefore appears to be general[10] for α,β-unsaturated ketones and for ketols which dehydrate under the reaction conditions to form α,β-unsaturated ketones.

Other workers[11,12,13] have presented considerable evidence to show that the C_8-unsaturated ketone obtained by condensation of methyl ethyl ketone in the presence of alkaline agents is 3-methyl-3-hepten-5-one. Abbott, Kon and Satchell[11] have further shown that this C_8-ketone contains some of the tautomeric 3-methyl-2-hepten-5-one and that the unsaturated ketone obtained by acidic condensation of methyl ethyl ketone consists of 3,4-dimethyl-3-hexen-5-one and its tautomer 3,4-dimethyl-2-hexen-5-one. Thus it would appear that basic catalysts induce condensation on the methyl group while acidic catalysts cause reaction on the methylene group of methyl ethyl ketone.

Results of cleavage studies on C_8-ketol and C_8-unsaturated ketone indicate that the basic condensation may not be completely selective and that both 3-methyl-3-hydroxy-5-heptanone and 3,4-dimethyl-3-hydroxy-5-hexanone are present in the condensation products of methyl ethyl ketone formed over soda lime. Likewise the C_8-unsaturated ketone apparently contains 3-methyl-3-hepten-5-one and 3,4-dimethyl-3-hexen-5-one, although the latter may be present in small amount and the former probably predominates as would be expected from the work referred to above.

This conclusion was reached because the final products isolated from cleavage of C_8-ketol and C_8-unsaturated ketone were acetic and propionic acids and an amylene and a hexylene. The two hydrocarbons apparently were tertiary in structure and, by their boiling points, appeared to be 2-methyl-1-butene and 3-methyl-2-pentene. If the reactions are strictly analogous to those of diacetone and mesityl oxide, the reaction of the ketol may be written as

$$C_2H_5C(CH_3)OHCH_2COC_2H_5 \longrightarrow$$
$$C_2H_5C(CH_3){=}CHCOC_2H_5 + H_2O \longrightarrow$$
$$C_2H_5C(CH_3){=}CH_2 + C_2H_5COOH$$
$$C_2H_5C(CH_3)OHCH(CH_3)COCH_3 \longrightarrow$$
$$C_2H_5C(CH_3){=}C(CH_3)COCH_3 + H_2O \longrightarrow$$
$$C_2H_5C(CH_3){=}CHCH_3 + CH_3COOH$$

The cleavage reaction might serve as a general method for the determination of the structure of β-ketols and α,β-unsaturated ketones. The final reaction is a hydrolytic fission of the carbon to carbon linkage between the carbonyl group and the substituted vinyl group, yielding an organic acid and an olefin. By identification of these products, a choice can be made among the several structures theoretically possible for the ketone in question. This method of structural determination should be used with discretion, however, since rearrangement or non-catalyzed pyrolysis might give products which would invalidate conclusions based upon the cleavage reaction alone. In dealing with the closely related homologs of diacetone alcohol and mesityl oxide, at least, this method of structural determination should be fairly satisfactory and should serve to fix the position of the carbonyl group.

Summary

1. A new type of fission of diacetone alcohol which produces acetic acid and isobutylene has been studied in some detail.

2. The reaction has been shown to proceed

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[8] A reaction which is essentially the reverse of the hydrolytic cleavage has been studied previously. Kondakow, *J. Russ. Phys.-Chem. Soc.*, **26**, 12, 232 (1894), using zinc chloride as a catalyst, prepared mesityl oxide from isobutylene and either acetyl chloride or acetic anhydride.

[9] During the course of the present investigation, Hardy, *J. Chem. Soc.*, 464 (1938), reported that acetic acid and liquid hydrocarbons, possibly isobutylene polymers, are formed when water and acetone are passed through liquid phosphoric acid at about 200 atmospheres pressure and temperatures of 189° or higher. It was shown that the reaction probably proceeded through mesityl oxide. Likewise in the present investigation some mesityl oxide, acetic acid and isobutylene were formed when acetone was passed over the cleavage catalyst, but the conversion was slight (less than 15%). The advantage of the present procedure, particularly when mesityl oxide and water or diacetone is used, rests upon the fact that acetic acid and unpolymerized isobutylene are obtained in almost quantitative yields.

[10] McAllister, Bouton and Bailey, U. S. Patent 2,148,294, Feb. 21, 1939.

[11] Abbott, Kon and Satchell, *J. Chem. Soc.*, 2514 (1928).

[12] Colonge, *Bull. soc. chim.*, [4] **49**, 441 (1931).

[13] Powell and Secoy, This Journal, **53**, 765 (1931).

through the dehydration of the ketol and subsequent hydrolytic cleavage of a carbon to carbon bond in the unsaturated ketone.

3. The reaction has been applied to other ketols and unsaturated ketones.

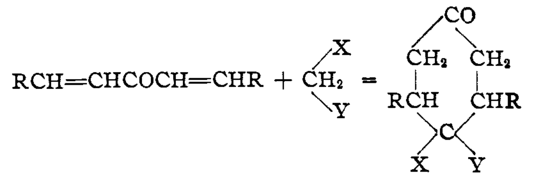
EMERYVILLE, CALIFORNIA RECEIVED MAY 6 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

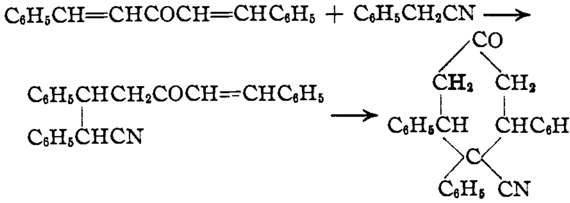
Some Michael Condensations Involving Benzyl Cyanide

BY R. W. HELMKAMP, LEO J. TANGHE AND JOHN T. PLATI

Kohler and co-workers[1,2] have shown that methyl cyanoacetate and methyl malonate under the influence of a small amount of sodium methylate add readily to dibenzalacetone and similar pentadienones to form cyclohexanone derivatives



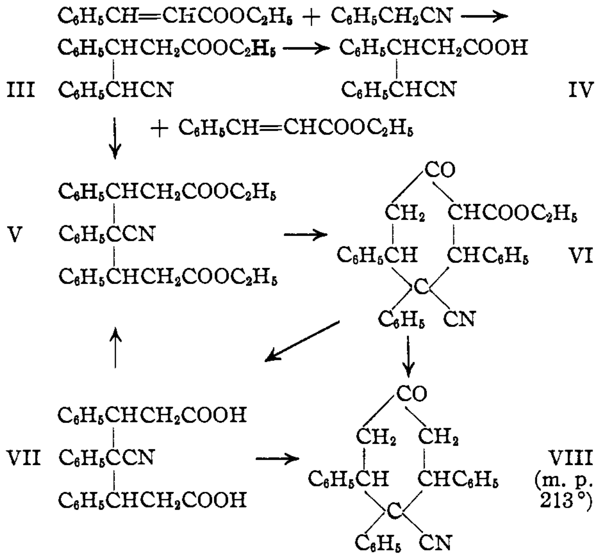
We have found that an analogous cyclic ketone is formed with similar ease when benzyl cyanide and dibenzalacetone are brought together in the presence of the same condensing agent



I II (m. p. 191°)

From the reaction mixture it is possible to isolate, in addition to the cyclohexanone derivative, two compounds isomeric with it. These substances are evidently stereoisomers having the open-chained structure I, for they readily reduce permanganate and are transformed, when dissolved in hot ethyl alcohol containing a trace of sodium hydroxide, into the saturated cyclic compound II. No open-chained addition products have ever been detected in the reactions of methyl cyanoacetate with pentadienones irrespective of the condensing agent used. Similarly, when methyl malonate adds to pentadienones in the presence of sodium methylate, the only condensation products which can be isolated, unless special precautions are taken, are the cyclohexanone derivatives.

Our object in condensing benzyl cyanide with dibenzalacetone was to compare the cyclohexanone II with the structurally identical ketone VIII formed in the following reaction sequence.



The formation of the products III and VI by the action of sodium ethylate on a mixture of benzyl cyanide and ethyl cinnamate was first reported by Erlenmeyer[3] and the structures of these compounds were later investigated by Avery.[4] Although the trimolecular open-chained addition product V has not been isolated from the condensation reaction, it can be assumed, as has been suggested by Avery, to be the precursor of the β-keto ester VI. He prepared V by the esterification of the pimelic acid VII, obtained by hydrolysis of VI, and he showed that the ester is reconverted into VI when treated with sodium ethylate.

On reinvestigating the condensation of benzyl cyanide with ethyl cinnamate, we were able to isolate a hitherto unreported product, which proved to be a stereoisomer of the ester III obtained by Erlenmeyer and Avery. Both compounds yield the same acid IV on hydrolysis.

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[1] Kohler and Helmkamp, THIS JOURNAL, **46**, 1018 (1924).

[2] Kohler and Dewey, *ibid.*, **46**, 1267 (1924).

[3] Erlenmeyer, *Ber.*, **33**, 2006 (1900).

[4] Avery, THIS JOURNAL, **50**, 2512 (1928).