Summary

The addition products obtained by the action of phenyl, *o*-tolyl, *p*-tolyl and *p*-bromo mustard oils on diethylmalonate condense with hydroxylamine and hydrazine to form, respectively, isoxazoles and pyrazoles.

MEDFORD HILLSIDE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE KETENIC DECOMPOSITION OF KETONES. KETENE AND METHYL KETENE

BY CHARLES DEWITT HURD

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Undoubtedly, the best way to prepare ketene is to decompose acetone vapors at high temperatures. Recently, it has been demonstrated that ketene may be prepared in a similar manner, but with poorer yields, from methylethyl ketone. It was considered probable that methyl ketene would also be formed in this reaction, but there seemed to be no positive evidence for such an occurrence.[1]

Ketene was identified as acetanilide, its reaction product with aniline. Methyl ketene would have formed propionanilide. This was not isolated, but there was found an unidentified crystalline product that melted at 80°, about 25° lower than the melting point of propionanilide. A similar low-melting toluidine reaction product was observed. One purpose of the present investigation was to establish the identity of these substances.

A second problem with which this paper deals was to ascertain whether or not methyl ketene was decomposed by heat. An opinion was expressed by Hurd and Kocour[2] that methyl ketene may actually have been prepared in their experiment, but that it may have decomposed at the temperature to which it was exposed. In order to answer this question, it was approached from two angles. First, an apparatus was built which heated the ketone vapors for a briefer period of time than formerly. The heating unit of this consisted of an electrically heated platinum filament, described below. If methyl ketene is susceptible to heat, an apparatus of this type should result in an augmented yield of methyl ketene. It seems probable that a short combustion furnace instead of the long one employed formerly, might also produce an increased yield of methyl ketene. This idea has not been tried experimentally as yet, however.

In the second place, a study was made of the ketenic decomposition of diethyl ketone. Because of its symmetrical structure, this ketone should

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[1] (a) Hurd and Kocour, THIS JOURNAL, **45**, 2167 (1923). For the preparation of ketene from acetone, see (b) Hurd and Cochran, *ibid.*, **45**, 515 (1923); also, a footnote to the article by Hurd and Kocour.

[2] Ref. 1a, p. 2168.

give as a primary decomposition product, methyl ketene: $CH_3—CH_2—CO—C_2H_5 \longrightarrow CH_3—CH{=}CO + C_2H_6$. There is no chance for other ketenes to be formed, except as decomposition products of the methyl ketene. Therefore, it bears upon the question to study this reaction and to study the fate of the methyl ketene.

The general results may be conveniently classified under three headings: (1) comparison of results due to the change of apparatus; (2) the identity of the low-melting aniline (or toluidine) reaction product, noted in the paper of Hurd and Kocour; and (3) the behavior of diethyl ketone towards heat.

1. Acetone vapors give a better yield of ketene with the former apparatus, namely, the long combustion furnace. Methylethyl ketone, on the contrary, gave with the present platinum wire apparatus both a better yield of ketene, identified as acetanilide, and also a larger quantity of the 80° material. No work was done with diethyl ketone in the former type of apparatus. This substance was decomposed by the hot platinum wire filament, however, to produce both ketene and methyl ketene in comparatively high yields. This is discussed in more detail below.

Diethyl ketone formed a considerable quantity of higher-boiling condensation products, and very little of the original ketone could be recovered in the distillate. In this respect, it differed from acetone and methylethyl ketone. With diethyl ketone, also, a larger carbon deposit was formed in the apparatus.

2. The 80° material was shown to be a mixture of acetanilide and propionanilide. This was indicated by its appearance and by its solubility characteristics. It was conclusively demonstrated by tests and by analysis. A mixture with identical properties was prepared from pure acetanilide and pure propionanilide. To form it, merely recrystallization of these 2 anilides from appropriate solvents was necessary. Similarly, the low-melting substance formed when toluidine was used in the place of aniline was found to be a mixture of aceto- and propiono-toluidides. Both of these mixtures appeared homogeneous, both melted completely within 0.5°, and both solidified rapidly when cooled a few degrees below the melting point. Several recrystallizations from various solvents did not change the melting point. Therefore, it was erroneously thought for a time that the substances might be pure chemical individuals. That they are mixtures, however, is now settled definitely.

3. It will be recalled that methyl ketene alone was anticipated in the decomposition of diethyl ketone. However, both ketene and methyl ketene were shown to be present. It appears rather obvious that ketene could not have been a primary decomposition product of diethyl ketone. Preferably, ketene must have been formed by the action of heat upon methyl ketene, which is a primary decomposition product. This would

indicate that the methyl ketene molecule will rupture at the single bond, $CH_3—CHCO$, to form ketene and ethylene. Undoubtedly, the molecule also is ruptured at the double bond, $CH_3CH=CO$, to form butylene, or its decomposition products, and carbon monoxide. Both of these decompositions necessarily diminish the yield of methyl ketene.

The explanation that ketene is formed from methyl ketene is substantiated by a comparison of the relative yields of ketene and methyl ketene from the 2 ketones, methylethyl ketone and diethyl ketone. With methylethyl ketone, both acetanilide and propionanilide were formed as reaction products of the ketenes, but propionanilide could not be isolated as such. Diethyl ketone, however, must have given rise to a greater relative ratio of methyl ketene to ketene, because in this case it was possible to isolate propionanilide in the pure state by fractional recrystallization. The relatively lower yield of ketene from diethyl ketone is to be expected because it is formed only as a result of a secondary reaction, whereas two effects conspire to diminish the yield of methyl ketene from methylethyl ketone. The first is the fact that both ketene and methyl ketene are formed concurrently, and the second is that methyl ketene, once formed, is decomposed by heat. As was explained above, the relative yield of ketene is somewhat enriched by this decomposition.

Methyl ketene has been prepared previously by the action of zinc shavings upon α-bromopropionyl bromide.[3] The yield was small. Therefore, the present method is interesting since it is the only other method available by which methyl ketene may be obtained. It possesses the disadvantages that methyl ketene alone is not produced. However, it is anticipated that modifications of the experimental procedure may be found to eliminate the secondary reaction by which ketene is formed.

Experimental Part

Purification of the Three Ketones

The acetone was distilled, refluxed with a small quantity of potassium permanganate, and redistilled. The methylethyl ketone was the commercial product, purified by several fractional distillations, and was the same material as that used by Hurd and Kocour.[1a] The diethyl ketone was obtained from manufacturers who claimed for it the highest purity. The claim was an optimistic exaggeration; nevertheless, by fractionation, a good portion was obtained which distilled between 102° and 103.5°.

Apparatus

The apparatus was built in 4 units, the first of which was the *decomposition bulb*. This, except for minor details, was similar to the apparatus used by Ott and Schmidt[4] for the preparation of carbon suboxide from diacetyltartaric anhydride. It was blown from

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[3] Staudinger, *Ber.*, **44,** 535 (1911).

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

76mm. Pyrex tubing. Such differences in detail as were adopted are as follows. The openings of the 2 glass tubes through which the copper wires entered the apparatus were made gas tight in the following manner. A copper wire was fused[5] to each end of a solid brass rod, 2 cm. long and of the same diameter as the glass tube. One of the wires entered the glass tube and was pulled snugly so that the brass rod touched the glass. This permitted an air-tight seal to be made simply by covering the glass and brass with a piece of rubber tubing. The loose end of this copper wire was sealed to an end of the platinum wire filament. The copper wire, fastened to the other end of the brass rod, was connected with the electric current. The other opening was sealed in identical fashion.

The platinum wire filament was 0.3 mm. in diameter and about 165 cm. in length. The top of the glass support upon which this wire was mounted terminated with a glass handle to which the copper wires were fastened. Instead of employing an annular rubber washer between the ground glass joint of the upper and lower halves of the apparatus, the seal was effected by stopcock grease. Rubber would be essential if a constant high vacuum were to be maintained. That was not essential, nor was it desired in this experiment.

The second unit of the apparatus was a *condensing flask* for the distillate. This was a double-necked, round-bottomed flask, identical with the second unit of Ott's apparatus.[4]

The *reaction tube* formed the third unit. This consisted of a large U-tube,[6] one arm of which was larger than the other. The small arm was connected to the second unit. The tube was of such capacity that 50 cc. of liquid filled the bottom and extended a short distance up the sides.

The fourth unit was a manometer and a *vacuum oil pump*. The vacuum was desirable in the apparatus to remove oxygen, to make any possible leaks inward ones, and to maintain a constant, rapid gaseous flow.

Details of Manipulation and General Remarks

Previous to a run, there were placed in the decomposition bulb the desired amount of ketone, and in the reaction tube an excess of aniline (or toluidine) dissolved in xylene. The 4 units were then assembled and the condensing flask was surrounded by crushed ice. After the evacuation of the whole apparatus to about 20 mm., the electric current was turned on, and the resistance adjusted so that a current of 6 amperes was maintained. An asbestos board was inserted between the first two units. The pressure in the apparatus gradually rose to 300–400 mm. as the reaction progressed. This gain in pressure was characteristic of every run. It prevented a too rapid volatilization of the ketone. The duration of the runs, when a 50cc. sample of ketone was used, was about 2 hours. It was necessary in some cases to apply heat beneath the decomposition bulb to volatilize the final portion of ketone.

The first experiments were conducted in an atmosphere of carbon dioxide, but inasmuch as the results did not differ from those obtained when the original atmosphere before evacuation was air, this procedure was disregarded.

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[5] The copper-to-brass, and the copper-to-platinum joints are readily made with the flame of the blast lamp. The oxidized copper surface is reduced, while hot, by thrusting it into methanol.

[6] When 2 tubes were used, the second was considerably smaller than the first.

Decomposition of Acetone

Fifty cc. of acetone was vaporized and heated in the decomposition bulb during the course of 2 hours. The resistance wire was heated by a current of 6 amperes; 28 g. of aniline was used in 2 reaction tubes, 24 g. in the first, and 4 g. in the second. The aniline was diluted with xylene, about 28 cc. being used in the first tube and 6 cc. in the second. It was found that no more than traces of ketene escaped reaction in the first tube.

Nine cc. of distillate was collected in the condenser. For the most part, this was undecomposed acetone.

The xylene and the excess of aniline were removed by distillation. The acetanilide that remained was cooled and crystallized from a mixture of benzene and ligroin; m. p., 113–114°; yield, 7.5 g., or 9.8%, based upon the acetone that was not recovered.

There was some carbonization in the decomposition bulb.

Decomposition of Methylethyl Ketone

Reaction with Aniline.—Fifty g. of methylethyl ketone was poured into the first bulb. Somewhat over 21 g. of freshly distilled aniline, diluted with 50 cc. of xylene was inserted in the reaction tube. Only a negligible amount of product was formed in a second reaction tube, placed in series with the first. The current used was 6 amperes; the duration of the experiment was 110 minutes.

Thirteen g. of distillate was collected, 14 cc. of which distilled between 76° and 83°. One cc. of foully smelling liquid remained. This did not solidify at —10°, nor was a solid obtained when part of it was evaporated. A solid was expected because crystals were noticed in the receiving arm of the condensing flask, early in the run; later, these dissolved in some of the liquid distillate. The same occurrence was noted in the decomposition of acetone.

The xylene was evaporated from the reaction product, following which the excess of aniline was removed by steam distillation. A non-volatile oil remained that solidified when the flask was cooled. This solid was filtered out and dissolved in hot alcohol. The aniline evidently had been imperfectly removed, for the addition of an equal volume of water caused the separation of oily crystals. These were collected and discarded; any possible reaction product contained therein was not calculated in the final yield. The filtrate was evaporated upon a watch glass nearly to dryness, and the crystals were collected upon a filter; weight, 2.6 g. The solid was insoluble in cold ligroin, only moderately soluble in cold carbon tetrachloride or in boiling ligroin (110°), and soluble in ethyl acetate. It was divided into 2 fractions by successive recrystallizations from these solvents or from appropriate mixtures of them. The more insoluble fraction was acetanilide; it melted at 110–112°. No purer product could be obtained by further crystallization.

By repeated recrystallizations of the more soluble portion, a fraction was obtained that melted sharply at 79.5–80°. The crystals were needle-shaped, and appeared to be perfectly homogeneous. In spite of the sharp melting point and the apparent homogeneity this material was proved to be not a chemical individual, but a mixture of acetanilide and propionanilide.

Analyses. Subs., 0.1368: CO_2, 0.3578; H_2O, 0.0892. Subs., 0.1551: N, 14.5 cc. (33.9°, 738.6 mm. (30.5°)), 40% KOH used. Calc. for $C_6H_6N—COCH_3$: C, 71.1; H, 6.71; N, 10.4. Calc. for $C_6H_6N—COC_2H_5$: C, 72.5; H, 7.45; N, 9.40. Found: C, 71.4; H, 7.28; N, 9.8.

An empirical formula, calculated from the observed values, is $C_{3.5}H_{10.3}ON$. This is seen to be between the two formulas, C_8H_9ON and $C_9H_{11}ON$, required for acetanilide and propionanilide. In the above reaction, these two anilides must have been prepared from the reactions of ketene and methyl ketene with aniline. Further analytical proof that the gaseous mixture of ketene and methyl ketene was formed is given below in the case of the toluidides.

To secure more evidence to confirm the belief that the 80° material was a mixture, an attempt was made to prepare such a mixture from the pure reagents. Slightly more acetanilide, m. p., 114°, than propionanilide, m. p., 103–104° (see p. 3101), was dissolved in a mixture of carbon tetrachloride and ligroin. The crystals that formed when the mixture was cooled were collected by filtration, and disregarded; m. p., 85–90°. The filtrate, however, was evaporated and the residue crystallized from boiling ligroin. Needle-shaped crystals resulted that melted sharply at 79–80°. These were identical in appearance with those formed in the work with methylethyl ketone. A mixed-melting-point determination of these two sets of 80° crystals gave 79–79.5°.

The 2.6 g. of reaction product corresponds to a yield of 3.7% if the material is assumed to be entirely acetanilide, or 3.4% if it is assumed to be propionanilide. This percentage is somewhat smaller than the true yield, for some of the reaction product was discarded, as explained above.

Reaction with *p*-Toluidine.—The details of this run were the same as those of the previous one, save that the aniline was replaced by 25 g. of *p*-toluidine. The *p*-toluidine had been previously recrystallized from benzene and ligroin. About 29.5 g. of methylethyl ketone entered the reaction; this was shown by the fact that there was 20.5 g. of distillate.

The xylene and the excess of toluidine were removed from the reaction product by vacuum distillation. The residue solidified quickly when cooled. It was crystallized from a mixture of benzene and ligroin. This material, which was later shown to be a mixture of acetotoluidide and propionotoluidide, weighed 3.2 g. Based upon the unrecovered ketone, this corresponds to a 5.3% yield of acetotoluidide, or a 4.8% yield of propionotoluidide.

The mixture was separated into two fractions both by crystallization from a mixture of carbon tetrachloride and ligroin, and by the use of each of these solvents independently. The more insoluble portion was acetotoluidide; m. p., 144°. The more soluble portion, m. p., 105.5–106°, was shown to be a mixture of acetotoluidide and propionotoluidide. The weight of the former was about 3.6 times that of the latter. Therefore, in this reaction, the ratio of methyl ketene to ketene is small.

Analyses(105.5–106° material). Subs., 0.1438: CO_2, 0.3846; H_2O, 0.0997. Subs., 0.1629: N, 13.4 cc. (32.5°, 744.3 mm. (31°)), 40% KOH used. Calc. for $C_7H_8N—COCH_3$: C, 72.5; H, 7.45; N, 9.40. Calc. for $C_7H_8N—COC_2H_5$: C, 73.6; H, 7.98; N, 8.60. Found: C, 73.0; H, 7.75; N, 8.73.

An empirical formula calculated from the experimental values is $C_{9.8}H_{12.4}ON$. Acetotoluidide is $C_9H_{11}ON$ and propionotoluidide is $C_{10}H_{13}ON$.

Decomposition of Diethyl Ketone

Forty g. of diethyl ketone and 14 g. of freshly distilled aniline were placed in the apparatus. The aniline was diluted with 50 cc. of xylene. Six amperes of current was used, and the duration of the experiment was 100 minutes. There was more carbonization on the surface of the decomposition bulb in this experiment than was the case with acetone or with methylethyl ketone, and very little recoverable ketone was found in the distillate. Instead, higher-boiling condensation products were formed.[7] The 13 g. of liquid thus obtained distilled as follows: 2 g. between 100° and 110°; 2 g. between 110° and 124°; 7 g. between 124° and 150°; and 2 g. of higher-boiling residue. Thus, little

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[7] Various reactions of diethyl ketone are discussed by Samec, *Monatsh.*, **28**, 739 (1907).

of the ketone which did not decompose into gaseous products escaped decomposition. Twenty-seven g. may have undergone ketenic decomposition.

The xylene and the aniline were removed from the reaction product by vacuum distillation. The residue, which solidified as it cooled, was dissolved in hot carbon tetrachloride and was precipitated by ligroin; weight, 4.8 g. This corresponds to a yield of 10.3% assuming that the material is propionanilide, or 11.3%, assuming that the material is acetanilide. These yields are based upon 27 g. of diethyl ketone. It may be fairer to base the yield upon 40 g., since very little of the ketone was recovered as such. In this case the yields become 7.0% or 7.6%, respectively.

Both propionanilide, m. p., 101.5–102.5°, and acetanilide, m. p., 110–112°, were isolated from the reaction product. The solvents used were carbon tetrachloride and ligroin. Lower-melting mixtures of these two compounds were also obtained in the fractionation.

Propionanilide was prepared for purposes of comparison by refluxing 5 g. of aniline and 8 g. of propionic acid for 5 hours. A white solid was obtained when this liquid mass was poured into 100 cc. of cold water; weight, 6.5 g. A further yield of 0.7 g. was obtained by evaporation of the water. The solid, after recrystallization from a mixture of carbon tetrachloride and ligroin, melted at 103–104°. A mixture of this with equal parts of the 101.5–102.5° material melted at 102–103.5°.

No idea of the relative amounts of acetanilide and propionanilide was obtained. At least, there was enough propionanilide to be easily isolated, but it seemed that there was a greater quantity of acetanilide in the mixture.

Summary

A further study of the ketenic decomposition of acetone and of methyl ketone has been made. Diethyl ketone, which has not been investigated heretofore in this connection, also was found to decompose ketenically. All three ketones give ketene as a decomposition product. Both methylethyl ketone and diethyl ketone produce methyl ketene, the larger relative yield coming from the latter.

A heating unit is described that differs from the apparatus used in the earlier work. It gives better results with methylethyl ketone and with diethyl ketone; with acetone, however, this is not the case.

Heat apparently ruptures the molecule of methyl ketone at the single bond to give ketene. This conclusion is reached because both ketene and methyl ketene were observed as decomposition products of diethyl ketone, whereas methyl ketene alone is accountable for as a primary decomposition product. The greater yield of methyl ketene when the ketone vapors were heated for a short period of time, in preference to a longer period, is further confirmation of the destructive effect of high temperatures upon methyl ketene. Decomposition undoubtedly occurs at the double bond as well as at the single bond, not to give another ketene as decomposition product, however.

Methyl ketene has been prepared by only one other method. Therefore, the present procedure, in spite of certain drawbacks, should prove to be of value.

URBANA, ILLINOIS