[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Ketene and its Dimer

BY CHARLES D. HURD AND ARTHUR S. ROE

Toward some hydroxyl-containing compounds ketene behaves as an efficient acetylating agent but toward others it is either non-reactive or sluggish. In the latter category are phenols and tertiary alcohols. Van Alphen[1] reported no reaction at room temperature between ketene and phenol, but Rice and co-workers[2] showed that the acetylation proceeded quantitatively at the boiling point. With *t*-butyl alcohol, there was no acetylation at room temperature[3] and the reaction was very slow at its boiling point.[2]

In view of the established catalytic effect[4] of a trace of sulfuric acid or *p*-toluenesulfonic acid on the analogous acetylation of carbohydrates, it was decided to try these catalysts on the reaction between ketene and phenol or tertiary alcohols. The results were striking. With only a trace of either acid it was found possible to effect complete conversion at room temperature of phenol to phenyl acetate, *t*-butyl alcohol to *t*-butyl acetate,[5] and *t*-pentyl alcohol to *t*-pentyl acetate.

Ketene and Aldehydes.—Ketene, in the presence of potassium acetate, is known to react with aldehydes like benzaldehyde[6] and cinnamic aldehyde[3] to yield anhydrides of unsaturated acids. Benzaldehyde yields cinnamic acetic anhydride, as follows

$$C_6H_5CHO + 2CH_2CO \longrightarrow C_6H_5CH{=}CHCOOCOCH_3$$

No such reaction occurs, however, between ketene and butyraldehyde.

Benzaldehyde differs from butyraldehyde in that it has no hydrogen on the α-carbon. Cinnamaldehyde differs in that it is unsaturated on the α-carbon. Acrolein and crotonaldehyde resemble cinnamaldehyde in this respect. Formaldehyde, like benzaldehyde, has no α-hydrogen. If methyl formate may be regarded as an aldehyde because of its CHO group, it also falls in the group of compounds with no α-hydrogen. These four aliphatic compounds—formaldehyde, acrolein, crotonaldehyde and methyl formate—were tested for their reactivity toward ketene. Reaction occurred in all instances, but the substances obtained were unsaturated red oils of high molecular weight (1500–2000).

If the reaction had proceeded like the reaction with benzaldehyde, acrolein would have produced β-vinylacrylic acetic anhydride (I), formaldehyde would have yielded acrylic acetic anhydride (II), and methyl formate would have given rise to methoxyacrylic acetic anhydride (III).

(I) $CH_2{=}CH{-}CH{=}CH{-}CO{-}OCOCH_3$
(II) $CH_2{=}CH{-}CO{-}OCOCH_3$
(III) $CH_3OCH{=}CH{-}CO{-}OCOCH_3$

The course of the reaction was affected little by temperature, for the polymeric products were formed when the reaction was performed at 20° or $-80°$.

Ketene and Formic Acid.—The general reaction of ketene with acids yielding mixed acetic anhydrides[6,7] was applied to formic acid: $HCOOH + CH_2{=}CO \rightarrow HCOOCOCH_3$. Formic acetic anhydride, thus produced, was pure by analysis and possessed the boiling point reported by Béhal[8] who prepared it from acetic anhydride and formic acid.

Graves' patent,[9] which appeared since completion of our work, should be mentioned. He states: "Ketene-containing gases from the pyrolysis of acetone were passed into 101.5 grams of 99% formic acid until the gain in weight was 90 grams. The product was acetoformic anhydride." Presumably acetic formic anhydride was in mind rather than "acetoformic anhydride," which would be $(CH_2COCO)_2O$, the anhydride of acetoformic acid. The substance was not purified by distillation nor characterized by reactions and no claim for it was made in the patent. The only claims were for acetic pyruvic anhydride, made from pyruvic acid and ketene.

Formic acetic anhydride proved to be an excellent formylating agent toward aniline

$$C_6H_5NH_2 + HCOOCOCH_3 \longrightarrow C_6H_5NHCHO + CH_3COOH$$

No acetanilide was produced. Since aniline reacts with acetic benzoic anhydride[7] to yield acetanilide and benzoic acid, this places the phenyl,

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(1) Van Alphen, *Rec. trav. chim.*, **43**, 760 (1924); **44**, 838 (1925).

(2) Rice, Greenberg, Waters and Vollrath, THIS JOURNAL, **56**, 1760 (1934).

(3) Hurd and Williams, *ibid.*, **58**, 962 (1936).

(4) Hurd, Cantor and Roe, *ibid.*, **61**, 426 (1939).

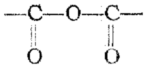
(5) Morey, *Ind. Eng. Chem.*, **31**, 1129 (1939).

(6) Hurd and Thomas, THIS JOURNAL, **55**, 275 (1933).

(7) Hurd and Dull, *ibid.*, **54**, 3427 (1932).

(8) Béhal, *Compt. rend.*, **128**, 1460 (1899).

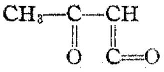
(9) Graves, U. S. Patent 2,135,709, Nov. 8, 1938.

methyl and hydrogen radicals in this decreasing order of electron attraction: $C_6H_5 > CH_3 > H$. This follows because the splitting of the symmetrical  $-\underset{O}{\underset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}-$ group in the mixed anhydrides must be governed by the terminal groups (R or R′ in R—CO—O—CO—R′).

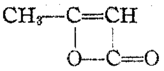
Non-reaction of Ketene and Tetraethyllead.—Ketene was found to be indifferent toward tetraethyllead. After passing 0.3 mole of ketene into 0.11 mole of tetraethyllead, the latter was poured slowly into concd. hydrochloric acid. The ethane evolved measured 2.38 liters (S. T. P.), compared with the calculated 2.4 liters. This non-reaction with ketene is in contrast to its violent behavior toward diethylmagnesium,[3] and its smooth reaction with diethylzinc.

The Dimer of Ketene

The dimer is known to be either acetylketene (IV) or β-crotonolactone (V) or, more probably, an equilibrium mixture of them, because on ozonolysis[3] it yielded pyruvic aldehyde. Since electron readjustment is all that is necessary to maintain the equilibrium between IV and V, they are resonance isomers. This should cause lessened chemical reactivity and it is well known that acetylketene is more sluggish than ketene.


$CH_3-\underset{O}{\underset{\|}{C}}-\underset{C=O}{\underset{\|}{CH}}$

IV



V

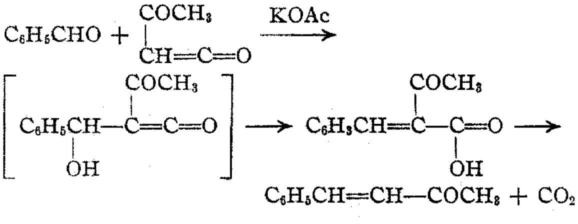
Parachor.—In the earlier work[3] the parachor of acetylketene was reported to be 182. This value was redetermined on material of greater purity and was found to be 188.0. Since that part of the calculated parachor which is contributed by the atoms alone is 127.6, the structural correction factor for the functional group involved (IV $\rightleftarrows$ V) is 60.4.

Enolization.—Acetylketene is a ketone as well as a ketene, so it is capable of enolization. Grignard and Blanchon[10] showed that enolization could be induced by branched-chain Grignard reagents, the amount of enolization being registered by the quantity of hydrocarbon evolved. Kohler and Thompson[11] showed that in some instances one might mistake reduction by the Grignard reagent for enolization, in which case propylene would be formed. The reaction of *i*-propylmagnesium bromide and acetylketene yielded propane, in an amount pointing to 23% enolization. A trace of propylene was present but the gas was chiefly propane.

Pyrolysis.—The pyrolysis of acetylketene at 550° yielded[3] methane, carbon monoxide, carbon, and dehydroacetic acid, but no ketene. It was thought that ketene might be formed at higher temperatures. At 650° over half of the dimer was depolymerized to ketene. As would be expected much gas was formed concurrently.

$$CH_3COCH=C=O \longrightarrow 2CH_2=C=O$$

Acetylketene and Benzaldehyde.—By analogy with the synthesis of cinnamic acid from ketene, benzaldehyde and potassium acetate, one would anticipate the synthesis of benzalacetone from acetylketene. This reaction was found to occur.



Carbon dioxide was evolved copiously and a 31% yield of benzalacetone was obtained.

A similar experiment was performed with carbon suboxide, O=C=C=C=O, which is a diketene,[12] but no reaction occurred. This non-reaction with benzaldehyde in the presence of potassium acetate must be associated with the absence of the —CH=C=O group in C_3O_2.

In view of the fact that ketene and diethylzinc react[3] to produce 2-butanone, it was hoped that acetylketene and diethylzinc might react smoothly. An immediate yellow precipitate formed when diethylzinc was added to acetylketene but in a few minutes this material congealed exothermically to a black tar, too stiff to stir. It was possible to keep the yellow precipitate, however, if toluene or benzene were used as diluents; but no products could be obtained from it by hydrolysis with steam, or with sulfuric acid solution, or with benzoyl chloride. Only tars resulted.

Experimental Part

Ketene was prepared in a ketene lamp[3] which delivered 0.1 mole per hour. A liberal supply of acetylketene ("Diketene") was donated by the Carbide and Carbon Chemicals Corporation through the courtesy of Dr. R. W. Mc-

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(10) Grignard and Blanchon, *Bull. soc. chim.*, **49**, 27 (1931).

(11) Kohler and Thompson, THIS JOURNAL, **55**, 3822 (1933).

(12) This term is not to be confused with the trivial name "Diketene" which is used sometimes for acetylketene. The latter is a monoketene, not a diketene, and in its resonance modification it is not a ketene at all.

Namee. For it, we are deeply grateful. Part of the acetylketene was stored for a year in a glass-stoppered bottle in a refrigerator. It gradually became quite dark in color, but the greater part of the acetylketene was still present as such at the end of the year. Pure acetylketene will leave a residue of dehydroacetic acid if distilled at atmospheric pressure but no such residue occurs on vacuum distillation. The acetylketene was always distilled prior to use, b. p. 43° (28 mm.).

Ketene and Tertiary Alcohols.—To 0.1 mole of *t*-butyl or *t*-pentyl alcohol was added either 1 drop of concd. sulfuric acid or 0.01 g. of *p*-toluenesulfonic acid. Then the stream of ketene was passed in for seventy minutes. Heat developed at once so the reaction was cooled in an ice-bath. The solutions became slightly yellow in color, less color being apparent in the solution containing the toluenesulfonic acid.

The solutions were treated with 10 cc. of 6 *N* sodium hydroxide and washed with 10 cc. of water. Both of these aqueous solutions were extracted with ether, the ether solution being added to the ester layer. The ether solution was dried with potassium carbonate, the ether carefully removed on a water-bath, and the residue distilled. The *t*-butyl acetate was collected at 94–95° and no liquid came over at 82°, indicating that all the alcohol had been esterified. Similarly, the *t*-pentyl acetate was collected at 123–124°, with no distillate at 100°. The yields of esters in all four experiments were uniformly high at 86–89%.

Ketene and Phenol.—To a solution of 9.4 g. (0.1 mole) of phenol in 40 cc. of dry ether was added a drop of concd. sulfuric acid (A) or 0.01 g. of *p*-toluenesulfonic acid (B). Ketene was bubbled through for an hour and a half. It was necessary to cool the reaction to prevent volatilization of the solvent. The solution was yellow at the end of the reaction, more so with A than with B. It was washed with 20 cc. of 6 *N* sodium hydroxide and then with 20 cc. of water. The aqueous solutions were washed with ether, which was added to the ester layer. The ether solution was dried with potassium carbonate. The ether was removed on a water-bath and the product distilled. In both runs, the yield of phenyl acetate, b. p. 190–191°, was 12.1 g. or 89%.

Ketene and Acrolein.—The acrolein used in these experiments contained the trace of hydroquinone (1:1000) which was added as a preservative. Ten grams (0.18 mole) of it with 1.5 g. of anhydrous potassium acetate were placed in a flask fitted with inlet and exit tubes and a mercury-sealed stirrer. Then 0.2–0.3 mole of ketene was passed into the flask. Heat was evolved so an ice-bath was used after the first hour of reaction. The reaction product was a viscous red oil which decomposed to a black tar on attempted distillation at 19 mm. The red oil was soluble in dioxane and in dilute sodium hydroxide. From the alkaline solution acids precipitated an amorphous brown solid which melted between 75–150°.

The red oil was dried for a week in a vacuum desiccator over sulfuric acid. Pure dioxane, kindly furnished by Dr. R. Umhoefer of this Laboratory, was used as a cryoscopic solvent. The apparent molecular weight of the polymer was 1987, since the freezing point lowering caused by dissolving 0.7014 g. in 18.4906 g. of dioxane was 0.089°.

The course of the reaction with ketene was similar at −80°. The reaction mixture changed slowly to a dark red, viscous liquid, then solidified after two hours. This solid melted at room temperature, then decomposed with evolution of gas, and congealed to a red glass. An intractable oily product was formed by addition of the red solid to a solution of aniline in ether.

In two subsequent experiments of the same size at −80°, the red reaction product was treated in one case with ice water, and in the other with 50 cc. of ethyl alcohol.

From the former, 15.5 g. of brown tar separated and from the latter 11 g. of similar product. The material was soluble in acetone, but could not be crystallized from it. Extraction of the tar with ether yielded 1 cc. of oil on evaporation but it contained no β-vinylacrylic acid for none of the tetrabromide (m. p. 160°) was obtained on treatment with bromine.

Ketone and Monomeric Formaldehyde at −80°.—Liquid formaldehyde was prepared[13] by condensing formaldehyde gas in a trap at −80°. To 4 cc. of this liquid was added 0.05 g. of fused potassium acetate, then ketene was passed into the tube for one hour at −80°. The mixture turned yellow at once and became red before the reaction was over. A small portion of the reaction product was removed and allowed to come to room temperature. It turned a darker red and became viscous after a few minutes. Part of the polymer was dried *in vacuo* over sulfuric acid for a week. The freezing point lowering caused by dissolving 0.6140 g. in 17.1042 g. of dioxane was 0.097°. This indicates a molecular weight of 1740.

The remainder of the mixture was kept at −80° and 30 cc. of a solution of bromine in carbon tetrachloride was added. The solution was left at room temperature overnight. The solvent was removed under diminished pressure, leaving a small amount of a red oil which gave a positive halogen test. Three cc. of water was added to the oil without apparent reaction. The water was removed on the steam-bath and the residue extracted with hot benzene. Any dibromopropionic acid would dissolve in this solvent, but only a trace of red tar remained after evaporation of the benzene. No dibromopropionic acid was isolated, which proved that no acrylic acid, as such, was in the reaction mixture.

Ketene and Methyl Formate.—Ketene was passed for seven hours into a stirred mixture of 28.7 g. of methyl formate and 1.5 g. of fused potassuim acetate, the temperature being maintained at −15° by an ice–salt bath. The color change was from yellow to deep red. The final red sirup weighed 55.2 g. On distillation there was obtained 16.8 g. of a mixture of methyl formate and acetone at 42–45°, and 4.1 g. of acetic anhydride at 39° (30 mm.). The latter, with *p*-toluidine, yielded aceto-*p*-toluidide, m. p. 146–147°. There appeared to be considerable decomposition during the distillation.

To perform the reaction at a lower temperature, 8.4 g. (0.2 mole) of ketene was liquefied and distilled slowly into 12 g. (0.2 mole) of methyl formate and 1 g. of fused potassium acetate at −80°. The yellow color appeared at once but the color did not become red as in the other experiment. When all the ketene was introduced the reaction product was an orange solid. When a little of it was brought to

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[13] Spence and Wild, *J. Chem. Soc.*, 338 (1935).

room temperature it melted to a yellow liquid which changed rapidly to the thick red oil mentioned before.

Half of the orange solid was transferred to a flask containing 30 cc. of aniline. The product was a red oil which could not be crystallized or identified.

One-quarter of the orange reaction product from another identical run at −80° was added to water, another quarter to methanol, another to ethanol, and the remainder to 1-butanol. The solutions were kept at 0° for six hours. Orange-brown solids separated in all instances. They were soluble in acetone or dioxane. For purification they were dissolved in acetone and precipitated by petroleum ether. Then the yellow solids were dissolved in dioxane and precipitated by methanol. The melting points of the material from the reactions with water (A), methanol (B), ethanol (C) and butanol (D), respectively, were 71–73°, 67–69°, 66–68°, 64–66°.

Saponification equivalents were determined in the usual manner by heating with standard alcoholic potash. These values were obtained for A–D: 44.5, 48.5, 49.7, 51.5.

Molecular weights were taken cryoscopically in dioxane as before. The values for A, B and C were 1498, 1524, 1533.

Ketene and Crotonaldehyde.—Twenty grams of crotonaldehyde (b. p. 103–104°) and 0.2 g. of potassium acetate were taken. When ketene was introduced heat and a slight coloration developed immediately, so the reaction was cooled in an ice-bath. After three hours the reaction had stopped. The brown reaction mixture was poured into 50 g. of ice. About 22 cc. of a brown liquid separated. It was soluble in acetone or dioxane but was insoluble in benzene, alcohol, ethyl acetate and petroleum ether. The apparent molecular weight of the tar, taken cryoscopically in dioxane as before, was 1761.

Ketene and Formic Acid.—Anhydrous formic acid (13.8 g., 0.3 mole), prepared from the 85% acid by refluxing with phthalic anhydride,[14] was treated with a stream of ketene gas (0.3 mole) freed from acetone vapors. The reaction product was distilled at 19 mm. and 15 cc. of formic acetic anhydride was collected at 33–33.5°: $n^{20}{}_D$ 1.3940; $d^{20}{}_4$ 1.1458.

Anal. Subs. 0.7216, 0.9094. Cc. of 0.0854 *N* base, 190.31, 240.32. Cc. calcd. for $HCOOCOCH_3$, 192.04, 242.01. Per cent. purity, 99.1, 99.3.

Aniline was added to 8 g. of ice-cold formic acetic anhydride. Distillation of the products at 29 mm. yielded 4 g. of acetic acid up to 50°, 2.5 g. of an intermediate fraction, and 9.2 g. of formanilide at 178–179°. The small amount of residue contained no acetanilide, crystallizable from hot water. The formanilide melted at 46°.

Acetylketene

Surface Tension and Parachor.—The capillary rise method of determining the surface tension was used. The radius of the capillary was found to be 0.0219 cm. by using pure thiophene-free benzene as a standard for calibration. Pure water served as a check on this result. Then pure acetylketene was taken. The latter was freshly distilled (b. p. 43.0–43.1° at 28 mm.). The density of this acetylketene was found to be 1.0817 at 25° since 0.8956 cc. weighed 0.9688 g. The data on surface tension are:

Substance	Water	Acetylketene
Temperature, °C.	25	25
Density	0.9971	1.0817
Av. capillary rise, cm.	6.73	2.92
Surf. tension, dynes/cm., found	71.98	33.89
Value in "Int. Crit. Tables"	71.97	...

From this, the parachor, $M\,\gamma^{1/4}/D - d$, is calculated to be 188.0 for acetylketene.

Enolization.[15]—*i*-Propylmagnesium bromide was prepared in 75 cc. of dry *n*-butyl ether from 12.3 g. of *i*-propyl bromide and 2.5 g. of magnesium. Then 4.561 g. of pure acetylketene (in 50 cc. butyl ether) was placed in a 250-cc. three-necked flask fitted with a mercury-sealed stirrer. The exit tube led from the flask through a small vertical condenser to an inverted, brine-filled bottle. The apparatus was swept out with nitrogen, placed in an ice-bath, and 36 cc. of Grignard solution was added slowly until no more gas was evolved. An excess of 4 cc. was then added and the reaction was allowed to come to room temperature while it was stirred for three hours.

The volume of the gas evolved at S. T. P., also corrected for the 40 cc. of Grignard solution, was 286.2 cc. This was 0.0128 mole. Since 0.0543 mole of acetylketene was used, there was 23.6% enolization, assuming that only one carbonyl enolized.

Analysis of the gas revealed only propane, propylene and nitrogen (no CO_2, H_2, O_2, CO). The propylene was 1.8% by volume, as determined by absorption in 83% sulfuric acid. The propane was 21.8% by volume. In duplicate analyses, the ratio of contraction (after combustion of the C_nH_{2n+2}) to absorption (of CO_2 after combustion) was 1.03 and 0.97. For propane this ratio should be 1.

Pyrolysis at 650°.—Acetylketene was introduced slowly by mercury displacement into the top of a vertical Pyrex tube maintained at 650° by automatic control. The effective volume of the tube was 156 cc. The exit gas flowed through two ice-cooled traps, vertically through a water-cooled condenser, and then through two aniline traps. The acetylketene taken was 51.4 g. and that recovered in the trap was 12.6 g. (chiefly acetylketene, but it contained a little dehydroacetic acid). The duration of the experiment was seventy-eight minutes, hence, the contact time was about ten seconds.

There was an indication of 19.8 g. of ketene because 63.5 g. of acetanilide, m. p. 114–115°, was obtained.

Reaction with Benzaldehyde.—A 200-cc. three-necked flask was fitted with a dropping funnel, mercury-sealed stirrer and condenser. Into it was placed 19.8 g. (0.18 mole) of freshly distilled benzaldehyde and 2 g. of fused potassium acetate.

During ninety minutes, 15.7 g. (0.187 mole) of acetylketene was added. Heat was applied to start the reaction, after which the heat generated sufficed to sustain it. A light yellow color soon developed which changed to a dark red. Between 1–1.5 liters of carbon dioxide (proved by lime-water test) was evolved.

The reaction mixture was poured into 50 cc. of dilute

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[14] Pryanishnikov and Shakhova, *J. Gen. Chem.* (U. S. S. R.), **2**, 84 (1932); *C. A.*, **27**, 2672 (1933).

[15] Preliminary work on this was performed by Jonathan W. Williams.

hydrochloric acid. No visible reaction occurred though a heavy oil separated. The aqueous layer was washed with 25 cc. of benzene, which was added to the oil. The solution was placed on a water-bath to remove the solvent, then distilled at 13 mm.

Fraction	Temp., °C.	Wt., g.	Remark
1	to 60	0.52	.....
2	60–63	8.31	Benzaldehyde
3	63–125	0.84	.....
4	125–128	1.94	Benzalacetone
5	128–130	6.44	Benzalacetone
Residue		7.07	

Fraction 2 was identified as benzaldehyde by preparation of the phenylhydrazone, m. p. 154–155° (literature value 156°). Fractions 4 and 5 were identified as benzalacetone. They solidified in the icebox to crystals which melted at 37–38° (literature, 42°); 0.1 g. gave 0.17 g. of benzalacetone phenylhydrazone, m. p. 154–155° (literature, 156–157°). The total yield of benzalacetone was 8.38 g., or 0.0574 mole. Mixed melting point of phenylhydrazones of fractions 2 and 4 was 125–130°.

Summary

Ketene, in the presence of a trace of sulfuric acid or *p*-toluenesulfonic acid, causes complete acetylation of phenol, *t*-butyl alcohol, or *t*-pentyl alcohol at room temperature.

Ketene, in the presence of potassium acetate, reacts with acrolein, crotonaldehyde, formaldehyde (monomer), or methyl formate to yield in all cases complex reaction products of high molecular weight. These reactions proceeded even at −80°.

Formic acid and ketene give rise to formic acetic anhydride which, in turn, reacts with aniline to yield formanilide, not acetanilide.

Ketene does not react with tetraethyllead.

Pyrolysis of acetylketene at 650° brings about depolymerization to ketene.

Toward *i*-propylmagnesium bromide, acetylketene displays 23% enolization.

The parachor of acetylketene was found to be 188 instead of 182 as previously reported.

Acetylketene, in the presence of potassium acetate, reacts with benzaldehyde with the production of benzalacetone and carbon dioxide. No such reaction occurs between carbon suboxide and benzaldehyde.

The product of reaction of acetylketene and diethylzinc is a yellow solid which yielded nothing but tars on hydrolysis or on reaction with benzoyl chloride.

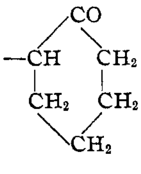
EVANSTON, ILLINOIS RECEIVED SEPTEMBER 16, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, NORTHWESTERN UNIVERSITY]

Preparation and Pyrolysis of Cyclohexanone

BY CHARLES D. HURD, HARRY GREENGARD AND ARTHUR S. ROE

Ordinarily, ketene is prepared by pyrolysis of acetone. A chain mechanism involving radicals has been proposed[1] to explain it. One would predict analogously that cyclohexanone should give rise to ketene because of the three possible radicals (I–III) formed by dehydrogenation of cyclohexanone, ketene and ethylene appear to be plausible products from each. No ketene was observed, however, when cyclohexanone was pyrolyzed in a tube at 700° or in a ketene lamp.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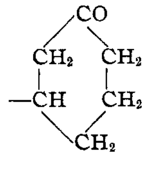
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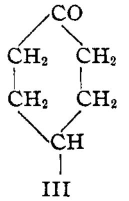
III

The observed products were water, cyclohexadiene, ethylene, carbon monoxide, and small amounts of hydrogen and methane.

When cyclohexanone was refluxed for five days, five-sixths of it was still intact but the remainder condensed to cyclohexylidenecyclohexanone.

An interesting development of the present work was the synthesis of cyclohexane in 60% yield by dehydrogenation of cyclohexanol over copper chromite.

Experimental

Cyclohexanone.—A horizontal Pyrex tube (25 × 2 cm.) was filled with pumice coated with the Adkins copper chromite catalyst, prepared as directed by Dunbar and Cooper.[2] It was heated electrically to 290–310°. The vapor of 150 g. of cyclohexanol was forced through the hot tube during eight hours by dropping the liquid slowly into an attached flask at 220°. The reaction products were condensed, dried with potassium carbonate, and distilled Twelve grams of cyclohexene was collected at 75–85°

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[1] Rice and co-workers, THIS JOURNAL, **53**, 1959 (1931); **56**, 1761 (1934).

[2] Dunbar and Cooper, *ibid.*, **58**, 1053 (1936).