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.

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# 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
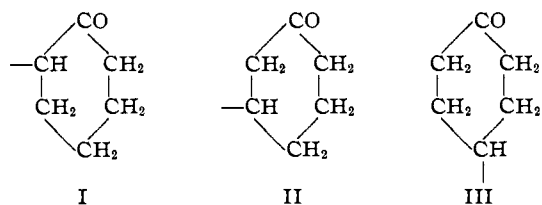
plausible products from each. No ketene was observed, however, when cyclohexanone was pyrolyzed in a tube at 700° or in a ketene lamp.

The observed products were water, cyclohexa-

diene, 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°

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

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

There was 8 g. of an intermediate fraction between 85–155°, then 91 g. of cyclohexanone was collected at 155–156.5°. The residue weighed 30 g. The yield was 60% of the theoretical. The cyclohexanone was identified as the semicarbazone, m. p. 165°.

### Pyrolysis

**By Refluxing.**—Twenty-four grams of cyclohexanone was refluxed for one hundred and fifteen hours. The solution became orange-colored. On vacuum distillation, 20 g. of the ketone was recovered at 60–64° (30 mm.), and 2.5 g. of cyclohexylidenecyclohexanone was collected at 158–162° (30 mm.). The oxime of the latter melted at 147–152°.

**Through Hot Tube.**—During one hour, 24 g. of cyclohexanone was passed through a Pyrex combustion tube heated to 700–725°. The tube was 120 × 2 cm. and was filled with pieces of porcelain. Condensables were removed from the gas stream by a coil condenser, then the gas was passed through aniline. The condensate, on distillation at 85–100°, yielded 1 g. of a mixture of water (droplets visible) and cyclohexadiene. At 150–160°

there was collected 2.5 g. of cyclohexanone (oxime, m. p. 87°). The cyclohexadiene was converted into 1,2,3,4-tetrabromocyclohexane, m. p. 140°, on treatment with bromine in carbon tetrachloride.

No acetanilide was found in the aniline trap; hence, no ketene was formed.

**With Ketene Lamp.**—Ninety grams of cyclohexanone was placed in the ketene lamp[3] and decomposed during one hour. The effluent gas was conducted through aniline. The volume of unabsorbed gas (S. T. P.) was 6.8 liters. No acetanilide was obtained from the aniline trap.

### Summary

Cyclohexanone is formed in good yields by dehydrogenation of cyclohexanol. The cyclohexanone yielded no ketene on pyrolysis at 700° but some cyclohexadiene was identified. Prolonged refluxing gave rise to small amounts of cyclohexylidenecyclohexanone.

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

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# The Reaction of Bromine with Anthracene in Dioxane

BY CHARLES C. PRICE AND CLAY WEAVER

In experiments on the reaction of anthracene with bromine using dioxane as a solvent,[1] it was noted that more hydrogen bromide was evolved than could be accounted for on the basis of bromination of the hydrocarbon, since two-thirds to three-fourths of the bromine consumed appeared as hydrobromic acid after addition of water to the reaction mixture.

As a tentative explanation, it was assumed that the bromination of a mole of anthracene induced the bromination of one or two moles of dioxane by an ionic mechanism. It has been discovered,

however, that the anomalous formation of hydrobromic acid in dioxane, even with material which had been distilled from sodium, was due to the presence of traces of water. In the presence of the basic solvent, the water and bromine react with the anthracene as hypobromous acid, leading to the formation of 9-bromoanthrone (I) and anthraquinone, thus accounting for the high percentage of acid formed. When precautions were taken to exclude atmospheric moisture from freshly dried dioxane, the normal reaction took place.
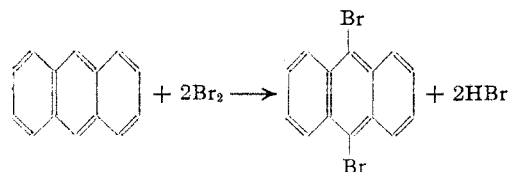




Since this eliminates the evidence for the ionic mechanism suggested by Price and Thorpe[2] for the *cis–trans* isomerization of diethylmaleate in the presence of bromine and anthracene, the alternative atomic–free radical mechanism they suggested is therefore to be preferred, not only from analogy with the photochemical reaction,[3]

(1) Price, THIS JOURNAL, **58**, 1834 (1936).

(2) Price and Thorpe, *ibid.*, **60**, 2839 (1938).

(3) Wachholtz, *Z. physik. Chem.*, **125**, 1 (1929); Schmidt, *ibid.*, **B1**, 205 (1930).