introduced into the reaction chamber very slowly in the course of twelve hours. At the end of the run the gases were analyzed and found to contain 80% carbon dioxide, no unsaturated hydrocarbons, small amounts of oxygen and saturated hydrocarbons (assumed to be methane). About 10 cc. of water-like liquid having an ethereal odor was collected in the liquid air trap. A test for hydrogen peroxide was negative, although a positive test for organic peroxides was obtained. A clean platinum gauze failed to destroy the peroxides. Both the fuchsin–aldehyde test and the "dimedon" reaction were negative. Both the resoninol–sulfuric acid and the U. S. P. tests[17] for methyl alcohol were strongly positive. Formic acid was also found to be present.

In a second run an excess of methane was used and it was allowed to enter the discharge chamber giving a blue-white glow at one end with the pink (water) glow limited to the end of the tube at which the water vapor entered. A volume of 3 liters of methane was used in this run. The gases were not analyzed. About 16 cc. of a liquid was obtained in the liquid air trap, and was found to give the same positive tests as that of the previous run, but in addition it gave a positive iodoform reaction indicating the presence of small amounts of ethanol.

Reaction of Free Hydroxyl Radicals with Isobutylene.—Isobutylene was prepared by the dehydration of *t*-butyl alcohol (80 g.) with oxalic acid (27 g.) and the vapors collected in a trap immersed in acetone–carbon dioxide ice. It was then distilled from the trap by allowing the vapors to pass through a 2-foot vertical column packed with calcium chloride and condensed in another trap to which was attached a stopcock and a ground glass female joint. The isobutylene (10 g.) was introduced into the reaction chamber through the connection E (Fig. 1) by allowing it to evaporate slowly. During the run some isobutylene entered the discharge tube thereby forming purple rings nearer to the reaction chamber while the pink glow (water) persisted in the left half of the discharge tube. At the end of four hours the reaction was stopped and the products condensed in the liquid air trap examined. A liquid (4 cc.) was obtained having a strong odor of formaldehyde. It gave a positive fuchsin–aldehyde test and the formaldimethone prepared from it melted at 188° (cor.). After the removal of formaldehyde the remaining solution gave a strong test for acetone using the sodium nitroprusside reaction.[18] The original liquid also gave a positive test for organic peroxides showing that hydrogen peroxide was probably bound either to formaldehyde or to acetone. The gases were not analyzed.

Summary

1. The reaction between free hydroxyl radicals formed in a glow discharge and methane, ethylene and isobutylene was studied in the gaseous phase.

2. It has been found that free hydroxyl radicals are much more reactive in the gaseous phase than in solution.

3. Methane was mainly converted to carbon dioxide. Other products found were small amounts of peroxides, methanol, ethanol and formic acid.

4. Ethylene was converted mainly to carbon dioxide, small amounts of peroxides, formaldehyde, formic acid and possibly ethylene glycol. With a large excess of ethylene no carbon dioxide was formed, but formaldehyde, formic acid, traces of ethanol and possibly ethylene glycol, acetylene and a solid polymer were noted.

5. With isobutylene, peroxides, formaldehyde and acetone were the chief products detected.

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(17) Reference 16, p. 427.

(18) Reference 16, p. 357.

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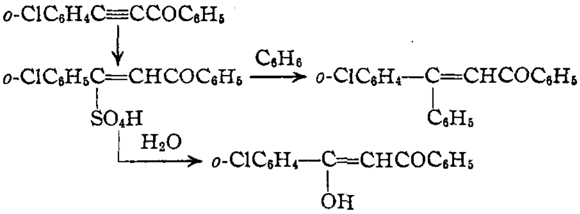
[CONTRIBUTION FROM THE THOMPSON LABORATORY OF THE PHILLIPS EXETER ACADEMY]

The Addition of Benzene to an Acetylenic Ketone

BY CHARLES L. BICKEL AND AUGUSTUS J. FABENS[1]

The literature contains several reports on the reaction of benzene and some of its simple substitution products with α,β-unsaturated ketones. Vorländer and Friedberg,[2] as well as Fuson and co-workers,[3] used a mixture of aluminum chloride and hydrogen halide as the condensing agent, Fuson reporting that these reactions are reversible. Kohler[4] found that benzene adds to chalcone in the presence of sulfuric acid, giving β,β-diphenylpropiophenone as the only identified product. This reaction is also assumed to be reversible,[5] although the nature of the aromatic residues does not permit a study of reversibility in this case.

The reaction of aromatic compounds with the more highly unsaturated acetylenic ketones has not been reported. The present investigation is a study of the reaction of *o*-chlorophenylbenzoyl acetylene with benzene in the presence of sulfuric acid. Two products have been isolated from this reaction, *o*-chlorodibenzoylmethane and β-(*o*-chlorophenyl)-chalcone. The diketone is the sole product when a sulfuric acid solution of the acetylenic ketone is treated with water[6]; thus, the isolation of the diketone in this instance indicates either incomplete reaction with benzene or a reversible reaction. β-(*o*-Chlorophenyl)-chalcone is the product of the net addition of benzene to the acetylenic ketone. A mechanism which is consistent with the known facts is formulated as follows



$$o\text{-ClC}_6\text{H}_4\text{C}{\equiv}\text{CCOC}_6\text{H}_5 \longrightarrow o\text{-ClC}_6\text{H}_5\underset{\text{SO}_4\text{H}}{\underset{|}{\text{C}}}{=}\text{CHCOC}_6\text{H}_5 \xrightarrow{\text{C}_6\text{H}_6} o\text{-ClC}_6\text{H}_4\text{—}\underset{\text{C}_6\text{H}_5}{\underset{|}{\text{C}}}{=}\text{CHCOC}_6\text{H}_5$$

$$\text{SO}_4\text{H} \xrightarrow{\text{H}_2\text{O}} o\text{-ClC}_6\text{H}_4\text{—}\underset{\text{OH}}{\underset{|}{\text{C}}}{=}\text{CHCOC}_6\text{H}_5$$

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[1] A senior in the Phillips Exeter Academy during the school year, 1948–1949.

(2) Vorländer and Friedberg, *Ber.*, **56**, 1144 (1923).

(3) Fuson, Eaton and Black, THIS JOURNAL, **56**, 687 (1934).

(4) Kohler, *Am. Chem. J.*, **31**, 650 (1904).

(5) Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, 1938, p. 585.

(6) Bickel, THIS JOURNAL, **69**, 74 (1947).

Certain observations indicate that the reaction with benzene is not reversible. Reversibility would lead to the formation of dibenzoylmethane and β-phenylchalcone, assuming that the *o*-chlorophenyl group is as easily loosed as the phenyl group.[7] Neither of these compounds was detected in the reaction products. The most conclusive evidence of irreversibility was obtained by treating β-(*o*-chlorophenyl)-chalcone with benzene and sulfuric acid. None of the β-diketone was produced.

The substituted chalcone, like other ethylenic compounds, is soluble in sulfuric acid. The extended period of exposure to the acid appears to convert the chalcone into other products. Thus, as the reaction time is increased in order to decrease the yield of the diketone, the yield of chalcone is decreased. The product or products of this reaction are being investigated and may be reported at a later date.

Attempts to decrease the side-reactions have so far met with no success. The acetylenic ketone was recovered when seventy-five per cent. sulfuric acid was substituted for concentrated sulfuric acid; the use of fuming sulfuric acid decreased the yield of diketone but also materially decreased the yield of chalcone.

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Experimental[8]

Since there were no significant variations in the procedure used in all of the runs, the general procedure is described in detail and the results for all runs are summarized in tabular form.

Concentrated sulfuric acid was added to a solution of *o*-chlorophenylbenzoylacetylene[9] in benzene contained in a 250 ml. glass-stoppered Erlenmeyer flask equipped with a Pyrex-enclosed bar magnet, the magnet being rotated at a rate which assured efficient mixing of the two layers. At the end of the stirring operation, the mixture was poured onto ice, the benzene layer washed with water and the benzene evaporated by a current of air. The residue was taken up in ether, the ether solution washed with water and then shaken with saturated cupric acetate solution. The copper salt of the β-diketone was filtered off, washed, dried, weighed and finally converted to the diketone which was isolated and identified.[10] The filtrate from the cupric acetate treatment was shaken with dilute hydrochloric acid, the ether layer washed with water, dried and concentrated, giving β-(*o*-chlorophenyl)-chalcone or unchanged acetylenic ketone.

TABLE I

SUMMARY OF RESULTS[a]

Time, days	H_2SO_4	Cu salt	Chalcone	Acetylene
2	46	6.30	4.0	None
7	46	5.70	3.55	None
14	46	2.00	0.5	None
4	5	Trace[b]	<0.1	None
3	0.8	None	None	>9.5
3	46[c]	5.56	2.35	None
9	37[d]	None	None	10

[a] Ten grams of acetylenic ketone and 125 ml. of benzene were used in each run. The times are in days; all other figures are weights in grams. [b] Dark green color in the ether layer but no solid copper salt. [c] Twenty-four grams of concentrated sulfuric acid and 22 g. of 30% fuming sulfuric acid. [d] Twenty-eight grams of concentrated sulfuric acid and 9 g. of water.

β-(*o*-Chlorophenyl)-chalcone.—The chalcone is quite soluble in ether, very sparingly soluble in petroleum ether, and crystallizes in sulfur-yellow stout needles melting at 106–107°.

Anal. Calcd. for $C_{21}H_{15}OCl$: C, 79.0; H, 4.74. Found: C, 78.4, 78.8; H, 4.78, 4.80.

Chromic acid oxidation of the chalcone in glacial acetic acid solution gave the calculated quantities of benzoic acid and *o*-chlorobenzophenone. The *o*-chlorobenzophenone, melting at 47°, was identified by comparison with a known sample synthesized by the reaction of phenylmagnesium bromide with *o*-chlorobenzaldehyde and by the subsequent oxidation of the *o*-chlorobenzhydrol to *o*-chlorobenzophenone.

The Reaction of the Chalcone with Benzene and Sulfuric Acid.—A mixture of 10 g. of the chalcone, 125 ml. of benzene and 46 g. of concentrated sulfuric acid was stirred (magnetic stirrer) for one week and then worked up as described above. Cupric acetate gave no evidence of a β-diketone. Three grams of the chalcone was recovered and the residual oil has as yet yielded no solid products.

Summary

o-Chlorophenylbenzoylacetylene reacts with a mixture of benzene and sulfuric acid to give *o*-chlorodibenzoylmethane and β-(*o*-chlorophenyl)-chalcone. The evidence indicates that the benzene reaction is irreversible.

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[7] Fuson (ref. 3) obtained β,β-diphenylpropiophenone by the action of benzene on 2-chlorochalcone.

[8] A magnetic stirrer was used in all of the experiments in which a long period of stirring was required. This made possible the use of a glass-stoppered Erlenmeyer flask and the elimination of the ordinary sleeve type stirrer and the vibration inherent in most stirrers of this type.

[9] Bickel, THIS JOURNAL, **69**, 2135 (1947).

[10] Bickel, *ibid.*, **68**, 866 (1946).