one-unit oxidizing agents can be readily explained on the peroxy-radical theory.

To make the above theory more concrete we append the following hypothetical series of reactions for the autoxidation of hydroquinone:

$$H_2O + C_6H_5O_2^- + O_2 \longrightarrow C_6H_5O_3 + OH + OH^- \quad (1)$$

$$C_6H_5O_3 + O_2 \rightleftarrows C_6H_5O_5 \quad (2)$$

$$C_6H_6O_6 + C_6H_5O_2^- \longrightarrow C_6H_5O_3 + C_6H_5O_4^- \quad (3)$$

$$C_6H_5O_5 + C_6H_5O_3 \rightleftarrows (C_6H_5O_3)_2O_2 \quad (4)$$

$$(C_6H_5O_3)_2O_2 + C_6H_6O_2 \longrightarrow 2C_6H_6O_4 + C_6H_4O_2 \quad (5)$$

$$OH + C_6H_6O_2 + O_2 \longrightarrow H_2O_2 + C_6H_5O_3 \quad (6+7)$$

Assuming equilibrium to be nearly reached in those steps given as reversible, the rate law for this series of reactions is $-d(O_2)/dt = k(CO_2)(C_6H_6O_2)(OH^-)^{3/2}$. By using the first ion $C_6H_5O_2^-$ in reaction 5 the mechanism is applicable to the autoxidation of catechol.

The product of the reaction $C_6H_6O_4$ or its ion can be taken as either a definite substance (Reinders and Dingemans) or as an equivalent mixture of quinone and hydrogen peroxide (LaMer and Rideal). In either case complex condensation products or quinhydrone, depending on the *p*H of the solution, will be formed by reactions with hydroquinone.

Summary

The expression $(-d(O_2)/dt = k(O_2)(C_6H_6O_2)(OH^-)^{3/2})$ obtained by LaMer and Rideal for the rate law of the autoxidation of hydroquinone has been confirmed.

A chain mechanism has been proposed for the reaction. By a change of the state of ionization of the phenol in one of the steps, this mechanism is applicable to the autoxidation of catechol.

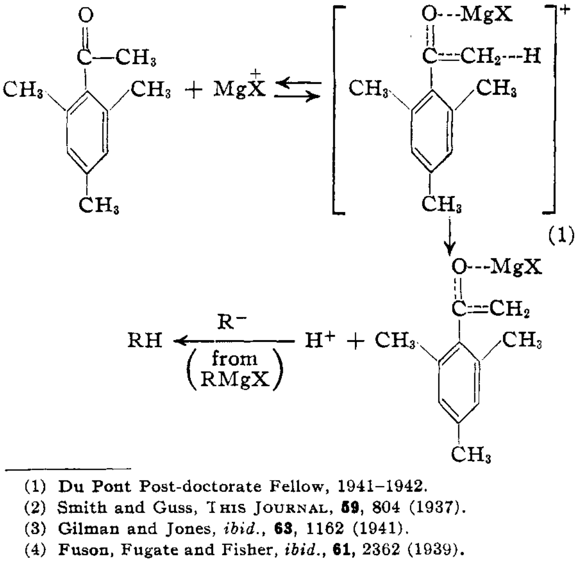
Berkeley, Calif. Received June 11, 1941

[Contribution from the School of Chemistry of the University of Minnesota]

Resonance and the Hindered Carbonyl–Grignard Reaction. I

By Richard T. Arnold, Harold Bank and R. Winston Liggett[1]

It is well known that many sterically hindered ketones (such as acetomesitylene) react with the Grignard reagent to form enolates and hydrocarbons.[2,3,4] This reaction is not necessarily preceded by simple enolization of the ketone. In fact, a more probable mechanism involves the coördination of a solvated halomagnesium cation (MgX^+) with the carbonyl oxygen atom followed by the direct ionization of a proton from the α-carbon atom according to the scheme below.[3]



The thermodynamic stability of such resonating ions as allyl, crotyl, benzyl, etc., should allow them to act qualitatively like the proton in the above type of reaction.

To test this hypothesis we have, for convenience, studied the reaction between allylic esters with sterically hindered carbonyl groups and the Grignard reagent. It was predicted that the reaction between phenylmagnesium bromide and allyl β-isodurylate should take the course shown by equation (2).

Actually allylbenzene was isolated in 67–70% yield and the magnesium halocarboxylate almost quantitatively. *o*-Tolylmagnesium bromide gave *o*-allyltoluene in comparable yield.

This type of cleavage is important only when normal addition to the carbonyl group is exceedingly slow or impossible. Allyl benzoate reacts with phenylmagnesium bromide to give triphenylcarbinol (86%) and small amounts of allylbenzene.[5]

We have now shown that one *o*-methyl group does not greatly interfere with normal addition. Thus allyl *o*-toluate with the Grignard reagent gives the carbinol (68%) and an unresolvable mixture.

In the aliphatic series the reaction of allyl tri-

---

[1] Du Pont Post-doctorate Fellow, 1941–1942.

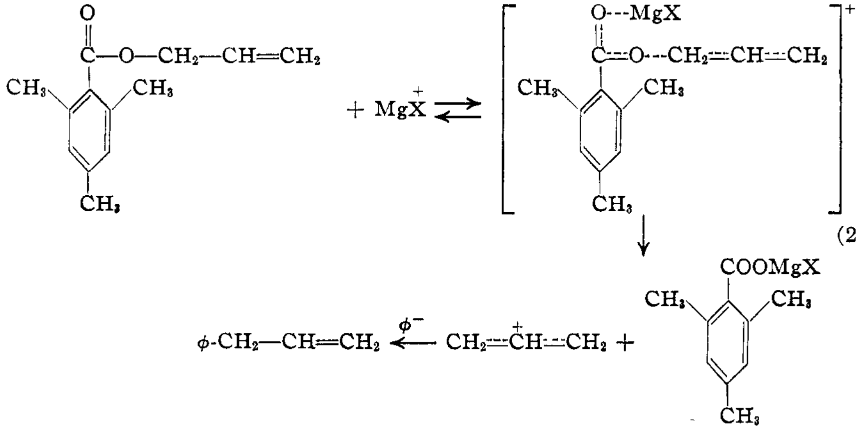
[2] Smith and Guss, This Journal, **59**, 804 (1937).

[3] Gilman and Jones, *ibid.*, **63**, 1162 (1941).

[4] Fuson, Fugate and Fisher, *ibid.*, **61**, 2362 (1939).

[5] Gilman and Robinson, *Bull. soc. chim.*, **45**, 636–641 (1929).

methylacetate was investigated. Since ethyl trimethylacetate reacts without difficulty with the Grignard reagent,[6] we assumed that no abnormal cleavage of the allyl group would take place with phenylmagnesium bromide. This was found to be true for *t*-butyldiphenylcarbinol was obtained in good yield.



(2)

In a preliminary run we were not able to cleave benzyl isodurylate with phenylmagnesium bromide in diethyl ether.

At present a detailed and systematic study of the reaction between allylic esters and Grignard reagents is being conducted in this Laboratory. The nature of the Grignard reagent, hindered carbonyl group, and allyl residue will be varied over wide ranges.

By allowing a solution of mesitylmagnesium bromide to drop slowly into dry ether through which a sustained stream of carbon dioxide passed, an extraordinary yield (84%) of β-isodurylic acid was obtained. Conventional methods of carbonation give 50–57% yields.[7,8] Pouring the Grignard solution onto dry-ice resulted in a yield of 60%.

Experimental

β-Isodurylic Acid.—A solution of Grignard reagent prepared from 50 g. of bromomesitylene was added dropwise to dry ether (150 cc.) through which a sustained stream of dried carbon dioxide passed. The gas flow was started fifteen minutes before addition of the Grignard reagent, and continued for thirty minutes after the addition was completed. Loss of ether by evaporation during the carbonation was made up by separate additions while the reaction was in progress. The mixture was decomposed with dilute hydrochloric acid and the ether layer extracted repeatedly with dilute sodium hydroxide. Acidification gave 34.5 g. of isodurylic acid; m. p. 150–151° (uncorr.).

Allyl Isodurylate.—In a Carius tube there were placed 10 g. of sodium isodurylate and 15 g. of freshly distilled allyl bromide. The sealed tube was heated at 130–160° for seven hours. The contents of the tube were extracted with ether and the ether layer washed with sodium carbonate solution, dried, and fractionated. Allyl isodurylate (6.25 g.) was collected at 115–117° (1 mm.).

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.49; H, 7.84. Found: C, 76.22; H, 7.76.

Allylbenzene.—Allyl isodurylate (33.7 g.) in 100 cc. of dry ether was added to a Grignard solution prepared from 32 g. of bromobenzene. Slow but persistent refluxing took place, and in forty-five minutes a white precipitate appeared. After standing overnight, the solid mass was treated with ammonium chloride solution containing a few drops of hydrochloric acid. The ether layer was washed with water and then extracted with dilute potassium hydroxide. Acidification of this solution gave a quantitative yield (95%) of β-isodurylic acid.

The ether layer was dried, and on careful fractionation gave 13.5 g. of a colorless, unsaturated liquid with characteristic hydrocarbon odor; b. p. 157° (755 mm.). The substance resembled allylbenzene in every respect.

Anal. Calcd. for C_9H_{10}: C, 91.5; H, 8.5. Found: C, 90.17; H, 8.99.

This hydrocarbon gave benzoic acid on permanganate oxidation.

Allyl Trimethylacetate.—Using four Carius tubes, 65 g. of sodium trimethylacetate was treated with 65 g. of allyl bromide at 160° for ten hours. An ether extract of the resulting mixture was washed with sodium carbonate solution, dried, and fractionated. The ester weighed 45 g. (60%); b. p. 55-56° (36 mm.).

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.69; H, 9.93. Found: C, 67.20; H, 9.86.

***t*-Butyldiphenylcarbinol.**—Allyl trimethylacetate (34.6 g.) was added to a Grignard solution prepared from 76.7 g. of bromobenzene. The mixture was allowed to stand twenty-four hours before decomposition with very dilute hydrochloric acid. Besides 7–10 g. of the original ester there was obtained 35 g. of a thick viscous oil; b. p. 190–220° (40 mm.). This carbinol was converted to its chloride by means of thionyl chloride; m. p. 69–70°, (Ramart-Lucas[9] gives 70–71°).

Allyl *o*-Toluate.—This ester was prepared from its sodium salt as described above; b. p. 148° (45 mm.); yield 69%.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.96; H, 6.86. Found: C, 75.06; H, 6.82.

***o*-Tolyldiphenylcarbinol.**—Allyl *o*-toluate (15 g.) was added to an excess of Grignard reagent prepared from 30 g.

---

[6] Bateman and Marvel, This Journal, **49**, 2914 (1927).

[7] Gilman and Heck, *Ber.*, **62**, 1379 (1929).

[8] Smith and Byrkit, This Journal, **55**, 4305 (1933).

[9] Ramart-Lucas, *Ann. chim. phys.*, [8] **30**, 367 (1913).

of bromobenzene in 100 cc. of ether. Refluxing started immediately, and the solution was stirred for three hours. After standing overnight, decomposition was effected with ammonium chloride. A tertiary carbinol (15.4 g.) was obtained on evaporation of the ether which melted at 100–101° after recrystallization from methanol and petroleum ether.[10] As described by Blicke,[10] this carbinol gave a yellow color with sulfuric acid which disappeared on dilution, and a yellow coloration with hydrochloric acid in acetic acid.

Benzyl Isodurylate.—To sodium isodurylate (23 g.) was added 20 cc. of benzyl bromide and 100 cc. of toluene. The mixture was refluxed and stirred mechanically for eight hours. The precipitated salt gave only a slight cloudiness on acidification. The toluene layer was fractionated, and 21 g. of the ester distilled at 175–180° (6–8 mm.).

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.33; H, 7.08.

Summary

1. It has been shown that allylic esters with greatly hindered carbonyl groups are cleaved by the Grignard reagent to give magnesium salts and hydrocarbons.

2. It is believed that the mechanism of this cleavage is comparable to that of acetomesitylene and the Grignard reagent.

MINNEAPOLIS, MINNESOTA

RECEIVED SEPTEMBER 29, 1941

---

[10] Blicke and Weinkauff, THIS JOURNAL, **54**, 1446 (1932).

[CONTRIBUTION NO. 252 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Identification of Organic Compounds. IV. Chlorosulfonic Acid as a Reagent for Identification of Alkylbenzenes

BY ERNEST H. HUNTRESS AND JOHN S. AUTENRIETH[1,2]

The use of chlorosulfonic acid as a tool for the characterization of organic compounds, whose application to the identification of aryl halides[3a] and aromatic ethers[3b] was reported in the first two papers of this series, has now been extended to a substantial group of alkylbenzenes.

The principle employed involves two stages, *viz.*, direct introduction of one sulfonyl chloride group into the aromatic nucleus by direct treatment with excess chlorosulfonic acid in chloroform followed by conversion of the resultant sulfonyl chlorides into the corresponding sulfonamides.

The specific application to these hydrocarbons was similar to that designated in the earlier paper[3a] as Procedure I. However, the amount of chlorosulfonic acid employed was 5 ml. (instead of 5 g.), and the chlorosulfonylation product was stirred forty-five minutes before pouring it onto ice. Conversion of the sulfonyl chloride was effected with solid ammonium carbonate substantially as in Procedure B[3a] of the first paper.

The structures of the ultimate sulfonamides from the monoalkylated benzenes were established by permanganate oxidation of the side chain. The resultant *p*-sulfamidobenzoic acid indicated that chlorosulfonylation had occurred para to the single side chain. For the polyalkylbenzene derivatives this oxidation was infeasible and the structures of the products have been inferred from previous work.

The various sulfonamides were subjected to combustion analyses for nitrogen and gave satisfactory values. In the interest of space economy their details are not reported. They served as evidence, however, that only one sulfonamido group was introduced under the conditions employed.

Experimental Work

The melting points reported in this paper are uncorrected. They were determined on a standard rod form 360° melting point thermometer in a copper block of the Berl and Kullmann type as described by Morton.[4]

The chlorosulfonic acid was obtained by fractional distillation of commercial material through a large bore six-foot column of about 40 theoretical plates. The colorless fraction boiling at 150.2° cor. was preserved in small colored glass sealed bottles.

The solvent chloroform was prepared from U. S. P. product by thorough washing with dilute aqueous sodium bicarbonate solution, then with distilled water, drying over phosphorus pentoxide and distilling from a fresh sample of the same agent. The fraction boiling at 61.5–62° was collected in lightly stoppered brown bottles and stored in a dark place.

The alkylbenzenes were obtained from a variety of

---

[1] This paper is constructed from part of a dissertation submitted in March, 1941, by John S. Autenrieth to the Faculty of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Present address: Hercules Powder Company, Wilmington, Delaware.

[3] (a) Huntress and Carten, THIS JOURNAL, **62**, 511 (1940); (b) **62**, 603 (1940).

[4] Morton, "Laboratory Technique in Organic Chemistry," first ed., McGraw-Hill Book Company, New York, N. Y., 1938, pp. 32–33.