reaction. With a little experience it is simple to adjust the inert gas pressure, length and bore of capillary desired in a particular experiment.

The practical advantages of the capillary vessels are evident from the fact that they have been used now for a period of over six years at the Riverside laboratories in thousands of experiments on many miscellaneous reactions, up to temperatures of 500° and pressures up to 500 atmospheres. The vessels had a capacity from 20 cc. up to about 3 liters. The capillaries ranged in length from 5 to 50 cm. and in bore from 0.1 to 2.0 mm. The usual material of construction was glass, but fused quartz, copper, nickel and other metals were also used.

In principle the method is not limited to capillaries and in industrial practice capillary spaces may be used to advantage.[6]

(6) See A. V. Grosse, U. S. Patent 1,986,196.

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Supplement to a Recent Paper on the Paramagnetism of Semiquinones

BY L. MICHAELIS, R. K. REBER AND J. A. KUCK

The results obtained by a potentiometric method[1] concerning the structure of a quinhydrone in the dissolved state, with phenanthrenequinone-3-sulfonate as a model, recently were confirmed by the measurement of the paramagnetic susceptibility.[2] The method was based on the change of susceptibility of the solution of the quinone while it is slowly being reduced. This method had thus far to be restricted to strongly alkaline solutions, in which glucose could be used as a slowly acting reducing agent. We have succeeded now in finding an agent of similar properties for acid solutions. According to the potentiometric method, the quinhydrone of the dye mentioned, when produced in acid solution, is essentially a valence saturated dimeric compound. This result is now confirmed by the magnetic method.

The method is based on a reaction, clarified in detail by Smythe,[3] who showed that methylglyoxal in the presence of potassium cyanide as catalyst is a reducing agent. The rate of the reduction

(1) L. Michaelis and E. S. Fetcher, THIS JOURNAL, 59, 2460 (1937).
(2) L. Michaelis, G. F. Boeker and R. K. Reber, ibid., 60, 202 (1938).
(3) C. V. Smythe, Biochem. Z., 257, 372 (1933).

exerted on a reducible substance depends on the concentration of potassium cyanide and can be regulated by a proper choice of this concentration. In absence of oxygen or any other reducible substance, one molecule of methylglyoxal is reduced to a substance of a structure not yet fully known, probably a polymerization product, at the expense of another molecule which is oxidized to pyruvic acid. In the presence of another reducible substance of a potential range not more negative than that of indigo disulfonate, this substance is reduced while methylglyoxal is oxidized to pyruvic acid. This reaction can be used at any $pH < 7$. In alkaline solution methylglyoxal is converted rapidly to lactic acid and so becomes ineffective for the reaction wanted.

Methylglyoxal can now be prepared easily by oxidation of acetone with selenium dioxide.[4,5] It is best stored in the form of a one molar aqueous solution and can be kept in the ice-box for several weeks.

A typical experiment follows: 0.1214 g. of potassium phenanthrenequinone-sulfonate and 0.0145 g. of potassium cyanide are dissolved in 5 cc. of acetate buffer (0.1 M in acetic acid and 0.1 M in sodium acetate), made up to a volume of 10 cc. with a 0.5 M aqueous solution of methylglyoxal, and sucked into the container of the magnetic balance. Before the first reading could be taken reduction, recognizable by the brown color, had already begun. The readings were continued until the complete discharge of color was reached, and longer. The change of volume susceptibility was

Time after mixing, min.	Volume susceptibility $K \times 10^6$	$\Delta K \times 10^6$	Color
17	0.72108	0.00014	Distinctly brown
20	.72103	.00019	
30	.72110	.00012	
34	.72108	.00014	
49	.72112	.00010	
71	.72122	.00000	Brown
77	.72122	.00002	Lighter brown
89	.72122	.00000	Fading
111	.72121	.00001	Colorless
127	.72122	.00000	

As stated in the previous paper, the limit of error may be estimated as 0.0002×10^{-6}. The changes are, accordingly, just within the limits of error. Since, however, this very slight change was observed also in a duplicate experiment, it may be real. If it be here also permitted to neglect all

(4) Hahn and Schales, Ber., 67, 1816 (1930).
(5) Riley, Morley and Friend, J. Chem. Soc., 1875 (1932).

changes in diamagnetism and attribute the whole change to the appearance and disappearance of a paramagnetic molecular species, a calculation on the principle presented in the previous paper would show 0.4% of the total dye in the radical form *in maximo*. Practically speaking, there is no distinctly measurable amount of a radical, and all of the deep-brown material developed is a valence-saturated compound. This is in agreement with the results of the potentiometric method and shows the contrast to the result in alkaline solution.

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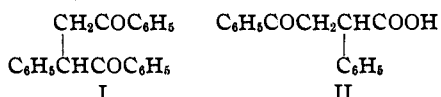PHYSICS DEPARTMENT OF
COLUMBIA UNIVERSITY
NEW YORK, N. Y.   RECEIVED DECEMBER 4, 1937

## Some Reactions of Maleic and Dimethylmaleic Anhydrides with Organometallic Compounds

BY D. STANLEY TARBELL[1]

The reaction of aryl Grignard reagents with aromatic and aliphatic anhydrides has proved to be superior to the Friedel–Crafts reaction in some cases in the preparation of aroyl acids,[2] and it seemed of interest to investigate the utility of a similar process applied to maleic anhydride for the preparation of aroyl acrylic acids.

When one mole of maleic anhydride is added in the usual manner to four moles of phenylmagnesium bromide, the principal product is desyl acetophenone[3] (I)

$$CH_2COC_6H_5 \quad\quad C_6H_5COCH_2CHCOOH$$
$$| \quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$C_6H_5CHCOC_6H_5 \quad\quad\quad\quad C_6H_5$$
$$\text{I} \quad\quad\quad\quad\quad\quad\quad\quad \text{II}$$

but there is also formed a small amount of phenylbenzoylpropionic acid (II); this product was not reported by the English workers. When one mole of Grignard reagent is added to one mole of anhydride at 0°, small amounts of II can be isolated from the resulting oil, but no benzoylacrylic acid (III) is found. Compounds I and II are prob-

$$C_6H_5COCH=CHCOOH$$
$$\text{III}$$
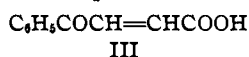
ably products of 1,4-addition to the conjugated system in maleic anhydride, but this mechanism of their formation has not been proved.
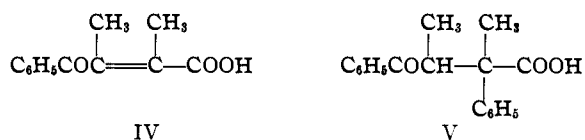
(1) Present address: University of Illinois, Urbana, Illinois.

(2) Weizmann, E. Bergmann and F. Bergmann, *J. Chem. Soc.*, 1367 (1935); Fieser and Newman, THIS JOURNAL, **58**, 2376 (1936); Newman, *ibid.*, **59**, 1003 (1937); E. Bergmann and Blum-Bergmann, *ibid.*, **59**, 1441, 1572 (1937).

(3) Arup and Purdie, *J. Chem. Soc.*, **97**, 1545 (1910).

The less reactive phenylzinc chloride seemed to offer a way of avoiding the 1,4-addition of the Grignard reagent, and it was possible to isolate III in 26% yield from this reaction. This method might prove useful in reactions with succinic anhydride, which gives a poor yield of the aroyl propionic acid by the Grignard reaction.[4]

Dimethylmaleic anhydride showed its diminished reactivity compared to maleic anhydride by giving a much cleaner reaction with phenylmagnesium bromide; the unsaturated keto acid (IV)

$$CH_3 \; CH_3 \quad\quad\quad\quad\quad CH_3 \; CH_3$$
$$| \quad | \quad\quad\quad\quad\quad\quad\quad | \quad |$$
$$C_6H_5COC=C-COOH \quad\quad C_6H_5COCH-C-COOH$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad C_6H_5$$
$$\text{IV} \quad\quad\quad\quad\quad\quad\quad\quad\quad \text{V}$$

was isolated in this case, along with an acid to which the structure V is assigned by analogy with II.

I wish to thank Professor L. F. Fieser for suggesting this problem and Professor P. D. Bartlett for helpful suggestions.

Experimental

Reaction of Phenylmagnesium Chloride and Maleic Anhydride.—The Grignard reagent prepared from 15.7 g. of bromobenzene and 2.4 g. of magnesium was added dropwise to 8.8 g. of maleic anhydride dissolved in ether at 0° with stirring; each drop of the Grignard solution caused an instantaneous precipitation of white solid. The product was worked up in the usual way and separated into neutral and acidic fractions by sodium carbonate extraction; the neutral fraction (1.2 g.) consisted mainly of diphenyl; the acidic fraction was a red oil (5.9 g.). The oil was taken up in benzene, and ligroin precipitated three lots of uncrystallizable oil. Then 0.7 g. of solid (m. p. 135–145°) was obtained after recrystallization from acetone–petroleum ether. Less pure material (1 g.) was obtained by further concentration. The solid was an impure sample of II; in other runs purer samples melting at 145–148° were obtained which gave a mixed m. p. with an authentic sample of II of 148–150°.

The run in which 0.1 mole of anhydride was added to 0.4 mole of Grignard reagent need not be described in detail; I, m. p. 125–127°, was found in the neutral fraction, and II in the acid fraction.

Reaction of Phenylzinc Chloride with Maleic Anhydride.[5]—Freshly fused zinc chloride (16.4 g., 0.12 mole) was dissolved in 40 cc. of dry ether by shaking, and added dropwise to a Grignard reagent prepared from 15.7 g. of bromobenzene and 2.4 g. of magnesium (0.1 mole). Phenylzinc chloride crystallized suddenly with much evolution of heat. Maleic anhydride (8.8 g., 0.09 mole) in 90 cc. of dry ether was added dropwise over one-half

(4) Weizmann, Blum-Bergmann and Bergmann, *J. Chem. Soc.*, 1370 (1935).

(5) Conant and Carlson, THIS JOURNAL, **54**, 4056 (1932).