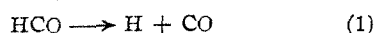


NOTES

The Stability of the Free Formyl Radical

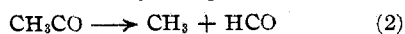
BY MILTON BURTON

The stability of formyl has a direct bearing on the mechanism of reactions such as the decomposition of the aldehydes. In recent papers¹ indirect evidence has been cited relating to the possibility of the reaction

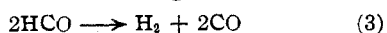


It consequently seems advisable to call attention to direct evidence on this point, which unfortunately has been published where it is obscured by other findings.

The evidence is of two kinds. Incidentally to a paper on the photolysis of formic acid,² it has been shown by the use of the guard mirror method³ that, although CH_3 radicals are formed in the photolysis of acetaldehyde, no H atoms are produced. Since part at least of the primary reaction must be by the path



this is equivalent to the statement that the HCO radicals so formed do not decompose at 100° (which was the temperature of the test) but enter some other reaction, *e. g.*



The objection may be made that the lead guard mirror itself prevents the passage of HCO radicals but that is beside the point. The HCO radicals have ample time to dissociate before they reach the lead mirror. If any H atoms are formed, the antimony mirror would detect them.³ The failure to detect such atoms by this sensitive method is very pertinent.

In some comments on a paper by Rollefson⁴ the writer⁵ presented other evidence on this point. Calculations from data by Leighton and Blacet⁶ and Blacet and Roof^{1a} were used to establish the fact that if hydrogen atoms are formed in the photolysis of acetaldehyde they take no further part in the reaction or, which is

(1) (a) Blacet and Roof, *THIS JOURNAL*, **58**, 278 (1936); (b) Leighton, Levanas, Blacet and Rowe, *ibid.*, **59**, 1843 (1937); (c) Blacet, Fielding and Roof, *ibid.*, **59**, 2375 (1937).

(2) Burton, *ibid.*, **58**, 1655 (1936).

(3) Burton, *ibid.*, **58**, 1645 (1936).

(4) Rollefson, *J. Phys. Chem.*, **41**, 259 (1937).

(5) Burton, *ibid.*, **41**, 322 (1937).

(6) Leighton and Blacet, *THIS JOURNAL*, **55**, 1766 (1933).

more probable, that no hydrogen atoms are formed.

It is interesting to note that the stability of HCO has been established from two distinctly different types of experiments (one involving direct test, the other kinetic studies) and that the radical appears to be stable even at 100°. This stability is to be compared with that of the CH_3CO radical which, according to Spence and Wild,⁷ is stable at room temperatures but is completely decomposed at 60°.

(7) Spence and Wild, *J. Chem. Soc.*, 352 (1937).

DEPARTMENT OF CHEMISTRY
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RECEIVED NOVEMBER 26, 1937

Reaction Vessels for Pressure Experiments¹

BY ARISTID V. GROSSE

There are a great number of chemical reactions which cannot be studied at elevated or high pressures in the usual type of apparatus because their material is either attacked by reagents or catalyzes the reactions investigated in an undesirable manner. Such material is practically always iron in the form of steel or ferrous alloys. On the other hand, the usual corrosion-resistant and non-catalytic materials are unsuitable for constructing high pressure apparatus because they lack tensile strength and other necessary mechanical properties.

The following simple type of reaction vessels equipped with a capillary, as illustrated in Fig. 1, and inserted into a cylindrical Ipatieff high pressure autoclave,² allows circumvention of these difficulties. It is based on the fact that the diffusion of gases and vapors through capillaries is extremely slow under pressure. Furthermore, the capillary provides a resistance to sudden mass flow from or into the vessel, but at the same time this resistance does not prevent pressure differences between the outside and inside of the reaction vessel from equalizing fairly rapidly, so that gases can be readily pressed in or released from the vessel. By choosing suitable capillary dimensions

(1) Presented before the Division of Organic Chemistry, at the Rochester Meeting, Sept., 1937, of the American Chemical Society.

(2) As shown in Fig. 1, *THIS JOURNAL*, **57**, 1618 (1935).

and providing sufficient pressure in the autoclave by means of an inert gas,² usually nitrogen, the losses from the liner can be limited to negligible quantities. (Under "sufficient pressure of an inert gas" pressure substantially higher than the total pressure of the reacting chemicals is understood.)

The total losses from such vessels, due either to *diffusion* or more generally to *mass flow*, vary to a great extent and depend, outside of factors just mentioned, *i. e.*, length and diameters of capillaries, total pressure and mass density of reactants, also on temperature, rate of heating or cooling, nature of the reactants⁴ and the inert gas, nature of the reaction itself (whether violent or smooth, exo- or endothermic, connected with pressure increase or decrease, etc.), ratio of pressure of reactants to pressure of inert gas and a few other less important factors.

In the more limited case of a pure inert liquid heated in an inert gas the losses from a capillary vessel during the usual procedure of experimentation may be attributed logically to three distinct periods (1) the time during which the autoclave is being heated, (2) the time during which the temperature is being kept constant or the actual diffusion period and (3) the time during which the autoclave is being cooled. By a proper technique the losses during periods 1 and 3, due *entirely* to mass flow, can be avoided practically completely.

For instance in Period 1 this is accomplished if the *rate of inert gas* input is so adjusted (for example by a precision needle valve) that it *always* remains *higher* than the rate of gas or vapor pressure increase of the reactants. In practice such an adjustment is not necessary in the numerous cases when a reaction takes place with gas absorption (for instance in hydrogenations or alkylations and polymerizations with gaseous olefins) because then the mass flow is only inward, into the capillary vessel. In Period 3 the gas flow will also be inward, since the vapors in the capillary vessel will condense more rapidly than the gas outside, except when the rate of cooling is too rapid.

An *example of losses* occurring during Period 2 is given in Table I.⁵

In each experiment 41.1 g. of *pure benzene* (crit. temp. 289°, press. 48 atm.) was heated in a ves-

(3) Under the term "inert gas" any reacting gas may also be understood provided it is inert toward the autoclave material.

(4) In case of subliming substances care should be taken to avoid clogging of the capillary. As a precaution against clogging due to any cause one should either seal on a thin walled tube to the glass reaction vessel, which can be readily broken inside the autoclave, or use ground-in joints with springs, as illustrated in Fig. 1.

(5) See Dissertation of Leroy A. Johnson, Dept. of Chem., Univ. of Chicago, Aug., 1932.

TABLE I

Run	Diffusion time, hrs.	Temp. of run, °C.	Total av. pressure, (C ₆ H ₆ & N ₂) kg./cm. ²	Diffusion per hr. in mg.	Loss in weight, % of total benzene/hour
1	2.7	303	105	57	0.14
2	4.1	309	107	53	.13
3	8.0	314	111	53	.13
4	19.5	317	111.5	40	.10

sel of 137.3 cc. volume, with a capillary 41.7 cm. long and 0.646-mm. bore. Nitrogen was used as the inert gas. To decrease losses it is preferable to work *substantially* below the critical densities. In our case the density of benzene vapors (=0.299) was very near its critical density (=0.305). We see, however, that even under these conditions the losses are small—of the order of 0.1% per hour. For this reason high pressure experiments can be performed *quantitatively with great ease*, since all reagents, except gases pressed in or released from the autoclave, *will be found in the capillary vessel* and can be weighed accurately before and after each

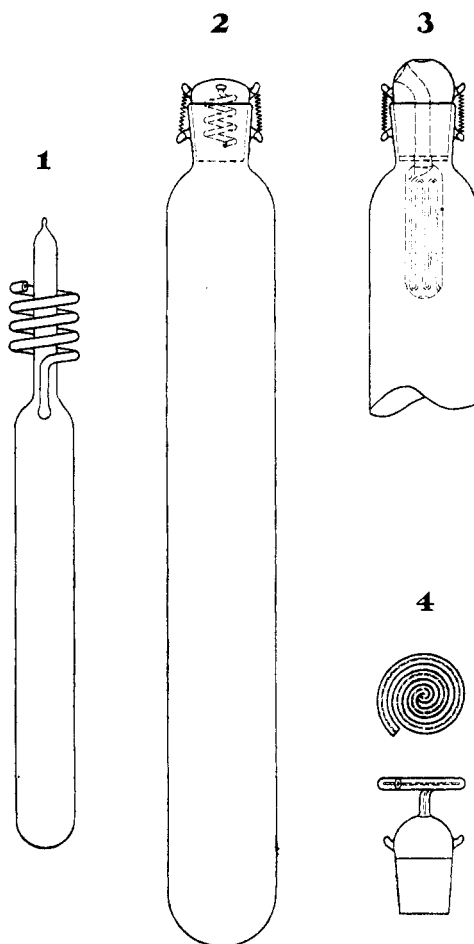


Fig. 1.

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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RECEIVED SEPTEMBER 30, 1937

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 method¹ 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

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

(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).

(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.

ROCKEFELLER INSTITUTE FOR
MEDICAL RESEARCH AND
PHYSICS DEPARTMENT OF
COLUMBIA UNIVERSITY
NEW YORK, N. Y.

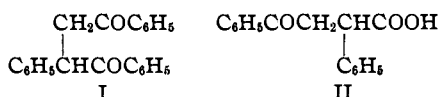
RECEIVED DECEMBER 4, 1937

Some Reactions of Maleic and Dimethylmaleic Anhydrides with Organometallic Compounds

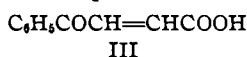
BY D. STANLEY TARBELL¹

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 acetophenone³ (I)



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-



ably products of 1,4-addition to the conjugated system in maleic anhydride, but this mechanism of their formation has not been proved.

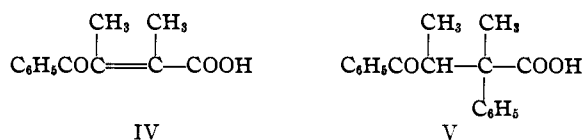
(1) Present address: University of Illinois, Urbana, Illinois.

(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)



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).

hour, while stirring the gray solid mass and refluxing. The gray solid gradually became yellow and slightly sticky and stirring with refluxing was continued for one-half hour after the addition of the anhydride was complete. The reaction mixture was worked up in the usual way, giving 0.9 g. of diphenyl and an acidic fraction of 10.2 g. of red oil. The latter was taken up in benzene and 3.6 g. of oily yellow solid was obtained by adding ligroin; the solid was taken up in ligroin and on crystallization a crop of yellow plates (1.9 g.) was obtained, m. p. 94–95° after recrystallization from benzene–petroleum ether. The mother liquor from the first fraction gave 2.3 g. of impure material crystallizing from ligroin, so that total crystalline solid obtained was 4.2 g. (26%). The pure sample gave no depression when mixed with a sample of III prepared by the Friedel–Crafts reaction.

Reaction of Phenylmagnesium Bromide with Dimethylmaleic Anhydride. 1. **One Mole of Each.**—The Grignard reagent prepared from 1.2 g. of magnesium and 7.9 g. of bromobenzene (0.05 mole) was added at 0° to 5.7 g. of dimethylmaleic anhydride (0.045 mole) dissolved in 300 cc. of dry ether. Reaction was immediate but not as violent as with maleic anhydride. The acid fraction (6.2 g.) was extracted with hot benzene and a residue of 1.1 g. of 1-phenyl-1-methyl-2-benzoylbutyric acid (V) was collected. The filtrate was treated with petroleum ether and 2.2 g. of solid was obtained; this consisted mainly of starting material and dimethylbenzoylacrylic acid (IV), which were separated by fractional crystallization from water; 0.3 g. of the latter turned up in the neutral fraction, from which it had not been extracted completely by sodium carbonate. The total yield after further fractional crystallization was 1.25 g. V, 0.7 g. IV, and 0.7 g. starting material. Compound IV melted at 92–94° and its identity was established

by mixed melting point with a sample prepared by the Friedel–Crafts reaction.⁶

Compound V is insoluble in hot water, very slightly in hot benzene, soluble in hot acetone, alcohol, and ethyl acetate and crystallizes from alcohol in needles, m. p. 183–185°.

Anal. Calcd. for $C_{19}H_{18}O_3$: C, 76.6; H, 6.4. Found: C, 76.7; H, 6.5.

Preparation of IV by the Friedel–Crafts Reaction.—When the reaction was carried out as described⁶ the first product obtained crystallized from benzene–petroleum ether as needles, m. p. 65–67° instead of 94°; on recrystallization from hot water it melted at 92–94° and did not change back into the low melting form on recrystallization from benzene–petroleum ether. Apparently IV can exist in two forms.

2. **Two Moles of Grignard Reagent and One of Anhydride.**—Phenylmagnesium bromide (0.1 mole) was added to 5.7 g. of dimethylmaleic anhydride (0.045 mole) in 150 cc. of dry ether at room temperature. The acidic fraction yielded 3.8 g. of V, no IV and 5.6 g. of a white compound, m. p. 65–68° which seemed to lose solvent, finally melting at 85–94° but not identical with IV; when recrystallized from benzene–petroleum ether the low melting form reappeared, and on drying for four hours at 65° melted at 90–93°. It is soluble in carbonate and bicarbonate solution, almost insoluble in hot water, readily soluble in ether, alcohol, benzene and acetone. Its structure was not investigated further, but it may be stereoisomeric with V.

(6) Lutz and Taylor, *ibid.*, **55**, 1593 (1933).

CHEMICAL LABORATORY OF RADCLIFFE COLLEGE
CAMBRIDGE, MASSACHUSETTS

RECEIVED OCTOBER 20, 1937

COMMUNICATIONS TO THE EDITOR

DIENE SYNTHESIS OF POLYCYCLES, WITH OR WITHOUT ANGULAR SUBSTITUENTS, FROM HEXATRIENE

Sir:

A new approach to the total synthesis of polycyclic compounds similar to the steroids has been investigated in this Laboratory. The method consists essentially in the use of a six-carbon chain containing conjugated double bonds which can be condensed successively with two compounds containing activated multiple bonds in the Diels–Alder sense. Thus the six-carbon chain forms the “backbone” of the polynuclear product, *e. g.*, carbons 6–7–8–9–11–12 in the steroid nucleus.

It was anticipated that the simplest chain of this type, 1,3,5-hexatriene, might not serve because the double bonds remaining after the first diene addition might not assume the required conjugated position, and therefore work with 1,3-hexadienes has been planned. Nevertheless condensations with the hexatriene were tried and evidence has been obtained that the primary adduct can add a second molecule.

The hexatriene was heated with 5-acetoxy-*p*-toluquinone in alcohol at 90–95°. Removal of alcohol from the reaction products and addition of benzene gave a crystalline substance part of which was removed for analysis. The compound was