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.

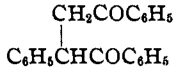
ROCKEFELLER INSTITUTE FOR
MEDICAL RESEARCH AND
PHYSICS DEPARTMENT OF
COLUMBIA UNIVERSITY
NEW YORK, N. Y.
RECEIVED DECEMBER 4, 1937

Some Reactions of Maleic and Dimethylmaleic Anhydrides with Organometallic Compounds

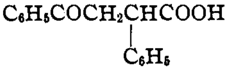
BY D. STANLEY TARBELL[1]

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)


$C_6H_5CH(CH_2COC_6H_5)COC_6H_5$

I


$C_6H_5COCH_2CH(C_6H_5)COOH$

II

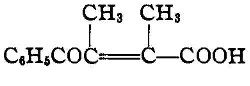
but there is also formed a small amount of phenylbenzoylpropionic acid (II); this product was not reported by the English workers. When one mole of Grignard reagent is added to one mole of anhydride at 0°, small amounts of II can be isolated from the resulting oil, but no benzoylacrylic acid (III) is found. Compounds I and II are probably products of 1,4-addition to the conjugated system in maleic anhydride, but this mechanism of their formation has not been proved.

$$C_6H_5COCH{=}CHCOOH$$

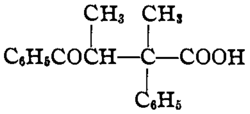
III

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)


$C_6H_5COC(CH_3){=}C(CH_3){-}COOH$

IV


$C_6H_5COCH(CH_3){-}C(CH_3)(C_6H_5){-}COOH$

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

---

(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).

(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 $C_{18}H_{18}O_3$: 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 described[6] 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