following a procedure similar to that shown above for II. After hydrolytic treatment in the usual manner, the crystalline material that had formed in two hours was removed and purified by recrystallization from dilute methyl alcohol to which a little acetic acid had been added. Compound IV was thus obtained as short diamond-shaped crystals, greenish-yellow in color, and showing greenish fluorescence in solution; m. p. 116–117°; yield, 56%. The residual benzene–ether solution, from which the crude IV was obtained originally after the hydrolysis of the Grignard complex, was set aside for ten days, after which time compound V was isolated (see below).

Anal. Calcd. for $C_{22}H_{19}ON$: N, 4.47. Found: N, 4.29.

3,3-Diphenyl-1-ethyloxindole (V). By the Action of Phenylmagnesium Bromide upon N-Ethylisatin.—The residual benzene–ether solution, from which IV had separated (see above), was allowed to stand for ten days and then was concentrated by distillation. Compound V, yield 16%, separated and was purified by crystallization from dilute methyl alcohol; long white needles, m. p. 156–157°, giving no fluorescence in solution.

Anal. Calcd. for $C_{22}H_{19}ON$: N, 4.47. Found: N, 4.40.

Compound V. By the Friedel–Crafts Reaction.—Compound V was prepared by the reaction of benzene with 3,3-dichloro-1-ethyloxindole, as for III. The product was identical with the V obtained from the Grignard reaction in melting point and physical characteristics. A mixture of samples from the two sources showed no depression of the melting point.

Summary

3,3-Diphenyl-1-methyloxindole and 3,3-diphenyl-1-ethyloxindole accompany the respective 2,3-diphenyl-1-alkylindole-oxide-2,3 as products of the reaction of phenylmagnesium bromide with N-methylisatin and N-ethylisatin.

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Friedel–Crafts Reactions on *m*-Diphenylbenzene[1]

BY H. GAINES GOODMAN, JR., AND ALEXANDER LOWY

In the process for the preparation of biphenyl from benzene, considerable amounts of high boiling products are produced. *m*-Diphenylbenzene is one of the constituents of this high boiling material. Wardner and Lowy[2] have reported references to the literature concerned with the preparation of this hydrocarbon and its derivatives up to 1932. Since then the additional articles[3] listed have dealt with the subject.

Because a search of the literature has revealed that no attempt has been made previously to apply the Friedel–Crafts type of reaction to *m*-diphenylbenzene, a study was undertaken, with the object of synthesizing and identifying several new compounds of the ketonic types, prepared by the action of acyl halides and anhydrides on *m*-diphenylbenzene in the presence of anhydrous aluminum chloride.

The Friedel–Crafts reaction needs no discussion here since it is covered admirably by several comprehensive reviews.[4]

The structure of the *m*-diphenylbenzene molecule is such that six theoretical monosubstitution products are possible. It was desirable, therefore, to determine the position of attack in the case of each reactant, and, in order to accomplish this, an oxidation of each acylation product was carried out and a study of the oxidation products made. The oxidation products isolated indicated that, in each reaction, the para position of an end ring had been attacked, except in the case of *m*-diphenylbenzene-phthaloylic acid,[5] the exact structure of which was not determined. This was in agreement with numerous examples contained in the literature, which indicated the para position of a substituted benzene ring to be the one generally attacked in the Friedel–Crafts syntheses.

Experimental

The writers are indebted to Mr. R. E. Bowman, of Wilmington, Delaware, who is investigating the high boiling material furnished by the Monsanto Chemical Co., for a generous supply of *m*-diphenylbenzene. The *m*-diphenylbenzene thus obtained was recrystallized twice from ethyl alcohol, producing white needle-shaped crystals, m. p. 85°. Redissolving these crystals in boiling ethanol, and filtering after cooling to 70°, resulted in the

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[1] Abstracted from a thesis presented by H. Gaines Goodman, Jr., to the Graduate School in partial fulfilment of the requirements for the Ph.D. degree.

[2] Wardner and Lowy, THIS JOURNAL, **54**, 2510 (1932).

[3] Cook and Cook, *ibid.*, **55**, 1212 (1933); Wulff and Roell, U. S. Patent 2,004,546; Busch and Weber, *J. prakt. Chem.*, **146**, 1 (1936).

[4] Kränzlein, "Aluminiumchlorid in der organischen Chemie," Verlag Chemie, G. m. b. H., Berlin, 1932; Calloway, *Chem. Rev.*, **17**, 327 (1935); Groggins, "Unit Processes in Organic Syntheses," McGraw-Hill Book Co., Inc., New York, N. Y., 1935.

[5] *m*-Diphenylbenzene-phthaloylic acid is the term selected for use here, in order to embrace all of the six monosubstitution products which might be obtained theoretically by the action of phthalic anhydride on *m*-diphenylbenzene. Groggins, *Ind. Eng. Chem.*, **22**, 620 (1930), has suggested a better nomenclature in the event that the structures of the acids are definitely known.

TABLE I

FRIEDEL–CRAFTS REACTIONS

m-ϕ_3 = m-Diphenylbenzene. A = Aluminum Chloride. B = Reactant.

	Grams used					
Expt.	m-ϕ_3	A	B	Inert solvent	Conditions (See text)	Product (See Table II)
1	30	20.7	10.2(Acetyl chloride)	Nitrobenzene	28(0.5)–45°(5)	(A)
2	20	25.5	9.1(Acetic anhydride)	Nitrobenzene	28(11)–45°(0.5)	(B)
3	(See text)	21.6	7.9(Acetyl chloride)	Nitrobenzene	30(2)–50°(1)	(C)
4	20	15.4	13.3(Benzoyl chloride)	Nitrobenzene	28°(5)	(D)
5	23	14.6	11.3(Chloroacetyl chloride)	Carbon bisulfide	4°(5)	(E)
6	23	14.6	19.4(Benzenesulfonyl chloride)	None	50(4)–100°(0.5)	(F)
7	23	29.3	14.8(Phthalic anhydride)	o-Dichlorobenzene	30(7)–50°(1)	(G)

separation from the cooled filtrate of crystals melting at 87°.

The apparatus described by Riddell and Noller[6] was used throughout the investigation.

In general, the procedures followed throughout the investigation were essentially the same, as is exemplified in the method used in the first experiment, described completely herewith.

Preparation and Identification of *p*-Acetyl-*m*-diphenylbenzene.—To a solution of 30 g. (0.13 mole) of *m*-diphenylbenzene in 100 cc. of nitrobenzene, a solution of 20.7 g. (0.15 mole) of anhydrous aluminum chloride in 100 cc. of nitrobenzene was added and mixed thoroughly. With the above mixture at 28°, 10.2 g. (0.13 mole) of acetyl chloride was added dropwise from the dropping funnel, stirring continuously. A vigorous evolution of hydrochloric acid gas continued for thirty minutes. Then the temperature was raised to 45° and held for five hours. The charge was hydrolyzed by the addition of ice, and the nitrobenzene layer separated and washed thoroughly with water. The nitrobenzene was removed by steam distillation and the resulting crude product dissolved in acetone and filtered. The acetone was then removed by evaporation and the residue subjected to a vacuum distillation. The distillate which passed over from 232 to 246° at 1 mm. pressure was further purified by three recrystallizations from ethanol, whereupon 10 g. of white *p*-acetyl-*m*-diphenylbenzene, melting at 104°, was obtained.

This compound was also produced by the use of acetic anhydride instead of acetyl chloride under the conditions given for experiment 2, Table I. Isolation of the reaction product was accomplished by the method described above.

One gram of *p*-acetyl-*m*-diphenylbenzene was refluxed for five hours with 5 g. of chromic anhydride and 40 cc. of glacial acetic acid. The charge was then poured into ice water, and the precipitated acid filtered and washed thoroughly with distilled water. The free acid was then dissolved in a small amount of 10% sodium hydroxide solution and filtered through asbestos. The filtrate was acidified with concentrated hydrochloric acid to reprecipitate the free acid which was washed thoroughly with distilled water and dried. The acid thus obtained was identified as terephthalic acid by conversion to dimethyl terephthalate, m. p. 140°, thus indicating that acylation had taken place in the para position of *m*-diphenylbenzene.

The essential data concerning each preparation are given in Table I. In this table the conditions are described by giving the initial and final temperatures, followed in parentheses by the duration of each temperature in hours. In each experiment the inert solvent was removed from the crude product by steam distillation. In Experiment 3, *p*-acetyl-*m*-diphenylbenzene, the product of Experiment 1, was used instead of *m*-diphenylbenzene in order to produce *p,p'*-diacetyl-*m*-diphenylbenzene. All efforts to produce this material from *m*-diphenylbenzene failed. After removal of the solvent, the crude product was extracted with ethyl ether and the residue recrystallized. This procedure also was used in working up the crude product of Experiment 4. In Experiment 5, after completion of the reaction, the inert solvent, carbon bisulfide, was decanted from the insoluble complex compound, which was then hydrolyzed, steam distilled to remove any residual carbon bisulfide, and the crude product extracted twice with 100 cc. of boiling ethanol. Upon cooling these extracts, crystals were deposited which were recrystallized from small amounts of ethanol. Benzenesulfonyl chloride was found to react very sluggishly upon *m*-diphenylbenzene if an inert solvent was used. In Experiment 6, therefore, the hydrocarbon and reactant were mixed, raised to 50°, and the aluminum chloride added in small increments. After hydrolysis, the crude product was boiled successively with several large portions of water to remove any remaining benzenesulfonyl chloride. The residue was then recrystallized from large quantities of ethanol. The procedure used in isolating the product of Experiment 7 differed so markedly from the others that it is given in detail, thus. The charge was hydrolyzed by pouring into a mixture of crushed ice containing 10% of concentrated hydrochloric acid. After hydrolysis, the solvent layer was separated and washed thoroughly to remove all the mineral acid, and the *o*-dichlorobenzene removed by steam distillation. The crude product was separated and boiled with 350 cc. of 10% sulfuric acid to remove any residual aluminum salts, and finally with several successive portions of water to remove any residual sulfuric acid and phthalic acid. The remaining solid matter was dissolved in 500 cc. of water containing 50 cc. of concentrated ammonium hydroxide, a small amount of boneblack added, and the solution boiled for one hour. After cooling, the boneblack and any insoluble hydrocarbon or phthalides were filtered off. The carboxylic acid was then reprecipitated by the addition of concentrated hydrochloric acid. After removal by filtration and washing to remove any residual hydrochloric acid or soluble chlorides, this product, 35.5 g., was dried over concentrated sulfuric acid, under reduced pressure. All efforts to purify this product by crystallization were futile. It is very soluble in methanol, ethanol, benzene, toluene,

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(6) Riddell and Noller, THIS JOURNAL, **52**, 4368 (1930).

TABLE II

CHARACTERISTICS OF PRODUCTS

m-ϕ_3 = *m*-Diphenylbenzene

Product	Solvent for recrystallization	Yield, g.	M. p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found		Hydrogen, % Calcd.	Hydrogen, % Found	
(A) *p*-Acetyl-*m*-ϕ_3	EtOH	10	104	$C_{20}H_{16}O$	88.24	88.09	87.95	5.88	5.74	5.82
(B) *p*-Acetyl-*m*-ϕ_3	EtOH	5	104	......	.....	.....	.....	....	....	....
(C) *p,p'*-Diacetyl-*m*-ϕ_3	EtOH	1.4	152	$C_{22}H_{18}O_2$	84.08	84.15	83.95	5.73	5.45	5.64
(D) *p*-Benzoyl-*m*-ϕ_3	Benzene, EtOH, 1:4	13	117	$C_{25}H_{18}O$	89.82	89.92	89.73	5.39	5.30	5.34
(E) *p,p'*-Di-(-ω-chloroacetyl)-*m*-ϕ_3	EtOH	3	150	$C_{22}H_{16}O_2Cl_2$						
				Cl,	18.53	18.23	18.27			
(F) *p*-Benzenesulfonyl-*m*-ϕ_3	EtOH	4	119	$C_{24}H_{18}O_2S$ S,	8.64	8.61	8.65			
(G) *m*-ϕ_3-Phthaloylic acid[5]	..	35.5	.	$C_{26}H_{18}O_3$	82.54	82.47	82.52	4.76	4.95	4.91
				Neut. eq.	378	385	387			

acetic acid, acetone, and ethyl ether, from any of which it may be recovered by evaporation of the solvent as a glassy, resinous film. The dried product fuses at 90–100° to a straw-colored, opaque, resinous mass.

Table II gives essential data concerning the products obtained.

Table III lists the oxidation products of each of the compounds with the melting points of their derivatives used for identification. These oxidations were all performed in the heretofore described manner, using a mixture of chromic anhydride and acetic acid. All esters were prepared by the method given by Mulliken.[7]

TABLE III

IDENTIFICATION OF PRODUCTS

Compound	Oxidation products	M. p. °C. DME = Dimethyl ester ME = Methyl ester
(A)	Terephthalic acid	DME, 140
(C)	Terephthalic acid	DME, 140
(D)	*p*-Benzoylbenzoic acid	194; ME, 107
(E)	Terephthalic acid	DME, 140
(F)	*p*-Phenylsulfonebenzoic acid	273
(G)	No identifiable products	...

Ring Closure of *m*-Diphenylbenzene-phthaloylic Acid.—Several experiments were performed with the idea of determining the susceptibility of *m*-diphenylbenzene-phthaloylic acid to ring closure, to form a substituted anthraquinone type. Of the five dehydrating agents used, acetic anhydride, anhydrous aluminum chloride, anhydrous ferric chloride, phosphorus pentoxide, and sulfuric acid, positive results were obtained only by the use of the last named reagent, when heated at 136°. Sulfonation, however, was shown to occur simultaneously. The resulting product was water soluble and when treated with zinc dust and 10% sodium hydroxide solution produced a deep red color, which disappeared upon blowing air through the solution.

***m*-Diphenylbenzene-*p*-carboxylic Acid.**—The method of oxidation described below is based upon that described by Bogert and Hasselström[8] for the preparation of retene-α-carboxylic acid from acetylretene.

One gram of *p*-acetyl-*m*-diphenylbenzene was dissolved in 50 cc. of hot methanol and, with stirring, 15 cc. of a strong sodium hypochlorite solution was added drop by drop. Stirring was continued for one hour. The formed suspension of white solid in methanol was poured into ice water and heated until the solid material had dissolved, filtered hot, and allowed to cool. The solid which crystallized was filtered and boiled with water to which sufficient hydrochloric acid had been added to convert the sodium salt to the free acid. This was cooled, filtered, and the residue washed thoroughly with water. The crude product, 0.9 g., was then recrystallized twice from benzene, after which 0.4 g. of white *m*-diphenylbenzene-*p*-carboxylic acid, melting at 221°, was obtained.

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.21; H, 5.11; neut. equiv., 274. Found: C, 82.78, 83.03; H, 5.21, 5.26; neut. equiv., 274, 267.

The sodium salt is very insoluble in cold water, soluble in hot water.

Summary

1. The following hitherto undescribed compounds were prepared by means of the Friedel–Crafts synthesis, using *m*-diphenylbenzene as the hydrocarbon: (a) *p*-acetyl-*m*-diphenylbenzene, which was converted to *m*-diphenylbenzene-*p*-carboxylic acid; (b) *p,p'*-diacetyl-*m*-diphenylbenzene; (c) *p*-benzoyl-*m*-diphenylbenzene; (d) *p,p'*-di-(-ω-chloroacetyl)-*m*-diphenylbenzene; (e) *p*-(benzenesulfonyl)-*m*-diphenylbenzene; and (f) *m*-diphenylbenzene-phthaloylic acid.

2. Oxidation experiments upon (a), (b), (c), (d), and (e) yielded products which indicated that, in each case, the substitution had taken place in the para position of an end ring of the *m*-diphenylbenzene molecule. The structure of *m*-diphenylbenzene-*p*-carboxylic acid follows from its synthesis from (a) by oxidation. Most likely (f) is a mixture of two or more isomeric keto acids.

3. Attempts to form a substituted anthraquinone type by ring closure of (f) indicated that, of the five dehydrating agents tried, sulfuric acid alone gave positive results. Sulfonation, however, occurred simultaneously.

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[7] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1904, Vol. I, p. 85.

[8] Bogert and Hasselström, *Proc. Natl. Acad. Sci.*, **18**, 417 (1932).