

CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE AND THE DEPARTMENT OF BIOLOGICAL CHEMISTRY OF THE AMERICAN UNIVERSITY OF BEIRUT]

The Condensation of 1,1-Diarylethylenes with Maleic Anhydride

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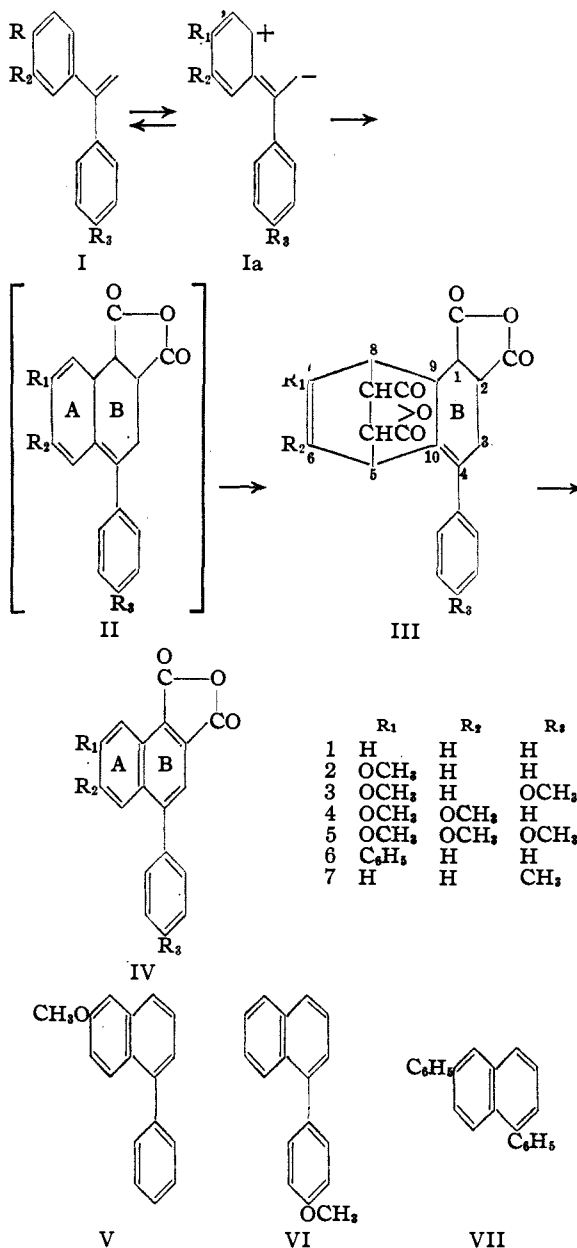
The addition of maleic anhydride to asymmetrical diphenylethylene, first observed by Wagner-Jauregg,² is a most peculiar example of Diels-Alder condensation for two reasons. In the first place, it shows that under specific structural conditions conjugation of a benzene ring with an exocyclic double bond gives a reactive dienic system, whereas styrene itself forms only copolymers with maleic anhydride.³ This behavior is undoubtedly due to enhanced resonance in the styrene system owing to the presence of another α -phenyl group. Sterical interaction of the ortho hydrogens in the two rings of I forces one of the rings out of the plane and enhances the coplanarity of the other with the unsaturated side-chain.⁴ In the second place, the intermediate (II), instead of reestablishing an aromatic ring by double bond migration, adds another molecule of the dienophile to form a bis-adduct (III). The structure of this labile product has not yet been established in a decisive manner.²

The object of the present research was to study the mechanism of the Wagner-Jauregg reaction and to investigate its applicability to the preparation of certain substituted naphthalenes and phenanthrenes. As shown in Table I, various substituted 1,1-diphenylethylenes give bis-adducts (III) in good yields. The reaction conditions are rather narrowly defined and sometimes, as in case 6, a slight departure from these conditions results in complete failure. In several cases it proved advantageous to condense the 1,1-diarylethanol directly, *i. e.*, without previous dehydration, a procedure first employed in this Laboratory⁵ and later used successfully by Arnold.⁶

Wagner-Jauregg accomplished the aromatization of the bis-adducts by a tedious three-step process. We have found that this transformation is most easily achieved by heating III with sulfur: one molecule of maleic anhydride and four hydrogen atoms are lost and 1,6-disubstituted naphthalene-3,4-dicarboxylic acid anhydrides (IV) are formed. These are intensely yellow compounds with strong, generally blue-violet fluorescence.⁷ Decarboxylation of IV was best effected by barium hydroxide and copper. Dry distillation of the potassium salts usually gave low yields and failed completely in the case of the methoxylated

derivatives owing to the cleavage of the ether group and subsequent decomposition of the resulting phenols.

On the basis of the tentative structure III for the bis-adducts, the spatial restrictions of the diene reaction (*cis* addition of the bridge, *cis* position of both carboxyls in the endo bridge) permit the formation of two racemates. In each case, however, the adducts were homogeneous, only one



(1) Part of a thesis submitted to the Hebrew University, Jerusalem, 1946.

(2) Wagner-Jauregg, *Ber.*, **63**, 3218 (1930); *Ann.*, **491**, 1 (1931).

(3) Compare, however, the successful diene reactions of isosafrol and isoeugenol, Hudson and Robinson, *J. Chem. Soc.*, 715 (1941).

(4) Coates and Sutton, *ibid.*, 567 (1942).

(5) F. Bergmann and Eschinazi, *THIS JOURNAL*, **65**, 1413 (1943).

(6) Arnold and Coyner, *ibid.*, **66**, 1542 (1944).

(7) The absorption and fluorescence spectra of this interesting class of compound are now under investigation.

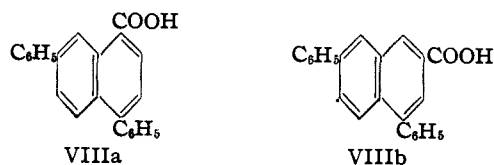
of the racemates being formed. When the two aryls in I are not identical an additional possibility of isomerism is introduced. However, in cases 2, 4, 5 and 6 the reaction products were homogeneous, indicating that one ring reacts in preference to the other. If we assume that the resonance form Ia is the actual reaction partner, we may foresee that the ring with greater energy of resonance stabilization is the participating one. Evidence in favor of this assumption is available in two cases. The decarboxylation product of IV (2; $R_1 = \text{OCH}_3$; $R_2 = R_3 = \text{H}$) proved to be identical with authentic 1-phenyl-6-methoxynaphthalene (V) and different from the isomeric 1-(*p*-anisyl)-naphthalene (VI). Decarboxylation of IV (6; $R_1 = \text{C}_6\text{H}_5$; $R_2 = R_3 = \text{H}$) gave 1,6-diphenylnaphthalene (VII), different from 1-(*p*-xenyl)-naphthalene. It seems probable that in cases 4 and 5 the predictions of the resonance theory are likewise valid. The ethylene I (7; $R_1 = R_2 = \text{H}$; $R_3 = \text{CH}_3$) gave an unexpected result. Decarboxylation of the corresponding aromatic anhydride (IV, 7) yielded an oil which was identified as 1-(*p*-tolyl)-naphthalene by comparison of the crystalline mononitro derivative. Thus the *p*-methyl group appears to have an adverse effect on the ability of the aromatic ring to participate in the condensation reaction.

The following observations cast some light on the mechanism of the Wagner-Jauregg reaction. The bis-adducts (III) readily dissociate into their components when heated. However, under the influence of hydrobromic or hydriodic acid, only one mole of maleic anhydride is split off and ring A becomes aromatic. These experiments do not answer the question as to whether the original bis-adducts already contain the naphthalene ring system or whether cyclization takes place only under the influence of strong mineral acids. However, the ease with which III is dehydrogenated by sulfur to form the anhydrides IV makes it probable that the ring system of IV was already present in III, since instances of cyclization during sulfur dehydrogenation are rare.⁸ The fact that the additional molecule of maleic anhydride is removed both by mineral acids and during dehydrogenation makes formula III appear quite reasonable and is also evidence that in both cases the driving force for the removal of the bridge is to be found in the tendency of ring A in III to become aromatic, following aromatization of Ring B (dehydrogenation) or a shift of the double bond from the 4,10- to the 9,10-position.

When the bis-adduct III, 6 was dehydrogenated without special precautions, a yellow product was obtained that appeared from the analysis to still contain the second molecule of maleic anhydride. Later a procedure was worked out whereby the desired naphthalene-1,2-dicarboxylic acid anhydride IV, 6 is readily obtained and the substance

(8) Compare the cyclization of zingiberene to cadalene, Ruzicka and Van Veen, *Ann.*, **468**, 133 (1929).

was found to have a marked tendency to form a molecular complex with maleic anhydride. Spectrographic results of Dr. R. N. Jones,⁹ as well as our own determinations of the fluorescence spectra, showed the substance IV, 6 to be optically identical with the initially isolated yellow product which therefore can be regarded as a complex of IV, 6. Treatment of IV, 6 with copper carbonate in boiling quinoline gave a monocarboxylic acid which may have either of the structures VIIIa or VIIIb.



Experimental¹⁰

I. Synthesis of 1,1-Diarylethylenes (I)

1-Phenyl-1-(*p*-anisyl)-ethylene (I,2),¹¹ 1,1-di-(*p*-anisyl)-ethylene (I,3),¹² 1-phenyl-1-(*p*-xenyl)-ethylene (I,6)¹³ and 1-phenyl-1-(*p*-tolyl)-ethylene (I,7)¹⁴ were all prepared according to literature.

1-Phenyl-1-(3,4-dimethoxyphenyl)-ethylene (I,4).—The starting material, 3,4-dimethoxybenzophenone, could not be prepared by Friedel-Crafts condensation of veratroyl chloride and benzene. Only the alternative method, condensation of benzoyl chloride with veratrole,¹⁵ was successful. The ketone reacted in the usual way with methylmagnesium iodide, to give a 90% yield of the ethylene (I,4), m. p. 93°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_2$: C, 80.0; H, 6.7. Found: C, 79.7; H, 7.0.

1-(*p*-Anisyl)-1-(3,4-dimethoxyphenyl)-ethylene (I,5).—The starting material, 3,4,4'-trimethoxybenzophenone, is prepared successfully by condensation of veratroyl chloride with anisole.¹⁶ The Grignard reaction with methylmagnesium iodide was performed as usual and gave a 70% yield of the ethylene (I,5), m. p. 106–107° (from ethanol).

Anal. Calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_3$: C, 75.6; H, 6.7. Found: C, 75.3; H, 6.7.

II. Condensation with Maleic Anhydride

General Procedure: 1 mole of ethylene and 10 moles of maleic anhydride were heated together in a stoppered Erlenmeyer at 140–160° for three hours. The red-brown reaction mixtures were then treated according to one of the following methods:

Method 1.—The excess anhydride was distilled off *in vacuo*, the residue dissolved in the minimum amount of boiling alcohol and left for twenty-four hours.

Method 2.—The crude mixture was dissolved directly in the minimum amount of hot acetic acid and left for crystallization, which started after one-half to twenty-four hours. The results are summarized in Table I. In the case of 1-phenyl-1-(*p*-xenyl)-ethylene (I,6) the only successful procedure was to heat the components exactly at 125°.

When diphenylmethylcarbinol (3 g.) was heated for three hours with maleic anhydride (12 g.) at 160° and the

(9) Results to be published separately.

(10) All melting points are uncorrected.

(11) Stoermer and Simon, *Ber.*, **37**, 4163 (1904).

(12) Pfeiffer and Wizinger, *Ann.*, **461**, 144 (1928).

(13) Schlenk and E. Bergmann, *ibid.*, **464**, 32 (1929).

(14) Tiffeneau, *Ann. chim.*, [8] **10**, 360 (1907).

(15) Sachs and Thonet, *Ber.*, **37**, 3332 (1904).

(16) Kostanecki and Tambor, *ibid.*, **39**, 4022 (1906).

TABLE I

No.	Ethylene		Pro- cedure (see experimental) a	M. p., °C.	Yield, %	Crystal form	Recrystallized from	Formula	Analyses, %			
	R =	R' =							Calcd.		Found	
1	Phenyl	Phenyl		279	42	Needles	Acetic acid	C ₂₂ H ₁₆ O ₆				
2	<i>p</i> -Anisyl	Phenyl	1	213-214	60	Plates	Acetic acid	C ₂₂ H ₁₆ O ₇	68.0	4.4	67.9	4.3
3	<i>p</i> -Anisyl	<i>p</i> -Anisyl	1	256	60	Rods	Acetic anhyd.	C ₂₄ H ₂₀ O ₆	66.1	4.6	66.4	4.8
4	3,4-Dimethoxyphenyl	Phenyl	1	245-246	60	Prismatic rods	Acetic anhyd. + acetic acid	C ₂₄ H ₂₀ O ₆	66.1	4.6	65.9	4.8
5	<i>p</i> -Xenyl	<i>p</i> -Anisyl	2	284-285	45	Microcryst.	Acetic anhyd.	C ₂₅ H ₂₄ O ₁₀ ^b	62.0	5.0	62.4	4.9
6	<i>p</i> -Xenyl	Phenyl	1 and 2	271	40	Microcryst.	Acetic acid	C ₂₃ H ₁₈ O ₆	74.3	4.4	73.9	4.5
7	<i>p</i> -Tolyl	Phenyl	2	238-239	60	Short needles	Butyl acetate	C ₂₃ H ₁₈ O ₆	70.8	4.6	70.6	4.5

^a The carbinol was condensed directly with maleic anhydride (see Experimental). See ref. (2). ^b This bis-adduct crystallizes with one mole of water, C₂₅H₂₂O₆·H₂O.

TABLE II

1,6-DISUBSTITUTED NAPHTHALENE-3,4-DICARBOXYLIC ACID ANHYDRIDES (IV)

No.	R ₁ =	R ₂ =	R ₃ =	Temp. of dehydro- genation, °C.	Yield, %	M. p., °C.	Recrystallized from	Crystal form	Formula	Analyses, %			
										Calcd.		Found	
1	H	H	H ^a	220 → 300	65	172	Xylene	Cubes	C ₁₈ H ₁₀ O ₅	78.8	3.6	78.8	4.0
2	OCH ₃	H	H	240 → 260	60	178	Acetic acid	Needles	C ₁₉ H ₁₂ O ₄	75.0	3.9	74.9	4.1
3	OCH ₃	H	OCH ₃	240 → 260	60	207	Acetic anhyd.	Hex. prisms	C ₂₀ H ₁₄ O ₅	71.9	4.2	71.8	4.4
4	OCH ₃	OCH ₃	H	240 → 260	60	187	Acetic anhyd. + acetic acid	Rods	C ₂₀ H ₁₄ O ₅	71.9	4.2	71.8	4.3
5	OCH ₃	OCH ₃	OCH ₃ ^b										
6	C ₆ H ₅	H	H	240 → 260	70	185	Acetic anhyd. + acetic acid	Prisms	C ₂₄ H ₁₄ O ₅	82.3	4.0	82.2	4.0
7	H	H	CH ₃ ^c	240 → 280	64	179-180	Benzene + pet. ether	Rods	C ₁₉ H ₁₂ O ₅	79.2	4.2	79.0	4.2

^a This anhydride was separated mechanically from a very small amount of brown prismatic plates, m. p. 166°. The quantity isolated was insufficient for analysis. ^b Aromatization of the bis-adduct III, 5 by heating with sulfur resulted in decomposition of the product. ^c The anhydride IV, 7 was separated mechanically from a small amount of a second substance, which crystallized from benzene-petroleum ether in clusters of dark-yellow needles of m. p. 189-190°. Its amount was insufficient for analysis.

reaction product dissolved in ethanol, 2.5 g., (42%) of the bis-adduct (III,1) was obtained, m. p. 280°.²

III. Dehydrogenation with Sulfur

The bis-adducts (III) were ground thoroughly with 2 equivalents of sulfur and heated in a Pyrex tube until evolution of hydrogen sulfide started (lower temperature limit in Table II, column 4). Heating was continued at this temperature usually for one and one-half hours and the temperature then raised about 50° for five minutes (upper limit in Table II). The resulting black tar was extracted with boiling acetic acid, in which, with the exception of case IV,2, the aromatic anhydrides are insoluble. The black residue was then dried in a desiccator over sodium hydroxide and sublimed *in vacuo*.

In case IV,2 the main part of the expected reaction product was found in the acetic acid solution. The solvent was distilled off *in vacuo* and the residue dried over sodium hydroxide. It was then extracted with hot alcohol, and the insoluble part sublimed *in vacuo*.

If, in any case, extraction was omitted before sublimation, the whole mass foamed over on heating *in vacuo*.

The adduct III,7 was aromatized with sulfur for ten minutes only. Longer heating caused complete decomposition.

Dehydrogenation of the bis-adduct III,6 was accomplished at 220-240°. The crude product was distilled in a tube at 190-230° (0.1 mm.), and crystallized spontaneously. This substance (IV,6) is dimorphic: from butyl acetate brown prisms of m. p. 187° are formed (A). Acetic anhydride-acetic acid as solvent yields a mixture of brown prisms (A) and, as the main product, yellow needles (B), which were separated mechanically; m. p. and mixed m. p. 187°. The two modifications are easily interchangeable. Pure A, when recrystallized from acetic acid, gives a mixture of A and B. Pure B, upon recrystallization from butyl acetate, is converted into pure A.

Sometimes, instead of IV,6, a molecular complex with maleic anhydride is isolated, m. p. 181° (yellow-red prisms from acetic anhydride-acetic acid).

Anal. Calcd. for C₂₃H₁₆O₆: C, 75.0; H, 3.6. Found: C, 75.1; H, 3.6.

A similar product can be obtained from A or B by recrystallization in the presence of maleic anhydride. This complex upon dry distillation at ordinary pressures again suffers dissociation and regenerates IV,6.

IV. Decarboxylation

After many trials, the following method was found to give the best results: The aromatic anhydride was dissolved in dioxane and poured slowly into a hot solution of barium hydroxide. After cooling, the barium salt was filtered off and dried in an oven at 100°. It was then ground thoroughly with half its weight of copper bronze and distilled at ordinary pressure.

A. 1-Phenylnaphthalene-3,4-dicarboxylic acid anhydride (IV,1) gave a 25% yield of an oil which was dissolved in acetic acid and treated with concentrated nitric acid. The solution, when poured onto ice, deposited the known 1-phenyl-4-nitronaphthalene of m. p. 132°.¹⁷

B. 1-Phenyl-6-methoxynaphthalene-3,4-dicarboxylic acid anhydride (IV,2), upon decarboxylation at 300°, gave a 30% yield of an oil which, when treated in the same way as before, gave a mononitro product, m. p. 148-149°, which crystallized from alcohol in yellow prismatic rods. It was shown by mixed melting point to be identical with the nitration product of authentic 1-phenyl-6-methoxynaphthalene (V) (see below).

Anal. Calcd. for C₁₇H₁₂O₃N: C, 73.1; H, 4.7; N, 5.0. Found: C, 73.3; H, 4.9; N, 5.1.

C. 1-(*p*-Anisyl)-6-methoxynaphthalene-3,4-dicarboxylic acid anhydride (IV,3) (0.2 g.) underwent decarboxylation at 320-350° and gave 0.04 g. = 25% of a colorless oil, which solidified upon treatment with ethanol. Recrystallization from the same solvent gave plates, m. p. 95°, identical with the specimen of 1-(*p*-anisyl)-6-meth-

(17) Weiss and Woidlich, *Monatsh.*, **46**, 453 (1925); Vesely and Stursa, *Chem. Listy*, **29**, 257 (1935); *Chem. Zentr.*, **107**, 1, 1221 (1936).

TABLE III
 1,6-DISUBSTITUTED NAPHTHALENES

R(1)	R'(6)	Temp. of dehydrogenation with sulfur, °C.	B. p., °C.	M. p., Mm.	M. p., °C.	Yield, %	Recrystallized from	Crystal form	Formula	Analyses, %			
										Calcd. C	Calcd. H	Found C	Found H
Phenyl	OCH ₃	190 → 240	158-162	0.1	...	95	C ₁₇ H ₁₄ O	87.2	6.0	86.9	6.1
<i>p</i> -Anisyl	H	220 → 280	205-206	6	120	90	Butyl acetate	Prismatic columns	C ₁₇ H ₁₄ O	87.2	6.0	87.3	5.8
<i>p</i> -Anisyl	OCH ₃	200 → 250	150-160	0.2	96-97	90	Ethanol	Plates	C ₁₉ H ₁₆ O ₂	81.8	6.1	81.5	5.9
Phenyl	Phenyl ^a				86-87	55	Methanol	Needles	C ₂₂ H ₁₈	94.3	5.7	94.5	5.7
<i>p</i> -Xenyl	H	220 → 280	260-265	0.8	147-148	60	Butanol	Prisms	C ₂₂ H ₁₈	94.3	5.7	94.2	5.9

^a This hydrocarbon was obtained by decarboxylation of the anhydride IV,6 (see Experimental).

 TABLE IV
 1,6-DISUBSTITUTED 3,4-DIHYDRONAPHTHALENES

R (1)	R' (6)	Yield, %	M. p., °C.	Recrystallized from	Crystal form	Formula	Analyses, %			
							Calcd. C	Calcd. H	Found C	Found H
Phenyl	OCH ₃	70	65	Ethanol	Plates	C ₁₇ H ₁₆ O	86.4	6.8	86.6	6.8
<i>p</i> -Anisyl	H	40	77-78	Methanol	Prismatic columns	C ₁₇ H ₁₆ O	86.4	6.8	86.7	7.1
<i>p</i> -Anisyl	OCH ₃	65	102	Isopropanol	Hexagonal plates	C ₁₉ H ₁₈ O ₂	81.2	6.8	81.5	6.9
<i>p</i> -Xenyl	H	45	113	Butanol	Lancets	C ₂₂ H ₁₈	93.6	6.4	93.5	6.6

oxynaphthalene, obtained by dehydrogenation of 1-(*p*-anisyl)-6-methoxy-3,4-dihydronaphthalene (see Table III).

D. The asymmetrical dimethoxy derivative (IV,4) underwent decarboxylation only at very high temperatures (about 400°). Most of the material decomposed. The small amount of yellow oil which distilled over gave analytical results which leave some doubt as to the purity of the sample. No crystalline substance could be isolated from the nitration mixture.

Anal. Calcd. for C₁₉H₁₆O₂: C, 81.8; H, 6.1. Found: C, 80.9; H, 6.3.

E. 1,6-Diphenylnaphthalene-3,4-dicarboxylic acid anhydride (IV,6) (0.5 g.) was decarboxylated between 320-400°. A colorless oil was obtained which crystallized upon trituration with methanol; yield 210 mg. (55%). From methanol, the substance (VII) crystallized in clusters of short needles, m. p. 86-87° (see Table III).

The picrate was prepared in ethanolic solution. It suffered dissociation when dissolved in ethanol or acetic acid, and was therefore recrystallized from a cold-saturated solution of picric acid in ethanol; m. p. 106-108°.

Anal. Calcd. for C₂₃H₁₈O₇N₂: N, 8.3. Found: N, 8.2.

When the bis-anhydride or the mono-anhydride (IV,6) (0.5 g.) was heated in quinoline (10 cc.) in the presence of basic copper carbonate (0.1 g.) for thirty minutes, and the mixture poured into dilute hydrochloric acid, a solid precipitate was obtained, which crystallized from acetic acid in rods, m. p. 205-207° (VIII a or b). It titrated as a monobasic acid.

Anal. Calcd. for C₂₂H₁₆O₂: C, 85.2; H, 4.9. Found: C, 85.4; H, 4.7.

F. The crude aromatic anhydride (IV,7) obtained from 1-phenyl-1-(*p*-tolyl)-ethylene, suffered decarboxylation at 320° and yielded an oil which, upon nitration as before, gave a yellowish product. It crystallized from ethanol in branched prisms, m. p. 126-127°, and was identical with the second nitration product, described below.

1-(*p*-Tolyl)-naphthalene¹⁸ was nitrated in hot acetic acid and the crude products, obtained by pouring the mixture onto ice, crystallized from methanol. There appeared first red-brown, dense clusters, m. p. 129-130° (substance A). The filtrate after several hours deposited a yellowish product which crystallized from ethanol in branched prisms, m. p. 126-127° (substance B) identical with the nitration product described before.

According to the analytical figures, A and B represent isomeric mononitro derivatives.

Anal. Calcd. for C₁₇H₁₅O₂N: N, 5.3. Found: Substance A: N, 5.2; substance B: N, 5.5.

V. Grignard Synthesis of Naphthalene Derivatives

6-Methoxytetralone-1 was prepared according to Burnop, *et al.*¹⁹ As we did not find any details about the preparation of the starting material, tetralin-6-sulfonic acid, we have worked out the following method:

To tetralin (440 g.) is added at room temperature concentrated sulfuric acid (400 g.) with stirring. The mixture is then heated for one-half hour at 70° and cooled again at 0°, whereupon tetralin-6-sulfonic acid crystallizes. Sodium hydroxide (180 g. in 300 cc. of water) is added slowly, until the solution becomes alkaline. The mixture is boiled with charcoal and filtered. The crude sodium tetralin-6-sulfonate is then dissolved in water (2 liters), boiled with charcoal and filtered. Sodium chloride (500 g.) is now added to the boiling solution, and stirring is continued until the salt dissolves completely. Upon cooling, the pure sodium sulfonate (300 g.) crystallizes in glistening leaflets.

A. The Grignard reaction between tetralone (14.5 g.) and *p*-anisylmagnesium bromide (from 19 g. of *p*-bromoanisole) was carried out in an ether-benzene mixture. The crude carbinol was dehydrated directly with sodium bisulfate at 160°. Distillation gave a fraction, b. p. 167° (0.15 mm.), which crystallized upon treatment with methanol (see Table IV). Its dehydrogenation product (IV) was crystalline and different from the decarboxylation product of the anhydride (IV,2) (see Table IV).

B. The reaction product from 6-methoxytetralone-1 (15 g.) and phenylmagnesium bromide was distilled at 159-161° (0.05 mm.). It crystallized upon trituration with ethanol (see Table III).

1-Phenyl-6-methoxy-3,4-dihydronaphthalene (3 g.) was dehydrogenated with sulfur (0.5 g.) at 190-240°. Distillation over copper gave a colorless oil, b. p. 158-162° (0.1 mm.) (V); yield, quantitative.

V (1 g.) was dissolved in acetic acid (5 cc.) and nitric acid (d. 1.48; 2 cc.) added while stirring. The mixture was then heated to 40-50° for one to two minutes and poured onto ice. The granular precipitate was recrystallized from acetic acid. The mononitro derivative of V formed flat, prismatic rods of m. p. 148-149°, identical with the product described above.

C. The product from the Grignard reaction between 6-methoxytetralone-1 and *p*-bromoanisole, distilled at 170-180° (0.6 mm.) and crystallized upon treatment with ethanol (see Table IV). Its dehydrogenation product was identical with the decarboxylation product of the anhydride IV,3 (see above and Table III).

(18) F. Bergmann and A. Weizmann, *J. Org. Chem.*, **9**, 352 (1944).

(19) Burnop, Elliott and Linstead, *J. Chem. Soc.*, 727 (1940).

D. The Grignard reaction between *p*-bromodiphenyl and tetralone was carried out according to the directions of Schmidlin.²⁰ After addition of the ketone, the solvent was distilled off and the pasty residue heated for three hours on a boiling water-bath. The crude carbinol was dehydrated with sodium bisulfate at 180° and the product distilled. The fraction of b. p. 210–215° (0.8 mm.) consisted of 0.5 g. of a yellow-brown oil, which solidified upon trituration with ethanol (see Table IV). Its dehydrogenation product (see Table III) was different from 1,6-diphenylnaphthalene (VII).

Acknowledgment.—The authors wish to thank Prof. L. F. Fieser for his kind advice in the preparation of this and the following manuscripts.

Summary

1. The Wagner-Jauregg condensation between

(20) Schmidlin, *Ber.*, **45**, 3171 (1912).

1,1-diphenylethylene and maleic anhydride has been applied to a number of 1,1-diarylethylenes and a convenient method worked out for conversion of the bis-adducts into 1,6-disubstituted naphthalenes.

2. When the two aryls are different, the reaction follows the course predicted by the theory of resonance, *i. e.*, the ring with larger resonance contribution participates exclusively in the addition to the dienophile.

3. The reaction mechanism, as proposed by Wagner-Jauregg, is supported by the new experimental results.

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The Use of Diarylvinyl Bromides as Diene Components in the Wagner-Jauregg Reaction

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In addition to procedures that achieve the aromatization of Diels-Alder adducts by use of external dehydrogenating agents, investigations have been made of the use of halogenated reaction partners such that the adducts can undergo dehydrohalogenation to give partially or completely aromatized products. Thus Fieser and Dunn,² in an extension of observations recorded in a patent³ concerning the addition of dienes to 2-chloro-1,4-naphthoquinone, found that adducts from 3-halo-1,2-naphthoquinones easily lose hydrogen halide to give dihydrides that undergo air oxidation to aromatized phenanthrenequinones. Synerholm⁴ employed chloromaleic anhydride as the dienophilic component in a Wagner-Jauregg reaction in boiling xylene and found that hydrogen chloride was eliminated under the conditions of the addition with the production of a stable dihydronaphthalene derivative. Halogenated diene partners have been used only rarely. Favorsky and Favorskaya⁵ found that the adduct from 1-chloro-3-methylbutadiene-1,3 and maleic anhydride loses hydrogen chloride readily to give a cyclohexadiene derivative that adds a second molecule of the dienophile.

We have found that the Wagner-Jauregg reaction of the type described in the first paper of this series⁶ can be applied to the condensation of diarylvinyl bromides (I) with maleic anhydride. The reaction affords bromine-containing non-crystalline adducts of the probable structure II,⁶

and these on sublimation *in vacuo* lose one molecule each of hydrogen bromide, hydrogen and maleic anhydride with the production of crystalline aromatic anhydrides of the type III. A possible sequence of reactions is through the intermediates IIa and IIb; the acid liberated in the formation of IIa may be responsible for the elimination of the endo-bridge in the next step. The last step can be regarded as proceeding by enolization of the hydrogen atoms adjacent to the carbonyl groups and autoxidation of the resulting dienediol.^{6a} The ready aromatization of the 1,2-dihydronaphthalene-1,2-dicarboxylic anhydride derivatives IIa is in marked contrast to the stable character of the 3,4-dihydro derivatives isolated by Synerholm⁴; the latter contains a double bond between the carboxylated carbon atoms.

1-Phenyl-1-(*p*-bromophenyl)-vinyl bromide (Ic) was prepared according to the literature⁷ and the crude mixture of the two isomers (m.p. 55°) was used. Di-(*p*-anisyl)-vinyl bromide (Ib) was prepared by Pfeiffer and Wizinger⁸ by bromination in benzene or carbon tetrachloride. We attempted to effect bromination in acetic acid solution, but obtained only the dimer of di-(*p*-anisyl)-ethylene. Schmitz-Dumont⁹ was unable to dimerize this ethylene with sulfuric-acetic acid at room temperature, and we have found that the ethylene is not altered by the same reagent at the reflux temperature, and we also observed that boiling hydrobromic-acetic acid does not effect dimerization but merely causes partial demethylation. The dimerization by bromine in acetic acid thus represents an unusual reaction, and the phenomenon is being investigated further. The

(1) Part of a thesis submitted to the Hebrew University, Jerusalem, 1947.

(2) Fieser and Dunn, *THIS JOURNAL*, **59**, 1016, 1024 (1937).

(3) I. G. Farbenindustrie, British Patent 320,375 (1929).

(4) Synerholm, *THIS JOURNAL*, **67**, 345, 1229 (1945).

(5) Favorsky and Favorskaya, *Compt. rend.*, **200**, 839 (1935); *C. A.*, **33**, 928 (1939); **134**, 7844 (1940).

(6) F. Bergmann, Szmuszkowicz and Fawaz, *THIS JOURNAL*, **69**, 1778 (1947).

(6a) F. Bergmann, *ibid.*, **64**, 176 (1942).

(7) E. Bergmann, Engel and Meyer, *Ber.*, **65**, 446 (1932).

(8) Pfeiffer and Wizinger, *Ann.*, **461**, 132 (1928).

(9) Schmitz-Dumont, Thömske and Diebold, *Ber.*, **70**, 175 (1937).