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 160° 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 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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[20] Schmidlin, *Ber.*, **45**, 3171 (1912).

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

BY FELIX BERGMANN AND JACOB SZMUSZKOWICZ[1]

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 patent[3] 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. Synerholm[4] 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 Favorskaya[5] 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 series[6] can be applied to the condensation of diarylvinyl bromides (I) with maleic anhydride. The reaction affords bromine-containing noncrystalline 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 Synerholm[4]; the latter contains a double bond between the carboxylated carbon atoms.

1-Phenyl-1-(*p*-bromophenyl)-vinyl bromide (Ic) was prepared according to the literature[7] and the crude mixture of the two isomers (m.p. 55°) was used. Di-(*p*-anisyl)-vinyl bromide (Ib) was prepared by Pfeiffer and Wizinger[8] 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-Dumont[9] 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

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[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).

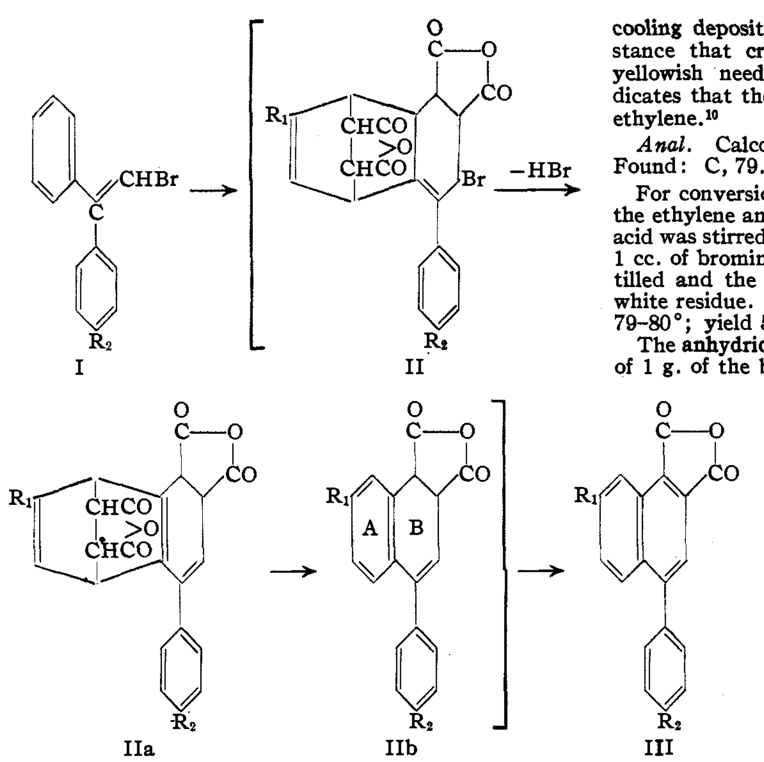
[6] F. Bergmann, Szmuszkowicz and Fawaz, THIS JOURNAL, **69**, 1773 (1947).

[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, Thömke and Diebold, *Ber.*, **70**, 175 (1937).



a: R_1, R_2 = H
b: R_1, R_2 = OCH_3
c: R_1 = Br, R_2 = H
d: R_1 = C_6H_5, R_2 = H

vinyl bromide Ib desired for the present study was obtained in 75% yield by bromination of the ethylene in acetic acid in the presence of one mole of sodium acetate.

The condensation of 1,1-diaryl-2,2-dihalogenoethylenes was attempted without success. Thus 1,1-di-(*p*-chlorophenyl)-2,2-dichloroethylene was recovered unchanged after being heated with maleic anhydride under a variety of conditions. It appears also that substituents in the vinyl group other than halogen render the diarylethylene unreactive. Triphenylethylene, for example, could not be brought into reaction with maleic anhydride. A further observation is that ω-bromostyrene when heated with maleic anhydride gave no addition product but merely lost hydrogen bromide and yielded phenylacetylene.

Experimental

1-Phenylnaphthalene-3,4-dicarboxylic Acid Anhydride (IIIa).—A mixture of 1 g. of diphenylvinyl bromide and 4 g. (10 equiv.) of maleic anhydride was heated at 160–180° for four hours and the dark brown mass was dissolved in alcohol and the product precipitated with water. The well-dried, granular precipitate was sublimed at 270–340° (2 mm.); trituration with ethanol gave a solid that crystallized from ligroin (b. p. 130°) in clusters of needles, m. p. 172° (no depression with previous sample[6]); yield 400 mg. (38%).

1-*p*-(Anisyl)-6-methoxynaphthalene-3,4-dicarboxylic Acid Anhydride (IIIb).—In an attempted bromination, a solution of 1 g. of 1,1-di-(*p*-anisyl)-ethylene in 10 cc. of acetic acid was treated with 0.2 cc. of bromine in 2 cc. of acetic acid. The solution became hot and developed a dark blue color that quickly faded, and the solution on cooling deposited in quantitative yield a yellowish substance that crystallized from butyl acetate in faintly yellowish needles, m. p. 203–204°. The analysis indicates that the substance is a **polymer** (dimer ?) of the ethylene.[10]

Anal. Calcd. for $(C_{16}H_{16}O_2)_n$: C, 80.0; H, 6.7. Found: C, 79.8; H, 6.4.

For conversion to the **bromide Ib**, a solution of 5 g. of the ethylene and 8 g. of sodium acetate in 50 cc. of acetic acid was stirred vigorously in an ice-bath and treated with 1 cc. of bromine, added by drops. The solvent was distilled and the product extracted with ethanol from the white residue. The bromide crystallized in plates, m. p. 79–80°; yield 5 g. (75%).

The **anhydride IIIb** was prepared by refluxing a solution of 1 g. of the bromide and 4.2 g. of maleic anhydride in 10 cc. of acetic acid for ten minutes. A heavy precipitate that separated immediately, was identified as fumaric acid. The addition of water to the filtrate precipitated a dark oil that was dried at 110° and then sublimed at 260–320° (0.3 mm.). A brown oil distilled and was triturated with ethanol to give a solid that could be crystallized from butyl acetate. The product melted at 205–206° and was identical with the earlier sample[6]; yield 300 mg. (29%).

1-Phenyl-6-bromonaphthalene-3,4-dicarboxylic Acid Anhydride (IIIc).—The bromide Ic (2 g.) was treated with maleic anhydride (6 g.) as above. The reaction mixture, when warmed briefly with acetic acid, deposited some fumaric acid, which was separated. The filtrate on dilution deposited brown oil that was sublimed at 280–330° (0.3 mm.). The reddish distillate was triturated with alcohol and the resulting solid crystallized from ligroin (90°). The anhydride formed yellow needles showing a strong blue fluorescence; m. p. 201–202°; yield 600 mg. (29%).

Anal. Calcd. for $C_{18}H_9O_3Br$: C, 61.2; H, 2.55. Found: C, 61.5; H, 2.7.

1-Phenyl-1-(*p*-xenyl)-vinyl Bromide (Id).[11]—The ethylene (5 g.) was dissolved in boiling acetic acid (40 cc.) and precipitated in a finely divided state by cooling and stirring. Bromine (1.5 cc.) in acetic acid (15 cc.) was then added dropwise at 0°, until a yellowish color persisted. Stirring was continued for ten minutes and the solution was boiled briefly to complete the decomposition of the dibromide and allowed to cool. The bromide Id separated as clusters of white needles, m. p. 165°; yield 4 g. (60%).

Anal. Calcd. for $C_{20}H_{15}Br$: C, 71.6; H, 4.5. Found: C, 71.7; H, 4.4.

1,6-Diphenylnaphthalene-3,4-dicarboxylic Acid Anhydride (IIId).—When the above bromide (1 g.) was heated with maleic anhydride (3.6 g.) a vigorous evolution of hydrobromic acid started at about 220° and ended after heating for one hour at 220–235°. The brown mass was dissolved in acetic acid, water was added, and the precipitated product dried and sublimed at 250–300° (1 mm.). Crystallization of the brown sublimate (0.5 g.) from acetic acid gave brown prisms (A), and dilution of the filtrate gave a yellow substance (B). The substances both melted at 187° and proved to be the two dimorphic modifications of IIId previously described.[6]

Anal. Calcd. for $C_{24}H_{14}O_3$: C, 82.3; H, 4.0. Found: A: C, 82.0; H, 4.0; B: C, 82.2; H, 4.2.

Summary

Diarylvinyl bromides condense with maleic an-

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[10] Regarding the two dimers of 1,1-diphenylethylene, see E. Bergmann and Weiss, *Ann.*, **480**, 49 (1930).

[11] Compare Pfeiffer and Schneider, *J. prakt. Chem.*, [2] **129**, 129 (1931).

hydride in the Wagner-Jauregg reaction to give adducts that upon sublimation in vacuum lose one mole each of maleic anhydride, hydrogen bromide, and hydrogen with conversion to the fully aromatized naphthalene-1,2-dicarboxylic acid anhydrides.

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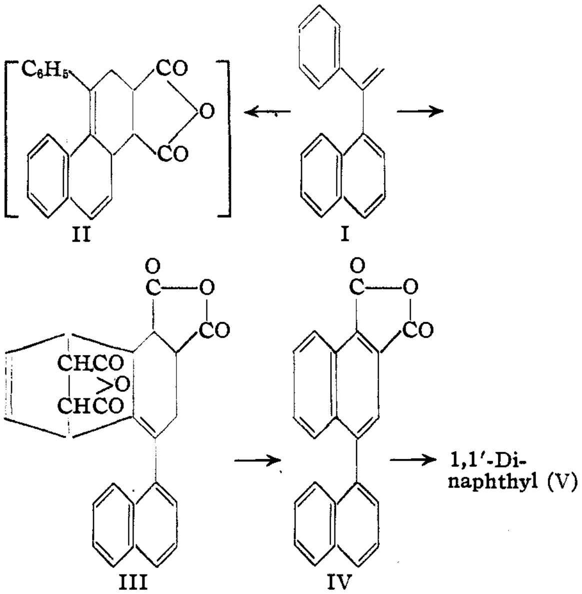
[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

Ortho Effects in the Wagner-Jauregg Reaction

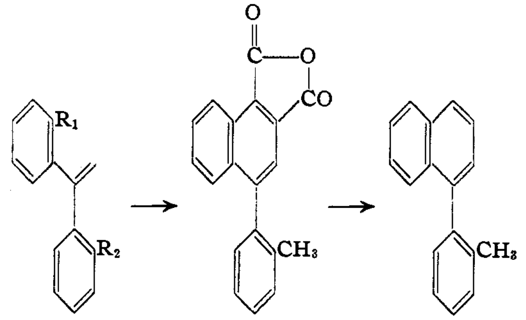
BY JACOB SZMUSZKOWICZ[1] AND FELIX BERGMANN

In view of the observations reported in the first paper of this series[2] it was expected that 1-phenyl-1-(α-naphthyl)-ethylene (I) would condense with maleic anhydride as a derivative of 1-vinylnaphthalene rather than of styrene, particularly since ordinarily the former structure represents a reactive dienic system and the latter a refractory one. The expected product II could hardly add a second molecule of maleic anhydride, as in the usual Wagner-Jauregg reaction. We were therefore surprised to obtain from I a bis-adduct that was shown to have the structure III by aromatization to IV and decarboxylation to 1,1'-dinaphthyl.



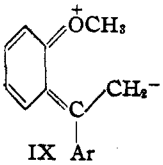
II I III IV

It thus appears that the resonance effect[2] is obscured by a second factor. A possible explanation is that the ring *ortho* to the α-naphthyl linkage interferes with the coplanarity of the aryl–vinyl system required for a condensation to II; indeed 1,1-di-(α-naphthyl)-ethylene is inactive toward maleic anhydride. However, a study of three *ortho*-substituted 1,1-diarylethylenes has led to apparent inconsistencies. Both the mono- and di-*ortho* methoxy derivatives VIa and VIb failed to react with maleic anhydride, even though the former contains one unsubstituted phenyl ring and would be expected to be comparable to I. The *o*-methyl substituted diphenylethylene VIc reacted in the normal manner to give a bis-adduct that was converted by aromatization (VII) and decarboxylation to the known α-(*o*-tolyl)-naphthalene (VIII).[3] A possible explanation of the lack of reactivity of the ortho methoxyl-substituted compounds is that the specific properties of the methoxyl group make IX the prevalent resonance structure of VIa.



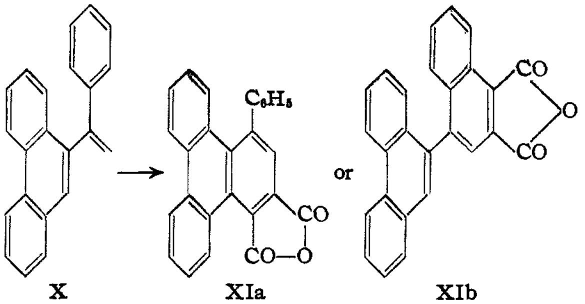
VI VII VIII

(a) $R_1 = OCH_3$; $R_2 = H$
(b) $R_1 = OCH_3$; $R_2 = OCH_3$
(c) $R_1 = H$; $R_2 = CH_3$



IX

A few experiments were made with ethylenes containing other polycyclic aryl substituents. 1-Phenyl-1-(β-naphthyl)-ethylene gave only minute amounts of reaction product. 1-Phenyl-1-



X XIa XIb

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

(2) F. Bergmann, Szmuszkowicz and Fawaz, THIS JOURNAL, 69, 1773 (1947).

(3) Cook and Lawrence, *J. Chem. Soc.*, 1431 (1936).