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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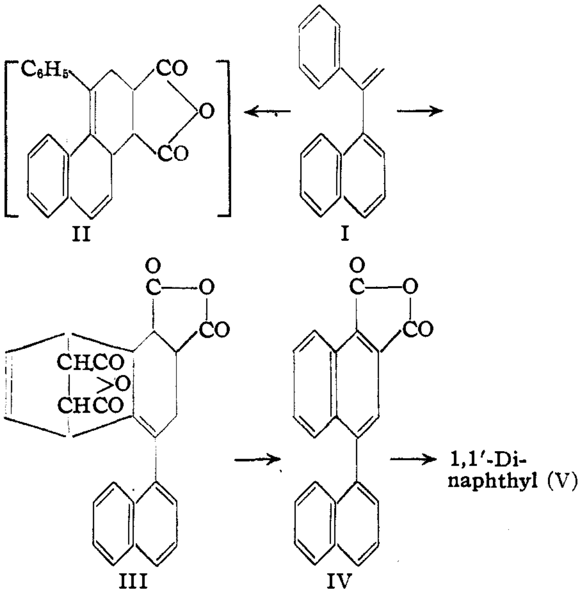
[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

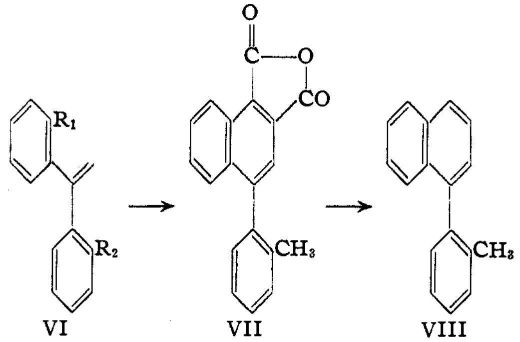
Ortho Effects in the Wagner–Jauregg Reaction

BY JACOB SZMUSZKOWICZ[1] AND FELIX BERGMANN

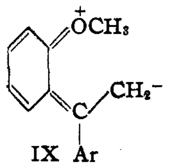
In view of the observations reported in the first paper of this series[2] it was expected that 1-phenyl-1-(α-naphthyl)-ethylene (I) would condense with maleic anhydride as a derivative of 1-vinylnaphthalene rather than of styrene, particularly since ordinarily the former structure represents a reactive 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.



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.

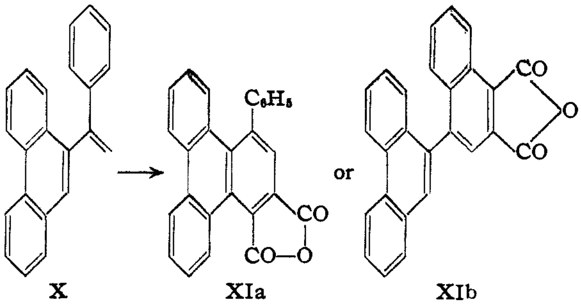


(a) $R_1 = OCH_3$; $R_2 = H$
(b) $R_1 = OCH_3$; $R_2 = OCH_3$
(c) $R_1 = H$; $R_2 = CH_3$



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-



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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).

(9′-phenanthryl)-ethylene (X) has been reported to be inert to maleic anhydride.[4] We have reinvestigated the reaction and found that on aromatization a very small amount of aromatic anhydride can be isolated of composition corresponding to either XIa or XIb.

Experimental[5]

The required **ethylenes** were all prepared according to the literature: 1-phenyl-1-(α-naphthyl)-ethylene (I),[6] 1-phenyl-1-(β-naphthyl)-ethylene,[7] 1-phenyl-(9′-phenanthryl)-ethylene (X),[4] 1-phenyl-1-(*o*-anisyl)-ethylene (VIa),[8] 1,1-di-(*o*-anisyl)-ethylene (VIb),[9] 1,1-di-(α-naphthyl)-ethylene[10] and 1-phenyl-1-(*o*-tolyl)-ethylene (VIc).[7] In the preparation of VIc a solid **by-product** was isolated; it formed needles, m. p. 120°, from ethanol.

Anal. Calcd. for $(C_{15}H_{14})_n$: C, 92.8; H, 7.2. Found: C, 92.5; H, 7.5.

Condensation with Maleic Anhydride. (a) 1-Phenyl-1-(α-naphthyl)-ethylene (I).—A mixture of 2.3 g. of I and 10 g. of maleic anhydride was heated at 160° for three hours and the red brown mass dissolved in warm glacial acetic acid (20 cc.). After one hour crystallization set in and 0.7 g. (16%) of white, practically pure prisms of III were obtained. Recrystallization of the anhydride from acetic anhydride was attended with heavy losses but gave prismatic rods, m. p. 333–334°.

Anal. Calcd. for $C_{26}H_{18}O_6$: C, 73.2; H, 4.2. Found: C, 73.0; H, 4.5.

The bis-adduct III (2.6 g.) was heated with sulfur (0.5 g.) at 325° for five minutes and then to 340° for one minute. The black mass was powdered while still hot and sublimed at 245–320° (0.2 mm.). The yellow sublimate was triturated with ethanol and crystallized from butyl acetate or acetic anhydride. **1,1′-Dinaphthyl-3,4-dicarboxylic acid anhydride** (IV) was thus obtained in 61% yield as beautiful yellow prismatic rods, m. p. 205°; the solutions show yellow-green fluorescence.

Anal. Calcd. for $C_{22}H_{12}O_3$: C, 81.5; H, 3.7. Found: C, 81.4; H, 3.9.

The anhydride IV (0.5 g.) was converted to the barium salt as described previously[2] and this was heated with copper bronze (0.5 g.) at 300° at ordinary pressure. A colorless oil distilled and solidified readily. Crystallization from alcohol afforded a mixture of white plates and brown prisms. The plates on recrystallization melted at 153–154° and gave no depression when mixed with authentic **1,1′-dinaphthyl**.

Anal. Calcd. for $C_{20}H_{14}$: C, 94.5; H, 5.5. Found: C, 94.4; H, 5.3.

The prisms, when recrystallized from alcohol, melted at 160–161° (found: C, 93.1, 93.0; H, 5.3, 5.7).

(b) 1-Phenyl-1-(β-naphthyl)-ethylene reacted with maleic anhydride only in boiling xylene solution (all other experiments were negative). The amorphous residue remaining after removal of solvent and excess reagent in vacuum could not be crystallized satisfactorily and was dehydrogenated with sulfur at 240–340°. Sublimation at 275–330 (1 mm.) gave an oil that crystallized on treatment with acetone and ligroin (80°). The substance crystallized from acetic anhydride as microcrystals, m. p. 221–222°; the analysis indicates that it is an **isomer of IV**.

Anal. Calcd. for $C_{22}H_{12}O_3$: C, 81.5; H, 3.7. Found: C, 81.5; H, 3.9.

(c) 1-Phenyl-1-(9′-phenanthryl)-ethylene (X) condensed with maleic anhydride only in boiling xylene. The mixture was worked up as in (b) and the crude adduct heated with sulfur at 220–300° for thirty minutes. Sublimation at 260–310° (8 mm.) and trituration of the sublimate with acetone gave a dark yellow substance; on crystallization from acetic anhydride and then from butyl acetate the anhydride (XIa or XIb) formed prisms, m. p. 258–259°.

Anal. Calcd. for $C_{26}H_{14}O_3 \cdot {}^1/_2H_2O$: C, 81.5; H, 3.9. Found: C, 81.5; H, 3.9.

(d) 1-Phenyl-1-(*o*-tolyl)-ethylene, VIc (2 g.) was heated with maleic anhydride for four hours at 155° and the product obtained crystalline from ethanol (10 cc.) by scratching. The bis-adduct (1.8 g., 60%) crystallized slowly from acetic acid, containing a little acetic anhydride in cubes, m. p. 288–289°.

Anal. Calcd. for $C_{23}H_{18}O_6$: C, 70.8; H, 4.6. Found: C, 70.6; H, 4.5.

Aromatization of the bis-adduct (1.5 g.) was effected with sulfur (0.5 g., ten minutes at 300°) and the product sublimed (340°, 1 mm.) and crystallized from ligroin (80°) and a little benzene. **1-(*o*-Tolyl)-naphthalene-3,4-dicarboxylic acid anhydride** (VII) formed clusters of leaflets, m. p. 161–162°.

Anal. Calcd. for $C_{19}H_{12}O_3$: C, 79.2; H, 4.2. Found: C, 79.5; H, 4.3.

The anhydride is extremely sensitive. A solution in hot isopropanol on cooling deposited white needles (m. p. 153°) of a substance that is acidic to litmus and is thus probably the half-ester of the diacid.

Decarboxylation of 0.2 g. of VII by heating the barium salt with copper as in (a) gave 70 mg. (47%) of hydrocarbon, m. p. 67–68°, that showed no depression on admixture with authentic α-(*o*-tolyl)-naphthalene.

Summary

1-Phenyl-1-(α-naphthyl)-ethylene reacts with maleic anhydride to give a Wagner-Jauregg type bis-adduct, that has been shown to be a derivative of 1,1-dinaphthyl. The unexpected participation of the phenyl rather than the naphthyl group is attributed to an ortho effect.

An *o*-methyl substituent in one of the phenyl groups of 1,1-diphenylethylene likewise orients an addition involving the unsubstituted aryl group. An *o*-methoxyl substituent in either or both of the phenyl groups blocks the addition of maleic anhydride. Diarylethylenes containing the β-naphthyl and the 9′-phenanthryl groups gave low yields of adducts of unestablished structure.

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[4] E. Bergmann and F. Bergmann, THIS JOURNAL, **59**, 1443 (1937).

[5] All melting points are uncorrected.

[6] Acree, *Ber.*, **37**, 2753 (1904); Stoermer and Simon, *ibid.*, **37**, 4163 (1904).

[7] E. Bergmann and Bondi, *ibid.*, **66**, 286 (1933).

[8] Stoermer and Kippe, *ibid.*, **36**, 3992 (1903).

[9] E. Bergmann and Bondi, *Ber.*, **64**, 1455 (1931).

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