[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

The Influence of Substituents on the Course of Addition of Maleic Anhydride to Diarylethylenes

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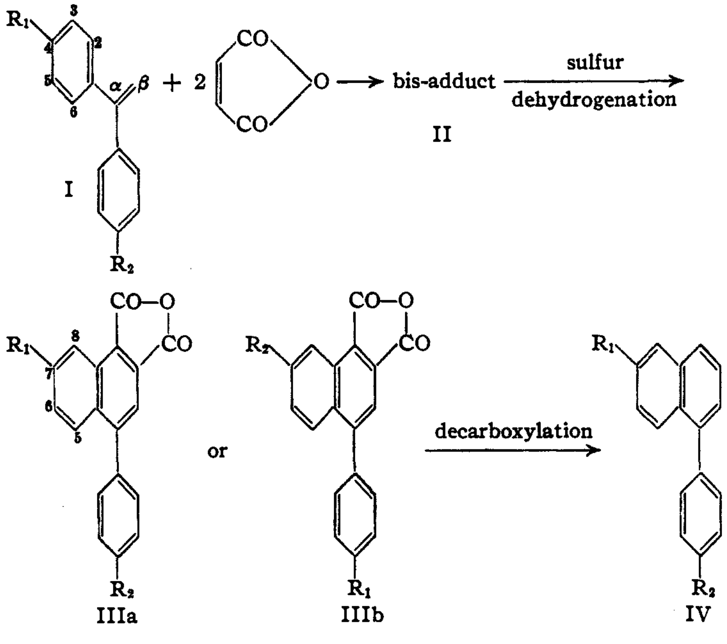
When an unsymmetrical diarylethylene of the general formula I is subjected to a Wagner–Jauregg type addition of maleic anhydride,[2] the reaction can lead to two isomeric products (IIIa or IIIb). However, as indicated in our earlier paper[3] and elaborated upon in the present investigation, only a single product is obtained in every case.[4] Proof of the structure of the addition product was obtained either by degradation of the aromatic anhydrides III to simple naphthalene derivatives, which could be synthesized in an unequivocal way or identified by exclusion of the isomeric structure, or by spectrographical analysis.[5]

TABLE I

FORMATION OF 4-ARYLNAPHTHALENE-1,2-DICARBOXYLIC ACID ANHYDRIDES (III)

	Ethylene used (I)		Aromatic anhydride (III)		
	R_1 =	R_2 =	R_1 =	R_2 =	Proof of structure
1	Phenyl	H	Phenyl	H	By exclusion
2	CH_3	H	H	CH_3	By independent synthesis
3	C_2H_5	H	H	C_2H_5	By spectroscopic analogy
4	$(CH_3)_2CH$	H	H	$(CH_3)_2CH$	By spectroscopic analogy
5	$(CH_3)_3C$	H	H	$(CH_3)_3C$	By spectroscopic analogy
6	OCH_3	H	OCH_3	H	By independent synthesis
7	OCH_3 (and OCH_3 at C_5)	H	OCH_3 (and OCH_3 at C_6)	H	By spectrographical analysis
8	F	H	H	F	By independent synthesis
9	Cl	H	H	Cl	By independent synthesis
10	Br	H	H	Br	By analogy
11	F	CH_3	(F	CH_3?)	None



Our results, which are summarized in Table I, enable us to divide all the aromatic substituents investigated into two classes: (a) substituents which promote participation of the substituted ring in the addition reaction (methoxyl, phenyl); (b) substituents which prevent participation of the substituted ring (halogen, alkyl).

For a full understanding of this classification we have to take into consideration that a substituent of group b does not interfere *per se* with the successful addition to the substituted ring. Thus, although in the unsymmetrical halogenated ethylenes (I,8 and 9) the substituted ring is excluded from reaction, the symmetrical dihalogenated derivatives (I,13 and 14) react very smoothly with maleic anhydride and the same is true for the di-(*p*-tolyl)-ethylene (I,12). Therefore in the unsymmetrically substituted ethylenes very accurately balanced electronic effects must result from the presence of two different aromatic rings.

If methoxyl and chlorine are taken as representatives of the two groups, it appears probable that the reaction starts by electrophilic attack of maleic anhydride to the β-carbon atom of the side chain. This attack is favored by the +T – effect of methoxyl and hindered by the –I – effect of chlorine (as compared to the unsubstituted ring), the effects being transmitted through the whole

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[1] Part of a thesis submitted to the Hebrew University, Jerusalem, 1947.

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

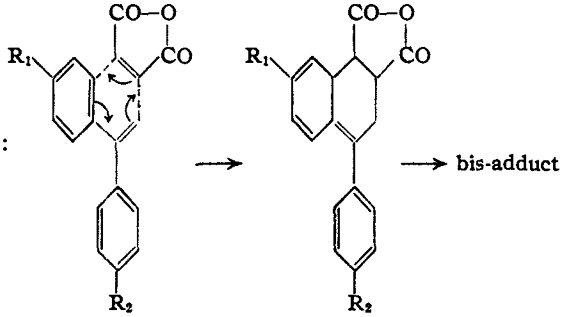
[3] F. Bergmann, J. Szmuszkowicz and Fawaz, THIS JOURNAL, **69**, 1773 (1947).

[4] About the possible exception from this rule of the *t*-butyl derivative I,5 see Experimental Part.

[5] Hirschberg and Jones, *Can. J. Res.*, in press.

conjugated system to the β-carbon atom. However, in electrophilic substitutions methyl usually behaves like methoxyl, whereas in the reaction under discussion the alkyls parallel the halogen group. This apparent contradiction can, however, be solved easily, if it is realized that the reaction involves a two-step addition to the β-carbon and the ortho position. If the first addition is electrophilic, the second step must be nucleophilic in character, so that the reacting system can pass through a complete electronic cycle, in which all electron shifts occur simultaneously (scheme A).

A:



The course of the reaction is therefore dependent on the electronic influence of a given substituent upon both the β- and ortho-position. If we assume that a substituent would—at least qualitatively—exert a similar influence on the diphenylvinyl system as it does on an isolated benzene ring, we can make use of Hammett's σ-constants for an estimate of the electronic shifts to be expected.[6] The pertinent figures are given in Table II and show very clearly, that an increased positive charge in the 2-position is at least as important as an increased electron density at the β-carbon atom. This is borne out especially by example I,1. The *p*-phenyl group has such a small positive σ-value, that no prediction can be made on this base. However the large positive δ-value for the *m*-position, directs addition toward the substituted ring. The figures of Table II thus support the reaction scheme A, as formulated above, and make it very probable that all Diels–Alder reactions follow a similar "polar" pattern.

An interesting case is represented by the dimethoxy compound I,7. Superficially both positions involved in the cyclization bear a negative charge and thus addition should be directed to the unsubstituted ring. However, the Wagner–Jauregg reaction involves a simultaneous addition of the dienophil at both the β-carbon and the *o*-position, and it is clear that the two methoxyl groups cannot resonate at the same time to produce a negative charge on their respective para positions and that the more extended conjugated systems associated with the 4-methoxyl is favored for resonance. Therefore, the 5-methoxyl can exert only its inductive effect. Although the I-effect of an aromatic methoxyl upon its para position cannot be determined separately, we have tried to estimate the electronic displacements in I,7 in the following way:

The β-carbon atom is under the *p*-effect of the resonating C_4-methoxyl ($\sigma = -0.268$) and the *m*-effect of the C_5-methoxyl ($\sigma = +0.115$). Assuming additivity of the two effects, we come to an over-all value of $\sigma_\beta = -0.153$. For the 2-position in the ring we have the *m*-effect of the resonating C_4-methoxyl, which certainly is $> +0.115$ and the purely inductive *p*-effect of the C_5-methoxyl, which is unknown, but certainly smaller than the *m*-effect (compare the values for *m*- and *p*-chlorine, *m*- and *p*-bromine), so that the increase of the meta-inductive effect of the C_4-methoxyl would be approximately balanced by the decrease of the para-inductive effect of the C_5-methoxyl. We assume σ_{ortho} to be approximately $2 \times 0.115 = +0.230$. Conditions in the 4,5-dimethoxylated ring are thus very favorable for the addition of maleic anhydride according to scheme A.

The symmetrically substituted diarylethylenes represent a different case. In general, resonance and coplanarity between the ring and the vinyl group in styrene is increased by the introduction of a second ring as in I. If both aromatic systems are identical, the symmetry of resonance favors the Wagner–Jauregg addition so much, that adversary electronic effects of individual substituents are overcome. If the two rings are not identical, any small difference in resonance energy is enlarged by the fact that only one aromatic group can be coplanar with the vinyl group at a time, whilst the other one is twisted out of the plane.[7]

The reaction scheme, as developed here, permits several predictions to be made about the course the reaction will take, if a single substituent is introduced in I into a *m*-position. This aspect of the problem is now under investigation.

TABLE II

σ-VALUES FOR *m*- AND *p*-SUBSTITUENTS

Substituent		σ-Value for *p*-Position	*m*-Position
Group a:	Methoxyl	−0.268	+0.115
	Phenyl	+ .009	+ .218
Group b:	Fluorine	+ .062	+ .337
	Chlorine	+ .227	+ .373
	Bromine	+ .232	+ .391
	Methyl	− .170	− .069

Experimental Part[8]

A. Preparation of Diarylethylenes (I)

Three methods are available for the synthesis of 1,1-diarylethylenes: (a) interaction of ethyl acetate with two moles of a Grignard compound (applicable only for cases with identical aryls); (b) reaction of an acetophenone with an arylmagnesium halide; (c) reaction of a benzophenone with methylmagnesium iodide.

Method (c) gives the best yields (nearly quantitative), but method (b) is often more economical inasmuch as a number of different diarylethylenes can be prepared from

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[6] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 188.

[7] R. N. Jones, THIS JOURNAL, 65, 1818 (1943); F. Bergmann and Israelashvili, *ibid.*, 68, 1 (1946).

[8] All m. p.'s are uncorrected.

the same acetophenone, whereas with method (c) a special synthetic route is required for every individual ethylene. The yields in reaction (a) are usually low, and this method is of little preparative value.

I,3: *p*-Ethyldiphenylethylene (I, $R_1 = C_2H_5$, $R_2 = H$).—*p*-Ethylbenzophenone was originally described by Söllscher.[9] The yield is reported as 75%. Norris and Blake,[10] however, found it necessary to purify the ketone, obtained "in the usual way," by four fractionations. We have observed that the Perrier modification[11] gave a 70% yield of a product of excellent purity. The reaction proceeded at room temperature and was completed by heating to 80° for one hour; b. p. 130–135° (0.5 mm.). The crude carbinol obtained from *p*-ethylbenzophenone and methylmagnesium iodide, was dehydrated by heating to 150° for one hour. Distillation yielded 85% of pure *p*-ethyldiphenylethylene; b. p. 118–120° (0.2 mm.); $n^{27.5}_D$ 1.5864.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.3; H, 7.7. Found: C, 91.9; H, 7.8.

I,4: *p*-Isopropyldiphenylethylene (I, $R_1 = CH(CH_3)_2$; $R_2 = H$).—*p*-Isopropylbenzophenone was prepared in 80% yield by Smith[9b] from cuminyl chloride and benzene. We applied again the Perrier technique. The benzoyl chloride–aluminum chloride complex reacted with isopropylbenzene at 0°; the reaction was completed at +15°. The ketone was obtained in 79% yield, b. p. 145–148° (0.1 mm.).

The Grignard reaction with methylmagnesium iodide was carried out as before. *p*-Isopropyldiphenylethylene boils at 122–123° (0.1 mm.); yield 86%; n^{17}_D 1.5823.

Anal. Calcd. for $C_{17}H_{18}$: C, 91.9; H, 8.1. Found: C, 92.1; H, 8.0.

I,5: *p*-*t*-Butyldiphenylethylene (I, $R_1 = C(CH_3)_3$; $R_2 = H$).—*p*-*t*-Butylbenzophenone was prepared by adding *t*-butylbenzene (60 g.) to the Perrier complex, prepared from benzoyl chloride (75 g.) and aluminum chloride (70 g.) in carbon disulfide (350 cc.) at +5°. The main reaction proceeded at room temperature and was completed by heating on a water-bath for one half-hour: yield 53%; b. p. 132–134° (0.1 mm.); n^{25}_D 1.5725.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.7; H, 7.6. Found: C, 85.3; H, 7.9.

The ethylene I,5 was prepared according to method (c). Dehydration of the intermediary tertiary carbinol was effected by heating to 150° for one hour: yield 95%; b. p. 123° (0.1 mm.); n^{27}_D 1.5767.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.5; H, 8.5. Found: C, 91.2; H, 8.7.

I,8: *p*-Fluorodiphenylethylene (I, $R_1 = F$; $R_2 = H$).—*p*-Fluorobenzophenone was obtained by Dunlop and Gardner[12] in 66% yield from benzoyl chloride and fluorobenzene. The Perrier technique yielded in this case only 45% of the ketone; b. p. 110–115° (0.4 mm.); m. p. 48°. The Grignard reaction with methylmagnesium iodide was carried out as before and yielded 96% of the ethylene I,8. It possesses a b. p. of 105–110° (0.3 mm.) and shows a strong blue fluorescence; n^{19}_D 1.5840.

Anal. Calcd. for $C_{14}H_{11}F$: C, 84.8; H, 5.6. Found: C, 84.7; H, 5.8.

I,9: *p*-Chlorodiphenylethylene (I, $R_1 = Cl$; $R_2 = H$) was prepared according to Bergmann and Bondi.[13]

I,10: *p*-Bromodiphenylethylene[14] (I, $R_1 = Br$; $R_2 = H$) was prepared according to method (b) in 67% yield.

I,11: 1-(*p*-Tolyl)-1-(*p*-fluorophenyl)-ethylene (I, $R_1 = CH_3$; $R_2 = F$) was obtained from *p*-methylacetophenone and *p*-fluorophenylmagnesium bromide in 40% yield as a clear yellow oil of b. p. 141–142° (0.03 mm.); $n^{27.5}_D$ 1.5738.

Anal. Calcd. for $C_{15}H_{13}F$: C, 84.9; H, 6.1. Found: C, 85.1; H, 6.1.

I,12: 1,1-Di-(*p*-tolyl)-ethylene (I, $R_1 = R_2 = CH_3$) was prepared in an unspecified yield by Anschütz and Hilbert[15] according to method (a). Repetition of their experiment gave only an 18% yield of the required ethylene. However, application of method (b) yielded the di-(*p*-tolyl)-ethylene in 58% yield, m. p. 60–61°.

I,13: 1,1-Di-(*p*-chlorophenyl)-ethylene[13] (I, $R_1 = R_2 = Cl$) was prepared according to method (b) from *p*-chloroacetophenone and *p*-chlorophenylmagnesium iodide in 73% yield, m. p. 91°.

I,14: 1,1-Di-(*p*-fluorophenyl)-ethylene (I, $R_1 = R_2 = F$).[16]—Method (a) yielded about 15% of this ethylene. As the preparation of *p*,*p*′-difluorobenzophenone according to Coates and Sutton is very tedious, we prepared the ethylene from *p*-fluoroacetophenone[17] and *p*-fluorophenylmagnesium bromide in 63% yield; b. p. 150–160° (30 mm.); m. p. 46°.

II. Condensation with Maleic Anhydride—Formation of bis-Adducts (II)

The formation of the bis-adducts (II) was carried out as before.[3] The optimal temperature had to be determined in each individual case, as the success of the condensation of the ethylenes I with maleic anhydride depends on narrowly defined temperature limits. When halogen was present in the ethylene, the bis-adduct always crystallized.[18] Among the alkyl-substituted ethylenes, only the mono- and di-tolyl derivative allowed the isolation of crystalline bis-adducts. In all other cases, the products were too soluble to permit crystallization. They were therefore dissolved in ethanol and precipitated by water as brownish powders. These crude, amorphous materials were purified by dissolution in sodium hydroxide and reprecipitation with hydrochloric acid. The white powders, so obtained, were then dried in an oven at 50–70° and used directly for the next step.

The properties of the bis-adducts (II) are summarized in Table II.

III. Dehydrogenation of bis-Adducts

All the aromatic anhydrides (III) were prepared by sulfur dehydrogenation of the bis-adducts. Details of these reactions together with the properties of the dehydrogenation products are given in Table III. Under the heading "Temperature of Dehydrogenation" two figures are given: The lower one designates the temperature at which the evolution of hydrogen sulfide started. The reaction mixture was usually kept at this temperature for ten to fifteen minutes. Thereafter the mixture was heated for five minutes to a temperature determined by the higher figure in the table, in order to complete the reaction. All the aromatic anhydrides are intensely yellow, beautifully crystalline substances, with a blue to violet fluorescence. When their alcoholic solutions were kept for some days, however, the color faded gradually due to the opening of the anhydride ring. The "dichloro" derivative (III,13) was so hygroscopic, that it could not be obtained in an anhydrous form, but rather as the semihydrate of the free dicarboxylic acid.

We have reported already in our first paper,[3] that some of the aromatic anhydrides are dimorphic, *e. g.*, the 4,7-diphenyl derivative (III, R_1 = phenyl; $R_2 = H$). We have observed now a further case of dimorphism: the fluoro derivative (III,8) crystallizes from acetic acid as

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(9) Söllscher, *Ber.*, **15**, 1680 (1882); (b) see also Smith, *ibid.*, **24**, 4025 (1891); (c) Vorländer, *ibid.*, **44**, 2455 (1911).

(10) Norris and Blake, THIS JOURNAL, **50**, 1808 (1928).

(11) See Fieser, "Experiments in Organic Chemistry," D. C. Heath Co., Boston, Mass., 1941, p. 192.

(12) Dunlop and Gardner, THIS JOURNAL, **55**, 1665 (1933); see also Kopal, *Rec. trav. chim.*, **34**, 157 (1915).

(13) E. Bergmann and Bondi, *Ber.*, **64**, 1468 (1931).

(14) Stoermer and Simon, *ibid.*, **37**, 4163 (1904).

(15) Anschütz and Hilbert, *ibid.*, **57**, 1697 (1924).

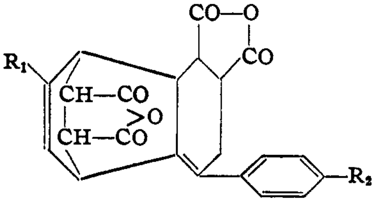
(16) Coates and Sutton, *J. Chem. Soc.*, 567 (1942).

(17) Renoll, THIS JOURNAL, **68**, 1160 (1946).

(18) In these cases, the crude melt was dissolved in ethanol and left for twenty-four hours. In the case of di-(*p*-fluorophenyl)-ethylene (I, $R_1 = R_2 = F$), the bis-adduct crystallized already in the hot melt and was isolated by treatment with methanol.

TABLE III

BIS-ADDUCTS (II)



No.	R₁	R₂	Ratio: e/m[a]	Optimal reaction temp., °C.	Time, hr.	Yield, %	M. p., °C.	Solvent[b]	Crystal form[c]	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
2	H	CH_3	1:5	150–160	4	80	238–239	A	s. n.	$C_{23}H_{18}O_6$	70.8	70.6	4.6	4.5
3	H	C_2H_5	1:8	150	3	(80)[d]	Amorph.							
4	H	$(CH_3)_2CH$	1:5	150	3	(75)	Amorph.							
5	H	$(CH_3)_3C$	1:5	135	3	(90)	Amorph.							
8	H	F	1:8	150–160	3¹/₂	25	302–303	B	t. c.	$C_{22}H_{15}O_6F$	67.0	67.2	3.8	4.1
9	H	Cl	1:5	150	3	60	275–277	C	s. n.	$C_{22}H_{15}O_6Cl$	64.4	64.1	3.7	3.8
11	F	CH_3	1:7	140–150	3	(75)[d]	Sirupy							
12	CH_3	CH_3	1:5	140–150	2	28	238–239	D	f. h. p.	$C_{24}H_{20}O_6$	71.3	71.5	5.0	5.0
13	Cl	Cl	1:10	170–180	1	44	303–305	B	h. c.	$C_{22}H_{14}O_6Cl_2$	59.5	59.7	3.2	3.5
14	F	F	1:7	140–150	3	22	347–348	E	t. r.	$C_{22}H_{14}O_6F_2$	64.1	64.4	3.4	3.7

[a] e/m = ethylene/maleic anhydride. [b] A = butyl acetate; B = acetic anhydride; C = acetic–acid + acetic anhydride; D = butyl acetate + toluene; E = acetic anhydride + butyl acetate. [c] s. n. = short needles; t. c. = triangular columns; f. h. p. = flat hexagonal prisms: h. c. = hexagonal columns; t. r. = thin rods. [d] Because of the amorphous condition of the products, no exact yield can be stated.

a mixture of elongated rods (main form), and prisms (a very small portion) both of m. p. 179° (no depression upon mixing!). The two forms were separated mechanically and recrystallized from acetic acid.

The methyl derivative III,2 formed a mixture of brownish rods of m. p. 183–184°, and pale yellow needles of m. p. 186–187°. The m. p. of a mixture of both forms was 183–184°. Analysis showed that the second form contains half a molecule of water.

The amorphous bis-adduct II,5 gave, upon dehydrogenation, a mixture of two (isomeric ?) anhydrides (III, 5a and b), which again were separated mechanically. The main form crystallized from petroleum ether as yellow blocks of m. p. 158-159°. The second isomer, which was obtained only in a small amount, formed thin rods when recrystallized from the same solvent, m. p. 184–185°. Absorption spectra of the two products give no indication, as to whether they possess isomeric structures.[5]

IV. Decarboxylation

For decarboxylation, the anhydrides were either mixed directly with barium hydroxide (5 parts) and copper bronze (1.5 parts) and subjected to heating (method A) or a dioxane solution of the anhydride was added dropwise to a warm aqueous solution of barium hydroxide, the precipitated salt washed and dried, and then mixed with copper bronze (1.5 parts) (method B).

The degradation of III,2 (III, R_1 = H; R_2 = CH_3) has already been described.[3] The higher alkyl homologs of this compound gave only oils, which upon nitration gave amorphous and non-crystallizable nitro derivatives, unsuitable for comparison. In these cases, therefore, assignment of a certain structure depends entirely on spectrographical evidence.[5] 4-(*p*-Chlorophenyl)-naphthalene-1,2-dicarboxylic acid anhydride (III,9; R_1 = H; R_2 = Cl) was decarboxylated according to method A at 320°. The clear, colorless oil, 1-(*p*-chlorophenyl)-naphthalene (IV,9), could not be induced to crystallization or converted into a crystalline picrate. It was therefore nitrated directly by heating its acetic acid solution with one equivalent of fuming nitric acid to 60° for thirty seconds and pouring on ice. The yellow oil, so obtained, was dissolved in alcohol. The filtered solution, upon cooling, deposited yellow prismatic rods of m. p. 119°.

Anal. Calcd. for $C_{16}H_{10}O_2NCl$: C, 67.8; H, 3.5; N, 4.9. Found: C, 67.7; H, 3.7; N, 5.1.

An authentic sample of IV,9 was prepared in the following manner. To a Grignard solution, prepared from *p*-chloroiodobenzene (18.5 g.), magnesium (2.2 g.) ether (40 cc.) and benzene (40 cc.), was added at 0° a solution of tetralone (10 g.) in benzene (25 cc.). The mixture was refluxed for four hours and then decomposed in the usual way. The crude reaction product was dehydrated by heating to 150° for one hour in the presence of an equal weight of sodium bisulfate. Distillation gave a colorless oil of b. p. 150–152° (0.2 mm.). This product represents 1-(*p*-chlorophenyl)-3,4-dihydronaphthalene; yield 45%.

Anal. Calcd. for $C_{16}H_{13}Cl$: C, 80.0; H, 5.4. Found: C, 80.0; H, 5.6.

The dihydronaphthalene derivative was dehydrogenated with sulfur at 190 → 270° and the product distilled over copper bronze. 1-(*p*-Chlorophenyl)-naphthalene (IV,9) was obtained in quantitative yield; b. p. 151-153° (0.4 mm.).

Anal. Calcd. for $C_{16}H_{11}Cl$: C, 80.7; H, 4.6. Found: C, 80.9; H, 4.9.

Nitration in acetic acid, under the same conditions as described before, gave a mononitro derivative, which crystallized from ethanol in yellow prismatic rods, m. p. 121–122°; mixed m. p. with the above nitro derivative, 119°.

Both nitro compounds were converted by reduction with tin and hydrochloric acid in ethanol into the corresponding amine, which was acetylated directly by acetic anhydride. Water precipitated the crude acetamino derivative, which was recrystallized from dilute acetic acid; short rods of m. p. 215–216°. The mixed m. p. of both acetamino compounds showed no depression.

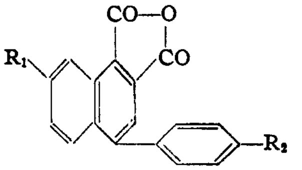
Anal. Calcd. for $C_{18}H_{14}ONCl$: C, 73.2; H, 4.7. Found: C, 73.5; H, 4.9.

4-(*p*-Fluorophenyl)-naphthalene-1,2-dicarboxylic acid anhydride (III,8) was decarboxylated according to method B at 320°. The colorless oil (IV,8), obtained in 27% yield, could not be induced to crystallize and was therefore nitrated directly in the same manner as described before. The nitration product, x(4?)-nitro-1-(*p*-fluorophenyl)-naphthalene, crystallized from ethanol in long yellow blocks of m. p. 104°.

Anal. Calcd. for $C_{16}H_{10}O_2NF$: N, 5.2. Found: N, 5.2.

TABLE IV

DERIVATIVES OF 4-PHENYLNAPHTHALENE-1,2-DICARBOXYLIC ACID ANHYDRIDE (III)



No.	R_1	R_2	Temp. of dehydrogenation, °C.	Range of sublimation temperature, °C.	Mm.	Yield, %	M. p., °C.	Solvent[a]	Crystal form[b]	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
2	H	CH_3[c]	240 → 270	270–320	0.2	88	183–184	a. a.	b. p.	$C_{19}H_{12}O_3$	79.2	79.4	4.2	4.5
3	H	C_2H_5	240 → 280	250–280	.4	75	162–163	a. a.	l. y. r.	$C_{20}H_{14}O_3$	79.5	79.3	4.6	4.8
4	H	$(CH_3)_2CH$	240 → 280	250–280	.4	Small	132–133	p. e.	t. y. p.	$C_{21}H_{16}O_3$	79.7	79.9	5.1	5.2
5a	H	$(CH_3)_3C$	280	250–300	.2	87	158–159	p. e.	y. p. b.	$C_{22}H_{18}O_3$	80.0	80.2	5.5	5.7
5b	[$(CH_3)_3C$	H ?]	280	250-300	.2	Very small	184–185	p. e.	b. y. r.	$C_{22}H_{18}O_3$	80.0	80.1	5.5	5.8
8	H	F[d]	265 → 300	250–280	.4	50	179	a. a.	y. n.	$C_{18}H_9O_3F$	74.0	74.1	3.1	3.1
9	H	Cl	270 → 300	240–280	.2	67	186–187	a. a.	e. y. r.	$C_{18}H_9O_3Cl$	70.1	70.0	2.9	3.0
11	F	CH_3	275 → 320	300–340	.4	40	195–196	a. a.	e. y. r.	$C_{19}H_{11}O_3F$	74.5	74.3	3.6	3.9
12	CH_3	CH_3	240 → 275	250–280	.5	100	182–183	a. a.	p. y. r.	$C_{20}H_{14}O_3$	79.5	79.3	4.6	4.7
13	Cl	Cl	280 → 310	280–310	.15	50	196–197	a. a.	l. b. p. r.	$C_{18}H_{10}O_4Cl_2\cdot{}^1/_2H_2O$	58.4	58.7	3.0	2.8
14	F	F	340	280–310	.8	Small	209	a. a.	p. l.	$C_{18}H_8O_3F_2$	69.7	69.4	2.6	2.9

[a] a. a. = acetic acid; p. e. = petroleum ether. [b] b. p. = brown prisms; l. y. r. = long yellow rods; t. y. p. = thin yellow plates; y. p. b. = yellow prismatic blocks; b. y. r. = bright yellow rods; y. n. = yellow needles; e. y. r. = elongated yellow rods; p. y. r. = pointed yellow rods; b. p. r. = light-brown prismatic rods; p. l. = prismatic leaflets. [c] This substance was already described in the first paper of this series.[3] The purest sample, now obtained, melts four degrees higher than before. On working with larger amounts, we obtained a second form; yellow needles of m. p. 186–187° (from acetic acid). Analysis shows this form to be a semihydrate of the anhydride III,2. *Anal.* Calcd. for $C_{19}H_{12}O_3\cdot{}^1/_2H_2O$: C, 76.8; H, 4.4. Found: C, 77.1; H, 4.6. [d] This anhydride appeared in two crystalline modifications of identical m. p. (see Experimental).

An authentic sample of IV,8 was prepared as in the foregoing case by interaction of tetralone with *p*-fluorophenyl magnesium bromide. 1-(*p*-Fluorophenyl)-3,4-dihydronaphthalene distilled at 120–125° (0.05 mm.) as a nearly colorless oil. It was obtained in 69% yield.

Anal. Calcd. for $C_{16}H_{13}F$: C, 85.7; H, 5.8. Found: C, 85.9; H, 6.0.

Dehydrogenation with sulfur proceeded at 200 → 220°. The product was distilled twice over copper bronze, b. p. 116–118° (0.04 mm.). This sample of 1-(*p*-fluorophenyl)-naphthalene (IV,8) formed a light yellow oil, which crystallized very slowly on standing; from methanol as colorless plates of m. p. 71–72°; yield, quantitative.

Anal. Calcd. for $C_{16}H_{11}F$: C, 86.5; H, 5.0. Found: C, 86.7; H, 4.8.

An acetic acid solution of IVa was heated with one equivalent of fuming nitric acid to 50° for ten seconds and the mixture poured onto ice. The nitro derivative crystallized from ethanol in yellow blocks of m. p. 104–105°, not depressed by admixture of the above nitration product.

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Summary

Unsymmetrically substituted 1,1-diarylethylenes react with maleic anhydride to yield only one of the two possible isomeric addition products. Substituents can be arranged in two groups: (a) substituents which promote addition to the substituted ring (methoxyl, phenyl); (b) substituents which prevent addition to the substituted ring (halogen, alkyl).

These effects are explained by the electronic influence of substituents on a meta and para position, applying Hammett's σ-values. The reaction mechanism is represented by an electronic cycle, involving electrophilic attack on the β-carbon atom and nucleophilic attack on the ortho position of the diarylethylene.

Symmetrically substituted diarylethylenes undergo the reaction even if they contain substituents of group b.

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