[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY OF THE HEBREW UNIVERSITY]

SYNTHESIS AND PROPERTIES OF 1,4-DIARYLBUTADIENES WITH HIGHER AROMATIC SYSTEMS

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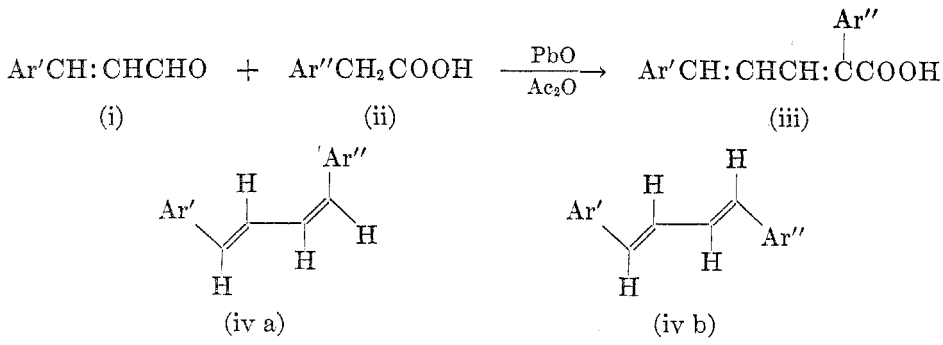
Stilbene and ethylenes with higher aryl substituents have found increased interest in recent years in view of their biological activities. For these studies, various substituents have been introduced into the aromatic rings to modify the reactivity of the stilbenes (1). In a series of papers the influence of higher aromatic nuclei on the reactivity of the olefinic double bond has been investigated (2). In this communication, we wish to report the synthesis of the corresponding 1,4-diarylated butadienes in order to study the degree of conjugation of the exocyclic double bonds with aromatic rings by chemical reactions, and by measurement of the absorption spectra and the susceptibility to photochemical changes. The new compounds synthesized are listed in Table I. Their absorption spectra have been reported by Hirshberg, Bergmann, and Bergmann (3).

For the synthesis of the diarylated butadienes, two different routes were used: (a) condensation of a β-arylacrolein with an arylacetic acid, and (b) condensation of two molecules of an aromatic aldehyde with succinic acid in presence of lead oxide and acetic anhydride, respectively (4).

It is clear that route (a) permits two different approaches, in those cases where the two aromatic substituents are different, as for example, in 1-phenyl-4-(9′-phenanthryl)butadiene (X).

The *trans* structure has been established for cinnamic aldehyde (5) and β-(α-furyl)acrolein (6). The *trans* structure of β-(9-phenanthryl)acrolein can be derived from the fact that the both condensations of 9-phenanthreneacetic acid with *trans*-cinnamic aldehyde and of β-(9-phenanthrene)acrolein with phenylacetic acid yielded the same *trans-trans* butadiene (X). It can therefore be assumed that all β-arylacroleins used in this investigation possess a *trans* structure. On this basis the decarboxylation of the substituted vinylacrylic acid



* Killed in the war of liberation of Israel, April 1948.

TABLE I

1,4-DIARYLBUTADIENES R′CH=CH—CH=CHR″

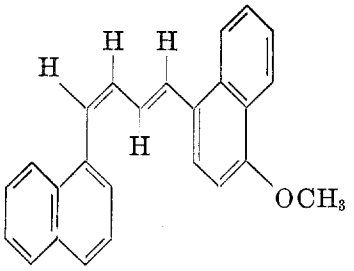
NO.	COMPOUND		CONFIGURATION	M.P., °C.	COLOR	FLUORESCENCE	SOLUTION IN COLD CONC'D H_2SO_4
	R′	R″					
I	Phenyl	2-Naphthyl	*trans-trans*	172	Bright yellow	Violet	—
II	1-Naphthyl	1-Naphthyl	*trans-trans*	170	Yellow	Green-violet	Brown-red
III	1-Naphthyl	2-Naphthyl	*trans-trans*	172	Yellow	Blue-violet	Green
IV	2-Naphthyl	2-Naphthyl	*trans-trans*	268	Green-yellow	Green-violet	Green
V	1-Naphthyl	4′-Methoxy-1-naphthyl	*cis-trans*	110	Brown-yellow	Yellow-green	Dark green
VI	1-Naphthyl	4′-Methoxy-1′-naphthyl	*trans-trans*	220	Yellow	Green-yellow	Dark green
VII	4′-Methoxy-1′-naphthyl	4′-Methoxy-1′-naphthyl	*cis-cis*	125	Yellow-brown	Blue	Blue-green
VIII	4′-Methoxy-1′-naphthyl	4′-Methoxy-1′-naphthyl	*cis-trans*	160	Yellow-brown	Green	Dark green
IX	4′-Methoxy-1′-naphthyl	4′-Methoxy-1′-naphthyl	*trans-trans*	194	Yellow-brown	Yellow	Dark-blue
X	Phenyl	9-Phenanthryl	*trans-trans*	156	Yellow-green	Violet	Blue

intermediate (iii) could lead to two isomers, namely, a *trans-cis* (iva) and the *trans-trans* form (ivb).

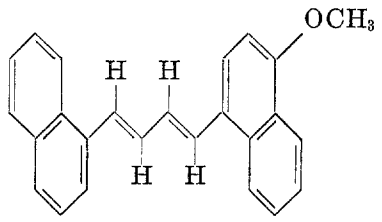
Actually, all reactions carried out according to this scheme yielded the *trans-trans* form only, if no substituent was present in the aromatic rings. The *trans-trans* structure is derived from the stability of our products towards iodine in boiling xylene.

For the stilbenecarboxylic acids, Taylor and Crawford (7) and Ruggli and Staub (8) established the *cis* position of the two aromatic nuclei by the observation that decarboxylation yielded the *cis*-stilbene as the primary product. If these rules are applied also to α,δ-diarylpentadienoic acids, the primary product of the decarboxylation of (iii) should be the *trans-cis* form (iva). In view of the fact that not even a trace of an isomeric *trans-cis* form could be detected by chromatographic analysis, it appears doubtful whether condensation of a β-arylacrolein (i) with an arylacetic acid (ii) puts the carboxylic group into the *cis* position with regard to the hydrogen at the same double bond. The steric conditions in a 1,4-disubstituted butadiene are probably different from those of a 1,2-disubstituted ethylene. It is thus conceivable that rules opposite to those formulated by Taylor (7) and Ruggli (6) control the special arrangement of (iii). That the rules may be broken even in the case of stilbenes is suggested by the fact that 1-(1′-naphthyl)-2-(9″-phenanthryl)ethylene is obtained from the corresponding carboxylic acid exclusively in the *trans* configuration. This deviation from the above rules might be due to the great bulk of the aromatic nuclei, which prevent the compound from assuming a *cis* configuration.

In this connection it is of interest that the condensation of β-(4-methoxy-1-naphthyl)acrolein with 1-naphthaleneacetic acid gave two isomers of m.p. 110° and 220°, respectively. The lower isomer is converted by iodine into the 220° compound, which itself is stable to such treatment. We thus ascribe to these two isomers the following structures, (iva) and (ivb).



isomer of m.p. 110°
(iv a)

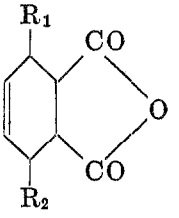


isomer of m.p. 220°
(iv b)

The formation of these two isomers could be due to two mechanisms: (a) during the condensation the two isomeric α,δ-diarylpentadienoic acids (iii) are formed, each one giving the corresponding diarylbutadiene (iv) upon decarboxylation, or (b) only one α,δ-diarylpentadienoic acid is formed during the condensation, in which the carboxyl group is *cis* to the hydrogen at the same double bond, but during the decarboxylation the primary *trans-cis* com-

pound is partially converted to the *trans-trans* configuration. The second reaction mechanism appears less probable in view of our experience with the unsubstituted diarylbutadienes (I–IV and X–XI). Furthermore, the condensation of 4-methoxy-1-naphthaldehyde with succinic acid gives all three possible isomers, indicating that the methoxy group has an influence on the formation of isomeric carboxylic acids. The influence of the methoxy group on formation of isomeric ethylenes and butadienes is now under investigation.

In the case of vinylnaphthalenes and 9-vinylphenanthrenes it has been shown that maleic anhydride adds to the conjugated system, resulting in one cyclic and the exocyclic double bond. It was thus of interest to find out whether our diarylbutadienes would behave as a butadiene or a tetraene. In all cases investigated here only one molecule of maleic anhydride was added. It is concluded that addition occurs only at the central conjugated system and yields monoadducts of the general structure (XII) [See, Kuhn and Wagner-Jauregg (9) and Arnold (10)].



XII

Likewise preferential bromination of the dienic system occurred. Usually the tetrabromides were isolated, but under appropriate conditions the reaction could be stopped at the dibromide stage.

The β-arylacroleins (i) were conveniently prepared by condensing the corresponding aromatic aldehydes with acetaldehyde in the presence of dilute ethanolic sodium hydroxide. The 1- and 2-naphthaleneacetic acids were prepared by known methods. 9-Phenanthreneacetic acid has been synthesized by Hewett (11a) by oxidation of 9-allylphenanthrene in a yield of 17%. A much more convenient method is the application of the Arndt-Eistert method to 9-phenanthroyl chloride.

The condensation of an arylacrolein with an arylacetic acid according to Kuhn and Winterstein (4) can be directed either towards the preferential formation of the carboxylic acid (iii) or the butadiene (iv). This depends on the reaction temperature and the amount of acetic anhydride in the mixture. A large excess of this reagent and a low reaction temperature (150°) favor the formation of (iii), whereas an equivalent amount of the anhydride and a higher reaction temperature (180°) yield almost exclusively the butadiene (iv).

EXPERIMENTAL PART[1]

A. STARTING MATERIALS

1-Naphthaldehyde. The preparation of 1-naphthaldehyde from 1-chloromethylnaphthalene with hexamethylenetetramine (11, 12) has been improved by substitution of acetic

[1] All melting points are uncorrected.

acid for alcohol as the solvent, and by using potassium iodide as catalyst. A solution of 1-chloromethylnaphthalene (13) (55 g.) and potassium iodide (solution of 10 g. in 10 cc. of water) in boiling glacial acetic acid (150 cc.) was treated with hexamethylenetetramine (44 g.), and the solution boiled until clear (10 min.). The mixture was poured into water and the oil which separated was purified through the bisulphite compound. The product distilled at 160°/20 mm. Yield, 32 g. (66%).

2-Naphthaldehyde (12) was prepared by the same method from 2-bromomethylnaphthalene (14) with, however, the omission of potassium iodide. B.p. 160°/19 mm. Yield, 72%.

4-Methoxy-1-naphthaldehyde was prepared in 78% yield by treating 1-methoxynaphthalene with N-methylformanilide in the presence of $POCl_3$, according to the method described for the preparation of 2-ethoxy-1-naphthaldehyde (15). B.p. 170–172°/2 mm., n_D^{29} 1.6725; upon cooling pale yellow needles were obtained, m.p. 34° (16).

The aldehyde was identified by converting it to the known 4-methoxy-1-naphthoic acid, m.p. 235° (17), with permanganate.

Picrate. The monopicrate was recrystallized from ethanol, yellow needles, m.p. 112°.

Anal. Calc'd for $C_{18}H_{13}N_3O_9$: N, 10.1. Found: N, 9.9.

The *2,4-dinitrophenylhydrazone* was recrystallized from glacial acetic acid, crimson needles, m.p. 259–260°.

Anal. Calc'd for $C_{18}H_{14}N_4O_{15}$: N, 15.3. Found: N, 15.4.

Oxime. The oxime crystallized from ethanol-water in colorless plates, m.p. 105°.

Anal. Calc'd for $C_{12}H_{11}NO_2$: N, 7.0. Found: N, 7.1.

The *semicarbazone* was recrystallized from ethanol-water in colorless plates, m.p. 216–217°.

Anal. Calc'd for $C_{13}H_{13}N_3O_2$: N, 17.5. Found: N, 17.3.

Formation of β-arylacroleins. For the preparation of β-arylacroleins the following procedure was used. Into a three-necked flask equipped with a stirrer, thermometer, and reflux condenser was placed a solution of an aromatic aldehyde (0.16 mole) and sodium hydroxide (1.0 g.) in ethanol (125 cc.); the mixture was cooled to 0°. Freshly distilled acetaldehyde (8 g.) in ethanol (20 cc.) was added dropwise with stirring during one hour at 5°, and stirring was continued for an additional four hours at room temp. (15°). The viscous orange mixture was poured into water and the oil which separated was taken up in ether, washed with water, and dried over $MgSO_4$. The residue was distilled *in vacuo*.

β-(1-Naphthyl)acrolein distilled at 220°/10 mm. Yield, 41%.

Oxime. The oxime was obtained from ethanol-water as yellow crystals of m.p. 152° [identical with the m.p. reported by Braun and Nelles (18)].

Anal. Calc'd for $C_{13}H_{11}NO$: N, 7.1. Found: N, 7.0.

Picrate. The monopicrate crystallized from ethanol in orange prisms, m.p. 103°.

Anal. Calc'd for $C_{19}H_{13}N_3O_8$: N, 10.2. Found: N, 10.1.

The *semicarbazone* was twice recrystallized from ethanol, yellow crystals, m.p. 208°.

Anal. Calc'd for $C_{14}H_{13}N_3O$: N, 17.5. Found: N, 17.3.

β-(2-Naphthyl)acrolein distilled at 250°/8 mm., and crystallized from petroleum ether (80°) in yellow prismatic rods, m.p. 118–119°. Yield, 35%.

Anal. Calc'd for $C_{13}H_{10}O$: C, 85.7; H, 5.4.
Found: C, 85.5; H, 5.3.

β-(4-Methoxy-1-naphthyl)acrolein was obtained as an orange oil, b.p. 195–200°/12 mm. Yield, 58%.

Anal. Calc'd for $C_{14}H_{12}O_2$: C, 79.2; H, 5.7.
Found: C, 85.5; H, 5.3.

Semicarbazone. The semicarbazone upon recrystallization from ethanol yielded yellow crystals, m.p. 224°.

Anal. Calc'd for $C_{15}H_{15}N_3O_2$: N, 15.6. Found: N, 15.8.

Besides the above product the reaction mixture yielded also a product of higher boiling point, b.p. 210–215°/12 mm., probably the aldol condensation product, 3-(4'-methoxy-1'-naphthyl)-3-hydroxypropionaldehyde. Yield, 32%.

Anal. Calc'd for $C_{14}H_{14}O_3$: C, 73.0; H, 6.1.
Found: C, 73.4; H, 5.9.

The *semicarbazone* crystallized from ethanol-water in colourless crystals, m.p. 205°.

Anal. Calc'd for $C_{15}H_{17}N_3O_3$: N, 14.6. Found: N, 14.3.

β-(9-Phenanthryl)acrolein crystallized from butyl acetate in yellow-orange prisms, m.p. 145°. Yield: 30%. Analysis shows this product to contain one molecule of water. It might therefore be the aldol or a hydrate of the acrolein.

Anal. Calc'd for $C_{17}H_{14}O_2$: C, 81.6; H, 5.6.
Found: C, 81.8; H, 5.9.

9-Phenanthryldiazoketone. A solution of 9-phenanthroyl chloride (19) (30 g.) in dry ether (300 cc.) was added at 10–15° to a solution of diazomethane (20) [prepared from N-nitrosomethylurethane (21)] (55 g.) in ether (500 cc.), and the yellow solution allowed to stand overnight at room temperature, whereupon yellow needles crystallized out. Recrystallization from ethanol gave yellow needles, m.p. 122°. Yield, 24 g. (80%).

Anal. Calc'd for $C_{16}H_{10}N_2O$: C, 78.1; H, 4.0.
Found: C, 78.0; H, 4.2.

9-Phenanthreneacetic acid. A solution of the diazoketone (15 g.) in dioxane (100 cc.) was added dropwise with stirring to a mixture of silver oxide (1.6 g.), anhydrous sodium carbonate (4 g.), and sodium thiosulphate (2.4 g.) in 160 cc. of water at 60–70°, during one hour. Thereafter the mixture was raised to 100°, and stirring was continued for six hours. The solution was cooled, diluted with water, and acidified with dilute nitric acid. The 9-phenanthreneacetic acid was recrystallized twice from methanol. Colorless plates, m.p. 219–220° [Compare, Mosettig and van de Kamp (19a)]. Yield, 65%.

B. SYNTHESIS OF 1,4-DIARYLBUTADIENES

Method (a). A mixture of β-arylacrolein (0.03 mole), arylacetic acid (0.03 mole), lead oxide (3.2 g.), and acetic anhydride (8 cc.) was refluxed for five hours. The reaction mixture was poured into boiling acetic acid-water, boiled for several minutes, and filtered.

Method (b). A mixture of 4-methoxy-1-naphthaldehyde (15 g.), succinic acid (5 g.), lead oxide (17.4 g.), and 30 g. of acetic anhydride was refluxed for ten hours with stirring. The reaction mixture was diluted with water, extracted with ether, and the ether solution washed with sodium carbonate, dried, and the solvent removed. The residue was triturated with ethanol and the product chromatographed (see below).

1-Phenyl-4-(2'-naphthyl)butadiene (I) upon recrystallization from glacial acetic acid yielded bright green plates, m.p. 172°. Yield, 60%.

Anal. Calc'd for $C_{20}H_{16}$: C, 93.7; H, 6.2.
Found: C, 93.9; H, 6.4.

From the mother liquor the corresponding α,δ-diarylpentadienoic acid was isolated, which crystallized from acetic acid in yellow needles, m.p. 188–189°.

Anal. Calc'd for $C_{21}H_{16}O_2$: C, 84.0; H, 5.3.
Found: C, 84.0; H, 5.6.

Compound I formed a *monopicrate* which was recrystallized from glacial acetic acid, in orange-red needles, m.p. 152°.

Anal. Calc'd for $C_{26}H_{19}N_3O_7$: N, 8.7. Found: N, 8.9.

1,4-Di-(1'-naphthyl)butadiene (II) gave yellow needles from glacial acetic acid, m.p. 168°. Yield, 35%.

Anal. Calc'd for $C_{24}H_{18}$: C, 94.1; H, 5.9.
Found: C, 93.8; H, 6.2.

From the mother liquor the dinaphthylpentadienoic acid was isolated. It was crystallized from xylene in yellow plates, m.p. 212°.

Anal. Calc'd for $C_{25}H_{18}O_2$: C, 85.7; H, 5.1.
Found: C, 85.8; H, 5.4.

The *dipicrate* of II was recrystallized from glacial acetic acid in red needles, m.p. 219–220°.

Anal. Calc'd for $C_{36}H_{24}N_6O_{14}$: C, 56.5; H, 3.2.
Found: C, 56.7; H, 3.4.

1-(1'-Naphthyl)-4-(2"-naphthyl)butadiene (III) crystallized from acetic acid in yellow prisms, m.p. 171–172°. Yield, 31%.

Anal. Calc'd for $C_{24}H_{18}$: C, 94.1; H, 5.9.
Found: C, 93.9; H, 5.9.

1,4-Di-(2'-naphthyl)butadiene (IV) gave upon recrystallization from xylene fine green plates, m.p. 268°. Yield, 28%.

Anal. Calc'd for $C_{24}H_{18}$: C, 94.1; H, 5.9.
Found: C, 94.2; H, 5.7.

1-Phenyl-4-(9'-phenanthryl)butadiene (X) was crystallized from acetic acid in yellow prismatic rods, m.p. 156°. Yield, 18%.

Anal. Calc'd for $C_{24}H_{18}$: C, 94.1; H, 5.9.
Found: C, 93.6; H, 6.1.

From the reaction mixture the corresponding diarylpentadienoic acid was isolated, and recrystallized from glacial acetic acid, yellow prisms, m.p. 230°. Yield, 21%.

Anal. Calc'd for $C_{25}H_{18}O_2 \cdot H_2O$: C, 81.5; H, 5.4.
Found: C, 81.7; H, 5.6.

Decarboxylation. The pentadienoic acid was converted to X as follows: A mixture of the carboxylic acid (1 g.), copper-bronze (1 g.), and freshly distilled quinoline (15 cc.) was refluxed for 30 min. The mixture was extracted with ether and washed with dilute hydrochloric acid (5%), a solution of sodium bicarbonate, and water, respectively. After drying over sodium sulphate, the residue recrystallized from acetic acid, m.p. 156°.

Picrate. The monopicrate of X crystallized from acetic acid in red-orange prisms, m.p. 164–165°.

Anal. Calc'd for $C_{30}H_{21}N_3O_7$: N, 7.8. Found: N, 8.0.

The same hydrocarbon is obtained, either by condensation of cinnamic aldehyde with 9-phenanthreneacetic acid, or alternatively, by condensation of β-(9-phenanthryl)acrolein with phenylacetic acid.

When a solution of X in xylene containing a trace of iodine was boiled for an hour, the original compound was recovered unchanged.

The condensation of 9-phenanthreneacetic acid with β-(9-phenanthryl)acrolein according to the procedure given above yielded the α,δ-di-(9-phenanthryl)pentadienoic acid. It crystallized from acetic acid in yellow-orange crystals, m.p. 225°. Yield, 20%.

Anal. Calc'd for $C_{33}H_{22}O_2 \cdot 3H_2O$: C, 78.6; H, 5.6.
Found: C, 79.0; H, 5.9.

1,4-Di-(9-phenanthryl)butadiene (XI) was obtained in small yield by decarboxylation of the corresponding carboxylic acid in quinoline with copper-bronze. Recrystallization from ethyl benzoate gave orange crystals, m.p. 208°.

Anal. Calc'd for $C_{32}H_{22}$: C, 94.6; H, 5.4.
Found: C, 94.1; H, 5.0.

1-(4'-Methoxy-1'-naphthyl)-4-(1"-naphthyl)butadiene (V and VI). The yellow product obtained by the condensation of β-(4-methoxy-1-napthyl)acrolein with 1-naphthaleneacetic acid was dissolved in carbon tetrachloride and chromatographed on activated alumina (80–200 mesh). Two yellow rings were obtained. They were separated by elution with a solution of ethanol in chloroform (5%). After removal of the solvent from the separate percolates, the two products were isolated. The product of the lower ring crystallized from carbon tetrachloride-petroleum ether in yellow needles, m.p. 110° (V).

Anal. Calc'd for $C_{25}H_{20}O$: C, 89.3; H, 5.95.
Found: C, 89.5; H, 5.96.

The *dipicrate* of V was recrystallized from glacial acetic acid, yellow-brown crystals, m.p. 155°.

Anal. Calc'd for $C_{37}H_{26}N_6O_{15}$: N, 10.57. Found: N, 10.60.

The product of the upper ring was crystallized from benzene-ethanol in yellow crystals, m.p. 220° (VI).

Anal. Calc'd for $C_{25}H_{20}O$: C, 89.3; H, 5.9.
Found: C, 89.6; H, 5.8.

Compound V was converted to compound VI when boiled in xylene containing a trace of iodine, whereas VI was recovered unchanged after the same treatment.

1,4-Di-(4'-methoxy-1'-naphthyl)butadiene (VII, VIII, and IX). The yellow-brown product obtained by the condensation of 4-methoxy-1-naphthaldehyde with succinic acid was dissolved in carbon tetrachloride and chromatographed on activated alumina (80–200 mesh). The three yellow rings obtained were separated by elution with chloroform and treated as described above. The product of the lower ring crystallized from carbon tetrachloride-benzine in yellow-brown crystals, m.p. 123–125° [presumably of the *cic-cis* configuration (VII)]. Yield, 12%.

Anal. Calc'd for $C_{26}H_{22}O_2$: C, 85.2; H, 5.9.

Found: C, 85.6; H, 5.6.

The product of the middle ring was crystallized from *n*-propanol in yellow-brown crystals, m.p. 159–160° [presumably of the *cis-trans* form (VIII)]. Yield, 20%.

Anal. Found: C, 85.8; H, 5.8.

The product of the upper ring upon recrystallization from glacial acetic acid-water gave yellow prisms of m.p. 178–180° [presumably of the *trans-trans* configuration (IX)]. Yield, 35%.

Anal. Found: C, 85.5; H, 5.7.

TABLE II

REACTION WITH BROMINE

COMPOUND	M.P., °C.	RECRYSTALLIZATION SOLVENT	CRYSTAL FORM	FORMULA	ANALYSIS			
					Calc'd		Found	
					C	H	C	H
I	219	Butyl acetate	Needles	$C_{20}H_{16}Br_4$	41.8	2.8	42.2	3.1
II	187	*n*-Butanol	Prisms	$C_{24}H_{18}Br_4$	46.0	2.9	46.2	3.1
III	198	*n*-Butanol	Prisms	$C_{24}H_{18}Br_4$	46.0	2.9	46.1	3.2
III[a]	194	*n*-Butanol	Prisms	$C_{24}H_{18}Br_2$	61.8	3.9	62.4	4.3
X	168	*n*-Butanol	Prismatic rods	$C_{24}H_{18}Br_4$	46.0	2.9	46.0	2.9

[a] The dibromide was obtained when compound III was treated with the calculated amount of bromine in carbon tetrachloride at 0°.

Compounds VII and VIII were converted to compound IX when treated with a trace of iodine in boiling xylene, whereas IX was stable to such treatment.

Addition of bromine. The new hydrocarbons were treated with an excess of bromine in carbon tetrachloride at 0°. After removal of solvent the residues were triturated with ethanol and recrystallized. Details of the bromination products are given in Table II.

Reaction with maleic anhydride. The monoadducts were obtained when one mole-equivalent of the unsaturated hydrocarbons (I, II, III, and IV) was heated with 10 mole-equivalents of maleic anhydride at 180° for two hours. The reaction mixture was poured into ethanol and left overnight. The solid product was collected and recrystallized. Details of the reaction products obtained are given in Table III.

Synthesis of 1-(1'-naphthyl)-2-(9''-phenanthryl)ethylene. A mixture of sodium 1-naphthaleneacetate (15 g.), 9-phenanthrenealdehyde (22) (15 g.), and acetic anhydride (75 cc.) was heated at 150° for ten hours. The product was poured into water and allowed to decompose overnight. The brown gum obtained was extracted with benzene, washed with dilute sodium hydroxide solution, dried, and the solvent removed. From the residue 6 g. of 9-phenanthrenealdehyde was obtained upon distillation at reduced pressure; the remain-

ing substance (10 g.) gave yellow prismatic plates, m.p. 179–180°, upon recrystallization from toluene. Yield, 43%.

Anal. Calc'd for $C_{26}H_{18}$: C, 94.5; H, 5.4.
Found: C, 94.8; H, 5.6.

From the sodium hydroxide washings, a yellow product was obtained. Recrystallization from toluene yielded α-(1-naphthyl)-β-(9′-phenanthryl)acrylic acid, yellow prisms of m.p. 232° (2 g.).

Anal. Calc'd for $C_{27}H_{18}O_2 \cdot H_2O$: C, 82.7; H, 5.1.
Found: C, 83.0; H, 5.1.

Decarboxylation. The corresponding ethylene was obtained by heating the stilbenecarboxylic acid with copper powder at 270–280° for 30 min. (23). Recrystallization from toluene gave yellow plates, m.p. 180°.

Picrate. The dipicrate crystallized from toluene in orange-red needles, m.p. 220°.

Anal. Calc'd for $C_{38}H_{24}N_6O_{14}$: C, 57.9; H, 3.0.
Found: C, 57.6; H, 3.3.

TABLE III

REACTION WITH MALEIC ANHYDRIDE[a]

COMPOUND	M.P., °C.	RECRYSTALLIZATION SOLVENT	CRYSTAL FORM	FORMULA	ANALYSIS			
					Calc'd		Found	
					C	H	C	H
I	225	Acetic anhydride	Needles	$C_{24}H_{18}O_3$	81.4	5.1	81.2	5.4
II	185	Acetic acid	Needles	$C_{28}H_{22}O_4$	79.6	5.2	78.9	5.8
III (a)	212	Acetic anhydride	Prisms	$C_{28}H_{20}O_3$	83.2	5.0	83.1	5.4
III (b)	242	Acetic anhydride	Needles	$C_{28}H_{20}O_3$	83.2	5.0	83.2	5.1
IV	264	Acetic anhydride	Needles	$C_{28}H_{20}O_3$	83.2	5.0	83.4	5.3

[a] The nature of the adducts has not yet been established.

Reaction with maleic anhydride. When a mole equivalent of the ethylene was treated with ten equivalents of maleic anhydride, in an analogous way to that previously described, the monoadduct was obtained. It crystallized from acetic anhydride in colorless crystals, m.p. 190°.

Anal. Calc'd for $C_{30}H_{20}O_3$: C, 84.1; H, 4.5.
Found: C, 83.7; H, 4.7.

SUMMARY

1. The synthesis of nine new 1,4-diarylbutadienes is described. When one of the naphthyl rings contains a methoxyl group, geometrical isomers are obtained. In all cases where no substituents were introduced in the aromatic rings only the *trans-trans* forms were isolated.

2. In the addition of bromine and maleic anhydride only the central dienic system participates.

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