[Contribution from the Daniel Sieff Research Institute]

SUBSTITUTED STILBENES AND 1,4-DIPHENYLBUTADIENES. PART III. MEERWEIN REACTION WITH *p*-AMINOBIPHENYL A NEW SYNTHESIS OF *lin.*-QUATERPHENYL

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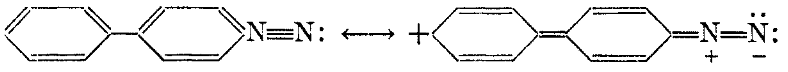
Among the factors which influence the successful achievement of the Meerwein reaction, an important role is played by the nature and the position of substituents in the diazo component. The mechanism by which substituents influence the course of the coupling reaction has not yet been cleared up. The most obvious feature, which varies from one substituent to another, is the stability of the diazo compounds. Snow (1), in a comprehensive study, has shown that certain groups, preferably halogens, alkoxyl, or nitro groups, stabilize the diazo compound appreciably. As coupling with the olefinic component in the Meerwein reaction usually proceeds at about 20° or higher, the stability of the diazotized amine up to this temperature is one fundamental condition. This is clearly pointed out by experiments with aniline itself, which in the stability scale of Snow stands near to the end. Coupling with cinnamic acid gives a very low yield of stilbene (1–2%), and with cinnamalacetic acid only traces of 1,4-diphenylbutadiene. A phenyl group in the para position stabilizes the diazonium ion enormously by resonance (*e.g.*, I ↔ Ia).



I Ia

Therefore, *p*-aminobiphenyl gives a 12% yield of *p*-phenylstilbene (II) (2) and 20% of 1-phenyl-4(*p*-phenylphenyl)-1,3-butadiene (III), respectively. On the other hand, a phenyl group in the ortho position completely prevents coupling, presumably because of its large size.

The enhanced resonance in the conjugated systems II and III is reflected in their physical properties (Table I). Light absorption is shifted to longer wavelengths, and the melting points are raised considerably.

When the diene (III) was heated to 140° with 10 moles of maleic anhydride, the adduct (IV) resulted in 80% yield. The melting point of IV is lowered during recrystallization from 260° to 250°, a phenomenon which may be explained by the shift of the double bond in the cyclohexene ring (2). In contrast to similar cases (3), nitrobenzene effected aromatization of the adduct with great difficulty. After boiling the reactants 2 hours in this solvent, only IV was obtained. After 10 hours, a mixture of IV and V was obtained, but an appreciable part of the product was decomposed. The method of Kuhn (2),[1] who achieved dehydrogenation of the disodium salt with ferricyanide, also gave negative results. On the other hand, dehydrogenation with sulfur yielded V

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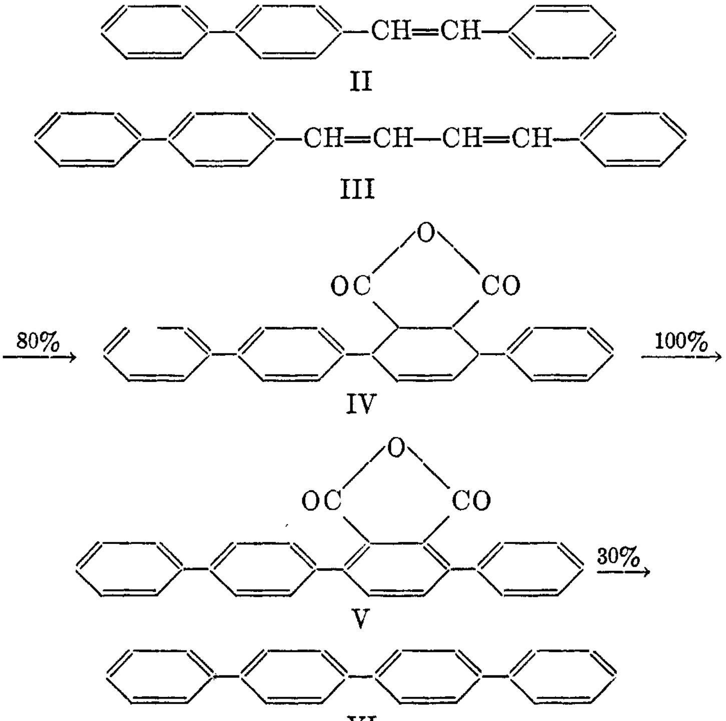
[1] Lohaus (4) prepared terphenyl in quantitative yield from 3,6-diphenyldihydrophthalic acid with potassium ferricyanide in one step.

quantitatively. Decarboxylation by basic copper carbonate in boiling quinoline then produced quaterphenyl (VI) in 30% yield. Although the last step gave only a moderate yield, the present method provides a convenient route to VI, as regards availability of starting materials and purity of end product (5).



II

III

IV

V

VI

EXPERIMENTAL

All melting points are uncorrected.

Stilbene. Coupling of diazotized aniline (0.1 mole) with cinnamic acid[2] gave a resinous product which, after distillation in a high vacuum, yielded 200 mg. (1.2%) of stilbene, the melting point and mixed melting point of which was 123°.

1,4-Diphenylbutadiene. The same reaction with cinnamalacetic acid (8.5 g. or 0.05 mole) yielded a sirupy product which was dissolved in methanol-acetone. After several days it deposited a few mg. of crystals melting at 143°. After the compound had been recrystallized from glacial acetic acid the melting point and mixed melting point was 151–152°.

p-Phenylstilbene (II) (2). *p*-Aminobiphenyl (8.6 g. or 0.05 mole) was dissolved in ethanol (400 cc.), and concentrated hydrochloric acid (6 cc.) added dropwise to the boiling solution. On cooling, the hydrochloride crystallized in shiny yellowish plates melting at 285°.

The hydrochloride (10.5 g.) was suspended in 10 cc. of concentrated hydrochloric acid and 20 cc. of ice-water, and diazotized with sodium nitrite (4 g.). The clear diazo solution was added at 5° to a solution of cinnamic acid (7.4 g.) in acetone (150 cc.). After addition of sodium acetate (10 g.) and cupric chloride (2 g.), the temperature was allowed to rise slowly. Evolution of gas started at 16°, but for completion of the reaction it was necessary

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[2] This reaction is already mentioned by Meerwein (6).

to heat at 40° for 4 hours. After steam distillation of the crude substance a granular product remained, which was distilled in a vacuum (boiling point *ca.* 300° at 1 mm.), and which crystallized on trituration with ethanol. From petroleum ether (130°) ill-defined crystals (needles?) formed, melting at 209°; yield 1.2 g. or 12%. Kuhn (2) reports the melting point 221° (corr.).

Anal. Calc'd for $C_{20}H_{16}$: C, 93.75; H, 6.25.
Found: C, 93.9; H, 6.5.

The dibromide, which was prepared in chloroform, crystallized on trituration with ethanol. From petroleum ether (130°) it crystallized in colorless long rods melting at 229°.

Anal. Calc'd for $C_{20}H_{16}Br_2$: C, 57.7; H, 3.9.
Found: C, 57.6; H, 3.9.

Catalytic reduction of 300 mg. of II over palladium-barium sulfate in ethyl acetate proceeded smoothly. After distillation of the solvent, the residue was recrystallized from ethanol, giving branched plates melting at 109°.

Anal. Calc'd for $C_{20}H_{18}$: C, 93.0; H, 7.0.
Found: C, 92.9; H, 7.0.

1-Phenyl-4-(p-phenylphenyl)-1,3-butadiene (III). Coupling with cinnamalacetic acid (8.8 g.) in acetone (150 cc.) was carried out as described above. Evolution of gas became rapid at about 30° and was completed by heating to 37° for 3 hours. After steam distillation, the residue was heated with acetic acid. Recrystallization from butyl acetate, then from xylene (brown solution with intense violet-red fluorescence) gave thin yellow plates melting at 214–215°; yield 2.8 g. or 20%. With concentrated sulfuric acid, a deep violet color is obtained, which changes on heating to violet red, then to brown.

TABLE I

PHYSICAL PROPERTIES

COMPOUND	M.P., °C	COLOR	REACTION WITH CONC'D H_2SO_4	FLUORESCENCE	BROMIDE M.P., °C	ADDUCT WITH MALEIC ANHYDR., M.P., °C	HYDROGENATION PRODUCT M.P., °C
Stilbene	124	none	none	blue	237		52
II	209	yellowish	blue	violet	229		109
1,4-Diphenyl-butadiene	152	yellowish	none	blue-violet	236	207	52
III	215	deep yellow	deep violet	bright blue	238	250	77

Anal. Calc'd for $C_{22}H_{18}$: C, 93.6; H, 6.4.
Found: C, 93.8; H, 6.5.

The tetrabromide was triturated with ligroin and recrystallized from petroleum ether (130°) and xylene. Clusters of plates appeared, melting at 238°. Although the substance was recrystallized four times, analysis showed a deficit of 2% in carbon. It is possible that a small amount of a nuclear brominated product was present.

Anal. Calc'd for $C_{22}H_{18}Br_4$: C, 43.9; H, 3.0.
Found: C, 42.0, 42.0; H, 3.1, 3.0.

Catalytic reduction of III (0.4 g.) in ethyl acetate (20 cc.) over palladium-barium sulfate was accomplished during one hour. Absorbed hydrogen: 60 cc.; calc'd: 62 cc. The 1-phenyl-4-(*p*-phenylphenyl)butane crystallized from ethanol in coarse blocks melting at 77°.

Anal. Calc'd for $C_{22}H_{22}$: C, 92.3; H, 7.7.
Found: C, 92.3; H, 7.6.

III (1.4 g.) and maleic anhydride (5 g. or 10 equivalents) were heated together at 140–150° for one hour. The mass was dissolved in boiling acetic acid, and deposited on cooling 1.5 g. or 80% of the adduct, IV. The crude product showed the melting point 260°, which after one recrystallization from butyl acetate decreased to 255°, and after a second one from xylene, to 250°. The colorless solution showed a weak blue fluorescence and deposited stars of long slender needles.

Anal. Calc'd for $C_{26}H_{20}O_3$: C, 82.1; H, 5.3.
Found: C, 81.8; H, 5.3.

When the adduct (1 g.) was suspended in ethanol (20 cc.) and 10% sodium hydroxide (10 cc.), it dissolved on gentle heating. On dropping the solution upon ice and hydrochloric acid, a snow-white precipitate was obtained. Recrystallization from ethanol gave colorless lancets. The dicarboxylic acid derived from IV sinters at 190°, and gives a clear yellow melt at 206°. It can be heated up to 230°, above which temperature decomposition occurs (dehydration?).

Anal. Calc'd for $C_{26}H_{22}O_4$: C, 78.4; H, 5.5.
Found: C, 78.3; H, 5.8.

Dehydrogenation of the dicarboxylic acid with potassium ferricyanide (2, 4) gave an amorphous product. The diene reaction in boiling nitrobenzene for 2 hours gave the tetrahydro product, IV, in 20% yield, the melting point and mixed melting point of which is 250°. When the reaction time was extended to 10 hours, the product, on recrystallization from xylene, presented a mixture of needles (IV) and boats (V). The yield was, however, so small that this method was abandoned.

The adduct, IV, (1.5 g.) and sulfur (0.3 g.) were intimately mixed and heated to 240°, whereupon evolution of hydrogen sulfide started. The violent reaction ceased after 10 minutes and was completed by heating to 300° for 2 minutes. The product was triturated with hot acetic acid and recrystallized from xylene with addition of charcoal. Yellow boatlike crystals (V) were formed, melting at 218° (with previous sintering); yield 1.5 g. (quantitative).

Anal. Calc'd for $C_{26}H_{16}O_3$: C, 83.0; H, 4.3.
Found: C, 82.8; H, 3.7.

3-Phenyl-6-(*p*-phenylphenyl)phthalic anhydride (V) (1 g.) and basic copper carbonate (2 g.) were heated in quinoline (30 cc.) to 140°. At this temperature reaction started. The water which formed was slowly distilled off with quinoline during one hour; then the mixture was boiled for 30 minutes. The quinoline was removed by steam, the water decanted, and the residue extracted with boiling xylene. After two recrystallizations from xylene, 250 mg. (31%) of quaterphenyl (VI) were obtained as plates melting at 312°.

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

SUMMARY

p-Aminobiphenyl easily undergoes the Meerwein reaction, yielding *p*-phenylstilbene and 1-phenyl-4-(*p*-phenylphenyl)-1,3-butadiene. The latter, through diene reaction with maleic anhydride, opens up a new route to quaterphenyl.

REHOVOTH, PALESTINE.

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