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APPLICATIONS OF THE MEERWEIN REACTION. PART IV. THE SYNTHESIS OF NEW MONO- AND DI-SUBSTITUTED STILBENES

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The ability of unsaturated acids to undergo a Meerwein coupling with *meta*-substituted anilines (1, 2) was exploited for the synthesis of the new *meta*-nitrostilbene (Ia). This compound is of special interest because of the many reaction possibilities of an aromatic nitro group. Several conversion products of Ia are described in the Experimental Part. 1-(*m*-Nitrophenyl)-4-phenyl-1,3-butadiene (II) was prepared in an analogous manner. It condensed with maleic anhydride in the same way as did the *p*-nitro compound, to yield the adduct III.

Selective reduction of nitrostilbenes to aminostilbenes is usually carried out by Pfeiffer's method (3) (stannous chloride in acetic acid). During catalytic reduction of these nitro compounds with palladium or Raney nickel, no marked inflection in the hydrogenation curve was observed after absorption of three moles of hydrogen. If the reaction is interrupted at this point, only the completely reduced amino ethane can be isolated. It is thus apparent that in the nitrostilbenes the speed of reduction of the two reducible groups is similar, although stilbene and nitrobenzene react at very different rates under comparable experimental conditions.

TABLE I

MELTING POINTS OF *trans*-NITROSTILBENES AND THEIR DERIVATIVES, °C

	UNSUBST.	*o*-SUBST.	*m*-SUBST.	*p*-SUBST.
Nitrostilbene	124	78[a]	112	157[b]
Nitrostilbene dibromide	237	156[c]	185	198[b]
Aminostilbene		106[a]	120	151[b]
Acetaminostilbene		144[a]	192	225[b]
Aminodiphenylethane		33[d]	51	48[e]
Acetaminodiphenylethane		117[d]	129	134[f]

[a] Sachs and Hilpert, *Ber.*, **39**, 899 (1906).

[b] See Ref. 4.

[c] Pfeiffer, *Ber.*, **48**, 1048 (1915).

[d] Ruggli and Staub, *Helv. Chim. Acta*, **20**, 37 (1937).

[e] v. Braun, Deutsch, and Koscielski, *Ber.*, **46**, 1511 (1913).

[f] This substance, *p*-$CH_3CONHC_6H_4CH_2CH_2C_6H_5$, crystallized from petroleum ether (130°) in long rods. *Anal.* Calc'd for $C_{16}H_{17}NO$: C, 80.3; H, 7.1. Found: C, 80.9; H, 6.6.

In Tables I and II the melting points of the isomeric *trans*-nitrostilbenes and *trans,trans*-nitrophenylphenylbutadienes and their derivatives are collected for comparison. It is seen that the large differences between the *m*- and *p*- series vanish almost completely if the unsaturated linkages disappear, either by hydrogenation, or bromination, or addition of maleic anhydride. The high melting points of the *p*-substituted derivatives are therefore ascribed to the strong mesomeric effect of the *p*-nitro group.

Ortho-substituted anilines usually give low yields of coupling products. This was again found to be the case with *o*-toluidine, which yielded 12% of *o*-methylstilbene (see Table III) and still more with α-naphthylamine, which produced only traces of 2-(α-naphthyl)-1-phenylethylene (IV). The melting point of our product, 148–149°, differs from that given by Balla (4), 72.5–73.5°, and therefore the two compounds are probably *cis-trans* isomers.[1] The Meerwein reaction between cinnamic acid and *o*-anisidine gave very impure samples of *o*-methoxystilbene (V), which could not be induced to crystallize. When we attempted to purify the substance *via* its dibromide (2), a tribromo derivative (VI) was obtained, which upon debromination yielded 5-bromo-2-methoxystilbene (VII). The latter structure was proved by comparison with the coupling product of cinnamic acid and diazotized 5-bromo-2-methoxyaniline.

TABLE II

MELTING POINTS OF *trans,trans*-1-(NITROPHENYL)-4-PHENYL-1,3-BUTADIENE, °C

	UNSUBST.	*o*-SUBST.	*m*-SUBST.	*p*-SUBST.
Nitrodiphenylbutadiene	152	97^a	146	172^b
Tetrabromide	255	193	206	245–246^b
Adduct with maleic anhydride	207^c	196	211	213^b
Aminodiphenylbutadiene		132^a		167^b
Acetaminodiphenylbutadiene			203	260

[a] See Ref. 10.
[b] See Ref. 11.
[c] Diels and Alder, *Ber.*, **62**, 2081 (1929).

TABLE III

METHYLSTILBENES

	M.P., °C	YIELD %	DIBROMIDE M.P., °C	DIHYDRO DERIV. B.P., °C
o-Methylstilbene	(b.p. 125/0.15 mm.)	12	159	95–98/0.05
m-Methylstilbene^a	48	14		
p-Methylstilbene	120^b	40	188^b	98–99/0.05^c

[a] See Ref. 12.
[b] Compare Klages and Tetzner, *Ber.*, **35**, 3967 (1902); Späth, *Monatsh.*, **35**, 469 (1914).
[c] Compare Mann, *Ber.*, **14**, 1645 (1881).

It was previously reported (2) that *o*-chloroaniline gave a 9% yield of *o*-chlorostilbene and 10% of 1-(*o*-chlorophenyl)-4-phenyl-1,3-butadiene. We have now carried out the analogous coupling with *p*-methoxycinnamic acid and obtained an 8% yield of 2-chloro-4′-methoxystilbene (VIII). 2,6-Dichloroaniline gave no

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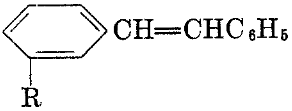
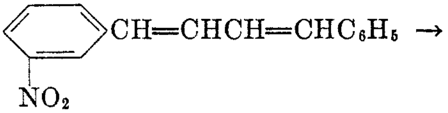
[1] β-Naphthylamine gave somewhat better yields. See Experimental Part.



I

a:R = NO_2

b:R = CH_3



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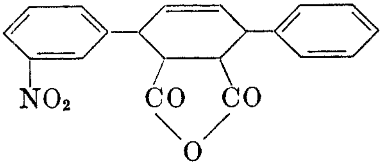

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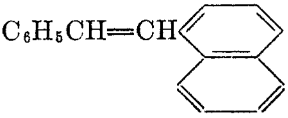

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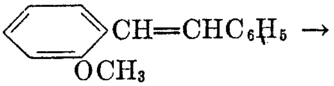

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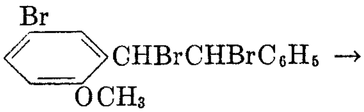

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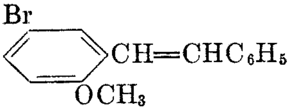

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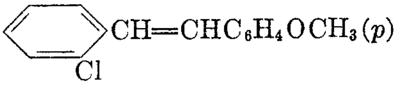

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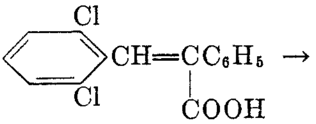

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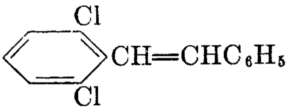

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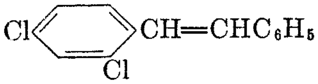

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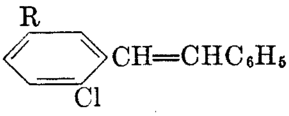
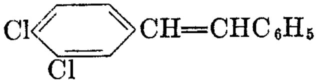


XII

a:R = Cl

b:R = CH_3



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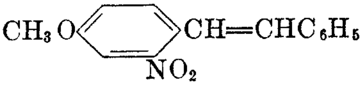

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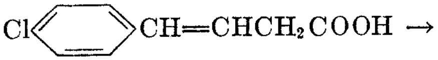

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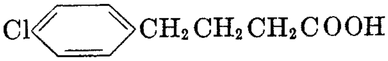

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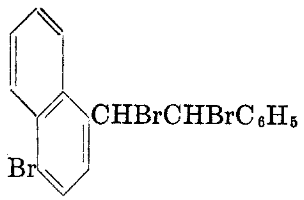
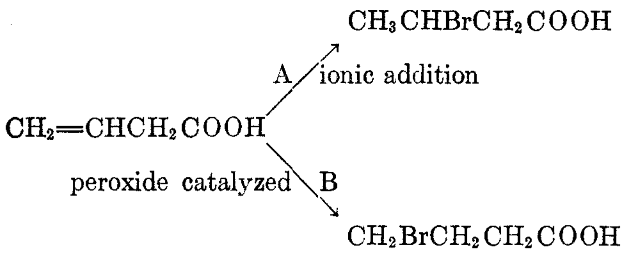


XVII



coupling product at all. The desired 2,6-dichlorostilbene (X) was, however, easily obtained by the classical method of Perkin from 2,6-dichlorobenzaldehyde and phenylacetic acid through decarboxylation of the intermediate carboxylic acid.

The Meerwein reaction of *ortho*-substituted anilines is markedly influenced by the presence of a second substituent. Thus 2,4-dichlorostilbene (XI) was obtained in 26% yield, 2,5-dichlorostilbene (XIIa) in 28%, and the 3,4-isomer (XIII) in 40% yield. 2-Chloro-5-methylaniline gave the corresponding stilbene (XIIb) in 27% yield. Comparison with *o*-chlorostilbene itself (9%) shows that the presence of an additional substituent diminishes the ortho-effect. 4-Methoxy-2-nitroaniline (5) was converted into 4-methoxy-2-nitrostilbene (XIV) in 18% yield.

The mechanism of the Meerwein reaction is still a controversial matter. Whereas Meerwein himself (6) proposed an ionic mechanism, consisting in the addition of the aryl cation to the α-carbon atom, *e.g.* of cinnamic acid, Koelsch (7) showed that acrylic and crotonic acids, which as catio-enoid systems add the anion of a hydrohalogen acid at the β-carbon atom, attach the aryl group at the same point. They thought it therefore probable that an aryl radical is the actual reacting form, and that the point of attack is determined by structural influences in the unsaturated acid. Thus, according to Koelsch, cinnamic acid adds the aryl radical at the α-carbon atom, because the odd electron on the β-carbon atom will be stabilized by resonance into the β-phenyl ring. Acrylic and crotonic acids, on the other hand, combine with their β-carbon atom, so that the odd electron on the α-carbon can resonate into the neighboring C=O group.

Now it must be borne in mind that all the β-unsaturated acids, which have been so far used for the Meerwein reaction, usually do not give different results when hydrohalogens are added to them, either as ions or by a radical mechanism (8). It appears therefore necessary to use an unsaturated acid, in which the disturbing catio-enoid system is absent, and therefore a clear distinction between the two reaction mechanisms can be made (9). When vinylacetic acid was coupled with diazotized *p*-chloroaniline, an acid was isolated in 5% yield, which represents one of the possible isomers of γ-(*p*-chlorophenyl)vinylacetic acid (XV). It was hydrogenated to γ-(*p*-chlorophenyl)butyric acid (XVI), identical with an authentic specimen (8). Kharasch and his co-workers have shown (9) that vinylacetic acid gives different results when hydrogen bromide is added by an ionic (scheme A) or radical mechanism (scheme B). Accordingly one would expect that the aryl cation would add at the β-carbon atom, and an aryl radical (which is less electrophilic than a halogen atom) to the γ-carbon atom. However, before final conclusions regarding the mechanism can be made, extension of these experiments to some more acids with terminal ethylenic groups appears necessary.

EXPERIMENTAL

m-Nitrostilbene (Ia) and derivatives. m-Nitroaniline (27 g.) was diazotized in hydrochloric acid solution and the clear diazo solution was added to cinnamic acid (30 g.) dissolved in acetone (150 cc.). The coupling reaction occurred at 14–16° during four hours. The solution was steam distilled, and the residue was extracted with benzene and washed with ammonia solution. Distillation gave a yellow oil, b.p. 170–175° (0.2 mm.), which crystallized on trituration with ethanol; yield 14.5 g., 33%. *m*-Nitrostilbene (Ia) crystallized from butanol in straw-yellow flat rods of m.p. 112°.

Anal. Calc'd for $C_{14}H_{11}NO_2$: C, 74.7; H, 4.9; N, 6.2.
Found: C, 74.7; H, 4.7; N, 6.0.

The *dibromide* was prepared in chloroform solution and crystallized from xylene-petroleum ether (130°) in branched leaflets of m.p. 184–185°.

Anal. Calc'd for $C_{14}H_{11}Br_2NO_2$: C, 43.6; H, 2.9; N, 3.6.
Found: C, 43.9; H, 2.6; N, 3.5.

m-Aminostilbene. m-Nitrostilbene (3 g.) was dissolved in acetic acid (50 cc.), containing 20 g. of stannous chloride, and saturated with dry hydrogen chloride (3). After a few minutes an exothermic reaction set in, and the complex salt crystallized out. It was filtered off and boiled with sodium hydroxide for two minutes. The supernatant oil solidified immediately. It was recrystallized first from ethanol, then from butyl acetate. *m*-Aminostilbene forms beautiful blocks of m.p. 119–120°.

Anal. Calc'd for $C_{14}H_{13}N$: C, 86.2; H, 6.7; N, 7.2.
Found: C, 86.0; H, 6.5; N, 7.5.

The acetyl derivative crystallized from acetic acid in tablets of m.p. 191–192°.

Anal. Calc'd for $C_{16}H_{15}NO$: C, 81.0; H, 6.3.
Found: C, 80.6; H, 6.3.

m-Aminodibenzyl. m-Nitrostilbene (3.5 g.) was dissolved in ethyl acetate (60 cc.) and reduced in the presence of Pd-$BaSO_4$. During 30 minutes about 1200 cc. of hydrogen was absorbed (calc'd: 1120 cc. for 760 mm. and 20°). The product distilled at 180° (6 mm.) as a thick yellow oil, which crystallized spontaneously. From petroleum ether (80°) thin, rhombic plates were obtained of m.p. 51°.

Anal. Calc'd for $C_{14}H_{15}N$: C, 85.3; H, 7.6; N, 7.1.
Found: C, 84.9; H, 7.7; N, 7.0.

3-Acetaminodibenzyl crystallized from a benzene-petroleum ether (80°) mixture in quadrangular plates of m.p. 128–129°.

Anal. Calc'd for $C_{16}H_{17}NO$: C, 80.3; H, 7.1; N, 5.9.
Found: C, 80.6; H, 7.0; N, 6.0.

1-(m-Nitrophenyl)-4-phenyl-1,3-butadiene (II) and derivatives. The Meerwein reaction between diazotized *m*-nitroaniline (18 g.) and 1-carboxy-4-phenyl-1,3-butadiene (22 g.)

proceeded at 24–30° during four hours. The mixture was worked up as above and yielded, after steam distillation, a crude product which crystallized directly upon treatment with hot acetic acid. II was recrystallized first from butanol, then from acetic acid, m.p. 146°, yield 4 g., 12%.

Anal. Calc'd for $C_{16}H_{13}NO_2$: C, 76.5; H, 5.2; N, 5.6.
Found: C, 76.1; H, 5.5; N, 5.8.

The tetrabromide, which was prepared in chloroform solution, had the m.p. 206° after recrystallization from xylene-petroleum ether (130°).

Anal. Calc'd for $C_{16}H_{13}Br_4NO_2$: C, 33.6; H, 2.3.
Found: 33.8; H, 2.3.

When the tetrabromide was treated with potassium iodide in acetone solution, the original butadiene was recovered.

1-(*m*-Nitrophenyl)-4-phenyl-1,3-butadiene (1 g.) was heated on a water-bath with maleic anhydride (2 g.) for four hours and the mixture was thereafter dissolved in hot acetic acid. On cooling, the adduct (III) was deposited, which crystallized from acetic anhydride in tablets of m.p. 211°; yield quantitative.

Anal. Calc'd for $C_{20}H_{15}NO_5$: C, 68.8; H, 4.3.
Found: C, 68.9; H, 4.2.

1-(*m*-Aminophenyl)-4-phenyl-1,3-butadiene was obtained in a manner analogous to the preparation of *m*-aminostilbene. As it was difficult to purify it from the last traces of stannic oxides, it was acetylated directly. 1-(*m*-Acetaminophenyl)-4-phenyl-1,3-butadiene crystallized from xylene in rods of m.p. 203°.

Anal. Calc'd for $C_{18}H_{17}NO$: C, 82.1; H, 6.5.
Found: C, 81.8; H, 6.0.

1-(*o*-Nitrophenyl)-4-phenyl-1,3-butadiene was prepared according to Bachman and Hoaglin (10) by the appropriate Meerwein reaction of *o*-nitroaniline.

Its tetrabromide was recrystallized from petroleum ether (130°) and had m.p. 193°.

Anal. Calc'd for $C_{16}H_{13}Br_4NO_2$: C, 33.6; H, 2.3.
Found: C, 33.4; H, 2.3.

The adduct with maleic anhydride was prepared as above. It crystallized from butyl acetate in rods, m.p. 196°.

Anal. Calc'd for $C_{20}H_{15}NO_5$: C, 68.8; H, 4.3,
Found: C, 69.0; H, 4.5.

The following new derivatives of 1-(*p*-nitrophenyl)-4-phenyl-1,3-butadiene (11) were prepared:

1-(*p*-Acetaminophenyl)-4-phenyl-1,3-butadiene crystallized from butyl acetate in yellowish short rods of m.p. 260°.

Anal. Calc'd for $C_{18}H_{17}NO$: C, 82.1; H, 6.5.
Found: C, 82.0; H, 6.5.

1-(*p*-Aminophenyl)-4-phenyl-1,3-butadiene reacted with diphenylketene in benzene solution. 1-(*p*-Diphenylacetaminophenyl)-4-phenyl-1,3-butadiene crystallized from ethyl benzoate in short rods of m.p. 240–241°.

Anal. Calc'd for $C_{30}H_{25}NO$: C, 86.75; H, 6.0; N, 3.4.
Found: C, 86.8; H, 6.4; N, 3.6.

Catalytic reduction produced 1-(*p*-aminophenyl)-4-phenylbutane of m.p. 32°, b.p. 178° (0.1 mm.).

Anal. Calc'd for $C_{16}H_{19}N$: C, 85.3; H, 8.4.
Found: C, 85.0; H, 8.2.

Its acetyl derivative crystallized from ethanol in glistening plates of m.p. 135°.

Anal. Calc'd for $C_{18}H_{21}NO$: C, 80.9; H, 7.9; N, 5.2.
Found. C, 80.6; H, 8.0; N, 5.6.

Methylstilbenes (see Table III). *o*-Methylstilbene was obtained by the appropriate Meerwein reaction in 12% yield; colorless oil of b.p. 120–125° (0.15 mm.).

Anal. Calc'd for $C_{15}H_{14}$: C, 92.8; H, 7.2.
Found: C, 92.4; H, 7.6.

Its dibromide crystallized from isopropanol and showed the m.p. 158–159°.

Anal. Calc'd for $C_{15}H_{14}Br_2$: C, 50.8; H, 4.0.

Found: C, 50.6; H, 4.4.

Catalytic reduction yielded *o*-methyldibenzyl as a colorless oil of b.p. 95–98° (0.05 mm.)

Anal. Calc'd for $C_{15}H_{16}$: C, 91.8; H, 8.2.

Found: C, 91.8; H, 8.2.

m-Methylstilbene (I b) (12) was obtained as an oil of b.p. 135–140° (0.1 mm.,) which crystallized slowly. After two recrystallizations from methanol it was obtained as yellowish leaflets of m.p. 48°; yield 14%.

Anal. Calc'd for $C_{15}H_{14}$: C, 92.8; H, 7.2.

Found: C, 93.1; H, 7.4.

The dibromide of (I b) crystallized from petroleum ether (130°) is prismatic plates of m.p. 174–176°.

Anal. Calc'd for $C_{15}H_{14}Br_2$: C, 50.8; H, 4.0.

Found: C, 50.6; H, 4.1.

Coupling with α-naphthylamine. The Meerwein reaction between diazotized α-naphthylamine and cinnamic acid was accomplished at 22–26°. The black tar which remained after steam distillation, was distilled *in vacuo* and yielded a very small fraction of b.p. 170° (14 mm.), which crystallized from petroleum ether (130°) in flakes of m.p. 148–149°.

Anal. Calc'd for $C_{18}H_{14}$: C, 93.9; H, 6.1.

Found: C, 93.6; H, 5.9.

With bromine in chloroform simultaneous addition at the ethylenic double bond and substitution in the ring took place, to yield a tribromo derivative of the possible structure XVII. The substance crystallized from petroleum ether (130°) in colorless leaflets of m.p. 165°.

Anal. Calc'd for $C_{18}H_{14}Br_2$: C, 55.4; H, 3.6.

for $C_{18}H_{13}Br_3$: C, 46.1; H, 2.8.

Found: C, 45.9; H, 2.6.

Coupling with β-naphthylamine. The reaction between diazotized β-naphthylamine and cinnamic acid proceeded at 5–15°. The tar, which remained after steam distillation, crystallized upon trituration with methanol. Recrystallization from petroleum ether (130°) gave 2-(β-naphthyl)-1-phenylethylene as white leaflets of m.p. 143°; yield 5%.

Anal. Calc'd for $C_{18}H_{14}$: C, 93.9; H, 6.1.

Found: C, 94.0; H, 6.4.

The dibromide was prepared in chloroform solution. It crystallized from petroleum ether (130°) in prisms of m.p. 186–187°.

Anal. Calc'd for $C_{18}H_{14}Br_2$: C, 55.4; H, 3.6.

Found: C, 55.3; H, 3.7.

Coupling with o-anisidine. The crude *o*-methoxystilbene (13) was obtained as a reddish oil of b.p. 138–140° (0.15 mm.). For purification, it was brominated in chloroform solution. The product crystallized from a mixture of xylene and petroleum ether (130°) in beautiful prisms of m.p. 190–192° (VI).

Anal. Calc'd for $C_{15}H_{14}Br_2O$: 48.6; H, 3.8; OCH_3, 8.4.

for $C_{15}H_{13}Br_3O$: C, 40.1; H, 2.9; OCH_3, 6.9.

Found: C, 39.9; H, 3.0; OCH_3, 6.8.

Dehalogenation of VI with potassium iodide in acetone gave an oil which crystallized after one weeks standing. The product (VII) crystallized from ethanol in colorless needles of m.p. 74°.

Anal. Calc'd for $C_{15}H_{13}BrO$: C, 62.3; H, 4.5.

Found: C, 62.1; H, 4.5.

Synthesis of 5-bromo-2-methoxystilbene (VII). 5-Bromo-2-methoxyaniline was prepared according to Kohn and Karlin (15). Its diazo derivative coupled with cinnamic acid under the usual conditions at 20–25°. The crude product was purified by distillation, b.p. 225–230°

(1.25 mm.), the distillate solidified spontaneously. It and its dibromide did not depress the melting points of the substances VI and VII described above.

2-Chloro-4′-methoxystilbene (VIII). The coupling between diazotized *o*-chloroaniline and *p*-methoxycinnamic acid proceeded at 17–20°. The crude product was distilled *in vacuo*, b.p. 180–185° (0.05 mm.). The oil so obtained solidified upon treatment with methanol. The substance (VIII) crystallized from the same solvent in prisms of m.p. 64°;[2] yield 14%.

Anal. Calc'd for $C_{15}H_{13}ClO$: C, 73.8; H, 5.3.
Found: C, 73.4; H, 5.3.

The dibromide crystallized from petroleum ether (130°) in clusters of leaflets, m.p. 148°.

Anal. Calc'd for $C_{15}H_{13}Br_2ClO$: C, 44.6; H, 3.2.
Found: C, 44.9; H, 3.5.

The stilbene VIII could not be demethylated by boiling 48% hydrobromic acid.

Dichlorostilbenes (see Table IV). 2,4-, 2,5-, and 3,4-Dichlorostilbene were prepared by the appropriate Meerwein reactions. The coupling of diazotized 2,6-dichloroaniline with cinnamic acid was unsuccessful. The compound X was therefore synthesized by Perkin's method.

2,6-Dichlorostilbene (X). 2,6-Dichlorobenzaldehyde (26 g.) and dry sodium phenylacetate (26 g.) were heated in boiling acetic anhydride (60 cc.) for eight hours. Then acetic acid (200 cc.) was added and the solution filtered. The filtrate, on standing overnight, deposited 25 g. (57%) of crystals (IX). This product crystallized from acetic acid in prismatic columns of m.p. 235°.

Anal. Calc'd for $C_{15}H_{10}Cl_2O_2$: C, 61.4; H, 3.4.
Found: C, 61.2; H, 3.8.

Decarboxylation. The acid (IX) (20 g.) was dissolved in quinoline (200 cc.) and basic copper carbonate (20 g.) added. Reaction started at 140° and was over after about half an hour. The solution was then boiled for ten minutes and steam-distilled. The non-volatile residue crystallized from propanol in prismatic plates of m.p. 89–90° (X), yield 10 g., or 60%.

Anal. Calc'd for $C_{14}H_{10}Cl_2$: C, 67.7; H, 4.0.
Found: C, 67.6; H, 4.4.

The dibromide of X crystallized from petroleum ether (130°) in prismatic plates of m.p. 136°.

Anal. Calc'd for $C_{14}H_{10}Br_2Cl_2$: C, 41.2; H, 2.5.
Found: C, 40.9; H, 2.2.

Bromination of the acid IX, on the other hand, was unsuccessful.

Coupling with vinylacetic acid. *p*-Chloroaniline (12 g.) was diazotized in the usual way, and the diazo solution added to vinylacetic acid (8.6 g.) in ice-cold acetone (200 cc.). The coupling reaction proceeded at 15°. After steam distillation, the non-volatile syrup was dissolved in benzene and the organic acids extracted from it by sodium hydroxide solution. This solution was boiled with charcoal, filtered, and stirred into ice-cold hydrochloric acid. A small precipitate was obtained which crystallized from petroleum ether (80°) in twinned plates of m.p. 107° (XV), yield 1 g., 5%.

Anal. Calc'd for $C_{10}H_9ClO_2$: C, 61.2; H, 4.6.
Found: C, 61.5; H, 4.4.

The unsaturated acid (XV) (0.8 g.) in acetic acid (20 cc.) was reduced over palladium-barium sulfate at 23° (758 mm.). The required amount of hydrogen was absorbed during 15 minutes. Distillation at 140–150° (1 mm.) gave an oil which solidified spontaneously (XVI), m.p. 55° [Lit. (16) 62°].

For easier identification, the chloride of XVI was prepared with thionyl chloride in boil-

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[2] Thus all the three isomeric chloro-4′-methoxystilbenes are now known: 3-Chloro-4′-methoxystilbene m.p. 96° [Jenkins and Richardson *J. Am. Chem. Soc.* **55**, 3874 (1933)]; 4-chloro-4′-methoxystilbene, m.p. 184° [v. Walter and Wetzlich *J. prakt. Chem.* (2) **67**, 175 (1900)].

TABLE IV

UNILATERAL DISUBSTITUTED STILBENES AND THEIR DERIVATIVES

STILBENES, Ar—CH=CH—C_6H_5

Ar =	YIELD %	M.P., °C	SOLVENT	CRYSTAL FORM	FORMULA	ANALYSES			
						Calc'd		Found	
						C	H	C	H
2,4-Dichlorophenyl[a]	26	79–80	Pet. ether 80°	Leaflets	$C_{14}H_{10}Cl_2$	67.7	4.0	67.6	3.8
2,5-Dichlorophenyl[b]	28	62	Methanol	Needles	$C_{14}C_{10}Cl_2$	67.7	4.0	67.6	4.0
3,4-Dichlorophenyl	40	86–87	Ethanol	Leaflets	$C_{14}H_{10}Cl_2$	67.7	4.0	67.6	3.8
2,6-Dichlorophenyl[c]	60	89–90	Propanol	Prismatic plates	$C_{14}H_{10}Cl_2$	67.7	4.0	67.6	4.4
2-Chloro-5-methylphenyl	27	b.p. 150/3 mm.			$C_{15}H_{13}Cl$	78.9	5.7	79.1	5.7
4-Methoxy-2-nitrophenyl	18	116	Acetic acid	Prismatic blocks	$C_{14}H_{13}NO_3$	70.6	5.1	71.2	5.5
5-Bromo-2-methoxyphenyl	28	74	Ethanol	Needles	$C_{15}H_{13}BrO$	62.3	4.5	62.1	4.5

DIBROMIDES, Ar—CHBr—CHBr—C_6H_5

Ar =	YIELD %	M.P., °C	SOLVENT	CRYSTAL FORM	FORMULA	Calc'd C	Calc'd H	Found C	Found H
2,4-Dichlorophenyl		146	Pet. ether 80°	Prismatic plates	$C_{14}H_{10}Br_2Cl_2$	41.2	2.5	41.3	2.9
2,5-Dichlorophenyl		188	Xylene	Prismatic blocks	$C_{14}H_{10}Br_2Cl_2$	41.2	2.5	41.7	2.2
3,4-Dichlorophenyl		182	Xylene	Prismatic rods	$C_{14}H_{10}Br_2Cl_2$	41.2	2.5	41.6	2.3
2,6-Dichlorophenyl		136	Pet. ether 130°	Prismatic plates	$C_{14}H_{10}Br_2Cl_2$	41.2	2.5	40.9	2.2
2-Chloro-5-methylphenyl		158	Pet. ether 130°	Prismatic rods	$C_{15}H_{13}Br_2Cl$	46.4	3.3	46.2	3.1

DIHYDRO DERIVATIVES, Ar—$CH_2CH_2C_6H_5$

Ar =	YIELD %	M.P., °C	SOLVENT	CRYSTAL FORM	FORMULA	Calc'd C	Calc'd H	Found C	Found H
2,4-Dichlorophenyl		b.p. 128–130/0.1 mm.			$C_{14}H_{12}Cl_2$	67.2	4.8	67.3	4.7
2,5-Dichlorophenyl		b.p. 133/0.06 mm.			$C_{14}H_{12}Cl_2$	67.2	4.8	67.4	4.8
3,4-Dichlorophenyl		53 b.p. 173/0.6 mm.			$C_{14}H_{12}Cl_2$	67.2	4.8	67.5	4.7

[a] Meerwein (6), who first prepared this stilbene, reports m.p. 77.5°

[b] This stilbene could be obtained pure only by decomposition of its dibromide with sodium iodide.

[c] This dichlorostilbene was prepared by Perkin's method (see Experimental Part).

ing benzene and converted directly into the anilide. The latter was recrystallized from petroleum ether (60°), forming elongated, sharp needles of m.p. 102°.

Anal. Calc'd for $C_{16}H_{16}ClNO$: C, 70.3; H, 5.9.

Found: C, 70.0; H, 5.7.

Both the acid (XVI) and its anilide did not depress the m.p. of γ-(*p*-chlorophenyl)butyric acid and its anilide, prepared according to Skraup and Schwamberger (16).

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SUMMARY

1. The Meerwein reaction between diazotized anilines and cinnamic acids has been applied to vairious meta-, ortho-, and di-substituted anilines. The coupling with α-naphthylamine gave a 2-(α-naphthyl)-1-phenylethylene, isomeric with the compound of the same structure described by Balla (4). 2,6-Dichlorostilbene could not be prepared in this way, but was obtained by the Perkin condensation of 2,6-dichlorobenzaldehyde with phenylacetic acid.

Selective catalytic reduction of the nitrostilbenes in the nitro group only could not be achieved.

2. The Meerwein reaction between diazotized *p*-chloroaniline and vinylacetic acid gave γ-(*p*-chlorophenyl)vinylacetic acid. If the reaction is regarded as ionic, the point of attachment of the diazo cation at the γ-carbon atom corresponds to the point of addition of the proton in the reaction with hydrobromic acid. If, however, comparison is made with the peroxide-catalyzed addition reaction, one should expect attachment of the aromatic radical at the β-carbon atom. Our result, therefore, points to an ionic mechanism, at least in the case of vinylacetic acid.

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