

TABLE II
MELTING POINTS AND ANALYSES OF 4-SUBSTITUTED 4'-HYDROXYBENZANILIDES

XC ₆ H ₄ - CONHC ₆ H ₄ OH, X	Mp, °C	Calcd, %			Found, %		
		C	H	N	C	H	N
OCH ₃	230-232	69.12	5.39	5.76	68.96	5.44	5.71
CH ₃	215-216	73.99	5.77	6.16	74.00	5.73	6.10
Cl	245-246	63.04	4.07	5.65	62.99	3.96	5.50
NO ₂	265-266	60.46	3.90	10.85	60.44	3.77	10.77

in which resonance stabilization of the conjugate base (phenolate anion) results in dispersal of charge rather than in charge creation. The ρ value for ionization of IIIb in 1.6% acetonitrile-water was found to be 0.05 ± 0.02 . This is 10 times less than the ρ for ionization of V (20% ethanol-water) and 6 times less than the ρ for ionization of substituted 4-hydroxystilbenes (1.6% acetonitrile-water).⁶ Clearly, the amide linkage is a poor transmitter of electronic effects despite the considerable double-bond character of the C-N bond.⁷

In recent work, Johnson and coworkers⁹ showed that Michael addition of ethanol to acrylanilides and elimination of HBr from β -bromopropionanilides (ethanol, 55°) have a Hammett ρ of 1.77 and 1.74, respectively. The amide linkage, it was concluded, is an excellent transmitter of activation effects. On the basis of our results with the benzanilide systems, it would appear that the large ρ values for the addition and elimination reactions are due mainly to an efficient transmission of polar effects, and that there is little direct resonance interaction between the substituents and the reactive sites.

The reason for the lack of electronic transmission through the amide linkage is not clear. Perhaps the 60% reduction in double-bond character is sufficient to suppress completely any conjugative effects. Alternatively, the nature of the partial double bond of the amide group may be different from that of ethylenic and azo double bonds. The partial double bond of the amide could involve overlap between the unshared pair of electrons on the nitrogen and an empty carbon orbital in the 3 shell. This is consistent with an amide carbonyl bond length that is shorter than that of acetaldehyde.¹⁰ Our results might also be related to Pauling's idea that polarization of the σ bond between the carbonyl carbon and the nitrogen effectively liberates a p orbital of carbon lying in the plane of the group, and permits a π bond to be formed with an unshared pair of electrons on the oxygen.¹

Experimental Section

Compounds.—The general procedure used for the preparation of the substituted 4'-hydroxybenzanilides was as follows. A *para*-substituted benzoyl chloride (0.01 mol) was dissolved in 20

(6) The ρ was determined from a two-point Hammett plot.

(7) The ionization of *para*-substituted N-methylbenzhydroxamic acids has a ρ of 0.86 in 80% Methyl Cellusolve-water.⁸ This ρ is less than that for the ionization of benzoic acid in water, and it suggests that there may be also little direct resonance interaction through the carbonyl carbon-nitrogen bond of the hydroxamic acids. Moreover, the pK_a values correlate with σ rather than with σ^- .

(8) O. Exner and W. Simon, *Collect. Czech. Chem. Commun.*, **30**, 4078 (1965).

(9) H. W. Johnson, E. Ngo, R. C. Stafford, and Y. Iwata, the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Organic Abstract No. 31.

(10) H. A. Bent, *Chem. Rev.*, **68**, 587 (1969).

ml of pyridine that had been dried over Linde 4A Molecular Sieve. This solution was added dropwise to 20 ml of a pyridine solution of recrystallized *p*-hydroxyaniline (0.01 mol). The reaction mixture was then boiled under reflux for 12 hr, after which the pyridine was removed with the aid of a rotary evaporator. The residue was crystallized from ethanol-water and sublimed. The properties of the products are given in Table II.

Substituted 4'-aminobenzanilides were prepared by the method of Izmail'skii and Malygina.²

pK_a Determinations.—The pK_a values of the benzanilides and stilbenes were determined spectrophotometrically by the method of Albert and Serjeant.¹¹

Registry No.—IIIa (X = OCH₃), 23600-43-3; IIIa (X = CH₃), 23600-44-4; IIIa (X = H), 17625-83-1; IIIa (X = Cl), 23600-46-6; IIIa (X = NO₂), 6409-40-1; IIIb (X = OCH₃), 23600-48-8; IIIb (X = CH₃), 23646-69-7; IIIb (X = H), 15457-50-8; IIIb (X = Cl), 19207-92-2; IIIb (X = NO₂), 13160-56-0.

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(11) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen and Co. Ltd., London, 1962, p 69.

Stereochemistry of α -Phenethyl Radical Dimerization¹

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It has been reported³ that the reduction of α -bromoethylbenzene and α -chloroethylbenzene by chromous sulfate produces 85–90% *meso*-2,3-diphenylbutane and 10–15% the *dl* forms, the disparity being attributed to conformational effects. If correct, this observation would connote a mechanism of final product formation other than simple dimerization of free radicals, because there is abundant qualitative and semiquantitative evidence⁴ based on yields in other free-radical situations

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(2) Summer Student Training Program, Argonne National Laboratory, 1969, supported in part by the National Science Foundation.

(3) C. E. Castro and W. C. Kray, Jr., *J. Amer. Chem. Soc.*, **85**, 2768 (1963).

(4) Comparable yields of *meso*- and *dl*-2,3-diphenylbutane have been reported in (a) the reaction of α -chloroethylbenzene with magnesium and moist ether [E. Ott, *Chem. Ber.*, **61**, 2124 (1928)]; (b) α -bromoethylbenzene with sodium [K. T. Serijan and P. H. Wise, *J. Amer. Chem. Soc.*, **74**, 365 (1952)]; (c) α -bromoethylbenzene with magnesium and cupric chloride [J. B. Conant and A. H. Blatt, *ibid.*, **50**, 551 (1928)]; (d) coupling of Grignard reagent [W. T. Somerville and P. E. Spoerri, *ibid.*, **74**, 3803 (1952)]; (e) decomposition of diacetyl peroxide in ethylbenzene [M. S. Kharasch, H. McBay, and W. H. Urry, *J. Org. Chem.*, **10**, 401 (1945)]; (f) decomposition of di-*t*-butyl peroxide in ethylbenzene [E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, **1951**, 131]; (g) decomposition of benzoyl peroxide in ethylbenzene [R. L. Dannley and B. Zaremsky, *J. Amer. Chem. Soc.*, **77**, 1588 (1955)]. In one instance, the reaction of hydrotropoyl chloride with sodium peroxide, the equality of yields was established by careful ir analysis [F. D. Greene, *ibid.*, **77**, 4869 (1955)].

to show that α -phenylethyl radicals dimerize in the two modes nearly equally. It seemed desirable in connection with concurrent studies on reduction by the hydrated electron to recheck the chromous sulfate reduction and, also, with the more refined analytical procedures now available, to test more rigorously for the presence or absence of measurable stereo discrimination in some conventional free-radical dimerizations.

The conventional reactions giving rise to 2,3-diphenylbutane mixtures, and believed to occur by dimerization of α -phenethyl radicals, were (1) decomposition of di-*t*-butyl peroxide in ethylbenzene at 135°;^{4f} (2) decomposition of benzoyl peroxide in ethylbenzene at 100°;^{4g} (3) reaction of ethylbenzene with aqueous potassium persulfate at 80°;⁵ (4) reaction of α -bromoethylbenzene with iron powder in water suspension;⁶ (5) reaction of α -bromoethylbenzene vapor with a silver mirror film at 25°;⁷ (6) benzophenone-sensitized photolysis of ethylbenzene at three different temperatures, -25, -73, and -110°.⁸ The choices were influenced by the thought that reactions at the lowest possible temperature, or on surfaces, would be most likely to reveal any small measure of steric control. No attempt was made to maximize yields and care was taken to avoid fractional separation of isomers prior to a determination of the *meso*/*dl* ratio by gas chromatography. All of the results (cf. Table I) agreed, within

TABLE I
ISOMER RATIOS IN REACTIONS FORMING
2,3-DIPHENYLBUTANE

Reaction no.	Reactants	Temp, °C	Time, hr	<i>meso</i> / <i>dl</i> ratio
1	Ethylbenzene, di- <i>t</i> -butylperoxide	135	3	1.08
2	Ethylbenzene, benzoyl peroxide	100	2	1.02
3	Ethylbenzene, aq K ₂ S ₂ O ₈	100	4	1.01
4	α -Bromoethylbenzene, Fe, aq suspn	80	3.5	1.03
5	α -Bromoethylbenzene (vapor), Ag mirror	25	46	0.98
6a	0.12 M ethylbenzene, 0.02 M benzophenone in benzene, 3600-Å irrads	25	0.5	1.00
			1.5	1.04
			3.0	1.03
6b	0.02 M benzophenone in ethylbenzene	-25	1.0	1.02
		-73	1.0	0.98
		-110	1.0	1.03
7	α -Bromoethylbenzene, aq CrSO ₄	25	0.2	1.05
		0	0.5	1.06

the limits of experimental error, with the assignment of equal probability to *meso* and *dl* product formation. The overall average, 1.020 \pm 0.020 (average deviation), deviated slightly in favor of the *meso* form but the direction and magnitude of the deviation is about what

might be expected from slight tailing of the *dl* peak into the region of the *meso* peak.

Likewise the product ratio from the chromous sulfate reduction of α -bromoethylbenzene (cf. Table I, reaction 7) showed no clearly significant departure from random orientation of the combining radicals. It follows that yields of isolated crystalline *meso* isomer in excess of 50% of theoretical cannot be reconciled with these measurements and hence that the reported³ actual yields, 56 and 81% from α -bromo- and α -chlorobenzene, respectively, are too imprecise to be mechanistically significant. The new measurements are consistent with, but of course do not uniquely validate, the currently accepted⁹ free-radical interpretation of halide reduction by chromous salts.

Experimental Section

Gas chromatographic analyses were performed on 7-m QF-1 columns operated at 125–150° or, in a few instances, on an 8-m OV-101 column at 195°. The latter provided a somewhat cleaner separation of *dl*- and *meso*-2,3-diphenylbutane, eluting in the order named, but the higher operating temperature was a disadvantage. Isomer ratios were based on peak areas as determined by disk integration.

Reactions 1–4, as enumerated above, were conducted on a gram scale and under a nitrogen atmosphere but otherwise under reaction conditions as described in the literature. Upon termination of the reactions in homogeneous mixtures, as in reactions 1, 2, and 6, samples were injected directly into the chromatograph. In other cases, namely reactions 3, 4, 5, and 7, ether extracts were made and samples thereof were injected. Reaction 5 was conducted by introducing a few milligrams of liquid α -bromoethylbenzene into a side arm on an evacuated silvered flask which, after sealing, was stored in the dark at room temperature for 2 days. In the photolysis experiments, solutions of benzophenone (0.02 M) in ethylbenzene, contained in Pyrex tubes and purged with nitrogen gas, were suspended in an alcohol-filled, windowed dewar flask and exposed for 60 min to 3600-Å illumination from a General Electric H 100 BL lamp. Some photolysis experiments were performed, at room temperature, with benzene as solvent.

The chromous sulfate reagent was prepared for us¹⁰ as described in an earlier paper by Castro¹¹ and was diluted to the required 0.45 N immediately before use. The reduction of α -bromoethylbenzene, 1.4 g in 25 ml of dimethylformamide, was done, first at room temperature, by addition to 25 ml of the reagent, vigorously stirred in a nitrogen-purged system. There was an immediate color change to dark green and noticeable warming of the mixture. After about 10 min, the separated product became semicrystalline and no further change was apparent on continued stirring for 2 hr. Extraction with three 20-ml portions of ether, followed by backwashing of the combined ether extracts with water and evaporation of most of the ether (after removal of a sample for chromatographic analysis), furnished 0.26 g (36%) of crystalline *meso*-2,3-diphenylbutane and 0.50 g of mother liquor. In a similar experiment, in which the reactants were cooled to ice-bath temperature before mixing, the initial color change occurred in a period of about 1 min, semicrystalline product appeared very quickly, and no further change was seen on continued stirring for 5 hr. The ether extract upon concentration deposited 0.19 g of *meso* isomer and the mother liquor (0.54 g) assayed 34% *dl* and 3% *meso*.

Registry No.—*meso*-2,3-Diphenylbutane, 3755-79-1; *dl*-2,3-diphenylbutane, 4656-85-3.

(5) C. Moritz and R. Wolfenstein, *Chem. Ber.*, **32**, 432 (1899).

(6) K. Sisido and H. Plozaki, *J. Amer. Chem. Soc.*, **70**, 778 (1948).

(7) This particular application of silver to effect dimerization appears not to have been previously mentioned but the prototype is well known.

(8) E. Paternò and G. Chieffi, *Gazz. Chim. Ital.*, **39** [II], 415; *Chem. Abstr.*, **5**, 682 (1911).

(9) The subject of mechanism in chromium(II) reductions has been reviewed by J. R. Hanson and E. Premuzic, *Angew. Chem. Int. Ed. Engl.*, **7**, 247 (1969).

(10) We are indebted to J. C. Sullivan and D. L. Toppen for a supply of the reagent.

(11) C. E. Castro, *J. Amer. Chem. Soc.*, **83**, 3262 (1961).