

soned that the "steric interaction" argument might hold true for the diesters in producing a more stable meso form. The results of the equilibrium experiments with methyl and isopropyl esters of 2,3-dimethylsuccinic acid are given in Table I. The methyl esters of the meso and racemic diastereoisomers are present in almost equal amounts at equilibrium, whereas in the case of the isopropyl esters, the meso is definitely the more stable form. Presumably the steric interaction of the more bulky isopropyl groups outweighs any interaction of the polar portions of the molecule.

In the glc analysis of the diastereoisomer esters, the racemic methyl and isopropyl esters were found to have greater retention times than those of the corresponding meso ones (Table II). This was expected⁸ as was the

TABLE II
RELATIVE RETENTION TIMES OF THE DIASTEREISOISOMERS
OF 2,3-DIMETHYLSUCCINIC ACID AND ITS ESTERS^a

Diastereoisomers	Relative retention time, racemate/meso
Acids	0.76
Methyl esters	1.18
Isopropyl esters	1.05
Trimethylsilyl esters	1.00

^a All esters were chromatographed under the same conditions.

observation that the presumably hydrogen-bonded racemic acid had a retention time less than that of the meso form. The direction of the change in the relative retention time of the methyl (1.18), isopropyl (1.05), and trimethylsilyl (1.00) esters can be explained by the increased shielding of the polar groups in going to the more bulky ester groups.

The ratios of the two diastereoisomeric dimethyl esters present in partly esterified mixtures, shown in Table III, indicate that the racemic acid esterifies

TABLE III
RESULTS OF THE ESTERIFICATION EXPERIMENTS

% acid groups reacted (a)	% of the methyl ester diastereoisomers		$k_{\text{racemate}}/k_{\text{meso}}$
	Meso (m)	Racemate (r)	
32	30.2	69.8	1.30
74	30.9	69.1	1.33
90	34.7	65.3	1.23
(100)	37.2	62.8	

faster than the meso. Unimolecular rate constants for the two acid forms were compared as if the two acid groups esterify independently. From these calculations, discussed in the Experimental Section, a rate constant 30% greater for the racemic acid is indicated. An actual determination of the esterification rates k_1 and k_2 for each acid form would be necessary in order to interpret the esterification rate differences.

Experimental Section

Materials.—By means of melting point and gas-liquid chromatography, 2,3-dimethylsuccinic acid (K and K Laboratories, Plainview, N. Y.) was found to consist of 99.8% of the meso form. Mixtures of the meso and racemic acid forms from which esters were prepared were obtained by heating the meso form with 5 *N* hydrochloric acid. The trimethylsilyl esters were pre-

pared with the silylation reagent Tri-Sil (Pierce Chemical Co., Rockford, Ill.).

Gas-Liquid Chromatography.—For chromatography of the esters, a 20 ft \times $\frac{1}{8}$ in. column packed with 3% XE-60 on 80-100 mesh Chromosorb W was used. The column temperature was 200° and the helium flow was 30 ml/min. Even when chromatographed separately (a sample of the racemic acid was obtained from the equilibrium mixture of the acids by means of crystallization from concentrated hydrochloric acid), the retention times of the two trimethylsilyl esters showed no difference. The acid diastereoisomers were chromatographed on a column 6 ft \times $\frac{1}{8}$ in. packed with 20% diethylene glycol adipate and 3% phosphoric acid on 60-80 mesh Gas-Chrom P. Peak shapes for the acids were distorted so that this method would not be suitable for analytical purposes.

Equilibrium Experiments.—Samples of the meso acid, approximately 0.2 g in 10 ml of 5 *N* hydrochloric acid, were sealed in glass tubes and kept at 125°. Analysis of the samples by glc of the methyl esters showed that equilibrium had been reached within 100 hr. Methyl and isopropyl esters prepared from the meso acid, approximately 0.2-g samples in 10 ml of the corresponding alcohol containing 0.1 *N* sodium alcoholate, reached equilibrium within 50 hr. Analyses of the diastereoisomers are based on peak-area measurements. Results are given in Table II.

Relative Esterification Rates.—A sample of the meso acid heated to 125° in 5 *N* hydrochloric acid for 80 hr provided a mixture of 37.2% meso and 62.8% racemic acids. Samples of this acid mixture (0.2 g) were partly esterified by refluxing in 25 ml of methanol containing 0.1 g of concentrated sulfuric acid for approximately 12, 30, and 60 min. The per cent of carboxylic acid groups reacted was determined by titration and the ratio of the two diesters formed was analyzed by glc. Relative esterification rates of the two acids were calculated on the assumption that the acid groups react independently, by use of the equation

$$\frac{k_{\text{racemate}}}{k_{\text{meso}}} = \frac{\log [1 - (\text{fraction of racemate diester formed})^{1/2}]}{\log [1 - (\text{fraction of meso diester formed})^{1/2}]} \\ = \frac{\log [1 - (a/100)(r/62.8)^{1/2}]}{\log [1 - (a/100)(m/37.2)^{1/2}]}$$

where a is the per cent of the acid groups reacted, and m and r are the per cent areas of the chromatogram for the meso and racemate diesters. The results are shown in Table III.

Registry No.—*meso*-2,3-Dimethylsuccinic acid, 608-40-2; *rac*-2,3-dimethylsuccinic acid, 608-39-9; meso methyl ester, 29800-12-2; racemic methyl ester, 29913-52-8; meso isopropyl ester, 29800-13-3; racemic isopropyl ester, 29800-14-4; meso trimethylsilyl ester, 29800-15-5; racemic trimethylsilyl ester, 29800-16-6.

¹³C-H Coupling Constants as a Probe of Ortho-Substituent Effects

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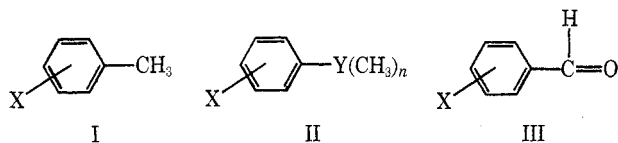
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Although attempts at semiquantitative correlations of structure with reactivity in substituted aromatics have been made, ortho substituents are usually not included in linear free energy relationships. It has generally been assumed that steric factors as well as electronic ones would be an important consideration in

(8) D. Nurok, G. L. Taylor, and A. M. Stephen, *J. Chem. Soc. B*, 291 (1968).

such systems. However, recent work has indicated that, in fact, steric factors should not have an effect in many of these ortho-substituted systems, but that no one universal set of σ_o constants could be derived.¹

Recently we have shown the existence of linear correlations between σ_m and σ_p and the magnitude of the ^{13}C -H coupling constants in compounds of types I, II, and III, where Y = C ($n = 3$), N ($n = 2$), and O ($n = 1$).²



Since ^{13}C -H coupling constants are independent of anisotropy effects and are generally believed to be a function of the effective nuclear charge of carbon and the s character in the C-H bond,³ this parameter should be an excellent probe into the electronic nature of the ground state of ortho-substituted aromatics. We have, therefore, measured the ^{13}C -H coupling constants of ortho-substituted toluenes, anisoles, and benzaldehydes. These three series were chosen because of the relatively large values of the J - σ slopes of the meta and para analogs and also because these systems contain C-H sites on electron-releasing (toluene and anisoles) and electron-withdrawing (benzaldehydes) groups.

Methyl ^{13}C -H coupling constants and ortho σ constants are presented in Table I. The ortho σ constants

TABLE I

 ^{13}C -H COUPLING CONSTANTS (± 0.2 Hz) AND σ_o CONSTANTS

X	CH ₃ ^a		OCH ₃ ^a		CHO ^b	
	<i>J</i>	σ	<i>J</i>	σ	<i>J</i>	σ
NO ₂	129.4	2.0	145.4	1.7	192.1	2.26
CHO	127.8	1.1	144.6	1.2	183.0	1.10
CO ₂ H	128.0	1.2				
CN	127.9	1.2				
F	127.9	1.2	144.1	0.8	182.5	1.04
Cl	127.9	1.2	144.1	0.8	182.8	1.08
Br	127.8	1.1	144.3	0.9	183.4	1.15
I	128.2	1.3	144.2	0.9		
OH	126.9	0.6			177.7	0.43
OCH ₃	126.9	0.6	143.3	0.2	180.3	0.76
H	125.8	-0.06	143.0	0.0	174.9	0.076
CH ₃	125.7	-0.12	143.0	0.0	173.8	-0.063
C ₂ H ₅	125.6	-0.17				
NH ₂	125.6	-0.17	143.3	0.2	171.8	-0.32
N(CH ₃) ₂	126.4	0.3				

^a 0.30 g or ml of solute per 1.0 ml of CCl₄. ^b 0.80 g or ml of solute per 1.0 ml of CHCl₃.

were obtained from the equation $J = \rho\sigma + C$, where J is the ortho coupling constant and ρ and C are the least-squares slope and intercept, respectively, for the J - σ plot of the appropriate meta- and para-substituted series. For the toluene series, $\rho = 1.72$ and $C = 125.9$;^{2a} for the anisole series the slope obtained by using σ^* values for the p -CHO, p -NO₂, and p -CN de-

derivatives was chosen, $\rho = 1.38$ and $C = 143.0$;^{2a} for the benzaldehyde series $\rho = 7.89$ and $C = 174.3$.^{2b,4} σ_o constants derived from the toluene and anisole series are believed to have uncertainties of ca. ± 0.1 - 0.2 ; those from the benzaldehyde, $\pm < 0.05$.

An examination of the data presented in Table I leads to several interesting observations.

(1) The σ_o constants for a particular substituent are roughly similar in all three series of compounds, but it is also obvious that σ_o for a given substituent in some cases is sensitive to the nature of the remainder of the molecule. Thus because of the relatively large uncertainties in the toluene and anisole ortho σ constants, σ_o for fluorine is the same for all three series within experimental error; on the other hand, the difference between σ_o for the nitro group obtained from the anisole derivative relative to the value obtained from the benzaldehyde derivative is outside experimental error.

(2) The σ_o constants are generally considerably greater in magnitude than the related σ_m and σ_p constants. This appears to be true primarily for electron-attracting substituents and is probably due to the greater inductive (field) effect in the ortho position.

(3) The quite positive σ_o values for the OH and OCH₃ groups indicate the predominance of the electron-withdrawing inductive effect over the electron-releasing resonance effect.

(4) The fact that the σ constants for the o -NH₂ group derived from the benzaldehydes and toluenes are negative argues for the predominance of the resonance effect over the inductive effect. The difference in electronic function between the OH(OCH₃) and NH₂ groups can be rationalized on the basis of oxygen's greater electronegativity. The positive σ_o constant derived from the anisole series can probably be attributed to intramolecular hydrogen bonding.

(5) The positive σ_o constant for the dimethylamino group can be ascribed to steric inhibition of resonance. Steric interaction of the ring methyl and N -methyl groups reduces electron release by resonance and thus produces a higher coupling constant and σ constant. This effect (in coupling constants) has been previously discussed.⁵

(6) The σ_o values for F and Cl are nearly identical in each of the three series. Since the σ_{p-F} (+0.062) is considerably smaller than σ_{p-Cl} (+0.277), the much greater inductive effect of F in the ortho position must be relatively more important than the +R resonance effect.

Experimental Section

Compounds studied were all commercial samples. Spectro-quality CCl₄ and CHCl₃ (C₂H₅OH removed with alumina) were used as solvents. Coupling constants were obtained on a Varian A-60D nmr spectrometer using standard side-banding techniques.

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(4) For the least-squares analysis of 13 compounds (CHCl₃), standard deviation of residuals was found to be 0.416, correlation coefficient 0.993.

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