were heated in a small modified Claisen–Vigreux flask under a slight (20 mm) vacuum while the IPA formed distilled off. The temperature was maintained for 5 min at 130° and the residue was then decomposed with 30% NaOH to yield about 3 g of reaction product consisting of 58% **2**, 39% **3**, and traces of unreacted **6**.

B.—3-*p*-Menthen-8-ol (**5**) (5 g) and 1 g of AIP were treated under the same conditions as described in A and afforded 3 g consisting of 60% **2** and 40% **3**.

Registry No.—**4**, R = Et, 24301-81-3; **4**, R = IP, 24301-82-4; **5**, 24302-23-6; **6**, 22472-80-6.

The Additivity of Mass Spectral Substituent Effects. Cleavage of Benzophenones

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It would be of interest to extend mass spectral steric-effect studies to simple cleavage reactions, but in known examples the observed electronic substituent effect is not great, and it can be expected that the effect of steric inhibition of resonance will not be great either. The theory of mass spectra suggests that multiple substitution may cause a great scattering of points about the correlation line against Hammett σ constants compared with the scatter for singly substituted compounds. This work shows that for doubly substituted benzophenones, the increase in scattering is not so large as to preclude observation of a moderate change in relative intensities owing to steric inhibition of resonance.

The formation of benzoyl ions in the mass spectra of singly substituted benzophenones can be correlated remarkably well with Hammett σ constants.[2] This general type of correlation, in which the relative intensities of benzoyl ion $[A^+]$ with respect to the intensities of the molecular ions $[M^+]$ are plotted against substituent constants as in eq 1, where $Z = [A^+]/[M^+]$, has been found for unsubstituted ions in the spectra of

$$\log (Z/Z_0) = \rho\sigma \qquad (1)$$

other aromatic compounds.[3] An interesting observation made recently is that *ortho*-substituent effects on ion intensities calculated in this fashion may be correlated[4] with *ortho*-substituent constants derived[5] from rates of gas-phase ester pyrolyses; the good correlation supports the validity of the interpretation of the pyrolysis data.

The relationship of eq 1 does not follow[6] from the quasiequilibrium theory of mass spectra,[7] and other explanations have been suggested. It is generally recognized that the equation of relative "rates" of mass spectral processes with intensity ratios is a simplification, and that other factors, notably appearance potentials of fragment ions[8] and the energy distribution of the molecular ions,[9] in principle govern the intensities of peaks in such a fashion that a Hammett plot may be extracted from them. These factors have been summarized.[10-12] Recently attempts have been made to work backward from the existence of correlations with σ constants in mass spectra, specifically correlations of ion intensities, ionization potentials, and appearance potentials of fragments, to derive the form which the energy distribution of molecular ions must have to meet the requirement of an exact fit of the ion intensity data to eq 1.[13] The restrictions imposed for mathematical tractability make this solution of mostly theoretical interest, but the calculation shows that reasonable distributions produced from consideration of the physical processes occurring in electron impact and the energy distribution in the original molecule[14] are fairly similar in form to this distribution, and allows the hope that further refinement of the model employed will give a better understanding of the importance of the energy distribution.

One would anticipate, on the basis of the good correlation of *meta*- and *para*-substituent constants with relative intensities in benzophenone spectra[2] and on the basis that the correlation can be extended remarkably well to *ortho* substituents,[4] that a good correlation could be routinely expected. The present considerations of substituent effects on ion intensities, irrespective of their author, would all predict this in the first approximation, for substituent effects would be expected to be cumulative on electron density, affecting ionization potentials and bond energies in closely similar patterns. It is more important to consider why substituent effects may *not* be cumulative in ion intensity data. The major reason would be the fact that the introduction of more substituents into the aromatic ring affords more routes for decomposition, which will then compete more effectively with formation of the ion of interest, benzoyl. Fewer ions will then decompose by the desired route, and the degree of correlation will be reduced. Further, the introduction of additional complex substituents could alter the effective number of degrees of freedom in the molecular ion to the extent that ion intensities will be noticeably affected. In practice, this alteration has been observed for metastable

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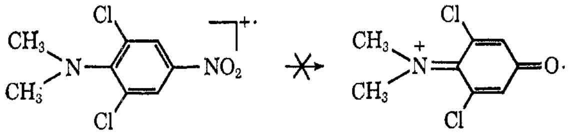
decompositions of the benzoyl ion to $C_6H_5^+$,[15] but it is not significant for the normal benzoyl ions.

Recently, attempts to define effects due to steric inhibition of resonance in mass spectral decompositions have been made.[16–18] In the first examples studied, the stability of the product ion very obviously depended on the ability of an electron donor in the *para* position to interact with the reaction site (eq 2).[16,17] When the group in the *para* position is large, substituents *ortho* to it seem to have the expected effect: there is a very great reduction, by a factor of more than



(2)

20, in the relative intensity of the daughter ion when the group is dimethylamino, which is so large that it is twisted in the ground state, and presumably then cannot interact with the oxygen atom to form a quinonoid structure in the daughter ion.

It is empirically found that the stability of the product ion is a very important "driving force" in governing the intensities of mass spectral peaks.[19–20] It is of interest, therefore, to look at cases where stability of the product ion is not so greatly influenced by the substituent, in order to determine the magnitude of steric effects in cases where the resonance demand is weak; one would expect that, for example, the removal of direct resonance interaction of the substituent and reaction site might reduce the substituent effect to something approaching the field- or induction-effect-dominated *meta*-substituent characteristics, but, before this experiment can be done, it is necessary to establish whether, superimposed upon this presumed steric effect, there will also be a scattering introduced by the increased number of substituents discussed earlier, and, if there is an increase in scattering, whether it will be so great as to imperil the extraction of information about interactions of multiple substituents.

We chose to examine the characteristics of intensity pattterns for the best correlated reaction for single substituents in mass spectra, eq 3, in a very similar

$$YC_6H_4COC_6H_5\cdot^+ \longrightarrow C_6H_5CO^+ \qquad (3)$$

$$Y_2C_6H_3COC_6H_5\cdot^+ \longrightarrow C_6H_5CO^+ \qquad (4)$$

study for doubly substituted compounds, eq 4. Since the data are highly correlated with σ (or σ^+) values for a single substituent, it seemed acceptable to assume that the correlation of the sum of their σ values (or σ^+ values) with ion intensities would be a measure of the additivity of substituent effects. It is, of course, necessary that one use only substituents which are incapable of exerting an effect other than electrical on neighboring substituents if one wishes to use 3,4-disubstituted compounds. We therefore chose substituents that are cylindrically symmetrical or nearly so to avoid steric effects, or else, as in the case of the nitro group, substituents whose effect is primarily not a resonance effect, as comparison[21] of the *meta* and *para* σ constants seems to suggest.

The point of our experiment, then, was to set up a model to test the additivity of substituent effects on ion intensities in mass spectra. This would determine whether the anticipated scattering of data for the formation of benzoyl ion by competing reactions would be so great that it would prevent the extension of model reactions for the study of steric inhibition of resonance to systems in which the resonance demand of the product ion is low.

Experimental Section

Preparation of Benzophenones.—The compounds were either commercially available or synthesized according to standard procedures in the literature which were checked where advisable to avoid ambiguity in the orientation of products formed by Friedel–Crafts reactions. The compounds were homogeneous by thin layer chromatography and had melting points in agreement with the values reported in the literature.

Mass Spectra.—All the mass spectra were recorded on a Hitachi RMU-6E single-focusing instrument, using 75-eV electrons (emission current 80 μA). The source pressure was always in the range of $5–10 \times 10^{-7}$ Torr; the source temperature was maintained at 185 ± 5°. Samples were introduced through the liquid–solid sample introduction port into a reservoir held at 185 ± 5°. The reproducibility of peak heights was at least 3% for four replicate determinations, and in many cases was less than 1%. Ratios of fragment ion intensities to molecular ion intensities were reproducible from day to day to within 4–5%.

Results and Discussion

Our data are presented in Table I, in the form of simple intensity ratios. When these data are plotted against the sum of the σ constants for each substituent, the correlation illustrated in Figure 1 is obtained. The slope of the correlation line is 0.77; the correlation coefficient is 0.918. When the data are plotted against the sum of the σ^+ constants for each substituent, the correlation shown in Figure 2 is found. Here the slope of the correlation line is 0.55 and the correlation coefficient is 0.956.[22]

TABLE I

RELATIVE INTENSITIES OF *m/e* 105 IN THE MASS SPECTRA OF DOUBLY SUBSTITUTED BENZOPHENONES ($Z = [105^+]/[M\cdot^+]$)[a]

Substituents	Z	Substituents	Z
3-CH_3O, 4-CH_3O	−0.48	3-Br, 4-OH	+0.05
3-Br, 4-NH_2	−0.47	H	+0.08
3-CH_3, 4-CH_3O	−0.42	3-Cl, 4-Cl	+0.41
3-CH_3, 4-OH	−0.28	3-Br, 4-Br	+0.42
3-Cl, 4-CH_3O	−0.14	3-Cl, 5-Cl	+0.52
3-Br, 4-CH_3O	−0.10	3-NO_2, 4-Cl	+0.54
3-CH_3, 4-CH_3	0.00	3-Br, 5-Br	+0.63
3-Cl, 4-OH	+0.01		

[a] The ratio found for benzophenone was divided by a statistical factor of 2.

For singly substituted benzophenones, the slope against σ is 1.01 and the correlation coefficient is 0.976; against σ^+, the slope is 0.66 and the correlation coeffi-

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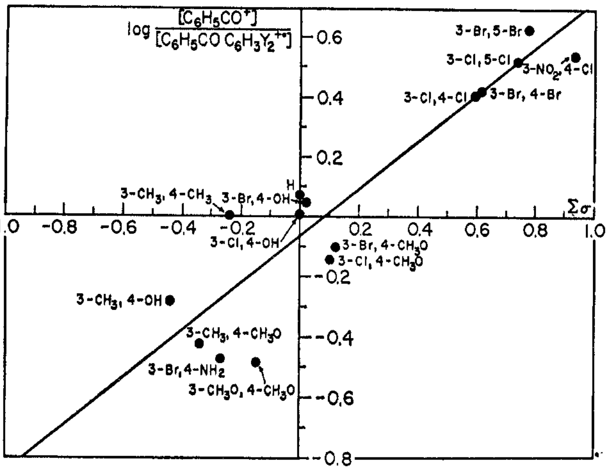


Figure 1.—Correlation of intensity ratios in doubly substituted benzophenones with sums of individual σ values of substituents.[22]

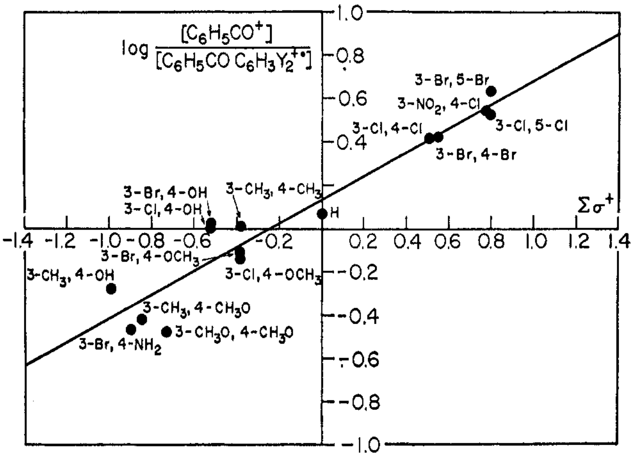


Figure 2.—Correlation of intensity ratios in doubly substituted benzophenones with sums of individual σ^+ values of substituents.[22]

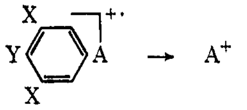
cient is 0.963.[2] These values were determined for more substituents than are represented in Table I, including several whose intensity ratios deviate markedly from the correlation line for explicable reasons. If we consider the correlation of only those single substituents that were actually used in the double-substituent study, their correlation with σ is better: $r = 0.990$. The correlation of data for this limited number of substituents with σ^+ is also improved: $r = 0.982$.

In terms of standard deviations of data points from the correlation line, the standard deviation of the new data from the line against σ is 0.15 log unit, compared with 0.09 for the old data (0.06 for those members of the old data actually used). The standard deviation of the new data from the line against σ^+ is 0.06 log unit, compared with 0.11 for the old data (0.07 for those members of the old data actually used).

As measured by the correlation coefficient, then, the doubly substituted benzophenones do show a decreased correlation with both σ and σ^+ constants, when compared with the data for the singly substituted benzophenones. The correlation against σ^+ is superior for the doubly substituted benzophenones, a distinction that was not noted for the singly substituted benzophenones first studied[2] but noted later when the reaction was examined for the *ortho*-substituted compounds.[4] As measured by the standard deviation of the data points from the correlation line, the correlation with σ^+ is still the better one for the doubly substituted compounds. There is, in fact, a slight decrease in the standard deviation from that of the data points of the single substituents used, but it may not be meaningful.

The data therefore indicate that, first of all, a recognizable correlation still exists for data from doubly substituted benzophenones. The slope of the line is somewhat different from that for the monosubstituted benzophenones, but this could be explained in light of the scattering of the data. The second obvious point is that for the correlation against σ, the scattering is markedly increased, as both the decreased correlation coefficient and simple inspection suggest. The loss in correlation is not so great, however, that much information would be lost about *expected* deviations from the line in other systems because of substituent–substituent interactions, provided that the *expected* deviations from additivity were large enough. For the correlation against σ^+, the loss in correlation is in fact insignificant.

It should be possible, as a result, to uncover deviations from additivity as a result of steric inhibition of resonance or other substituent–substituent interactions. The scattering due to the multiple substitution of systems suggested by eq 5 will increase the probable deviation of the intensity ratio, in the benzophenones by a predictable amount, and we can therefore state how large the steric effect on intensity ratios must be in order to assign the deviation from additivity with confidence to the predicted effect, not to the scattering because of multiple pathways.



(5)

For the benzophenones, the standard deviation of relative intensity values from the expected values (the correlation line) is 0.06 for the σ^+ correlation. Twice the standard deviation sets the 95% confidence level; that is, outside of this range there is only a 5% chance that any observed effect is due entirely to scattering. Provided that we can find examples where the expected change in substituent effect is greater than 0.12 log unit as a result of steric inhibition of resonance, we can assign deviations from additivity in the proper direction to this cause with a high level of confidence that this is indeed the source of the deviation. If one chooses the worse correlation, that with σ values, then the substituent effect must be greater than 0.30 log unit to ascribe the same level of confidence to the interpretation.

The deviation seems sufficiently small that we have anticipation of finding large enough expected changes in substituent behavior for eq 5 as a result of steric inhibition of resonance in such reactions. We plan to report our results of this new study later.

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