# Charge Localization in the Mass Spectra of Substituted Phenylbutyrophenones

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A study of the McLafferty rearrangement of substituted phenylbutyrophenones relative to butyrophenones and 1-(4-butyrophenyl)-2-ethanes shows a peculiar non-linear relationship with the type of substituent and the distance of the substituent from the reaction site.

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#### Introduction

The role of electron-donating and -withdrawing substituents in localizing charge in unimolecular ion reactions observed in mass spectra has been investigated in substituted butyrophenones (1), valerophenones (2), nitro- and butyryldiphenyl ethers (3), and methyl butyrates (4). Among the conclusions reached for the McLafferty rearrangements of substituted butyrophenones are that the reaction is (i) enhanced by an increased positive charge at the reaction site (the ratio  $[M-C_2H_4]/[M]$  is greater for an electron-withdrawing substituent than for an electron-donating substituent) (1a), and (ii) much slower when the substituent has been removed and "isolated" from the reaction site (1b, 2). The influence of a remote but conjugated substituent in the McLafferty rearrangement has been discussed only briefly in connection with the fragmentation of nitrodiphenylethers (3). In this note we discuss new information on remote substituent effects.

### Experimental

All mass spectra were determined on an AEI MS-9 mass spectrometer at varied ionizing voltages using a 100  $\mu$ A electron beam. The i.r. spectra were taken on a Perkin–Elmer Model 137 spectrophotometer and n.m.r. spectra were determined on a Varian Model A-60 instrument. All melting points (capillary) are uncorrected. Satisfactory micro analyses were performed on all compounds in this work.

In a typical experiment, the substituted (except amino and hydroxy) phenylbutyrophenones were obtained by acylation of the substituted biphenyl with butanoyl chloride and a molar excess of anhydrous aluminum chloride in gently refluxing carbon disulfide. The aminophenylbutyrophenones were prepared by stannous chloride reduction (5) of corresponding nitro compounds, and the hydroxy isomer via diazotization of the corresponding amino isomer. Most substituted butyrophenones may be obtained as indicated (6) or synthesized by modification (R. Nicoletti, this laboratory) of established procedures (7, 8).

### **Results and Discussion**

In our work we have investigated the behavior of substituted phenylbutyrophenones (1 and 2) and have noted several new effects (see Table 1) which were not observed for the [M-28] fragmentation of substituted butyrophenones (3)(1a)or 1-(4-butyrophenyl)-2-phenylethanes (4) (1b).(1) Whereas electron-donating substituents have a very similar influence on the [M-28] rearrangement in 1, 2, and 3, electron-withdrawing substituents do not, and (2) the influence of an electron-withdrawing substituent in enhancing the [M-28] fragmentation is an order of magnitude greater in 3 than in 1 and 2 but is smaller (by a factor of 2) in  $1 (Y = NO_2)$  compared to 4 (Y = NO<sub>2</sub>),<sup>2</sup> wherein the substituent is not only remote from but incapable of conjugation with the reaction site. The behavior mentioned under (2) may be contrasted with that of electrondonating substituents in 1, 2, and 3 in which the closeness of the [M-28] values suggests that fragmentation behavior here is relatively insensitive to the substituent's distance from the reaction center. Considering the very large difference shown by 1, 2, and 3 for electronwithdrawing groups, the behavior noted for

 $^{2}$ At 75 eV, [M-28] in 4 (Y = NO<sub>2</sub>) is 94 for M = 100 %. See ref. 1b.

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NOTES

	[M-28], 20	Taninatian natantial			
Y (M = 100.0)	Phenylbutyrophenones	Butyrophenones	of $C_6H_5Y$ ,‡ (eV)		
н	20.0	27.2	9.24§		
$m-NH_2$ $p-NH_2$	8.0 10.4	5.5 19.5	7.70		
p-OCH <sub>3</sub>	12.8	27.6	8.22		
p-OH	13.8	31.0	8.50		
$p-CH_3$	18.5	25.6	8.82		
<i>p</i> -Br	27.5	228	8.98		
p-Cl	28.9	204	9.07		
p-F	29.0	173	9.20		
p-CN	44.2		9.71		
$p-NO_2$ $m-NO_2$	42.0	945 733	9.92		

TABLE 1. Substituent effects\* on the abundance of M-C<sub>2</sub>H<sub>4</sub> ions from p-(Y-C<sub>6</sub>H<sub>4</sub>)-C<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+.

\*The effect of these substituents on further fragmentations of the [M-28] ion is negligible. †The values are essentially the same as those determined at 70 eV, and they closely parallel the percent ionization values. 1See ref. 9.



electron-donating groups is rather surprising. Also, judging from the usual behavior of an electron-donating substituent far removed from the reaction site, e.g.,  $4 (Y = NH_2)^3$  the [M-28] intensities of 1 and 2 are expected to be considerably smaller than those of 3.

The peculiar non-linear effects in 1, 2, 3, and 4 noted by varying distance from the reaction site and changing from electron-withdrawing to electron-donating substituents suggest that the qualitative arguments of charge localization (1-4)do not sufficiently explain certain types of fragmentation behavior. Conjugation of the substituent Y of 1 with the carbonyl group (presumed transfer site) by resonance appears to have no special influence on the [M-28] intensities which are very similar for the meta- and para-nitro or amino isomers.<sup>4</sup> Thus, canonical resonance

<sup>3</sup>At 75 eV, [M-28] in 4 (Y = NH<sub>2</sub>) is < 1 for M = 100%. See ref. 1b. <sup>4</sup>This behavior holds for the nitrobutyrophenones 3 (Y = NO<sub>2</sub>) as well and suggests that biphenyl twisting is not responsible for the observed effects is not responsible for the observed effects.

structures such as 5 and 7 apparently contribute no more to the total picture than either 6 or 8, although the rationalization (1) for the butyrophenone (3) behavior was interpreted using the concept of radical site and positive charge localization on the carbonyl oxygen.

Probably a more satisfying explanation of the data of Table 1 is lodged in the quasi-equilibrium treatment (4) and a knowledge of how given substituents perturb the energy profile for excited states leading to product. Even though a clear linear parallel is observed between the effect of a substituent on the [M-28] fragmentation of phenylbutyrophenones and the ionization poten-



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tial of the corresponding substituted benzene (9), no satisfactory explanation for the reported data is available.

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# X-Ray and Infrared Studies of Lead Apatites

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The cell constants and infrared spectra of lead apatites have been investigated. The lowering of the molecular symmetry  $T_d$  of the phosphate ion, and the nature and extent of changes in vibration frequencies of lead apatites with the ionic substitution of PO<sub>4</sub><sup>3-</sup> by AsO<sub>4</sub><sup>3-</sup> and VO<sub>4</sub><sup>3-</sup> are discussed.

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We are investigating the infrared spectra of apatites in the light of detailed knowledge of atomic positions provided by X-ray studies. A previous study (1) was on the investigation of synthetic apatites and the present work is a report on the study of mineralogical apatites. The mineral specimens of this investigation were obtained from the United States National Museum. A description of them has been reported (2). The unit cell dimensions of these samples calculated from the X-ray powder diffraction patterns are given in Table 1. There seems to be no variation of X-ray data for phosphatianmimetite of this work with the replacement of

TABLE 1.	Unit cell	dimensions	of	lead	apatites

Apatite	a-Axis (Å)	c-Axis (Å)	c/a
$\frac{Pb_{10}(PO_4)_6Cl_2}{Pb_{10}(AsO_4)_6Cl_2}$	9.98	7.33	0.734
$Pb_{10}[(As,P)O_4]_6Cl_2$	10.25	7.45	0.726
$Pb_{10}[(As,P)O_4]_6Cl_2$	10.25	7.45	0.726
$Pb_{10}(VO_4)_6Cl_2$	10.33	7.34	0.710

arsenic by phosphorus. In fact, the unit cell dimensions should have different values with the changing composition. Our observation is confirmed by the interesting work of Adler (3) who could not determine in his X-ray spectrogram the presence of phosphate in his phosphatianmimetite sample.

Although pyromorphite, mimetite, and vanadinite are isomorphous, their infrared spectra

<sup>&</sup>lt;sup>1</sup>This work was carried out at Fisk University, Nashville, Tennessee, U.S.A., and Faculté des Sciences de Toulouse, Toulouse, France.