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APPLICATION OF THE INDO MOLECULAR ORBITAL METHOD TO *ortho* EFFECTS IN MASS SPECTRA. CLEAVAGE OF *cis*-β-METHOXYSTYRENE

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Abstract—The principal fragmentation of the *cis*-β-methoxystyrene molecular ion is loss of the methyl group. Although this compound has a π system similar to that of phenyl acetate, the substituent effect of a strongly electronegative *ortho* substituent is insignificant for this fragmentation; but for the same substitution in phenyl acetate, it had been shown to be important. The INDO method was used to show that bond orders confirm the lack of the substituent effect in the *cis*-β-methoxystyrene system.

THERE has been increasing interest in the application of molecular orbital theory to the fragmentation of molecular ions. A recent study of the Iterative Extended Hückel Theory[1] summarizes earlier uses of Perturbation Molecular Orbital Theory[2] and a limited Hückel LCAO model,[3] and points to earlier work on simpler molecules as well. There has also been considerable investigation of the structures of simple even-electron ions, but these results were not interpreted in terms immediately applicable to interpretation of fragmentation patterns in mass spectra.

Recently we have been interested in the application of semi-empirical molecular orbital methods to the interpretation of various problems in mass spectrometry.[4] One problem which serves as a background for the present one is the peculiar *ortho* effect on the loss of ketene from *o*-fluorophenyl acetate and related compounds.[5,6] The *ortho*-fluoro compound has a much tighter activated complex than the *para* isomer. Application of the INDO molecular orbital method to this problem took the form of examining interactions in the energy-minimized ground state configuration of each ion; according to the results, the *ortho*-fluoro substituent holds the carbonyl group in a planar position, with a bond order calculated to be 0·40 between carbonyl oxygen and fluorine.[7]

We have begun a program of examining related molecules. In this first example, we examine the correlation of the bond order of the weakest bond in substituted *cis*-β-methoxystyrenes. These molecules are chosen to permit the same interactions as those found between oxygen and fluorine in the corresponding substituted phenyl acetates. On the other hand, the cleavage studied is the simple loss of the methyl group, which ought not to depend on this sort of interaction.

The synthesis of the key compounds is outlined by the sequence of reactions in Scheme 1. The parent compound, *cis*-β-methoxystyrene (I), was prepared by the addition of methanol to phenylacetylene by a reported procedure.[8] On treatment of *o*-fluoroacetophenone (IIa) with phosphorus pentachloride, a mixture of the corresponding α,α′-dichloroethylbenzene (IIIa) and α-chlorostyrene (IVa) was obtained.

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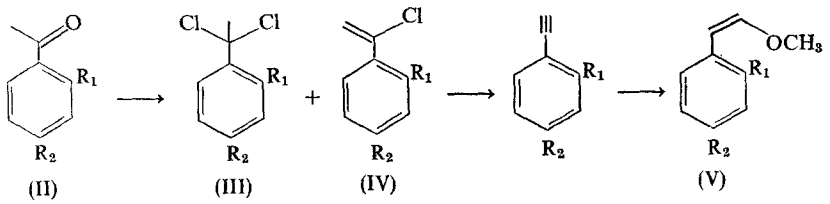

a: $R_1 = F, R_2 = H$
b: $R_1 = H, R_2 = F$

SCHEME 1

Without further purification the chloro derivatives were treated with sodium methoxide in methanol to give compound Va. Compound Vb was prepared similarly. The structure assignments for I, Va and Vb were made on the basis of their n.m.r. spectra: in all cases, the olefinic protons exhibited an AB pattern with J_{AB} in the range 6·9 to 8·3 Hz, indicating *cis* geometry. The electron-impact spectra are consistent with structures vinylogous to anisole: $[M]^+$ for I loses CH_3, then CO, to give peaks at *m/e* 119 (22%) and *m/e* 91 (100%) at 70 eV. Compounds Va and Vb behaved similarly. Other peaks were observed for the loss of CO and HCO directly from $[M]^{+\cdot}$ for I and Va; these peaks were insignificant in the spectrum of Vb. Ionization and appearance potential data were collected by our usual method[9] and are shown in Table 1; the precision of the data was ±0·03 eV, as usual.

TABLE 1. IONIZATION AND APPEARANCE POTENTIALS IN *cis*-β-METHOXYSTYRENES

Onset V	(I)	(Va)	(Vb)
IP	7·5	7·9	7·7
AP, $[M - 15]^+$	10·6	10·7	10·5
AP, $[M - 28]^{+\cdot}$	9·2	9·6	—
AP, $[M - 29]^+$	9·9	10·4	—
AP, $[M - 43]^+$	11·9	11·9	11·9

There is virtually no substituent effect upon the activation energy for the loss of CH_3, 2·8 eV in each of the fluoro compounds vs 3·1 eV in the parent compound; also, the *ortho* compound does not differ from the *para* in this respect. There are some differences in the other decompositions, but we must note that the structure(s) of the ion giving rise to these decompositions is (are) speculative in the extreme, and therefore we do not discuss them.

For our study of this problem, we used the INDO/2 molecular orbital program available from the Quantum Chemistry Program Exchange, modified for our purposes. The bond lengths and initial bond angles used are given in Fig. 1. Bond lengths were left unchanged throughout the energy minimization, since the INDO method does not yield accurate bond lengths.* Four of the bond angles were varied in pairs in

* Professor J. A. Pople has informed us privately that useful results are obtainable with crystallographic bond lengths.

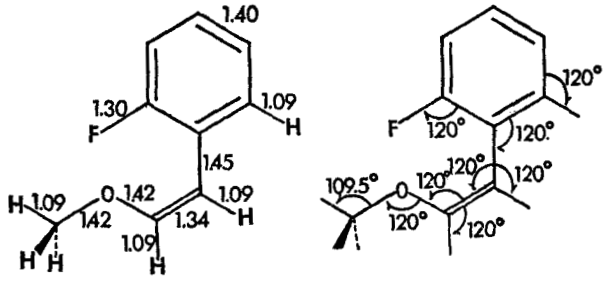

FIG. 1. Bond lengths and initial bond angles for *cis*-β-methoxystyrenes, illustrated for the *o*-fluoro compound.

5° increments. These angles were: the ring-side chain angle; the ring C—C=C, the C=C—O angle and the =C—O—C angle. Since major distortion of the aromatic ring and the methyl group are most unlikely, and since we have never found such distortions in other systems, we consider that minimization of the energy by adjustment of these parameters effectively corresponds to a minimization of all pertinent parameters. The final energy-minimized values for these angles are given in Fig. 2.

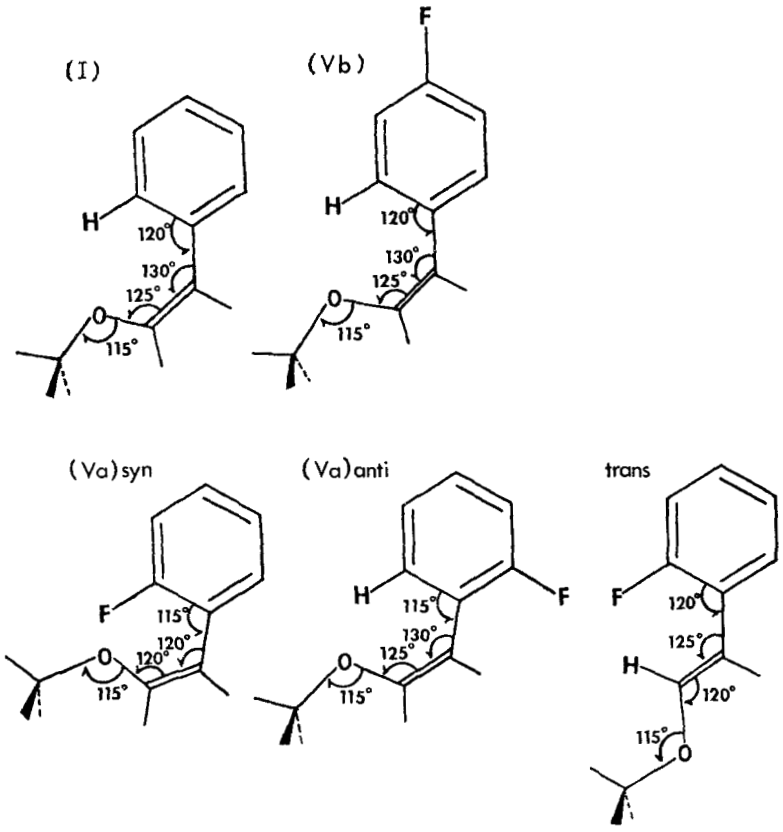

FIG. 2. Final bond angles for *cis*-β-methoxystyrenes.

The initial and final energies are given in Table 2. The conformation of Va in which fluorine and oxygen are adjacent is seen to be more stable than that in which the side chain is rotated 180° (here called *anti*). Additionally, the *cis* isomer is more stable than the *trans*. Both the bond angles and the bond orders quoted in Table 2 suggest a tightening of the 6-membered ring formed by the side chain and the *ortho* substituent when the substituent is fluorine. This is analogous to our findings for the phenyl acetates.[7]

TABLE 2. INITIAL AND FINAL ENERGIES OF β-METHOXYSTYRENES AND BOND ORDERS BETWEEN FORMALLY NONBONDED ATOMS

Molecular ion	E_{init}	E_{final}	Weak bond	Bond order
cis-β-methoxystyrene (I)	−86·39708	−86·41090	*o*-H—O	0·0035
o-F (O and F *syn*) (Va)	−112·16786	−112·20689	*o*-F—O	0·2454
o-F (O and F *anti*) (Va)	−112·07286	−112·08535	*o*-H—O	0·0017
p-F (Vb)	−112·07362	−112·08506	*o*-H—O	0·0038
trans-*o*-F-β-MeOstyrene	−112·08417	−112·08696	*o*-F—H	0·0082

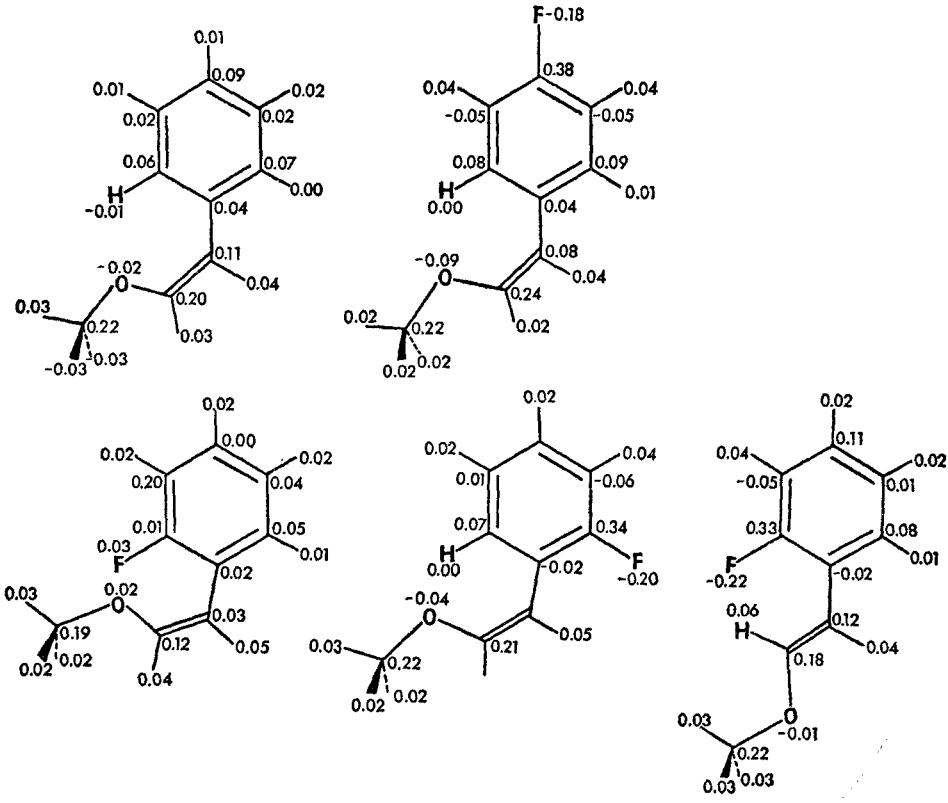

FIG. 3. Charge densities in energy-minimized *cis*-β-methoxystyrenes.

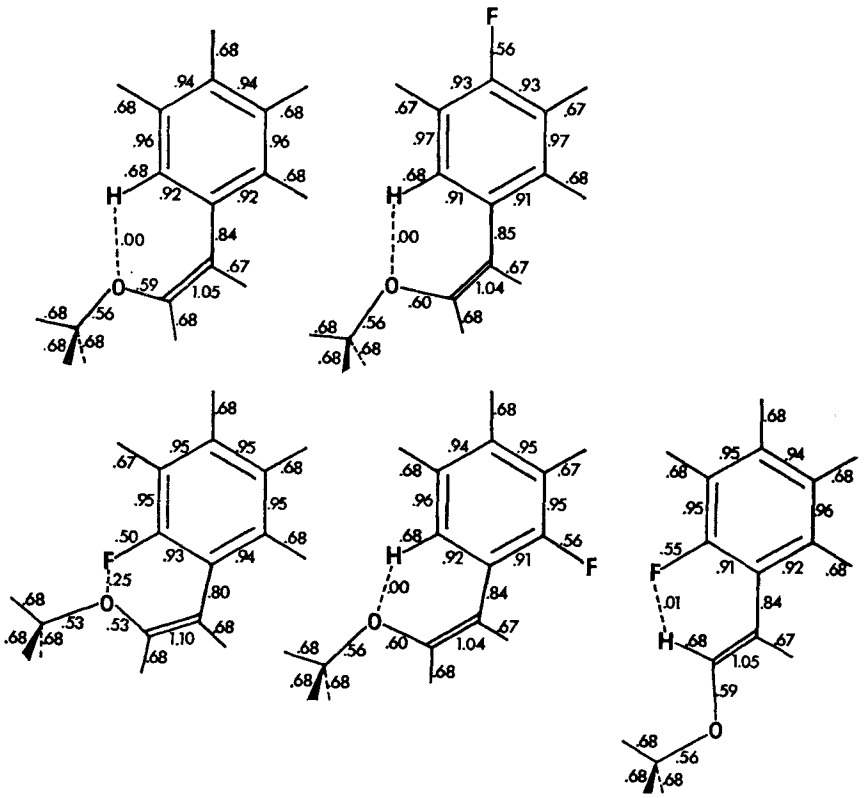

FIG. 4. Bond orders in energy-minimized *cis*-β-methoxystyrenes.

A peculiar interaction for the *ortho*-fluoro substituent may also be observed in the charge density distributions (Fig. 3). This too is analogous to our findings with the phenyl acetates.[7] Fluorine in the *para* position pulls electrons off the carbon to which it is attached, leaving the rest of the molecular ion essentially unchanged. Fluorine in the *ortho* position shows a much different pattern in which the charge is distributed, so that there is no buildup of negative charge on fluorine nor positive charge on the carbon to which it is attached.

The crux of the difference between the systems, however, is the fact that in the *cis*-β-methoxystyrenes we are dealing with a simple cleavage which obviously is not associated with any 6-membered ring; in the phenyl acetates, we are dealing with a rearrangement whose progress demands first loosening and then rupture of this ring. Thus, a correlation of fragmentation with bond order of the affected bond can be expected in the former compounds. This is neatly found in Fig. 4.

The weakest bond in the molecular ion in each case is either the C—F bond or the CH_3—O bond. Rupture of aromatic carbon–fluorine bonds is not a common process and on this point the correlation does not give useful results; but, of course, the calculations do suggest that otherwise the lowest-energy cleavage should be the loss of methyl, which is what we observe. Even more importantly, the results also indicate that there should be only a negligible substituent effect of fluorine in either the *ortho*

or the *para* position on the activation energy for loss of methyl, and this too is what we observe (Table 1). This is important in light of the recurrence of the peculiar *ortho*-fluorine interaction with the side chain: in spite of the fixing of the conformation, no unusual strengthening of the exocyclic bonds is found, either in the experiment or in the calculation. Finally, we note that the reactivity of this set of compounds is correctly predicted by the *ground-state* calculations. Thus, some of the statistical methods which make this assumption can now be applied to the problem.

We have completed an initial RRK calculation, which indeed also supports our finding of a lack of substituent effect for this simple cleavage. Because of the supposed oversimplification of this method, we plan to complete a set of RRKM calculations as well, which we will describe at a later date.

CONCLUSIONS

(1) The unusual 6-membered ring found in *o*-halophenyl acetates is found also in *o*-fluoro-*cis*-β-methoxystyrene, but it does not influence the loss of methyl. (2) Molecular orbital calculations point to the correct cleavage as the lowest energy simple cleavage, except that carbon–fluorine bond orders seem too low. (3) The calculations suggest that the reaction may occur from the ground state of the ion, so that it is a good candidate for study by statistical methods.

EXPERIMENTAL

The mass spectra were recorded on an Hitachi RMU-6E single focusing mass spectrometer using 80 μa emission current at 75 eV and 2·5 V repeller voltage. Low voltage data were collected as before.[5] Ionization and appearance potentials were obtained by a technique outlined previously,[9] using Kr, C_6H_6 and $(C_2H_5)_3N$ as internal standards. No special claim is made for the absolute values of the numbers, but internally the method gives remarkable consistent sets of data.[9] This last point is the crux of the applicability of the technique to substituent effect problems.

Boiling points and pressures are uncorrected. I.r. spectra were obtained on a Perkin–Elmer 257 instrument; n.m.r. spectra, on a JEOL C-60HL instrument and reported as δ values (ppm downfield from tetramethylsilane).

cis-*β-Methoxystyrene*. Using the procedure of Moureu,[8] from 5·0 g (49 mmol) phenylacetylene, 5·0 g (0·22 g-atom) Na and 40 ml anhydrous MeOH, there was obtained 1·7 g (26%) colorless oil, b.p. 80 to 85 °C/40 mm (lit. 210 to 213 °C); i.r. (CCl_4) 3090, 3060, 3040, 3000, 2960, 2910 (aromatic and olefinic C—H), 2870, 2830 (sym stretching OCH_3), 1650 (C=C), 1275 (asym stretching C—O—C) and 1105 cm^{-1} (sym stretching C—O—C); n.m.r. (CCl_4): 3·6δ (s, 3H, OCH_3), 5·5δ (center of AB, 2H, J = 6·9 Hz, *cis*-CH=CH), and 7·0 to 7·6δ (m, 5H, C_6H_5).

o-*Fluoroacetophenone*. To a cooled solution of 22·5 g (0.16 mol) *o*-fluorophenylmethylcarbinol[10] in 250 ml acetone, 36 ml 8N CrO_3 stock solution[11] was added; the mixture was stirred at room temperature 30 min. Excess CrO_3 was decomposed by adding 50 ml MeOH. After removal of solvent on the rotary evaporator, the Cr salts were dissolved in water. Extraction, drying (Na_2SO_4), concentration and distillation gave 19·8 g (89%) colorless oil, b.p. 73 to 75 °C/12 mm.

cis-*β-Methoxy-o-fluorostyrene*. To 19·5 g (94 mmol) PCl_5 was added dropwise 12·0 g (87 mmol) *o*-fluoroacetophenone. The mixture was heated in an oil bath (70 °C) 10 min and then distilled under reduced pressure. After removal of $POCl_3$ a mixture (13·2 g) of α,α'-dichloro-*o*-fluorobenzene and α-chloro-*o*-fluorostyrene was obtained. This mixture was used immediately without further purification. To a solution of 16·5 g (0·72 g-atom) Na in 150 ml anhydrous MeOH was added 13·2 g of chloro derivatives, and the mixture was heated 20 h. Precipitated NaCl was dissolved by adding 200 ml water. Extraction, washing, drying, concentration, and distillation gave 7·5 g colorless oil, b.p. 87 to 91 °C/10 mm. G.l.c. analysis (6 ft × $\frac{1}{4}$ in 10% Carbowax 20M, 125 °C, 40 ml/min) indicated 80% desired product (retention time 8·4 min) and several unidentified products. Analytical and spectral samples were collected by g.l.c.; i.r. (CCl_4): 3060, 3040, 3000, 2960, 2940 (aromatic and olefinic C—H), 2875, 2840 (sym stretching OCH_3), 1660 (C=C), 1280 (asym stretching

C—O—C) and 1090 cm^{-1} (sym stretching C—O—C); n.m.r. (CCl_4): 3·75δ (s, 3H, OCH_3), 5·8δ (center of AB, 2H, J = 8·3 Hz, *cis*-CH=CH) and 6·7 to 7·4δ (m, 4H, aromatic H). (Found: C, 70·86; H, 5·76. C_9H_9OF requires C, 71·04; H, 5·96).

cis-*β-Methoxy*-p-*fluorostyrene*. The procedure described above was followed. From 22·9 g (0·10 mol) *p*-fluoroacetophenone (Aldrich), 6·4 g colorless oil, b.p. 88 to 90 °C/11 mm, was obtained. G.l.c. analysis (80 in × ½ in, 20% Carbowax 20 M, 150 °C, 400 ml/min) indicated the oil to contain 67% desired product (13 min) and 33% unidentified product (11 min). The analytical and spectral samples were collected by g.l.c.; i.r. (CCl_4): 2875, 2815 (sym stretching OCH_3), 1660 (C=C), 1270 (asym stretching C—O—C), and 1100 cm^{-1} (sym stretching C—O—C); n.m.r. (CCl_4): 3·76δ (s, 3H, OCH_3), 5·6δ (center of AB, 2H, J = 7·3 Hz, *cis*-CH=CH) and 6·8 to 7·75δ (m, 4H, aromatic H).

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REFERENCES

1. G. Loew, M. Chadwick and D. Smith, *Org. Mass Spectrom.* **7,** 1241 (1973).
2. R. C. Dougherty, *J. Amer. Chem. Soc.* **90,** 5780 (1968).
3. F. P. Boer, T. W. Shannon and F. W. McLafferty, *J. Amer. Chem. Soc.* **90,** 7239 (1968).
4. C. E. Parker, M. M. Bursey and L. G. Pedersen, *Org. Mass Spectrom.* **9,** 204 (1974) and references contained therein.
5. S. A. Benezra and M. M. Bursey, *J. Chem. Soc.* (*B*) 1515 (1971).
6. S. A. Benezra and M. M. Bursey, *Z. Naturforsch.* **27A,** 670 (1972).
7. C. E. Parker, J. R. Hass, L. G. Pedersen and M. M. Bursey, *Org. Mass Spectrom.* **7,** 1189 (1973).
8. Ch. Moureu, *Bull. Soc. Chim. France*, [*3*], **31,** 526 (1904).
9. M. M. Bursey and P. F. Rogerson, *Inorg. Chem.* **10,** 1313 (1971) and references contained therein.
10. L. A. Brook, *J. Amer. Chem. Soc.* **66,** 1295 (1944).
11. K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.* **39,** (1946).