Journal of Organometallic Chemistry, 67 (1967) C4–C6

Preliminary communication

THEORY AND APPLICATION OF PHOTOELECTRON SPECTROSCOPY

XLIV*,**. A QUANTITATIVE ACCOUNT OF HYPERCONJUGATION IN ALLYL AND BENZYL COMPOUNDS OF ELEMENTS OF GROUP IVB

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(Received December 12th, 1973)

Summary

It is shown that the destabilization of the π-MOs in allyl and benzyl compounds of elements M of Group IVB can be quantitatively predicted on the basis of the hyperconjugative M—C/π interaction model.

We present below a quantitative analysis of the M—C (M = C, Si, Ge, Sn) hyperconjugation*** in allyl ($CH_2{=}CH{-}CH_2MR_3$) and benzyl ($C_6H_5{-}CH_2MR_3$) compounds. The results provide a definitive interpretation of this phenomenon, which has recently been intensively studied [1]

To account quantitatively for the interaction between two basis orbitals (in our case the M—R′ σ-MO of compounds $R'MR_3$ on the one hand, and the vinyl and phenyl (e_{1g}) π-MO with non-zero coefficient at the position of substitution on the other) of energies E_1 and E_2 (assuming $E_1 > E_2$) we have, according to the variation method:

$$\delta E = ½[E_1 + E_2 + \sqrt{(E_1 - E_2)^2 + 4\beta^2}\ ] - E_1 \qquad (1)$$

Here β denotes the interaction between the two basis orbitals and δE the rise in energy of the higher orbital due to this interaction. The values of the energies E_1,

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*For part XLIII see ref. 5.

**After this paper was submitted a paper by Pitt [6] appeared. This publication is based largely on results disclosed in our earlier papers (see our perturbational account of the variation of the effect of M—C hyperconjugation with M [1b, 1h] and our discussion of the role of p_π—d_π conjugation in Group IV chemistry [1a, 1b].

***For leading references see ref. 1h.

TABLE 1

MEASURED VERTICAL IONIZATION POTENTIALS (IP_1 to IP_3), EXPERIMENTAL ENERGIES (E_1 and E_2) OF THE BASIS ORBITALS, AND EXPERIMENTAL AND CALCULATED HYPERCONJUGATIVE ORBITAL DESTABILIZATIONS (δE)

Compound	IP_1 (eV)	IP_2 (eV)	IP_3 (eV)	E_1 (eV)	E_2 (eV)	δE (eV)	
						found	calc.
CH_2=CH—CH_2CH_3	9.72 π [e]	11.75 σ(CC)		10.51 [m]	12.1 [i]	0.48	0.6
CH_2=CH—CH_2SiH_3	9.49 π [e]	11.72 σ(SiC)		10.51 [m]	≈11.7 [g]	0.71	0.7
CH_2=CH—CH_2CMe_3	9.5 π [c]	11.0 σ(CC)		10.51 [m]	11.3 [i,j,k]	0.7	0.8
CH_2=CH—CH_2SiMe_3	9.0 π [b]	10.5 σ(SiC)		10.51 [m]	10.57 [h,j,k]	1.2	1.12
CH_2=CH—CH_2GeMe_3	8.85 σ(GeC)	10.2 σ(GeC)	10.4 π	10.21 [j,k]	10.51 [m]	1.1	1.01
CH_2=CH—CH_2SnMe_3	8.50 σ(SnC)	9.7 σ(SnC)	10.7 π	9.7 [j,k]	10.51 [m]	0.9	0.8
C_6H_5—CH_2CH_3	8.85 π_s [a]	9.20 π_a [a]		9.25 [m]	12.1 [i]	0.28	0.4
C_6H_5—CH_2CMe_3	8.7 π_s	9.0 π_a		9.25 [m]	11.3 [i,j,k]	0.4	0.5
C_6H_5—CH_2SiMe_3	8.4 π_s [d]	9.1 π_a	10.6 σ(SiC)	9.25 [m]	10.57 [h,j,k]	0.7	0.62
C_6H_5—CH_2GeMe_3	8.25 π_s	9.0 π_a	10.35 σ(GeC)	9.25 [m]	10.21 [j,k]	0.9	0.71
C_6H_5—CH_2GeEt_3	8.1 π_s	9.05 π_a,σ(GeC)	10.2 σ(GeC)	9.25 [m]	9.35 [f]	1.0	1.04
C_6H_5—CH_2SnMe_3	8.1 π_s	9.15 π_a,σ(SnC)	10.2 σ(SnC)	9.25 [m]	9.70 [j,k]	1.0	0.89
C_6H_5—CH_2SnEt_3	7.9 σ(SnC)	8.9 π_a,σ(SnC)	9.95 π_s(?)	8.8 [l]	9.25 [m]	0.9	0.9
C_6H_5—CH_2SnBu_3	7.9 σ(SnC)	8.9 π_a,σ(SnC)	9.8 π_s(?)	8.7 [f]	9.25 [m]	0.8	0.9

[a] $\pi_s(\pi_a) = \pi(e_{1g})$MO with non-zero (zero) coefficient at the position of substitution. [b] Ref. 1a. [c] Ref. 1b. [d] Ref. 1c. [e] Ref. 1g. [f] Ref. 1h. [g] Ref. 3a. [h] Ref. 3b. [i] Ref. 3c. [j] Ref. 3d. [k] Ref. 3e. [l] $SnEt_4$: IP_1 = 8.8 eV [σ(SnC)] [3f]. [m] Ref. 3g.

E_2, and δE are available from photoelectron (PE) spectroscopy*.

Table 1 summarizes the measured vertical ionization potentials (*IP*), the assignment of corresponding PE bands, and the E_1 and E_2 values for a series of allyl and benzyl compounds. The δE values are obtained from the IP_1 and E_1 values with a correction for the C—H hyperconjugation of the CH_2MR_3 group (allyl compounds 0.31 eV [4a], benzyl compounds 0.12 eV [4b])**. By varying β in (1) and looking for the best correlations (least-squares method) between the observed and calculated (from (1)) δE values, straight lines are obtained which pass through the origin. The best β values are found to be 1.15 ± 0.07 eV for the allyl compounds and 1.09 ± 0.09 eV for the benzyl compounds. These results show quantitatively and unambiguously that the interaction between π systems and CH_2MR_3 substituents is hyperconjugative. They further show the interaction parameter β to be independent of M.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Dr. M.T. Reetz for providing us with a sample of $CH_2{=}CH{-}CH_2GeMe_3$.

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*Based on the validity of Koopmans' theorem [2].

**It follows from the PE spectra of the compounds $C_6H_5MR_3$ that the inductive effect of the substituents CH_2MR_3 is negligible.