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THE "EXTENDED SELECTIVITY TREATMENT" FOR ELECTROPHILIC SUBSTITUTIONS AT THE *ALPHA* POSITION OF THE FURAN RING[1]

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Brown and Stock[2] solved the problem of testing the applicability of a linear free energy treatment for electrophilic substitutions of a given substrate by reversing the conventional Hammett procedure. The substituent group is maintained constant and log k/k_H's are plotted against the reaction constant ρ for several substitutions. This treatment was called by these authors[2] "Extended Selectivity Treatment".

Satisfactory linear correlations were obtained when the treatment was applied to several derivatives of benzene, having substituents of different character.[3] Recently we have successfully applied the same treatment to an heteroaromatic ring, thiophene.[4]

Quantitative rate data, ample enough for an analogous test, are now also available for the electrophilic reactions at the *alpha* position of furan.

The presently available *alpha* partial rate factors (α_f) are summarized in table 1. They are derived from three types of reactions: a) "conventional" electrophilic substitutions in which a proton is substituted (1, 2 and 3); b) "displacement" reactions which involve the replacement of groups other than hydrogen (5 and 6); and c) side-chain electrophilic reactions in which a resonance-stabilized carbonium ion is formed in the transition state (4 and 7).

Table 1

Alpha partial rate factors for electrophilic reactions of furan

N	Reaction	α_f	Ref.
1	Bromination, Br_2, AcOH, 25°	6.1×10^{11}	5
2	Chlorination, Cl_2, AcOH, 25°	1.9×10^{9}	6
3	Acetylation, Ac_2O, $SnCl_4$, DCE, 25°	3.2×10^{7}	7
4	Solvolysis of 1-arylethylacetates 30% EtOH, 25°	1.5×10^{5}	8
5	Protodesilylation, $HClO_4$, MeOH, 50°	1.7×10^{4}	9
6	Protodemercuration, HCl, 10% EtOH, 70°	4.0×10^{3}	10
7	Pyrolysis of 1-arylethylacetates, 327°	3.8	11

The data closely follow a straight line with the theoretical origin (r = 0.995; s = 0.79) as shown in figure 1. The linearity argues for a constancy of the resonance contributions of the furan ring in the diverse reactions.

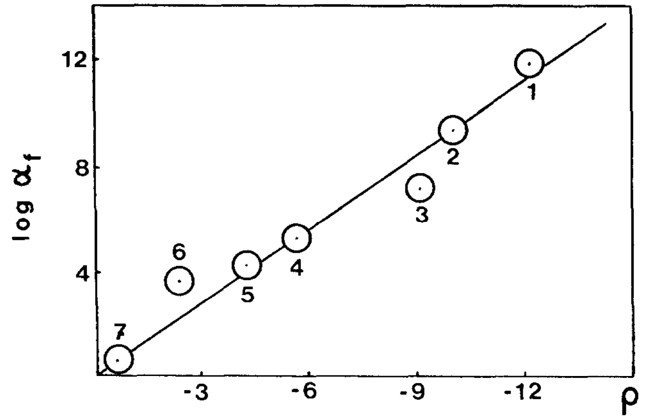

Figure 1: The "Extended Selectivity Relationship" for electrophilic reactions at the alpha position of furan. The numbers identify the reactions: see table 1.

From the slope a substituent constant σ_α^+ relative to the structural modification caused by the substitution of an oxygen atom for a CH=CH in the benzene ring may be calculated. The value obtained, -0.93, is noticeably more negative than the σ_α^+ for thiophene[4], -0.79.

Research is currently in progress in this laboratory, in order to obtain data necessary for testing the applicability of the relationship to the reactions at the beta position.

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REFERENCES

1. Part XI of the series: Electrophilic substitutions in five-membered heterocyclic systems. Previous part: S. Clementi and G. Marino, Gazzetta Chim. Ital., in the press.
2. H.C. Brown and L.M. Stock, J. Am. Chem. Soc., **24**, 3298 (1962).
3. For a review see: L.M. Stock and H.C. Brown, Adv. Phys. Org. Chem., **1**, 35 (1963).
4. S. Clementi, P. Linda, and G. Marino, J. Chem. Soc. (B), in the press.
5. P. Linda and G. Marino, J. Chem. Soc. (B), 392 (1968).
6. The α_f for chlorination has been calculated from the 2nd order rate constants of chlorination in anh. AcOH at 25° of the 2-methoxycarbonyl derivatives of furan (5.5×10^{-2} l. mole^{-1} sec^{-1}) and thiophene (1.1×10^{-3} l. mole^{-1} sec^{-1}), and the relative rate of chlorination, thiophene to benzene, 1.3×10^7, [G. Marino, Tetrahedron, **21**, 843 (1965)].
7. P. Linda and G. Marino, Tetrahedron, **23**, 1739 (1967).
8. M.L. Gross, Ph. D. Thesis, Minnesota University (1966).

9. C. Eaborn and J.A. Sperry, J. Chem. Soc., 4921 (1961).

10. R.D. Brown, A.S. Buchanan, and A.A. Humffray, Austr. J. Chem., **18**, 1513 (1965).

11. R. Taylor, J. Chem. Soc. (B), 1397 (1968).