Tetrahedron Letters No.7, pp. 611-612, 1971. Pergamon Press. Printed in Great Britain.

THE RELATIVE IMPORTANCE OF PRIMARY STERIC EFFECTS IN ACETYLATION OF BENZENE AND THIOPHEN DERIVATIVES

Sergio Clementi, Paolo Linda, and Marco Vergoni
Istituto di Chimica Organica, Università di Perugia, Italy

(Received in UK 22 December 1970; accepted for publication 13 January 1971)

Recent papers of Bak and coworkers[1] have pointed out the molecular geometry of five-membered heteroaromatic compounds: thiophen, furan, and pyrrole. The internal angles of these systems are different from each other, and always smaller than those of benzene.

In connection with our previous studies[2] on structure-reactivity relationships in the thiophen ring, we have now investigated the influence of molecular geometry on the importance of steric effects in electrophilic substitutions at this ring.

The differences in angles between thiophen and benzene rings might cause a remarkable difference in the relative importance of primary steric effects in these two systems. Such a problem has not previously been studied and now we are able to report some data to make a comparison possible.

The partial rate factors for the tin tetrachloride catalyzed acetylation by acetic anhydride in dichloroethane at 25° C of toluene, <u>t</u>-butylbenzene, **3-methylthiophen and 3-<u>t</u>-butylthiophen have been calculated from isomer distributions and relative rates to unsubstituted rings (Table 1).**

The magnitude of the <u>steric ratio</u>, defined as the ratio of the o_f/m_f ratios obtained respectively for toluene and <u>t</u>-butylbenzene and the ratio of the $2_f/5_f$

ratios for 3-methylthiophen and 3-t-butylthiophen (i.e., 44500 for benzene and 17.6 for thiophen), shows that the steric hindrance is less significant in thiophen than in benzene, since the results cannot be interpreted only in terms of the differences of polar effects between the methyl and t-butyl group. In fact the predicted steric ratio would be 2.1, as calculated from Brown's σ^+ constants (considering $\sigma_o^+ = \sigma_p^+$) and a ρ constant equal to -5.6 for the title reaction.[2b]

Table 1. Partial rate factors for the acetylation of alkylderivatives

Compound	o_f	m_f	p_f
Toluene	16.3	3.90	746
t-Butylbenzene	0.001	10.6	687
	^2f	^4f	^5f
3-Methylthiophen	10.3	0.065	3.40
3-t-Butylthiophen	0.87	0.002	5.03

Of course this argument is sound so long as the transition states for all the considered systems are very similar. There are many experimental data to support this, but even so the position is not yet completely resolved.

The "Consiglio Nazionale delle Ricerche" is thanked for financial support. The authors are also grateful to prof. G.Marino for encouragement and discussion.

REFERENCES

1. B.Bak, D.Christensen, L.Hansen-Nygaard, and J.Restrup-Andersen, J.Mol.Spectr., 7, 58, (1961).
2. a) G.Marino, Atti Acc. Naz. Lincei, 38, 700 (1965); b) P.Linda and G.Marino, Tetrahedron, 23, 1739 (1967); c) S.Clementi and G.Marino, Tetrahedron, 25, 4599 (1969); d) S.Clementi, P.Linda, and G.Marino, J.Chem.Soc. (B), 1153 (1970).