Tetrahedron Letters No.15, pp. 1-4, 1960. Pergamon Press Ltd. Printed in Great Britain

SUBSTITUENT EFFECTS IN AROMATIC SUBSTITUTION

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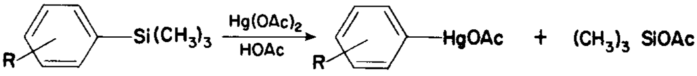
(Received 1 June 1960)

RECENTLY[1] we reported that mercuridesilylation [equation (I)] constitutes a convenient method for determining the reactivity of a particular ring position in an aromatic system. The mercuriacetate enters the position occupied by the trimethylsilyl group at a convenient rate to measure.



I

We are hereby reporting the results of an application of this method to a study of the electrical effects of alkyl groups on an aromatic ring (equation I, where R = m and p-CH_3, C_2H_5, i-C_3H_7 and t-C_4H_9). As will be noted from Table 1, the meta alkyl series shows a gradual increase in rate of cleavage which is readily explainable in terms of the gradually increasing inductive effect of the meta alkyl substituent. Surprisingly however, the para alkyl series also shows the same gradual increase in rate. This becomes

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[1] R.A. Benkeser, D.I. Hoke and R.A. Hickner, J.Amer.Chem.Soc. 80, 5294 (1958).

[2] For other exceptions see: W.M. Lauer, G.W. Matson and G. Stedman, J.Amer.Chem.Soc. 80, 6437 (1958); H. Cohn, E.D. Hughes, M.H. Jones and M.G. Peeling, Nature, Lond. 169, 291 (1952); C. Eaborn and R. Taylor, Chem. & Ind. 949 (1959).

TABLE 1.

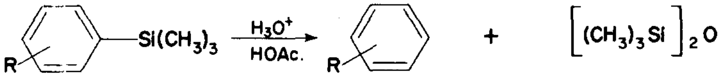
Cleavage of Alkylphenyltrimethylsilanes by Mercuric Acetate in Glacial Acetic Acid at 25° (a)

Alkyl Group	k/k_H (b)
m-CH_3	2.51
m-i-C_3H_7	3.96
m-t-C_4H_9	5.50
p-CH_3	10.60
p-C_2H_5	11.50
p-i-C_3H_7	12.00
p-t-C_4H_9	14.00

(a) The solution was 0.1788 M in mercuric acetate and 0.017 M in silane.

(b) These rates are relative to the unsubstituted compound, phenyltrimethylsilane.

one of the rare electrophilic substitution wherein *p*-alkyl groups do not activate in the Baker - Nathan (hyperconjugative) order.[2] On the other hand, preliminary results of protodesilylation [equation (II)] from our Laboratory indicate that *p*-alkyl groups follow the Baker - Nathan order.



II

In view of recent disclosures regarding the influence of solvation upon the electron release of alkyl groups, one is tempted to explain these anomalous results in terms of a solvent effect.[3-6] This becomes a particularly attractive explanation when one considers that protodesilylations, which follow the Baker - Nathan order, are routinely carried out in a highly polar medium (mineral acid in aqueous acetic acid), while the mercuridesilylations reported in Table 1 are carried out in a relatively non-polar medium (mercuric acetate in glacial acetic acid).

While solvation effects may indeed be the sole explanation for the anomalies observed, a second possibility exists which cannot be overlooked at this time. The mercuridesilylation reaction is one of low selectivity,[7] having an S_f factor of 0.63.[8] In terms of the Hammond[9] postulate, the transition state for mercurisesilylation will resemble the reactants, in that very little breaking of the carbon-silicon bond has occurred. Hence very little positive ion character is developed in the aromatic ring in the transition state, and hence there is very little demand upon the electron releasing properties of the para alkyl groups. An interesting corollary to

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[3] See series of papers in Tetrahedron 5, 166 (1958).

[4] R.S. Mulliken, Tetrahedron 6, 68 (1959).

[5] W.A. Sweeney and W.M. Schubert, J.Amer.Chem.Soc. 76, 4625 (1954);and subsequent papers.

[6] R.A. Clement and J.N. Naghizadeh, J.Amer.Chem.Soc. 81, 3154 (1959).

[7] See L.M. Stock and H.C. Brown, J.Amer.Chem.Soc. 81, 5621 (1959) for leading references to this concept.

[8] The S_f factor for aromatic mercuration at 25° is 1.01. [H.C. Brown and C.W. McGary, Jr., J.Amer.Chem.Soc. 77, 2306 (1955)]. From these and other data, it would appear that reactions which involve the breakage of a carbon-silicon bond are uniformally less selective than the corresponding reaction involving a carbon-hydrogen bond breakage (e.g. mercuridesilylation and aromatic mercuration).

[9] G. Hammond, J.Amer.Chem.Soc. 77, 334 (1955).

this second explanation would be that mercuridesilylation rates should correlate more satisfactorily with Hammett's sigma constants than with Brown's σ^+ constants,[10] sonce the latter reflects resonance interactions to a greater extent than the former. We plan to check this point.

Acknowledgement - The authors are grateful to the National Science Foundation for a fellowship grant which made this work possible.

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[10] H.C. Brown and Y. Okamoto, J.Amer.Chem.Soc. 79, 1913 (1957).