Influence of σ–π Conjugation on the Rate of Protodemetallation Reactions: A Comment

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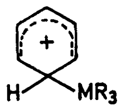
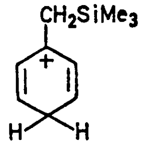
Summary Comments are offered on the novelty of a recent explanation of the ease of cleavage of R_3MPh bonds as M is varied from C to Si, Ge, Sn, and Pb.

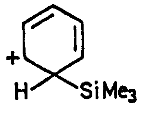
After dismissing an alternative explanation offered by Eaborn and Pande in 1960 (not 1970 as stated in his communication),[1] Berwin recently suggested that the relative rates of acid cleavage of $Ph–MR_3$ bonds as M is varied from C to Si, Ge, Sn, and Pb, can be regarded as reflecting the ease of electron release from the $C–MR_3$ bonds, which is mainly hyperconjugative (σ–π conjugative) in origin.[2] In 1964, having previously withdrawn the earlier proposal,[3] my colleagues and I ourselves interpreted the rate variations in terms of this electron release,[4] and furthermore drew attention to the relationship between the electron release by CH_2MR_3 groups and the ease of cleavage of $Ph–MR_3$ bonds by pointing to the analogy between the stabilization of the intermediate (I) and that of the intermediate (II), and by presenting both intermediates in the canonical forms involving a carbonium ion centre β to the MR_3 group [see (III)], to the significance of which Berwin has redirected attention. (Since the effects of the CH_2MR_3 groups on the stability of (II) correlate with σ^+-constants,[5] the existence of a linear relationship between the logarithms of the relative rates of cleavage of aryl–MEt_3 bonds and the lowering of the charge-transfer energy between Ph_3MCH_2Ph compounds and tetracyanoethylene, which was noted by Berwin,[2] was to be expected in the light of this analogy.) While we did not always in 1961—1967 attribute the electron release from CH_2MR_3 groups mainly to hyperconjugation, as we had done earlier,[6] we have consistently done so since 1968.[7]



(I)



(II)



(III)

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[1] C. Eaborn and K. C. Pande, *J. Chem. Soc.*, 1960, 1566.

[2] H. J. Berwin, *J.C.S. Chem. Comm.*, 1972, 237.

[3] C. Eaborn and J. A. Waters, *J. Chem. Soc.*, 1961, 542; R. W. Bott, C. Eaborn, K. C. Pande, and T. W. Swaddle, *ibid.*, 1962, 1217.

[4] R. W. Bott, C. Eaborn, and P. M. Greasley, *J. Chem. Soc.*, 1964, 4804.

[5] See, for example, R. Baker, C. Eaborn, and R. Taylor, *J.C.S. Perkin II*, 1972, 97 and refs, therein.

[6] C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 1954, 939; C. Eaborn, *ibid.*, 1956, 4858; C. Eaborn, 'Organosilicon Compounds,' Butterworths, London, 1960, p. 486.

[7] C. Eaborn, Plenary Lecture at the Second International Symposium on Organosilicon Chemistry, Bordeaux, 1968, as published in *Pure and Appl. Chem.*, 1969, **19**, 375; A. R. Bassindale, C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Organometallic Chem.*, 1969, **20**, 49; A. R. Bassindale, C. Eaborn, and D. R. M. Walton, *ibid.*, 1970, **21**, 91; M. A. Cook, C. Eaborn, and D. R. M. Walton, *ibid.*, 1970, **24**, 301.