CARBON-METAL HYPERCONJUGATION. THE EXTRAORDINARY

ELECTRON DONATION BY α-METALLOALKYL GROUPS[1]

W. Hanstein and T. G. Traylor
Department of Chemistry, Revelle College
University of California, San Diego
La Jolla, California
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We wish to report a very strong ortho, para directing, electron donating effect of

the metallomethyl group ($M-CH_2-$) which acts through carbon-metal hyperconjugation.

Nesmeyanov and co-workers[2] have proposed that carbon-metal hyperconjugation (called

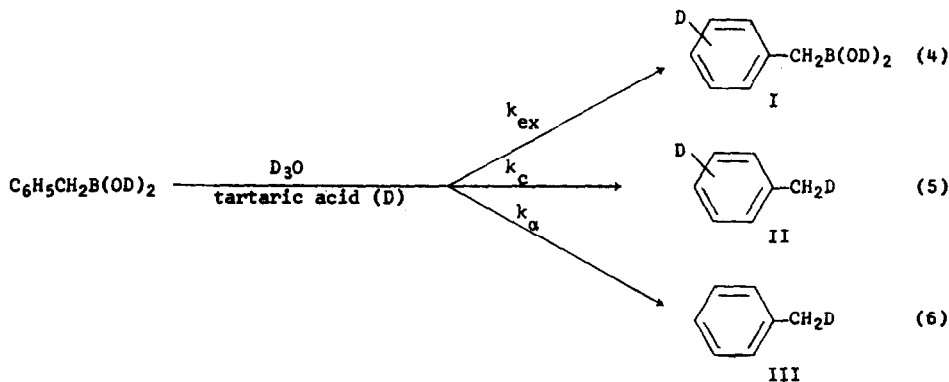σ-π conjugation),[2a] exemplified below for ketones, is an important factor in spectroscopic

and chemical properties of organometallic compounds.[3,4,5] Such conjugation leads to

elimination during solvolyses of β-metalloalkyl derivatives.

$$CH_2-CH_2 \longrightarrow CH_2=CH_2 + M^+ + X^- \tag{1}$$
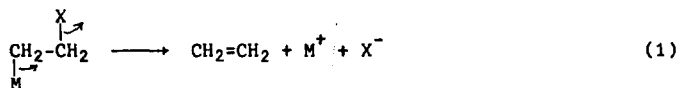
We have suggested[6] that such σ-π conjugation should be transmitted through a phenylene

group as illustrated in equations 2 and 3.

$$(2)$$

$$(3)$$
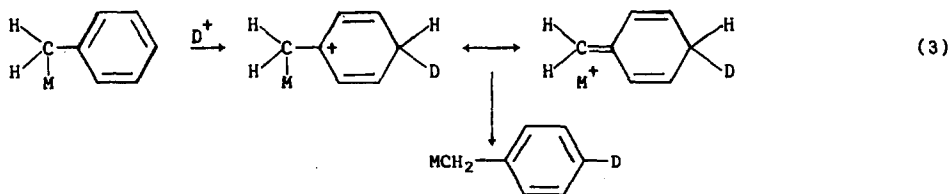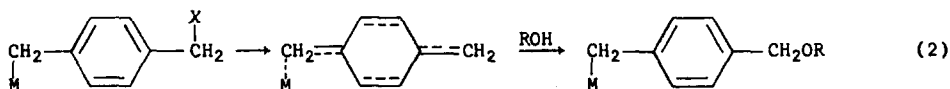
We find two examples of very facile deuteriodeprotonation[7] which occur according to

reaction 3 (M = BX_3^-, $HgCH_2C_6H_5$). Whereas benzylboronic acid was converted to $C_6H_5CH_2D$

in alkaline D_2O, reaction with 3 M tartaric acid at pH = 0.7 in D_2O at 100°C resulted

in the following reactions.[9]

$$C_6H_5CH_2B(OD)_2 \xrightarrow[\text{tartaric acid (D)}]{D_3O}$$

Reaction scheme:

- k_{ex} → I: D-substituted ring —CH$_2$B(OD)$_2$ (4)
- k_c → II: D-substituted ring —CH$_2$D (5)
- k_α → III: ring —CH$_2$D (6)

The _ortho_ to _para_ ratio $\frac{1}{2}\left(D_o/D_p\right)$ was 1.1 in II[10] and the ratios of $k_{ex} : k_\alpha : k_c$ were approximately 1 : 2.2 : 4.7.[11]

A second and more facile reaction was observed upon treatment of dibenzylmercury with a 4.3 M solution of trifluoroacetic acid in chloroform at 35°C. After 82 minutes, 29% cleavage had occurred,[12] accompanied by extensive exchange in the recovered dibenzyl-mercury.[13,16] Analyses of all products as described above[17] indicated that reactions analogous to 4, 5 and 6 had occurred. The _ortho_ to _para_ rate for exchange[17] was 0.84, similar to that reported above, k_{ex} was $2.1 \times 10^{-4} \text{sec}^{-1}$ and the ratio $k_{ex}/\left(k_c + k_\alpha\right)$ at least 3.[19]

A comparison of these with other deuteriodeprotonation rates indicates that the σ^+ constants are roughly[20]

$$\sigma^+_{p-CH_2\bar{B}X_2OH} = -1.11 \qquad \sigma^+_{p-CH_2HgCH_2C_6H_5} = -1.14$$

Clearly, σ-π conjugation involving metals is remarkably large. These results (especially with $R\bar{B}X_2OH$ which has no d-orbitals) strengthen our postulate of σ-π conjugation for the much smaller effect of the ferrocenyl group $(\sigma^+_{p-Fer} = -0.71)$.[21]

The reactions of benzylboronic acid (and dibenzylmercury) are best explained by a mechanism similar to that proposed by Bundel, Antonova and Reutov[8a] for _ortho_ substitution in benzyl mercuric chloride.

$$C_6H_5CH_2B\bar{X}_2OD \xrightarrow{\underset{S_E2}{D^+}}$$

X = tartaric Acid

$$(7)$$
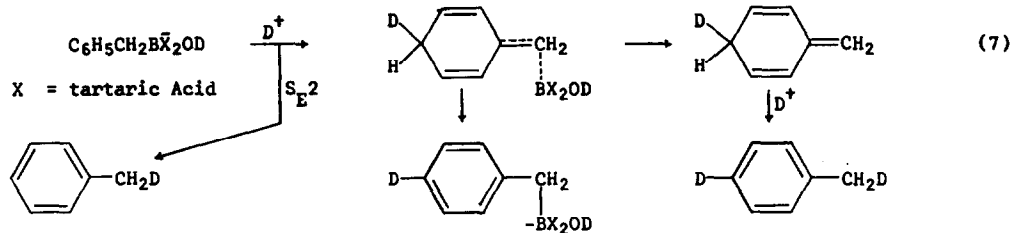
Studies of the effects of electrophiles and various metals on these kinds of reactions are in progress.[21]

References

1. Supported by the National Science Foundation Grants GP-2829 and 6391.

2. (a) A. N. Nesmeyanov and I. F. Lutsenko, Doklady Akad. Nauk. SSSR 59, 707 (1948).

   (b) A. N. Nesmeyanov, K. A. Perchskaya, A. N. Akramovich, and L. M. Miakova,

   Doklady Akad. Nauk. SSSR·121, 660 (1958). (c) A. N. Nesmeyanov and I. I. Kritskaya,

   ibid. 477.

3. I. P. Beletskaya, L. A. Fedorov, V. A. Moskalenko, and O. A. Reutov, Izvestiya

   Akad. Nauk. 1965, 933.

4. P. P. Shorygin, V. P. Roshchupkin, and L. G. Stolyarova, Russian Journal of Physical

   Chemistry 39, 321 (1965).

5. M. M. Kreevoy, R. J. Steinwand and T. S. Straub, J. Org. Chem. 31, 4291 (1966).

6. T. G. Traylor and J. C. Ware, J. Amer. Chem. Soc. 89, 2304 (1967).

7. Bundel, Antonova and Reutov[8a,b] have suggested the possibility of reactions such as

   5 and have observed deuterodeprotonation of benzylmercuric chloride. This was

   attributed to a combination of σ-π conjugation and a favored cyclic transition state

   since ortho/para ratios were ten to twenty.

$$C_6H_5CH_2HgCl + DCl \longrightarrow$$
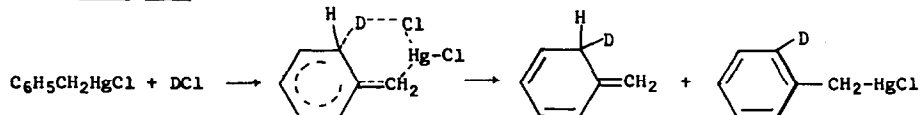
Ring reactions of benzylmagnesium halides have been observed[8b,c] by Gilman and Harris[8c] and by Benkeser.[8d]

8. (a) Yu. G. Bundel, N. D. Antonova and O. A. Reutov, Doklady Akad. Nauk. SSSR 166, 1103 (1966). (b) I. P. Beletskaya, L. A. Fedorov, and O. A. Reutov, Zh. Org. Khim. 3, 225 (1967). (c) H. Gilman and S. A. Harris, J. Am. Chem. Soc. 53, 3541 (1931). (d) R. A. Benkeser and W. DeTalvo, ibid. 89, 2141 (1967).

9. The products were analysed by mass spectra, nmr and IR spectra. The positions and extents of deuteration may be determined readily from these analyses. Analyses of I were carried out on the toluene obtained by alkaline cleavage in H_2O.

10. (a) G. V. Tiers, J. Chem. Phys. 19, 1072 (1951). G. V. D. Tiers and J. H. Tiers, ibid. 20, 761 (1952).

11. The mass spectrum of the toluene, obtained by alkaline H_2O cleavage of I, was used to obtain $k_{ex} = 5 \times 10^{-7} sec^{-1}$. The overall cleavage rate ($k_{\alpha} + k_c = 3.4 \times 10^{-6} sec^{-1}$) was obtained from the rate of toluene production in the deuterated reaction medium.

12. Determined by weighing the metallic mercury which resulted from the rapid solvolysis of benzylmercuric trifluoroacetate.[15b] Benzylmercuric trifluoroacetate is stable under some cleavage conditions (less polar solvent like 2.2 $\underline{M}$ trifluoroacetic acid in benzene) and can be isolated. Under the above conditions it solvolyzed as fast as it was formed.

13. This cleavage reaction is strongly acid dependent and is therefore not S_E1. We first tried the cleavage with DCl under conditions which were reported by Reutov et al.[3b] to result in a S_E1 reaction. Even with thirtyfold higher concentrations of the reactants we obtained some benzaldehyde and no toluene under these conditions. We therefore suggest that the acid independent reaction studied by Reutov et al. might be air oxidation rather than cleavage by DCl or HCl. A reported S_E1 cleavage of dibutylmercury[14] was shown to be air oxidation by Jensen and Heyman.[15a]

14. C. R. Hart and C. K. Ingold, J. Chem. Soc. 4372 (1964); C. K. Ingold, Helv. Chim. Acta 47, 1191 (1964); Record Che. Progr. 25, 145 (1964).

15. (a) F. R. Jensen and D. Heyman, J. Am. Chem. Soc. 88, 3438 (1966). (b) F. R. Jensen and R. J. Ouellette, ibid. 83, 4477, 4478 (1961).

16. The exchange $DC_6H_4CH_2HgOOCCF_3 + (C_6H_5CH_2)_2Hg \rightarrow C_6H_5CH_2HgOOCCF_3 + DC_6H_4CH_2HgCH_2C_6H_5$
    would be slow at this temperature and furthermore this reaction would reduce the
    observed deuteration of dibenzyl mercury.

17. Recovered dibenzyl mercury was first analysed for _ortho_ and _para_ deuterium
    (631 cm^{-1} and 602 cm^{-1} respectively; 0.5 _ortho_/_para_ = 0.76 using the intensity ratio
    given by Tiers[10] for d-toluenes), then cleaved with mercuric chloride and the result-
    ing benzylmercuric chloride reduced to toluene with lithium aluminum hydride in
    ether.[18]

18. S. Winstein and T. G. Traylor, _J. Am. Chem. Soc._ __78__, 2597 (1956).

19. The total rate of cleavage, estimated by determination of toluene, was $4 \times 10^{-5} sec^{-1}$
    (k_c/k_α = 1.7).

20. An additional correction has to be made for the fact that at pH = 0.7 in 3 __M__ tartaric
    acid only 0.3% of benzylboronic acid is in the anionic form with tetrahedral boron
    which is the reacting species. (Unpublished results.)

21. For example, dibenzyl mercury has been acetylated under very mild conditions (J. A.
    Mangravite, unpublished data). See also the following communication.