Tetrahedron Letters No.52, pp. 4821-4825, 1965. Pergamon Press Ltd.
Printed in Great Britain.

INTRAMOLECULAR CATALYSIS OF A FRIEDEL-CRAFTS ACYLATION REACTION

H. W. Whitlock, Jr., C-Y. Hsu and K. Sundaresan
Department of Chemistry, University of Wisconsin,
1112 W. Johnson St., Madison, Wis.

(Received 7 September 1965; in revised form 5 November 1965)

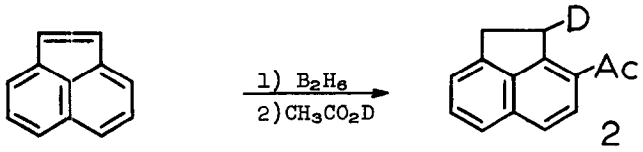
Selective transfer of a substituent-bound electrophile to a carbon ortho to the substituent is often invoked to explain anomalous ortho-para ratios in electrophilic aromatic substitution (1,2). We wish to report a particularly clear cut example of this. Hydroboration of acenaphthylene in diglyme by either the ex situ or in situ procedure (3) followed by acetolysis of the resulting organoborane affords, in addition to a poor yield of a mixture of acenaphthene and acenaphthylene, substantial amounts (25-45 percent yield) of 3-acetylacenaphthene (1). That this ketone is derived from an intramolecular acylation reaction follows from the following observations.

1) Only 1 is produced; no 5-acetylacenaphthene could be detected. In contrast, acetylation of acenaphthene, using acetic anhydride and boron acetate or magnesium perchlorate gave mixtures of 3- and 5-acetylacenaphthene with the latter predominating. This, of course, is in agreement with

the known pattern of electrophilic attack on acenaphthene (4,5,6).

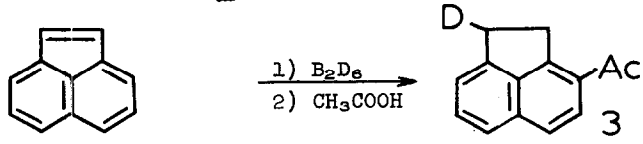
2) Both acenaphthene and 1 appear to share a common precursor. Monitoring of an acetolysis reaction mixture (120°) by vpc showed that the ratio of 1 to acenaphthene remained relatively constant at from 1.8 after ten minutes heating to 1.5 after fourteen hours.

3) The acyl-bearing carbon in 1 is that adjacent to the boron-bearing carbon of the intermediate organoborane. When the hydroboration reaction mixture was subjected to acetolysis with deuteroacetic acid (eq. 1), 2-deutero-3-acetylacenaphthene (2) was produced. On the other hand, reaction of acenaphthylene with hexadeuterodi-



(1)

borane followed by acetolysis (eq. 2) afforded 1-deutero-3-acetylacenaphthene (3). The structural assignments follow



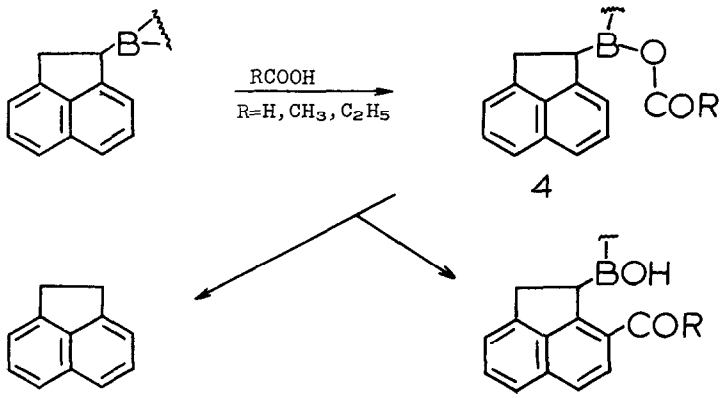
(2)

from the NMR spectra of the ketones. In the spectrum of 1 the bridge methylenes appear as two multiplets (7) at δ 3.35 and 3.65 in a typical (8) A_2B_2 pattern. In the spectrum of

2 the low field multiplet (assigned to the C-2 methylene group) corresponded to only one hydrogen and in the spectrum of 3 the high field multiplet corresponded to one hydrogen (9). Repetition of the sequences in equations one and two, using propionic acid and deuteropropionic acid gave deuterated 3-propionylacenaphthene (10) with the same positioning of deuterium as above.

4) Formolysis of the intermediate organoborane gave an eight percent yield of acenaphthene-3-carboxaldehyde, an oil, homogenous by vpc, which was identified by oxidation (silver oxide) to acenaphthene-3-carboxylic acid.

From these results we conclude that the intermediate organoborane may serve as an intramolecular acylating agent as shown. Neither the production of the ketones and



aldehyde nor the highly specific directive effect seems to be consistent with an intermolecular acylation. Intramolecular acyltransfer should be especially favorable in the above case since not only is the geometry of 4 favorable for this, but acenaphthene is known to possess abnormally high reactivity toward electrophilic substitution (11). The yields of the two 3-acylacenaphthenes are high enough to make the reaction preparatively interesting. Several other examples of high ortho-para ratios in electrophilic substitution which presumably arise from coordination of the attacking electrophiles with ring substituents (12,13) have kindly been pointed out by a referee. Particularly to the point is the nitration of phenylboronic acid (13). These and the previously cited examples differ from the present case in that they involve complexing of a performed electrophile with ring substituents while the example reported here involves intramolecular formation and transfer of the electrophile. Mechanistically, however, the two types of reaction are quite similar.

Acknowledgment. Partial support by the National Institutes of Health is acknowledged.

REFERENCES

1. P. Kovacic and J. J. Hiller, Jr., J. Org. Chem., 30, 1581 (1965), and references contained therein.
2. M. J. S. Dewar in "Molecular Rearrangements", P. de Mayo editor, Wiley, New York, 1963.
3. H. C. Brown, "Hydroboration", W. A. Benjamin, Inc., New York, 1962.
4. L. F. Fieser and E. B. Hershberg, J. Am. Chem. Soc., 61, 1272 (1939).

5. L. F. Fieser and J. Cason, ibid., 61, 1740 (1939).

6. L. F. Fieser and M. A. Peters, ibid., 54, 4347 (1932).

7. The methylene hydrogens of 5-acetylacenaphthene appear as a single peak (width at half-height ~ 3 c.p.s.) at δ 3.25. In the spectrum of 1 the multiplet at δ 3.65 is assigned to the C-2 methylene group and the multiplet at δ 3.35 is assigned to the C-1 methylene group on the basis of the expected deshielding effect of the 3-acetyl group on the C-2 methylene hydrogens. NMR spectra were determined at 60 Mc in carbon tetrachloride. Peak positions (δ) are given in p.p.m. downfield from internal tetramethylsilane.

8. K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra", W. A. Benjamin, Inc., New York, 1962.

9. Deuterium content was checked by mass spectrometry. Monodeuteroketones from deuteration with deuteroacids persistently had only 0.75-0.8 D per molecule.

10. Unlabelled 3-propionylacenaphthene, m.p. 120-121° (oxime, m.p. 142-143°) was identified spectrally. Infrared; $\lambda_{max}^{CHCl_3}$ 5.99 u: NMR; CH_3 at δ 1.25 (triplet, J = 7 c.p.s. 3H), CH_2 at δ 3.01 (quartet, J = 7 c.p.s., 2H), C-2 methylene at δ 3.35 (mult., 2H), C-1 methylene at δ 3.68 (mult., 2H): Mass spectrum; m/e 210 (P), 181 (base, P-C_2H_5), 153 (P-COC_2H_5).

11. E. Berliner, D. M. Falcione and J. L. Riemenschneider, J. Org. Chem., 30, 1812 (1965).

12. R. O. C. Norman and G. K. Radda, J. Chem. Soc., 3030 (1961).

13. D. R. Harvey and R. O. C. Norman, ibid., 3822 (1962).