Tetrahedron Letters No. 15, pp 1289 - 1290.
© Pergamon Press Ltd. 1979. Printed in Great Britain.

0040-4039/79/0408-1289$02.00/0

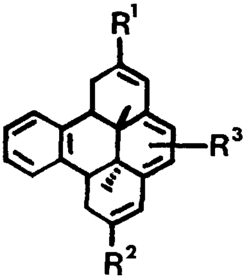
THE FIRST EXAMPLE OF ELECTROPHILIC SUBSTITUTION ON A BENZANNULENE.[1]

Reginald H. Mitchell* and Joseph Shue-Hen Yan,
Department of Chemistry, University of Victoria,
Victoria, B. C., V8W 2Y2 CANADA

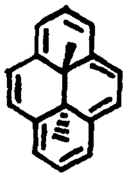
Summary: Electrophilic substitution (nitration, acylation) proceeds readily in the macro ring of the benzannelated [14]annulene **1** to give products similar to that of the non annulated parent **6**.

Recently, there has been a tremendous resurgence of interest in benzannulenes,[2,3] perhaps prompted in part by an ability to detect diatropicity in such systems by simple magnetic resonance measurements. Interestingly there have been no reports of such molecules undergoing electrophilic substitution reactions, despite the fact that such reactions are amongst the best studied for their benzenoid counterparts.

Here we report the first examples of electrophilic substitution reactions on the macrocyclic ring of a benzannulene. The benzannelated dihydropyrene **1**, which we recently synthesised,[3b] is relatively stable and obtainable on the gram scale, and thus seemed an ideal candidate to test.



1 : $R^1 = R^2 = R^3 = H$
2 : $R^1 = NO_2$; $R^2 = R^3 = H$
3 : $R^1 = R^2 = NO_2$; $R^3 = H$
4 : $R^1 = R^2 = R^3 = NO_2$
5 : $R^1 = COCH_3$; $R^2 = R^3 = H$


6

Treatement of **1** with copper(II) nitrate in acetic anhydride readily forms its mono-, di- an trinitroderivatives. At 0°C, 2-nitro-trans-12c,12d-dimethyl-12c,12d-dihydrobenzo(e)pyrene[4] **2**, is obtained in 35% yield as blue crystals, mp 163-164°, whereas at 20°C the 2,7-dinitro derivative, **3**, mp 197°C (dec) is the major product. The structure of the latter is readily apparent from its molecular ion at m/e 373 (MH^+, chemical ionisation), and the ^1H and ^{13}Cmr spectra. The latter shows five strong signals between 131-111 ppm corresponding to aromatic carbon atoms each bearing a hydrogen atom, and indicates a symmetrical product. The ^1Hmr spectrum shows H-1,8 at δ 9.09 (2H, d, J=1.5 Hz), H-9,12 as part of an AA'XX' at δ 9.2-8.6, H-4,5 at δ 7.92 (2H, s) and H-3,6 at δ 8.71 (2H, d, J=1.5 Hz) and hence allows assignment of **3** as the 2,7-derivative. A green trinitro derivative, **4**, mp 198°C (dec), (M^+ = 417.0961; calc. for $C_{22}H_{15}N_3O_6$, M = 417.0961) is obtained using copper(II) nitrate at 20°C.

The internal methyl protons appear at δ -1.85 (**1**), -1.85 (**2**), -1.60 (**3**) and -1.50 and -1.55 ppm (**4**) respectively, consistent with results obtained for toluene[5] and clearly indicated that no substantial change took place to the system or its diatropicity on electrophilic substitution.

Similarly treatment of **1** with acetic anhydride and a few drops of BF_3-etherate at 20°C readily yielded 76% of the purple mono-acetyl derivative, **5**, mp 140-142°C.

These results are very similar to those obtained[7] for the parent system **6** and show that the annulated benzene ring does not appear to have an effect on the position of substitution.

On the basis of classical electrophilic substitution reactions, **1** can thus be regarded as chemically aromatic and as such joins the rather elite group[7,8] of macrocyclic annulenes which have thus far been electrophilically substituted. The success obtained with **1** should prompt others to test analogous systems.

We thank the National Research Council of Canada and the University of Victoria for financial support.

References

1. Benzannelated Annulenes. 4. For Part 3, see R. H. Mitchell, R. J. Carruthers and L. Mazuch, *J. Am. Chem. Soc.*, **100**, 1007 (1978).
2. See for example R. T. Weavers and F. Sondheimer, *Angew. Chem., Int. Ed. Engl.*, **13**, 141 (1947); A. Yasuhara, T. Satake, M. Iyoda and M. Nakagawa, *Tetrahedron Letters*, 895 (1975); M. Iyoda, M. Morigaki and M. Nakagawa, *Tetrahedron Letters*, 1043 (1975); J. Ojima, A. Kimura and T. Yokoyama, *Chemistry Letters*, 1261 (1974) and 207 (1975); H. A. Staab, F. Graf and B. Junge, *Tetrahedron Letters*, 743 (1966); U. E. Meissner, A. Gensler and H. A. Staab, *Angew. Chem., Int. Ed. Engl.*, **15**, 365 (1976).
3. (a) R. H. Mitchell and R. J. Carruthers, *Tetrahedron Letters*, 4331 (1975).
   (b) R. H. Mitchell and J. S-H. Yan, *Can. J. Chem.*, **55**, 3347 (1977).
4. The structure of all new compounds were fully supported by mass and NMR spectral data and elemental analysis.
5. Perhaps surprisingly, the chemical shift of the methyl group in toluene is almost the same as in the nitrotoluenes,[6] similarly for the methyl group of nitro-**6** (δ-4.03) relative to **6**(δ-4.25)[7].
6. C. J. Pouchert and J. R. Campbell, "The Aldrich Library of NMR Spectra", Aldrich Chemical Co., Vol IV, 1B; Vol V, 144C, 148D, and 151D, (1974).
7. J. B. Phillips, R. J. Molyneux, E. Sturm and V. Boekelheide, *J. Am. Chem. Soc.*, **89**, 1704 (1967).
8. I. C. Calder, P. J. Garrett, H.C. Longuet-Higgins and F. Sondheimer, *J. Chem. Soc. (C)*, 1041 (1967); E. Vogel and W. A. Boll, *Angew. Chem., Int. Ed. Engl.*, **3**, 642 (1964); E. Vogel W. A. Boll and M. Biskup, *Tetrahedron Letters*, 1569 (1966); Y. Gaoni and F. Sondheimer, *J. Amer. Chem. Soc.*, **86**, 521 (1964).

(Received in USA 7 February 1979)