Tetrahedron Letters No.52, pp.4567-4570, 1969. Pergamon Press. Printed in Great Britain

REACTIONS IN THE π-CLOUD OF [2.2](2,7)NAPHTHALENOPHANE

Rodger W. Griffin Jr.[1a] and Nancy Orr[1b]

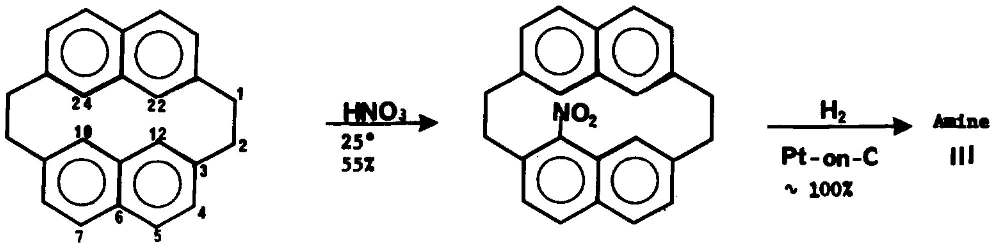
The William G. and Marie Selby Science Laboratory

Division of Natural Sciences, New College

Sarasota, Florida 33578

(Received in USA 31st July 1969; received in UK for publication 3rd October 1969)

One of the primary objectives in the investigation of meta-bridged aromatic compounds[2,3] has been the study of substituents and their reactions in the π-cloud. We now report the <u>direct introduction</u> of the nitro group into a π-cloud position of [2.2](2,7)naphthalenophane (I) and describe further transformations in this meta-bridged series.



I

II

These results are in striking contrast to those observed with [2.2]metacyclophane[4,5] its derivatives[6,7] and [3.2]metacyclophane-2-carboxylic acid.[8]

To date, only one investigation of [2.2](2,7)naphthalenophane (I) has been reported, which describes the synthesis and aromatization of I[9,10] The nmr of hydrocarbon I (in C_6D_6) shows absorption of <u>alpha</u> (d,2.30τ) and <u>beta</u> aromatic protons (d, 2.90τ), highfield aromatic protons as a singlet at 4.88τ, and $-CH_2-$(eq) and (ax) at 7.05 and 7.92τ. Although we have isolated only traces of the half-coupled, half-reduced compound reported by Baker et. al., the cyclic trimer [2.2.2](2,7)naphthalenophane, was isolated from the coupling reaction in 2.0% yield and showed nmr absorption ($CDCl_3$) at 3.02τ for the highfield aromatic protons and a sharp singlet, as expected, for the $-CH_2-$ (6.90τ).

We have found that nitration of hydrocarbon I in benzene-acetic acid under dilute conditions at room temperature affords at least six products; the major product (55% yield) is 10-nitro[2.2](2,7)naphthalenophane (II), obtained as yellow rhombic crystals, mp 217-218° (corr). The structure and spectra of the other products will be discussed in a full paper; however, it is noted here that 5-nitro[2.2](2,7)naphthalenophane was obtained in 15% yield as yellow cubic crystals, mp 240.0-241.5° (corr).

The structure of II was established by combustion analysis (Anal. Calcd for $C_{24}H_{19}NO_2$: C, 81.37; H, 5.42; N, 3.96. Found: C, 81.37; H, 5.66; N, 3.59), infrared (KBr) absorption of the $-NO_2$ bands at 6.5μ (1520 cm^{-1}) and 7.45μ (1390^{-1}), ultraviolet absorption maxima (95% EtOH) at 217 mμ (log 5.1) and 286 (3.8), and the nmr spectrum (C_6D_6): normal Ar-H (m, 8 H, 2.15-3.25τ), highfield aromatic protons at 3.85, 5.27 and 5.38τ, and $-CH_2-$ (m,8 H,7.10-8.02τ).[11] The absorption of three, distinct, single highfield aromatic protons unequivocally establishes the substitution of the nitro group on a carbon bearing a hydrogen atom in the π-cloud of I.

Catalytic reduction of II (Brown hydrogenator) produces the corresponding, air-sensitive amine III (ca. 100% yield, crude), whose structure was established by combustion analysis and spectral data. This represents an additional example of a simple transformation of a functional group in the π-cloud of a meta-bridged compound.[12,13] Of particular interest is the nmr spectrum ($CDCl_3$) of III, which clearly shows three single highfield aromatic protons (4.68, 4.90, and 5.13τ); the $-NH_2$ protons are hidden in the complex multiplets of the $-CH_2-$ region, but integration shows them to be present at ca 8.2τ. In contrast, the $-NH_2$ protons of 1-amino-2,7-dimethylnaphthalene absorb as a sharp singlet at 6.22τ ($CDCl_3$).[14,15] Further, the $-NH_2$ protons of 5-amino[2.2](2,7)naphthalenophane show nmr absorption ($CDCl_3$) at 5.97τ.

Many other reactions of 2,7-dimethylnaphthalene and of hydrocarbon I have been carried out and we are vigorously pursuing further studies in the naphthalenophane series since it is clear that the products from the reactions of I are quite different in character from those obtained from [2.2]metacyclophane.[16]

REFERENCES

1. (a) We are grateful for funds from ACS-PRF Grant #3385-B, which made possible this investigation.

   (b) This represents part of the work submitted by N. O. to the Division of Natural Sciences of New College in partial fulfillment of the requirements for the B. A. degree, May 1969.
2. R. W. Griffin Jr., *Chem. Revs.*, **63**, 45 (1963).
3. B. H. Smith, "Bridged Aromatic Compounds," Academic Press, New York, N. Y., 1964.
4. N. L. Allinger, M. A. DaRooge, and R. B. Herman, *J. Am. Chem. Soc.*, **83**, 1974 (1961).
5. M. Fujimoto, T. Sato, and K. Hata, *Bull. Chem. Soc. Japan*, **40**, 600(1967).
6. N. L. Allinger, B. J. Gorden, S-E. Hu, and R. A. Ford, *J. Org. Chem.*, **32**, 2272 (1967).
7. T. Sato, S. Akabori, S. Muto, and K. Hata, *Tetrahedron*, **24**, 5557 (1968).
8. R. W. Griffin and R. A. Coburn, *J. Org. Chem.*, **32**, 3956 (1967).
9. W. Baker, F. Glockling, and J. F. W. McOmie, *J. Chem. Soc.*, 1118 (1951).
10. We wish to acknowledge several private communications from R. A. Coburn (to R.W.G.), June 1964, which describe preliminary, small-scale work in this series.
11. We are deeply indebted to Prof. Erich Blossey of Rollins College for his assistance in determining nmr spectra, which were obtained on a Varian T-60 spectrometer.
12. While this manuscript was in preparation, a report was published describing the substitution and transformation of substituents in the π-cloud of 5,13-dimethoxy[2.2]metacyclophane: V. Boekelheide, C. Ramey, E. Sturm, T. Miyasaka, and B. A. Hess, Jr., *J. Org. Chem.*, **34**, 1956 (1969).
13. Boekelheide has also recently reported several *rearrangements* of substituents in the π-cloud position of various [2.2]metacyclophane derivatives: (a) B. A. Hess Jr., A. S. Bailey, B. Bartusek, and V. Boekelheide, *J. Am. Chem. Soc.*, **91**, 1665 (1969).

    (b) V. Boekelheide and E. Sturm, *J. Am. Chem. Soc.*, **91**, 902 (1969). We attempted the thermal rearrangement of II at 400° for 15 min in a nitrogen-flushed evacuated capillary but found no significant changes in the compound.

14. Very few reactions of 2,7-dimethylnaphthalene have been reported in the literature.[15] We have studied this hydrocarbon and its derivatives as a model compound throughout this investigation and a complete discussion of our results will be reported in a full paper.

15. For example, nitration under oxidizing conditions: D. Kalman and U. Kramer, *Ber.*, **93**, 2316 (1960); halogenation: E. Clar and H. D. Wallenstein, *Ber.*, **64B**, 2076 (1931); and Friedel-Crafts acylation: R. Lesser and G. Gad, *Ber.*, **60B**, 242 (1927).

16. ADDED IN PROOF: We wish to thank the referee who called our attention to P. G. E. Alcorn and P. R. Wells, *Aust. J. Chem.*, **18**, 1377 (1965) which describes the nitration of 1- and 2-methylnaphthalene. The latter hydrocarbon affords the 1-nitro isomer as the major product.