Tetrahedron Letters No. 22, pp 1921 - 1923, 1974. Pergamon Press. Printed in Great Britain.

Preparation of 9,10-Dimethylanthracene. Formation and Photocyclization of 1,2-bis(9'-anthranyl)ethanes

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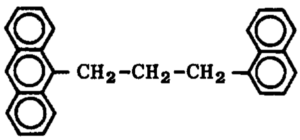
(Received in USA 13 February 1974; received in UK for publication 23 April 1974)

The recent report of Chandross and Schiebel[1] on the reversible photocyclization of 1-(9-anthranyl)-3-(1-naphthyl)propane (1) prompts us to report similar findings on 1,2-bis(10'-methyl-9'-anthryl)ethane (2). Our original interest lay in the synthesis of 9,10-dimethylanthracene (3) and the procedure selected was that of Badger and Pearce.[2] In that procedure, 9-methyl-10-iodomethylanthracene (4-I) is synthesized from anthraquinone and then reduced with stannous chloride in acidic p-dioxane. In our hands, a side product reported by Badger and Pearce to be 2 was the predominant product isolated. Although the white solid possessed the correct molecular formula $C_{32}H_{26}$ (by elemental analysis, mass spectrum, and Rast's method), the color and spectral evidence did not support structure 2. The PMR spectrum of the product (δ 2.2, 3H, s; 2.7, 2H, s; and 6.7-7.7, 8H, m) and



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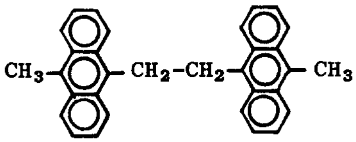

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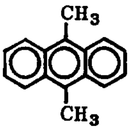

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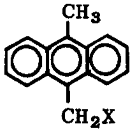

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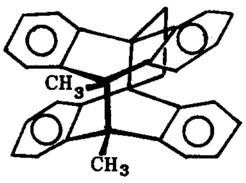

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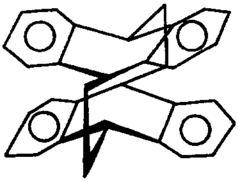
the UV spectrum [λ max 274 nm (ε 2160) and 265 nm (ε 1950)] suggested structure 5 for the product, the result of a (4πs + 4πs) photocyclization of 2 caused by ordinary light in the laboratory.[3] When 2 was prepared[5] by coupling of 4-Cl with magnesium and allowed to stand in the laboratory, the yellow material rapidly turned white. Beckwith and Waters do not report this phenomenon; perhaps the light qualities and intensities in the laboratories in Oxford in 1955 and in Boulder in 1972 differed considerably.

Chandross and Schiebel reported that 1 was photocyclized when irradiated in highly dilute solutions with light of wave length greater than 350 nm, and that 70% of the original intensity of the absorption spectrum of 1 was restored upon irradiation at 254 nm. When an 0.01 M solution of 5 in tetrahydrofuran was irradiated at 254 nm, about 5-10% of the intensity of the spectrum[5] for 2 was restored. However, 5 was readily converted to 2 upon heating to just below its decomposition temperature (305°).

Related to these results are those of Golden[6] on paracyclophane 6 undergoes a similar intramolecular photochemical (4πs + 4πs) addition. Similarly, Weinshenker and Greene[7] have isolated the cyclopropanol 7, formed upon irradiation of 9,9'-dianthrylcarbinol (8) in dioxane. Some time ago, Roitt and Waters[8] reported that treatment of 9-methylanthracene with benzoyl peroxide gave a yellow solid [the anticipated 1,2-di-9'-anthrylethane (9)], as well as a white substance



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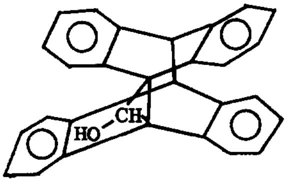

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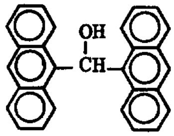

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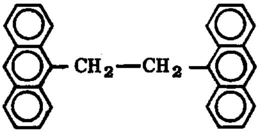

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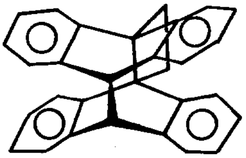

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with the same analysis, for which they proposed a dimeric structure. Based upon our results on 2 and 5, we propose structure 10 for the Roitt and Waters compound.

As stated earlier, our initial interest was in a convenient synthesis of 9,10-dimethylanthracene (3). The following procedure is to be recommended. 4-I is made by the procedure of Badger and Pearce[2] by treatment of 9,10-anthraquinone with excess methylmagnesium iodide followed by treatment with concd hydriodic acid, or the analogous chloride (4-Cl) by use of concd hydrochloric acid. Either halide is reduced with excess sodium borohydride in dimethylformamide. The product may be readily purified by chromatography on alumina and elution with hexane. Yields range from 68-79% (based upon anthraquinone).[9]

Acknowledgment: The authors are indebted to the National Science Foundation for support of this work via grant GP-8913X.

REFERENCES AND FOOTNOTES

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2. G. M. Badger and R. S. Pearce, *J. Chem. Soc.*, 2314 (1950).
3. It is of interest that Lalonde and Calas, who made a detailed study[4] of dimerization of anthracenes analogous to the 2 → 5 transformation, reported that 9,10-dialkylanthracenes did not photodimerize, presumably due to steric strain. This restriction apparently does not hold in intramolecular photocyclization.
4. R. Lalonde and R. Calas, *Bull. Soc. Chim.*, 144 (1960).
5. A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1108 (1956).
6. J. H. Golden, *ibid.*, 3741 (1961).
7. N. M. Weinshenker and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 506 (1968).
8. I. M. Roitt and W. A. Waters, *J. Chem. Soc.*, 2695 (1952).
9. G. A. Russell and S. A. Werner, *J. Org. Chem.*, **31**, 248 (1966), have reported that 9,10-dimethylanthracene (3) can be made readily by treatment of anthracene with the sodium salt of dimethylsulfoxide in DMSO. In our hands, the yields obtained were low and the product work-up difficult.