9,10-DEWAR-ANTHRACENE

Wolfgang Pritschins and Wolfram Grimme^{*} Institut für Organische Chemie der Universität zu Köln Greinstraße 4, D-5000 Köln, Germany

Summary: The title compound $\underline{8}$ has been synthesized and the kinetic parameters of its aromatization have been measured. In the key-step of the synthesis 3,6-dihydrobenzocyclobutadiene is used, a new and powerful diene that cycloadds along its axis.

The bicyclo[2.2.0]hexadiene structure, visualized by J. Dewar^[1] as one of several possible structures for a $C_{6}H_{6}$ hydrocarbon two years after Kekulé's structure elucidation of benzene, was never considered an alternative for the benzene hexagon. For anthracene, on the other hand, the analogous 9,10-Dewar structure with a para bond, originated by Graebe and Liebermann, was used well into the present century. The quinoid structure, first proposed by Armstrong^[2], met doubts until it was proved by refractometry in 1920^[3]! Within the last twenty years Dewar isomers of benzene, naphthalene and anthracene have been prepared^[4] and their highly exothermic transformation into the Kekulé structure of anthracene, however, became only known recently in form of some derivatives^[5].

We now report on the synthesis of the parent compound <u>8</u> (scheme 1): A straightforward synthetic concept for 9,10-Dewar-anthracene would consist in the Diels-Alder reaction of phthalic anhydride with benzocyclobutadiene followed by an oxidative bisdecarboxylation. Phthalic anhydride, however, is no dienophile and benzocyclobutadiene performs badly as a diene and not so along its axis ^[6]. Nevertheless, we could use this naive approach by activating

both reaction partners by the same method, i.e. the reversible interruption of their aromatic sextets by 1,4-dihydrogenation. The activated dienophile 3,6dihydrophthalic anhydride (1), already exploited by Alder ^[7], served also for the synthesis of the activated diene, 3,6-dihydrobenzocyclobutadiene. Photoaddition of 1,2-dichloroethene to 1 gave the three isomeric tricyclic anhydrides $\frac{2}{2}$ [8], which were hydrolysed to the diacids and bisdecarboxylated with lead tetraacetate to the 1,2-dichloro-3,6-dihydrobenzocyclobutene stereoisomers 3 (50%). Treating the dichlorides with diiron nonacarbonyl by the standard procedure [9] led to 3,6-dihydrobenzocyclobutadiene iron tricarbonyl $(\underline{4})$ (48%), which was oxidized in the presence of 3,6-dihydrophthalic anhydride (1) with ceric ammonium nitrate in acetone. The thus generated 3,6-dihydrobenzocyclobutadiene cycloadded to the dienophile 1 along its axis to give adduct 5 (43%). The two aromatic sextets were reestablished successively into the para bonded skeleton of 5 by (1) dehydrogenation with dichloro-dicyano-p-benzoquinone (DDQ) yielding $\underline{6}$ (95%), (2) bisdecarboxylation with lead tetraacetate to produce 7 (10%) and (3) a second dehydrogenation with DDQ that afforded the

title compound 8 (86%).

Scheme 1



Physical Data of $\underline{3}$, $\underline{4}$, $\underline{5}$, $\underline{6}$, $\underline{7}$ and $\underline{8}$

- 3 (trans); mp 46°; δ^{CC1} 4 5.78 (2H,s), 4.78 (2H,s), 2.68 (4H,s).
- <u>4</u> mp 17^o; m/e 244 (M⁺), 216 (M⁺-CO), 188 (M⁺-2CO), 160 (M⁺-3CO), 132 (C₆H₄Fe⁺) 56 (base, Fe⁺); ν^{film} 2035, 1900, 1640, 1435 cm⁻¹; δ^{CCl}4 5.72 (2H,s), 3.90 (2H,s), 2.88 (4H, AB, Δν 20 Hz, J 18 Hz).
- 5 mp 179°; m/e 210 (M⁺-CO₂), 77 (base); ν^{KBr} 1855, 1780, 1205, 920 cm⁻¹; δ^{CDC1_3} 5.97 (2H,t), 5.70 (2H,s), 3.38 (2H,s), 2.62 (4H,s), 2.55 (4H, AB, $\Delta\nu$ 30 Hz, J 15 Hz).
- $\frac{6}{(\epsilon \ 1000)}, \frac{1}{267} (\text{dec.}); \text{ m/e } 252 (\text{M}^+), 198 (\text{M}^+-\text{C}_4\text{H}_6), 179 (\text{base}); \lambda_{\text{max}}^{\text{acetonitrile } 261 (\epsilon \ 1000), 267 (1450), 274 (1400); \nu^{\text{KBr}} 1855, 1785, 1205, 920 \text{ cm}^{-1}; \delta^{\text{CDCl}} 3 7.30 (4\text{H}, AA'BB', J+J' 7.8 \text{Hz}), 6.09 (2\text{H}, t), 3.89 (2\text{H}, s), 2.64 (4\text{H}, AB).$
- <u>7</u> δ^{CC1}4 6.93 (4H,s), 5.56 (2H,s), 4.36 (2H,s), 2.60 (4H, AB).
- <u>8</u> mp 73[°] (dec.); λ_{max}^{hexane} 263 (ϵ 2000), 271 (3500), 277 (4000); $\delta^{CC1}4$ 7.05 (8H,m), 5.00 (2H,s); ¹³C-NMR, 75.5 MHz, $\delta^{acetone-d}6$ 149.07, 127.70, 124.19, 52.47; ¹H-NMR, 300 MHz, $\delta^{acetone-d}6$ 7.253, 7.149 (AA'BB', J_{AB} 7.26 Hz, J_{AB} , 0.90 Hz, J_{AA} , 0.93 Hz, J_{BB} , 7.57 Hz), 5.088 (s).

Crystalline 9,10-Dewar-anthracene is stable at room temperature and reverts violently, in a sealed tube under argon, to the crystalline Kekulé isomer at 73° C. In solution, the rearrangement takes place readily at 20° C. Its progress was monitored in degassed dodecane solution at seven temperatures between 25° and 50° C by registration of the increasing anthracene adsorbtion at 382 nm. Kinetic analysis for a first order reaction gave the Arrhenius equation

$$\log k = (12.22 \pm 0.41) - (21600 \pm 600)/2.303 \text{ RT}$$

The activation parameters $\Delta H^{\ddagger} = 21.0 \text{ kcal/mol}$ and $\Delta S^{\ddagger} = -4.7$ eu fall into the narrow range of 21 -24 kcal/mol and -5 - +3 eu, respectively, found for other Dewar isomers of aromatic hydrocarbons without a substituent at the bridgehead; they indicate that neither the heat of aromatisation nor the potential

resonance stabilisation of one centre of the intermediate diradical as a pentadienyl, cinnamyl or benzhydryl system have much influence on the transition state of these rearrangements.

Acknowledgement: We thank the Verein der Freunde und Förderer der Universität Köln for stringless financial support.

REFERENCES AND NOTES

- [1] J. Dewar, Proc. Roy. Soc. Edinburgh 1867, 84; cf. W. Baker, Chem. Brit. 1965, <u>1</u>,191.
- [2] H. E. Armstrong, Proc. Chem. Soc. 1890, <u>6</u>, 101.
- [3] K. von Auwers, Chem. Ber. 1920, 53, 941.
- [4] (a) E. E. van Tamelen, S. P. Pappas and K. L. Kirk, J. Am. Chem. Soc. 1971, <u>93</u>, 6092; (b) R. N. McDonald, D. G. Frickey and G. M. Muschik, J. Org. Chem. 1971, <u>37</u>, 1307; (c) N. C. Yang, R. V. Carr, E. Li, J. K. McVey and S. A. Rice, J. Am. Chem. Soc. 1974, <u>96</u>, 2297.
- H. Hart and B. Ruge, Tetrahedron Lett. 1977, 3143; (b) W. Pritschins and W. Grimme, Tetrahedron Lett. 1979, 4545; (c) H. Güsten, M. Mintas and L. Klasinc, J. Am. Chem. Soc. 1980, <u>102</u>, 7936.
- [6] M. P. Cava and M. J. Mitchell, J. Am. Chem. Soc. 1959, <u>81</u>, 5409.
- [7] K. Alder and K. H. Backendorf, Chem. Ber. 1938, <u>71</u>, 2199.
- [8] T. Tsuji, Z. Komiya and S. Nishida, Tetrahedron Lett. 1980, 3583.
- [9] R. Pettit and J. Henery, Org. Synth. 1970, <u>50</u>, 21.

(Received in Germany 29 December 1981)

1154