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A TRIMERIC $C_{48}H_{30}$ HYDROCARBON OF UNUSUAL STRUCTURAL INTEREST DERIVED FROM 9,10-DIHYDRO-9,10-ETHENOANTHRACENE

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Although the acidity of the vinyl proton is recognized (1), little use of this property has been made in preparative organic chemistry except when the ethylenic function is substituted by one or more chlorines (2). Among the few recent examples are the deuterium labeling of benzobarrelene (3) and the metalation of norbornadiene (4). We have found that 9,10-dihydro-9,10-ethenoanthracene (Ia), its 11-chloro (Ib) and 11-carboxylic acid derivative (Ic) may be metalated in excellent yield at the vinyl proton positions in tetrahydrofuran at -70° by treatment with butyl lithium. Carbonation gives, respectively, the known acid IIa (5), m p 250-51°, the chloro acid $C_{17}H_{11}ClO_2$*,IIb, m p 260-261° and the known dicarboxylic acid IIc (6) m p 255°, in over 75% yield. The structure of IIb was indicated by the nmr spectrum (DMSO) (acidic proton region; 10.1 ppm, 1H: aromatic region, A_2B_2 pattern centered at 7.16 ppm, 8H: benzylic region; singlets at 5.7 ppm, 1H and 5.1 ppm, 1H) and the found mass spectral molecular weight of 262. Exchange in Ib of the vinyl proton by lithium rather than chlorine is not entirely unexpected in view of the work of Köbrich (2) which shows, for example, proton-lithium exchange at the α-position of vinyl chloride at low temperature. If, however, reaction of Ib with butyl lithium is run at 25° rather than -70° (initial cooling is necessary), the yield of acid is greatly decreased and the Fittig type coupling reaction intervenes. From the neutral

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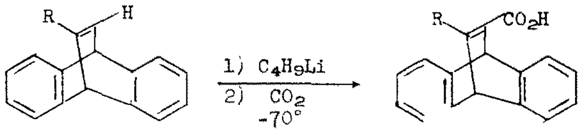
*Analytical data were in good agreement with the molecular formula indicated. nmr at 60 MHz.

fraction of 30% yield of a chlorine containing compound and a much smaller amount of a hydrocarbon can be isolated. The chlorine containing compound, mp 268°, was shown to be the dimeric $C_{32}H_{21}Cl$ (III) by its nmr spectrum ($CDCl_3$) (aromatic + vinyl region, 7.42-6.85 ppm, 17H: benzylic region; H at C_9', doublet centered at 5.75 ppm, J = 1 Hz; H at C_{10}', doublet centered at 5.15 ppm, J = 7 Hz; H's at C_9 and C_{10}, singlets at 5.06 and 4.98 ppm) and the mass spectral molecular weight of 440. The hydrocarbon, $C_{46}H_{30}$, which could readily be separated and purified because of its high insolubility must be the structurally fascinating Byzantine molecule IV. The structure of this ethenoanthracene trimer was established by its high resolution mass spectrum showing a prominent $M^{\dagger}$ 606.235 (theor. for $C_{48}H_{30}$: 606.2347) and an intense fragment ion at m|e = 428 representing the loss of anthracene presumably by a retro Diels-Alder type mechanism, and its nmr spectrum (DMSO at 160° to keep in solution) (aromatic region; A_2B_2 pattern centered at 7.25 ppm, 24H: benzylic region; singlet at 6.30 ppm, 6H). The considerably downfield position of the bridgehead proton signal from that of the model trypticene (5.65 ppm) is undoubtedly due to steric compression. The uv spectrum of IV (CH_3CN for solubility purposes) (max: 241 mμ, log ∈ 4.42; 263 mμ, log ∈ 4.21) is in general similar to that of trypticene (CH_3CN) (max: 269 mμ, log ∈ 3.52; 277 mμ, log ∈ 3.64) but with a hypsochromic and hyperchromic shift. A most striking property of IV is its high melting point and thermal stability. It melts in a sealed tube at 580° with some sublimation and may be repeatedly remelted after cooling without any noticeable darkening of the colorless crystals.

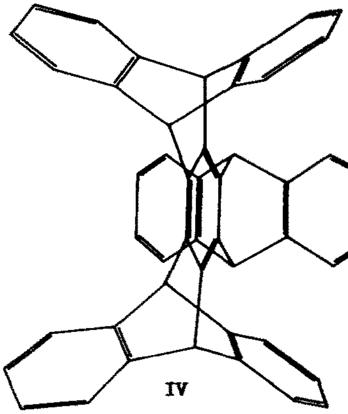
The structure IV was further supported by the preliminary results of an X-ray structure analysis now in progress. Colorless prisms belonging to the orthorhombic system and containing compound IV in a 1:1 ratio with chlorobenzene were obtained from chlorobenzene solution (presence of C_6H_5Cl demonstrated mass spectrally and by microanalysis). Crystal data are a = 17.10 Å, b = 21.20 Å, c = 10.62 Å, Z = 4, ρ_{exp} = 1.23 g|cm³, ρ_{calc} = 1.24 g|cm³ for $C_{46}H_{30} \cdot C_6H_5Cl$, space group Cmcm, Cmc2 or C2cm (systematic extinctions observed for hkl when h+k odd and hol when l odd). These systematic extinctions coupled with the observed fact that Z = 4 requires that the $C_{48}H_{30} \cdot C_6H_5Cl$ unit be placed in a uniquely determined special position in the unit cell of each of the three possible space groups and that it adopt the crystallographic symmetry of this respective position. In

Cmcm the molecular symmetry must be at least mm (i.e. two mutually perpendicular mirror planes) while in the latter two possibilities the minimum symmetry is reduced to m (one mirror plane). In either case the chlorobenzene can be placed on the mirror planes in such a way that it conforms to the crystallographic symmetry and to packing requirements of the molecule. Thus, the $C_{48}H_{30}$ hydrocarbon IV has been shown to have a minimum symmetry of m. It is believed at the present time that the correct space group is Cmcm (molecular symmetry mm). This point and the full symmetry of the molecule will be revealed only by successful refinement of the structure.

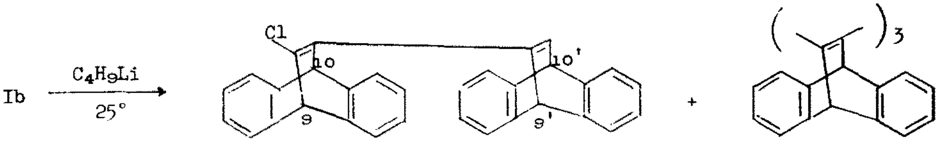


Ia, R = H
Ib, R = Cl
Ic, R = CO_2H

IIa, b, c



IV



III

IV

The experimental measurement of the thermodynamic acidities of ethylenes is a meagerly studied subject. Since the ethenoanthracenes I may be metalated in excellent yield, such a study becomes possible. For example, following Conant and Wheland (7), equilibration of the lithium salt of Ia with the hydrocarbon Ib in tetrahydrofuran at -70° followed by carbonation and analysis of the mixture of IIa and b (vpc separation of the trimethylsilyl derivatives on a 6 foot Chromosorb G column coated with 5% methylsilicone at 270°) shows the chlorine substituted ethylene Ib to be more acidic than the parent Ia by 3.0 pKa units.

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