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'LEPIDOPTERENE' AND ITS DIMETHYLDERIVATIVE ; FORMATION OF THREE σ BONDS THROUGH FORMAL $5\pi_s + 5\pi_s$ THERMAL CYCLOADDITION

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Summary : In contrast to previous reports [2,3,7,8], the colourless products obtained in the preparation of 1,2 bis (9'-anthranyl) ethanes are not the photoisomers 4 but new polycyclic compounds of type 3 which we propose to call lepidopterenes [1] , on account of their suggestive shape.

It is possible to obtain 1,2-bis (9' anthranyl) ethane 2a in several ways, among which are the action of peroxides on 9-methylanthracene [2a] and the action of grignard reagents on 9-halogenomethylanthracenes [3,4]. In every case, the yellow compound 2a is accompanied by one or two unexpected colourless compounds [5] which give 2a on melting. Waters [2] assigned the structure 4a to one of the compounds, assuming it to be the photoisomer of 2a ; the other compound, he believed, was a polymer. Stewart [3] found only one colourless derivative, which, he believed, was a photodimer of 2a, but Livingston [6] showed it to be the photoisomer 4a.

When the grignard reaction is carried out on the methyl derivative of 1a, i.e. 1b [3,4] the main products are 2b and a white solid which was assigned the structure 4b by Stewart [3]. The same structure was recently attributed [7] to the white product isolated in the reaction of 9-iodomethyl 10-methyl anthracene with stannous chloride in acidic p-dioxane [8].

A few years ago, in order to prepare a sample of 2b [9] we repeated the grignard reaction with 1b and found a white side-product, different from 4b even when the reaction was carried out in the dark.

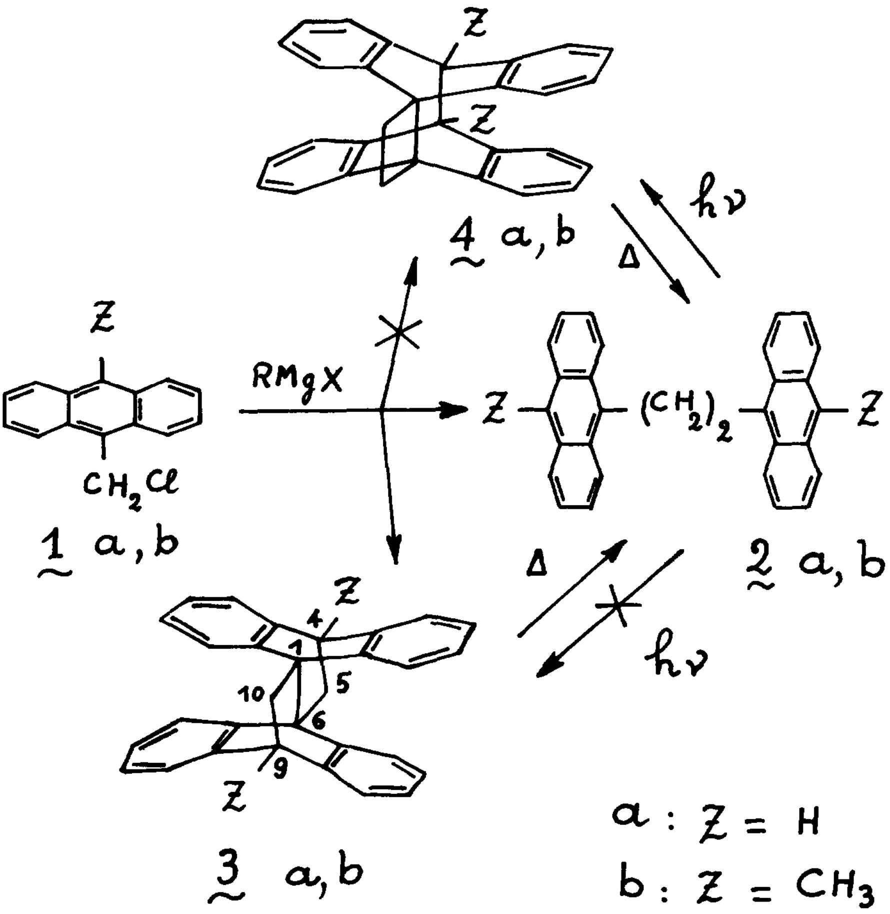
W.W. Henderson studied the reactions of 9-halogenomethyl anthracenes with grignard reagents. In 1962 he proposed in his thesis [4] the correct structure 3a and 3b for the white side products obtained. Probably for the lack of a definitive structure proof, his results were, to our knowledge, not published.

We report here spectroscopic evidence for the structure of 3a, 3b and a short discussion on the mechanism.

RESULTS

the parent compound : The reaction of 1a with MeMgI gave 2a (30 %) and 3a (35 %) which separated mechanically. Significant NMR data are given in table 1 ; the coupling between meso hydrogens (positions 4 and 9) and the methylene protons (positions 5 and 10) : $^3J_{HH} \simeq 3$ Hz is in accord with the formula 3a. A crucial proof of the structure was obtained by X-ray structural analysis[11]

(R factor : 3.4 %) ; an interesting feature is the considerable length (1.64 Å) of the bond C(1) - C(6).



In the solid state, both 3a and 4a are decomposed quantitatively into 2a when they are heated in an evacuated tube until all the material has melted ; however, in solution, the photoisomer 4a is readily converted to 2a at a temperature much lower than its melting point, in contrast to 3a.

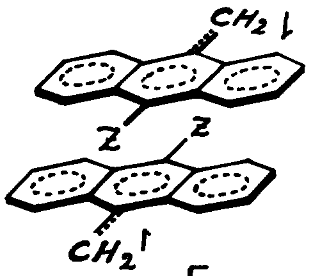
the methyl derivative : In the reaction of 1b with MeMgI, we obtained 2b (major product) and a small amount of a white product identified to 3b. The I.R. spectrum of 3b is different from that of 4b but superimposible upon that of the white product resulting from the reaction of 9-iodomethyl 10-methylanthracene with SnCl$_2$[8]. Evidence for the structure of 3b rests on analogy with 3a in the mode of preparation (grignard reaction) and NMR data : comparing the chemical shifts of the protons of the CH_2 groups (n° 5 and 10) underlined in table 1 leaves little doubt in our minds that the structure of 3b is as indicated. Both, 3b and 4b are thermally convertible to 2b but 4b is much less stable in solution than 3b.

Table 1

	2a (320°C)	3a (298°C)	4a$^{\Delta}$ (320°C)
H(meso) n°9 CH_2 (n°5 and 10)	7,85 (s) 2 H 4.02 (s) 4 H	4.62 (t) 2 H 2.91 (d) 4 H $^3J_{HH} \simeq 3$ Hz	
	2b (271°C)	3b (345°C)	4b (305°C)
CH_3 (meso) CH_2 (n°5 and 10)	3.15 (s) 6 H 4.07 (s) 4 H	2.21 (s) 6 H 2.71 (s) 4 H	2.35$^{\neq}$ (s) 3.60$^{\neq}$ (s)

^{1}H chemical shift δ(ppm) ref TMS in $CDCl_3$ at 30°C , ≠ (in benzene)
obtained with a P.E.R 12 or a Varian A60A,
For 3 and 4 melting points are not sharp. $^{\Delta}$ 4a is not soluble enough.

DISCUSSION Preceding authors have considered anionic as well as radical mechanisms [3,4] to account for the formation of 2 and 3 . Although more work is required to elucidate the mechanism recent works on grignard reactions [12] suggest the intermediacy of free radicals. As a working hypothesis, we have represented two delocalized free radicals forming two types of sandwich complexes because of radical-radical singlet attraction in a pre-transition state (see below) : head-to-head coupling (6) should result in the formation of 2 which does not react any more



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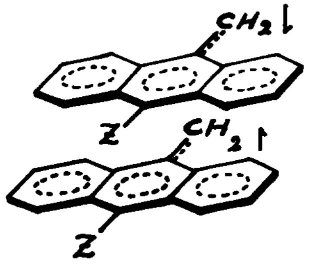

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thermally but photochemically by (4 + 4) cycloaddition ; head-to-tail coupling (**5**) should generate **3** in one or two steps.

In any case, this reaction provides a new type of formal $5\pi_s + 5\pi_s$ cycloaddition resulting in the formation of three σ bonds. We are investigating the scope and mechanism of the reaction.

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(1) According to IUPAC nomenclature rules, the parent compound should be named : 2,3 : 7,8 : 11, 12 : 13, 14 - tetrabenzotetracyclo$[4.4.2^{1,4}.2^{6,9}.0]$ tetradeca 2,7,11,13 - tetraene.

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