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HELICENES: AN INTRAMOLECULAR INSERTION REACTION INVOLVING THE HELICENE SKELETON

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Abstract—1-Formyl[6]helicene tosylhydrazone (**1a**) heated in benzene solution in the presence of NaH gave a carbene insertion product, whose structure (2) was determined by ^{1}H and ^{13}C-NMR spectroscopy and fully confirmed by an X-ray diffraction study carried out by A. Van Meerssche *et al.* The resolution of the new hydrocarbon (2) has been achieved by hplc, using a silica-gel column impregnated with (-)TAPA.

We wish to report briefly a third type[1,2] of a chemically induced modification of a [6]helicene skeleton, namely: an intramolecular carbene insertion reaction.

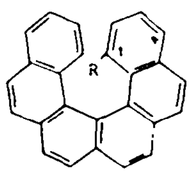
1-Formyl[6]helicene tosylhydrazone (**1a**) was planned to be used for the production of carbene **1c** from the corresponding anion **1b**.

In the course of this work, we have observed the formation of a new hydrocarbon $C_{27}H_{16}$ (M^+ for *m/e* 340) in the reaction step leading to the tosylhydrazone. The same hydrocarbon is also formed very slowly by refluxing a benzene/ethanol solution of the isolated tosylhydrazone. The mass spectrum of this tosylhydrazone shows no molecular ion; the first ion in the high mass region (*m/e* 340) corresponds to the loss of $C_7H_8N_2O_2S$ (−184).

The new product is however best prepared (75% yield) by refluxing the tosylhydrazone (**1a**) in benzene solution in the presence of NaH.

To our surprise, the $C_{27}H_{16}$ hydrocarbon 2, was also isolated, as a by-product, after reduction of 4-bromo-1-menthyloxycarbonyl[6]helicene (3) with $LiAlH_4$ followed by $LiAlH_4 + AlCl_3$ in ether at room temperature. The hydrocarbon 2 was fully characterized by its NMR spectrum. This skeletal rearrangement may involve, like the rearrangement of 7-substituted norbornadienes described by Franzus and Snyder,[3] a hydride transfer to one of the cyclic double bonds. A speculative hypothesis along this line, which could be studied using $LiAlD_4$, is shown in Scheme 1.†

The structure of the (dl)$C_{27}H_{16}$ hydrocarbon (2), an isomer of the spirohydrocarbon obtained by acid treatment of 1-hydroxymethyl[6]helicene,[1] was determined by ^{1}H and ^{13}C-NMR spectroscopy and fully confirmed by an X-ray diffraction study kindly carried out by Professor A. Van Meerssche *et al.* (personal communication). Catalytic hydrogenation of 2 (H_2; 5% Pd/C; C_6H_6) gave the corresponding 5,6-dihydro derivative (M^+ for *m/e* = 342), the UV spectrum of which is very similar to the UV spectrum of benzo[c]phenanthrene.

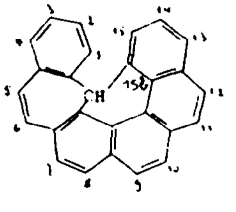


1

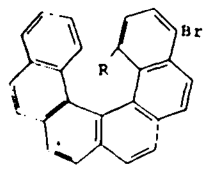
a R= $-CH{=}N{-}\overset{(-)}{N}HTs$

b R= $-CH{=}N{-}\overset{(-)}{N}Ts\ \overset{(+)}{Na}$

c R= $-CH:$

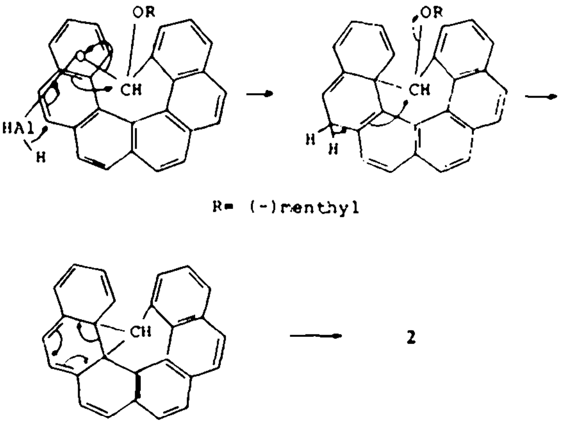


2



3

R= (−)-CO_2menthyl



Scheme 1. $3\ LiAlH_4 + AlCl_3 \longrightarrow 3\ LiCl + 4\ AlH_3$

^{1}H *and* ^{13}C*-NMR spectra**

The ^{1}H-NMR spectrum of 2 contains 14 protons in the aromatic region and 2 isolated protons at 6.10 ppm (multiplet) and 5.17 ppm (singlet), respectively.

The ^{13}C-NMR spectrum shows that the only Csp^3 (δ = 45.36 ppm) is a tertiary C atom, the hydrogen of which resonates at 5.17 ppm (s). The twenty-six Csp^2 give signals located between 125.11 and 141.74 ppm.

The assignment of the protons and of their sequence in

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†Being short of material, we have unfortunately been unable, so far, to repeat and to study this reaction.

*Bruker HX90; CS_2; TMS = 0; ^{1}H 90 MHz; ^{13}C 22.63 MHz.

Table 1. ^{1}H-NMR spectrum of hydrocarbon 2

H	δ_{ppm}	J	H	δ_{ppm}	J
1	6.101	$J_{1-2} = 8.2$	9	7.725	
2	6.916	$J_{1-3} = 0.9$	10	7.725	
3	6.951	$J_{1-4} = 0.5$	11	7.765	$J_{11-12} = 8.6$
4	7.198	$J_{2-3} = 7.3$	12	7.847	
5	7.322	$J_{2-4} = 1.3$	13	7.821	$J_{13-14} = 8.2$
6	7.322	$J_{3-4} = 7.7$	14	7.538	$J_{13-15} = 0.8$
7	7.597	$J_{7-8} = 8.3$	15	7.299	$J_{14-15} = 7.4$
8	7.425		15b	5.173	$\nu_{\frac{1}{2}} = 2.5$

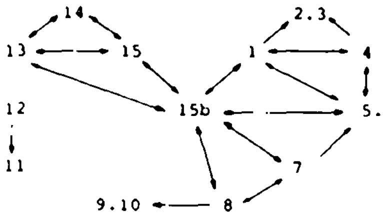

Fig. 1. Indor experiments on hydrocarbon 2.

the molecule was carried out by an Indor study (cf. Table 1 and Fig. 1.).

The spectrum consists of: one ABCD system which contains a strongly shielded proton (6.10 ppm; multiplet), one ABC system and four AB systems, two of which appear as singlets. The $C_{27}H_{16}$ hydrocarbon must be heptacyclic and structure 2 is fully compatible with the NMR data.

The Csp^3-$H_{(15b)}$ proton belongs to a cycloheptatriene ring and, at the same time, to a 1,12-methanobenzo[c]phenanthrene (or 6-H-benzo[c,d]pyrene) system. Benzylic couplings with $H_{(1,7,8,13 \text{ and } 15)}$ and ^{5}J couplings with $H_{(5 \text{ and } 6)}$ justify the width ($\nu_{\frac{1}{2}} = 2.5$ Hz) of the $H_{(15b)}$ signal.

The chemical shift of this proton ($\delta = 5.173$ ppm) is in the range expected for a H-C(Ar)$_3$ system.

The conformation of the hydrocarbon 2 fully justifies the shielding of $H_{(1)}$ and $H_{(15)}$, which experience the anisotropy of the terminal rings.

The chiral hydrocarbon 2 has been resolved by hplc using a silica-gel column impregnated with (-)TAPA following the technique described by Gil Av *et al.*[4] (S. H. Wilen, F. Geerts-Evrard and V. Libert, Brussels, personal communication).

We now plan to attempt to prepare the tropylium salt of the new heptacyclic hydrocarbon described in this communication.

EXPERIMENTAL

1-*Formyl*[6]*helicene tosylhydrazone* **1a**. A mixture of 1-formyl[6]helicene (0.645 g; 1.81 × 10^{-3} mol) and tosylhydrazine (1.860 g; 10^{-2} mol) in benzene-EtOH (3:2) was refluxed for 28 hr.

The product, purified by column chromatography [silica-gel (150 g); benzene] gave the following main fractions:

(a) 0.081 g (14%) M$^+$ for *m/e* = 340 ($C_{27}H_{16}$), m.p. 242–43° (1,2-dimethoxyethane). This product is identical to the product 2 described below.

(b) 0.139 g (21%) M$^+$ for *m/e* = 358 ($C_{27}H_{18}O$). The NMR spectrum of this compound is identical with the NMR spectrum of 1-hydroxymethyl[6]helicene (unpublished spectrum).

(c) 0.494 g (52%) M$^+$ − 184 for *m/e* = 340. m.p. 197–198° (acetonitrile). (Found: C, 77.9; H, 4.4; N, 5.5; S, 6.1. Calc. for $C_{34}H_{24}N_2SO_2$ (524): C, 77.84; H, 4.61; N, 5.34; S, 6.11%).

15b - H - *benzo*[c,d] - (*benzo*[6,7]*cyclohepta*) [1,2,3-f,g]*pyrene* (2). NaH (7.4 × 10^{-4} mol) was added to a soln of **1a** (0.190 g; 3.6 × 10^{-4} mol) in anhyd benzene (60 ml) and the mixture refluxed for 3 hr. The product was purified by column chromatography [silica-gel (50 g); benzene] and recrystallized from 1,2-dimethoxyethane, m.p. 242–243°, yield 0.09 g (75%); M$^+$ for *m/e* = 340. (Found: C, 95.5; H, 4.7. Calc. for ($C_{27}H_{16}$): C, 95.26; H, 4.74%).

5,6 - *Dihydro* - 15b - H - *benzo*[c,d] - (*benzo*[6,7]*cyclohepta*) [1,2,3-f,g] *pyrene*. The catalytic hydrogenation of 2 (10 mg) was carried out in benzene soln with 5% Pd/C as catalyst. M$^+$ for *m/e* 342 ($C_{27}H_{18}$). UV spectrum very similar to the UV spectrum of benzo[c]phenanthrene.

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REFERENCES

[1] R. H. Martin, J. Jespers and N. Defay, *Tetrahedron Letters* 1093 (1975).

[2] R. H. Martin, J. Jespers and N. Defay, *Helv. Chim. Acta* **58**, 776 (1975).

[3] B. Franzus and I. Snyder, *J. Am. Chem. Soc.* **87**, 3423 (1965).

[4] F. Mikes, G. Boshart and E. Gil Av, *J. Chem. Soc. Chem. Commun.* 99 (1976).