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THE PHOTOREARRANGEMENT OF THE OVERCROWDED HYDROCARBON 10,10a-DIHYDRO-9-METHYL-10,15-DIPHENYL-9H-BENZO[5,6]INDENO[2,1-c]PHENANTHRENE

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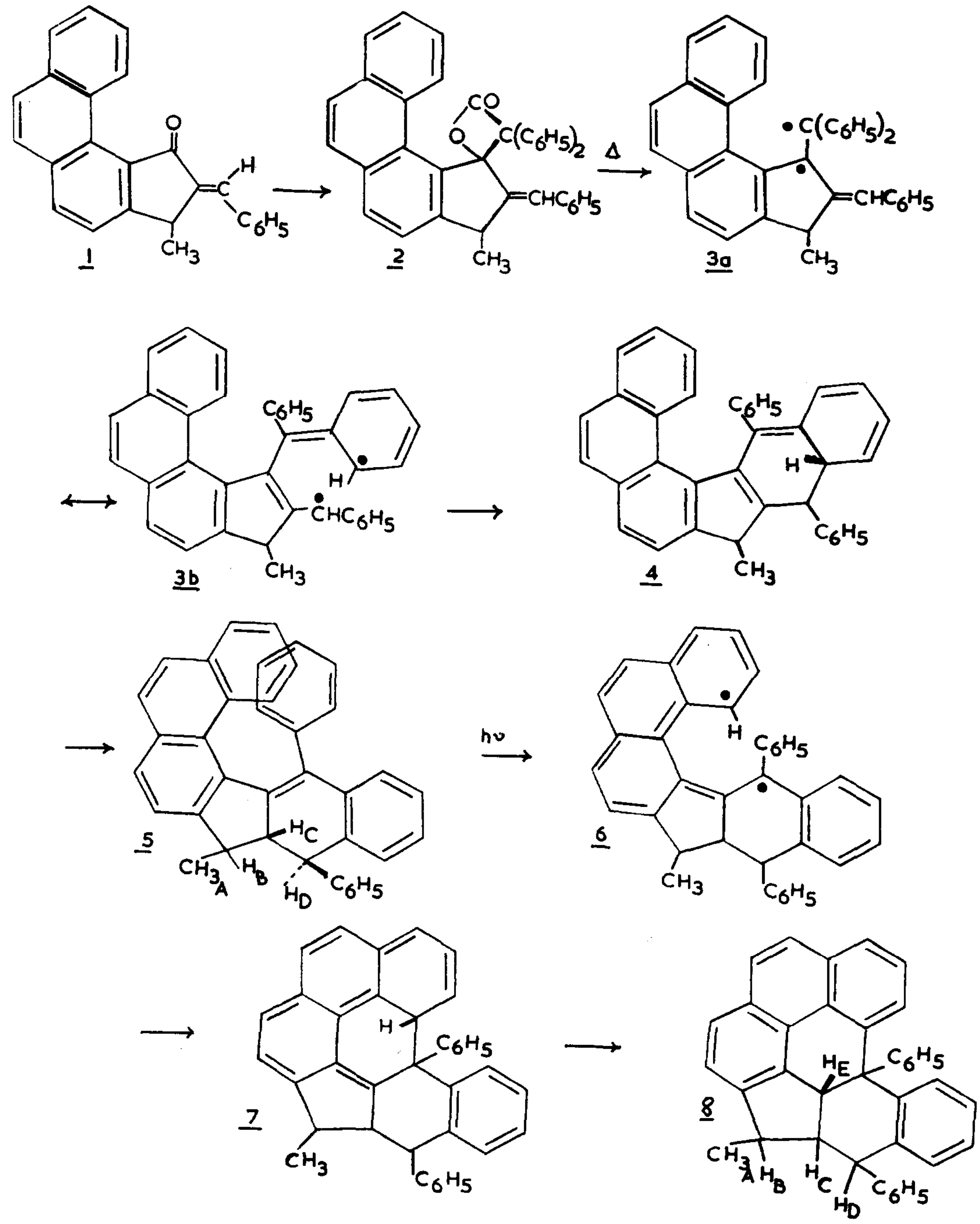
Recently we reported a number of intramolecular hydrogen transfer reactions of sterically hindered compounds[1]. We now wish to report the novel rearrangement reaction of the overcrowded hydrocarbon 10,10a-dihydro-9-methyl-10,15-diphenyl-9H-benzo[5,6]indeno [2,1-c]phenanthrene (5). 1-Oxo-2-benzylidene-3-methyl-cyclopenta[c]phenanthrene (1) reacts with diphenylketen at 180° to give the thermally unstable β-lactone (2), which eliminates carbon dioxide to give the excited state of 1-diphenylmethylene-2-benzylidene-3-methyl -cyclopenta[c]phenanthrene (3a,3b), which does not relax to the ground state as does 1-diphenylmethylene-2-benzylideneindane[2], but cyclises to the intermediate (4) which undergoes a 1,5-hydrogen shift through a six-membered transition state to yield the overcrowded hydrocarbon (5), bright yellow crystals with a green fluorescence, m.p. 231-232°. When this hydrocarbon in light petroleum is exposed to 366 mμ radiation, it rearranges to 5a,6,10b,13e-tetrahydro-5-methyl-6,10b-diphenyl-5H-cyclo-penta[def] naphtho[8,2,1-pqr]chrysene (8), colourless crystals with a blue fluorescence, m.p. 264-265°. This photorearrangement is pictured as activation of the hydrocarbon (5) to a low lying excited singlet state (6), followed by cyclisation to the intermediate (7), which undergoes a 1,5-intramolecular hydrogen shift through a six-membered transition state as outlined below.

The structures of hydrocarbons (5) and (8) follow from their n.m.r. and u.v. spectra. Both compounds gave satisfactory analyses.


O
H
C6H5
CH3
1
CO
O
C(C6H5)2
=CHC6H5
CH3
2
Δ
•C(C6H5)2
=CHC6H5
CH3
3a
C6H5
H
•CHC6H5
CH3
3b
C6H5
H
C6H5
CH3
4
HC
CH3A
HB
HD
C6H5
5
hν
H
C6H5
CH3
C6H5
6
H
C6H5
CH3
C6H5
7
HE
C6H5
CH3A
HB
HC
HD
C6H5
8

TABLE

N.m.r. and u.v. spectral data

		Compound (5)	Compound (8)
u.v.	λ_{max} mμ	245, 303, 318, 360, 375, and 395	268, 276, and 310
	(logϵ)	4.63, 4.14, 4.10, 4.10, 4.07, and 4.05	4.34, 4.31, and 3.83
n.m.r.			
H_A		τ 8.55 doublet	τ 8.14 doublet
H_B		6.90 quintet	6.00 quintet
H_C		6.18 quartet	6.52 multiplet
H_D		5.34 doublet	5.59 doublet
H_E		----	5.02 doublet
$J_{AB}=J_{BC}$		3.5 c./sec.	4.0 c./sec.
J_{CD}		4.75	6.3
J_{CE}		----	5.8

Double-resonance irradiation of hydrocarbon (5) at τ 5.34 caused H_C to become a doublet (J_{BC} = 3.5 c./sec.); at τ 6.18, H_D to become a singlet; and at τ 6.9, H_A to become a singlet and H_C to become a doublet (J_{CD} = 4.75 c./sec.). Double-resonance irradiation of hydrocarbon (8) at τ 5.02 caused the multiplet at τ 6.52 to become resolved into a quartet (J_{CD} = 6.3 c./sec., J_{BC} = 4.0 c./sec.). Irradiation at τ 6.52 caused H_D and H_E to become singlets; at τ 6.00, H_A to become a singlet; and at τ 8.14, H_B to become a doublet (J_{BC} = 4.0 c./sec.).

REFERENCES

1. H.G. Heller, D.Auld, and K. Salisbury, J. Chem. Soc., (C), 682, 1552, and 2457 (1967).
2. N.Campbell, P.S.Davison, and H.G.Heller, J. Chem. Soc., 993 (1963).