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THE CHEMISTRY OF PHENALENIUM SYSTEM. XIII.[1]
SYNTHESIS AND PROPERTIES OF 4H-CYCLOPENTA[cd]PHENALEN-4-ONE

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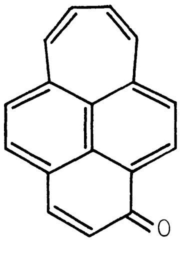
The synthesis of the title compound 3 from benzo-4,5-indan-3-one 4 is described. Upfield chemical shifts of the protons attached to the phenalenone moiety of 3 relative to those of the dihydro derivative 9 are interpreted in terms of an induced paramagnetic ring current in the periphery of this molecule.

Our previous papers[2,3] demonstrated that condensed tetracyclic conjugated ketones having a phenalenone skeleton such as 7H-cyclohepta[cd]phenalen-7-one 1 and 5H-cyclopenta[cd]phenalen-5-one 2 are regarded as peripheral [15]- and [13]annulenones, respectively, perturbed by the central ethylenic pi-system. In order to gain further insight into this proposal we have examined the synthesis and properties of 4H-cyclopenta[cd]phenalen-4-one 3 as the one of the other possible model compounds for perturbed [13]annulenone.



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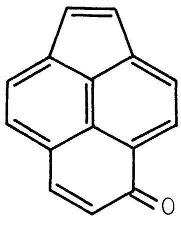

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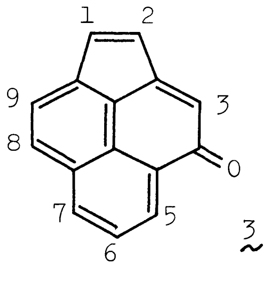

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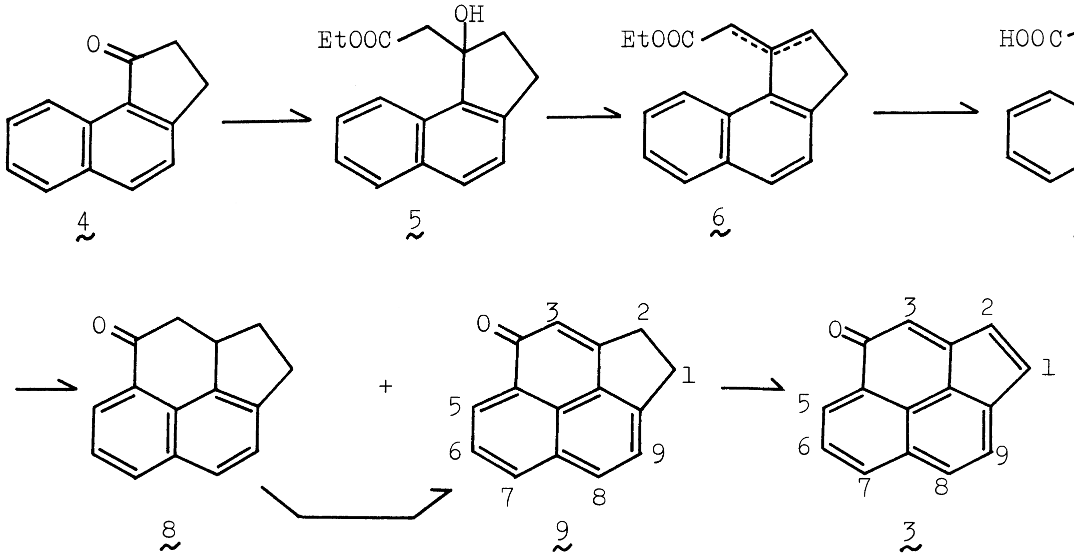
The following series of reactions [Scheme 1] were used for the preparation of 3. The Reformatsky reaction was used to convert benzo-4,5-indan-3-one 4[4] into the hydroxy-ester 5 which was in turn transformed into a mixture of the unsaturated esters 6 by dehydration with formic acid. Without isolation, hydrolysis of 6 with sodium hydroxide followed by hydrogenation in the presence of palladium-on-carbon gave the acid **7**, mp 70-76°C, ν 1700 cm^{-1}. The tetracyclic skeleton was constructed by cyclizing **7** with liquid hydrogen fluoride at room temperature for 2 hr. Two products were obtained by usual work-up followed by alumina column chromatography. The major product was obtained (60% yield) as colorless crystals, mp 149.5-150.5°C, whose physical constants were in good agreement with the expected ketone **8**. The minor product (5% yield), mp 150°C, m/e 206 (M^+, 6%) and 204 (100%), ν 1638 and 1590 cm^{-1}, was assigned to the unsaturated ketone **9** by its nmr spectral data [Table 1]. This ketone **9** was also obtained from **8** by treatment with chloranil in refluxing benzene. Full dehydrogenation of **8** and/or **9** could be carried out with excess 2,3-dichloro-5,6-dicyano-p-benzoquinone in refluxing benzene, affording **3** as dark-red needles (pet.benzine), mp 180°C, in 5% yield. Compound **3** exhibits infrared carbonyl bands (KBr) at 1650 and 1620 cm^{-1}. The electronic spectrum of **3** shows no solvent dependence for the band of the longest wavelength: λ_{max}(methanol), 213 nm (ε 40,500), 250 (sh, 17,000), 302 (11,700), 415 (sh, 4,600), 425 (4,700) and 490 (950); λ_{max}(cyclohexane), 215 (37,300), 268 (9,800), 300 (11,100), 405 (5,000), 410 (sh, 4,700), 430 (5,900) and 490 (920).

[Scheme 1]



If 4H-cyclopenta[cd]phenalen-4-one **3** hides a 12-pi-electron system, the nmr spectrum should indicate the presence of an induced paramagnetic ring current by resonances of the perimeter protons at relatively high fields. A reference compound for the evaluation of the ring current effect is the dihydro derivative **9**. The nmr spectral data on **3** and **9** in deuteriochloroform are summarized in Table 1. In completing the full conjugation by going from **9** to **3**, all the vinyl protons

Table 1. Nmr data on **3** and **9** in $CDCl_3$ at 100 MHz.

Chemical Shifts [δ-values]

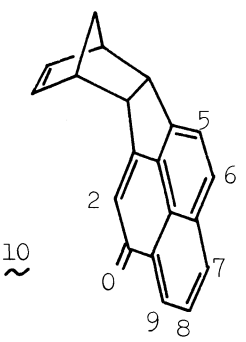
	H-1	H-2	H-3	H-5	H-6	H-7	H-8	H-9
9	- 3.04 -		6.56	8.50	7.72	8.14	7.32	7.96
3	6.74	6.31	6.38	7.96	7.22	7.72	7.22	7.56
Δδ[**9** - **3**]			0.18	0.54	0.50	0.42	0.10	0.40

Coupling Constants [Hz]

	$J_{1,2}$	$J_{5,6}$	$J_{6,7}$	$J_{8,9}$	$J_{5,7}$
9		8.3	8.5	8.6	0.5
3	5.5	8.0	8.3	8.4	0.5

moved upfield by 0.1-0.5 ppm as in the case of **2** [upfield shifts of 0.2-0.5 ppm].[2) Furthermore, the resonances due to the five-membered ring protons of **3** were shifted upfield by 0.4-0.8 and 1.0-1.4 ppm than those of acenaphthylene[5) and aceplei-adylene,[6) respectively. These fingings are reasonably interpreted in terms of the shielding effect due to the existence of an induced paramagnetic ring current in the periphery of this molecule. Although the conversion of **3** to the protonated species was expected in 96% sulfuric acid and in trifluoroacetic acid, we could not detect the ionic species in such conditions since **3** decomposed in these acids at room temperature.

The chemical test for the stability of **3** is the Diels-Alder reaction with cyclopentadiene. In a benzene solution, the reaction of **3** with cyclopentadiene was complete in only three hours even at room temperature. The adduct, obtained as yellow crystals, mp 148-149°C, in a quantitative yield, was assigned to be the endo [4+2]adduct **10** by its nmr spectral data. Thus the spectrum of adduct **10** shows multiplet centered at δ 1.82 (2H, $-CH_2-$), multiplets centered at 3.26 (2H, allylic) and 4.00 (2H, benzylic), an AB-quartet further split into doublets at 5.75 and 5.43 (J=6 and 2 Hz; vinyl), a singlet at 6.53 (1H, H-2), an AB-quartet at 7.44 and 7.93 (J=8.8 Hz, H-5 and H-6) and AMX-type signals at 7.68, 8.15 and 8.53 ppm ($J_{7,8}$=8.4 Hz, $J_{8,9}$=8.0 Hz, $J_{7,9}$=1.6 Hz; H-8, H-7



10

and H-9). It was shown by double-resonance experiments that the signals at 3.26 and 4.00 were coupled each other ($J \approx 4$ Hz), strongly suggesting the endo-configuration. The facility of this Diels-Alder reaction affords additional evidence that proceeding to a full conjugated system produces a significant decrease in its stability.

These experimental results presented in this paper are interpreted in terms of the paratropic nature of **3**, being in accord with the proposed peripheral electronic model such as perturbed [13]annulenone.$^{7)}$

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