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THE CHEMISTRY OF PHENALENIUM SYSTEM X1)

7H-CYCLOHEPTA[cd]PHENALEN-7-ONE. A MODEL COMPOUND OF PERTURBED [15]ANNULENONE*

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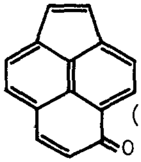
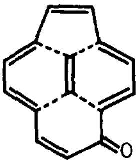
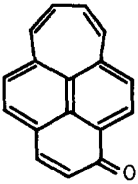
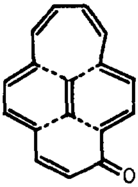
Polycyclic conjugated ketones are expected to be aromatic or nonaromatic if they possess a [4n+3] or a [4n+1] monocyclic array with an internal vinyl cross-link according to the idea2) of peripheral conjugation. One of the model compounds for such prediction is 5H-cyclopenta[cd]phenalen-5-one (1)3) where the molecule has a 13-membered ring ketone with an internal vinyl pi-system. Available experimental evidences clearly indicated that the compound (1) is best represented by perturbed [13]annulenone such as (1a).


(1)


(1a)


(2)


(2a)

In order to gain further evidence regarding the possible peripheral nature of condensed polycyclic conjugated ketones having a phenalene moiety, it appeared desirable to prepare a next higher vinylog containing [15]annulenone framework, 7H-cyclohepta[cd]phenalen-7-one (2) which should sustain a diamagnetic ring current in an applied magnetic field. We now describe the recognition of this purpose, that is, the synthesis and the properties of (2).

Tetrahydropleiadiene (3), prepared from tetralone according to the known procedure of Horton et. al.,4) was allowed to react at 0° with one mole equivalent of acetyl chloride in nitrobenzene in the presence of aluminum chloride. Usual work-up and distillation gave the acetyl derivative (4)5) in 73% yield. bp 160-

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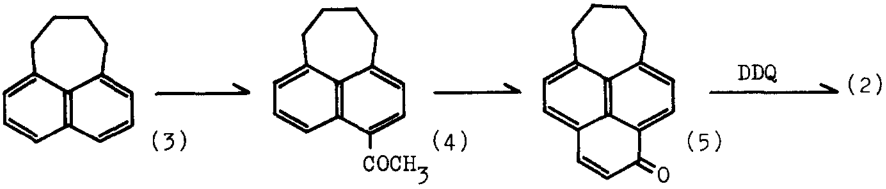
* This paper is dedicated to Emeritus Professor Tetsuo Nozoe in Commemoration of his 70th birthday.

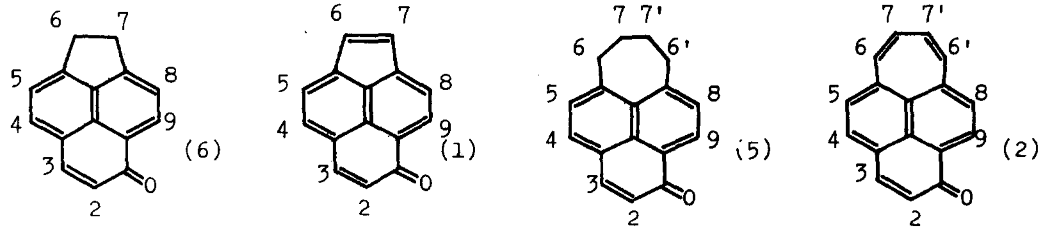
170°/2 mm Hg; $\nu_{C=O}$ 1675 cm^{-1}; δ, 1.8-2.05(m, 4H), 3.0-3.3(m, 4H), 2.50(s, 3H), 6.95-7.80(m, 5H). Treatment of (4) with sodium hydride in dry ether at 0°, and



then with one mole equivalent of ethylformate in dry ether at 35-40°, followed by 85% sulfuric acid at room temperature for 2 hr, gave the tetrahydro ketone (5)[5] in 48% yield as stable yellow crystals with mp 135-137°(from pet. ether-benzene). The nmr spectrum of (5) confirms the structure [see Table-1]. Compound (5) was treated directly with two mole equivalents of dichlorodicyano-p-benzoquinone in refluxing toluene under nitrogen atmosphere for 72 hr. Chromatography on alumina with ethanol-ether (1:10) as an eluting solvent afforded the desired fully unsaturated ketone (2)[5] in 25% yield as dark red needles with mp 193-194°: m/e 230 (M^+); $\nu_{C=O}(CHCl_3)$, 1625 cm^{-1}. The electronic spectrum of the ketone (2) in cyclohexane showed maxima at 214 nm(log ε 4.51), 242(4.34), 266(4.35), 281(4.33), 319 (3.76), 362(3.30), 452(s, 4.03), 473(4.16), 498(4.14), 508(4.08) and 529(3.85), but in methanol there was observed a considerable bathochromic shift on the long wavelength absorption : 217 nm(log ε 4.49), 238(4.34), 283(4.43), 325(s, 3.87), 358(s, 3.42), 503(s, 4.21), 523(4.23), 535(s, 4.24) and 566(4.12). The substantial solvent effect on the electronic spectrum coupled with a low carbonyl streching frequency of (2) is suggestive of highly polarized ground state.

Table-1 summarizes the nmr chemical shift data for the pertinent compounds.[6] Numbering shown in the Figures and the Tables of this paper is not in accord with the nomenclature but is used conveniently for the ready comparison of the chemical shift data. The nmr spectrum of (2) indicated the existence of a diamagnetic ring current, since all of the ring protons resonated at considerably lower magnetic field than those of the perturbed [13]annulenone, (1)[3] [downfield shifts of about 0.5-0.8 ppm except H-5 and H-8; see Table-1, Entry G]. In completing the full conjugation by going from the dihydro ketone (6) to (1), all the vinyl protons moved upfield by 0.2-0.5 ppm [Table-1, Entry-E].[3] On the other hand, however, the introduction of two double bonds into (5) causes the vinyl protons to shift downfield

Table-1. Nmr Spectra of the Ketones (5) and (2) Compared with the Models (6) and (1). (δ-values)



Entry		H-2	H-3	H-4	H-5	H-6(6')	H-7(7')	H-8	H-9
A	(6)	6.63	7.63	7.43	7.29	3.36	3.37	7.61	8.42
B	(1)	6.17	7.17	7.14	7.10	6.65	6.60	7.32	7.94
C	(5)	6.63	7.61	7.51	7.27	3.15-3.35	1.9-2.1	7.46	8.48
D	(2)	6.95	7.80	7.64	7.17	6.8-7.0	6.2-6.4	7.34	8.58
E	Δ(6-1)	+0.46	+0.46	+0.29	+0.19			+0.29	+0.48
F	Δ(5-2)	-0.32	-0.19	-0.13	+0.10			+0.12	-0.10
G	Δ(1-2)	-0.78	-0.63	-0.50	-0.07			-0.02	-0.64

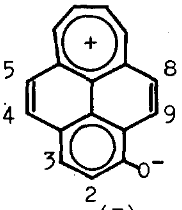
by 0.1-0.3 ppm [Table-1, Entry-F, except H-5 and H-8]. The most plausible explanation suggests that these downfield shifts arise from deshielding due to the existence of a diamagnetic ring current in the periphery of (2). Furthermore, the chemical shifts of seven-membered ring protons in the present ketone (2) are lower field than those of acepleiadiene [δ, 5.05 and 5.73 ppm]7) but are similar to those noted in the peripheral 14-pi system, acepleiadylene [δ, 6.79 and 6.85 ppm].7) These fingings are presumably attributable to the diamagnetic ring current effect expected in this ketone (2).

As expected, the diamagnetic ring current is enhanced when (2) is protonated. The nmr spectrum of (2) in trifluoroacetic acid [Table-2, Entry-A] shows downfield shifts for the all vinyl protons of 1.2-1.5 ppm as compared with that in deuteriochloroform [Table-2, Entry-D]. Again, it can be seen that the ketone (2) exhibits substantial downfield shifts (0.3-0.7 ppm) relative to the corresponding tetrahydro-derivative (5) [Table-2, Entries-A, B and C]. Differences in the chemical shifts between the neutral and the protonated species of (2) are even larger than those of (5).

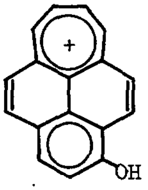
In order to determine to what extent the diene moiety in the seven-membered ring of (2) would behave as an aliphatic diene we have examined the reactivity of (2) to maleic anhydride. Although the reaction of maleic anhydride with acepleiadiene in boiling benzene was complete in 3 days,[8] with the present ketone (2) there was no reaction after six days.

Table-2. Nmr Spectra of (2) and (5) in CF_3COOH (δ-values)

Entry		H-2	H-3	H-4	H-5	H-6(6')	H-7(7')	H-8	H-9
A	(2)	8.31	9.11	9.15	8.71	8.9-9.1	8.4-8.6	8.74	9.74
B	(5)	7.65	8.74	8.86	8.01	3.5-3.7	21.-2.3	8.12	9.35
C	Δ(5-2)	-0.66	-0.37	-0.29	-0.70			-0.62	-0.39
	$\delta(CDCl_3) - \delta(CF_3COOH)$								
D	(2)	-1.36	-1.31	-1.51	-1.54	-2.1	-2.2	-1.40	-1.16
E	(5)	-1.02	-1.13	-1.35	-0.74	-0.35	-0.2	-0.66	-0.87



(7)



(8)

Alternative possibilities such as (7) and (8) for the neutral and the protonated species, respectively, are easily eliminated since the vicinal coupling constants are considerably smoothed out [$J_{2,3}$=9.2, $J_{4,5}$=7.9 and $J_{8,9}$=8.2 Hz for neutral species; $J_{2,3}$=8.7, $J_{4,5}$=8.4 and $J_{8,9}$=8.9 Hz for protonated species] as compared with those expected for (7) and (8).

The observations described in this communication are best understood by assuming that the ketone (2) is the peripheral [15]annulenone[9] perturbed by a internal vinyl crosslink such as (2a).

REFERENCES AND FOOTNOTES

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