SYNTHESIS AND PROPERTIES OF A BRIDGED PHENALENONE INCORPORATED INTO BICYCLO[3.2.2]NONANE SKELETON. 6,9-DIHYDRO-6,9-ETHENOCYCLOHEPTA[gh]PHENALEN-1-ONE¹⁾

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Summary: 6,9-Dihydro-6,9-ethenocyclohepta[gh]phenalen-1-one (1) has been synthesized starting from the Diels-Alder adduct (6) of acepleiadiene (5) and maleic anhydride through 10 steps with reasonable yields. Spectroscopic properties of 1 suggested the intramolecular electron supply from the remote ethylenes to the phenalenone π -systems in the ground-state of this molecule.

In spite of the extensive investigation on the tropylium ions incorporated into a bicyclo[2.2.2]octane skeleton,²⁾ studies on the ionic species based on bicyclo[3.2.2]nonane system are seemingly focused only to the labile bicyclo-[3.2.2]nonatrienyl cation.³⁾ In order to gain insight into the stable ionic species incorporated into a bicyclo[3.2.2]nonane skeleton we synthesized 6,9dihydro-6,9-ethenocyclohepta[gh]phenalen-1-one (1), which is expected not only to be a likely precursor of the bridged phenalenyl systems (2) but also to behave as the fully charged hydroxyphenalenium ion (3) in strong acidic media.⁴⁾



Since acepleiadylene (4) is known to be fairly inert to Diels-Alder reaction as 4π addend,⁵⁾ our synthesis of 1 was started from the Diels-Alder adduct 6^{5a} of acepleiadiene (5) and maleic anhydride according to the sequence of reactions shown in Scheme I.⁶⁾ Oxidative decarboxylation of 6 into the diene 7 [colorless needles, mp 116-117°C, 96% yield], which was unsatisfactory when attempted with lead tetraacetate,⁷⁾ was effected smoothly by using bis-triphenylphosphinenickel dicarbonyl⁸⁾ in refluxing diglyme for 16 h. The formation of a large amount of triphenylphosphine during the reaction made the separation of the product χ difficult. This tedious separation was supplanted by the more facile chemical separation. Thus, the reaction mixture was filtered through short column of silica gel and then refluxed in a mixture of ethanol and carbon tetrachloride to convert triphenylphosphine into its oxide, the chromatographic property of which allowed easy separation from the desired product χ . Oxidation of χ with t-butylhydroperoxide in the presence of cuprous bromide followed by treatment with lithium aluminum hydride gave the benzylic alcohol § [mp 150.5-151°C, 87% yield]⁹) which was then oxidized with an equivalent pyridinium chlorochromate to

Scheme I



give the ketone 9 [mp 138.5-139°C, 95% yield]. Successful ring expansion of the acenaphthenone ring to the phenalenone skeleton required considerable experimentation.¹⁰⁾ An effective achievement of the ring expansion, though quite multistep sequence, was found as follows: Reaction of 9 with two equivalents of phenyl benzenethiosulfonate¹¹⁾ in the presence of sodium hydride in THF at -78 \sim 0°C produced the bis-sulfenylated compound <u>10</u> [mp 182-183°C, 86% yield] which was transformed into the keto-ketal 11 [mp 148-150°C, 92% yield] by treatment with mercuric perchlorate and calcium carbonate in methanol at room temperature. The keto-ketal 11 thus obtained was converted to the methylated keto alcohol 13 [mp 240°C (decomp.), 77% yield from 11] through the ketal 12 by treatment with methyllithium in THF at -78°C followed by hydrolysis with dilute hydrochloric acid. The compound 13 could be converted into its acetate (Ac₂0/ py.), which without isolation, afforded the cis-glycol 14 [mp 198-199°C, 62% yield] on treatment with 1.2 equivalent of lithium tri-sec-butylborohydride in THF. Finally, the cis-glycol 14 was cleaved with periodic acid and then cyclized with a catalytic amount of p-toluenesulfonic acid in refluxing benzene to give

the bridged phenalenone 1 in 70% yield. Alternatively, reduction of 13 with sodium borohydride in methanol afforded mainly the *trans*-glycol, which, without separation, was treated with lead tetraacetate followed by *p*-toluenesulfonic acid to give the final product 1 in 67% yield from 13.

The bridged phenalenone 1 [yellow plates, mp 160°C (decomp. in a sealed tube)] can be stored under argon atmosphere in refrigerator, however, it decomposes gradually at room temperature. The substantial instability of 1 makes a sharp contrast to the stability of the parent phenalenone (12).⁴⁾ The comparison of the visible spectra of 1 in acetonitrile and in trifluoroacetic acid with those of the parent phenalenone 12 is illustrated in Figure 1. Despite the absence of direct conjugation between the phenalenone and ethylene moieties in 1,



Figure 1. Visible spectra of the bridged phenalenone (1) and phenalenone (12). 1 in CH_3CN (----), 1 in CF_3COOH (----), 12 in CF_3COOH (-----), and 12 in CF_3COOH (-----).

the spectra of which showed appreciable bathochromic shifts in both solvents compared to those of phenalenone suggesting the existence of an intramolecular interaction between two chromophores in the present molecule 1.

The interaction is also seen in other physical properties of 1. Thus, the streching frequency of the carbonyl group of 1 was found to be 1633 cm⁻¹ which is 10 cm⁻¹ lower frequency than that of phenalenone 12.⁴⁾ At the same time, the pK_{BH}^{+} value of 1 measured spectrophotometrically in HClO₄-aqueous dioxane using Ho-function, ¹²⁾ was found to be -0.8, indicating that the basicity of 1 is increased by a factor of 0.6 as compared with that of the parent phenalenone 12 (pK_{BH}^{+} = -1.4 measured at the same conditions).

The comparison of the ¹H-NMR chemical shifts of 1 and 12 is summarized in Table I. Although the factors affecting the proton chemical shift are complicated, it is apparent that all of the protons attached to the phenalenone skeleton of 1 resonated at higher field than those of the corresponding protons of phenalenone 12.¹³



Comparison of the chemical shifts of 1 and 12 Table I.

		H-2	H-3	H-4	H - 5	H - 8	H-9	bridge head	olefin
in CDC1 ₃	42	6.66	7.63	7.63	7.48	7.67	8.52	4.38	6.74
	ł	6.59	7.59	7.50	7.35	7.55	8.44		
	Δδ	0.07	0.04	0.13	0.13	0.12	0.08		
in CF ₃ COOD	łż	7.76	8.88	8.78	8.20	8.30	9.46		
	ł	7.53	8.61	8.46	7.94	8.06	9.22	4.92	7.15
	Δδ	0.23	0.27	0.32	0.26	0.24	0.24		

The numbering of 1 is used conveniently for the ready comparison with that of 12.

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- All new compounds reported in this paper gave satisfactory elemental analyses 6) and spectroscopic data consistent with the proposed structures.
- In this case the maximum yield of 7 obtained was less than 10%. 7)
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- Functionalization at the benzylic position of $\underline{7}$ by other reagents such as 9) NBS or lead tetraacetate resulted in destruction of the etheno-bridges.
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