

THE CHEMISTRY OF PHENALENIUM SYSTEM XIV,¹⁾ 2,3-HOMOPHENALENONE

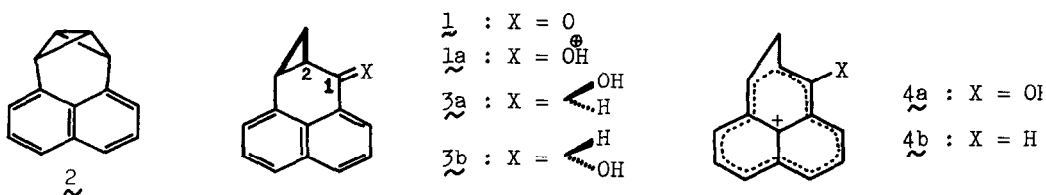
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The chemistry of the homoaromatic compounds is currently a topic of great interest.²⁾ Although various studies for homotropones,³⁾ homotropylium ions⁴⁾ have been known for several years, a homo-derivative of phenalene which is a highly polarized ketone, resembling in many of its properties to tropone, has not been reported to date. We now wish to describe the synthesis and properties of 2,3-homophenalene (1).

Naphto[1,8]tricyclo[4.1.0.0^{2,7}]heptene (2) now conveniently available through the reaction of lithium phenalene with dichloromethane in the presence of n-butyllithium in ether reported independently by us⁵⁾ and by Pagni and Watson,⁶⁾ reacts smoothly at 50° with 2N phosphoric acid in THF for 2 hr to give a mixture



of the epimeric endo- (3a) and exo-alcohol (3b) [in the ratio 1.0 : 0.6] in nearly quantitative yield. The stereochemistry of the epimeric alcohols, 3a and 3b, was established by examination of the nmr spectra of these alcohols. For the endo alcohol, 3a, the proton α to the hydroxy group appears as a doublet at δ 5.18 ppm with vicinal coupling constant of 6 Hz denoting the presence of cis arrangement between H-1 and H-2.⁷⁾ This observation served to differentiate 3a from the epimer 3b where the signal assignable to H-1 appears as a broad singlet at δ 5.23 ppm suggesting the small coupling between H-1 and H-2.⁷⁾ Additional support for the plausibility of the stereochemical assignments of 3a and 3b are also gained

from a reduction of 2,3-homophenalenone 1 [vide post], thus sodium borohydride reduction of 1 gave exclusively the endo alcohol 3a. The predominant formation of 3a from 2 by the endo attack of nucleophile is strongly remind of the observation by Wiberg and Szeimies⁸⁾ that the tricyclo[4.1.0.0^{2,7}]heptane reacts with deuterioacetic acid to give chiefly cis-2-acetoxynorcarane.

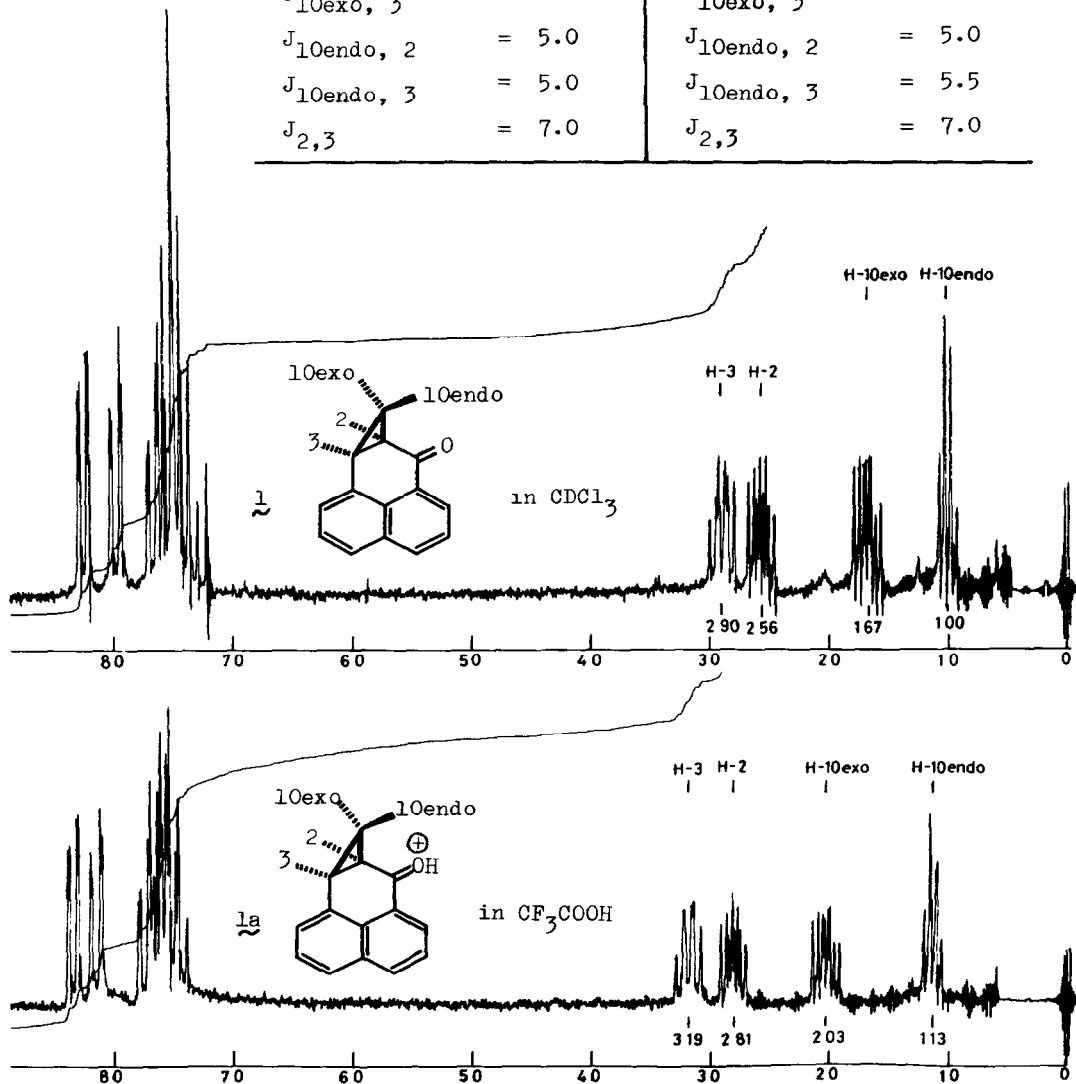
Oxidation of a mixture of 3a and 3b with chromic oxide in pyridine gave 2,3-homophenalenone 1 after usual work-up in 85% yield. Final purification was achieved by reduced pressure sublimation, pale yellow crystals, mp 62-65°. Anal. Calcd. for C₁₄H₁₀O : C, 86.57; H, 5.19. Found : C, 86.49; H, 5.19%. The ir and uv spectra of 2,3-homophenalenone, $\nu_{C=O}$ (KBr) 1665 cm⁻¹; λ_{max} (ethanol) 212 (log ϵ 4.53), 249 (4.29), 323 (3.69), 335 (3.74), 355 nm (sh, 3.62), λ_{max} (cyclohexane) 212 (4.56), 248 (4.35), 319 (3.75), 334 (3.74), 350 (sh, 3.45), 365 (sh, 3.18), 383 (sh, 2.65), λ_{max} (CF₃COOH) 240 (4.03), 295 (3.40), 364 (3.71), 440 (sh, 3.14), strikingly resembled the spectra of phenalanone.⁹⁾ These spectroscopic properties suggest that the electron delocalization in 2,3-homophenalenone through the cyclopropane ring is relatively small.¹¹⁾ The mass spectrum of 2,3-homophenalenone shows a parent ion at m/e 194 (18%), an ion at m/e 166 (24%) due to loss of carbon monoxide and an ion at m/e 165 (100%) attributable to the stable phenalenium ion.

The nuclear magnetic resonance spectra of 2,3-homophenalenone in deuteriochloroform and trifluoroacetic acid at 100 MHz are shown in Fig-1 and Table-1. Protonation of 2,3-homophenalenone 1 to homoaromatic species was expected in CF₃COOH, but we could not observe the hydroxyhomophenalenium ion 4a in this condition. From Fig-1 it is apparent that the all of the protons shift downfield slightly (0.13-0.36 ppm) in CF₃COOH even an endo proton, H-10endo, to give a chemical shift difference between H-10exo and H-10endo, $\Delta\delta=0.9$ ppm. This is comparable to the difference seen with the unprotonated species ($\Delta\delta=0.67$ ppm). If we adopt the chemical shift difference of these protons as a criterion of homoaromatic electron delocalization²⁾ it could be concluded that 1a is not homoaromatic. Furthermore, the same coupling constant (Table-1) observed for neutral and protonated species ($J_{10exo, 10endo}=4.5$ Hz)¹²⁾ is also consistent with our conclusion.

The formation of the parent homophenalenium ion 4b from 3a and/or 3b was

Table-1. Coupling Constants of $\underline{1}$

for neutral species $\underline{1}$ (in CDCl_3)	for protonate species $\underline{1a}$ (in CF_3COOH)
$J_{10\text{exo}, 10\text{endo}} = 4.5 \text{ Hz}$	$J_{10\text{exo}, 10\text{endo}} = 4.5 \text{ Hz}$
$J_{10\text{exo}, 2} = 10.0$	$J_{10\text{exo}, 2} = 9.5$
$J_{10\text{exo}, 3} = 8.0$	$J_{10\text{exo}, 3} = 8.0$
$J_{10\text{endo}, 2} = 5.0$	$J_{10\text{endo}, 2} = 5.0$
$J_{10\text{endo}, 3} = 5.0$	$J_{10\text{endo}, 3} = 5.5$
$J_{2,3} = 7.0$	$J_{2,3} = 7.0$

Fig-1. 100 MHz Nmr Spectra of $\underline{1}$ in CDCl_3 (top) and CF_3COOH (bottom).

anticipated in strong acidic media but we have failed in detecting the expected ion $4b$ in conc. sulfuric acid or trifluoroacetic acid because of the instability of $3a$ and $3b$ in these acids at room temperature. We are investigating other case to detect the homophenalenium ion $4b$.

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