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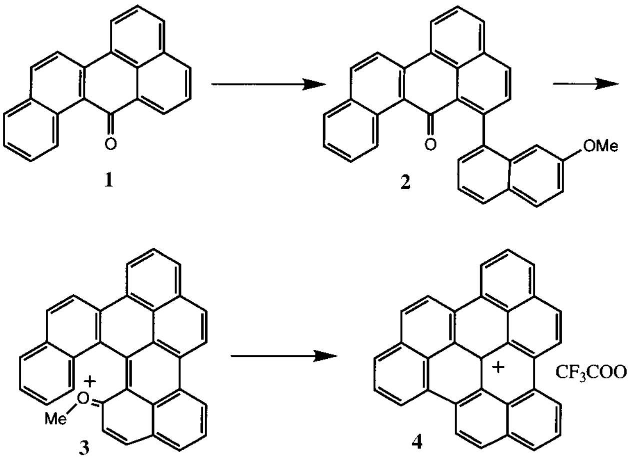
Synthesis of the Trinaphthophenalenium Cation**

Masahiko Suenaga,* Yuji Miyahara, Nobujirou Shimizu, and Takahiko Inazu

The unique feature of odd-alternant hydrocarbons (i.e., polycyclic hydrocarbons with alternating double bonds and an odd number of carbon atoms), is the readily interconvertible redox triad (cation–radical–anion), which has been the subject of many experimental and theoretical studies. Recently we have disclosed a novel synthetic approach[1] to extended phenalenones as potential precursors of the corresponding odd-alternant hydrocarbons. Here we report the application of this method to the synthesis of the hitherto unknown trinaphthophenalenium cation **4**, a cation of a novel C_{3h}-symmetric odd-alternant hydrocarbon.

Treatment[2] of 7*H*-benzo[*hi*]chrysen-7-one (**1**)[3] with 7-methoxy-1-naphthyllithium (prepared from 7-methoxy-1-naphthyl iodide[4, 5] and *n*BuLi in ether at room temperature) and autooxidation of the resulting adduct in the usual workup afforded 6-(7-methoxy-1-naphthyl)-7*H*-benzo[*hi*]chrysen-7-one (**2**)[6] in 75% yield (Scheme 1). This molecule contains the necessary number of carbons for the construction of the desired trinaphthophenalene skeleton. The methoxy group was deliberately introduced to serve as an auxiliary in the following three key steps of the condensation to the target structure. First, it acts as an electron-donating group to make position 8 reactive enough to react with the central carbonyl group to give **3**. Second, it stabilizes the adjacent cationic center as shown in **3** to increase the chance for the ring-closing condensation with the facing benzene ring. Finally, it can leave as methanol to provide the trinaphthophenalenium cation **4**. Our system worked as beautifully as we had originally conceived.



Scheme 1. Synthesis of $4 \cdot CF_3COO$.

The reaction proceeded in steps and we could isolate the intermediate **3** as a blue-violet solid after heating **2** in 30% HBr/HOAc at 95°C for 1 h. Although **3** was not fully characterized, the presence of 16 different aromatic protons and three methyl protons in the ^1H NMR spectrum supports the proposed structure. When the reaction temperature was increased to 110°C, the final transannular condensation occurred very smoothly to furnish trinaphthophenalenium trifluoroacetate $\mathbf{4} \cdot CF_3COO$ as a dark violet solid (71% from **2**) after chromatographic purification (silica gel, CF_3COOH).

The characteristic absorption of **4** in acetonitrile ($\lambda_{max}(\varepsilon) = 568$ (10400)) supports its extensively delocalized π system. The ^1H NMR spectrum[7] of **4** consists of four doublets at $\delta = 9.74$, 9.42, 9.05, and 9.02 and one triplet at $\delta = 8.65$ in accord with the expected C_{3h} symmetry. The FAB mass spectrum (**4** in CF_3COOH/*m*-nitrobenzyl alcohol matrix) shows a peak for the trinaphthophenalenium cation at m/z 387.1172 (calcd for $C_{31}H_{15}$: 387.1174). As a measure of the thermodynamic stability of the trinaphthophenalenium cation, its pK_{R+} value was determined by spectrophotometric titration in buffered 50% aqueous acetonitrile. Although the titration curve was discontinuous[8] between pH 2.65 and 2.96, the preliminary pK_{R+} value was estimated to be roughly 4.2. Therefore, the stability of cation **4** is comparable to that of the tropylium ion ($pK_{R+} = 4.7$).

The electrochemical behavior of **4** was examined by cyclic voltammetry using a microelectrode (Table 1). Two quasi-reversible redox waves were observed. While the first reduction potential is much higher than that of phenalenium ion, the reverse is true with the second reduction potential. The electrochemical properties of the trinaphthophenalenium system are consistent with the results of semiempirical calculations.[11, 12] Thus, while the LUMO energy of cation **4** (−6.04 eV) is higher than that of phenalenium cation

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Table 1. Results of cyclic voltammetric studies.[a]

Cation	E_{red1}	E_{red2}
4	-0.066	-0.762
phenalenium[b]	0.5 (0.7)	-1.1 (-0.9)

[a] Tetrabutylammonium tetrafluoroborate (4 mM) as the supporting electrolyte, scan rate 50 mV s^{-1}, 25°C; potential in volts vs. Ag/Ag$^+$, measured with a 25 μm Pt working microelectrode in MeCN; reduction peak potentials are for a quasi-reversible redox reaction; the observed potentials were corrected with reference to ferrocene/ferrocenium (Fc/Fc$^+$; $E_{1/2} = +0.089$ V) as an internal standard. [b] The originally reported[9] reduction potentials for phenalenium tetrafluoroborate (listed in parentheses) were given in volts vs. SCE. For comparison these data were converted into values vs. Ag/Ag$^+$ reference electrode according to Equation (a).[10]

$$E(\mathrm{Ag/Ag^+}) = E(\mathrm{SCE}) - 0.226\ \mathrm{V} \qquad \text{(a)}$$

(-6.76 eV), the SOMO energy of the trinaphthophenalenyl radical (-4.55 eV) is lower than that of phenalenyl radical (-4.43 eV).

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[6] Yellow needles (from $CHCl_3$/EtOH), m.p. 165–167°C; elemental analysis calcd for $C_{32}H_{20}O_2$: C 88.05, H 4.62; found: C 87.94, H 4.73.

[7] ^{1}H HMR (400 MHz, CF_3COOD, $\delta(CF_3COOH) = 11.5$) All signals were fully assigned with a COSY-45 experiment.

[8] The buffer had to be changed from the Clark–Lubs (W. M. Clark, H. A. Lubs, *J. Biol. Chem.* **1916**, *25*, 479–510) to the McIlvaine (T. C. McIlvaine, *J. Biol. Chem.* **1921**, *49*, 183–186) in the course of titration. With the Britton–Robinson buffer (H. T. S. Britton, R. A. Robinson, *J. Chem. Soc.* **1931**, 458–473 and 1456–1462), which can cover the required pH range, the sigmoid titration curve was not obtained.

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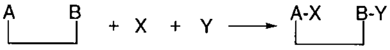
Parallel Differentiated Recognition of Ketones and Acetals**

Jian-xie Chen and Junzo Otera*

Integration of multistep chemical reactions into one-pot reactions is of great significance from both economical and ecological points of view. A number of one-pot processes, which are named tandem, cascade, domino reactions, etc., have received much attention.[1–3] In these protocols, similar or different types of reactions are performed in sequence without isolating intermediates. This strategy is particularly elegant in that the preceding reaction creates the necessary functionality for the subsequent one. Accordingly, the relevant reaction sites are inherited from one step to the next. In practical synthesis, however, we often need to carry out chemical transformations on separate reaction sites within a molecule. Conventionally, such transformations have been executed in a stepwise, not a one-pot, manner. If the manifold reactions could be performed simultaneously (that is, in parallel), the process would be efficient and expeditious [Eq. (1)]. Here we wish to advance a new concept based on such parallel (or horizontal) treatment rather than the conventional series (or vertical) strategy.



(1)

To arrive at the ultimate goal of parallel recognition [Eq. (1)], we require a new concept of chemoselectivity in which a mixture of substrates A and B reacts with a mixture of reagents X and Y to furnish products A–X and B–Y exclusively or predominantly over other possible products [Eq. (2)]. The requirement would be satisfied if product AX could be formed predominantly over BX in the competition reaction of substrates A and B with reagent X [Eq. (3)] and BY in preference to AY in the reaction with reagent Y [Eq. (4)]. To our knowledge, no such treatment has been put forth intentionally, although the analogous selectivity might have incidentally resulted from unintentional performances on rare occasions.[4]

$$\mathrm{A+B+X+Y \longrightarrow A{-}X + B{-}Y} \qquad (2)$$

$$\mathrm{A+B+X \longrightarrow A{-}X\ (+B{-}X)} \qquad (3)$$

$$\mathrm{A+B+Y \longrightarrow B{-}Y\ (+A{-}Y)} \qquad (4)$$

For reaction (2) to occur efficiently the substrates A and B should be similar to each other in chemical reactivity, so that reactions (3) and (4) can proceed under the identical reaction conditions. They should simultaneously undergo different reactions irrespective of the other. The reagents X and Y also

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