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Formation of keto-carbeniums from 1,2,2-triarylacenaphthen-1-ols by breaking a long C–C bond: unusual alcohol protonolysis accompanied by formal hydride abstraction☆

Takanori Suzuki,* Takayuki Nagasu, Hidetoshi Kawai, Kenshu Fujiwara and Takashi Tsuji

Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

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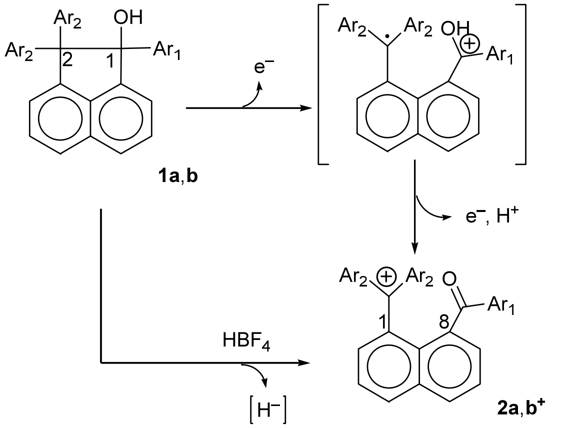
Abstract—Oxidation of 1,2,2-tris(4-dimethylaminophenyl)- and 2,2-bis(4-dimethylaminophenyl)-1-phenylacenaphthen-1-ols **1a**,**b** with I_2 induced the C_1–C_2 bond fission to give 8-aroylnaphthalen-1-yl-bis(4-dimethylaminophenyl)carbenium derivatives **2a**,**b**$^+$, the intramolecular Lewis acid–base pairs. Treatment of **1** with HBF_4 did not induce the expected C–OH bond heterolysis but caused fission of CO–H and C_1–C_2 bonds to give exactly the same carbenium **2**$^+$.

Covalent bond lengths such as 1.54 Å for C_{sp^3}–C_{sp^3} are basic parameters in chemistry, and large deviations from the standard values are diagnostic of novel steric and electronic features as exemplified by tetraarylbenzocyclobutenes with a C–C bond length of 1.72 Å.[1] Beside elucidating the origin of bond elongation,[2,3] exploring novel reactivities involving such weakened bonds is necessary to shed light on the boundary between long bonds and short nonbonds.[4] In our continuing studies on the oxidative cleavage of polyarylated long C–C bonds upon electron-transfer (ET),[5] we have found that the title acenaphthenols **1a**,**b** undergo C–C bond fission not only upon 2e-oxidation but also upon treatment with HBF_4 (Scheme 1). The latter reaction is quite unusual because the Brønsted acid induces formal hydride abstraction from the hydroxy group to give keto-carbeniums **2a**,**b**$^+$. We report here the details of these novel reactions along with precise geometrical features of the reactant and products determined by low-temperature X-ray analyses.

Reaction of 2,2-bis(4-dimethylaminophenyl)acenaphthen-1-one[6] with $4\text{-}Me_2NC_6H_4Li$ in THF gave **1a**[7] in 29% yield along with the conjugated addition–aromatization[8] product **3a**[7] (yield 37%) whose structure was confirmed by X-ray analysis.[9] Such an anomalous addition is resulted from the steric hindrance around the carbonyl group in the starting acenaphthone. By using PhLi, **1b**[7] was similarly obtained in 46% yield. Detailed geometrical data for the triarylacenaphthenol skeleton were determined by X-ray analysis[9] on **1b** at −100°C (Fig. 1). The notable feature is that the polyarylated C_1–C_2 bond is much longer [1.648 (4) Å] than the standard value (1.54 Å).[10] Such



[**a**: $Ar_1 = Ar_2 = 4\text{-}Me_2NC_6H_4$ **b**: $Ar_1 = C_6H_5$; $Ar_2 = 4\text{-}Me_2NC_6H_4$
c: $Ar_1 = Ar_2 = C_6H_5$]

Scheme 1.

Keywords: long bond; electron transfer; protonolysis; dye; *peri*-interaction.

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* Corresponding author. Tel.: +49-11-706-2714; fax: +49-11-706-2714; e-mail: tak@sci.hokudai.ac.jp

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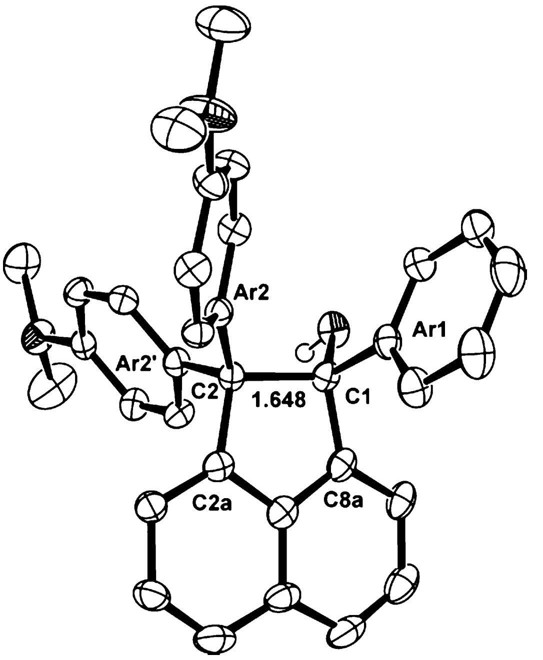


Figure 1. Molecular structure of **1b** determined by X-ray analysis.

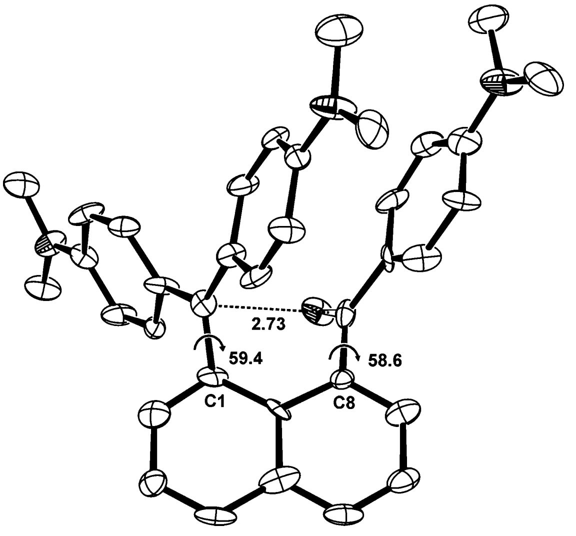


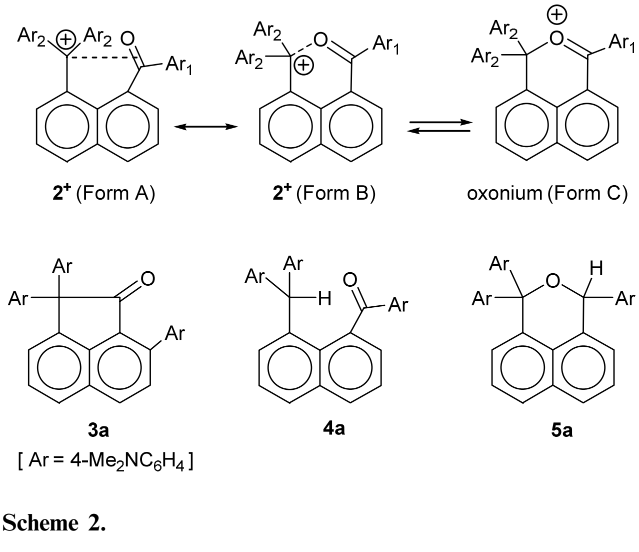
Figure 2. Molecular structure of **2a**$^+$ determined by X-ray analysis of I_3^- salt.

expansion can be accounted for by steric repulsion between aryl substituents,[3] which is inevitable due to the rigid five-membered-ring structure with small torsion angles [C^{8a}–C^1–C^2–C^{2a}: 17.0 (3)°; C^{Ar1}–C^1–C^2–C^{Ar2}: 22.2 (3)°; O–C^1–C^2–$C^{Ar2'}$: 27.9 (3)°].

According to the voltammetric analyses, acenaphthenols **1** are strong electron donors [E^{ox}: +0.42 V for **1a** and +0.53 V for **1b**][11] due to multiple substitution of the electron-donating aryl groups, and irreversibility of the oxidation waves suggests the facile fission of the weakened bond followed by ET.[12] Upon treatment with 3 equiv. of iodine, **1a** and **1b** underwent 2e-oxidation accompanied by C_1–C_2 bond fission and deprotonation, resulting in the formation of stable I_3^- salts[7] of keto-carbeniums **2a**$^+$ (yield 81%) and **2b**$^+$ (yield 72%), respectively. Their structures are assigned on the basis of spectral data, and finally confirmed by the X-ray analysis[9] on **2a**$^+I_3^-$ salt at −120°C.

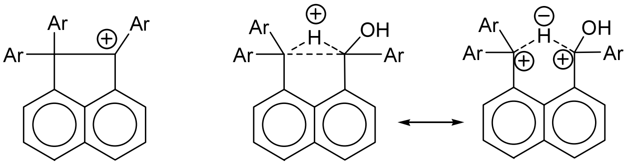
As shown in Figure 2, the Ar_2C^+-type carbenium unit and the carbonyl group at the 1,8-positions of naphthalene nucleus are rotated in the same direction [59.4 (5)° and 58.6 (4)°, respectively] in **2a**$^+$, thus furnishing the face-to-face overlap of these moieties. The methylium carbon is located 2.73 Å above the carbonyl plane, and separated by only 2.94 and 2.93 Å from the O and C atoms of the carbonyl group, respectively. This is the shortest carbenium–carbonyl contact in crystal ever reported. This structure is best described as a π-complex of Lewis acid and base (Form A in Scheme 2), suggesting the presence of *peri*-interaction[13] between the two moieties. Owing to such short-nonbonded interaction, treatment of **2a**$^+I_3^-$ with $NaBH_4$ in EtOH gave not only the triarylmethane derivative **4a** (yield 28%) but also the cyclic isomer **5a** (yield 21%), whose structural assignment was unambiguously carried out by X-ray analyses.[9] The former is the usual hydride adduct (leuco-base) of triarylmethylium dyes,[14] whereas the latter is the product through the hydride addition on the σ-complex (Form B) or the oxonium (Form C) generated from the π-complex, Form A. Although the presence of *peri*-interaction in **2**$^+$ is not so clear by comparisons of spectral data (**2a**$^+$: λ_{max} 630 nm in MeCN; δc 179 ppm in $CDCl_3$) with the reference carbenium without aroyl group [bis(4-dimethylaminophenyl)-1-naphthylcarbenium: 627 nm; 175 ppm], π-acidity of **2a**$^+$ (E^{red} −0.65 V) is much reduced than the reference carbenium (−0.56 V) due to the interaction with the aroyl π-base. Such a difference indicates that through-space interaction[15] stabilizes the carbenium unit in **2**$^+$.

The most striking reactivity of the acenaphthenols **1** is the acid-assisted long C–C bond fission to give the same stabilized keto-carbeniums **2**$^+$. Upon treatment of **1a**



Scheme 2.

with 1.2 equiv. of HBF_4 in THF at room temperature, **2a**$^+BF_4^-$ salt was isolated in 87% yield without giving the expected carbenium **6a**$^+$ by C–OH heterolysis.[14] Similarly, **2b**$^+BF_4^-$ was obtained by acid treatment of **1b** in 84% yield. By considering the fact that 1,1,2-triphenylacenaphthen-1-ol **1c** underwent the acid-catalyzed substitution reactions via **6c**$^+$,[16] not only the expansion of the C_1–C_2 bond by steric factors but also the strong donating property of amino substituents on aryl groups are responsible for this unusual behavior. One plausible explanation may be that both factors raise the orbital energy of C_1–C_2 σ bond, thus enhancing the affinity of this σ bond toward proton although the involvement of hydrogen-bridged[17,18] carbenium **7**$^+$ in this protonolysis is still unclear. In summary, this is one of the rare examples where Brønsted acid is proven to act as an oxidant or to assist oxidation to give the carbenium salt.[19] Studies on the relationship between this unusual alcohol protonolysis and the alkane protonolysis by superacid[18,20] are now in progress.[21]



6$^+$ **7**$^+$

[**a**: Ar = 4-$Me_2NC_6H_4$
c: Ar = C_6H_5]

Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 209572–209576. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk]. ORTEP drawings with atom numbering schemes for **1b**, **2a**$^+I_3^-$, **3a**, **4a**, and **5a** were submitted as electronic supplementary material (PDF).

Acknowledgements

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7. For **1a**: mp 172.0–174.0°C; ^1H NMR (300 MHz, $CDCl_3$) δ/ppm 7.76 (br. d, 1H, $J=7.5$ Hz), 7.69 (br. d, 1H, $J=7.5$ Hz), 7.58 (dd, 1H, $J=7.5$, 7.5 Hz), 7.50 (dd, 1H, $J=7.5$, 7.5 Hz), 7.34 (br. d, 1H, $J=7.5$ Hz), 7.20 (br. d, 1H, $J=7.5$ Hz), 7.10 (AA′XX′, 2H), 7.09 (AA′XX′, 2H), 6.64 (AA′XX′, 2H), 6.53 (AA′XX′, 2H), 6.41 (AA′XX′, 2H), 6.27 (AA′XX′, 2H), 3.26 (s, 1H), 2.86 (s, 6H), 2.81 (s, 6H), 2.74 (s, 6H); IR (KBr) ν/cm^{-1} 3556. For **1b**: mp 180.0°C (decomp.); ^1H NMR (300 MHz, $CDCl_3$) δ/ppm 7.78 (br. d, 1H, $J=7.5$ Hz), 7.72 (br. d, 1H, $J=7.5$ Hz), 7.58 (dd, 1H, $J=7.5$, 7.5 Hz), 7.53 (dd, 1H, $J=7.5$, 7.5 Hz), 7.32 (br. d, 1H, $J=7.5$ Hz), 7.23 (br. d, 1H, $J=7.5$ Hz), 7.16 (AA′XX′, 2H), 7.01 (AA′XX′, 2H), 6.84–6.74 (m, 5H), 6.50 (AA′XX′, 2H), 6.40 (AA′XX′, 2H), 3.48 (s, 1H), 2.85 (s, 6H), 2.81 (s, 6H); IR (KBr) ν/cm^{-1} 3520. For **2a**$^+I_3^-$: mp 241.0–242.5°C (decomp.); ^1H NMR (300 MHz, $CDCl_3$) δ/ppm 8.20 (br. d, 1H, $J=7.5$ Hz), 8.10 (br. d, 1H, $J=7.5$ Hz), 7.65 (dd, 1H, $J=7.5$, 7.5 Hz), 7.57 (dd, 1H, $J=7.5$, 7.5 Hz), 7.47 (br. d, 1H, $J=7.5$ Hz), 7.36 (br. d, 1H, $J=7.5$ Hz), 7.70–7.10 (br., 8H), 6.68 (br., 4H), 3.27 (s, 12H), 3.15 (br. s, 6H); IR (KBr) ν/cm^{-1} 1582. For **2b**$^+I_3^-$: mp 141.5–143.5°C (decomp.); ^1H NMR (300 MHz, $CDCl_3$) δ/ppm 8.22 (dd, 1H, $J=7.5$, 1.5 Hz), 8.14 (dd, 1H, $J=7.5$, 1.5 Hz), 7.70 (dd, 1H, $J=7.5$, 7.5 Hz), 7.56 (dd, 1H, $J=7.5$, 7.5 Hz), 7.51–7.42 (m, 6H), 7.23 (dd, 1H, $J=7.5$, 7.5 Hz), 7.40–7.00 (br., 4H), 6.63 (AA′XX′, br., 4H), 3.27 (s, 12H); IR (KBr) ν/cm^{-1} 1580. For **3a**: mp 250.0–255.0°C; ^1H NMR (300 MHz, $CDCl_3$) δ/ppm 8.05 (br. d, 1H, $J=7.5$ Hz), 7.77 (br. d, 1H, $J=7.5$ Hz), 7.73 (br. d, 1H, $J=7.5$ Hz), 7.66 (AA′XX′, 2H), 7.57 (dd, 1H, $J=7.5$, 7.5 Hz), 7.43 (br. d, 1H, $J=7.5$ Hz), 7.14 (AA′XX′, 4H), 6.80 (AA′XX′, 2H), 6.60 (AA′XX′, 4H), 3.01 (s, 6H), 2.88 (s, 12H); IR (KBr) ν/cm^{-1} 1706. For **4a**: mp 213.0–215.0°C (decomp.); ^1H NMR (300 MHz, $CDCl_3$) δ/ppm 7.92 (dd, 1H, $J=7.5$, 1.5 Hz), 7.78 (dd, 1H, $J=7.5$, 1.5 Hz), 7.40 (dd, 1H, $J=7.5$, 7.5 Hz), 7.39 (dd, 1H, $J=7.5$, 7.5 Hz), 7.29 (dd, 1H, $J=7.5$, 1.5 Hz), 7.14 (dd, 1H, $J=7.5$, 1.5 Hz), 7.75–6.10 (br., 12H), 6.17 (s, 1H), 3.02 (s, 6H), 2.95–2.70 (br., 12H); IR (KBr) ν/cm^{-1} 1590. For **5a**: mp 221.0–222.5°C; ^1H NMR (300 MHz, $CDCl_3$) δ/ppm 7.76 (dd, 1H, $J=7.5$, 1.5 Hz), 7.71 (br. d, 1H, $J=7.5$ Hz), 7.37 (dd,

1H, $J=7.5$, 7.5 Hz), 7.32 (AA′XX′, 2H), 7.27 (dd, 1H, $J=7.5$, 7.5 Hz), 7.20 (AA′XX′, 2H), 7.02 (AA′XX′, 2H), 6.93 (dd, 1H, $J=7.5$, 1.5 Hz), 6.74 (AA′XX′, 2H), 6.74 (br. d, 1H, $J=7.5$ Hz), 6.64 (AA′XX′, 2H), 6.62 (AA′XX′, 2H), 5.70 (s, 1H), 2.96 (s, 6H), 2.94 (s, 6H), 2.90 (s, 6H); IR (KBr) ν/cm^{-1} 1614.

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9. *Crystal data* for **1b**: $C_{34}H_{32}N_2O$, M 484.64, triclinic, $P\bar{1}$, $a=10.062$ (4), $b=11.677$ (4), $c=12.405$ (4) Å, $\alpha=72.69$ (2), $\beta=75.04$ (2), $\gamma=70.45$ (2)°, $U=1290.8$ (8) Å^3, D_{calcd} ($Z=2$) = 1.247 g cm^{-1}, $\mu=0.75$ cm^{-1}, $T=173$ K. The final R value is 0.063 for 3210 independent reflections with $I > 3\sigma I$ and 334 parameters. For **2a**$^+$$I_3^-$: $C_{36}H_{36}I_3N_3O$, M 907.41, monoclinic, $P2_1/c$, $a=10.847$ (5), $b=20.532$ (10), $c=15.410$ (7) Å, $\beta=100.214$ (9)°, $U=3377$ (2) Å^3, D_{calcd} ($Z=4$) = 1.784 g cm^{-1}, $\mu=28.10$ cm^{-1}, $T=153$ K. The final R value is 0.067 for 2881 independent reflections with $I > 3\sigma I$ and 388 parameters. The bond distance for C=O is 1.24(1) Å. For **3a**: $C_{36}H_{35}N_3O$, M 525.69, orthorhombic, $P2_12_12_1$, $a=11.236$ (6), $b=15.226$ (9), $c=16.221$ (9) Å, $U=2774$ (2) Å^3, D_{calcd} ($Z=4$) = 1.258 g cm^{-1}, $\mu=0.76$ cm^{-1}, $T=100$ K. The final R value is 0.060 for 2286 independent reflections with $I > 3\sigma I$ and 362 parameters. For **4a**: $C_{36}H_{37}N_3O$, M 527.71, triclinic, $P\bar{1}$, $a=9.610$ (8), $b=10.826$ (8), $c=15.28$ (1) Å, $\alpha=99.817$ (9), $\beta=98.46$ (1), $\gamma=108.93$ (1)°, $U=1446$ (1) Å^3, D_{calcd} ($Z=2$) = 1.212 g cm^{-1}, $\mu=0.73$ cm^{-1}, $T=153$ K. The final R value is 0.081 for 2779 independent reflections with $I > 3\sigma I$ and 361 parameters. The bond distance for C=O is 1.244(5) Å. For **5a**: $C_{36}H_{37}N_3O$, M 527.71, triclinic, $P\bar{1}$, $a=10.548$ (4), $b=11.934$ (6), $c=12.384$ (5) Å, $\alpha=86.20$ (2), $\beta=69.52$ (2), $\gamma=78.39$ (2)°, $U=1430$ (1) Å^3, D_{calcd} ($Z=2$) = 1.225 g cm^{-1}, $\mu=0.74$ cm^{-1}, $T=153$ K. The final R value is 0.062 for 3510 independent reflections with $I > 3\sigma I$ and 361 parameters.
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21. Keto-carbenium **2a**$^+$ was also generated when **1a** was treated with CCl_3COOH (1.1 equiv.) in chloroform. Preliminary results show that production of **2a**$^+$ obeys the similar kinetics under Ar and under air, suggesting that oxygen does not play an important role in this reaction.