アカデミックプログラム［B講演］ | 14. 有機化学—芳香族・複素環・ヘテロ原子化合物：口頭B講演

2024年3月18日(月) 15:55 ~ 17:15 E1141(11号館 [4階] 1141)

[E1141-1vn] 14. 有機化学—芳香族・複素環・ヘテロ原子化合物

座長：盛田 大輝、武藤 慶

英語
15:55 ~ 16:15
[E1141-1vn-01]
Non-electronic activation on anthracene ring by steric repulsion between substituents

○Annisa Indah Reza[1], Kento Iwai[1], Nagatoshi Nishiwaki[1] (1. Kochi University of Technology)

英語
16:15 ~ 16:35
[E1141-1vn-02]
鉄触媒による自己酸化イミンのアザ環化π拡張反応

○張 岩[1]、福間 翔太[1]、尚 睿[1]、中村 栄一[1] (1. 東京大学)

英語
16:35 ~ 16:55
[E1141-1vn-03]
ベンザインと窒素置換アルキンの新奇な分子内環化付加反応の開発

○田渡 司[1]、坂上 峻哉[1]、伊藤 琢磨[2]、原渕 祐[3,4]、前田 理[3,4,5]、高須 清誠[1]、瀧川 紘[1] (1. 京大院薬、2. 北大院総化、3. 北大WPI-ICReDD、4. JST-ERATO、5. 北大院理)

日本語
16:55 ~ 17:15
[E1141-1vn-04]
シクロドデシプチセンの合成

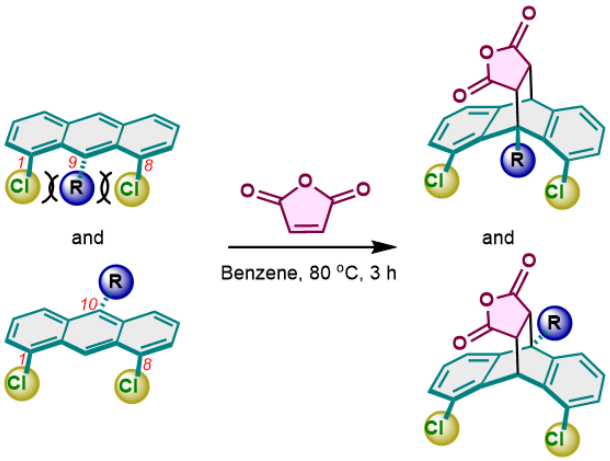
○兵頭 瑞樹[1]、岩田 隆幸[2]、新藤 充[2] (1. 九大院総理工、2. 九大先導研)

Non-Electronic Activation on Anthracene Ring by Steric Repulsion between Substituents

([1]*Graduate School of Engineering Science, Kochi University of Technology,* [2]*Research Center for Molecular Design, Kochi University of Technology*) ○Annisa Indah Reza,[1] Kento Iwai,[1,2] Nagatoshi Nishiwaki[1,2]

Keywords: Non-electronic activation; Steric repulsion; Ring distortion; Anthracene; Diels-Alder reaction

In our previous work, aromatic distortion of 1-methylquinolinium salts[1] and 1,8-dimethyl- and 1,8-diidonaphthalenes[2,3] was achieved using an intense steric repulsion between the *peri*-substituents. The reactivity was found to be higher as the substituent was bulkier. Herein, we extensively explored this non-electronic activation into another aromatic system using 1,8-dichloroantracene, where its 9- and 10-positions are separately substituted with methoxy and alkyl groups. The anthracene framework was distorted, especially in the vertical direction, compared to its 10-substituted counterparts, and the distortion was significant as the bulkiness of the substituent was larger. Thus, the distortion of the anthracene ring is due to the steric repulsion with chloro groups at the *peri*-positions. The Diels-Alder reactions with maleic anhydride were conducted to evaluate the distorted anthracenes' activation. Generally, the product yields became higher as the substituent was bulkier. Moreover, anthracene possessing an isopropyl group was more highly activated than derivative with a strongly electron-donating methoxy group, indicating the anthracene framework was activated non-electronically rather than influenced electronically.



R	Yield/%	Recovery/%
OMe	75	18
Me	79	15
Et	75	20
^{n}Pr	80	12
^{i}Pr	91	5

R	Yield/%	Recovery/%
OMe	53	36
Me	50	35
Et	63	20
^{n}Pr	58	30
^{i}Pr	75	12

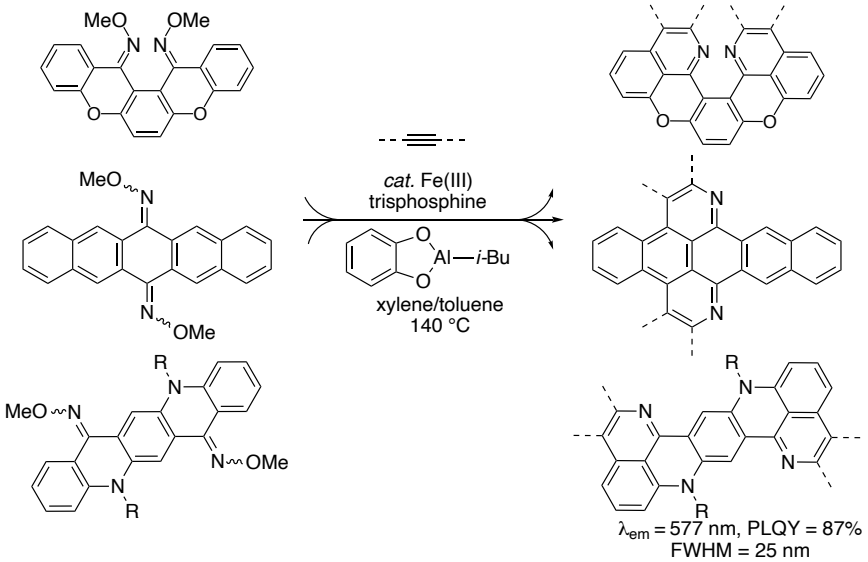
1) *Bull. Chem. Soc. Jpn.* **2020**, *93*, 50–58. 2) *Molecules* **2023**, *28*, 5343. 3) *J. Org. Chem.* **2023**, *88*, 9409–9412.

Iron-Catalyzed Aza-Annulative π-Extension using a Self-Oxidation Auxiliary

(*Graduate School of Science, The University of Tokyo*) ○Yan Zhang, Shota Fukuma, Rui Shang, Eiichi Nakamura

Keywords: Aza-Annulative π-Extension, Iron Catalysis, C–H Activation, Narrow-Band Emissive Molecules

Aza-annulative π-extension (**AAPE**) reactions[1] offer a potent pathway to create novel donor-acceptor conjugated materials by integrating an imine moiety into the conjugated system, serving as an electron-accepting unit[2]. However, the affinity of late-transition metals for conjugated π-systems, coupled with their elevated cost, has posed significant challenges, restricting efficient **AAPE** reactions on straightforward C–H substrates for developing conjugated new materials. In this study, we unveil an iron-catalyzed C–H activation methodology[3], facilitating **AAPE** with diverse internal alkynes and employing oxime ether as both a self-oxidizing auxiliary[4] and nitrogen source, derived seamlessly from accessible carbonyl compounds. The **AAPE** reaction was enabled by using trisphosphine as a ligand, and isobutyl aluminum(III) catecholate as a base.[5] By using the reaction, we discovered an aza-oxa[5]helicene from dixanthone as a potential circularly polarized luminescence material and two narrow-band-emissive molecules from easily accessible pentacene-6,13-dione and quinacridone, which emit blue and yellow light with high color purity and high fluorescence quantum yield. These findings emphasize the potential of iron-catalyzed C–H activation in expanding the range of donor-acceptor-type conjugated materials for organic electronics.



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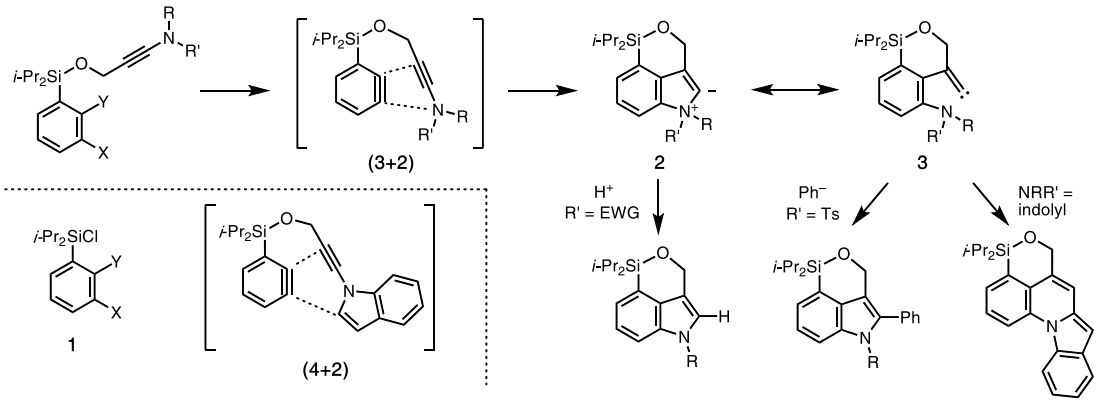
5. Shang, R.; Ilies, L.; Nakamura, E. *J. Am. Chem. Soc.* **2016**, *138*, 10132−10135.

ベンザインと窒素置換アルキンの新奇な分子内環化付加反応の開発

（京大院薬[1]・北大院総化[2]・北大 WPI-ICReDD[3]・JST-ERATO[4]・北大院理[5]）○田渡 司[1]・坂上 峻哉[1]・伊藤 琢磨[2]・原渕 祐[3,4]・前田 理[3,4,5]・高須 清誠[1]・瀧川 紘[1]
Novel Intramolecular Cycloadditions of Benzyne with Nitrogen-substituted Alkynes ([1]*Graduate School of Pharmaceutical Sciences, Kyoto University*, [2]*Graduate School of Chemical Sciences and Engineering, Hokkaido University*, [3]*WPI-ICReDD*, [4]*JST-ERATO*, [5]*Faculty of Science, Hokkaido University*) ○Tsukasa Tawatari,[1] Takaya Sakaue,[1] Takuma Ito,[2] Yu Harabuchi,[3,4] Satoshi Maeda,[3,4,5] Kiyosei Takasu,[1] Hiroshi Takikawa[1]

Herein, we report novel cycloaddition reactions of benzyne with nitrogen-substituted alkynes, using our originally-developed benzyne precursor **1**.[1,2] Our findings include intramolecular (3+2) cycloadditions of ynamides and *N*-alkynylindoles as three-atom components.[3] A notable feature is that indolium ylide intermediate **2**, whose resonance structure is vinylidene **3**, displays an ambivalent character with both nucleophilic and electrophilic properties, which facilitates the construction of various nitrogen-containing aromatic compounds. A further significant finding is the unprecedented (4+2) cycloadditions observed when employing *N*-alkynylindoles. In this presentation, the details of these reactions including substrate scope and mechanistic study by DFT calculations will be discussed.
Keywords : Benzyne; Ynamide; N-alkynylindole; Intramolecular reaction; Heteroaromatic

今回、我々は、ベンザインと窒素置換アルキンとの新奇な分子内環化付加反応を見出したので報告する。すなわち、独自に開発したベンザイン前駆体 **1**[1,2] を活用し、イナミドおよび *N*-アルキニルインドールとの分子内反応を検討した結果、窒素置換アルキンを三原子成分とする新奇な(3+2)環化付加反応が進行することが分かった[3]。また、環化付加反応の後に生じる中間体は、イリド **2** とその共鳴構造であるカルベン **3** の両方に相当する反応性を示し、多様な含窒素芳香族化合物の合成に展開できることを明らかにした。さらに、*N*-アルキニルインドールとの反応では、前例のない(4+2)環化付加反応が進行することも判明した。本講演では、基質一般性や DFT 計算による反応機構解析など、この反応の詳細について発表する。



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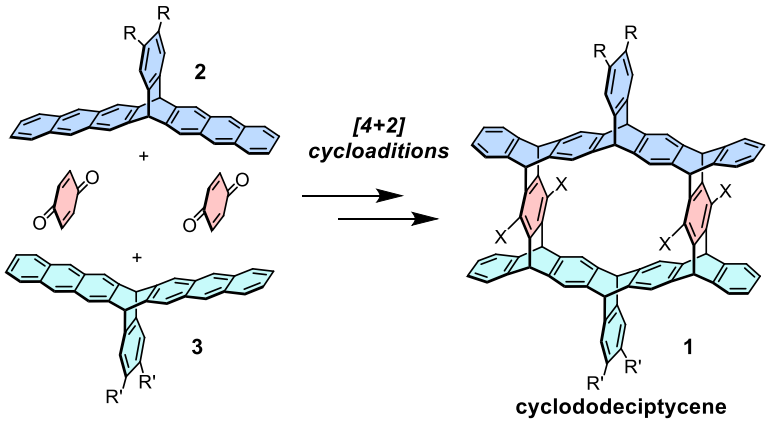
シクロドデシプチセンの合成

(九大総理工 [1]・九大先導研 [2]) ○兵頭 瑞樹 [1]・岩田 隆幸 [2]・新藤 充 [2]
Synthesis of cyclododeciptycene ([1]*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University,* [2]*Institute for Materials Chemistry and Engineering, Kyushu University*)
○Mizuki Hyodo,[1] Takayuki Iwata,[2] Shindo Mitsuru[2]

Cyclododeciptycene **1** is a macrocyclic compound consisting of six triptycene units, which was proposed by Hart. Although Hua synthesized its quinone derivative, and Itami and Segawa reported synthesis of its regioisomer, synthesis of compound **1** has not yet been achieved. In this study, based on our previous findings,[3,4] we constructed the cyclic structure through stepwise [4+2] cycloaddition reactions between the quinone unit and the anthracene unit. we have successfully synthesized cyclododeciptycene **1** for the first time by reducing the quinone.
Keywords : Cyclic Iptycenes; Macrocyclic compounds; Cycloaddition; Triptycenes

シクロドデシプチセン **1** は、6 つのトリプチセンユニットからなる大環状イプチセンである。1986 年に Hart らによりその構造が提唱された後、Hua らによるキノン体の合成 [1] や伊丹、瀬川らによる異性体の合成 [2] が報告されたが、**1** の合成は未だ達成されていない。我々は、これまでに活性アントラセンを用いた新規トリプチセン合成法を開発し [3]、これを基盤として、「ambident アントラセン」を用いた鎖状イプチセンの系統的合成の開発に成功した [4]。本研究では、これらの知見をもとに、シクロドデシプチセン **1** の合成について検討した。

トリプチセンを原料にアントラセン構造を 2 つもつトリプチセン **2** および **3** を合成した。これらに対して、キノンユニットを段階的に反応させることで、4 度の[4+2]環化付加反応を行い、環状構造を構築した。最後に、キノン部位の還元を経て、シクロドデシプチセン **1** の初の合成に成功した。



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