Facile Carbolithiation of Bent Alkyne without Catalyst. Tandem Route to Dibenzo[*b*,*f*]pentalenes from Dibenzocyclooctadiyne

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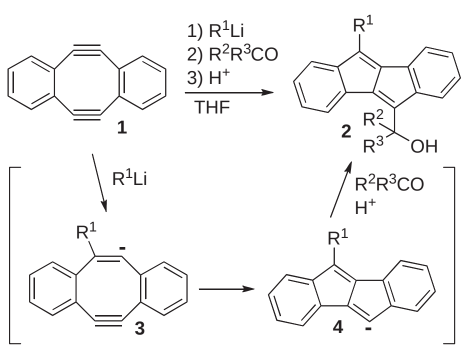
Nucleophilic addition of RLi to a triple bond of dibenzocycloocta[*a*,*e*]diyne provides dibenzo[*b*,*f*]pentalene motif through trans-annulation of the resulting vinyllithium. Dibenzopentalene anion thus formed reacts with various electrophiles such as aldehydes, alkyl halides, acid halide, and Me_3SiCl to give the corresponding products.

On account of its great promise for providing highly substituted alkenes,[1] carbometalation of alkynes with organometallic nucleophiles is still a challenge to synthetic chemists, because the acetylenic bond is rather inert towards nucleophilic attack unless alkynes bear heteroatom functions.[2] The superbase generated from *t*-BuOK and BuLi was employed for overcoming the low reactivity of diphenylacetylene, but double ortho metalation of the aromatic rings inevitably occurred leaving the triple bond untouched.[3] Although carbometalation with alkyllithium reagents in the presence of TMEDA has found limited utility,[4] recent progress of catalytic protocols has met with remarkable success even for unfunctionalized alkynes.[5] On the other hand, bent acetylenes undergo uncatalyzed reverse-demand Diels–Alder reactions induced by strain release.[6] We postulated therefore that strained alkynes must undergo nucleophilic attack even without catalyst. In this study, we investigated nucleophilic addition of alkyllithium reagents to highly strained 5,6,11,12-tetradehydrodibenzo[*a*,*e*]cyclooctene (**1**).[7] Moreover, it has been found that the initial nucleophilic addition triggers spontaneous trans-annular cyclization, and in situ trapping of the resulting intermediate with an electrophile affords diversely substituted dibenzo[*b*,*f*]-pentalenes, a unique class of molecules which have been receiving much attention due to their anti-aromaticity.[8]

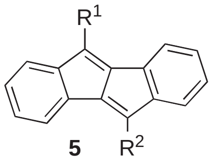
As expected, nucleophilic addition of alkyllithiums took place smoothly (Scheme 1). Presumably, a thermodynamic advantage gained by release of the strain upon sp-to-sp^2 hybridization change contributes to the facile addition. The resulting vinylic anions **3** spontaneously underwent trans-annular addition onto another triple bond. The newly formed vinylic anions **4** could be in situ trapped by various electrophiles. As an electrophile, various aldehydes were employable like benzaldehyde, *p*-chloro- and *p*-nitrobenzaldehyde, 2-naphthaldehyde, and heptanal. When the BuLi-initiated reaction was terminated with cyclohexenone, 1,2-adduct **2f** was obtained exclusively in 64% yield. As a nucleophile, EtLi and MeLi could be used,[9] and the corresponding adducts, **2g** and **2h**, were obtained in 69 and 72% yields, respectively.[10]

When other electrophiles such as PhCOCl, MeI, and Me_3SiCl were used, the three-component reaction also proceeded smoothly to afford the desired products **5**, respectively (Scheme 2). Notably, the present method is simpler and more convenient than those previously reported for the synthesis of pentalenes, i.e., nucleophilic addition,[11] flash vacuum pyrolysis (FVP),[12] dehydration[13] and transition-metal-catalyzed[14] or anionic trans-annulation.[15]



R^1= Bu, R^2= H, R^3= Ph (75%, **2a**), *p*-Cl-C_6H_4 (73%, **2b**),
p-$NO_2C_6H_4$ (76%, **2c**),
2-naphthyl (62%, **2d**), C_7H_{15} (64%, **2e**)
R^1= Bu, R^2, R^3= -$(CH_2)_5$- (64%, **2f**)
R^1= Et, R^2= H, R^3= Ph (69%, **2g**)
R^1= Me, R^2= H, R^3= Ph (72%, **2h**)

Scheme 1. Three component reaction through nucleophilic addition of R^1Li to a triple bond of **1** followed by trans-annulation.



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R^1= Bu, R^2= COPh (78%, **5a**)
R^1= Bu, R^2= Me (61%, **5b**)
R^1= Bu, R^2= Me_3Si (57%, **5c**)
R^1= Me, R^2= Me (63%, **5d**)

Scheme 2. Structures of **5**.

Aryl halides were not employable as an electrophile in the three-component process, but incorporation of aryl groups was feasible by the Suzuki–Miyaura or Stille coupling of iodopentalene **6**, which was easily prepared by treatment of **4** with iodine (Scheme 3). Because it was rather difficult to remove a dibutyldibenzo[*b*,*f*]pentalene by-product from the iodide on account of their similar polarity, the crude mixture obtained after usual workup was directly used for the next coupling reactions. The couplings proceeded smoothly to afford the desired products in good yields.[16]

In summary, we have shown that the strained acetylenic bond can readily undergo facile uncatalyzed carbolithiation. The tandem process initiated by nucleophilic addition of alkyllithium to **1** gives convenient access to diversely substituted dibenzo[*b*,*f*]pentalenes **2**, **5**, and **7**. Further development of this protocol and photochemical assessment of these compounds are now in progress.

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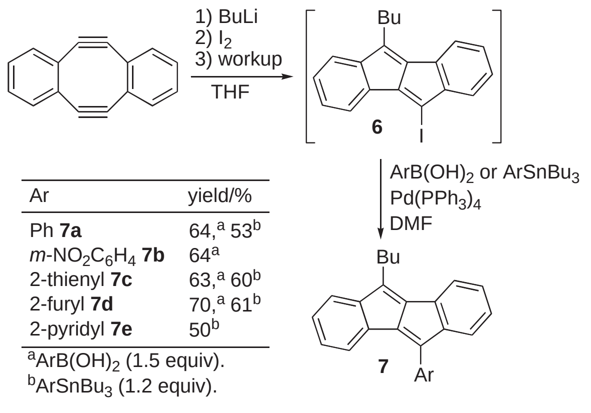

Ar	yield/%
Ph **7a**	64,[a] 53[b]
m-$NO_2C_6H_4$ **7b**	64[a]
2-thienyl **7c**	63,[a] 60[b]
2-furyl **7d**	70,[a] 61[b]
2-pyridyl **7e**	50[b]

[a] $ArB(OH)_2$ (1.5 equiv).
[b] $ArSnBu_3$ (1.2 equiv).

Scheme 3. Stepwise synthesis of **7**.

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9 Other nucleophiles such as PhLi, MeMgBr, Bu_2CuLi, BuCuLi, $Bu_2CuCNLi$, BuZnBr, L-selectride, and super-Hydride were not effective for the nucleophilic addition, and **1** was recovered.

10 Representative procedure for **2a**: BuLi (1.45 M in hexane, 0.84 mL, 1.21 mmol) was added to a THF solution (10 mL) of **1** (0.242 g, 1.21 mmol) at −78 °C, and the mixture was stirred for 30 min. Benzaldehyde (0.154 g, 1.45 mmol) in THF (4 mL) was added at this temperature, and the mixture was stirred for 1 h. After workup with aqueous NH_4Cl/AcOEt, the crude product was subjected to chromatography on silica gel (7:93 EtOAc/hexane) to give 0.330 g of **2a** (75%) as red powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, 2H, $J = 7.0$ Hz), 7.47 (d, 1H, $J = 7.0$ Hz), 7.35 (t, 2H, $J = 7.0$ Hz), 7.29 (t, 1H, $J = 7.5$ Hz), 7.12 (d, 1H, $J = 7.0$ Hz), 6.95–6.79 (m, 6H), 5.94 (d, 1H, $J = 2.5$ Hz), 2.62 (t, 2H, $J = 7.5$ Hz), 2.31 (d, 1H, $J = 2.5$ Hz), 1.67 (m, 2H), 1.49 (m, 2H), 0.96 (t, 3H, $J = 7.5$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.7, 147.9, 143.5, 143.2, 143.0, 140.9, 140.4, 135.2, 135.1, 128.7, 128.0, 127.7, 127.3, 126.9, 126.8, 124.3, 122.2, 121.8, 120.8, 71.4, 30.7, 26.3, 22.9, 13.9; Anal. Calcd for $C_{27}H_{24}O$: C, 88.97; H, 6.64%. Found: C, 89.08; H, 6.87%.

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