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Formation of stereodefined multiply substituted all-*cis* octatetraenes, tricyclo[4.2.0.$0^{2,5}$]octa-3,7-dienes and pentalenes via CuCl- or $FeCl_3$-mediated dimerization of 1-lithiobutadienes and 1,4-dilithiobutadienes

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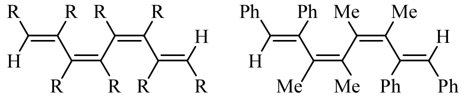
Abstract—Dimerization of 1-lithiobutadienes and 1,4-dilithiobutadienes depended remarkably on the substituents and metal halide reagents. Stereodefined multiply-substituted linear all-*cis* octatetraenes were prepared in moderate yields via $FeCl_3$-mediated dimerization of 1-lithiobutadienes, while CuCl induced the dimerization of alkyl-substituted 1,4-dilithio-1,3-dienes to form linear all-*cis* octatetraenes and tricyclo[4.2.0.$0^{2,5}$]octa-3,7-dienes. Interestingly, stereodefined pentalene derivatives were also obtained when 1,4-dilithio-1,3-dienes possessed both phenyl and alkyl substituents.

Development of synthetic methods for linear and cyclooctatetraenes is of great interest since these compounds are important as conjugated advanced materials.[1] Although several methods are known for the synthesis of octatetraenes derivatives, few methods can provide them with stereodefined skeletons.[2]

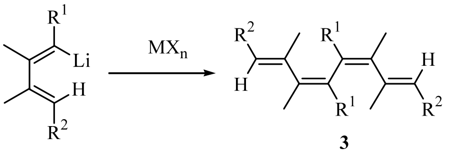
Dimerization of aryllithium compounds in the presence of metal salts has been one of the most important methods for the synthesis of biaryl compounds.[3] Tetraphenylenes have been also prepared by metal salt-mediated dimerization of 2,2′-dilithiobiphenyl.[4] This group has recently investigated the reaction of 1-lithiobutadienes **1** and 1,4-dilithiobutadienes **2** with a variety of organic substrates.[5–10] Since these lithiobutadiene derivatives can be readily obtained with high stereoselectivity,[11] we initiated a project to synthesis multiply-substituted octatetraenes **3** and **4** of stereodefined skeletons via metal salt-mediated dimerization (Eqs. (1), (2)). Interestingly, we found that dimerization products of 1-lithiobutadienes **1** and 1,4-dilithiobutadienes **2** depended remarkably on the substituents and metal halide reagents. In this paper, we would like to report our preliminary results.



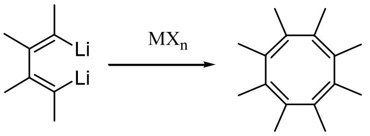
3a: R = Pr, 50%
3b: R = Bu, 56%

3c: 45%

Figure 1.



1 **3** (1)



2 **4** (2)

Keywords: dimerization; synthetic methods; CuCl; $FeCl_3$; 1-lithiobutadienes; 1,4-dilithiobutadienes; pentalenes; all-*cis* linear octatetraenes; tricyclo[4.2.0.$0^{2,5}$]octa-3,7-dienes.

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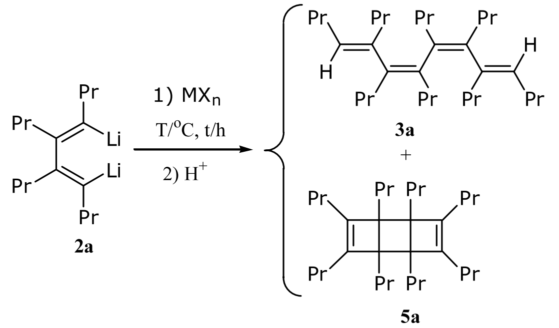
Table 1. CuX-mediated dimerization of 1,4-dilithio-1,3-diene **2a** affording octatetraene **3a** and tricyclooctadiene **5a**



Run	MX_n	T (°C)	t (h)	Yield (%)[a]	Ratio of **5a**:**3a**
1	2 equiv. $FeCl_3$	0	12	<5	–
2	2 equiv. $FeCl_3$	rt	12	<5	–
3	2 equiv. CuCl	0	4	81	1:0.8
4	2 equiv. CuBr	0	4	65	1:1.6
5	2 equiv. CuI	0	4	33	1:3
6	2 equiv. CuCl	−78	4	Trace	–
7	2 equiv. CuCl	rt	4	76	1:0.6
8	1 equiv. CuCl	0	4	46	1:0.9

[a] Combined isolated yields.

Although they are less studied, vinyllithium compounds have been reported to dimerize when treated with CuCl or CuI.[3b] However, when this treatment was applied to 1-lithiobutadiene derivatives **1**, we were surprised to note that this literature method did not induce the dimerization of **1**. The conjugated and multiply-substituted butadienyl skeletons of **1** must be responsible for this failure. We finally found that one equivalent of $FeCl_3$ at 0°C in diethyl ether solution could mediate the dimerization of **1** to afford multiply substituted and stereodefined all-*cis* octatetraenes **3a**–**c** in moderate isolated yields (Fig. 1). To the best of our knowledge, this reaction is the first example of its kind.

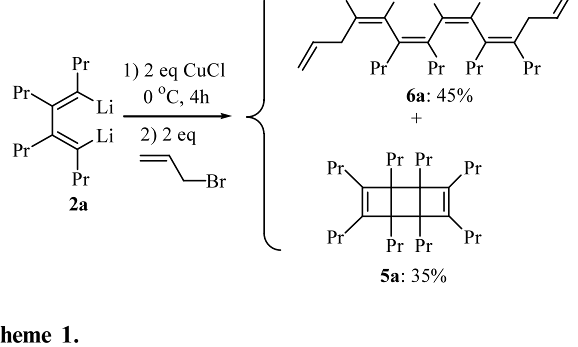
We then investigated the metal salt-mediated dimerization of 1,4-dilithiobutadienes **2**, expecting formation of cyclooctatetraenes **4** (Eq. (2)). One example has been reported regarding the formation of cyclooctatetraene from $NiBr_2$ complex-mediated dimerization of (*E*,*E*)-1,4-dilithio-1,4-diphenyl-1,3-butadiene by Carpenter and co-workers.[12] As shown in Table 1, neither $FeCl_3$ nor CuX afforded any expected cyclooctatetraenes **4**. Instead, a mixture of linear octatetraene **3a** and tricyclo[4.2.0.0^{2,5}]octa-3,7-diene **5a**[13] was obtained when 1,4-dilithio-1,2,3,4-tetrapropyl-1,3-diene **2a** was used. The best results in terms of the yields of products was realized when two equivalents of CuCl were used at 0°C. Although detectable amounts of **3a** and **5a** were formed, the reactions mediated by $FeCl_3$ afforded messy mixtures of products.

When a reaction mixture of CuCl and **2a** was treated with 2 equivalents of allyl bromide, the bisallylated product **6a** was obtained in 45% isolated yield, along with **5a** in 35% isolated yield (Scheme 1). This result indicates that two Cu–C bonds exist in the linear intermediate.

More interestingly, when the butadiene skeleton of a 1,4-dilithiobutadiene has both phenyl and alkyl substituents, CuCl-mediated dimerization reaction afforded, in addition to linear octatetraenes **3**, stereodefined pentalene derivatives **7** (Scheme 2).[14,15] Compounds **3d** and **7a** were obtained from **2b**, while compounds **3e** and **7b** were generated from **2c**. Formation of tricyclo[4.2.0.0^{2,5}]octa-3,7-diene **5** was not observed in these reactions.

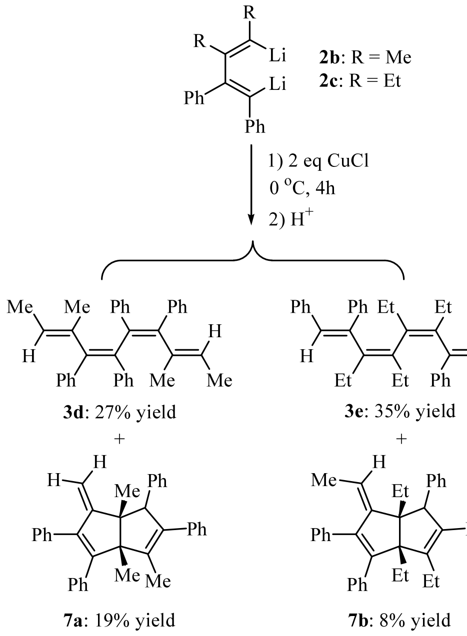
The structures of pentalene derivatives **7a** and **7b** have been determined by single-crystal X-ray analysis. The structure of **7b** is shown in Figure 2.[16]

It is interesting to compare the regiochemistry of **3c** with that of **3d**. In **3c**, the four phenyl groups are bonded to the two terminal double bonds, while the four phenyl groups are bonded to the two internal double bonds in **3d**. Although the reason is not yet



Scheme 1.

clear, the two terminal double bonds in **3e** bear the four phenyl groups, while those in **3d** bear the four alkyl groups (methyl groups).



Scheme 2.

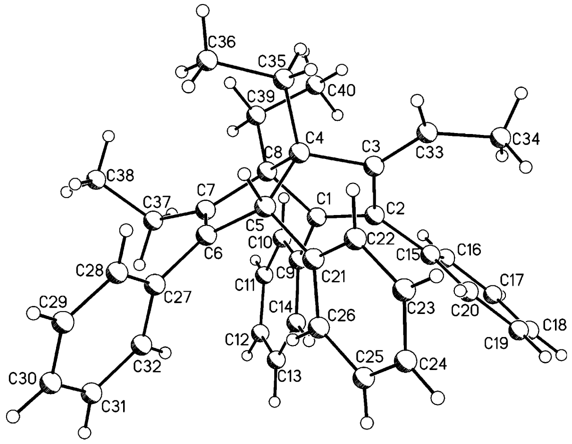
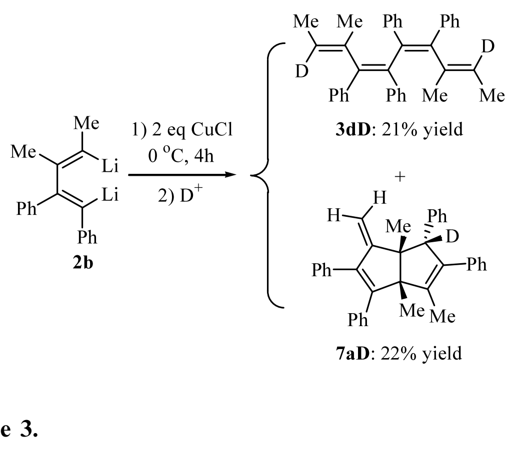


Figure 2. Single crystal X-ray structure of **7b**. Selected bond lengths (Å): C1–C2 1.342(2), C2–C3 1.479(2), C3–C4 1.522(2), C3–C33 1.335(2), C4–C5 1.583(2), C4–C8 1.576(2), C5–C6 1.479(2), C6–C7 1.341(2), C7–C8 1.515(2).



Scheme 3.

Deuteriolysis of the reaction mixture of **2b** instead of hydrolysis afforded the deuterated products **3dD** and **7aD** in 21 and 22% isolated yields, respectively (Scheme 3). This result sheds a clue for understanding the reaction mechanism.

Reaction mechanisms for the metal salt-mediated dimerization of aryl- and vinyllithium reagents have been discussed in the literature.[3] However, reaction mechanisms for the metal-mediated dimerization of 1,4-dilithiobutadienes affording linear octatetraenes, tricyclo[4.2.0.$0^{2,5}$]octa-3,7-dienes and stereodefined pentalene derivatives are not yet clear. It is obvious that a few competitive reaction paths are involved. Further investigations into the reaction mechanism, scope and limitations of this reaction are in progress.

Acknowledgements

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15. Selected characterization data for **7a**: Yellow crystalline solid. Mp 196–198°C. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.45–1.54 (m, 9H), 3.99 (s, 1H), 4.63 (d, $J=2.4$ Hz, 1H), 4.77 (d, $J=2.4$ Hz, 1H), 6.21–7.25 (m, 20H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.5, 19.7, 23.9, 58.3, 67.7, 69.6, 107.1, 125.8, 126.3, 126.3, 126.6, 127.1, 127.2, 127.8, 127.8, 128.8, 129.4, 129.9, 134.9, 137.8, 138.0, 138.1, 139.9, 141.0, 141.6, 150.3, 157.9. HRMS calcd for $C_{36}H_{32}$ 464.2504, found 464.2503. Anal. calcd for $C_{36}H_{32}$: C, 93.06; H, 6.94. Found: C, 92.82; H, 6.92. The structure of this compound was determined by single-crystal X-ray analysis.
16. X-Ray crystallographic data for **7b**: A colorless block crystal having approximate dimensions of 0.4×0.35×0.35 mm was mounted on a glass fiber. X-Ray data were collected on a Rigaku RAXIS RAPID IP diffractometer with graphite-monochromated Mo/Kα radiation ($\lambda=0.71073$ Å). $C_{40}H_{40}$, $f_w=520.72$, monoclinic, space group $C2/c$, $a=16.159(3)$, $b=13.112(3)$, $c=29.605(6)$ Å, $V=6169(2)$ Å^3; $Z=8$; $D_{calcd}=1.121$g cm^{-3}; $R_1=0.0455$, $wR_2=0.1173$. CCDC 213915.