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Tetrahedron Letters 45 (2004) 2671–2675

Tetrahedron Letters

Noncatalytic, solvent-free thermal formation of cyclic trimers using 1,6-bis(acyloxymethyl)hexa-2,4-diyne derivatives

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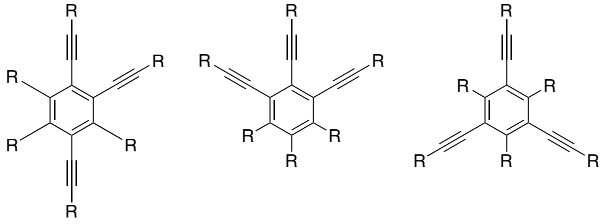
Received 22 October 2003; revised 22 January 2004; accepted 23 January 2004

Abstract—The thermal reactivity of diacetylenes in the liquid phase was studied extensively to elucidate the cooperative mechanism of polymerization.

Heat, UV light irradiation, or γ-irradiation can induce polymerization of diacetylenes in the solid state, especially when they are arranged in an appropriate orientation for 1,4-addition.[1] Polymerization can even occur in the liquid crystalline phase if the diacetylenes are sufficiently reactive in the temperature range over which the mesophase exists.[2]

Polymerization of diacetylenes in neat liquid without catalysts would be advantageous from the environmental standpoint. However, because the liquid-phase polymerization of diacetylenes requires extreme conditions,[3] it has scarcely been investigated. In this study, we carried out the liquid-phase polymerization of diacetylenes with long alkyl chains (**1**, **2**) and acyloxymethyl groups (**3**, **4**) at both ends of a 1,3-butadiynyl moiety and found that bis(acyloxymethyl)-1,3-butadiynes **3** and **4** polymerized rapidly in the melt state at 120 °C. Moreover, we isolated small amounts of cyclic trimers **5a** (1,2,4-triethynylbenzene derivative) and **5b** (1,2,3-triethynylbenzene derivative), and the corresponding heptyl analogues, respectively. This result provided clues about the cooperative mechanism of the cyclic trimerization.



5a **5b** **5c**

R = CH_2OCOCH_3

Symmetrically disubstituted diacetylenes **1**, **2** and **3**, **4** were prepared by Eglinton coupling of the monosubstituted acetylene derivatives (Scheme 1).[4] The differential scanning calorimetry thermogram (scanning rate 2 °C/min) of triaconta-14,16-diyne (**1**) exhibited only an endothermic peak at 54.5–55.0 °C, corresponding to the melting process, whereas the thermogram of bis(acetyloxymethyl) derivative **3** showed a broad exothermic peak above 120 °C ($\Delta H = 67.0$ kJ/mol), accompanied by an endothermic peak (melting process) at 30.0–30.5 °C (Fig. 1). The exothermic peak can be ascribed to the heat of oligomerization of diacetylene **3**.

The liquid-phase polymerization of diacetylenes **1**, **2** and **3**, **4** was carried out in a sealed Pyrex tube under a nitrogen atmosphere at 110 °C for 24 h. Although diacetylene monomer **1**, **2** did not polymerize under these conditions,[5] diacetylene **3** polymerized smoothly. The conversion yield of **3** was estimated to be 76% by gel

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Keywords: Liquid-phase polymerization; Diacetylene; Triethynylbenzene; Dewar benzene derivative.

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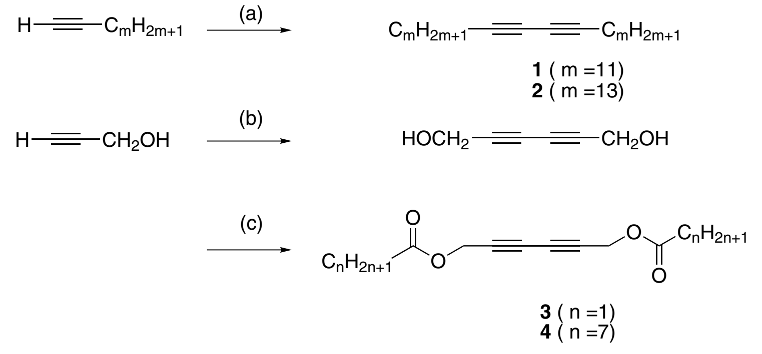
doi:10.1016/j.tetlet.2004.01.134



Scheme 1. Reagents and reactions: (a) $Cu(OAc)_2{\cdot}H_2O$/Pyridine, MeOH, **1** ($m = 11$); 41%, **2** ($m = 13$); 46%. (b) $Cu(OAc)_2{\cdot}H_2O$/Pyridine, MeOH, 56%. (c) $C_nH_{2n+1}COCl/Et_2O$, Et_3N, **3** ($n = 1$); 60%, **4** ($n = 7$); 56%.

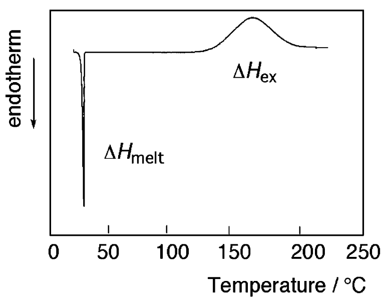


Figure 1. DSC thermogram of **3**.

permeation chromatography (GPC, JAIGEL 1H 2H, eluent: chloroform). The wide distribution of the molecular weights of the oligomers obtained from **3** was analyzed by GPC, and the fractions of the largest retention volume (161 mL) and the second largest one (140 mL) were isolated. The first fraction contained trimeric isomers, and the second fraction (broad peak) contained oligomers up to 12-mer as revealed by time-of-flight (TOF) mass spectroscopy.[6] The major and minor isomers (4:1 ratio) of the isolated trimeric mixture (6% yield) were separated by liquid column chromatography (eluent: 95:5 hexane–ethyl acetate). Elemental analysis, EI mass spectrometry, and ^1H NMR and ^{13}C NMR spectroscopy suggested that the major isomer was 1,2,4-triethynylbenzene derivative (**5a**).[7] An authentic sample of **5a** was prepared independently by heating **3** in the presence of $Ni(CO)_2(PPh_3)_2$ in refluxing benzene for 10 h.[8] The product (42% yield), which was isolated and purified by silica gel column chromatography, was identical with the isolated major isomer **5a**. Single crystals of **5a** were obtained by recrystallization from 1:1 (v/v) dichloromethane–hexane, and X-ray crystallographic analysis unequivocally confirmed the structure of **5a** (Fig. 2).[9] On the other hand, spectroscopic data[10] suggested that the minor trimeric isomer was 1,2,3-triethynylbenzene derivative (**5b**). Since this derivative has never been obtained from a transition metal catalyzed reaction, product **5b** is characteristic of the liquid-phase oligomerization. Diacetylene **4** also exhibited thermal reactivity, affording the corresponding products (data not shown). Incidentally, the transition metal catalyzed oligomerization of **3** using $CoCp(CO)_2$ (Cp = cyclopentadienyl) afforded **5a** (21% yield) and 1,3,5-triethynyl derivative **5c**[11] (15% yield), whereas the 1,2,3-triethynyl derivative **5b** was not obtained.[12] This result provides additional support for the assigned structure of **5a**–**c**. The formation of **5a** and **5c** by the cobalt complex catalyzed trimerization can be explained on the basis of previous reports.[13]

The distribution of products **5a** and **5b** provides a clue for elucidating the mechanism of the liquid-phase trimerization (Fig. 3). Since formation of **5b** with the 1,2,3-trisubstituted pattern can only be rationalized in terms of the intermediacy of Dewar benzene (**6b**), formation of **5a** is presumably also due to the thermally allowed ring opening of Dewar benzene derivative (**6a**,**a′**).[14] Viehe et al. reported[15] that Dewar benzene derivatives can be formed by $[_{\pi}4_s + {}_{\pi}2_s]$ addition of cyclobutadiene and acetylene derivatives. Taking this result into consideration, it is likely that cyclobutadiene (**7a**), which is formed transiently in a stepwise manner, reacts with monomer **3** immediately only when they are in close proximity, affording Dewar benzene derivatives **6**.

The formation of Dewar benzene **6a** can be explained by the addition of cyclobutadiene **7a** with diacetylene monomer **3**, which approaches from the other side of the ethynyl substituents of cyclobutadiene **7a** (Fig. 3; mode A). Judging from the symmetry of HOMO of **7a** and LUMO of **3** calculated by PM3 method (MOPAC 97)

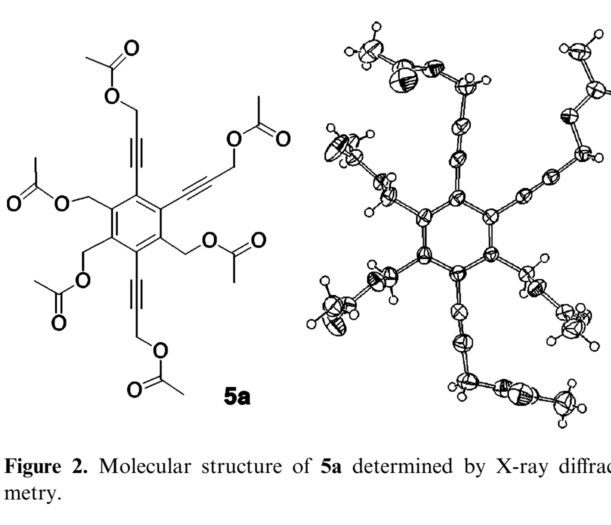


Figure 2. Molecular structure of **5a** determined by X-ray diffractometry.

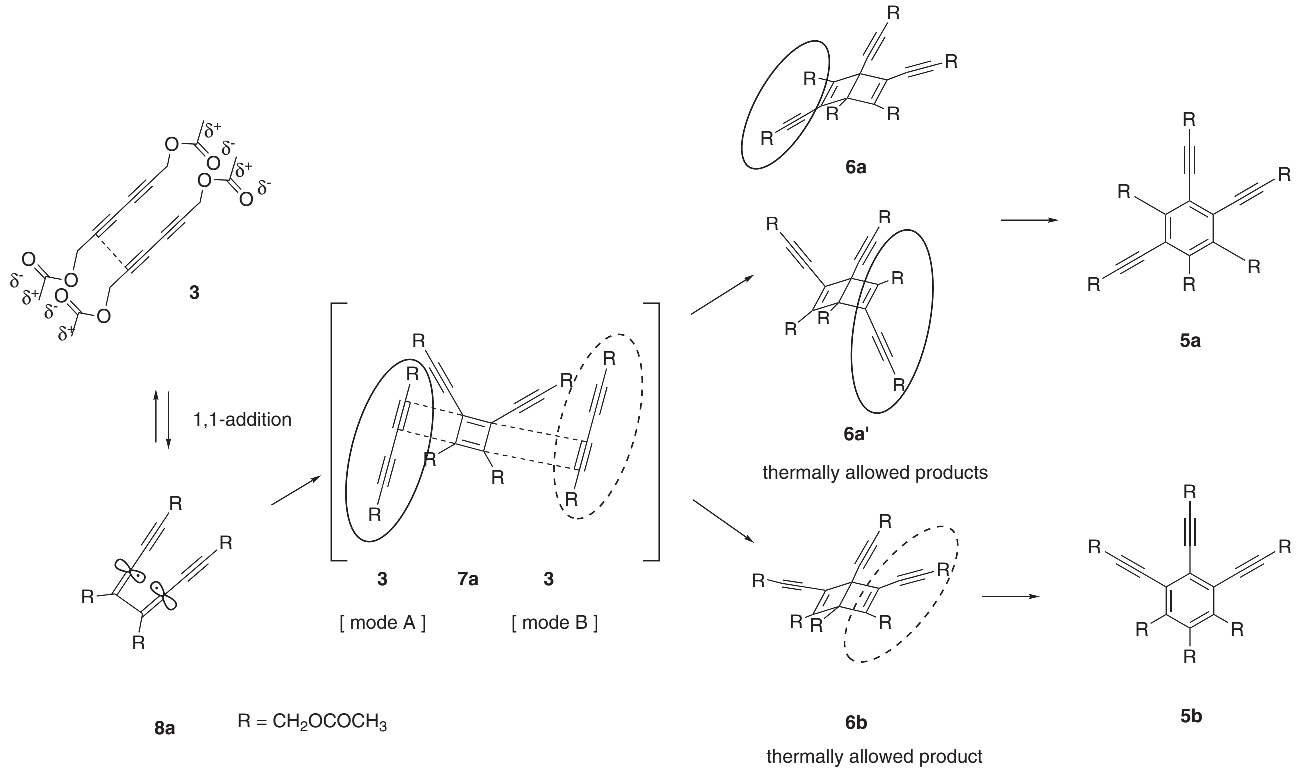


Figure 3. Reaction mechanism for the formation of 1,2,4-, 1,2,3-trisubstituted ethynylbenzene. Preorganized diacetylene **3** affords cyclobutadiene **7a**, which adds to diacetylene **3** in mode A or B, to give Dewar benzene **6a**, **6a′**, or **6b**, respectively.

(Fig. 4), the electro-cyclic reaction between **7a** and **3** is considered to occur in the thermally allowed [$_{\pi}4_s + {}_{\pi}2_s$] manner. If the reacting monomer **3** is located close to the substituent side of cyclobutadiene **7a** (Fig. 3; mode B), the addition reaction gives rise to Dewar benzene **6b** also through the thermally allowed [$_{\pi}4_s + {}_{\pi}2_s$] process. On the other hand, 1,3,5-derivative **5c**, which must be generated from Dewar benzene **6c**, is considered to be formed by the addition of 1,3-disubstituted cyclobutadiene derivative **7b** with diacetylene **3**. This product **5c**, however, was not detected at all because of the poor thermodynamic stability of biradical intermediate **8b** (Fig. 5).

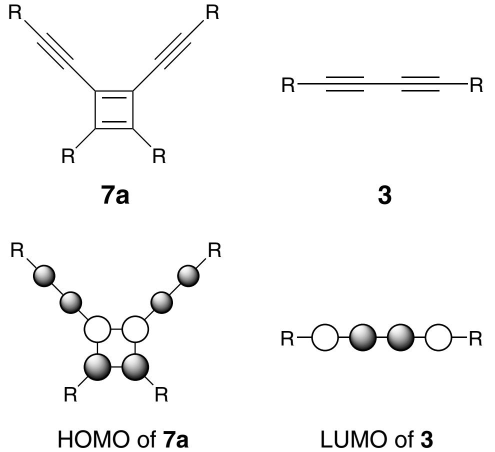
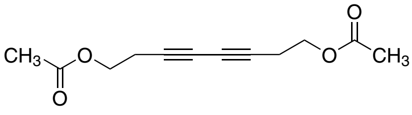


Figure 4. HOMO of cyclobutadiene **7a** and LUMO of diacetylene **3**.

Although it is difficult to elucidate the mechanism of the liquid-phase polymerization of diacetylenes **3** in detail at the present stage, local alignment of **3** enables to form 1,1-(1,4)-addition to give diradical **8a**.[16] The diradical is likely to afford Dewar benzene (**6a**,**a′**,**b**) through the transition state [**7a**···**3**], which can be accessed only when monomer **3** is prelocated closely to the transiently formed cyclobutadiene. If the transition state [**7a**···**3**] for affording Dewar benzene cannot be formed, diradical **8a** will decompose to two monomers **3**, because of the extremely short lifetime of cyclobutadiene **7a** at this temperature (Fig. 3).[17]

In contrast, monomer **9**, which has an ethylene unit as a spacer, does not exhibit any reactivity in the liquid phase. Presumably, the conformational freedom of the ethylene unit is too large to restrict monomers to the plausible transition state for the formation of Dewar benzenes. Incidentally, hybrid monomer **10** did not trimerize in the liquid phase.[18] The lack of oligomerization of diacetylenes with alkyl chains (**1**,**2**) also supports the foregoing interpretation.[5]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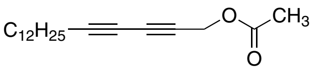
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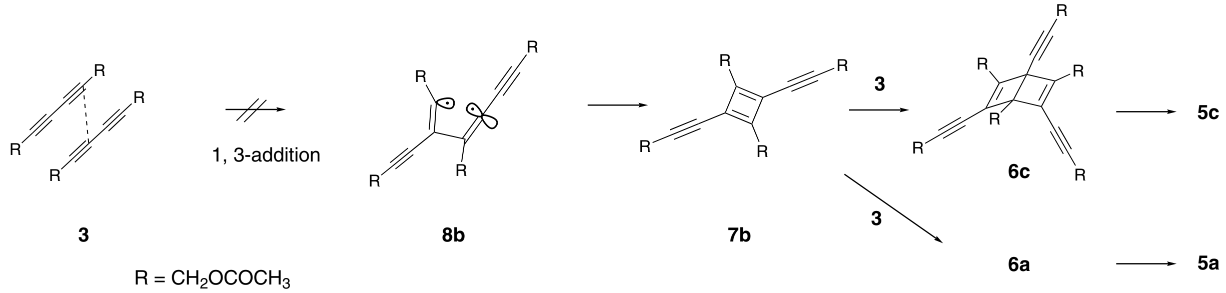

Figure 5. Reaction mechanism for the formation of 1,3,5-trisubstituted ethynylbenzene. This reaction, however, does not take place due to the instability of biradical **8b**.

In summary, we found that triethynylbenzenes **5** with a specific substitution pattern were obtained simply by heating an appropriate monomer without the use of solvents or catalysts. This result suggests that acetylene monomers are loosely preorganized for the 1,1- (1,4)-addition to occur even in the liquid phase, presumably due to the electro-static interaction between polar ester groups. Furthermore, the isolation of triethynylbenzenes **5a** and **5b** provides a clue for characterizing the structures of higher oligomers because triethynylbenzenes possibly react to form phenylene-type oligomers under the reaction conditions.[19]

Acknowledgements

We thank Dr. T. Kudo (Bruker Daltonics) for skillful TOF measurements. This work was supported by a grant-in-aid from The 21st Century COE (Center of Excellence) program (Research Center for Integrated Science) of the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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5. Either dialkyl-substituted diacetylene **1** or **2** did not exhibit any reactivity at all although these diacetylenes with long alkyl chains are likely to align side-by-side due to the dispersion force between alkyl groups. Although alkyl chains are close to each other, it does not necessarily mean that the reactive site of each **1** or **2** is located in proximity intermolecularly.
6. TOF mass spectra were obtained with a Bruker Daltonics Autoflex spectrometer, using α-cyano-4-hydroxycinnamic acid as a matrix.
7. Spectral data for **5a**: ^{1}H NMR (270 MHz, $CDCl_3$/TMS) δ 2.02 (s, 3H), 2.03 (s, 3H), 2.06 (s, 3H), 2.10 (s, 3H), 2.11 (s, 6H), 4.87 (s, 2H), 4.92 (s, 2H), 4.93 (s, 2H), 5.30 (s, 2H), 5.31 (s, 2H), 5.33 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.5, 20.6, 20.65, 20.70 (CH_3), 52.34, 52.46, 52.50, 61.64, 63.26 ($-CH_2O-$), 80.59, 81.41, 81.85, 93.33, 94.14, 94.63 ($C{\equiv}C$), 125.72, 127.43, 127.62, 137.79, 138.21, 140.10 (Ar), 170.09, 170.14, 170.37, 170.62 ($C{=}O$); EI mass spectrum *m*/*z* (rel intensity) 582.2 (M^+, 20), 420.2 (100). Anal. Calcd for $C_{30}H_{30}O_{12}$: C, 61.85; H, 5.19. Found: C, 61.75; H, 5.19.
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9. Crystal structure data for **5a**: colorless needles (crystallized from dichloromethane–hexane); crystal system monoclinic; space group $P2_1/n$; $Z = 4$; cell parameters $a = 8.237(1)$ Å, $b = 18.847(2)$ Å, $c = 19.131(3)$ Å, $\beta = 102.168(2)°$; $V = 2903.2(7)$ Å^3; radiation (Mo Kα) $\lambda = 0.71073$ Å; 379 variables for 2597 reflections; final $wR_2(F^2) = 0.114$; $R_1(F) = 0.057$; atomic coordinates have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication number CCDC221909. 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].
10. Spectral data for **5b**: ^{1}H NMR (270 MHz, $CDCl_3$/TMS) δ 2.04 (s, 3H), 2.06 (s, 6H), 2.13 (s, 3H), 2.14 (s, 6H), 4.96 (s, 4H), 4.99 (s, 2H), 5.23 (s, 2H), 5.36 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.69, 20.70, 20.76, 20.77 (CH_3), 52.50, 52.62, 59.60, 61.82 ($-CH_2O-$), 81.57, 82.76, 92.69, 93.49 ($C{\equiv}C$), 127.83, 129.19, 136.04, 137.94 (Ar), 170.13, 170.18, 170.37, 170.38 ($C{=}O$); EI mass spectrum *m*/*z* (rel intensity) 582.2 (M^+, 21), 420.2 (100).
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12. Spectral data for **5c**: ^{1}H NMR (270 MHz, $CDCl_3$/TMS) δ 2.10 (s, 9H), 2.13 (s, 9H), 4.90 (s, 6H), 5.38 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.56, 20.61 (CH_3), 52.25, 63.19 (–CH_2O–), 80.11, 93.89 ($C{\equiv}C$), 125.93, 139.75 (Ar), 170.04, 170.55 ($C{=}O$); EI mass spectrum *m*/*z* (rel intensity) 582.2 (M^+, 21), 420.2 (100).
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16. Possibility of formation of cyclobutadiene **7a** through 1,4-addition cannot be excluded. In this case, however, the ring closure of the geminate biradical **8a** to cyclobutadiene **7a** requires the conformational change of the biradical **8a**.
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18. Hybrid-type derivative **9** was synthesized as follows. To a solution of 0.3 mmol of 1-tetradecyne in 10 mL of dry diethyl ether was added dropwise 0.19 mL of a 1.58 M solution of *n*-butyllithium in hexane at −78 °C. After 1 h, I_2 powder was added, and the mixture was allowed to react for 3 h. The reaction mixture was hydrolyzed with ice water and extracted with hexane. The organic phase was washed with water and dried over $MgSO_4$. Thereafter, Glaser coupling was performed according to the procedure reported in the literature. Ben-Efraim, D. A. *Tetrahedron* **1973**, *29*, 4111–4125.
19. Snow, A. W. *Nature* **1981**, *292*, 40–41, and references cited therein. The proposed structure of the polymers in this earlier work may be re-examined on the basis of the present results. Preliminary experiment revealed that the relative yield of cyclic trimers **5a**,**b** became maximum after 12 h, decreasing gradually thereafter. This tendency suggests that the cyclic trimers reacted with a monomer, or trimers, affording phenylene-type oligomers, at least, to some extent.