A direct route to conjugated enediynes from dipropargylic sulfones by a modified one-flask Ramberg–Bäcklund reaction †

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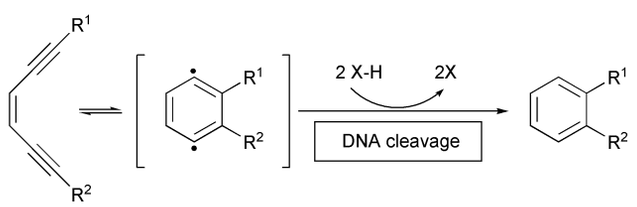
The reaction of dipropargylic sulfones with dibromodifluoromethane in the presence of alumina-supported KOH in dichloromethane solution results in facile rearrangement affording the corresponding conjugated linear and cyclic enediynes in good yields. This result shows that the direct transformation of α- and α′-hydrogen bearing sulfones assembles enediyne units without resorting to the prior preparation of the α-halo sulfone precursors in a separate step.

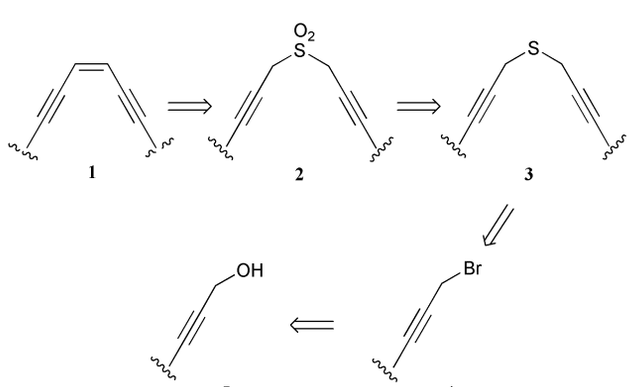
Introduction

The recent discovery of several potent antitumor antibiotics containing enediynes or analogues and models of enediynes has pushed the exploration of conjugated enediynes to the forefront of chemical and biological research. Not only a unique structural feature, but also their most fascinating aspect is the unprecedented mechanism of the cleavage of DNA that originates from the chemical reactivity of the enediyne moiety (Scheme 1).[1] The greatly increased demand for structurally



Scheme 1 Bergman cyclization of a typical enediyne moiety.

diverse enediynes has prompted synthetic chemists to seek novel and more efficient approaches to the enediyne functionality. Many strategies have been developed to construct or modify enediyne systems.[2] Perusal of the numerous reviews on the chemistry of the enediynes reveals that the field is dominated by palladium catalyzed cross coupling reactions of terminal alkynes with vinyl halides, or their equivalents, as a rapid convergent entry into the hex-3-ene-1,5-diyne moiety. Another method entails the anchoring of a carbon–carbon triple bond to each end of a latent olefinic double bond which is subsequently revealed by an eliminative process. The synthesis of a cyclic enediyne parent system calls for mild conditions with, at the same time, a strong driving force for the ring closure reaction. Most often, an acetylide carbonyl addition is used as the ring closure reaction.[2a] Danishefsky *et al.*, however, efficiently obtained highly substituted, 10-membered cyclic enediynes by two-fold palladium-catalyzed coupling of iodoacetylene with *cis*-1,2-bis(trimethylstannyl)ethylene.[2b] Jones' method was based on a sequence of tandem carbenoid coupling and elimination of two propynylic bromide units.[2c] In contrast to ring closure, the Ramberg–Bäcklund reaction has been put to good use by Nicolaou for the conversion of cyclic α-chlorodipropargylic sulfones into the corresponding enediyne arrays.[2d] We recently reported a new protocol of the Ramberg–Bäcklund reaction to effect the direct transformation of α- and α′-hydrogen bearing sulfones into alkenes.[3] We became interested in using our procedure to synthesize enediynes **1** (Scheme 2) without resorting to the prior preparation of the



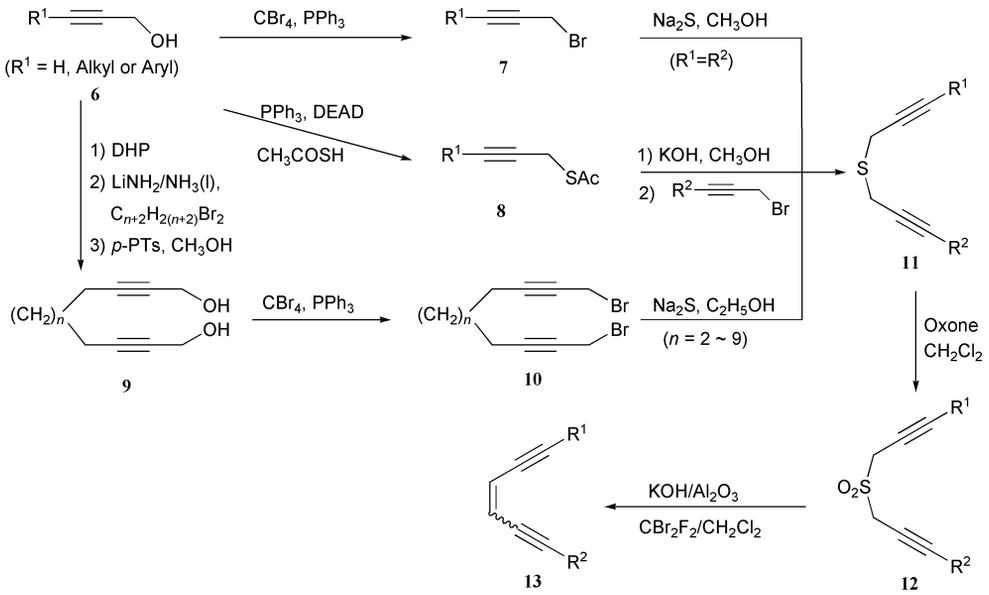
Scheme 2 Strategy of constructed enediyne.

α-halosulfone precursors in a separate step. In this paper we extend this methodology to include the synthesis of conjugated linear and cyclic enediynes as well as full details of their preparation.

Results and discussion

Scheme 2 outlines the strategy which we pursued in the quest for stereopure substituted enediyne **1**. We wished to prepare it from dipropargylic sulfone **2**. The strategy shown in Scheme 2 was thought to be feasible because of the successful application of our procedure to the formation of conjugated trienes from diallylic sulfones, and conjugated tetraenes from allylic dienylic sulfones.[3b,3d] Our synthetic method was also applied to the synthesis of natural products containing a triene unit such as galbanolenes. The procedure reported here started with a dipropargylic sulfone **2** with two triple bonds already in place and the new double bond to be realized by our modified Ramberg–Bäcklund procedure. This disconnection approach relied on the

† Electronic supplementary information (ESI) available: spectroscopic data for compound **8**, **9o**, **10o**, **11a**–**11g**, **11o**, **12a**–**12o**, **13a**–**13g** and **13o**. For direct electronic access see http://www.rsc.org/suppdata/p1/b2/b207296n/



Scheme 3 Synthesis of enediynes **13a**–**o** *via* Ramberg–Bäcklund reaction: (**a**) $R^1 = n\text{-}C_5H_{11}$, $R^2 = H$; (**b**) $R^1 = t\text{-}Bu$, $R^2 = H$; (**c**) $R^1 = Ph$, $R^2 = H$; (**d**) $R^1 = n\text{-}C_5H_{11}$, $R^2 = Ph$; (**e**) $R^1 = t\text{-}Bu$, $R^2 = Ph$; (**f**) $R^1 = n\text{-}C_5H_{11}$, $R^2 = n\text{-}C_5H_{11}$; (**g**) $R^1 = Ph$, $R^2 = Ph$; (**h**) $R^1,R^2 = (CH_2)_4$; (**i**) $R^1,R^2 = (CH_2)_5$; (**j**) $R^1,R^2 = (CH_2)_6$; (**k**) $R^1,R^2 = (CH_2)_7$; (**l**) $R^1,R^2 = (CH_2)_8$; (**m**) $R^1,R^2 = (CH_2)_9$; (**n**) $R^1,R^2 = (CH_2)_{10}$; (**o**) $R^1,R^2 = (CH_2)_{11}$.

synthesis of dipropargylic sulfone **2**, which was in turn prepared from propargylic bromide **4**. There are two general approaches for the assembly of linear or cyclic sulfide **3**, from which the corresponding sulfone **2** could be obtained after oxidation. One makes use of the coupling reaction between a propargylic bromide **4** and Na_2S, which afforded the symmetrical linear and cyclic sulfides. The alternative is to couple a propargylic thioacetate to a propargylic bromide, thus providing the unsymmetrical linear sulfides **3**. These procedures invariably demanded the preparation of propargylic alcohol **5**, the common intermediate for the requisite bromide **7**, **10** and thioacetate **8** (Scheme 3).

We used propargylic alcohols **6** (R^1 = H, alkyl or aryl) as starting materials. These alcohols (R = alkyl or aryl) were either transformed into the corresponding propargylic bromides **7** by reaction with CBr_4 and Ph_3P in nearly quantitative yield, or into the corresponding thioacetates **8** using the Mitsunobu reaction [4] with thioacetic acid in the presence of Ph_3P and DEAD (diethyl azodicarboxylate), respectively. Coupling of propargylic bromide **7** with Na_2S in CH_3OH furnished the symmetrical linear sulfide **11** ($R^1 = R^2$). Alternatively, *in situ* cleavage of the acetyl moiety of **8** with KOH in CH_3OH followed by alkylation of the resulting proparyglic thiol with proparygl bromide, provided the unsymmetrical linear sulfides **11** ($R^1 \neq R^2$) in good yields (Table 1). On the other hand, protection of propargylic alcohol **6** (R = H) with DHP (3,4-dihydro-2*H*-pyran), and conversion to the corresponding anion *via* $LiNH_2$ in liquid ammonia, followed by alkylation of the resulting anion with dibromides afforded the bis(acetylenic) compounds, which were deprotected under methanolic acid conditions leading to diols **9h**–**o** in good yields (Table 2). The dibromides **10h**–**o** were prepared from **9h**–**o** by the action of CBr_4 and Ph_3P. These substrates were then reacted with Na_2S under high dilution conditions to furnish the cyclic sulfides **11h**–**o**. All of the dipropargylic sulfides **11** were oxidized by oxone ($2KHSO_5{\cdot}KHSO_4{\cdot}KSO_4$) [5] in CH_2Cl_2 to give high yields of the corresponding sulfones **12**. Subjecting the dipropargylic sulfones **12** to our previously described modified Ramberg–Bäcklund reaction protocol (CBr_2F_2, KOH–Al_2O_3, CH_2Cl_2),[3a] they proceeded smoothly to give a readily separable mixture (approximate 1 : 1) of the linear (*E*)- and (*Z*)-enediynes and cyclic (*Z*)-enediynes **13**. For the linear enediynes synthesized in this series, the (*E*)-isomers had consistently larger R_f values than those of the corresponding (*Z*)-isomers and each pair was easily separated by flash column chromatography over silica gel. The configurations of the newly formed double bonds in the unsymmetrical enediynes (**13a**–**13e**) were readily diagnosed by the typical coupling constant of 16.1–16.0 Hz and 10.9–10.0 Hz for the *trans*- and *cis*-olefinic protons, respectively. For the symmetrical enediynes **13f** and **13g**, the issue of stereochemistry was confirmed by comparison of their physical and spectroscopic properties to those reported in the literature.[6,7] Furthermore, an X-ray crystallographic analysis of **13g** revealed an (*E*)-conformation. Similarly treatment of the 18-membered ring sulfone **12o** (n = 9) with KOH–Al_2O_3 led to the desired 17-membered ring enediyne **13o** (n = 9) along with the (*E*)-isomer (2%). Based on the preferential formation of the (*Z*)-isomer in all the cyclic enediynes studied and the fact that they had consistently smaller R_f values than those of the corresponding (*E*)-isomer, they were easily separated by flash column chromatography over silica gel. We therefore tentatively assigned the faster running isomers the (*E*)-geometry (δ_H = 5.96 ppm), and the slower the (*Z*)-geometry (δ_H = 5.74 ppm). This outcome was similar to the case of linear enediynes presented previously. Thus, this provides a rapid route to stereochemically defined linear and cyclic conjugated enediynes.

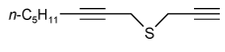
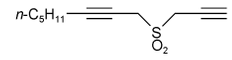
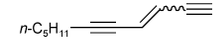
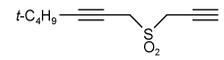
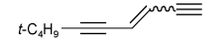
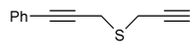
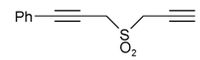
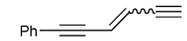
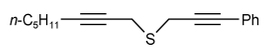
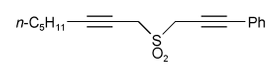
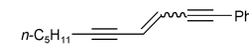
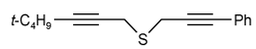
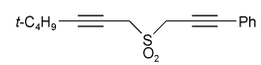
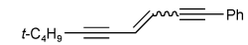
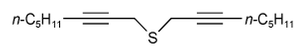
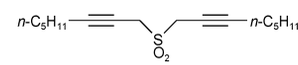
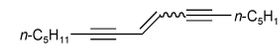
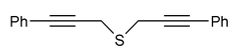
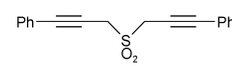
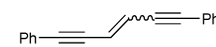
Conclusion

We have demonstrated the applicability of our protocol of the Ramberg–Bäcklund reaction in assembling the linear and cyclic hex-3-ene-1,5-diyne unit from dipropargylic sulfones without the necessity of preparing the α-halo dipropargylic sulfones beforehand. The synthesis transformation utilizes readily available propargyl alcohol and aliphatic bromides as starting material. The synthetic routes are facile and the reactions can be performed on molar scales. Direct application of the chemistry can be expected both in the design of antitumour agents and in the preparation of enediyne nanomaterials.

Experimental

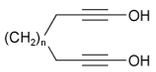
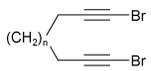
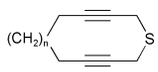
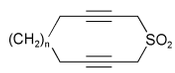
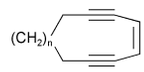
Melting points were measured on a Reichert Microscope apparatus and are uncorrected. IR spectra were recorded on a Nicolet 205 FT-IR spectrophotometer and reported in wavenumbers (cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on a Bruker Cryospec WM 250 spectrometer or Avance DRX–200 spectrometer. NMR spectra were recorded in

Table 1 Yields (%) of linear sulfides **11**, linear sulfones **12** and linear enediynes **13**

Entry	Sulfide **11**	Yield (%)	Sulfone **12**	Yield (%)	Enediyne	Yield (%) of (*E*)-**13** δ_H (*J*)[a]	Yield (%) of (*Z*)-**13** δ_H (*J*)
a		89		>95		43 6.10, 5.85 (16.1)	37 5.90, 5.72 (10.9)
b		33		>95		33 6.07, 5.84 (16.1)	27 5.90, 5.72 (10.9)
c		82		>95		49 6.30, 6.04 (16.1)	45 6.13, 5.88 (10.9)
d		81		87		33 6.13, 6.04 (16.0)	27 5.92, 5.84 (10.0)
e		80		87		43 6.10, 6.05 (16.0)	47 5.95, 5.86 (10.7)
f		75		90		41 5.88	40 5.73
g		95		89		40 6.29	30 6.10

[a] Coupling constants (*J*) reported in Hz for the newly formed C=C bond.

Table 2 Yields (%) of diols **9**, dibromides **10**, cyclic sulfides **11**, cyclic sulfones **12** and cyclic enediynes **13**

Entry	Diol **9**	Dibromide **10**	Sulfide **11**	Sulfone **12**	Cyclic enediyne **13**
					
h ($n = 2$)	75	85	70	55	50
i ($n = 3$)	78	66	67	65	65
j ($n = 4$)	88	70	65	70	70
k ($n = 5$)	71	80	77	70	73
l ($n = 6$)	87	73	66	68	70
m ($n = 7$)	67	74	66	60	66
n ($n = 8$)	65	76	76	70	71
o ($n = 9$)	82	85	61	75	74

$CDCl_3$, using tetramethylsilane (δ_H 0.00 ppm) or residual chloroform (δ_H 7.26 ppm, δ_C 77.0 ppm) as internal standard. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. Mass spectra (MS) data were obtained on a Finnegan MAT 95 or VGZAB–HS mass spectrometer. High-resolution mass spectra (HRMS) were obtained on an APEX II 47e mass spectrometer. Elemental analyses were carried out by Medac Ltd, Uxbridge, UK or the Shanghai Insititute of Organic Chemistry, P.R. China. UV–visible light spectra were recorded on a Hitachi U-2000 spectrometer. Propargyl alcohol and aliphatic bromides were purchased from Aldrich Chemical Company and used without further purification. Oct-2-yn-1-ol, 4,4-dimethylpent-2-yn-1-ol and 3-phenylprop-2-yn-1-ol were prepared according to literature methods.[8–10]

Propargylic bromide 7

The individual propargylic alcohol **6** (10 mmol) was added to a solution of Ph_3P (10 mmol) and CBr_4 (10 mmol) in C_6H_6 (10 cm^3) at 0 °C. After 2 h, the solvent was evaporated *in vacuo*. The residue was extracted with hexane and the combined extracts were washed (saturated NaCl solution), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give crude propargylic bromides **7**. The spectral data (NMR and MS) obtained for 1-bromooct-2-yne and 1-bromo-3-phenylprop-2-yne were identical with those in the literature.[11]

Propargylic thioacetates 8

A solution of DEAD (10 mmol) in dry benzene (10 cm^3) was added to a stirred solution of Ph_3P (10 mmol) in C_6H_6 (50 cm^3) at 0 °C. The resulting red solution was kept at 0 °C for 15 min and then a precooled (0 °C) mixture of the individual propargylic alcohol **6** (10 mmol) and CH_3COSH (10 mmol) in dry C_6H_6 (10 cm^3) was added in one portion. The mixture was stirred at rt for 1 h and the solvent was removed *in vacuo*. Flash chromatography of the residue over silica gel (hexane–EtOAc = 10 : 1) afforded the following propargylic thioactetes **8**: (*S*)-Oct-2-ynyl thioacetate, (*S*)-4,4-dimethylpent-2-ynyl thioacetate and (*S*)-3-phenylprop-2-ynyl thioacetate. Data for propargylic thioactetes **8** are available as supplementary data. †

Diol 9

Lithium amide (120 mmol) was suspended in dry liquid ammonia (100 cm^3) at −78 °C. Tetrahydro-2-(prop-2-ynyloxy)-2*H*-pyran (110 mmol, 2.2 equiv.) was added dropwise over 20 min to this suspension with vigorous stirring. This was followed by addition of the individual dibromide (50 mmol). The reaction was allowed to warm to rt over night. It was then added to a solution of saturated NaCl (200 cm^3) and EtOAc (100 cm^3). The organic phase was dried (Mg_2SO_4) and concentrated *in vacuo*. The residue was then dissolved in CH_3OH (100 cm^3), and *p*-PTs (pyridinium toluene-*p*-sulfonate, 5 mmol) was added. After one day, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography (hexane–EtOAc = 2 : 1) to give the products **9h–o**. The spectral data (IR, NMR and MS) and mp data obtained for diols **9h–n** were identical with those in the literature.[2d] Data for heptadeca-2,15-diyne-1,17-diol (**9o**) are available as supplementary data. †

Dibromide 10

The individual diol **9** (25 mmol) was added to a solution of CBr_4 (55 mmol, 2.2 equiv.) and Ph_3P (55 mmol, 2.2 equiv.) in C_6H_6 (50 cm^3). After 3 h, the solvent was evaporated *in vacuo*, and the residue was purified by flash chromatography (hexane–$CHCl_3$ = 10 : 1) to give the products **10h–o**. The spectral data (IR, NMR and MS) obtained for dibromides **10h–n** were identical with those in the literature.[2d] Data for heptadeca-2,15-diyne-1,17-diyl dibromide (**10o**) are available as supplementary data. †

General procedure for the preparation of sulfides 11

Method A. For the unsymmetrical linear sulfide, the individual propargylic thioacetate **8** (5 mmol) was added to a solution of KOH (5 mmol) and $Na_2S_2O_3 \cdot 5H_2O$ (10 mg) in methanol (10 cm^3) under nitrogen. The resulting mixture was stirred at 0 °C for 30 min. To this thioate solution was then added dropwise the individual propargylic bromide **7** ($R^1 \neq R^2$, 5 mmol) over a period of 5 min and stirring was continued for 1 h at 20 °C. The reaction mixture was poured into water (10 cm^3) and the solvent was evaporated *in vacuo*. The aqueous phase was extracted with Et_2O and the combined extracts were washed (saturated NaCl solution), dried ($MgSO_4$), filtered and concentrated *in vacuo*. Flash chromatography of the residue over silica gel (hexane–EtOAc = 100 : 1) afforded the unsymmetrical sulfides **11**.

Method B. For the symmetrical linear sulfides, individual bromide **7** (10 mmol) was added to a solution of Na_2S (5 mmol) in methanol (10 cm^3). The resulting mixture was stirred at 20 °C for 2 h. The reaction mixture was then worked up following the same procedure as that described in Method A.

Method C. For the cyclic sulfides, solutions of individual dibromide **10** (50 mmol in EtOH, 100 cm^3) and Na_2S (55 mmol, 1.1 equiv. in 80% EtOH–H_2O, 100 cm^3) were added separately and simultaneously *via* a funnel to cooled (−5 °C) EtOH (400 cm^3) over 4 h under stirring. The resulting mixture was stirred at 20 °C for 4 h. The reaction mixture was then worked up following the same procedure as that described in Method A.

Linear dipropargylic sulfides **11a–11e** were prepared using method A, **11f** and **11g** were prepared using method B. Cyclic sulfides **11h–o** were prepared using method C. Data for linear dipropargylic sulfides **11a–11g** and cyclic sulfide **11o** are available as supplementary data. † The spectral data (IR, NMR and MS) obtained for cyclic sulfides **11h–n** were identical with those in the literature.[2d]

General procedure for the preparation of sulfones 12

A mixture of the individual propargylic sulfide **11** (5 mmol) and Oxone (25 mmol) in CH_2Cl_2 (20 cm^3) was stirred at 50 °C for 2–3 days. The reaction mixture was filtered through a pad of silica gel and the filtered cake was washed with CH_2Cl_2–EtOAc (2 : 1, 50 cm^3). The filtrate was concentrated *in vacuo*. Flash chromatography of the residue over silica gel (hexane–EtOAc = 10 : 1gradient to 2 : 1) afforded linear and cyclic propargylic sulfones **12**. Data for sulfones **12a**–**12o** are available as supplementary data. †

General procedure for the preparation of linear and cyclic enediynes 13

A solution of sulfone **12** (2 mmol) in dry CH_2Cl_2 (10 cm^3) was added to a stirred suspension of KOH–Al_2O_3 (10 mmol of KOH) in CBr_2F_2–CH_2Cl_2 (1:10, 10 cm^3). The mixture was then stirred for 10 min to 1 h. The reaction mixture was filtered through a short column of silica gel. The filtrate was concentrated *in vacuo* to give the crude enediyne **13**. Flash chromatography of the crude enediyne over silica gel (hexane) afforded the pure enediynes. Disubstituted enediynes are more stable and can be stored at −30 °C for days in hexane solution. The terminal enediynes **13a**–**13c** are less stable and tend to polymerize even when stored at −30 °C for one day. Hence, we were unable to obtain elemental analysis or HRMS data of these compounds. Data for linear enediynes **13a**–**13g** [12–14] and cyclic enediyne **13o** are available as supplementary data. † The spectral data (IR, NMR and MS) for cyclic enediynes **13h**–**13n** were identical with those in the literature.[2d]

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