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Reductive coupling of alkynes by oxobis(diethyldithiocarbamato)molybdenum(IV)–sodium borohydride

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Abstract

The reductive coupling of terminal alkynes and the intramolecular cyclization of diynes by oxobis(diethyldithiocarbamato)molybdenum(IV) in the presence of sodium borohydride are reported. The reaction leads to a mixture of products resulting primarily from 'head to tail' coupling of the alkynes. 1,7-Octadiyne undergoes cyclization to afford cycloheptene-3-ylidene in 45% yield. The product distribution appears to be controlled by steric factors associated with the alkyne–molybdenum intermediate. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Alkyne coupling; Intramolecular cyclization; Molybdenum; Reductive coupling

1. Introduction

The reversible binding of acetylene to oxobis(diethyldithiocarbamato)molybdenum(IV) (**1**) (Fig. 1) [1,2] has been used to explore the role of oxomolybdenum(IV) in nitrogen fixation by metalloenzymes [2]. The reversible formation of this acetylene–oxomolybdenum complex is readily observed spectrophotometrically. The maroon colour of **1** is restored by simply passing nitrogen through a solution of the yellow acetylene complex (**2**). Our interest in alkyne–$MoO(S_2CNEt_2)_2$ chemistry arose from the observation that in the presence of sodium borohydride, the acetylene adduct of **1** formed ethene, along with small quantities of 1,3-butadiene [3]. Given this observation we sought to explore the potential of **1** as a reagent for the coupling of alkynes.

There are a number of publications, which have reported the coupling of alkynes using unrelated transition metal complexes. Some metal complexes used include CuCl [4], Ni phosphines [5], $RhCl(PPh)_3$ [7], $Ni(CN)_2$ [8], $PdCl_2(PhCN)_2$ [9], $NbCl_5$ [10] and WCl_6 [10]. The major products, linear dimers or substituted benzenes, formed by these reagents are presumed to arise via the intermediacy of metallocyclopropene (**3**), metallocyclopentadiene (**4**) and metallocycloheptatriene (**5**) complexes. The reaction scheme in Fig. 2 is based on mechanistic studies by Yamazaki [11], Bianchini [12] and Wigley [13].

The addition of nucleophiles to metal–alkyne complexes generally produce a *cis*- or *trans*-metalloalkene. From a mechanistic point of view, the two isomers are believed to arise from different mechanisms. Direct nucleophilic attack on the alkyne carbon leads to the *trans*-metalloalkene, while attack at the metal center, followed by 1,2-shift of the nucleophile to the alkyne leads to the *cis*-metalloalkene [14]. With regard to the regiochemistry of nucleophilic addition, electrophilic complexes, such as alkyne–$MoO(S_2CNEt_2)_2$ or alkyne–L_3RhH^+, are under steric control and undergo Markovnikov addition [15].

Probably the closest reported analogous reaction to that studied here, is the reaction of alkynes with nickel chloride and $Al(i\text{-}Bu)_3$ [16]. In this work a nickel hydride species is formed which then complexes with the

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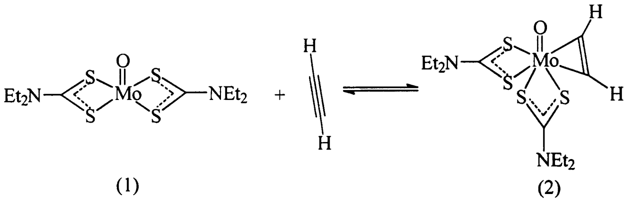

Fig. 1. Complexation of (**1**) with acetylene.

alkyne. A mechanism analogous to that shown in Fig. 2 was postulated based on extensive deuterolysis experiments. Products similar to those found here, that is arenes and dienes, were reported.

2. Results and discussion

In our initial investigations, we used 1-hexyne and 1-dodecyne as substrates. The latter proved somewhat more convenient in elucidating the scope of the reaction given the volatile nature of some of the products formed from the reaction with **1** and sodium borohydride. This was due to the formation of significant amounts of volatile alkenes, presumably formed by direct reduction and hydrolysis of the alkyne complex **2**. In all experiments the reaction mixtures were extracted and analysed by GC–MS.

A number of variables were examined including solvent, ratio of alkyne to **1** and the ratio of $NaBH_4$ to alkyne. A summary of these studies is shown in Tables 1 and 2. From these studies a number of trends can be seen. Firstly, the yield of dienes tend to increase with increasing amounts of reducing agent and **1**, and secondly the more water present, the greater the yield of the dimeric product. This latter point may simply reflect the improved solubility of $NaBH_4$. Another trend to emerge was that increasing the amount of the alkyne relative to **1**, leads to more aromatic products as expected given the mechanism shown in Fig. 2. It should also be noted that no reaction took place in the absence of borohydride.

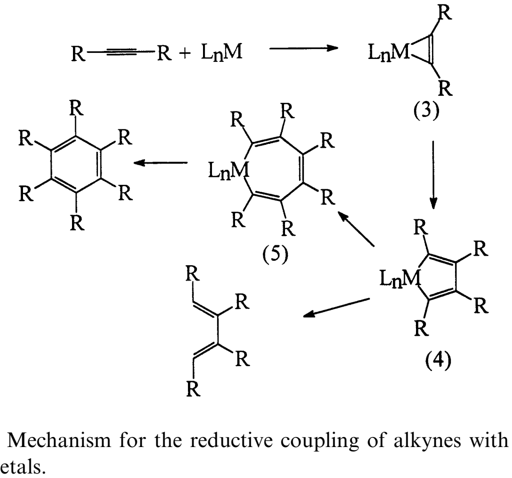

Fig. 2. Mechanism for the reductive coupling of alkynes with transition metals.

Mechanistically, it was of interest to determine the isomeric composition of the dienes and the aromatic components. The 1-hexyne reaction was selected for this purpose. Unfortunately, we were unable to separate the products formed by thin layer chromatography using either silica, boric acid or silver nitrate impregnated silica. However we were able to separate the dienes and the aromatic components from the other products, and this relatively pure mixture was analysed by 2D-NMR. GC–MS analysis of this mixture showed it to consist of a mixture of three isomeric dienes and two aromatic components. The ^{1}H-NMR spectrum of the mixture displayed four aromatic resonances, which corresponded to that expected from two trialkylbenzenes: a 1,2,4- and a 1,3,5-trialkylbenzene. Thus the 1,2,4-tributylbenzene produced a doublet at δ 7.07 ($J = 7.6$ Hz), a doublet at 6.95 ($J = 1.5$ Hz) and a doublet of doublets at 6.93 ($J = 7.6$ and 1.5 Hz). The fourth aromatic signal was a singlet at δ 6.81 corresponding to a symmetrically substituted trialkylbenzene. These four resonances correlated to literature values for the corresponding triethylbenzenes [17]. Integration showed the ratio of these peaks corresponded to a ratio of 1:0.4 for the 1,3,5-tributylbenzene to the 1,2,4-tributylbenzene, a value confirmed by GC–MS analysis. This ratio is larger than that expected from simply a random coupling, suggesting that, as was expected, steric effects influence the regiochemical composition.

For identification of the dienes formed, it proved convenient to synthesise some of the expected dienes. Apart from geometrical isomers, three positional isomers are possible, that is, 1,4-dibutylbuta-1,3-diene, 1,3-dibutylbuta-1,3-diene and 2,3-dibutylbuta-1,3-diene.[1] Given that steric effects on the product composition were evident for the aromatic products, they would also be expected to influence the regioisomeric distribution of the diene products.

In any case, we synthesised two of the geometric isomers of dodeca-5,7-dienes, specifically the (*E*,*E*)- and the (*E*,*Z*)-isomers by literature procedures [18,19]. The former was synthesized by in situ copper(I) catalysed oxidative coupling of the (*E*)-hex-1-enyl-1-diisobutylaluminium and the latter by in situ oxidative coupling of (*E*)-hex-1-enyl-1-thexylborate. Comparison of the ^{1}H-NMR of the diene/arene mixture with these isomers indicated that the (*E*,*E*)-isomer was the main dodeca-5,7-diene formed. Only traces of the (*E*,*Z*)-isomer were detected and no (*Z*,*Z*)-isomer was found.

The structures of the other two isomeric dienes formed in the reaction were readily determined from the ^{1}H-NMR spectrum after taking into consideration the presence of the (*E*,*E*)-isomer. The NMR showed four broad singlets due to the presence of two pairs of olefinic

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[1] Trivial nomenclature has been used in the discussion for these dienes for convenience.

Table 1
Reaction of 1-hexyne with **1**

Hexyne:(**1**) ratio	Solvent (DMF:H_2O)	$NaBH_4$	Temperature (°C)/time (h)	Recovered hexyne	Hexane	Hexene	Dienes	Arenes	Others
0.44	4:1	1.5	30/4	5	1	2	46	13	24 [c], 6 [d]
0.29	4:1 [a]	2	30/4	11	16	27	44	2	1 [c], 1 [d]
0.25	1:1 [a]	2.1	30/4	14	19	29	35	1	1 [c], 1 [d]
0.18	[b]	1.4	30/4	67	3	15	11	3	1 [c], 1 [d]
0.19	11:1 [a]	1.2	35/23	25	7	0	39	28	1 [d]
1.0	6:1	4.7	22/18	1	0	0	62	13	1 [d]

[a] THF used in place of DMF.
[b] Anhydrous DMF.
[c] Unidentified trimers.
[d] Unidentified dodecenes.

methylene resonances at δ 4.84 and 4.87, and δ 4.91 and 5.05. Calculation of the predicted shift for the first pair using Pascual, Meier and Simon's rule [20] showed that these corresponded to the shifts and coupling expected for (*E*)-2,4-dibutylbuta-1,3-diene[2] (δ 4.81 and 4.95), the product of 'head to tail' coupling. In addition to these olefinic resonances, a doublet of triplets (δ 5.73, $J = 15.7$, 7.1 Hz) was also present. This corresponded to an olefinic proton coupling to a (*E*)-olefinic proton and geminal coupling to an allylic methylene. This was confirmed by $^1H-^1H$-COSY experiments, as were all assignments. The remaining olefinic resonances corresponded to the product of tail to tail coupling, that is, the 2,3-dibutyl-1,3-butadiene. Once again the ^1H-NMR integration based on these assignments correlated well with the GC–MS analysis, which showed the diene ratio to be 10:7:1 for (*E*)-1,3-dibutylbutadiene: (*E*,*E*)-1,4-dibutylbutadiene: 2,3-dibutylbutadiene.

This product distribution is likely to arise from steric constraints on the coupling reaction, during the formation of oxomolybdenumcyclopentadiene (**4**) (Fig. 2). Steric factors are likely to control the orientation of insertion of the second alkyne into the C–Mo bond. Thus a 'head to tail' insertion leads to the least hindered metallocyclopentadiene (**6**) (Figs. 3 and 4) with alkyl groups oriented away from one another. Insertion in a 'head to head' fashion leads to **7** and 'tail to tail' fashion leads to **8**. Thus formation of **8** is least favoured, while the formation of **6** versus **7** may be further controlled by electronic factors.

Other minor products that were detected had molecular weights that corresponded to reduced dienes, that is dodecenes. The isomeric composition of these minor components was not further investigated. These products are likely to arise via hydride reduction, followed by hydrolysis of the metallocycopentadienes (**6**–**8**) (Fig. 4; note the oxidation state and the presence of ligands is not specified). GC–MS analysis also showed the presence of compounds with a molecular weight of 250. While their GC retention times were close to those observed for aromatic components, these products were assumed to be trimers, not cyclohexadienes. The trimers would arise by reduction, followed by hydrolysis of the metallocycloheptatriene intermediate (**5**). It is not possible to rationalize the formation of cyclohexadienes, given the likelihood that the mechanism in Fig. 2 operates. Once again, the isomeric composition of these compounds was not pursued, given their presence in trace amounts.

Berg and Hodgson reported that $Mo_2O_3(S_2CNEt_2)_4$, an oxo-bridged dimer, equilibrates in solution to $MoO(S_2CNEt_2)_2$ and $MoO_2(S_2CNEt_2)_2$ [21]. This prompted us to explore the potential of using this Mo(V) complex as a less oxygen-sensitive substitute for $MoO(S_2CNEt_2)_2$. Thus when $Mo_2O_3(S_2CNEt_2)_4$ was used in excess in place of $MoO(S_2CNEt_2)_2$ the same yields and product proportions were obtained for reductive coupling of 1-hexyne. While we did not explore this further, it does suggest a convenient alternative procedure for reductive coupling, given the air stability of this Mo(V) complex.

The other simple alkyne which was subjected to reductive coupling with oxobis(diethyldithiocarbamato)molybdenum(IV) was 2-pentyne. This was of interest as it further enabled steric effects to be evaluated. In contrast to palladium [9] and nickel [6] catalysts which form arenes from internal alkynes, no aromatic products were formed, supporting the importance of steric factors in the current case. The only products detected by GC–MS analysis were three isomeric dienes. ^1H-NMR analysis of this mixture was not straightforward;

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[2] See footnote 1.

Table 2
Reaction of 1-dodecyne with **1**

Dodecyne:**1** ratio	Solvent (DMF:H_2O)	$NaBH_4$	Temperature (°C)/ time (h)	Recovered dodecyne	Dodecane	Dodecene	Dienes	Arenes	Others [a]
1.0	10:1	6.7	22/20	14	4	10	45	9	5 [c]
1.0	10:1	4.0	22/20	12	16	26	43	0	1 [c]
1.0	10:1	1.0	30/4	18	5	9	37	13	3 [c]
1.0	20:1 [b]	5.0	22/20	69	11	9	3	0	0
0.30	2.3:1	3.0	22/20	0	0	0	88	0	7 [c]
1.0	7:1	1.0	22/20	36	6	9	44	2	2 [c]

[a] 1-Dodecanethiol found (1.3–3.5%).
[b] THF used in place of DMF.
[c] Unidentified eicostetraenes.

however, given the formation of only (*E*,*E*)-isomers in the case of both 1-hexyne and 1-dodecyne coupling, the same (*E*,*E*)-geometry is likely here. The structures tentatively assigned to the products are shown in Fig. 5. The ratio of the products, **13**, **14** and by GC–MS was approximately 1:1:0.3, based on analogy with the previous results.

The final alkyne to be examined was of particular interest from a synthetic point of view. Intramolecular coupling of diynes has been reported for a range of catalysts. While the majority of the literature concerns intramolecular eneyne cyclizations (for example Cp_2ZrCl_2 [22] and Pd(II) [23]), there are relatively few simple intramolecular diyne cyclizations (for example Pd(II) [24]). While these other complexes accomplish this task efficiently, providing good yields, the possibility of using oxomolybdenumdithiocarbamates would have the advantage of providing a relatively cheap alternative cyclization reagent. The observations made concerning the reactions of simple alkynes, suggest that the intramolecular cyclization of 1,7-octadiyne may lead to three possible products (Fig. 6). In the event, reaction of 1,7-octadiyne led to problems due to the volatility of the products resulting in poor recoveries. Thus the yields quoted do not necessarily reflect the efficacy of the reaction. The mixture of products was again identified using ^{1}H-NMR, COSY and GC–MS. As expected from the results obtained for intermolecular coupling, the major product was the result of 'head to tail' coupling, cyclohept-1-ene-3-ylidene (**16**), formed in 37% yield, along with oct-1-en-7-yne formed in 25% yield (Fig. 6). The remainder of the reaction product consisted of unidentified dimers (22%) and recovered 1,7-octadiyne (15%). Traces of a product tentatively identified as the result of 1,8-cyclization, that is cycloocta-1,3-diene (**15**), were also detected. Thus while the yield is poor, intramolecular cyclization is highly selective in this case. While 'head to tail' coupling was the main mode of cyclization for 1,7-octadiyne, other diynes may well form products via 'head to head' coupling. This cyclization mode may predominate as the distance between the alkynes increases.

The reduction of oximes [25] and nitroarenes [26] using mixtures of molybdenum oxides or complexes and borohydrides has been previously reported. While these workers do not address the precise nature of the molybdenum species involved, more recent work has demonstrated the formation of low mixed valency molybdenum species, formed on treatment of molybdate with potassium borohydride [27]. Given that in the absence of sodium borohydride no reaction took place, it is likely that a low valent molybdenum species is involved in the coupling step described here. The fate of the molybdenum, and the diethylthiocarbamate ligand, remains undetermined at this stage.

3. Conclusions

Alkynes are reductively coupled in the presence of oxomolybdenumdiethydithiocarbamate and sodium borohydride. The major products of intermolecular coupling of unsymmetrical alkynes arise via 'head to tail' coupling. Terminal alkynes afford dienes along with arenes, while internal alkynes form only dienes. Intramolecular cyclization of 1,7-octadiyne led predominantly to cyclohept-1-ene-3-ylidene in 44% yield based on recovered staring material. These yields are unacceptable from a synthetic viewpoint, however the results suggest that the use of more sterically demanding ligands may lead to greater selectivity in the mode of coupling.

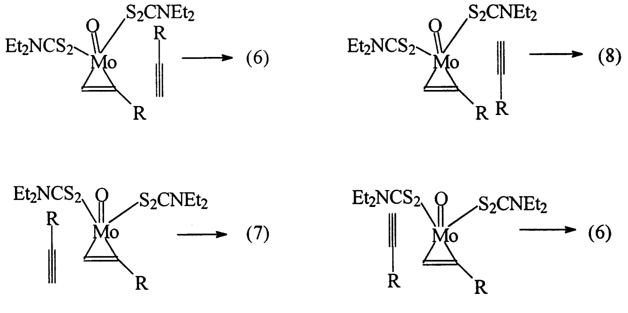


Fig. 3. Regiochemistry of coupling of unsymmetrical alkynes with **2**.

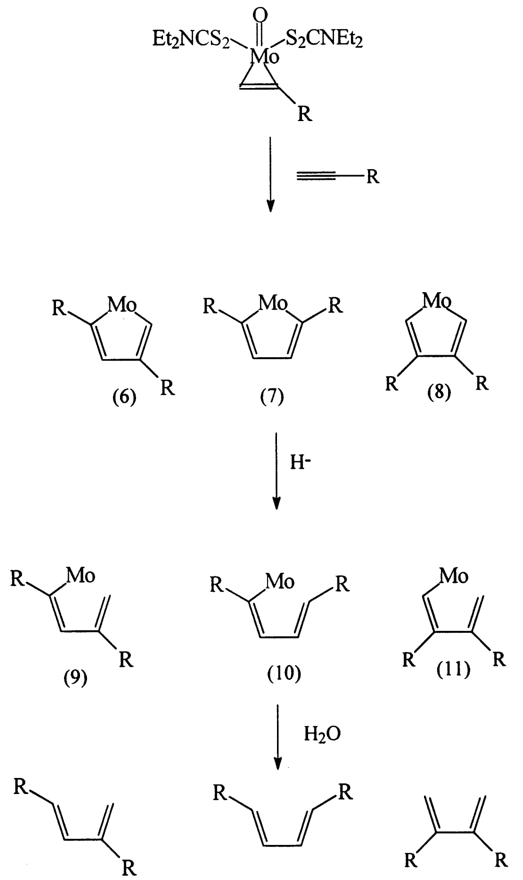
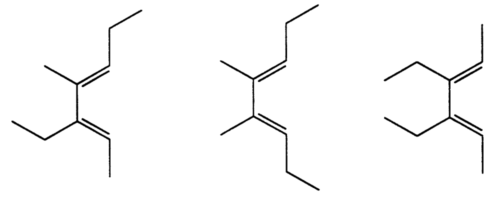


Fig. 4. Mechanism for the formation of butadienes from metallocyclopentadienes.

4. Experimental

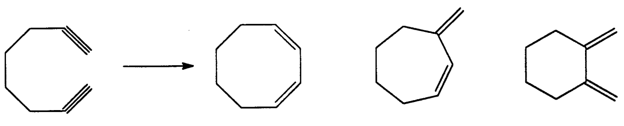
4.1. General

All infrared spectra were recorded on a Bio-Rad FTS-7 FT spectrophotometer as Nujol mulls. UV–vis spectra were obtained on a Shimadzu W-2 101 PC UV–vis scanning spectrophotometer. Solid probe mass spectra were obtained at 70 eV using a Jeol JMS DX303 Mass Spectrometer. All GC–MS analyses were performed using a HP5 column (0.25 mm ID × 30 m fused silica capillary column coated with 0.25 μm of 5% phenyl-silicone–95% methyl-silicone). The GC oven program consisted of 70°C, 1 min; 70–220°C at 16°C min^{-1}; 220°C, 1 min; 220–290°C at 8°C min^{-1}; 290°C, 4 min. Helium was used as the carrier gas, a 25:1 split ratio was employed with an inlet pressure of 275 kPa. Mass spectra were obtained at 70 eV. ^{1}H-NMR and all ^{13}C-NMR were recorded on Bruker DRX 300 operating at 300.166 and 75.47 MHz, or a Bruker DRX 500 operating at 500.132 MHz. Deuterated chloroform was used as the solvent. Preparative thin layer chromatography (TLC) was performed using Merck Silica Gel 60F$_{254}$. Flash chromatography was performed using BDH Silica Gel (40–63 μm). All solvents used with $MoO(S_2CNEt_2)_2$ were purged with nitrogen for 30 min before use.



(12) (13) (14)

Fig. 5. Butadienes from the reaction of **1** with 2-pentyne.



(15) (16) (17)

Fig. 6. Possible cyclization modes of 1,7-octadiyne.

4.2. *Dioxobis(diethyldithiocarbamato)molybdenum(VI)*

Hydrochloric acid (2 M) was slowly added to a rapidly stirring solution of sodium diethyldithiocarbamate trihydrate (14.0 g, 62.1 mmol), sodium acetate trihydrate (35.0 g) and sodium molybdate(VI) dihydrate (15.0 g, 62.0 mmol) in water (150 ml), until pH 5.5 was reached. The rusty-brown precipitate became yellow as the pH approached 5.5. The yellow solid was isolated by vacuum filtration, washed with water, ethanol and ether and dried at the pump. The product (15.2 g, 58%) was used without further purification. IR 878, 912 cm^{-1}.

4.3. *Oxobis(diethyldithiocarbamato)molybdenum(IV)*

To $MoO_2(S_2CNEt_2)_2$ (5.0 g, 11.8 mmol) in 1,2-dichloroethane (50 ml) in a Schlenk flask was added triphenylphosphine (7.0 g, 26.7 mmol) in 1,2-dichloroethane (20 ml) and the mixture was refluxed for 60 min under nitrogen. After the solvent was removed under vacuum and the residue was triturated with cold ethanol (250 ml) and filtered under nitrogen. The residue was washed with ethanol then ether and dried, affording maroon crystals (yield 4.0 g, 88%). ^{1}H-NMR: δ 1.36, br t ($J = 7.1$ Hz), 4 × CH_3; 3.86 and 3.94, each br sex ($J = 7.1$ Hz), 2 × CH_2. IR: 957, 1524 cm^{-1}.

5. Coupling reactions

The following method is representative of coupling reactions carried out using oxobis(diethyldithiocarbamato)molybdenum (IV). For the intramolecular coupling of 1,7-octadiyne, 9:1 dimethylformamide–water was used as the solvent and the concentration of the diyne was 0.01 M. All transfer steps were carried out in a nitrogen filled dry-box.

Oxobis(diethyldithiocarbamato)molybdenum (IV) (30 mg, 0.88 mmol) in 4:1 dimethylformamide–water (25 ml) was stirred for 5 min to dissolve the complex. 1-Hexyne (0.23 ml, 2.0 mmol) was added and the solution stirred for 30 min. Sodium borohydride (110 mg, 2.9 mmol in water (1 ml) was then added and the mixture stirred at room temperature for 20 h. The reaction mixture was extracted with *n*-pentane (4 × 50 ml) and the combined organic extracts washed with water (2 × 50 ml) followed by saturated sodium chloride solution (2 × 20 ml). The organic phase was concentrated under reduced pressure and purified by passing through a short silica gel column capped with anhydrous sodium sulfate, eluting with *n*-pentane. Removal of the solvent under vacuum afforded an oil which was further purified by preparative TLC using petroleum spirits (40–60°C): dichloromethane (9:1) as the mobile phase. The major band, which consisted of a mixture of dimers and trimers was then analysed by GC–MS and ^{1}H-NMR.

5.1. *(E,E)-Dodeca-5,7-diene*

1-Hexyne (0.27 ml, 2.4 mmol) and 0.7 M di-isobutylaluminium hydride (0.7 M in toluene, 3.3 ml, 2.3 mmol) was added, while maintaining the temperature at 25°C with cooling in a water bath. The solution was stirred at room temperature for 30 min and then heated at 50°C for 4 h. The solvent was removed under vacuum and dry THF (2 ml) was added. Copper(I) chloride (285 mg, 2.9 mmol) was added and the black suspension was stirred at room temperature for 30 min and then heated to 50°C for 4 h. The reaction mixture was poured slowly into dilute sulfuric acid (5%, 10 ml) and then extracted with *n*-pentane (5 × 10 ml). The combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate (50 ml) and dried. The solvent was then removed under reduced pressure and the residue was subjected to chromatography short column of silica gel, eluting with petroleum spirits (30–40°C). Removal of the solvent under vacuum afforded the diene (127 mg, 59%) as a colourless oil. ^{1}H-NMR: δ 0.89, t ($J = 7.2$ Hz), 1- and 12-CH_3; 1.33, m, 2-, 3-, 10- and 11-CH_2; 2.05, dt ($J = 7.2$, 7.2 Hz), 4- and 9-CH_2; 5.56, m, 5- and 8-CH; 6.00, m, 6- and 7-CH. $^{13}C\{^1H\}$-NMR: 13.9, 22.3, 31.6, 32.3, 130.3, 132.4. MS: $m/z = 166$ ($M^{+\cdot}$, 20%), 123 (10), 109 (10), 95 (18), 81 (62), 67 (100), 54 (23), 41 (48), 27 (24).

5.2. *(E,Z)-Dodeca-5,7-diene*

1-Hexyne (0.3 ml, 2.6 mmol) was slowly added to thexylborane in tetrahydrofuran (0.5 M, 2.9 ml, 1.4 mmol) at 0°C. The solution was stirred for 1 h at 0–5°C and then trimethylamine *N*-oxide dihydrate (138 mg, 1.24 mmol) was added at 0°C and stirred at this temperature for a further 1 h. The resulting solution was treated with sodium hydroxide solution (3 M, 1.2 ml), followed by iodine (310 mg) in tetrahydrofuran (1.5 ml). Excess iodine was decomposed by addition of a small amount of aqueous sodium thiosulphate. The reaction mixture was extracted with petroleum spirit (30–40°C, 5 × 50 ml) and the combined organic extracts were concentrated under reduced pressure and purified by flash chromatography on a short silica gel column, eluting with petroleum spirit 30–40°C. Removal of the solvent under vacuum yielded a colourless oil (231 mg, 92%) determined to be 86% pure by GC. ^{1}H-NMR: δ 0.93, t ($J = 7.2$ Hz), 1- and 12-CH_3; 1.40, m, 2-, 3-, 10- and C11-CH_2; 2.13, 2,15 each dt ($J = 7.2$, 7.2 Hz), 4- and 9-CH_2; 5.31, dt, ($J = 10.8$ and 7.5 Hz) 5-CH; 5.68, dt ($J = 14.9$, 7.5 Hz); 5.97, dd ($J = 10.8$, 10.8 Hz), 7-CH. 6.33, ddt ($J = 15.1$, 10.8 and 1 Hz) 6-CH. $^{13}C\{^1H\}$-NMR: 13.9, 22.3, 27.4, 31.6, 32.0, 32.6, 125.7, 128.7, 129.9 and 134.5. MS: $m/z = 166$ ($M^{+\cdot}$, 19%), 123 (10), 109 (10), 95 (17), 81 (62), 67 (100), 54 (28), 41 (52), 27 (31).

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