

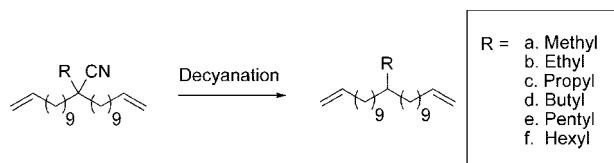
# Avoiding Olefin Isomerization During Decyanation of Alkylcyano $\alpha,\omega$ -Dienes: A Deuterium Labeling and Structural Study of Mechanism

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A two-step synthetic pathway involving decyanation chemistry for the synthesis of pure alkyl  $\alpha,\omega$ -dienes in quantitative yields is presented. Prior methodologies for the preparation of such compounds required 6–9 steps, sometimes leading to product mixtures resulting from olefin isomerization chemistry. This isomerization chemistry has been eliminated. Deuteration labeling and structural mechanistic investigations were completed to decipher this chemistry. Deuterium labeling experiments reveal the precise nature of this radical decyanation chemistry, where an alcohol plays the role of hydrogen donor. The correct molecular design to avoid competing intramolecular cyclization, and the necessary reaction conditions to avoid olefin isomerization during the decyanation process are reported herein.

## 1. Introduction

Olefin metathesis has proven to be an excellent synthetic tool for carbon–carbon bond formation via a variety of methodologies, two of which require dienes.  $\alpha,\omega$ -Dienes are usually employed in ring-closing metathesis (RCM) and acyclic diene metathesis (ADMET) chemistry, where the preparation of pure terminal olefins can be synthetically challenging.<sup>1</sup> In many cases, alkene isomerization occurs as a detrimental side reaction, not only reducing yield but also generating a difficult-to-purify mixture of products with internal olefins. Nitrile chemistry is often employed because of the high alkylation yield and ease of subsequent decyanation,<sup>2</sup> where decyanation is usually carried out by electron transfer chemistry initiated by alkali metals, such as Li,<sup>3–5</sup> Na,<sup>6–9</sup> or K.<sup>10,11</sup> The reaction proceeds in excellent yield via a radical anion intermediate, which eliminates a

cyanide moiety with concomitant formation of a radical.<sup>12</sup> Even so, reaction conditions can be harsh when other functionalities not compatible with alkali metals or radical species are present. For example, compounds containing olefin functionalities can undergo structural isomerization via radical intermediates. This is the case for  $\alpha,\omega$ -dienes, which can isomerize to internal olefins. To circumvent this isomerization problem, we have applied a previously reported method for the decyanation of alkylcyano  $\alpha,\omega$ -dienes while completely avoiding isomerization.<sup>13</sup> This paper describes the necessary conditions to do so.

## 2. Results and Discussion

### 2.1. Synthetic Approach to Alkyl $\alpha,\omega$ -Dienes via Decyanation Chemistry.

Most methods for the preparation of

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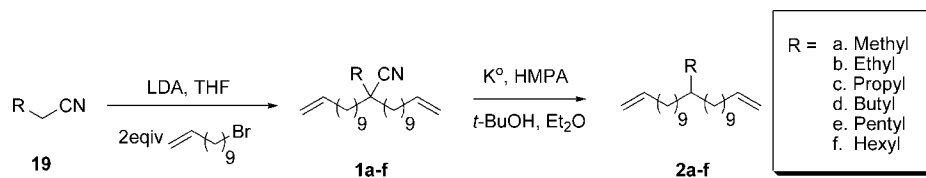
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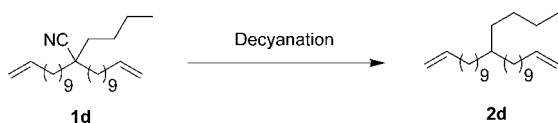
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SCHEME 1. Synthesis of Alkyl  $\alpha,\omega$ -DienesTABLE 1. Different Decyanation Systems for the Reduction of **1d** to 12-Butyltricoso-1,22-diene **2d**

entry	system	solvent	reaction time	yield (%) <sup>a</sup>	olefin isomerization (%) <sup>b</sup>
1	K <sup>0</sup> , Al <sub>2</sub> O <sub>3</sub>	hexane	5 min	20	7
		hexane	10 min	30	20
2	K <sup>0</sup> , Al <sub>2</sub> O <sub>3</sub> , toluene	hexane/toluene (1:1)	10 min	19	63
		toluene	10 min	22	75
3	K <sup>0</sup> , Ph <sub>3</sub> CH	hexane/ether (1:1)	3 h	41	BD
4	K <sup>0</sup> , HMPA, <i>t</i> -BuOH	ether	3 h	99	BD

<sup>a</sup> Yield after purification by column chromatography, <sup>b</sup> Percentage of olefin isomerization detected by NMR and confirmed by GC. BD = below <sup>1</sup>H and <sup>13</sup>C NMR detection limit.

SCHEME 2. Synthesis of 12-Butyltricoso-1,22-diene **2d**

alkyl  $\alpha,\omega$ -dienes require as many as 9 synthetic steps resulting in low yields.<sup>14–16</sup> We have reduced the number of steps to 2, previously reported alkylation<sup>2</sup> followed by decyanation, while producing analytically pure dienes. Further yet, a variety of synthetic routes can be required just for the preparation  $\alpha,\omega$ -dienes simply possessing different alkyl substituents. For example, three independent methodologies have been used for synthesizing  $\alpha,\omega$ -dienes possessing methyl,<sup>17–19</sup> ethyl,<sup>16,20</sup> and hexyl<sup>21</sup> substituents.

The need for a high yield, universal synthesis having fewer steps motivated us to explore more sophisticated nitrile chemistry, since primary nitriles **19** have been dialkenylated using lithium diisopropylamide (LDA) in quantitative yields.<sup>2</sup> Subsequent decyanation of the resulting alkylcyano  $\alpha,\omega$ -dienes **1** produces alkyl  $\alpha,\omega$ -dienes **2**, as shown in Scheme 1. This paper focuses on alkyl  $\alpha,\omega$ -dienes with 9 methylene spacers between the double bond and the tertiary carbon. Syntheses of analogous compounds with various spacer lengths can also be achieved.

Previous work has shown that reductive elimination of nitriles by electron transfer works for primary, secondary, and tertiary nitriles using various alkali metals in ammonia,<sup>3–8</sup> potassium in hexamethylphosphoramide (HMPA),<sup>22–25</sup> or potassium with dicyclohexyl-18-C-6 in toluene.<sup>26</sup> Although decyanation of alkyl nitriles by alkali metals in liquid ammonia is quite versatile, it does not offer utility when other functionalities are present in the molecule, such as olefins. For example, Marshall and

Bierenbaum reported the decyanation of  $\beta,\gamma$ -unsaturated nitriles using alkali metals in liquid ammonia with yields greater than 90%, yet they obtained a mixture of products due to olefin isomerization.<sup>27</sup> Cuvigny reported the use of alkali metals in HMPA and ether in the presence of various alcohols with yields from 16% to 89%.<sup>13</sup> Other groups have modified Cuvigny's methodology for the synthesis of vitamin D derivatives with yields from 70% to 90%.<sup>22–24</sup> While this methodology has proven to be useful with various substrates, studies containing alkene molecules susceptible to promote olefin isomerization as described here have not been reported.

Our investigation began by exploring several methods for the reductive elimination of the nitrile functional group from model compound **1d**. The different reaction conditions and observed results are shown in Scheme 2 and Table 1.

The first experiment (entry 1) involved the use of potassium metal on alumina in dry hexane, yielding 20% decyanation and giving 7% olefin isomerization after 5 min of reaction. After 10 min, the same reaction conditions produced 30% decyanation with 20% olefin isomerization, where the extent of isomerization was calculated from <sup>1</sup>H NMR spectra by comparison of the relative areas of the terminal and internal olefin signals (see Figure 1). The observed results suggested that a tertiary radical is formed after the reductive elimination of nitrile, where the translocation of this radical to a more stable allyl radical leads to the olefin isomerization product (Scheme 3).

Different systems involving a radical trap were developed in order to prove the concept of radical translocation. Formation of a more stable species must occur to avoid translocation of the tertiary radical to an allylic radical. Furthermore, the stable species must be produced at a higher rate than the allylic radical formation in order to tune the reaction toward decyanation without olefin isomerization. Toluene was added to the reaction mixture with the intent of forming a stable benzyl radical, as indicated in Table 1, entry 2. Decyanation occurred in 19–22%

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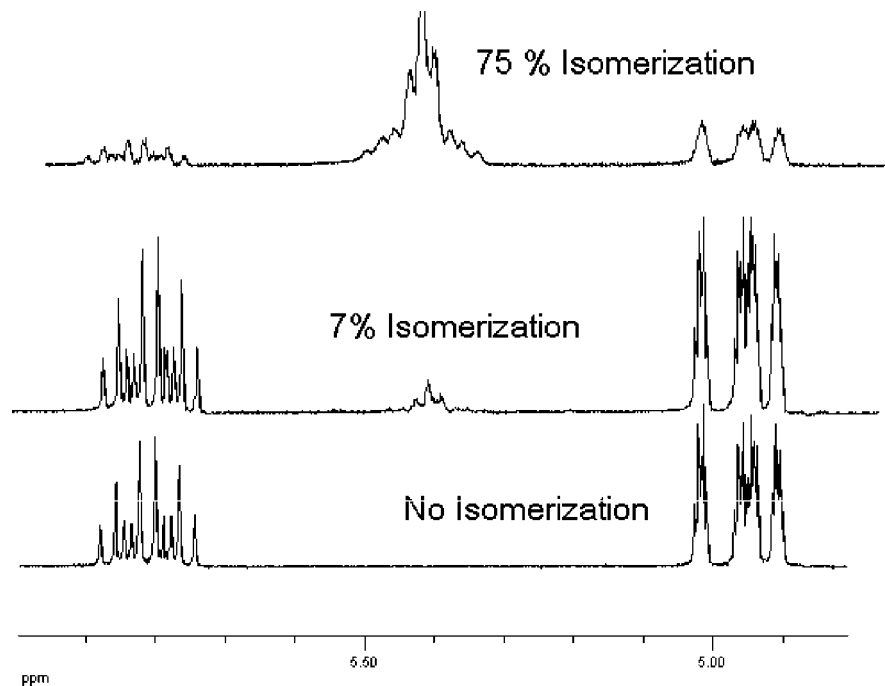
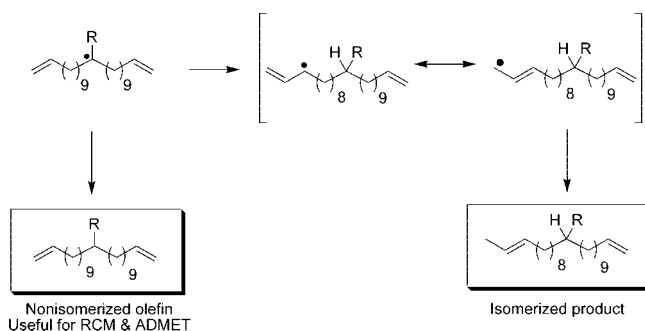


FIGURE 1. Expanded  $^1\text{H}$  NMR spectrum of 12-butyltricoso-1,22-diene **2d** at three different degrees of olefin isomerization.

**SCHEME 3. Proposed Mechanism for Olefin Isomerization via Formation of an Allylic Radical**



yield with 63–75% olefin isomerization. Although formation of benzyl radical cannot be ruled out, formation of the allylic radical seems to occur at a faster rate, thus promoting olefin isomerization.

The third entry in Table 1 shows the result of incorporation of triphenylmethane as a radical trap. The reductive elimination of the nitrile functional group in the presence of  $\text{Ph}_3\text{CH}$  in hexane/ether (1:1) produced the desired decyanation product in 41% yield; hydrogen radical transfer from the triphenylmethane molecule to the tertiary radical formed by decyanation occurs to produce the desired product without structural olefin isomerization. The absence of isomerized internal double bonds suggests that the more stable triphenylmethyl radical forms more quickly than does the allylic radical, which would lead to olefin isomerization. Although the triphenylmethyl radical was observed during the reaction by the appearance of a yellowish solution, competition between the radical trapping process and deprotonation of  $\text{Ph}_3\text{CH}$  initiated by potassium metal is also plausible.<sup>28–32</sup> The initial yellow solution gradually converted to an intense red color due to formation of the triphenylmethyl anion, which deactivates the decyanation process and decreases the reaction yield.

Entry 4 in Table 1 shows the decyanation of **1d** using potassium metal, HMPA, and *t*-BuOH with quantitative yields

**TABLE 2. Decyanation of Alkylcyano  $\alpha,\omega$ -Dienes Using Potassium Metal, HMPA, and *t*-BuOH in Ether**

substrate	product	overall yield (%) <sup>a</sup>	olefin isomerization (%) <sup>b</sup>
		99	BD
		98	BD
		99	BD
		99	BD
		98	BD
		99	BD

<sup>a</sup> Yield after purification by column chromatography. <sup>b</sup> Percentage of olefin isomerization detected by NMR and confirmed by GC. B.D = below  $^1\text{H}$  and  $^{13}\text{C}$  NMR detection limit.

without apparent olefin isomerization. The absence of isomerized product suggests that the tertiary radical formed after the reductive elimination of nitrile, before producing an allylic

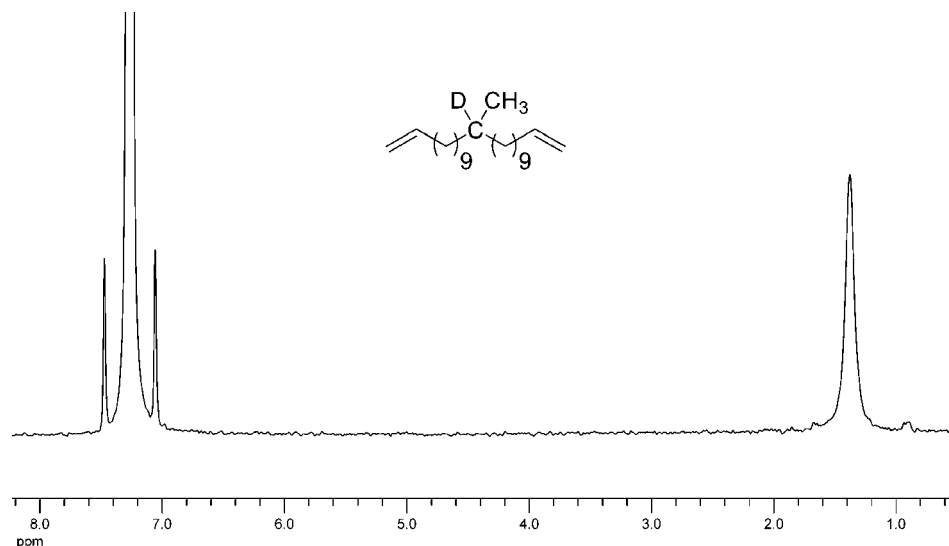


FIGURE 2. Deuterium-NMR of 12-*d*-12-methyl-tricosa-1,22-diene.

radical, quickly abstracts hydrogen from the alcohol or it is reduced yielding a carbanion, which inactivates the tertiary radical and consequently its structural isomerization. Although formation of *tert*-butoxyl radicals from *tert*-butanol is not common,<sup>33–35</sup> alkoxy radicals rapidly abstract hydrogen from the  $\alpha$ -carbon in the alcohol or solvent or disproportionate yielding a *tert*-butoxide anion.<sup>36–39</sup>

To further expand the scope of this method, a series of alkylcyano  $\alpha,\omega$ -dienes was decyanated resulting in quantitative yields with no apparent olefin isomerization, as shown in Table 2. Obviously the method has broad utility. Prior methodologies for the preparation of alkyl  $\alpha,\omega$ -dienes require 6–9 synthetic steps; this approach requires 2 steps, alkylation<sup>2</sup> and decyanation, and circumvents side reactions, providing a universal, high yielding route to pure alkyl  $\alpha,\omega$ -dienes.

## 2.2. Deuterium Labeling and Mechanistic Considerations.

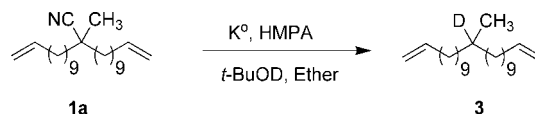
Cuvigny speculated that HMPA is the hydrogen donor in the reductive elimination of nitriles, but no chemical or spectroscopic proof has been reported to date.<sup>13</sup> Two possible sources of hydrogen radicals are present in the reactions we describe, HMPA and *t*-BuOH.<sup>40</sup> The reaction is carried out as a mixture of potassium metal and HMPA in ether, followed by dropwise addition of the nitrile dissolved in *t*-BuOH and ether. Experiments in deuterated alcohol were performed to determine the origin of the hydrogen captured after the reductive elimination of nitrile (Table 3). The first test involved the dropwise addition of a mixture of **1a** and *t*-BuOD in ether to a solution of

TABLE 3. Decyanation of **1a** in the Presence of Deuterated Compounds

entry	decyanation system	yield (%) <sup>a</sup>	extent of deuteration (%) <sup>b</sup>	olefin isomerization (%) <sup>c</sup>
1	K <sup>0</sup> , HMPA, <i>t</i> -BuOD	99	92	BD
2	K <sup>0</sup> , HMPA- <i>d</i> <sub>18</sub> , <i>t</i> -BuOH	99	not detected	BD
3	K <sup>0</sup> , <i>t</i> -BuOD	12	91	BD
4	<i>t</i> -BuO <sup>-</sup> K <sup>+</sup>	0		

<sup>a</sup> Yield after purification by column chromatography. <sup>b</sup> Extent of deuteration detected by <sup>1</sup>H NMR and deuterium-NMR. <sup>c</sup> Percentage of isomerized product detected by <sup>1</sup>H NMR and confirmed by GC. BD = below <sup>1</sup>H and <sup>13</sup>C NMR detection limit.

SCHEME 4. Decyanation of **1a** in the Presence of Deuterated *tert*-Butanol



potassium metal and HMPA in ether, yielding the decyanation product **3** (Scheme 4) in quantitative yield without apparent olefin isomerization. Figure 2 shows the deuterium-NMR spectrum of **3**, where one singlet at  $\delta$ 1.38, corresponding to the monodeuterated tertiary carbon, is observed. Figure 3 shows the <sup>13</sup>C NMR spectra of the products formed in the presence *t*-BuOH (Figure 3a) and *t*-BuOD (Figure 3b). The intensity of the tertiary carbon signal at 33.02 ppm is much smaller in the monodeuterated product **3** due to the larger <sup>13</sup>C relaxation time in the absence of directly bonded protons. The extent of deuteration of the final product was calculated by integration of the <sup>1</sup>H NMR signals from the methyl at the branch point, singlet in the deuterated product versus doublet in the product with <sup>1</sup>H on the tertiary carbon, as shown in Figure 4. The results indicated that **3** was 92% deuterated. The high extent of deuteration confirms that the hydrogen from the alcohol is captured by the tertiary radical from the reductive elimination of nitrile.

The second entry in Table 3 describes the decyanation experiment using HMPA with all methyl groups isotopically labeled with deuterium. As with the previous experiments, the reaction produced decyanation in quantitative yield without apparent olefin isomerization. Deuterium NMR experiments

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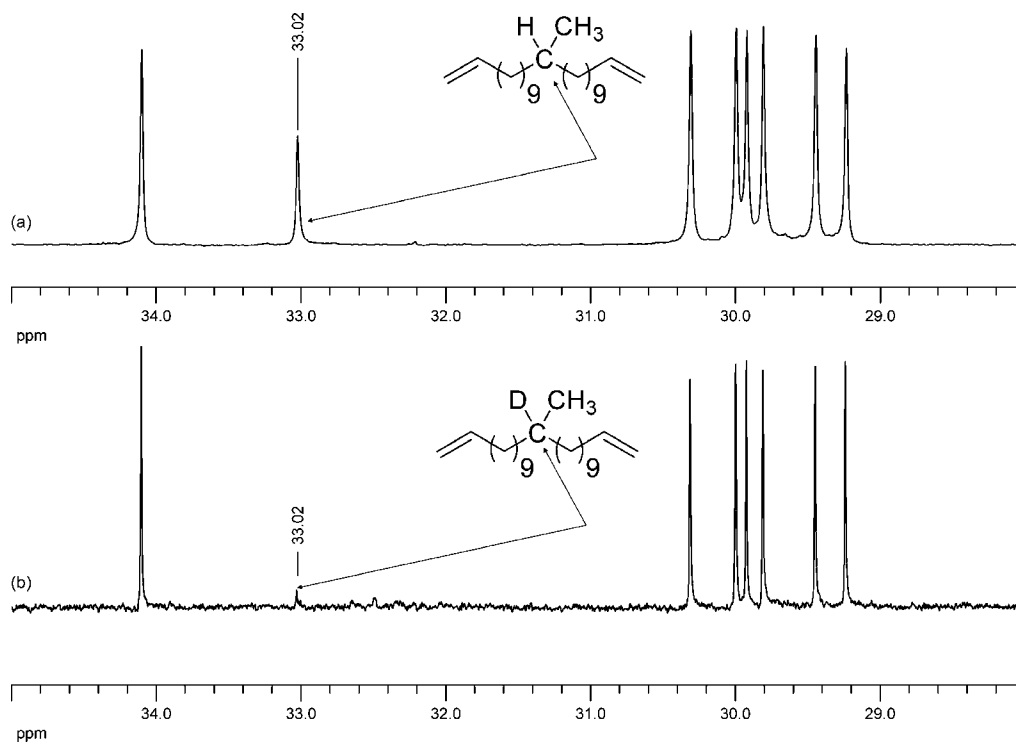


FIGURE 3.  $^{13}\text{C}$  NMR comparison of (a) 12-methyltricos-1,22-diene and (b) 12-*d*-12-methyl-tricos-1,22-diene.

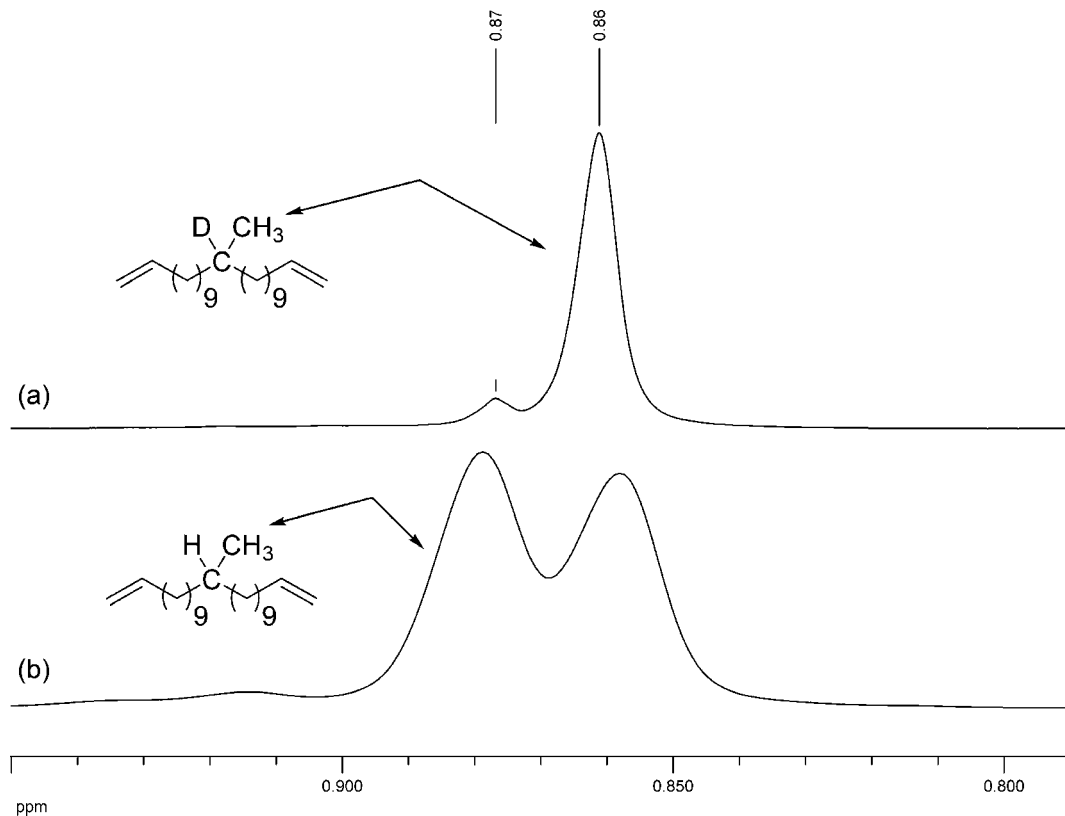


FIGURE 4.  $^1\text{H}$  NMR methyl resonances of (a) 12-*d*-12-methyl-tricos-1,22-diene (singlet with a small contribution of residual doublet) and (b) 12-methyltricos-1,22-diene (doublet).

showed no apparent deuteration in the final product when the isotopic label is carried by the HMPA, clearly showing that the hydrogen from the alcohol, and not from HMPA, is captured by the tertiary radical during the reductive elimination of nitrile.

The third entry in Table 3 shows the reaction conditions when decyanation occurs in the absence of HMPA, resulting in 12% decyanation with no apparent olefin isomerization. Deuterium-NMR showed a singlet at  $\delta 1.38$ , which corresponds to the



formation of **3**. The low yield in this reaction is explained by the absence of HMPA, which apparently stabilizes the formation of the intermediate species.

The fourth experiment in Table 3 was designed to determine if reductive elimination is carried out by potassium metal or by the potassium *tert*-butoxide possibly formed in situ. The reaction was performed via dropwise addition of **1a** in ether to a solution of potassium metal and *t*-BuOD in ether. The starting material **1a** was recovered and no decyanation product **3** was detected. These results demonstrate that reductive elimination of nitrile occurs by electron transfer from potassium metal and not via *t*-BuOK formed in situ.

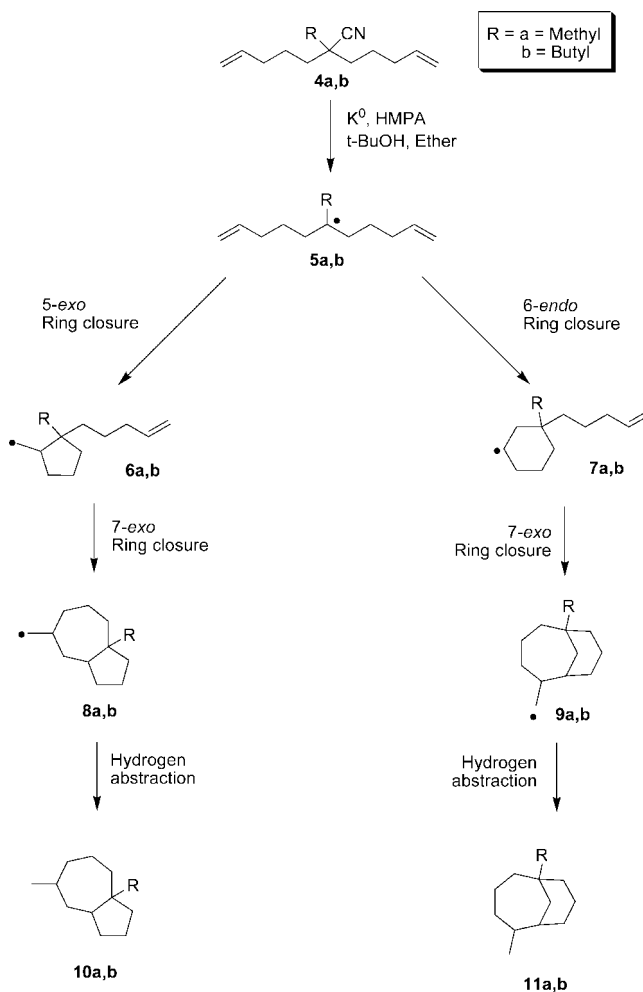
Although decyanation methodology using potassium metal and HMPA appears to occur through a radical-intermediate mechanism, no definitive proof of this has been clearly presented to date.<sup>41</sup> Formation of a carbanion via reduction of the radical-intermediate species cannot be ruled out.<sup>40</sup> One way to provide evidence for a free radical-intermediate would be to capture it via intramolecular cyclization before reduction to the carbanion occurs. Alkenes capture radical moieties which can subsequently undergo rapid intraradical cyclization to form cyclic radicals.<sup>42–45</sup>

To prove the point, decyanation was performed using alkylcyano  $\alpha,\omega$ -dienes **4a** and **4b** possessing only three methylene units between the terminal double bonds and the nitrile, in order to enhance the likelihood for cyclization to occur (Scheme 5).<sup>46–48</sup> In fact, bicyclic products **10** and **11** form as a result of intramolecular radical capture. Decyanation of **4** produces a tertiary radical **5**, which undergoes 5-*exo* and 6-*endo* ring closures **6** and **7**, leading to the bicyclic structures **10** and **11**.

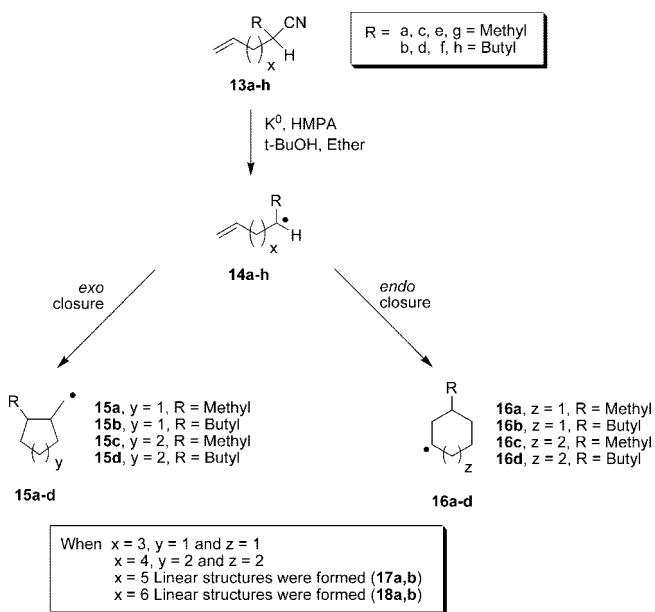
To further determine the influence of spacer length on the cyclization pathway, a series of experiments were performed using alkylcyano  $\omega$ -alkenes **13** possessing spacers of 3, 4, 5, and 6 methylene groups (Scheme 6). Compounds with three and four methylene units between the terminal double bond and the nitrile formed cyclic products **15** and **16**. Structures with five and six methylene spacers yielded only linear structures. These results verified that at least five CH<sub>2</sub> spacers are needed between the double bond and the carbon bearing the nitrile group to prevent radical-induced cyclization.<sup>49–51</sup>

All of these results suggest a plausible mechanism involving a radical-intermediate for the reductive elimination of CN in the presence of potassium, HMPA and *t*-BuOH (Scheme 7). Transfer of one electron from potassium metal to the nitrile group results in formation of a radical anion. Subsequent elimination of cyanide yields a tertiary radical that is rearranged to form cyclic molecules **10**, **11**, **15**, and **16**, quenched by abstraction of hydrogen from *t*-BuOH to yield **2a–f**, or reduced to a carbanion followed by protonation from *t*-BuOH to yield

### SCHEME 5. Decyanation of 2-Alkyl-2-pent-4-enyl-hept-6-enenitrile



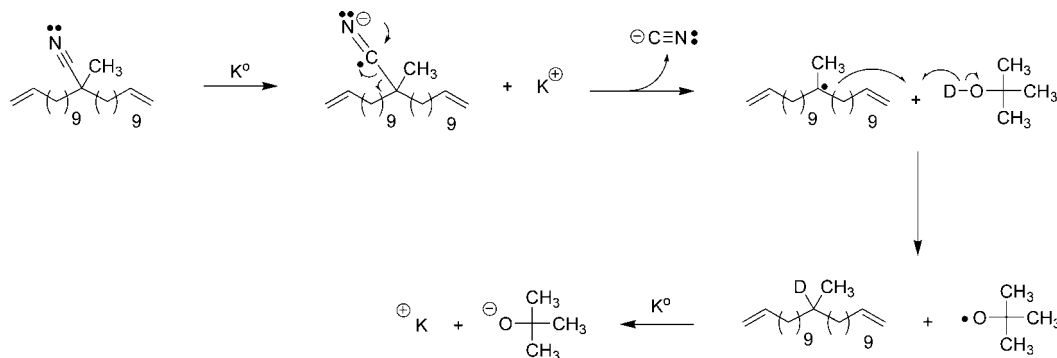
### SCHEME 6. Decyanation of Alkenylnitriles



**2a–f**. Abstraction of hydrogen from *t*-BuOH avoids formation of allylic radicals and consequent olefin isomerization.

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## SCHEME 7. Proposed Mechanism for the Reductive Elimination of Nitrile



## 3. Conclusions

The understanding of the mechanism for reductive elimination of nitriles opens the possibility for the synthesis of alkyl  $\alpha,\omega$ -dienes. Previously reported methodologies for the preparation of **2a**, **2b**, and **2f** require 6–9 synthetic steps. This new methodology allows quantitative synthesis of such dienes in 2 steps and circumvents side reactions such as structural olefin isomerization and intramolecular cyclization. We believe this to be a universal synthesis route for the preparation of alkyl  $\alpha,\omega$ -dienes.

## 4. Experimental Section

**Materials.** All starting materials were used as received, except for 11-bromoundec-1-ene and the alkylcyano  $\alpha,\omega$ -dienes, which were synthesized according to the literature procedures.<sup>1,2</sup> Tetrahydrofuran, toluene, and ether were freshly distilled from Na/K alloy using benzophenone as an indicator. The 11-bromoundec-1-ene, hexamethylphosphoramide, diisopropylamine, propionitrile, butyronitrile, pentanenitrile, hexanenitrile, heptanenitrile, and octanenitrile were freshly distilled from  $CaH_2$  prior to use. The *tert*-butanol was dried over calcium oxide and freshly distilled before use.

**4.1. Decyanation of 2-Butyl-2-(undec-10-enyl)tridec-12-enenitrile (1d) with Potassium Metal and Neutral Alumina.** The decyanation of **1d** (0.10 g, 0.3 mmol) was carried out in slurry of potassium and neutral alumina as reported by Umani-Ronchi.<sup>10</sup> The reaction was monitored by TLC plate using 5% ethyl acetate in hexane. When no trace of starting material was observed by TLC, the remaining excess of unreacted potassium was removed from the reaction flask. The reaction was quenched with water (20 mL), extracted three times with ether (600 mL), and washed with brine (150 mL). After drying over  $MgSO_4$ , the solution was filtered, concentrated by rotary evaporation, and purified by flash column chromatography (hexane). Decyanation was carried out in hexane, hexane/toluene (1:1), and toluene as described below.

**Decyanation of 2-Butyl-2-(undec-10-enyl)tridec-12-enenitrile (1d) in Hexane. Synthesis of 12-Butyltricoso-1,22-diene (2d).** After purification, 19 mg (20% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 0.90 (t, 3H), 1.23–1.41 (m, 39H), 2.04 (q, 4H), 4.97 (m, 4H), 5.42 (m, 0.15H), 5.82 (m, 2H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 14.4, 23.4, 24.5, 26.9, 29.2, 29.4, 29.8, 29.9, 29.9, 30.4, 33.6, 33.9, 34.1, 37.6, 114.3, 139.5; EI/HRMS  $[M]^+$  calcd for  $C_{27}H_{52}$  376.4069, found 376.4050. Anal. Calcd for  $C_{27}H_{52}$ : 86.09 C, 13.91 H; found 86.02 C, 13.98 H.

**Decyanation of 2-Butyl-2-(undec-10-enyl)tridec-12-enenitrile (1d) in Hexane/Toluene 1:1. Synthesis of 12-Butyltricoso-1,22-diene (2d).** After purification, 18 mg (19% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 0.90 (t, 3H), 1.23–1.41 (m, 39H), 2.04 (q, 4H), 4.97 (m, 4H), 5.42 (m, 3.4H), 5.82 (m, 2H);

$^{13}C$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 14.4, 23.4, 24.5, 26.9, 29.2, 29.4, 29.8, 29.9, 29.9, 30.4, 33.6, 33.9, 34.1, 37.6, 114.3, 139.5; EI/HRMS  $[M]^+$  calcd for  $C_{27}H_{52}$ : 376.4069; found 376.4035. Anal. Calcd for  $C_{27}H_{52}$ : 86.09 C, 13.91 H; found 86.09 C, 13.90 H.

**Decyanation of 2-Butyl-2-(undec-10-enyl)tridec-12-enenitrile (1d) in Toluene. Synthesis of 12-Butyltricoso-1,22-diene (2d).** After purification, 21 mg (22% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 0.90 (t, 3H), 1.23–1.41 (m, 39H), 2.04 (q, 4H), 4.97 (m, 4H), 5.42 (m, 6H), 5.82 (m, 2H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 14.4, 23.4, 24.5, 26.9, 29.2, 29.4, 29.8, 29.9, 29.9, 30.4, 33.6, 33.9, 34.1, 37.6, 114.3, 139.5; EI/HRMS  $[M]^+$  calcd for  $C_{27}H_{52}$ : 376.4069; found 376.4074. Anal. Calcd for  $C_{27}H_{52}$ : 86.09 C, 13.91 H; found 86.11 C, 13.91 H.

**4.2. Decyanation of 2-Butyl-2-(undec-10-enyl)tridec-12-enenitrile (1d) with Potassium Metal and Triphenylmethane. Synthesis of 12-Butyltricoso-1,22-diene (2d).** Potassium metal (49 mg, 1.25 mmol) and hexane (10 mL) were transferred to a three-neck round-bottom flask equipped with a stir bar, addition funnel, and argon inlet adaptor. A solution of **1d** (0.10 g, 0.3 mmol) and triphenylmethane (183 mg, 0.75 mmol) in hexane (10 mL) and ether (1.5 mL) was added dropwise to the reactor and stirred for 3 h. The reaction was quenched with water (5 mL), extracted three times with ether (300 mL), and washed with brine (100 mL). After drying over  $MgSO_4$ , the solution was filtered, concentrated by rotary evaporation, and purified by flash column chromatography (hexane). After purification, 38 mg (41% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 0.90 (t, 3H), 1.23–1.41 (m, 39H), 2.04 (q, 4H), 4.97 (m, 4H), 5.82 (m, 2H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 14.4, 23.4, 24.5, 26.9, 29.2, 29.4, 29.8, 29.9, 30.4, 33.6, 33.9, 34.1, 37.6, 114.3, 139.5; EI/HRMS  $[M]^+$  calcd for  $C_{27}H_{52}$ : 376.4069; found 376.4061. Anal. Calcd for  $C_{27}H_{52}$ : 86.09 C, 13.91 H; found 86.10 C, 13.90 H.

**4.3. General Methodology of Decyanation Using Potassium Metal and Hexamethylphosphoramide.** Potassium metal (8.285 g, 212 mmol), HMPA (27.238 g, 152 mmol), and ether (185 mL) were transferred to a three-neck round-bottom flask equipped with a stir bar, addition funnel, and argon inlet adaptor. A solution of the alkylcyano  $\alpha,\omega$ -diolefin (30 mmol) and *t*-BuOH (5.841 g, 79 mmol) in ether (130 mL) was added dropwise to the reactor and stirred for 3 h at 0 °C. The reaction was monitored by TLC plate using 5% ethyl acetate in hexane. When no trace of starting material was observed by TLC, the remaining excess of unreacted potassium was removed from the reaction flask. The reaction was quenched with water (20 mL), extracted three times with ether (600 mL), and washed with brine (150 mL). After drying over  $MgSO_4$ , the solution was filtered, concentrated by rotary evaporation, and purified by flash column chromatography (hexane).

**12-Methyltricoso-1,22-diene (2a).** After purification, 9.93 g (99% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 0.84 (d, 3H), 1.23–1.39 (m, 33H), 2.04 (q, 4H), 4.97 (m, 4H), 5.82 (m,

2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 20.0, 27.4, 29.2, 29.4, 29.8, 29.9, 30.0, 30.3, 33.0, 34.1, 37.4, 114.3, 139.4; EI/HRMS  $[\text{M}]^+$  calcd for  $\text{C}_{24}\text{H}_{46}$ : 334.3600; found 334.3607. Anal. Calcd for  $\text{C}_{24}\text{H}_{46}$ : 86.14 C, 13.86 H; found 86.15 C, 13.79 H.

**12-Ethyltricoso-1,22-diene (2b).** After purification, 10.24 g (98% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 0.84 (t, 3H), 1.28–1.37 (m, 35H), 2.04 (q, 4H), 4.96 (m, 4H), 5.82 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 11.1, 26.1, 27.0, 29.2, 29.4, 29.8, 29.9, 30.0, 30.4, 33.4, 34.1, 39.1, 114.3, 139.5; EI/HRMS  $[\text{M}]^+$  calcd for  $\text{C}_{25}\text{H}_{48}$ : 348.3756; found 348.3758. Anal. Calcd for  $\text{C}_{25}\text{H}_{48}$ : 86.12 C, 13.88 H; found: 86.25 C, 13.97 H.

**2-Propyltricoso-1,22-diene (2c).** After purification, 10.76 g (99% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 0.90 (t, 3H), 1.23–1.41 (m, 37H), 2.04 (q, 4H), 4.97 (m, 4H), 5.82 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 14.8, 20.1, 27.0, 29.2, 29.4, 29.8, 29.9, 30.0, 30.4, 34.0, 34.1, 36.4, 37.5, 114.3, 139.4; EI/HRMS  $[\text{M}]^+$  calcd for  $\text{C}_{26}\text{H}_{50}$ : 362.3913; found 362.3918. Anal. Calcd for  $\text{C}_{26}\text{H}_{50}$ : 86.10 C, 13.90 H; found 86.09 C, 13.91 H.

**12-Butyltricoso-1,22-diene (2d).** After purification, 11.18 g (99% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 0.90 (t, 3H), 1.23–1.41 (m, 39H), 2.04 (q, 4H), 4.97 (m, 4H), 5.82 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 14.4, 23.4, 27.0, 29.2, 29.4, 29.8, 29.9, 30.0, 30.4, 33.7, 34.0, 34.1, 37.6, 114.3, 139.4; EI/HRMS  $[\text{M}]^+$  calcd for  $\text{C}_{27}\text{H}_{52}$ : 376.4069; found 376.4061. Anal. Calcd for  $\text{C}_{27}\text{H}_{52}$ : 86.09 C, 13.91 H; found 86.10 C, 13.90 H.

**12-Pentyltricoso-1,22-diene (2e).** After purification, 11.48 g (98% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 0.90 (t, 3H), 1.23–1.41 (m, 41H), 2.04 (q, 4H), 4.97 (m, 4H), 5.82 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 14.4, 23.0, 26.7, 27.0, 29.2, 29.4, 29.7, 29.8, 29.9, 30.0, 30.4, 32.7, 33.9, 34.0, 34.1, 37.7, 114.3, 139.4; EI/HRMS  $[\text{M}]^+$  calcd for  $\text{C}_{28}\text{H}_{54}$ : 390.4226; found 390.4228. Anal. Calcd for  $\text{C}_{28}\text{H}_{54}$ : 86.07 C, 13.93 H; found 86.05 C, 13.96 H.

**12-Hexyltricoso-1,22-diene (2f).** After purification, 12.01 g (99% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 0.89 (t, 3H), 1.15–1.48 (m, 43H), 2.04 (q, 4H), 4.97 (m, 4H), 5.82 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 14.4, 23.0, 26.9, 29.2, 29.4, 29.8, 29.9, 29.9, 30.1, 30.4, 32.2, 33.9, 34.1, 37.6, 114.3, 139.5; EI/HRMS  $[\text{M}]^+$  calcd for  $\text{C}_{29}\text{H}_{56}$ : 404.4382; found 404.4386. Anal. Calcd for  $\text{C}_{29}\text{H}_{56}$ : 86.05 C, 13.95 H; found 86.38 C, 13.97 H.

**4.4. Decyanation Using Isotopic Labeling with Deuterium.** The decyanation of **1a** was carried out in presence of deuterated *t*-butanol or HMPA-*d*<sub>18</sub> using the general decyanation procedure described in section 4.3.

**Decyanation using Potassium Metal, Hexamethylphosphoramide, and 2-Methyl-2-propan- $^2\text{H}$ -ol. Synthesis of [12- $^2\text{H}$ ]-12-Methyltricoso-1,22-diene (3).** After purification, 9.9 g (99% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 0.84 (s, 3H), 1.23–1.39 (m, 32H), 2.04 (q, 4H), 4.97 (m, 4H), 5.82 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 19.9, 27.3, 27.4, 29.2, 29.4, 29.8, 29.9, 30.0, 30.3, 34.1, 37.3, 37.4, 114.3, 139.4; deuterium-NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 1.38 (s,  $\text{CH}_2\text{CD}(\text{CH}_3)\text{CH}_2$ ). EI/HRMS  $[\text{M}]^+$  calcd for  $\text{C}_{24}\text{H}_{45}\text{D}$ : 335.3662; found 335.3657. Anal. Calcd for  $\text{C}_{24}\text{H}_{45}\text{D}$ : 85.89 C, 14.11 H; found 85.92 C, 14.09 H.

**Decyanation Using Potassium Metal, Hexamethylphosphoramide-*d*<sub>18</sub>, and *tert*-Butanol. Synthesis of 12-Methyltricoso-1,22-diene (2a).** After purification, 9.91 g (99% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 0.84 (d, 3H), 1.23–1.39 (m, 33H), 2.04 (q, 4H), 4.97 (m, 4H), 5.82 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 20.0, 27.4, 29.2, 29.4, 29.8, 29.9, 30.0, 30.3, 33.0, 34.1, 37.4, 114.3, 139.4; deuterium-NMR ( $\text{CDCl}_3$ ): No signal detected for  $\text{CH}_2\text{CD}(\text{CH}_3)\text{CH}_2$ ; EI/HRMS  $[\text{M}]^+$  calcd for  $\text{C}_{24}\text{H}_{46}$ : 334.3600;

found 334.3605. Anal. Calcd for  $\text{C}_{24}\text{H}_{46}$ : 86.14 C, 13.86 H; found 86.12 C, 13.88 H.

**4.5. Decyanation of Alkylcyano-1,10-undecadienes and Alkenitriles.** The decyanation of **4and 13** was carried out as described in section 4.3. Characterization and purification of the respective products was carried out by NMR and HPLC/MS. Two columns were utilized: (1) analytical or scout scale column with dimensions of 10.0 mm (inner diameter) by 250.0 mm; (2) preparative scale with dimensions of 41.4 mm (inner diameter) by 250.0 mm. Both columns were silica packed with a particle size of 8  $\mu\text{m}$  and a pore size of 60 Å. Crude samples were diluted in a 25% solution (w/v) of HPLC grade hexanes and filtered prior to injection.

**3a,7-Dimethyl-decahydroazulene (10a).** After purification, 0.84 g (85% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 1.06 (d, 3H), 1.16 (s, 3H), 1.25–1.45 (m, 10H), 1.61–1.75 (m, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 21.3, 22.6, 22.1, 23.5, 32.0, 33.3, 38.2, 39.0, 39.9, 41.4, 47.0, 48.0; EI/HRMS  $[\text{M}]^+$  calcd for  $\text{C}_{12}\text{H}_{22}$ : 166.1722; found 166.1725. Anal. Calcd for  $\text{C}_{12}\text{H}_{22}$ : 86.67 C, 13.33 H; found 86.63 C, 13.36 H.

**3a-Butyl-7-methyl-decahydroazulene (10b).** After purification, 0.82 g (83% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 0.96 (t, 3H), 1.06 (d, 3H), 1.16–1.48 (m, 14H), 1.60–1.75 (m, 8H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 14.1, 21.3, 22.4, 23.4, 23.8, 27.8, 32.3, 33.3, 36.4, 37.7, 38.2, 39.2, 39.3, 44.8, 54.7; EI/HRMS  $[\text{M}]^+$  calcd for  $\text{C}_{15}\text{H}_{28}$ : 208.2191; found 208.2193. Anal. Calcd for  $\text{C}_{15}\text{H}_{28}$ : 86.46 C, 13.54 H; found 86.48 C, 13.52 H.

**1,5-Dimethylbicyclo[4.3.1]decane (11a).** After purification, 27 mg (3% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 1.06 (d, 3H), 1.16 (s, 3H), 1.10–1.26 (m, 9H), 1.31–1.51 (m, 6H), 1.61–1.70 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 18.8, 21.4, 22.1, 25.4, 31.7, 35.7, 37.2, 40.1, 40.9, 41.6, 42.7, 43.4; EI/HRMS  $[\text{M}]^+$  calcd for  $\text{C}_{12}\text{H}_{22}$ : 166.1722; found 166.1720. Anal. Calcd for  $\text{C}_{12}\text{H}_{22}$ : 86.67 C, 13.33 H; found 86.61 C, 13.39 H.

**1-Butyl-5-methylbicyclo[4.3.1]decane (11b).** After purification, 18 mg (2% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 0.96 (t, 3H), 1.06 (d, 3H), 1.10–1.51 (m, 21H), 1.61–1.70 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 14.1, 18.8, 21.7, 22.4, 23.4, 27.5, 31.7, 35.7, 37.5, 39.2, 39.4, 40.1, 40.5, 41.2; EI/HRMS  $[\text{M}]^+$  calcd for  $\text{C}_{15}\text{H}_{28}$ : 208.2191; found 208.2188. Anal. Calcd for  $\text{C}_{15}\text{H}_{28}$ : 86.46 C, 13.54 H; found 86.43 C, 13.56 H.

**1,2-Dimethylcyclopentane (15a).** After purification, 0.94 g (95% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 1.06 (d, 6H), 1.25–1.75 (m, 8H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 17.9, 25.4, 36.1, 45.3; EI/HRMS  $[\text{M}]^+$  calcd for  $\text{C}_7\text{H}_{14}$ : 98.1096; found 98.1094. Anal. Calcd for  $\text{C}_7\text{H}_{14}$ : 85.63 C, 14.37 H; found 85.61 C, 14.39 H.

**1-Butyl-2-methylcyclopentane (15b).** After purification, 0.89 g (90% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 0.96 (t, 3H), 1.06 (d, 3H), 1.29–1.60 (m, 14H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 14.1, 18.2, 23.1, 25.7, 30.0, 31.8, 33.9, 36.4, 43.1, 46.4; EI/HRMS  $[\text{M}]^+$  calcd for  $\text{C}_{10}\text{H}_{20}$ : 140.1565; found 140.1568. Anal. Calcd for  $\text{C}_{10}\text{H}_{20}$ : 85.63 C, 14.37 H; found 85.61 C, 14.40 H.

**1,2-Dimethylcyclohexane (15c).** After purification, 0.71 g (71% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 1.06 (m, 6H), 1.20–1.65 (m, 10H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 18.2, 25.8, 33.3, 40.3; EI/HRMS  $[\text{M}]^+$  calcd for  $\text{C}_8\text{H}_{16}$ : 112.1252; found 112.1250. Anal. Calcd for  $\text{C}_8\text{H}_{16}$ : 85.63 C, 14.37 H; found 85.67 C, 14.31 H.

**1-Butyl-2-methylcyclohexane (15d).** After purification, 0.68 g (68% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 0.96 (t, 3H), 1.06 (d, 3H), 1.20–1.50 (m, 16H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 14.1, 18.5, 23.1, 25.8, 26.1, 30.0, 31.1, 32.1, 33.6, 38.1, 42.5;



EI/HRMS  $[M]^+$  calcd for  $C_{11}H_{22}$ : 154.1722; found 154.1721. Anal. Calcd for  $C_{11}H_{22}$ : 85.63 C, 14.37 H; found 85.61 C, 14.36 H.

**Methylcyclohexane (16a).** After purification, 42 mg (4% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 0.96 (d, 3H), 1.01–1.75 (m, 11H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 22.9, 26.5, 26.6, 32.9, 35.6; EI/HRMS  $[M]^+$  calcd for  $C_7H_{14}$ : 98.1096; found 98.1097. Anal. Calcd for  $C_7H_{14}$ : 85.63 C, 14.37 H; found 85.64 C, 14.32 H.

**Butylcyclohexane (16b).** After purification, 91 mg (9% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 0.96 (t, 3H), 1.01–1.8 (m, 17H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 14.2, 23.1, 26.6, 26.9, 29.3, 33.6, 37.4, 37.8; EI/HRMS  $[M]^+$  calcd for  $C_{10}H_{20}$ : 140.1565; found 140.1561. Anal. Calcd for  $C_{10}H_{20}$ : 85.63 C, 14.37 H; found 85.60 C, 14.40 H.

**Methylcycloheptane (16c).** After purification, 0.27 g (28% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 0.96 (d, 3H), 1.01–1.4 (m, 12H), 1.65 (m, 1H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 21.0, 26.5, 29.3, 34.9, 37.3; EI/HRMS  $[M]^+$  calcd for  $C_8H_{16}$ : 112.1252; found 112.1256. Anal. Calcd for  $C_8H_{16}$ : 85.63 C, 14.37 H; found 85.59 C, 14.41 H.

**Butylcycloheptane (16d).** After purification, 0.31 g (31% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 0.96 (t, 3H), 1.25–1.45 (m, 18H), 1.50 (m, 1H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 14.1, 23.1, 26.8, 29.3, 29.7, 34.9, 35.1, 40.4; EI/HRMS  $[M]^+$  calcd for  $C_{11}H_{22}$ : 154.1722; found 154.1719. Anal. Calcd for  $C_{11}H_{22}$ : 85.63 C, 14.37 H; found 85.67 C, 14.31 H.

**Non-1-ene (17a).** After purification, 0.98 g (98% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 0.86 (t, 3H), 1.23–1.39 (m, 10H), 2.04 (q, 2H), 4.97 (m, 2H), 5.82 (m, 1H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 11.1, 22.8, 29.5, 29.8, 31.9, 33.9, 114.3, 139.5. EI/HRMS  $[M]^+$  calcd for  $C_9H_{18}$ : 126.1409; found 126.1410. Anal. Calcd for  $C_9H_{18}$ : 85.63 C, 14.37 H; found 85.67 C, 14.31 H.

**Dodec-1-ene (17b).** After purification, 0.99 g (99% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 0.89 (t, 3H), 1.23–1.39 (m, 16H), 2.04 (q, 2H), 4.97 (m, 2H), 5.82 (m, 1H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 11.1, 22.8, 29.4, 29.7, 29.8, 31.9, 33.9, 114.3, 139.5. EI/HRMS  $[M]^+$  calcd for  $C_{12}H_{24}$ : 168.1878; found 168.1875. Anal. Calcd for  $C_{12}H_{24}$ : 85.63 C, 14.37 H; found 85.61 C, 14.40 H.

**Dec-1-ene (18a).** After purification, 0.97 g (97% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 0.89 (t, 3H), 1.23–1.39 (m, 12H), 2.04 (q, 2H), 4.97 (m, 2H), 5.82 (m, 1H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 11.1, 22.8, 29.4, 29.7, 29.8, 31.9, 33.9, 114.3, 139.5. EI/HRMS  $[M]^+$  calcd for  $C_{10}H_{20}$ : 140.1565; found 140.1563. Anal. Calcd for  $C_{10}H_{20}$ : 85.63 C, 14.37 H; found 85.65 C, 14.39 H.

**Tridec-1-ene (18b).** After purification, 0.98 g (98% yield) of a colorless liquid was collected. The following spectral properties were observed:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 0.89 (t, 3H), 1.23–1.39 (m, 18H), 2.04 (q, 2H), 4.97 (m, 2H), 5.82 (m, 1H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  (ppm) 11.1, 22.8, 29.4, 29.7, 29.8, 31.9, 33.9, 114.3, 139.5. EI/HRMS  $[M]^+$  calcd for  $C_{13}H_{26}$ : 182.2035; found 182.2033. Anal. Calcd for  $C_{13}H_{26}$ : 85.63 C, 14.37 H; found 85.60 C, 14.42 H.

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**Supporting Information Available:** Characterization data for compounds **1a–f**, **4a,b**, and **13a–h**. Copies of  $^1H$  and  $^{13}C$  NMR spectra for compounds **2a–f**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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