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Construction of [4.3.1]Propellanes via Molybdenum Fischer Carbene Complexes

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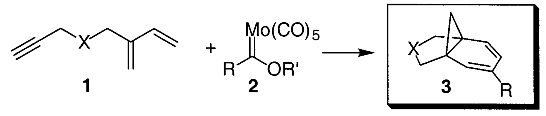
Abstract: Treatment of molybdenum Fischer carbene complexes with 6-methylene-7-octen-1-yne derivatives at 40 °C generates substituted tricyclo[4.3.1.$0^{1,6}$]deca-2,4-dienes in good yield. Pentacarbonyl(butylmethoxycarbene)molybdenum(0) afforded the highest cyclization yields (54%), while the analogous chromium carbene complex gave no reaction. The range of dienyne substrates that participate in this reaction is explored and its mechanism is analyzed and discussed.

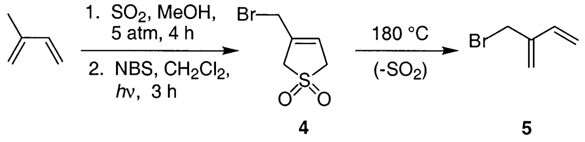
The propellanes, a class of hydrocarbons with two singly bonded carbon atoms joined by three other bridges, present a challenging task to synthetic organic chemists. In general, propellane syntheses are low-yielding and labor-intensive and require complex reaction conditions.[1,2] However, we have recently found that dienyne **1** cyclizes with molybdenum Fischer carbene complexes[3] (**2**) to produce [4.3.1]propellane[4] **3** (eq 1). Herein we describe this carbene-mediated transformation, which is a rapid and efficient approach to carbocyclic propellanes.



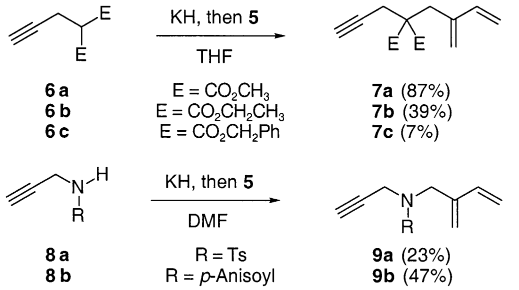
(1)

In this study, most of the cyclization substrates derived from **1** were prepared using bromodiene **5** as a key synthetic intermediate. Following the procedure of Krug and Yen,[5] condensation of isoprene with sulfur dioxide[6] followed by treatment with *N*-bromosuccinimide produced bromosulfolene **4** (Scheme 1). Subsequent pyrolysis of **4** generated **5**, which was used promptly after its production to avoid decomposition. Treatment of **5** with the potassium salts of propargylmalonates **6a**−**c** and propargylamides **8a** and **8b** gave the dienynes **7a**−**c**, **9a**, and **9b**, respectively (Scheme 2). Another cyclization substrate, dienyne **14**, was synthesized by a different route (Scheme 3).[7,8]

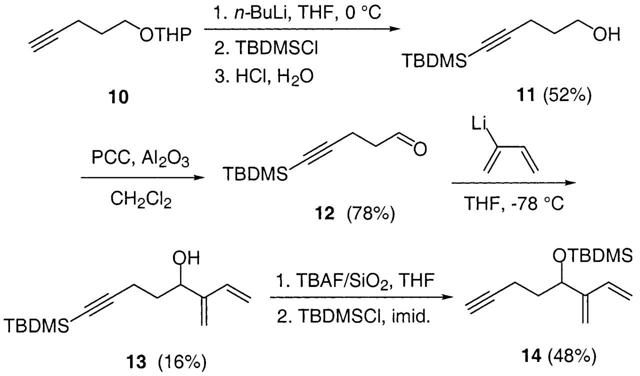
SCHEME 1



SCHEME 2



SCHEME 3



We first explored the reaction of *gem*-diester dienynes **7a**−**c** with butyl(methoxy)molybdenum carbene complex (**2a**, Scheme 4). Complex **2a** is relatively stable, easily isolable, and has performed well in related carbene−alkyne−alkene cyclizations.[9,10] Cyclization yields for these malonate dienynes are dependent upon the choice of ester: as the bulk of the diesters increases, the dienynes become less thermally stable (see the Experimental Section) and are prone to decomposition before cyclization can occur. Treatment of dienyne **14** with

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[1] For reviews, see: (a) Ginsburg, D. *Propellanes: Structure and Reactions*; Verlag Chemie: Weinheim, 1975. (b) Ginsburg, D. *Propellanes: Sequel I*; Technion-Israel Institute of Technology: Haifa, Israel, 1981.

[2] Wiberg, K. B. *Chem. Rev.* **1989**, *89*, 975−983 and references therein.

[3] For a recent review on metal carbene-mediated cyclization reactions, see: Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271−288.

[4] For a recently published crystal structure of a [4.3.1]propellane similar to **3**, see: Mackay, M. F.; Banwell, M. G.; Pallich, S.; Phyland, J. R. *Acta Crystallogr.* **1998**, *C54*, 378−380. [4.3.1]Propellanes are occasionally found in nature; examples include cnoerin C, a compound isolated from *Cneorum pulverulentum* (Mondon, A.; Callsen, H.; Epe, B. *Tetrahedron Lett.* **1975**, *9*, 703−706) and marasmic acid, an antibiotic sesquiterpene isolated from *Marasmius conigenus.* For a recent synthesis of (±)-marasmic acid and several leading references, see: Tobe, Y.; Yamashita, D.; Takahashi, T.; Inata, M.; Sato, J.-i.; Kakiuchi, K.; Kobiro, K.; Odaira, Y. *J. Am. Chem. Soc.* **1990**, *112*, 775−779.

[5] Krug, R. C.; Yen, T. F. *J. Org. Chem.* **1956**, *21*, 1082−1086.

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[10] Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* **1991**, *113*, 5066−5068.

10.1021/jo020378a CCC: $22.00

SCHEME 4

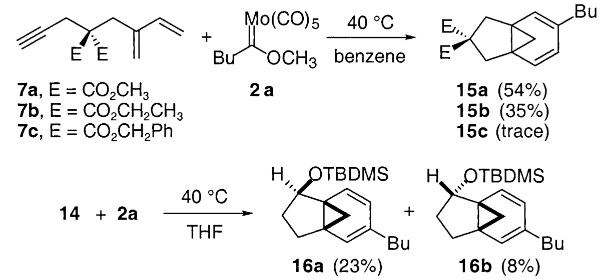
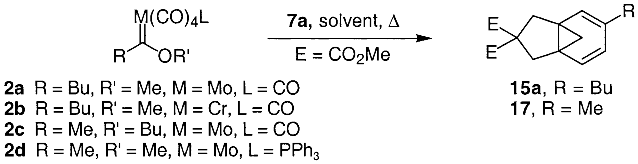


TABLE 1. Optimization of Cyclization Yields[a]



entry	L	R	R′	M	solvent	T (°C)	time (h)	yield (%)
1	CO	Bu	Me	Mo	benzene	40	5	54
2	CO	Bu	Me	Mo	THF	40	5	24
3	CO	Bu	Me	Mo	benzene	80	2.5	9
4	CO	Bu	Me	Cr	benzene	60	5.5	
5	CO	Me	Bu	Mo	benzene	60	4	5
6	PPh_3	Me	Me	Mo	benzene	60	4.25	7

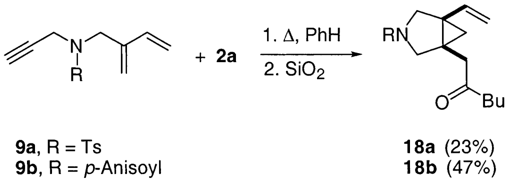
[a] Using 1.2 equiv of freshly purified carbene complex (silica gel chromatography with 100% hexanes), cyclizations were monitored by TLC until no starting material was present.

complex **2a** produced a 3:1 diastereomeric mixture of propellanes **16a** and **16b** in 33% yield. NOE studies confirmed that in the major diastereomer **16a** the siloxy substituent was syn to the CH_2 bridge.

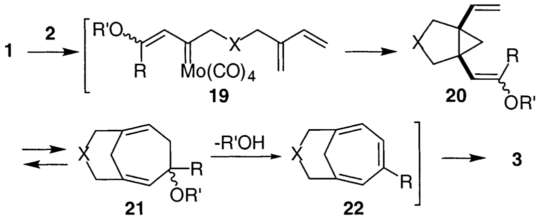
Optimization of cyclization yields of dienyne **7a** are presented in Table 1. While thermolysis of **7a** and **2a** in benzene generated propellane **15a** in 54% yield (entry 1), when this reaction was carried out in THF (entry 2) **15a** was produced in 24% yield. At higher temperature (entry 3), the yield was significantly lower, apparently due to competing thermal decomposition of the dienyne.[11] Previous studies have demonstrated that chromium carbene complexes do not readily participate in cyclizations of this type,[10] and this was again the case with dienyne **7a** (entry 4). Upon reaction with chromium complex **2b**,[12] decomposition of both the carbene complex and the dienyne was observed by TLC and no identifiable compounds were produced. The less stable molybdenum carbene complex **2c**[13] (entry 5) and the less reactive[13] triphenylphosphine complex **2d**[14] (entry 6) did react with **7a** to produce **17**, but higher reaction temperatures were required and yields were lower.

We next investigated whether nitrogen-containing dienynes **9a** and **9b** would participate in this reaction pathway (Scheme 5). Our earlier studies of related amine derivatives demonstrated that allyl propargyl amides cyclize with carbene complexes to give cyclopropylpyrrolidine derivatives.[15] Indeed, treatment of **9a** and **9b** with complex **2a** followed by silica gel chromatography generated ketocyclopropane **18a** and **18b** in 41% yield. It is noteworthy that following initial cyclopropane formation, rearrangement to the propellane framework did not occur (vide supra).

SCHEME 5



SCHEME 6



A possible mechanism for propellane formation (Scheme 6) begins with insertion of **2** into the alkyne of **1** to generate vinylcarbene **19**. Carbene cyclopropanation of the **19** methylene olefin produces *cis*-divinylcyclopropane **20**, which undergoes a [3,3]-sigmatropic rearrangement to 1,4-cycloheptadiene **21**.[16] Elimination of R′OH from **21** then gives the highly strained cycloheptatriene **22**, which irreversibly tautomerizes to **3**. Cycloheptatrienes are normally favored over their corresponding norcaradiene tautomers, either exclusively or as an equilibrating mixture.[17] Fortunately, [4.3.1]propellanes such as **3**, where the norcaradiene bridgehead carbons are incorporated into a five-membered ring, possess one of the few stable norcaradiene systems.[18]

Of particular mechanistic interest is the contrasting behavior of *gem*-diester derived dienynes **7a**−**c** that readily produced **15a**−**c**, and nitrogen derivatives **9a** and **9b** that reached the stage of cyclopropane **20** but did not form the [4.3.1]propellane system. We believe this reactivity difference is due to substituent-induced conformational preferences of **20**.[19] For the divinylcyclopropane intermediate derived from **7a**−**c**, there are four conformations that summarize the most critical steric interactions (Scheme 7). The two key issues are the conformation of the cyclopentane ring and the orientation of the enol ether. In the cyclopentane ring, the *gem*-diester carbon can be folded either "up," as in **23a** and **23b**, or "down," as in **23c** and **23d**. Both vinyl substituents are able to freely rotate, but rearrangement can only occur when

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[11] Dienyne **7a** was not stable when heated alone at 80 °C in benzene.

[12] Montgomery, J.; Wieber, G. M.; Hegedus, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 6255−6263.

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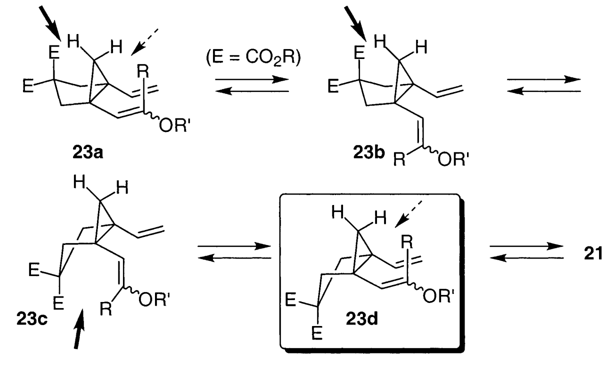
[17] For recent discussion of the cycloheptatriene−norcaradiene rearrangement, see: Jarzecki, A. A.; Gajewski, J.; Davidson, E. R. *J. Am. Chem. Soc.* **1999**, *121*, 6928−6935.

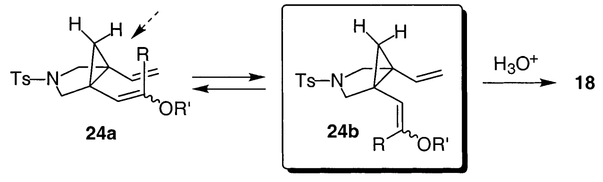
[18] Matsumoto, M.; Shiono, T.; Kasuga, N. C. *Tetrahedron Lett.* **1995**, *36*, 8817−8820.

[19] For a general discussion of substituent effects on *cis*-divinylcyclopropane rearrangements, see: Piers, E.; Morton, H. E.; Nagakura, I.; Thies, R. W. *Can. J. Chem.* **1983**, *61*, 1226−1238.

SCHEME 7



SCHEME 8



both are rotated syn to the CH$_2$ bridge, forming the boatlike conformations of **23a** and **23d** (for simplicity the unsubstituted vinyl group, though free to rotate, is kept constant). Rearrangement cannot occur when both vinyl substituents are rotated anti to the CH$_2$ bridge as rearrangement through this conformation would generated a highly strained *trans*,*trans*-1,4-cycloheptadiene. Conformations **23a** and **23b** are both highly disfavored because of the severe steric interaction between the *endo*-ester and the CH$_2$ bridge. Conformation **23c** is also disfavored because of the indicated severe steric interaction between the cis substituent of the enol ether and the *exo*-ester. In conformation **23d** there is only a relatively mild steric interaction between the cis enol ether substituent and the CH$_2$ bridge; therefore, **23d** is significantly preferred over conformations **23a**–**c**. Fortunately, the low-energy conformation of **23d** has two vinyl groups that are appropriately positioned for a [3,3]-sigmatropic rearrangement to **21**.

For the amide-based divinylcyclopropane **24**, there are no significant steric interactions between the amide, the CH$_2$ bridge, nor the vinyl substituents (Scheme 8). Therefore, the only significant conformational issue to consider is the orientation of the enol ether. When rotated "up" the cis substituent of the enol ether interacts with the CH$_2$ bridge (see arrow in **24a)**. When rotated "down" no significant steric interactions are apparent. Thus, the activation energy for rearrangement of **24a** is expected to be significantly higher than that of **24b**.

On the basis of the above analyses and because no enol ether nor ketone products were observed for the cyclization of **14** with **2a**, the TBDMS ether of **14** may provide enough steric bulk to favor the proper orientation of the vinyl groups achieved by **23d**. The 3:1 distribution of propellane products **16a** and **16b** suggests that the siloxy substituent does not significantly bias a single conformation through which divinylcyclopropane rearrangement is viable.

Experimental Section

General Methods. All reagents were obtained from commercial suppliers and used as received unless otherwise indicated. Benzene and tetrahydrofuran (THF) were glass-distilled from potassium/benzophenone ketyl under a nitrogen atmosphere. Diethyl ether was glass-distilled from sodium/benzophenone ketyl under a nitrogen atmosphere. Dimethylformamide (DMF) and dichloromethane were glass-distilled from calcium hydride under a nitrogen atmosphere. Melting points are uncorrected.

2-(Bromomethyl)-1,3-butadiene (5). Thermolysis of 3-(bromomethyl)-2,5-dihydrothiophene 1,1-dioxide **4**^{5} at 180 °C and 0.5 mmHg generated **5**, which was directly distilled into an aluminum foil covered receiving flask cooled to −78 °C and then used immediately without further purification.[20]

General Procedure for the Synthesis of Malonate Dienynes. Potassium hydride (1.15 mmol) was washed with Et$_2$O and suspended in THF (25.0 mL). After slow addition of the propargylmalonate (1.15 mmol), the reaction mixture was stirred for 1 h at rt. In the dark, freshly prepared bromide **5** (from pyrolysis of 2.30 mmol of **4**) in THF (2.0 mL) was then transferred via cannula to the resulting suspension. After 12 h at rt, the reaction mixture was concentrated in vacuo and the residue purified by chromatography on silica gel. Preparation of nitrogen-containing dienynes **9a** and **9b** was identical to this procedure; however, DMF was used as a solvent instead of THF.

Dimethyl 6-methylene-7-octen-1-yne-4,4-dicarboxylate (7a): clear, colorless liquid; ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.33 (dd, J = 17.6, 11.0 Hz, 1H), 5.36 (d, J = 17.6 Hz, 1H), 5.25 (s, 1H), 5.14 (s, 1H), 5.07 (d, J = 11.0 Hz, 1H), 3.74 (s, 6H), 3.06 (s, 2H), 2.85 (d, J = 2.6 Hz, 2H), 2.08 (t, J = 2.6 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$) δ 170.3, 141.0, 138.6, 120.0, 114.0, 79.3, 71.8, 56.8, 52.6, 32.4, 22.6 ppm; IR (KBr) 3269, 2955, 2156, 1739 cm^{-1}; LRMS *m/e* 237 (MH$^+$, 24), 205 (18), 177 (100); HRMS calcd for $C_{13}H_{17}O_4$ (MH$^+$) 237.1127, found 237.1115.

Diethyl 6-methylene-7-octen-1-yne-4,4-dicarboxylate (7b): clear, colorless liquid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.21 (dd, J = 11.2, 6.4 Hz, 1H), 5.26 (d, J = 17.6 Hz, 1H), 5.11 (s, 1H), 5.02 (s, 1H), 4.93 (d, J = 10.8 Hz, 1H), 4.14–4.00 (m, 4H), 2.92–2.89 (m, 2H), 2.72 (d, J = 2.4 Hz, 2H), 1.96–1.95 (m, 1H), 1.18–1.14 (m, 6H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.6, 140.8, 138.4, 119.7, 113.9, 79.5, 71.7, 61.6, 56.8, 32.3, 22.7, 14.0 ppm; IR (neat) 3308, 1728 cm^{-1}; LRMS *m/e* 219 (15), 117 (100); HRMS (FAB) *m/e* calcd for $C_{15}H_{21}O_4$ (MH$^+$) 265.1440, found 265.1442.

Dibenzyl 6-Methylene-7-octene-1-yne-4,4-dicarboxylate (7c). This compound, a clear yellow oil, is unstable and gradually decomposes during purification and spectroscopic identification: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33–7.22 (m, 10H), 6.28 (dd, J = 10.8, 6.8 Hz, 1H), 5.33 (d, J = 17.6 Hz, 1H), 5.16 (d, J = 18.4 Hz, 2H), 5.11 (s, 1H), 5.04 (d, J = 18.4 Hz, 2H), 5.05 (s, 1H), 5.00 (d, J = 10.8 Hz, 1H), 3.06 (s, 2H), 2.86 (d, J = 2.8 Hz, 2H), 2.01 (t, J = 2.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$) δ 169.2, 138.3, 134.8, 128.3, 128.2, 128.1, 128.0, 119.9, 114.0, 72.0, 67.4, 65.8, 57.1, 32.5, 15.4 ppm; IR (thin film) 3309, 3096, 3074, 1820, 1747 cm^{-1}; LRMS *m/e* 205 (100), 91 (36), 39 (44); HRMS (FAB) *m/e* calcd for $C_{25}H_{24}O_4Na$ (MNa$^+$) 411.1572, found 411.1558.

***N*-2-Methylene-3-butene-*N*-2-propynyltoluenesulfonamide (9a):** light yellow solid; mp 98.5–99.5 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.76 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 6.34 (dd, J = 17.7, 11.1 Hz, 1H), 5.62 (d, J = 17.7 Hz, 1H), 5.25 (s, 1H), 5.23 (s, 1H), 5.18 (d, J = 11.1 Hz, 1H), 4.04 (d, J = 2.4 Hz, 2H), 3.99 (s, 2H), 2.43 (s, 3H), 1.94 (t, J = 2.4 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$) δ 143.7, 139.2, 135.6, 135.5, 129.5, 128.0, 120.1, 116.4, 76.2, 74.0, 47.7, 35.4, 21.4 ppm; IR (neat) 3288, 2119, 1352, 1168 cm^{-1}; LRMS (CI) *m/z* 276 (MH$^+$, 100); HRMS calcd for $C_{15}H_{18}NO_2S$ (MH$^+$) 276.1058, found 276.1049.

***N*-Isoprenyl-*N*-propargyl-4-methoxybenzamide (9b):** light yellow oil; ^{1}H NMR (300 MHz, CDCl$_3$, 50 °C) δ 7.48 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 6.39 (dd, J = 11.1, 1.8 Hz, 1H), 5.32–5.20 (m, 3H), 4.38 (s, 2H), 4.15 (s, 2H), 3.83 (s, 3H),

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[20] Hegedus, L. S.; Varaprath, S. *Organometallics* **1982**, *1*, 259–263.

2.27 (t, J = 2.3 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$, 70 °C) δ 170.8, 161.5, 141.7, 136.9, 129.3, 128.6, 117.2, 114.8, 114.0, 79.6, 72.3, 54.8, 48.0 (br s), 37.0 (br s); IR (neat) 3292, 2118, 1638 cm^{-1}; LRMS (EI) *m/z* 255 (M$^+$, 49), 135 (100); HRMS calcd for $C_{16}H_{17}NO_2$ (MH$^+$) 255.1259, found 255.1260.

5-(*tert*-Butyldimethylsilyl)-4-pentyn-1-ol (11): clear liquid; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.77 (q, J = 5.8 Hz, 2H), 2.36 (t, J = 6.9 Hz, 2H), 1.78 (pentet, J = 6.4 Hz, 2H), 1.56 (t, J = 5.3 Hz, 1H), 0.92 (s, 9H), 0.08 (s, 6H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$) δ 107.2, 83.4, 61.9, 31.2, 26.0, 16.44, 16.39, −4.6 ppm; IR (neat) 3329, 2178 cm^{-1}; LRMS (EI) *m/z* 141 (9), 75 (100).

5-(*tert*-Butyldimethylsilyl)-4-pentynal (12): clear, citrus-smelling oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 9.79 (t, J = 1.0 Hz, 1H), 2.70−2.64 (m, 2H), 2.57−2.52 (m, 2H), 0.91 (s, 9H), 0.07 (s, 6H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$) δ 200.6, 105.3, 84.0, 42.6, 25.9, 16.4, 13.1, −4.7 ppm; IR (neat) 2855, 2724, 2176, 1731 cm^{-1}; LRMS (EI) *m/z* 139 (100), 109 (45), 57 (7).

8-(*tert*-Butyldimethylsilyl)-3-methyleneoct-1-en-7-yn-4-ol (13): clear, yellow oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.38 (dd, J = 17.9, 11.2 Hz, 1H), 5.37 (d, J = 17.9 Hz, 1H), 5.31 (s, 1H), 5.17 (s, 1H), 5.11 (d, J = 11.2 Hz, 1H), 4.66−4.64 (m, 1H), 2.51−2.27 (m, 2H), 1.98−1.85 (m, 2H), 1.77−1.65 (m, 1H), 0.93 (s, 9H), 0.09 (s, 6H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$) δ 148.8, 136.2, 114.43, 114.39, 107.4, 83.5, 70.1, 35.1, 26.0, 16.5, 16.4, −4.6 ppm; IR (neat) 3365, 2173 cm^{-1}; LRMS (CI, NH$_3$) *m/z* 268 (MNH$_4^+$, 18), 251 (MH$^+$, 82); HRMS (MH$^+$) calcd for $C_{15}H_{27}OSi$ 251.1831, found 251.1834.

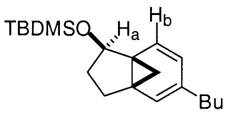
6-Methylene-5-(*tert*-butyldimethylsilyloxy)-7-en-1-yne (14): clear, colorless liquid; ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.31 (dd, J = 17.9, 11.2 Hz, 1H), 5.36 (d, J = 17.9 Hz, 1H), 5.23 (s, 1H), 5.11 (s, 1H), 5.07 (d, J = 11.3 Hz, 1H), 4.53 (dd, J = 7.8, 3.6 Hz, 1H), 2.37−2.16 (m, 2H), 1.95 (t, J = 2.5 Hz, 1H), 1.88−1.65 (m, 2H), 0.90 (s, 9H), 0.08 (s, 3H), 0.00 (s, 3H) ppm; ^{13}C NMR (100 MHz, C$_6$D$_6$) δ 149.2, 136.3, 115.0, 114.2, 84.2, 71.3, 69.4, 37.2, 26.3, 18.7, 15.5, −4.2, −4.7 ppm; IR (neat) 3317, 2121 cm^{-1}; LRMS (CI, NH$_3$) *m/z* 268 (MNH$_4^+$, 94), 251 (MH$^+$, 100); HRMS (MH$^+$) calcd for $C_{15}H_{27}OSi$ 251.1831, found 251.1833.

General Procedure for Carbene Cyclizations. A solution of the carbene complex (0.60 mmol) and the dienyne (0.50 mmol) in benzene or THF (10.0 mL) were heated until disappearance of the dienyne was observed by TLC. The reaction mixture was then concentrated in vacuo, and the remaining material was immediately purified by silica gel chromatography.

Dimethyl 3-butyltricyclo[4.3.1.0^{1,6}]deca-2,4-diene-8,8-dicarboxylate (15a): clear, colorless liquid; ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.12 (d, J = 9.4 Hz, 1H), 5.80 (s, 1H), 5.69 (d, J = 9.4 Hz, 1H), 3.76 (s, 3H), 3.67 (s, 3H), 2.82 (d, J = 13.4 Hz, 2H), 2.41 (d, J = 13.5 Hz, 2H), 2.05 (t, J = 7.3 Hz, 2H), 1.48−1.20 (m, 5H), 0.90 (t, J = 7.1 Hz, 3H), −0.24 (d, J = 4.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$) δ 173.0, 171.9, 131.7, 128.8, 123.1, 122.6, 59.1, 52.8, 41.4, 41.1, 35.9, 35.19, 35.15, 31.2, 22.1, 19.1, 13.8; IR (neat) 1737 cm^{-1}; LRMS (CI, CH$_4$) *m/z* 305 (MH$^+$, 38); HRMS calcd for $C_{18}H_{25}O_4$ (MH$^+$) 305.1753, found 305.1769.

Diethyl 3-butyltricyclo[4.3.1.0^{1,6}]deca-2,4-diene-8,8-dicarboxylate (15b): clear, pale yellow liquid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.12 (d, J = 9.2 Hz, 1H), 5.79 (s, 1H), 5.67 (d, J = 9.6 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 4.11 (q, J = 7.2 Hz, 2H), 2.82 (dd, J = 13.2, 2.4, 2H), 2.41 (dd, J = 13.6, 5.6 Hz, 2H), 2.06 (t, J = 7.2 Hz, 3H), 1.28−1.17 (m, 10H), 0.87 (t, J = 7.2 Hz, 3H), −0.26 (d, J = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 172.2, 171.1, 131.4, 128.7, 123.0, 122.4, 61.7, 59.2, 41.4, 41.0, 36.2, 35.5, 35.4, 31.4, 22.3, 19.4, 14.2 14.1 ppm; IR (neat) 1730 cm^{-1}; LRMS *m/e* 332 (M$^+$, 43), 258 (100); HRMS (EI) *m/e* calcd for $C_{20}H_{28}O_4$ 332.1987, found 332.1987.

Dibenzyl 3-Butyltricyclo[4.3.1.0^{1,6}]deca-2,4-diene-8,8-dicarboxylate (15c). Rapid degradation of **15c** prevented the calculation of an accurate yield; however, the following crude spectroscopic data were obtained: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32−7.20 (m, 10H), 6.10 (d, J = 9.2 Hz, 1H), 5.76 (s, 1H), 5.65 (d, J = 9.6 Hz, 1H), 5.11 (s, 2H), 5.02 (s, 2H), 2.84 (dd, J = 13.5, 2.4 Hz, 2H), 2.43 (dd, J = 13.4, 5.5 Hz, 2H), 1.36−1.09 (m, 7H), 0.86 (t, J = 7.2 Hz, 3H), −0.27 (d, J = 4.4 Hz, 1H) ppm; IR (neat) 1816, 1735 cm^{-1}; LRMS *m/e* 456 (M$^+$, 4), 413 (100); HMRS (FAB) *m/e* calcd for $C_{30}H_{32}O_4Na$ 479.2198, found 479.2212.



16a

3-Butyl-7-(*tert*-butyldimethylsilyloxy)tricyclo[4.3.1.0^{1,6}]-deca-2,4-diene (16). A 1D NOE difference experiment on **16a** (a clear, pale yellow liquid) exhibited a 5.8% enhancement of H$_b$ when H$_a$ was irradiated. Assignment of proton and carbon atoms was based on COSY, HETCOR, and DEPT experiments: ^{1}H NMR (500 MHz, CDCl$_3$) **16a** δ 6.24 (d, J = 9.3 Hz, 1H), 5.71 (d, J = 8.8 Hz, 1H), 5.70 (s, 1H), 4.32 (t, J = 7.8 Hz, 1H), 2.11−2.02 [(m, 3H) containing 2.06 (t, J = 7.5 Hz, 2H)], 1.71 (dt, J = 13.2, 8.3 Hz, 1H), 1.59 (ddd, J = 12.2, 8.8, 2.0 Hz, 1H), 1.40−1.34 (m, 2H), 1.26 (apparent sextet, J = 7.3 Hz, 2H), 0.91 (s, 9H), 0.88 (t, J = 7.1 Hz, 3H), 0.09 (s, 3H), 0.05 (s, 3H), −0.38 (d, J = 3.9 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$) **16a** δ 131.5, 128.0, 124.1, 122.8, 77.3, 39.5, 35.3, 35.2, 31.4, 29.7, 29.0, 25.9, 22.1, 18.1, 13.9, 12.7, −4.59, −4.62 ppm; **16b** δ 131.9, 127.8, 122.9, 122.7, 75.8, 39.5, 34.5, 32.6, 31.5, 30.8, 29.9, 25.7, 22.6, 22.1, 15.9, 14.0, −4.5, −4.8 ppm; IR (neat) 1269 cm^{-1}; LRMS (EI) *m/e* 318 (M$^+$, 17), 260 (100), 186 (70), 129 (74); HRMS (EI) calcd for $C_{20}H_{35}OSi$ (MH$^+$) 319.2449, found 319.2457. Anal. Calcd for $C_{20}H_{34}OSi$: C, 75.42; H, 10.77. Found: C, 75.08; H, 10.44.

Dimethyl 3-methyltricyclo[4.3.1.0^{1,6}]deca-2,4-diene-8,8-dicarboxylate (17): clear, colorless liquid; ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.13 (d, J = 9.4 Hz, 1H), 5.82 (s, 1H), 5.67 (d, J = 9.4 Hz, 1H), 3.76 (s, 3H), 3.68 (s, 3H), 2.87 (d, J = 13.4, 2H), 2.41 (d, J = 13.5 Hz, 2H), 1.82 (s, 3H), 1.24 (d, J = 4.7 Hz, 1H), −0.21 (d, J = 4.7 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 173.1, 172.0, 128.9, 127.0, 123.5, 123.4, 59.0, 52.9, 41.4, 41.1, 36.0, 29.6, 21.3, 18.9 ppm; IR (thin film) 1737, 1690 cm^{-1}; LRMS *m/e* 262 (M$^+$, 3), 143 (100); HRMS calcd for $C_{15}H_{18}O_4$ (MH$^+$) 262.1283, found 262.1273.

(5β)-*N*-(4-Toluenesulfonyl)-1β-(2-oxohexyl)-5β-vinyl-3-azabicyclo[3.1.0]hexane (18a): clear, pale yellow oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.68 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 5.59 (dd, J = 17.2, 10.6 Hz, 1H), 5.07 (d, J = 10.2 Hz, 1H), 4.98 (d, J = 17.0 Hz, 1H), 3.66 (d, J = 9.1 Hz, 1H), 3.58 (d, J = 9.1 Hz, 1H), 3.19 (d, J = 9.2 Hz, 1H), 2.94 (d, J = 9.2 Hz, 1H), 2.44 (d, J = 17.4 Hz, 1H), 2.43 (s, 3H), 2.34 (d, J = 17.4 Hz, 1H), 2.32 (t, J = 7.4 Hz, 2H), 1.48 (pentet, J = 7.5 Hz, 2H), 1.25 (sextet, J = 7.6 Hz, 2H), 1.02 (d, J = 5.6 Hz, 1H), 0.87 (t, J = 7.3 Hz, 3H), 0.75 (d, J = 5.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$) δ 208.9, 143.6, 134.7, 133.8, 129.8, 127.6, 115.9, 53.2, 52.4, 43.0, 42.4, 33.1, 30.2, 25.6, 22.1, 21.4, 17.9, 13.7 ppm; IR (KBr) 1714, 1341, 1161, 1099, 999, 814 cm^{-1}; LRMS (CI, NH$_3$) *m/z* 362 (M$^+$, 100); HRMS calcd for $C_{20}H_{28}NO_3S$ (MH$^+$) 362.1790, found 362.1805.

(5β)-*N*-(4-Methoxybenzoyl)-1β-(2-oxohexyl)-5β-vinyl-3-azabicyclo[3.1.0]hexane (18b): clear, colorless oil; ^{1}H NMR (300 MHz, C$_6$H$_6$, 70 °C) δ 7.49 (d, J = 8.6 Hz, 2H), 6.67 (d, J = 8.6 Hz, 2H), 5.63 (dd, J = 17.3, 10.8 Hz, 1H), 4.99 (d, J = 10.7 Hz, 1H), 4.96−4.85 (m, 1H), 3.63 (t, J = 10.7 Hz, 2H), 3.28 (s, 3H), 3.16 (s, 2H), 1.96−1.83 (m, 2H), 1.34−1.27 (m, 3H), 1.24−1.17 (m, 2H), 0.96 (d, J = 5.0 Hz, 1H), 0.90 (d, J = 4.9 Hz, 1H), 0.81 (t, J = 7.3 Hz, 3H), 0.25 (s, 1H); IR (C$_6$H$_6$ solution) 1631, 1610 cm^{-1}; LRMS (EI) *m/z* 342 (M$^+$, 28), 324 (14), 135 (100); HRMS calcd for $C_{21}H_{28}NO_3$ (MH$^+$) 342.2071, found 342.2069.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for **7a**−**c**, **9a**,**b**, **11**−**14**, **15a**−**c**, **16**, **17**, and **18a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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