Extended Unsaturated Carbenes.[1] Generation, Nature, and Chemistry of Alkatetraenylidenecarbenes, $R_2C{=}C{=}C{=}C{=}C{=}C$:

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Abstract: Base-initiated elimination of triflic acid from butadiynylvinyl triflates affords a ready entry to alkatetraenylidenecarbenes, $R_2C{=}C{=}C{=}C{=}C{=}C$:. Trapping with olefins results in the corresponding cumulenes or cumulene-derived products. Indirect evidence indicates that analogous to all presently known unsaturated carbenes these intermediates are unencumbered, electrophilic singlets. Insertion into silanes and germanes gives novel R_3Si– and R_3Ge– functionalized hexapentaenes albeit in low isolated yields. All new cumulenes are air sensitive, relatively unstable, but isolable compounds.

Carbenes are among the most versatile as well as synthetically useful organic reactive intermediates.[3] Recently unsaturated carbenes[4] have been of interest and to date the first three members of the homologous series **1**, namely alkylidenecarbenes, **2**, alkenylidenecarbenes, **3**, and alkadienylidenecarbenes,[5] **4**, have been observed and their chemistry explored.[4,5]

$$\underset{\mathbf{1},\ n\,=\,0\,\rightarrow\,\infty}{(R_2)C({=}C{=})_nC:}\qquad \underset{\mathbf{2}}{(R)_2C{=}C:}\qquad \underset{\mathbf{3}}{(R)_2C{=}C{=}C:}$$

$$\underset{\mathbf{4}}{(R)_2C{=}C{=}C{=}C:}$$

Attempts to generate the next member of the series, namely alkatrienyldenecarbene, **6**, by ϵ elimination from **5** have been unsuccessful:[6]

$$\underset{\mathbf{5}}{(C_6H_5)_2C(OCOCH_3)C{\equiv}C{-}C{\equiv}CH} \xrightarrow[\times]{t\text{-BuOK}} \underset{\mathbf{6}}{(C_6H_5)_2C{=}C{=}C{=}C{=}C:}$$

Despite this failure with a more extended unsaturated carbene, based on our experience in the generation of **4**, we were encouraged to try to generate and trap the six-carbon homologue (**1**, $n = 4$). In this paper we wish to report the generation, nature, and some chemistry of alkatetraenylidenecarbenes, **7**, the most extended unsaturated carbene to date.[7]

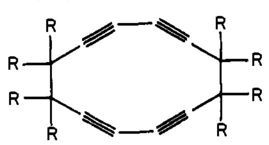
$$\underset{\mathbf{7}}{>C{=}C{=}C{=}C{=}C{=}C:}$$

Results and Discussion

Generation and Trapping of Alkatetraenylidenecarbenes. Reaction of butadiynylvinyl triflate **8**, prepared in three steps in 70% overall yield as previously reported,[8] with t-BuOK in glyme at 20 °C containing an excess olefin as trap proceeded as shown in Scheme I. Rate-determining loss of the triflate anion preceded by a rapid equilibrium formation of anion **9** were indicated by reisolation of deuterium-incorporated starting triflate **8** in deuterated media. This observation is consistent with a similar rapid preequilibrium and like conclusions, based on comparable experiments, in the base-catalyzed reaction of propargyl halides[9] as well as ethynylvinyl triflates[5] in the formation of carbenes **3** and **4**. Once formed carbene **10** is readily trapped by olefins. Addition to tetramethylethylene (TME) results in enediyne **12** via base-catalyzed isomerization of initial adduct **11**. Trapping with cyclohexene gives cyclyne **14** via dimerization of initial adduct **13**. Similarly, reaction of enediyne **15** via carbene **16** results in cumulene **17** in trapping with TME with only uncharacterized polymer being formed in the presence of cyclohexene, as shown in Scheme II.

Products **12**, **14**, and **17** were characterized by spectral means as summarized in Table I. Compound **12** as well as its spectral properties are unexceptional; the intense molecular ion in the mass spectrum, the consistent proton NMR spectrum, as well as the characteristic[10] infrared and UV all serve to unambiguously establish its structure.

The structure of cyclyne **14** is established by its molecular ion at m/z 368, its characteristic UV and infrared absorption, and the ^{13}C NMR with four distinct acetylenic carbons in the expected range[11] between 69 and 96 ppm, all in excellent agreement with the data for known cyclyne analogues **18a**[12] and **18b**.[13]



18a, R = H
b, R = CH_3

Adamantyl cumulene **17** is characterized by its molecular ion at m/z 278, a consistent ^1H NMR, and the very characteristic infrared absorption at 2010 cm^{-1} along with unique UV absorptions, all typical of cumulenes in general and hexapentaenes in particular.[14]

Several aspects of these olefin trapping reactions deserve further discussion. It is evident that the exact fate of the initial adduct

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[2] Fulbright-Hays postdoctoral fellow from the University of Zagreb, Zagreb, Yugoslavia.

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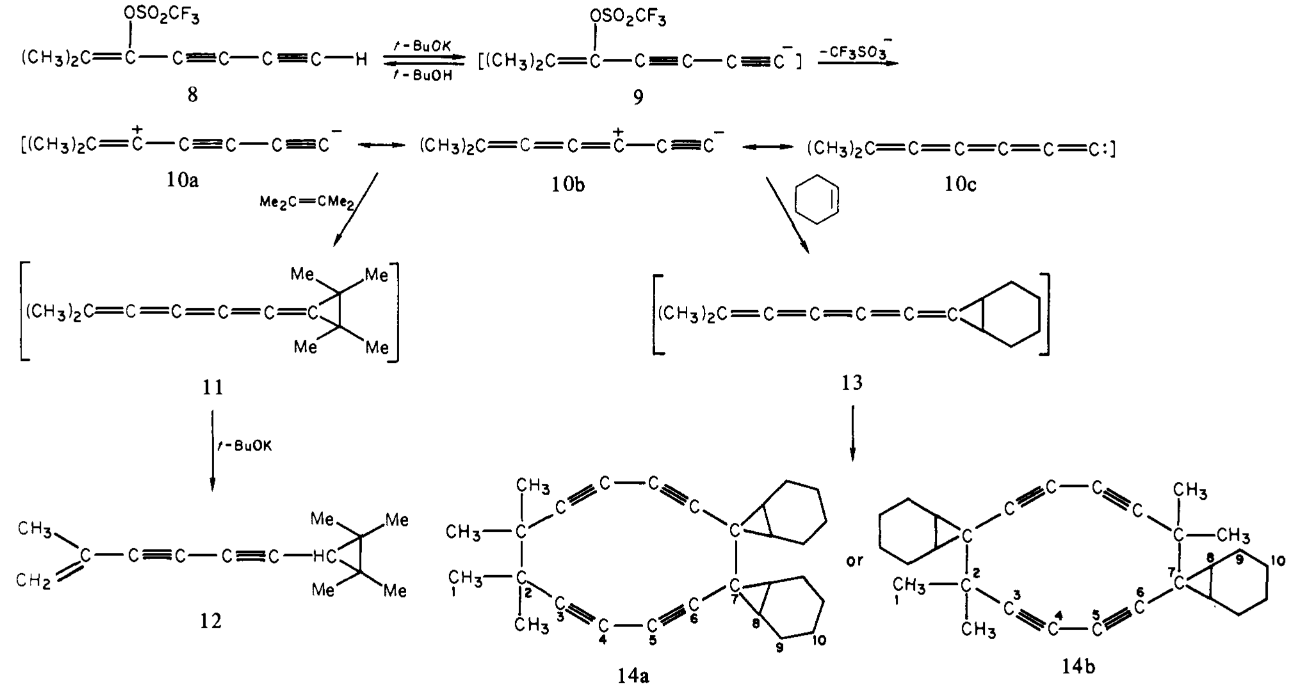
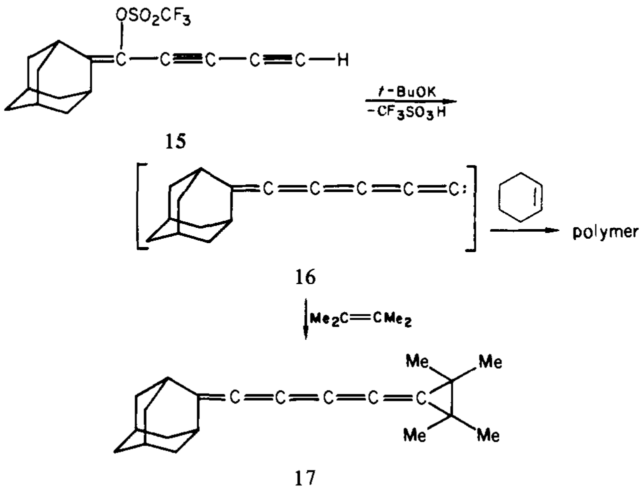
Scheme I



Scheme II

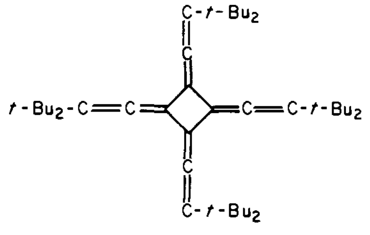


is very much a function of both the nature of the substitution of the carbene and the olefin. Bulky substituents such as adamantyl as well as the four methyl groups of the olefin prevent dimerization and allow isolation of the original cumulene adduct, i.e., **17**. In contrast, adduct **11** undergoes a base-catalyzed isomerization, not possible with adduct **17**, in preference to dimerization. Similarly, the bulky adamantyl group prevents the cyclohexene adduct of carbene **16** from cyclodimerizing, but the limited substituents on the olefin trap prevent isolation of the possible cumulene adduct itself and hence only polymerization is observed.

Perhaps the most interesting of all these reactions is dimerization of adduct **13** to cyclyne **14**. First of all, a priori cyclodimerization of cumulene **13** could result in a large number of diverse products. Yet only cyclyne **14** was isolated as a stable crystalline substance in 31% yield.[15] Moreover, no formally 2 + 2 dimers resulting in [4]radialenes were observed although such [4]radialenes are readily formed[16] from substituted tetratrienes and were the only products in the cyclohexene trapping of carbene **4**.[5] Furthermore, such formally 2 + 2 dimerization about the central π bond and concomitant formation of the corresponding [4]radialene, **20**, was the sole product in the cyclodimerization of tetra-*tert*-butylhexapentaene, **19**.[17] This discrepancy in behavior between the cyclohexene adducts of carbene **4** as well as cumulene **19** on the one side and adduct **13** on the other is not at present clearly understood—although qualitative calculations[18] based on bond additivity considerations[19] indicate that such cumulene cyclodimerizations in general, and the dimerization of **13** to **14** specifically, are not unreasonable on thermodynamic grounds. More specifically, cyclyne formation, but not [4]radialene formation, has the added advantage of relieving the approximately 12 kcal/mol strain energy of each methylenecyclopropane moiety in adduct **13**. No such relief of steric strain (of the methylenecyclopropane type) is of course possible in **19**, moreover cyclyne formation from **19** would place four *tert*-butyl groups on two adjacent saturated carbons, sterically clearly unfavorable. The possibility of two bulky adamantyl groups next to each other may also account for the lack of cyclyne formation and preferred polymerization in the case of the reaction of carbene **16** with cyclohexene.

$$t\text{-}Bu_2C{=}C{=}C{=}C{=}C{=}C\text{-}t\text{-}Bu_2 \xrightarrow{\Delta}$$

19



20

Unfortunately, neither the mode of formation nor the spectral data allow a clear distinction between the two possible cyclodimers,

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[15] No other viable products besides **14** were isolated or observed by TLC, besides some highly polar oligomers or polymers with strong IR absorption at 2150 cm^{-1}.

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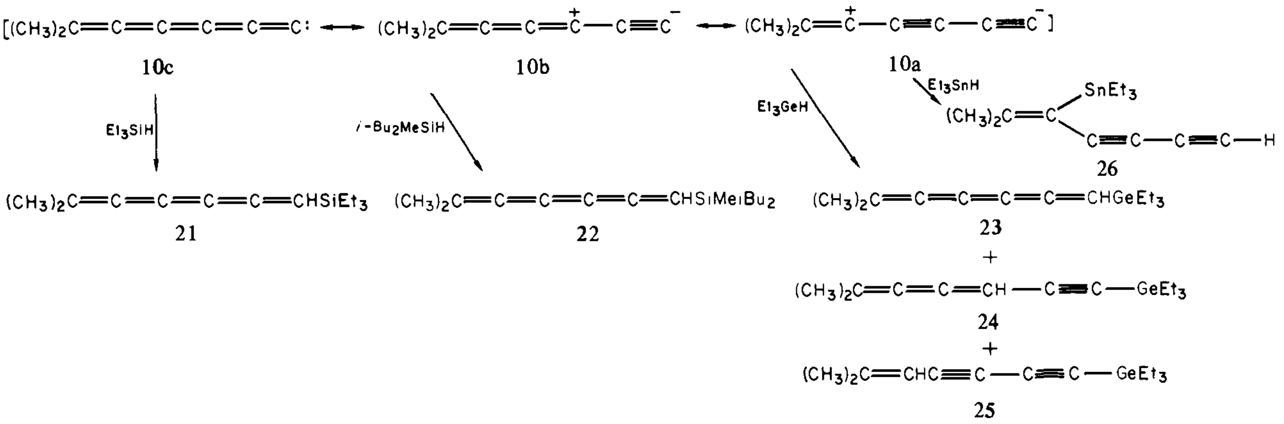
Scheme III



namely the head-to-head **14a** or head-to-tail adduct **14b**, although thermodynamic considerations[18,19] would suggest a preference for **14a**. This is in accord with the fact that *only* ten signals were observed in the ^{13}C NMR and that only a single sharp spot is seen on TCL strongly suggesting that only one of the two possible cyclodimers, specifically **14a**, is predominantly, if not exclusively, formed.

Nature of Alkatetraenylidenecarbenes. In general there are four major characteristics[3,4] of carbenes, including unsaturated carbenes, that are of interest: (a) its encumbrance (i.e., free carbene vs. carbenoid); (b) electrophilicity or nucleophilicity; (c) spin multiplicity; and (d) steric factors. Unfortunately, because of the extreme sensitivity of many of the cumulene adducts as well as the limited mode of generation it is very difficult, if not impossible, to obtain clear, reliable experimental data on these points. Nevertheless, we wish to address and comment on each of these points. Analogy to other unsaturated carbenes,[4,5] and specifically to alkylidenecarbenes[21] **2** generated by similar means via *t*-BuOK initiated elimination of CF_3SO_3H, suggests, but certainly does not prove, that alkatetraenylidenecarbenes **7** are likely to be unencumbered.

To date all unsaturated carbenes, including **4**, have been found to be electrophilic.[4,5] It may be reasonably argued that conjugation of the empty carbenic p orbital with the appropriate π bonds of the cumulene backbone should *decrease* the electrophilicity of these species with increasing conjugation. That is electrophilicity should *decrease* upon going from carbene **2** to **3** or **4** and again from **3** to **6** or **7**, with the major change presumably occurring between carbenes **2** and **3**. Because of the steric problems associated with the reaction[4,22] of carbene **2** (due to the coplanarity and close proximity of the β substituents and the reactive empty orbital) but not present in more extended unsaturated carbenes, it is difficult to determine the *exact* degree of electrophilicity of carbene **2**. More specifically, it is impossible to obtain a Moss[23] "carbenic selectivity index" for alkylidenecarbenes **2** and hence to make an accurate comparison between it and other unsaturated carbenes. Hence, although both carbenes **2** and **3** are known[4] to be electrophilic it is not possible to assess differences, if any, between them. Because of the instability of the adduct cumulenes it was not possible to obtain relative rates and hence the carbenic selectivity index[23] for alkatetraenylidenecarbenes **7**. Hence once again no real comparison is possible between the relative electrophilicities of **3** and **4** (m = 0.70–0.83 and m = 0.77, respectively)[5] and carbene **7**. However, it is unlikely that the additional conjugation in **7** compared to **3** or **4** should substantially diminish electrophilicity and therefore alkatetraenylidenecarbenes **7** are in all likelihood electrophilic.

No direct experimental data are available on the spin multiplicities of these novel extended carbenes. Theoretical calculations[24,25] indicate that unsaturated carbenes at least through alkadienylidenecarbenes **4** possess a singlet ground state with considerable (51 kcal/mol for **2** and 47 kcal/mol for **3**) singlet–triplet energy splitting. Trends that can be deduced from the ab initio calculations[25] and **2** and **3** indicate that increased conjugation favors the triplet state, whereas configuration interaction and d-orbital involvement favor the singlet state of extended unsaturated carbenes. Because of the opposing nature of these two trends it is difficult to make accurate extrapolations and predictions for the ground state of carbene **7** and species beyond. However, the large magnitude of the splitting energy in carbene **3** and the fact that configuration interaction and d-orbital involvement dominate[25] over conjugation effects would suggest a singlet ground state for alkatetraenylidenecarbene **7**. In light of the difficulty of obtaining good experimental data, reliable ab initio calculations on the singlet–triplet splitting energy of extended unsaturated carbenes **4**, **6**, **7**, and beyond, would be most welcome.

Finally, as all substituents are very far removed from the reactive carbenic carbon there should be no steric effects of any kind in the *initial* reaction of alkatetraenylidencarbene **7** or any species beyond **7** (i.e., **1**, $n > 5$). This is already the case for the shorter four-carbon species **4**.[5]

Chemistry of Alkatetraenylidenecarbenes. The reactions and chemistry of any carbene, including unsaturated carbenes, fall into three broad categories: (i) addition to π systems and concomitant formation of carbocycles (carbon–carbon π systems) or heterocycles (hetero-π systems); (ii) "insertion" reactions; and (iii) ylide formation and other miscellaneous reactions. In most cases addition to simple carbon π systems such as olefins is used to trap and hence establish the intermediacy as well as the nature of carbenes. From a synthetic and preparative point of view addition reactions are by and large more useful as they provide entry into certain cyclic systems otherwise not readily obtainable. In the case of alkylidenecarbenes **2** there is little doubt that addition reactions are far more important than insertions as they provide simple entry into a variety of small and strained ring systems,[26] whereas most potential insertion products are better made by other means. However, with more extended unsaturated carbenes **1** ($n > 2$) the reverse holds since many of the possible addition products, albeit interesting, are not likely to be stable. In contrast "insertion" products resulting in unknown, novel functionalized cumulenes, inaccessible by other means, may be isolated by this route. Hence we decided to examine the "insertion" of alkatetraenylidenecarbenes **10** and **16** into group

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Table I. Summary of Properties of Adducts 12, 14, and 17

compd	% yield^a	mass spectra m/z (rel intensity)	UV^b λ_{max}, nm (ϵ)	IR^c ν_{max}, cm^{-1}	^{1}H NMR^d δ (H's, mult)	^{13}C NMR,^{e} δ
12	41	186 (50.6; M^+), 171 (18.0; $M^+ - \mathrm{Me}$), 156 (29.4; $M^+ - 2\mathrm{Me}$), 141 (52.2; $M^+ - 3\mathrm{Me}$), 83 (100)	215.5 (42 300), 219 (41 300), 243 (5370), 256 (8470), 270.5 (11 100), 287 (8290)	3080 w (cyclopropyl-H), 2215 s, 2130 w (C≡C), 1603 m (C=C), 898 s (C=CH_2)	0.97 (1 H, s, cyclopropyl C–H), 1.18 (12 H, s, CH_3), 1.92 (3 H, m, C=C–CH_3), 5.40 (2 H, m, C=CH_2)	
14	31	368 (24.8; M^+), 353 (32.5; $M^+ - \mathrm{Me}$), 339 (17.5; $M^+ - C_2H_5$), 325 (37.5; $M^+ - C_3H_7$), 311 (24.2; $M^+ - C_4H_9$), 297 (59.4; $M^+ - C_5H_{11}$), 283 (60.2; $M^+ - C_6H_{13}$), 269 (80.6; $M^+ - C_7H_{15}$), 255 (100; $M^+ - C_8H_{17}$)	244 (2210), 257.5 (2190), 272.5 (1540)	3080 w (cyclopropyl-H), 2215 s, 2140 w (C≡C)	0.83 (4 H, m, cyclopropyl C–H), 1.26 (12 H, s, CH_3), 1.10–1.55 (8 H, m, cyclohexane C–H), 1.55–2.00 (8 H, m, cyclohexane C–H)	95.80 88.47 75.30 69.86 42.15 29.46 23.41 20.98 20.30 19.69
17	53	278 (31.4; M^+), 263 (13.4; $M^+ - \mathrm{Me}$), 254 (6.2; $M^+ - C_2$), 239 (6.7; $M^+ - C_2 - \mathrm{Me}$), 129 (100), 91 (20.8), 77 (13.4)	240 sh (54 500), 251.5, (185 000), 316 (18 200), 332.5 (29 400)	2010 s (cumulene), 1650 m (C=C)	1.26 (12 H, s, CH_3), 1.60–2.10 (12 H, m, adamantyl), 2.68 (2 H, br s, bridgehead CH)	

[a] All isolated yields. [b] 12 and 17 in hexane, 14 in EtOH. [c] 12 neat, 14 and 17 10% in CCl_4. [d] CCl_4, internal Me_4Si. [e] $CDCl_3$, proton decoupled.

Table II. Summary of Properties of Insertion Adducts

compd	% yield^a	mass spectra m/z (rel intensity)	UV^b λ_{max}, nm (ϵ)	IR^c ν_{max}, cm^{-1}	^{1}H NMR^d δ (H's, mult)
21	10	218 (18.4; M^+), 189 (54.2; $M^+ - \mathrm{Et}$), 161 (86.3; $M^+ - C_4H_9$), 133 (100; $M^+ - C_6H_{13}$)	226 (7300), 239 (5940), 251 (6900), 268 sh (8420), 300 (22 000), 318 (20 900), 368 (175), 398 (53)	2190 w, 2140 s, 2045 s (cumulene), 1615 m (C=C), 730 s [$Si(C_2H_5)_3$]	0.3–1.5 (15 H, m, Si–CH_2CH_3), 2.04 (6 H, s, C=C–CH_3), 5.27 (1 H, br s, C=C–H)
22	12	260 (11.2; M^+), 218 (4.6; $M^+ - C_3H_6$), 204 (27.7; $M^+ - C_4H_8$), 203 (13.9; $M^+ - C_4H_9$), 190 (11.2; $M^+ - C_5H_{10}$), 189 (59.9; $M^+ - C_5H_{11}$), 162 (28.3; $M^+ - C_7H_{14}$), 161 (22.7; $M^+ - C_7H_{15}$), 148 (44.5; $M^+ - C_8H_{16}$), 147 (100; $M^+ - C_8H_{17}$), 133 (57.6; $M^+ - C_9H_{19}$)	226 (3450), 240 (3690), 251 (4820), 267 sh (6400), 301 (18 930), 318 (18 560)	2190 w, 2140 s, 2045 s (cumulene), 1615 m (C=C), 795 s ($SiMeiBu_2$)	0.18 (3 H, s, Si–CH_3), 0.65 (4 H, d, $J = 7$ Hz, S–CH_2), 0.99 (12 H, d, $J = 7$ Hz, CH_3), 1.40 (2 H, m, CH), 2.01 (6 H, s, C=C–CH_3), 5.34 (1 H, br s, C=C–H)
23	1	240, 238, 236 (31.7, 22.8, 18.4; $M^+ - C_2$), 211, 209, 207 (88.5, 67.0, 51.9; $M^+ - C_2 - \mathrm{Et}$), 183, 181, 179 (42.9, 39.4, 27.5; $M^+ - C_2 - C_4H_9$), 155, 153, 151 (57.8, 74.3, 61.7; $M^+ - C_2 - C_6H_{13}$), 57 (100; $C_4H_9^+$)	220 (9500), 268.5 (27 000)	2045 s (cumulene), 1615 w (C=C), 1455 s, 1210 s, 1020 s, 705 s, [$Ge(C_2H_5)_3$]	0.75–1.40 (15 H, m, Ge–CH_2CH_3), 1.95 (6 H, s, C=C–CH_3), 5.57 (1 H, br s, C=C–H)
24	12.4	264, 262, 260 (16.1, 13.7, 9.9; M^+), 235, 233, 231 (92.0, 93.6, 71.2; $M^+ - \mathrm{Et}$), 207, 205, 203 (86.6, 66.6, 58.1; $M^+ - C_4H_9$), 179, 177, 175 (55.6, 57.5, 47.5; $M^+ - C_6H_{13}$), 240 (1.7; $M^+ - C_2$), 211 (5.2; $M^+ - C_2 - \mathrm{Et}$), 183 (7.7; $M^+ - C_2 - C_4H_9$), 155 (10.7; $M^+ - C_2 - C_6H_{13}$), 103 (97.5), 99 (100)	224 (6190), 236 (5950), 249.5 (7040), 267 sh (8380), 298 (23 610), 317 (23 970)	2185 m, 2130 s (C≡C), 2040 s (cumulene), 1610 m (C=C), 1455 s, 1205 m, 1020 s, 710 s [$Ge(C_2H_5)_3$]	0.75–1.40 (15 H, m, Ge–CH_2CH_3), 2.04 (6 H, d, $J = 1$ Hz, C=C–CH_3), 5.30 (1 H, d, $J = 1$ Hz, C=C–H)
25	18.6	264, 262, 260 (22.1, 16.5, 11.4; M^+), 235, 233, 231 (100, 72.8, 53.2; $M^+ - \mathrm{Et}$), 207, 205, 203 (54.5, 43.0, 31.5; $M^+ - C_4H_9$), 179, 177, 175 (47.2, 47.3, 36.8; $M^+ - C_6H_{13}$), 103 (11.8)	214 (39 260), 224 (52 600), 237 (5170), 249 (7320), 262.5 (14 150), 277.5 (19 500) 294 (15 030)	2190 s, 2095 m (C≡C), 1625 (C=C), 1455 s, 1200 m, 1030 s, 710 s [$Ge(C_2H_5)_3$]	0.75–1.40 (15 H, m, Ge–CH_2CH_3), 1.88 (3 H, s, C=C–CH_3), 1.97 (3 H, s, C=C–CH_3), 5.33 (1 H, br s, C=C–H)
26	10.6	310, 308, 306 (8.4, 6.9, 4.5; M^+), 281, 279, 277 (51.8, 41.8, 23.8; $M^+ - \mathrm{Et}$), 253, 251, 249 (2.5, 3.1, 2.6; $M^+ - C_4H_9$), 225, 223, 221 (24.7, 47.0, 34.5; $M^+ - C_6H_{13}$), 207, 205, 203 (11.9, 9.2, 7.3; Et_3Sn^+), 179, 177, 175 (35.6, 30.4, 20.0; Et_2SnH^+), 149, 147, 145 (81.0, 66.8, 47.8; $EtSn^+$), 105 (100), 91 (18.8)	212.5 sh (34 500), 216 sh (33 800), 224 sh (28 600), 252 (5720), 265 (8190), 280 (11 120), 296.5 (8230)	3308 s (C≡C–H), 2185 s (C≡C), 1090 m, 1020 m, 680 s [$Sn(C_2H_5)_3$]	0.80–1.40 (15 H, m, Sn–CH_2CH_3), 1.88 (3 H, s, C=C–CH_3), 2.10 (3 H, s, C=C–CH_3), 2.42 (1 H, s, C≡C–H)
27	25	286 (41.9; $M^+ - C_2$), 257 (100; $M^+ - C_2 - \mathrm{Et}$), 229 (34.6; $M^+ - C_2 - C_4H_9$), 201 (48.8; $M^+ - C_2 - C_6H_{13}$), 91 (13.5), 77 (8.4)	220 (3620), 275.5 (14 750)	2050 s (cumulene), 1615 m (C=C), 790 s, 735 s [$Si(C_2H_5)_3$]	0.30–1.40 (15 H, m, Si–CH_2CH_3), 2.01 (12 H, br s, adamantyl), 2.67 (2 H, br s, bridgehead CH), 5.41 (1 H, s, C=C–H)

28		196 (100; M^+), 167 (20.2; $M^+ - C_2H_5$), 153 (50.9; $M^+ - C_3H_7$), 139 (36.5; $M^+ - C_4H_9$), 102 (8.4), 91 (21.1)	219 (32 400), 235 (9000), 244 (9860), 257 (13 300), 271 (16 700), 286 (13 250)	3275 s (C≡C–H), 2195 s, 2115 w, (C≡C), 1617 s (C=C)	1.93 (12 H, br s, adamantyl), 2.29 (1 H, s, C≡C–H), 2.52 (1 H, br s, bridgehead CH), 3.21 (1 H, br s, bridgehead CH), 5.20 (1 H, s, C=C–H)
29	10.7	332, 330, 328 (25.8, 17.9, 13.7; $M^+ - C_2$), 303, 301, 299 (100, 72.7, 55.2; $M^+ - C_2 - Et$), 275, 273, 271 (5.8, 5.4, 3.8; $M^+ - C_2 - C_4H_9$), 247, 245, 243 (43.1, 35.8, 27.9; $M^+ - C_2 - C_6H_{13}$), 91 (9.6)	220 (9210), 227.5 (8830), 274.5 (22 640)	2180 w, 2040 s, (cumulene), 1615 m (C=C), 1445 s, 1215 m, 1020 m, 710 s [$Ge(C_2H_5)_3$]	0.55–1.40 (15 H, m, Ge–CH_2CH_3), 2.01 (12 H, br s, adamantyl), 2.69 (2 H, br s, bridgehead CH), 5.59 (1 H, s, C=C–H)
31	32.7	356, 354, 352 (24.4, 17.5, 12.9; M^+), 327, 325, 323 (100, 71.1, 54.7; $M^+ - Et$), 299, 297, 295 (35.3, 16.7, 11.0; $M^+ - C_4H_9$), 271, 269, 267 (15.0, 12.8, 9.5; $M^+ - C_6H_{13}$), 332, 330 (4.5, 8.2; $M^+ - C_2$), 303, 301 (27.4, 23.4; $M^+ - C_2 - Et$), 275, 273 (3.9, 5.6; $M^+ - C_2 - C_4H_9$), 247, 245, 243 (7.7, 8.1, 6.2; $M^+ - C_2 - C_6H_{13}$), 196 (44.9), 91 (18.2), 77 (13.2)	219 (51 000), 228 (65 600), 252 (9500), 265.5 (19 500), 280.5 (27 800), 297 (22 200)	2190 s, 2095 m (C≡C), 1620 s (C=C), 1445 s, 1200 m, 1030 s, 715 s [$Ge(C_2H_5)_3$]	0.60–1.40 (15 H, m, Ge–CH_2CH_3), 1.93 (12 H, br s, adamantyl), 2.51 (1 H, br s, bridgehead CH), 3.23 (1 H, br s, bridgehead CH), 5.22 (1 H, s, C=C–H)
32	16.2	402 (6.3; M^+), 373, 371 (19.4, 16.2; $M^+ - Et$), 345 (49.0; $M^+ - C_4H_9$), 315 (10.6; $M^+ - C_6H_{13}$), 378 (9.1; $M^+ - C_2$), 353, 351, 349, 347, 345 (19.4, 18.4, 100, 84.3, 49.0; $M^+ - C_2 - Et$), 293, 291, 289, 287 (24.8, 41.4, 30.4, 13.8; $M^+ - C_2 - C_6H_{13}$)	219 (26 200), 244 (18 500), 256 (17 600), 270.5 (11 500), 286 (8900)	3305 s (C≡C–H), 2180 s, 2075 m (C≡C), 1622 s (C=C), 1105 s, 1020 m, 680 s [$Sn(C_2H_5)_3$]	0.80–1.50 (15 H, m, Sn–CH_2CH_3), 1.91 (12 H, br s, adamantyl), 2.28 (1 H, s, C≡C–H). 2.50 (1 H, br s, bridgehead CH), 3.42 (1 H, br s, bridgehead CH)
33	16.6	310 (61.2; M^+), 281 (100; $M^+ - Et$), 253 (60.5; $M^+ - C_4H_9$), 225 (51.0; $M^+ - C_6H_{13}$)		2185 w, 2125 s (C≡C), 2040 s (cumulene), 1612 m (C=C), 745 s, 730 s [$Si(C_2H_5)_3$]	0.30–1.50 (15 H, m, Si–CH_2CH_3), 2.04 (12 H, br s, adamantyl), 2.60–3.00 (2 H, m, bridgehead CH), 5.31 (1 H, s, C=C–H)

[a] All isolated yields. [b] Hexane. [c] Neat, NaCl plates. [d] CCl_4, internal Me_4Si.

4 hydrides well precedented with carbenes in general[27] and recently with alkadienylidenecarbenes **4**.[1]

Reaction of carbene **10** with trialkylsilanes, germane, and stannane proceeded as shown in Scheme III, and reaction of carbene **16** is summarized in Scheme IV. Once again all products were identified by spectral means as summarized in Table II. All new compounds had good molecular ions and/or easily established fragmentation patterns in the mass spectrometer including proper isotope distributions for the germanium and tin adducts. Noteworthy is the ready loss of the m/z 24 C_2 fragment from most extended cumulenes (i.e., **17**, **23**, **27**, and **29**). All cumulenes are uniquely identified by the strong cumulenyl absorption in the infrared between 2010 and 2050 cm^{-1} as well as their UV absorptions, both very characteristic of hexapentaenes.[14,28] In contrast the isomeric conjugated enynes have strong C≡C absorptions between 2075 and 2195 cm^{-1} as well as UV absorption characteristic of such enynes.[10] The proton spectra are all consistent with the proposed structures. Unfortunately, due to the relative instability of these novel functionalized cumulenes few ^{13}C NMR spectra could be obtained. Specifically, due to the very long relaxation times of the quaternary carbons the compounds did not survive the overnight runs required as a consequence of long pulse delays and aquisition times. Nevertheless, there is little or no doubt about the identity and exact structure of all compounds in Table II.

Once again these results deserve comments. As seen, most isolated yields are rather low in the 1–33% range with the majority around 10–20%. This is clearly a function of the known[14,28] thermal instability, base and oxygen sensitivity,[29] etc. of all extended cumulenes and the consequent experimental difficulties in manipulations and handling of these compounds. Most of these reactions are accompanied by extensive polymerization and tar formation indicative and as a consequence of the sensitivity of the initial molecules formed.

It is evident from the data that alkatetraenylidenecarbenes **10** and **16** readily insert into silanes as well as germanes to give the corresponding cumulenyl silanes and germanes (Schemes III and IV). However, the two products **26** and **32** resulting by trapping with Et_3SnH are anomalous. Although we do not fully understand this anomalous behavior of tin hydride it may be a consequence of the relatively low pK_A of 24 for R_3SnH compared to the pK_A of >34 for R_3SiH and R_3GeH,[30] as well as the weaker bond dissociation energy for Me_3MH with Sn = 74 kcal/mol, with Ge = 82 kcal/mol, and with Si = 90 kcal/mol.[31] Products **26** and **32** may also be a consequence of some radical process well precedented with tin.[32] In contrast to the anomalous behavior of carbene **7** toward tin, the shorter homologue **4** gave the normal "insertion" products of cumulenylstannanes.[1,33]

In conclusion we have developed a simple, general means of alkatetraenylidenecarbene generation via base-initiated elimination of butadiynylvinyl triflates. Trapping with olefins results in the corresponding cumulenes or cumulene-derived products. Because of the considerable instability of such extended cumulenes it is presently impossible to obtain reliable direct experimental data on the exact nature of these carbenes. However, indirect data and analogy to the shorter homologous unsaturated carbenes indicate an unencumbered, singlet, electrophilic species with no steric problems. These carbenes readily undergo "insertion" into silanes and germanes to give novel Si– and Ge– functionalized

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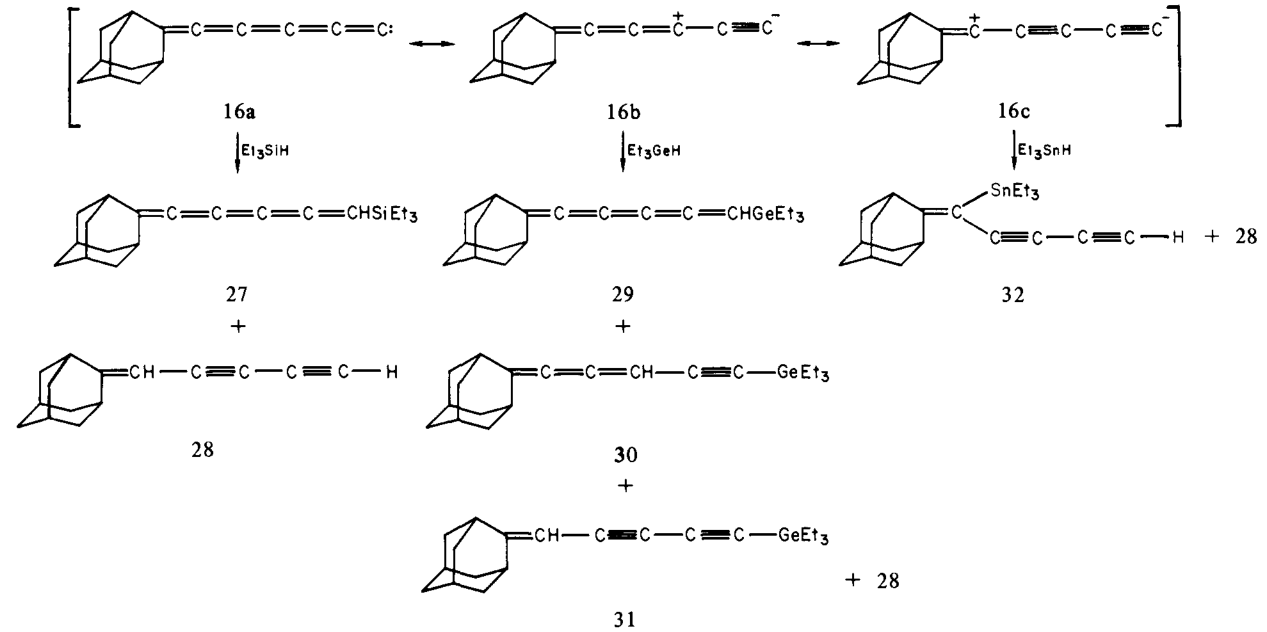
[33] It is however possible that some "normal" cumulenyl stannane indeed formed but did not survive the reaction conditions and hence could not be isolated or detected.

Scheme IV



hexapentaenes, albeit in low isolated yields. Although the present method of generating extended unsaturated carbenes is in *principle* applicable to *all* such carbenes **1** with even numbers of carbons it is likely that experimental difficulties due to the instability of extended cumulenes precludes formation of higher homologues beyond **7** (**1**, $n = 4$) or at best the next two even-membered intermediates (i.e., **1**, $n = 6$ or 8).

Experimental Section

General. Infrared spectra were recorded on a Beckmann Acculab 3 or Perkin-Elmer 298 spectrometer. Ultraviolet spectra were recorded on a Cary 14 UV–visible spectrophotometer. ^{1}H NMR spectra were recorded on a Varian EM-360 or EM-390 spectrometer and ^{13}C NMR spectra on a FT-80 spectrometer. Mass spectra were recorded on a Varian MAT 112 GC–mass spectrometer. All reactions, transfers, and manipulations were carried out under argon.

Materials. All commercial reagents were ACS reagent grade. Solvents were purified and vigorously dried immediately prior to use. Triethylsilane was purchased from Petrarch and tetramethylethylene from Chemical Samples and distilled prior to use. Triethylgermane, triethylstannane, and i-Bu$_2$MeSiH were prepared as previously reported,[1] as was starting vinyl triflate **8**.[8]

Vinyl Triflate 15. Following our literature procedure[8] this triflate was prepared from 11 mmol of the corresponding trimethylsilylvinyl triflate in 80.4% yield: mass spectrum 344 (M$^+$, 14.5%), 211 (13.5%), 183 (22.5%), 91 (24.4%), 77 (100%); IR (neat, NaCl) 3275 (C≡CH), 2200 (C≡C), 1630 (C=C), 1420, 1215, 1145 cm^{-1} (OSO$_2$CF$_3$); NMR (CCl$_4$, internal Me$_4$Si) δ 1.85–2.15 (12 H, br s, adamantyl), 2.22 (1 H, br s, bridgehead CH), 2.61 (1 H, s, C≡CH), 3.07 (1 H, br s, bridgehead CH). The precursor trimethylsilylvinyl triflate was prepared[8] from 56.7 mmol of the corresponding ketone in 58.3% yield: mass spectrum 416 (M$^+$, 90.6%), 255 (93.9%), 149 (20.1%), 73 (100%); IR (neat, NaCl) 2190 and 2090 (C≡C), 1633 (C=C), 1420, 1212, 1143 (OSO$_2$CF$_3$), 1253, 850 cm^{-1} (SiMe$_3$); NMR (CCl$_4$, internal Me$_4$Si) δ 0.23 (9 H, s, SiMe), 1.80–2.20 (12 H, m, adamantyl), 2.95–3.25 (2 H, m, bridgehead CH). The necessary (2-adamantyl)—C(=O)C≡C—C≡CSiMe$_3$ was prepared on a 75.5 mmol scale in 75.1% yield as previously described:[8] mass spectrum 284 (M$^+$, 3.3%), 269 (5.1%), 223 (100%); IR (neat, NaCl) 2195 and 2090 (C≡C), 1665 (C=C), 1251 and 850 cm^{-1} (SiMe$_3$); NMR (CCl$_4$, internal Me$_4$Si) δ 0.25 (9 H, s, SiMe), 1.60–2.05 (13 H, m, adamantyl), 2.15 (1 H, br s, bridgehead CH), 2.52 (1 H, br s, bridgehead CH).

General Procedure for the Generation, Trapping, and Reaction of Alkatetraenylidenecarbenes. Interaction of Vinyl Triflate 8 with Et$_3$SiH, Formation of 21. Into a 1000-mL three-neck round-bottom flask fitted with an addition funnel, magnetic stirring bar, and an argon inlet and outlet were added 1.2 g (4.76 mmol) of triflate **8**, 8.35 g (71.9 mmol) of Et$_3$SiH, and 500 mL of glyme containing 0.12% w/v of t-BuNO (as a radical trap). The solution was cooled to −20 °C and purged with argon. A solution of 668 mg (5.95 mmol) of freshly sublimed t-BuOK in 100 mL of glyme was added dropwise over a 2-h period, then the entire mixture was warmed to room temperature and stirred under argon overnight. To the darkened reaction mixture were added a few crystals of NH$_4$Cl to neutralize any excess base and the solvent and excess trap were removed on a Buchi rotary evaportator. The residue was extracted with four 50-mL portions of argon-flushed pentane and the pentane solution was quickly filtered and concentrated. The concentrated pentane solution was chromatographed on silica gel, using argon-flushed pentane as eluent. The leading pale yellow fraction was collected and the pentane evaporated in vacuo yielding 103 mg (10%) of cumulene **21** as a pale yellow oil. Besides cumulene **21** starting triflate **8** was recovered in about 25% yield. Cumulene **21** as well as **17** and all products of Schemes III and IV are very oxygen sensitive and rather unstable. They may be handled *neat* at room temperature for several minutes subsequently polimerizing. They are stable in pentane solution at −20 °C for several days. All spectral properties are summarized in Tables I and II. For **21**: ^{13}C NMR (CDCl$_3$, proton decoupled, rel. Me$_4$Si) δ 4.33, 7.26 (SiCH$_2$CH$_3$), 24.45, 24.59 (CH$_3$), 81.81, 94.57, 103.66, 122.01, 150.35, 166.04 (cumulenic C's).

Reaction of 8 with TME. Reaction of 2.38 mmol of triflate **8** with 4.76 mmol of t-BuOK and 35.7 mmol of TME in 370 mL of glyme over a 5-day period at 0 °C gave 181 mg (41%) of isomerized adduct **12**.[34]

Reaction of 8 with Cyclohexene. Reaction of 2.38 mmol of triflate **8** with 3.22 mmol of t-BuOK and 35.7 mmol of cyclohexene in 370 mL of glyme gave 136 mg (31%) of white crystalline **14**: mp 143–144 °C dec.

Reaction of 8 with i-Bu$_2$MeSiH. Reaction of 2.38 mmol of triflate **8** with 2.97 mmol of t-BuOK and 40 mmol of i-Bu$_2$MeSiH in 300 mL of glyme gave 74 mg (12%) of **22** as a yellow oil.

Reaction of 8 with Et$_3$GeH. Interaction of 2.38 mmol of triflate **8** with 2.97 mmol of t-BuOK and 9.95 mmol of Et$_3$GeH in 300 mL of glyme gave 6.0 mg (1%) of **23**, 77.5 mg (12.4%) of **24**, and 116 mg (18.6%) of **25** all as yellow oils. For **25**: ^{13}C NMR (C$_6$D$_6$, proton decoupled, rel. Me$_4$Si) δ 5.7, 8.9 (GeCH$_2$CH$_3$), 21.1, 24.3 (2 CH$_3$), 64.4, 73.5, 81.0, 90.0 (C≡C), 104.6, 119.9 (C=C).

Reaction of 8 with Et$_3$SnH. Reaction of 2.38 mmol of triflate **8** with 2.97 mmol of t-BuOK and 10.1 mmol of Et$_3$SnH in 300 mL of glyme gave 78 mg (10.6%) of **26** as a yellow oil.

Reaction of Vinyl Triflate 15 with TME. In general all reactions with triflate **15** were carried out on a smaller scale and at −78 °C with addition of t-BuOK over a 10-min period followed by workup after 10 min of stirring at −78 °C. The much greater reactivity of vinyl triflate **15** compared to **8** is not understood. Moreover in *all* reactions of this triflate with group 4 hydrides varying amounts of hydrocarbon **28** were formed. It is obvious that this is a reduction product but its origin is not at all clear; it was not observed in reactions of **15** with olefins. Reaction of 1.29 mmol of **15** with 1.61 mmol of t-BuOK and 19.5 mmol of TME in 200 mL of glyme gave 270 mg (75%) of nearly pure **17**. Rechromatography gave 190 mg (53%) of pure **17** as yellow crystals.

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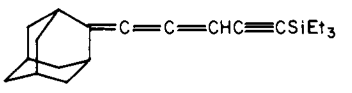
(34) Possible direct evidence for adduct 11 comes from the observation of a small close second spot on the TLC of product 12 and an additional band at 2050 cm^{-1} in the IR strongly characteristic of such cumulenes.[14,28]

Reaction of 15 with Cyclohexene. Reaction of 1.29 mmol of triflate **15** with 1.61 mmol of *t*-BuOK and 19.5 mmol of cyclohexene in 200 mL of glyme gave only polymeric material with no cumulenic, allenic, or acetylenic absorption in the infrared.

Reaction of 15 with Et_3SiH. Reaction of 1.29 mmol of triflate **15** with 1.61 mmol of *t*-BuOK and 19.5 mmol of Et_3SiH in 200 mL of glyme gave 100 mg (25%) of **27** and 86 mg (34%) of **28**. Hydrocarbon **28** was present in all cases after the extended cumulene fraction of the chromatography prior to the elution of the other adducts, except in the case of **32** were there was significant coelution. Similar reaction of 0.29 mmol of triflate **15** with 0.36 mmol of *t*-BuOK and 29 mmol (100-fold excess) of Et_3SiH in 40 mL of glyme gave 15 mg (16.6%) of adduct **33**; no cumulene **27** was observed in this reaction. For **33**: ^{13}C NMR ($CDCl_3$, proton decoupled, rel. Me_4Si) δ 97.4, 139.3, 149.9, 173.1 (C=C=C=C). The difference in behavior between a large and a moderate excess (100 vs. 14) of silane is not understood. On the other hand with less than a tenfold excess of silane a significantly lower yield of product was observed.



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Reaction of 15 with Et_3GeH. Reaction of 1.81 mmol of triflate **15** with 2.26 mmol of *t*-BuOK and 9.95 mmol of Et_3GeH in 250 mL of glyme gave 69 mg (10.7%) of **29**, 3 mg (0.5%) of **30**, and 210 mg (32.7%) of **31** as yellow oils and 49 mg (13.8%) of **28**. Because of the small amount and sensitivity it proved to be impossible to fully isolate, purify, and spectrally characterize **30**.

Reaction of 15 with Et_3SnH. Reaction of 1.81 mmol of **15** with 2.26 mmol of *t*-BuOK and 10.1 mmol of Et_3SnH in 250 mL of glyme gave 117.5 mg (16.2%) of **32** as a yellow oil and 62.6 mg (17.6%) of **28**.

Attempted *t*-BuOK Catalyzed Isomerization of Cumulene 29. A solution of 0.17 mmol of *t*-BuOK in 5 mL of glyme was added over a 2-min period under argon to a solution of 0.085 mmol of cumulene **29** and *t*-BuNO in 10 mL of glyme at −78 °C. After 5 min of stirring at −78 °C the mixture was warmed to −50 °C then worked up by the standard procedure. TLC as well as spectroscopy indicated only recovered **29** with no isomerization to **30** or **31**. Hence this result, together with the fact that excess base was used in all reactions, indicate that the enyne and enediyne products observed (i.e., **24**, **25**, **30**, and **31**) are primary products and not the result of base-catalyzed isomerization.

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Carbon Acidity. 58. Hydrogen Isotope Exchange Kinetics of Propylene with Lithium Cyclohexylamide

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Abstract: Rates for hydrogen isotope exchange with lithium cyclohexylamide (LiCHA) in cyclohexylamine-*N,N*-d_2 (CHA-d_2) and cyclohexylamine (CHA) are compared for propene and toluene. Benzyl hydrogens in toluene were found to be 6.2 times more reactive than allyl hydrogens in propene. Experimental primary isotope effects are also reported for propene: k^D(exptl)/k^T(exptl) = 2.9, k^H(exptl)/k^T(exptl) = 30, and k^H(exptl)/k^D(exptl) = 10.2. Derived internal return values show comparable values for propene and toluene. Analysis of polydeuteration rates shows that exchange is accompanied by complete equilibration of allyl positions. The high isotope effects and comparable acidities and internal return imply a transition state for propene which resembles that of toluene. An equilibrium pK_a on the CsCHA scale of ∼43 is deduced for propene.

Studies of the stability of allylic anions, the simplest of all π-conjugated species, have become more numerous in recent years.[1,2] Allylic anions appear frequently as intermediates in base-catalyzed proton-exchange and olefin isomerization reactions in larger systems;[1,3] however, there are few studies involving the parent allyl anion derived from propene undoubtedly because propene is a gas at normal temperatures. Proton transfer involving propene has been reported in the gas phase by the flowing afterglow technique[4] and by ion-cyclitron resonance.[5] These measurements provide estimates of the stability of allyl anion relative to other anions and also estimates of the relative pK_a's of propene, toluene, and a number of other hydrocarbons in the gas phase; the proton affinity of allyl anion is about kcal mol^{-1} greater than benzyl anion.[6] In solution phase, deuterium exchange of propene in dimethyl sulfoxide-d_6 catalyzed by potassium *tert*-butoxide has been used to establish unequivocally the intermediacy of the π-allyl anion.[7]

We recently reported an investigation of hydrocarbon acidities in which allylic anions were generated from a series of cycloalkenes.[1] In this paper, we now turn our attention to the parent hydrocarbon, propene. We have again approached this problem by measuring hydrogen isotope exchange of allylic hydrogens in propene in the lithium cyclohexylamide (LiCHA)–cyclohexylamine (CHA) system. This study provides the first reliable estimate of the solution ion pair pK_a of propene since the kinetic properties are found to show important similarities to toluene.

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