Regioselective Coupling of Ethynylcyclopropane Units: Hexaspiro[2.0.2.4.2.0.2.4.2.0.2.4]triaconta-7,9,17,19,27,29-hexayne[1]

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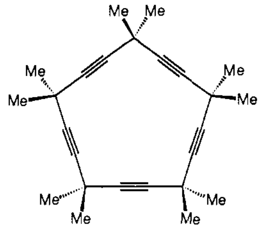
Abstract: Regioselective synthetic methods are reported for the head to head, head to tail, and tail to tail coupling of ethynylcyclopropanes. Oxidative cyclization of the head to head dimer $5\text{-}H_2$ under high dilution conditions gave the title compound, an 18-membered macrocycle comprising six acetylenic units and six spirocyclopropanes that alternate pairwise around the ring. An X-ray crystal structure and spectroscopic properties of this novel macrocycle are reported.

Cyclic polyacetylenes continue to attract considerable interest from both a theoretical and a synthetic viewpoint.[2,3] Our own well-documented research efforts in this area aim at the synthesis of new classes of such compounds that will provide detailed insights into general bonding phenomena and reaction behavior, such as electronic interactions between triple bonds and transition-metal complexation, respectively.

Recently we have reported the first members of a novel family of compounds, the "[*N*]pericyclynes," of which decamethyl[5]pericyclyne (**1**) provides compelling evidence for cyclic homoconjugation and homoaromaticity in neutral hydrocarbons.[4,5] These results prompted us to extend our studies to molecules related to **1** in which the *gem*-dimethyl groups are replaced by spirocyclopropane units. In view of the unusual bonding properties of the three-membered ring, with its high-energy HOMOs (Walsh e_A and e_S orbitals),[6-8] the cyclic electronic interaction among the homoconjugated acetylene units in **1** should be significantly enhanced by the presence of interspersed spirocyclopropyl groups, as in pentaspirocyclopropane[5]pericyclyne (**2**).[9]



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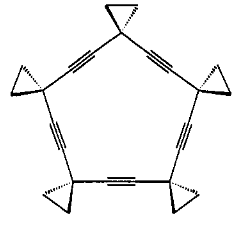

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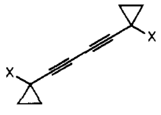
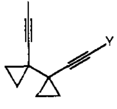
In order to gain access to various types of such cyclic polyacetylenes, we have developed methodology for all three possible regioselective couplings of two ethynylcyclopropane units **3**-X(Y) to the corresponding dehydro dimers **4**-X_2, **5**-Y_2, and **6**-X(Y).[10] A variety of difunctional cyclopropylacetylenes **3**-X(Y), versatile five-carbon building blocks, is readily available in multigram quantities by well-established literature procedures.[11,12]

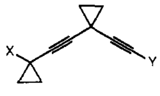
3-X(Y)



4-X₂



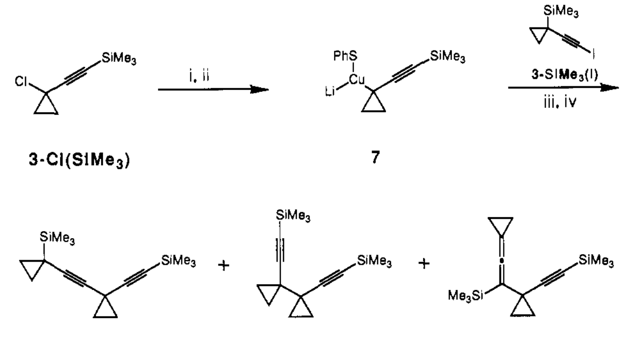
5-Y₂



6-X(Y)

X = H, Cl, I, SiMe₃; Y = H, I, SiMe₃

Scheme I[a]



[a] Key: (i) *n*-BuLi, C_6H_{14}/Et_2O, −78 to −10 °C, 1 h; (ii) PhSCu, THF, −30 °C, inverse addition, then −20 °C, 20 min; (iii) 3-$SiMe_3$(I), THF, −78 to −55 °C; (iv) MeOH.

The tail to tail coupling of terminal acetylenes under oxidative conditions is straightforward[13] and, when applied to monomer **3**-H_2, gives the conjugated diyne **4**-H_2 in 57% yield.

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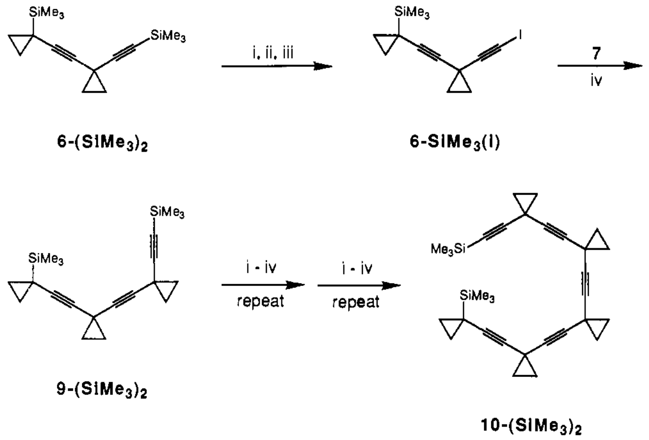
Scheme II[a]



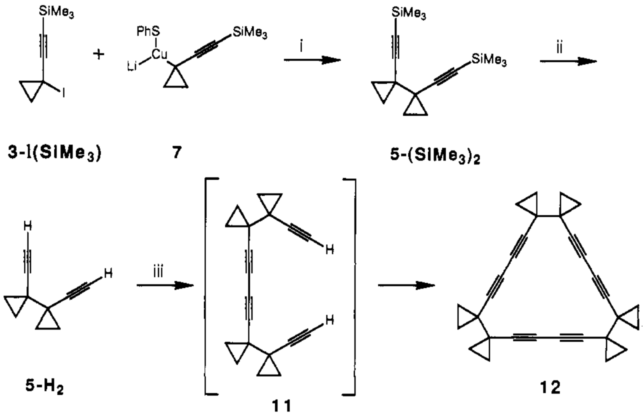
[a] Key: (i) KOH, MeOH, 25 °C, 14 h; (ii) MeLi, Et_2O, −78 °C; (iii) I_2, −78 °C; (iv) 7, THF/Et_2O/C_6H_{14}.

A reasonably selective head to tail coupling of two units of **3**-X(Y) was best achieved by treating 1-(iodoethynyl)-1-(trimethylsilyl)cyclopropane (**3**-SiMe$_3$(I)) with the 1-[(trimethylsilyl)ethynyl]cyclopropyl heterocuprate **7**[14] prepared from **3**-Cl(SiMe$_3$) by lithiation with butyllithium and conversion with (phenylthio)copper, following a procedure analogous to those of Posner[15] and Piers.[16] The three dimers **6**-(SiMe$_3$)$_2$, **5**-(SiMe$_3$)$_2$, and **8** were thus produced in a ratio of 10:2:3, the head to tail dimer **6**-(SiMe$_3$)$_2$ being obtained in yields of up to 45% after chromatographic separation (Scheme I). While **5**-(SiMe$_3$)$_2$ apparently arises by dimerization of the thermally labile cuprate **7**, the allene **8** can only have been formed after propargylic rearrangement of **7**[17] or via transmetalation between **7** (or its lithio precursor) and **3**-SiMe$_3$(I), which may have led to some **3**-I(SiMe$_3$).

Dimer **6**(SiMe$_3$)$_2$ can be transformed to the iodoacetylene **6**-SiMe$_3$(I) by protiodesilylation with potassium hydroxide in methanol, deprotonation with methyllithium, and iodination with elemental iodine in nearly quantitative yield (97%). Repetition of the coupling procedure with cuprate **7** provided trimer **9**-(SiMe$_3$)$_2$, and two more iterations of this sequence eventually lead to pentamer **10**-(SiMe$_3$)$_2$ in an overall yield of about 5% (Scheme II). After flash chromatography and subsequent crystallization from methanol at −30 °C, **10**-(SiMe$_3$)$_2$ was obtained as white crystals; mp 215 °C.[18]

An attempted cyclization of pentamer **10**-(SiMe$_3$)$_2$ was hampered by poor yields in its four-step transformation to **10**-I(H) (bis(protiodesilylation), terminal silyl protection, propargylic deprotonation, iodination) and nonoptimized conditions in the Pd(0)-catalyzed intramolecular coupling, although model studies performed on 1-iodo-1-[(trimethylsilyl)ethynyl]cyclopropane (**3**-I(SiMe$_3$)) and 1-ethynyl-1-(trimethylsilyl)cyclopropane (**3**-SiMe$_3$(H)) under the Jeffery conditions (Pd(OAc)$_2$, K_2CO_3, Bu_4NBr, DMF)[19] for a Heck coupling[20] gave the dimer **6**-(SiMe$_3$)$_2$ in reasonable yield.

Scheme III[a]



[a] Key: (i) THF/C_6H_{14}/Et_2O, − 75 °C, 1.5 h; (ii) KOH, MeOH, 25 °C, 14 h; (iii) CuCl, $CuCl_2$, pyridine, 0 °C, slow inverse addition over 3 days, then stir at 0 °C for 9 days.

The head to head dimer **5**-(SiMe$_3$)$_2$, first obtained as a by-product in the head to tail coupling of heterocuprate **7** with iodoacetylene **3**-SiMe$_3$(I), can be prepared more efficiently (77% yield) by directed alkylation of **7** with 1-iodo-1-[(trimethylsilyl)ethynyl]cyclopropane (**3**-I(SiMe$_3$)).[21] This is quite remarkable for a tertiary–tertiary coupling reaction in which two quaternary centers are formed.[22] Protiodesilylation with potassium hydroxide in methanol and trap to trap distillation gave pure 1,1′-diethynylbicyclopropyl (**5**-H_2 (83% yield, Scheme III)).[18]

An attempted cyclooligomerization of **5**-H_2 under high dilution conditions according to the Eglinton recipe (cupric acetate in pyridine at 50 °C[23,24]) gave only high molecular weight products, which were not characterized. On the other hand, slow addition of **5**-H_2 in pyridine to a large excess of cuprous chloride and cupric chloride in pyridine at 0 °C, followed by stirring at 0 °C for 12 days, according to the protocol of Breslow et al.,[25] afforded the title compound cyclotrimer **12** in 8.5% yield after chromatography.[26] The slightly contaminated product was finally recrystallized from acid-free methylene chloride at −30 °C to give pure crystals of **12** (2%).[27] When stored at room temperature in the absence of CH_2Cl_2 mother liquor, the clear crystals of **12** turned opaque. The ^{1}H NMR spectrum of **12** in C_6D_6 showed a typical AA′–BB′ pattern with two multiplets centered at δ 0.10 and 0.58.

In line with previous experience on cyclic arrays of conjugated multiple bonds and *bicyclopropyl* units,[28] the UV spectrum of **12** does not manifest any sign of cyclic conjugation. The longest wavelength absorption (λ_{max} = 267.5 nm, log ϵ = 3.46) is virtually identical with that of 1,4-dicyclopropylbuta-1,3-diyne (λ_{max} = 268 nm, log ϵ = 3.00), the subunit in **12**, except for a 3-fold increase in the molar extinction coefficient. Thus, the bicyclopropyl units in **12** completely block electronic transmission from one diyne unit to the next.

X-ray diffraction structure analysis revealed that the crystals of **12** trapped two molecules of methylene chloride per molecule of **12**. The fact that these CH_2Cl_2 molecules sit exactly on the C_3 axis of the hydrocarbon above and below the equatorial plane

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(14) This type of heterocuprate was selected because other *sec*- and *tert*-alkyl cuprates are thermally less stable. Cf. ref 15.

(15) Cf. Posner, G. H.; Whitten, C. E.; Sterling, J. J. *J. Am. Chem. Soc.* **1973**, *95*, 7788–7800.

(16) Cf. Piers, E.; Banville, J.; Lau, C. K.; Nakagura, I. *Can. J. Chem.* **1982**, *60*, 2965–2975.

(17) Cf. Jäger, V. In *Methoden der Organischen Chemie*; Houben-Weyl, 4th ed.; Müller, R., Ed.; Thieme: Stuttgart, 1977; Vol. V/2a, pp 282 ff. Klein, J. In *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; Wiley-Interscience: New York, 1978; Vol. 1, pp 343 ff.

(18) All new products and important intermediates were fully characterized by ^{1}H NMR, ^{13}C NMR, IR, MS, and elemental analyses.

(19) Jeffery, T. *Tetrahedron Lett.* **1985**, *26*, 2667. The original report by Jeffery calls for Bu_4NCl, but we have successfully used Bu_4NBr in a variety of applications. Cf. Reiser, O.; Reichow, S.; de Meijere, A. *Angew. Chem.* **1987**, *99*, 1285–1286; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1277–1278; Reiser, O.; Weber, M.; de Meijere, A. *Angew. Chem.* **1989**, *101*, 1071–1072; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1037–1038; Lansky, A.; Reiser, O.; de Meijere, A. *Synlett* **1990**, 405–407.

(20) Cf. Heck, R. F. *Org. React.* (*N.Y.*) **1982**, *27*, 345.

(21) Cyclopropyl to cyclopropyl coupling reactions via cyclopropyllithium derivatives have previously been reported. Cf. Slabey, V. A. *J. Am. Chem. Soc.* **1952**, *74*, 4928–4930; Merkel, B.; Köbrich, G. *Chem. Ber.* **1973**, *106*, 2025–2039; *Ibid.* **1973**, *106*, 2040–2048.

(22) Even the coupling of lithium (phenylthio)(*tert*-butyl)cuprate with a *sec*-alkyl halide does not proceed well. Cf. ref 15.

(23) Eglinton, G.; Glabraith, A. R. *Chem. Ind.* **1956**, 737–738.

(24) Cf. also Miller, S. P.; Whitlock, H. W., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 1492–1494.

(25) O'Krongly, D.; Denmeade, S. R.; Chiang, M. Y.; Breslow, R. *J. Am. Chem. Soc.* **1985**, *107*, 5544–5545.

(26) After 40 h, the open-chain dimer **11** was detectable by GC/MS, but it was no longer present during the latter course of the reaction.

(27) The high-resolution mass spectrum of **12** showed for $C_{30}H_{24}$, M^+ calcd 384.1878, found, 384.1876.

(28) de Meijere, A. *Chem. Ber.* **1974**, *107*, 1684–1701.

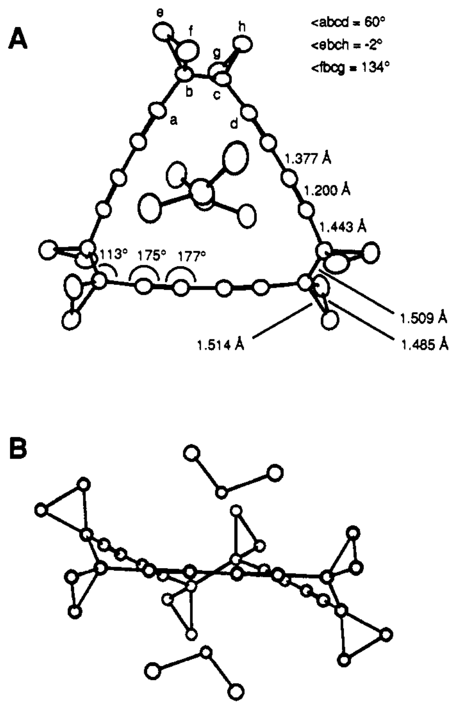

Figure 1. ORTEP plot and structural parameters of **12**: A, top view; B, side view. The X-ray diffraction data were collected at -100 °C to avoid crystal efflorescence due to loss of methylene chloride. The monoclinic crystal had space group $C2/c$ (no. 15), $Z = 4$, $a = 1738$ (8), $b = 1195$ (5), $c = 1417$ (6) pm, $\beta = 102.7$ (2)°, and $V = 2871 \times 10^6$ pm^3. A total of 2515 reflections were refined to a final $R_w = 0.044$.

is remarkable. Whether or not this is due to a special sort of molecular recognition is yet unknown.[29] The symmetry of **12** is D_3, but the overall symmetry of the solvate is lowered as the CH_2Cl_2 molecules are staggered along the C_3 axis (Figure 1). The solvent molecules form a zigzag layer between layers of the cyclic hexayne (Figure 2).

The puckering of the 18-membered ring in **12**, with dihedral angles of 60° in each of the three bicyclopropyl units, is the same as that in [6]rotane[30] with three buta-1,3-diyne units inserted into every other bond. As expected, the inversion barrier of **12** is much lower than that of [6]rotane.[31a] In the ^{1}H NMR spectrum of **12**, no temperature effect due to slowing down of its rapid inversions could be seen down to -80 °C.[31b]

The bond lengths in the cyclopropane rings of **12** alternate significantly (148.5 pm average for the distal and 151.4 pm for the proximal bonds). This is in accord with theoretical predictions[32] for acceptor substituted cyclopropane derivatives, as well as with X-ray[33] and microwave spectroscopic structure analyses[34,35] on such compounds. While the C–C bond length in cyclopropane is 151.0 pm,[33] the distal and proximal cyclopropyl C–C bonds in cyclopropylacetylene (and in cyclopropylcyanide) are 150.3 (150.0) and 152.7 (152.9) pm, respectively. The 1,3-diyne groups in **12** are only slightly bent and deviate from linearity by 2 to 5°.

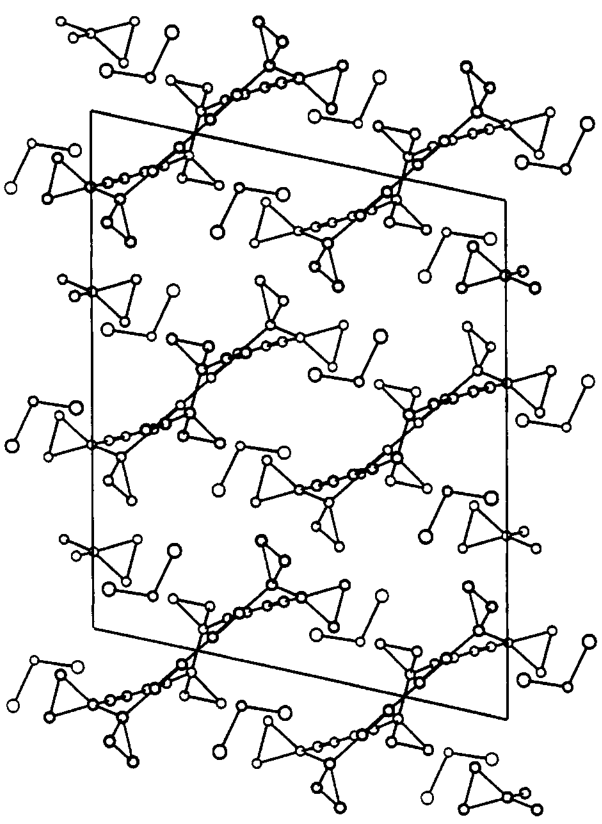

Figure 2. Packing arrangement of **12** and CH_2Cl_2 in the crystal lattice.

We are continuing our efforts to prepare cyclic polyacetylenes with only *one* spirocyclopropyl unit between adjacent π systems, e.g., **2**.

Experimental Section

General Remarks. ^{1}H NMR: IBM AF 80 (80 MHz), Bruker WP 80 (80 MHz), WH 270 (270 MHz), WM 400 (400 MHz), Nicolet NT-500 (500 MHz); δ 0 for tetramethylsilane, 7.15 for [d$_5$]benzene, 7.26 for chloroform, 5.35 for [d$_1$]methylene chloride; characterization of signals, s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, mc = centrosymmetric multiplet. ^{13}C NMR: IBM AF 80 (20.15 MHz), Bruker WP 80 (20.15 MHz), WH 270 (67.92 MHz), WM 400 (100.62 MHz); δ 0 for tetramethylsilane, 128.0 for [d$_6$]benzene, 77.0 for deuteriochloroform, 53.0 for [d$_2$]methylene chloride; assignment generally based on spectra obtained with the DEPT (distortionless enhancement by polarization transfer) technique, for DEPT spectra positive and negative phases designated as + and –, respectively, missing DEPT signal designated by the ϕ symbol. IR: Perkin-Elmer 125, 297, 399, 599. UV: Perkin-Elmer 552 and Varian Cary 219. MS: Varian MAT CH7 with Varian Aerograph 1740 and Varian MAT 112 with Varian Aerograph 1400 (GC–MS coupling; GC with 25-m quartz capillary Oribond SE 54; carrier gas, helium), Finnigan 4023 (GC–MS coupling; GC with 30-m "wide bore" capillary column Supelco SPB-1), VG ZAB-HS with Hewlett-Packard 5790A (GC–MS coupling; GC with 30 m "wide bore" capillary column DB 1), Varian MAT 311 A (high resolution) and VG 70-2509 (high resolution). GC analytical: Siemens L 402 (carrier gas, nitrogen; column A, 6 ft × $^1/_8$ in. V2A-steel, 3% SE 54 Chromosorb A-AW-DMCS, 80–100 mesh), Varian Aerograph 1400 (carrier gas, nitrogen), Siemens Sichromat 3 (carrier gas, hydrogen). GC preparative: Varian Aerograph 920 (carrier gas, hydrogen), Hewlett-Packard 5710 (carrier gas, helium), Carlo Erba FTV 2350 (carrier gas, hydrogen). Column chromatography: Kieselgel 60 (70–230 mesh, E. Merck, Darmstadt). Flash chromatography: column pressured with an aquarium aerator Elite 801 (~1.4 bar) or nitrogen from a pressure tank; silica gel, "chromatography medium" 60, 20–45 μm (Amicon). Thin-layer chromatography: Kieselgel 60 F$_{254}$ on aluminum foil (E. Merck, Darmstadt). Mp: melting point apparatus of Wagner & Munz; mp's uncorrected. Elemental analyses: Mikroanalytisches Laboratorium Beller, Göttingen, FRG, and Spang Microanalytical Laboratories, Eagle Harbor, MI, U.S.A. Anhydrous solvents were prepared following the

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(29) Coordination of CH_2Cl_2 albeit to metal cations via the chlorine lone pairs has recently been observed. Cf. Newsbound, T. D.; Colsman, M. R.; Miller, M. M.; Wulfsberg, G. P.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1989**, *111*, 3762–3764.

(30) Prangé, T.; Pascard, C.; de Meijere, A.; Behrens, U.; Barnier, J. P.; Conia, J. M. *Nouv. J. Chim.* **1980**, *4*, 321–327.

(31) (a) Fitjer, L. *Chem. Ber.* **1982**, *105*, 1047–1060. (b) The low-temperature ^{1}H NMR spectrum of **12** was recorded in [d$_2$]dichloromethane at 400 MHz. If one were arbitrarily to assume a chemical shift difference of δ 0.5 between the signals for the different inside cyclopropyl hydrogens in the static conformation of **12**, an upper limit of 9 kcal/mol could be placed on the inversion barrier (ΔG^*) for **12**. The inversion barrier in **12** should be much less than that in cyclohexane.

(32) Hoffmann, R. *Tetrahedron Lett.* **1970**, 2907–2909; Günther, H. *Ibid.* **1970**, 5173–5176.

(33) Cf. Allen, F. H. *Acta Cryst.* **1980**, *B36*, 81–96 and references cited therein.

(34) Harmony, M. D.; Nandi, R. N.; Tietz, J. V.; Choe, J. I.; Getty, S. J.; Staley, S. W. *J. Am. Chem. Soc.* **1983**, *105*, 3947–3951.

(35) Pearson, R., Jr.; Choplin, A.; Laurie, V. W.; Schwartz, J. *J. Chem. Phys.* **1975**, *62*, 2949–2951.

usual laboratory methods. All reactions with alkylmetal reagents were carried out under an inert atmosphere in flame-dried glassware.

1-Chloro-1-(trichloroethenyl)cyclopropane,[12,36] 1-(trimethylsilyl)-1-[(trimethylsilyl)ethynyl]cyclopropane,[11,12] and 1-ethynyl-1-(trimethylsilyl)cyclopropane[11,12] were prepared according to our previously published procedure. Methyl cyclopropyl ketone was prepared with use of a modification of the procedure of S. Takei and Y. Kawano,[37] according to W. Weber and A.d.M.[38] Vinylcyclopropane was prepared according to W. Kirmse et al.,[39] ethynylcyclopropane was prepared according to Y. M. Slobodin and I. Z. Egenburg,[40] and (phenylthio)copper was prepared according to G. H. Posner et al.[41]

1,4-Dicyclopropylbuta-1,3-diyne (**4**-H$_2$). To a solution of dry cupric acetate (6.0 g, 33.1 mmol) in dry methanol/pyridine (1:1 v/v 80 mL)) was added a solution of ethynylcyclopropane (**3**-H$_2$; 1.0 g, 15.1 mmol) in dry methanol (1 mL), and the mixture was stirred for 3 days at ambient temperature. The reaction mixture was poured into ice-cold 18 N sulfuric acid (100 mL), and the aqueous mixture was extracted with two 30-mL portions of ether. After the organic phase was dried over magnesium sulfate, the solvent was distilled over a 40-cm column packed with glass rings and the residue was purified by Kugelrohr distillation (100 °C (0.1 Torr)): yield 560 mg (57%); **4**-H$_2$; colorless liquid; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.63–0.81 (m, 8 H), 1.19–1.30 (m, 2 H); ^{13}C NMR (67.93 MHz, CDCl$_3$, broad-band decoupling) δ 0.07, 8.56, 61.08, 79.92; IR (film) 3090, 3020, 2240, 2190, 2160 cm^{-1}; UV (methanol) λ_{max} (10 g ϵ) 228.4 nm (2.905), 240.0 (3.103), 253.2 (3.18), 268 (3.00); MS (70 eV) m/z 130 (M$^+$), 128 (M – H$_2$), 115 (M – CH$_3$), 102 (M – C$_2$H$_4$).

Iodination of Terminal Cyclopropylalkynes. General Procedure (GP1). To a solution of the terminal alkyne **3**-SiMe$_3$(H), **6**-SiMe$_3$(H), **9**-SiMe$_3$(H), etc. (1 equiv) in dry diethyl ether was added at –78 °C a solution of methyllithium (1 equiv) in ether; the mixture was stirred for 1 h at this temperature and then for 1 h at room temperature and cooled to –78 °C again. Iodine (1.2 equiv) was added to the mixture with stirring, and then the mixture was warmed to room temperature again and stirred for 1 h. The reaction mixture was hydrolyzed with saturated ammonium chloride solution; the aqueous phase was extracted with three portions of ether (20–100 mL), and the combined organic layers were washed with several portions of saturated sodium bisulfite solution until no further decolorization was visible. The organic phase was dried over magnesium sulfate, the solvent removed on a rotatory evaporator, and the residue dried under reduced pressure. Yields of iodoacetylenes **3**-SiMe$_3$(I), **6**-SiMe$_3$(I), **9**-SiMe$_3$(I), etc. ranged from 94–98%.

1-(Iodoethynyl)-1-(trimethylsilyl)cyclopropane (**3**-SiMe$_3$(I)). The reaction mixture obtained from 1-ethynyl-1-(trimethylsilyl)cyclopropane[14] (**3**-SiMe$_3$(H); 20.0 g, 0.145 mol) and 1.4 M methyllithium solution (115 mL, 0.160 mol) in dry ether (230 mL) was treated with elemental iodine (46 g, 0.180 mol) at –78 °C according to GP1. After the workup, one obtained 36 g (94%) of **3**-SiMe$_3$(I) as a yellowish oil: ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.02 (s, 9 H), 0.64 (m, 2 H), 0.91 (m, 2 H); ^{13}C NMR (20.15 MHz, CDCl$_3$, broad-band decoupling) δ –15.75, –3.44, 0.45, 12.20, 99.70; IR (film) 3080, 3000, 2960, 2900, 2160, 1435, 1260 (br), 1200, 1060, 1030, 974, 840 (br), 755, 695, 645, 590, 465 cm^{-1}; MS (70 eV) m/z 264 (8, M$^+$), 209 (4), 185 (12), 137 (19, M – I), 97 (33), 73 (100).

Coupling of 1-Ethynylcyclopropyl 1-(Phenylthio)cuprate with Iodoalkynes and Iodocyclopropanes, General Procedure (GP2). To a solution of 1-chloro-1-[(trimethylsilyl)ethynyl]cyclopropane[14,15] (**3**-Cl(SiMe$_3$; 1.1 equiv) in dry diethyl ether was added dropwise with stirring a solution of n-butyllithium (1.2 equiv) in n-hexane; after 1 h, the mixture was slowly warmed to –10 °C until the [1-[(trimethylsilyl)ethynyl]cyclopropyl]lithium precipitated (warning: exothermic reaction!). The mixture was stirred for an additional 20 min and then transferred into a dropping funnel and added dropwise to a stirred suspension of (phenylthio)copper (1 equiv) in dry tetrahydrofuran kept at –30 to –40 °C in such a fashion that the internal temperature never raised above –30 °C. After it was stirred at –20 °C for an additional 20 min, the light brown suspension was cooled again to –78 °C and, within 5–10 min, a solution of the corresponding iodoacetylene **3**-SiMe$_3$(I), **6**-SiMe$_3$(I), **9**-SiMe$_3$(I), etc. (0.12–0.75 equiv) or iodocyclopropane **3**-I(SiMe$_3$) in dry tetrahydrofuran was added. The reaction mixture was kept between –75 and –55 °C for 1.5–3.5 h and then solvolyzed with dry methanol. The mixture was warmed to room temperature and poured into saturated ammonium chloride solution (50–350 mL), and the two-phase system was stirred for 30 min, at which time a deep blue aqueous phase had formed. The solution was filtered off the yellow precipitate over Celite, and the aqueous phase was extracted with three portions of ether (50–150 mL) and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the residual yellow oil was chromatographed over silica gel.

1-[2″-[1′-(Trimethylsilyl)cyclopropyl]ethynyl]-1-[2‴-(trimethylsilyl)ethynyl]cyclopropane (**6**-(SiMe$_3$)$_2$). The reaction mixture obtained from **3**-Cl(SiMe$_3$) (16.0 g, 93.0 mmol) in diethyl ether (10 mL) with 1.6 M n-butyllithium in n-hexane (66 mL, 106 mmol), (phenylthio)copper (14.5 g, 84.0 mmol) in THF (360 mL), and **3**-SiMe$_3$(I) (15.5 g, 59.0 mmol) in THF (25 mL) was stirred at –60 °C for 1.5 h, quenched with methanol (50 mL), and poured into saturated ammonium chloride solution (350 mL). The crude yellow oil collected after further workup was chromatographed over silica gel (800 g; column, 6 × 68 cm) eluting with petroleum ether (30:50).

Fraction I: R_f = 0.31; yield 820 mg (5%, based on **3**-SiMe$_3$(I)); 2″-[1′-[2‴-(trimethylsilyl)ethynyl]cyclopropyl]-2″-(trimethylsilyl)ethenylidenecyclopropane (**8**); ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.12 (s, 9 H), 0.20 (s, 9 H), 0.91 (m, 2 H, 2′-H, 3′-H), 1.10 (m, 2 H, 2′-H, 3′-H), 1.50 (mc, 4 H, 2-H, 3-H); ^{13}C NMR (100.62 MHz, CDCl$_3$, broad-band decoupling and DEPT) δ –0.36 (+), 0.11 (+), 8.09 (–), 13.48 (ϕ), 19.15 (–), 73.52 (ϕ), 80.08 (ϕ), 103.20 (ϕ), 112.35 (ϕ), 190.47 (ϕ); IR (film) 3090, 3060, 2960, 2160, 2000, 1400, 1247, 1000, 850 (br), 760 cm^{-1}; MS (70 eV) m/z 274 (3.5, M$^+$), 259 (19, M – CH$_3$), 231 (4.5, M – CH$_3$ – C$_2$H$_4$), 203 (3.8, M – CH$_3$ – (2 C$_2$H$_4$)), 201 (5.0, M – SiMe$_3$), 186 (6.0, M – CH$_3$ – SiMe$_3$), 185 (9), 171 (7, M – (2 CH$_3$) – SiMe$_3$), 155 (12.5), 97 (15), 73 (100).

Fraction II: R_f = 0.25; yield 7.95 g (49%, based on **3**-SiMe$_3$(I); purity according GC (column C), 85%; impurities, **6**-SiMe$_3$(H), **5**-(SiMe$_3$)$_2$, and 1-(phenylthio)-1-[(trimethylsilyl)ethynyl]cyclopropane (**3-SPh**(SiMe$_3$)); **6**-(SiMe$_3$)$_2$; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.02 (s, 9 H), 0.24 (s, 9 H), 0.55 (m, 2 H, 2′-H, 3′-H), 0.77 (m, 2 H, 2′-H, 3′-H), 1.09 (m, 2 H, 2-H, 3-H), 1.15 (m, 2 H, 2-H, 3-H); ^{13}C NMR (100.62 MHz, CDCl$_3$, broad-band decoupling and DEPT) δ –3.49 (+), –2.20 (ϕ), 0.05 (+), 3.63 (ϕ), 11.83 (–), 20.73 (–), 74.98 (ϕ), 79.68 (ϕ), 82.13 (ϕ), 108.44 (ϕ); IR (film) 3090, 3010, 2970, 2900, 2240, 2170, 1250, 1010, 918, 850 (br) cm^{-1}; MS (70 eV) m/z 274 (8, M$^+$), 259 (10, M – CH$_3$), 231 (9, M – CH$_3$ – C$_2$H$_4$), 203 (10, M – CH$_3$ – (2 C$_2$H$_4$)), 186 (13, M – CH$_3$ – SiMe$_3$), 171 (13, M – (2 CH$_3$) – SiMe$_3$), 73 (100). Anal. Calcd for C$_{16}$H$_{26}$Si$_2$: C, 69.99; H, 9.54. Found: C, 69.81; H, 9.38.

Fraction III: R_f = 0.22; yield 950 mg of crude product, which was purified by preparative GC (column D, 140 °C) and identified as 1,1′-bis[(trimethylsilyl)ethynyl]-1,1′-bicyclopropyl (**5**-(SiMe$_3$)$_2$); white solid; mp 52 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.09 (s, 18 H), 0.89 (m, 4 H), 1.04 (m, 4 H); ^{13}C NMR (100.62 MHz, CDCl$_3$, broad-band decoupling and DEPT) δ 0.14 (+), 14.55 (–), 15.26 (ϕ), 81.92 (ϕ), 108.78 (ϕ); IR (KBr pellet) 3100, 3010, 2950, 2890, 2160, 1415, 1245, 1155, 850, 760, 635, 560, 450 cm^{-1}; MS (70 eV) m/z 274 (0.74, M$^+$), 259 (9.3, M – CH$_3$), 201 (14, M – SiMe$_3$), 186 (21, M – CH$_3$ – SiMe$_3$), 171 (12 M – (2 CH$_3$) – SiMe$_3$), 97 (12), 73 (100). Anal. Calcd for C$_{16}$H$_{26}$Si$_2$: C, 69.99; H, 9.54. Found: C, 70.09; H, 9.59.

Protiodesilylation of (Trimethylsilyl)alkynes, General Procedure (GP3). To a solution of the respective (trimethylsilyl)alkyne **5**-(SiMe$_3$)$_2$, **6**-(SiMe$_3$)$_2$, 3,3:6,6:9,9-triethylene-11-(trimethylsilyl)-1-[1′-(trimethylsilyl)cyclopropyl]-1,4,7,10-undecatetrayne, **9**-(SiMe$_3$)$_2$, **10**-(SiMe$_3$)$_2$, etc. in dry methanol was added at 0 °C a solution of potassium hydroxide in methanol, and the mixture was stirred at room temperature for 14 h. Water (50–250 mL) was added and the aqueous phase extracted with five portions of pentane (50 mL each). The combined organic phases were dried over magnesium sulfate and the solvents removed under reduced pressure. The crude product was distilled or used without further purification.

1-[2″-[1′-(Trimethylsilyl)cyclopropyl]ethynyl]-1-ethynylcyclopropane (**6**-SiMe$_3$(H)). The product obtained from **6**-(SiMe$_3$)$_2$, (6.5 g, 23.7 mmol) in methanol (20 mL) and potassium hydroxide (10.0 g, 0.18 mol) in methanol (80 mL) according to GP3 was distilled under reduced pressure: yield 3.35 g (70%); **6**-SiMe$_3$(H); colorless oil; bp 100–105 °C (20 Torr); ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.0 (s, 9 H), 0.61 (m, 2 H, 2′-H, 3′-H), 0.83 (m, 2 H, 2′-H, 3′-H), 1.14 (mc, 4 H, 2-H, 3-H), 1.92 (s, 1 H); ^{13}C NMR (100.62 MHz, CDCl$_3$, broad-band decoupling and DEPT) δ –3.47 (+), –2.20 (ϕ), 2.59 (ϕ), 11.91 (–), 20.21 (–), 63.71 (+), 74.61 (ϕ), 82.36 (ϕ), 86.46 (ϕ); IR (film) 3310 (s), 3090, 3020, 2970 (s), 2240, 2130, 1430, 1255 (s), 1010, 950, 850 (s), 750 cm^{-1}; MS (70 eV) m/z 202 (5.1, M$^+$), 187 (6.1, M – CH$_3$), 159 (17, M – CH$_3$ – C$_2$H$_4$), 147 (8.4), 131 (13), 73 (100). Anal. Calcd for C$_{13}$H$_{18}$Si: C, 77.16; H, 8.96. Found: C, 76.94; H, 8.98.

1-[2″-[1′-(Trimethylsilyl)cyclopropyl]ethynyl]-1-(2‴-iodoethynyl)cyclopropane (**6**-SiMe$_3$(I)). To the reaction mixture obtained from **6**-

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SiMe$_3$(H) (4.7 g, 23.3 mmol) in diethyl ether (80 mL) and 1.2 M methyllithium solution in ether (25.0 mL, 30.0 mmol) according to GP1 was added at −78 °C elemental iodine (8.5 g, 33.5 mmol). After workup, the crude product was dried under reduced pressure: yield 7.4 g (97%); **6**-SiMe$_3$(I) as a yellow oil; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.0 (s, 9 H), 0.60 (m, 2 H, 2′-H, 3′-H), 0.84 (m, 2 H, 2′-H, 3′-H), 1.14 (mc, 4 H, 2-H, 3-H); ^{13}C NMR (20.15 MHz, CDCl$_3$, broad-band decoupling) δ −9.58, −3.46, −2.22, 5.01, 11.96, 20.40, 74.34, 82.74, 95.69; IR (film) 3040, 3005, 2955, 2895, 2230 (s), 2180 (w), 1420 (br), 1330, 1250 (s), 1215, 1190, 1055, 1025, 1005, 960, 905, 805 (br s), 750, 700, 620 cm^{-1}; MS (70 eV) *m/z* 328 (6.8, M$^+$), 313 (3.4, M − CH$_3$), 285 (6.9, M − CH$_3$ − C$_2$H$_4$), 257 (10), 201 (10, M − I), 185 (12), 173 (13), 145 (21, M − I − (2 C$_2$H$_4$)), 128 (9.6), 97 (7.4), 73 (100).

3,3:6,6-Diethylene-8-(trimethylsilyl)-1-[1′-(trimethylsilyl)cyclopropyl]-1,4,7-octatriyne (9-(SiMe$_3$)$_2$). The reaction mixture obtained from **3**-Cl(SiMe$_3$) (6.3 g, 36.8 mmol) in ether (2 mL), 1.5 M *n*-butyllithium in *n*-hexane (27.0 mL, 40.5 mmol), (phenylthio)copper (5.6 g, 32.6 mmol) in THF (120 mL), and **6**-SiMe$_3$(I), (4.7 g, 14.2 mmol) in THF (8 mL) was stirred at −60 °C for 2.5 h, quenched with methanol (20 mL), and poured into saturated ammonium chloride solution (150 mL). The crude product obtained after further workup was chromatographed over silica gel (350 g; column, 6 × 28 cm) eluting first with petroleum ether (60:70) and then gradually switching to diethyl ether. **9**-(SiMe$_3$)$_2$ eluted with petroleum ether/ether (4:1) as a yellow zone: R_f = 0.05, *n*-pentane; yield 3.54 g (46%); **9**-(SiMe$_3$)$_2$; yellowish viscous liquid; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.0 (s, 9 H), 0.13 (s, 9 H), 0.60 (m, 2 H), 0.82 (m, 2 H), 1.07 (mc, 4 H), 1.17 (br d, 4 H); ^{13}C NMR (100.62 MHz, CDCl$_3$, broad-band decoupling and DEPT) δ −3.46 (+), −2.18 (ϕ), 0.03 (+), 2.79 (ϕ), 3.46 (ϕ), 11.87 (−), 20.27 (−), 20.81 (−), 75.53 (ϕ), 76.55 (ϕ), 78.66 (ϕ), 80.06 (ϕ), 81.74 (ϕ), 107.72 (ϕ); IR (film) 3080, 3005, 2960, 2900, 2230 (w), 2170 (s), 1420, 1360, 1250 (s), 1060, 1030, 995, 920, 890, 845 (br s), 760, 695 cm^{-1}; MS (70 eV) *m/z* 338 (2.0, M$^+$), 323 (1.3, M − CH$_3$), 310 (1.3, M − C$_2$H$_4$), 295 (2.6, M − CH$_3$ − C$_2$H$_4$), 267 (3.0), 265 (3.3), 249 (4.0), 235 (6.7), 221 (3.6), 207 (3.4), 195 (3.0), 97 (4.0), 73 (100). Anal. Calcd for C$_{21}$H$_{30}$Si$_2$: C, 74.48; H, 8.93. Found: C, 74.49; H, 8.95.

3,3:6,6-Diethylene-1-[1′-(trimethylsilyl)cyclopropyl]-1,4,7-octatriyne (9-SiMe$_3$(H)). The reaction mixture obtained from **9**-(SiMe$_3$)$_2$ (3.54 g, 10.5 mmol) in methanol (10 mL) and potassium hydroxide (5.0 g, 90.0 mmol) in methanol (50 mL) according to GP3 gave, after drying the crude product under reduced pressure, 2.66 g (95.5%) of **9**-SiMe$_3$(H) as a slightly yellow, viscous oil: ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.0 (s, 9 H), 0.60 (m, 2 H), 0.83 (m, 2 H), 1.08 (mc, 4 H), 1.18 (br s, 4 H), 1.93 (s, 1 H); IR (film) 3290 (s), 3080, 3000, 2950 (s), 2220, 2110, 1420, 1360, 1300, 1245 (s), 1215, 1185, 1055, 1025, 1010, 990, 940, 920, 880 (br s), 750 cm^{-1}; MS (70 eV) *m/z* 266 (5.6, M$^+$), 251 (2.6, M − CH$_3$), 235 (3.4), 223 (8.0, M − CH$_3$ − C$_2$H$_4$), 195 (15, M − CH$_3$ − (2 C$_2$H$_4$)), 178 (12), 165 (12), 115 (5.4), 73 (100). Anal. Calcd for C$_{18}$H$_{22}$Si: C, 81.14; H, 8.32. Found: C, 80.89; H, 8.34.

3,3:6,6-Diethylene-8-iodo-1-[1′-(trimethylsilyl)cyclopropyl]-1,4,7-octatriyne (9-SiMe$_3$(I)). To the reaction mixture obtained from **9**-SiMe$_3$(H) (2.66 g, 10.0 mmol) in diethyl ether (80 mL) and 1.2 M methyllithium solution (12.0 mL, 14.5 mmol) according to GP1 was added at −78 °C iodine (4.0 g, 16.0 mmol). The crude product after drying under reduced pressure was 3.72 g (95%) of **9**-SiMe$_3$(I) as a dark oil: ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.0 (s, 9 H), 0.59 (m, 2 H), 0.83 (m, 2 H), 1.08 (mc, 4 H), 1.18 (mc, 4 H); IR (film) 3085, 3005, 2960 (s), 2230, 1420, 1355, 1305, 1245 (s), 1215, 1190, 1060, 1030, 995, 840 (br s), 750 cm^{-1}; MS (70 eV) *m/z* 392 (5.6, M$^+$), 364 (1.4, M − C$_2$H$_4$), 349 (1.6, M − CH$_3$ − C$_2$H$_4$), 321 (4.4, M − CH$_3$ − (2 C$_2$H$_4$)), 265 (3.8, M − I), 235 (12), 221 (7.5), 207 (9.0), 191 (10), 179 (9.0), 165 (9.0), 97 (4.5), 73 (100).

3,3:6,6:9,9-Triethylene-11-(trimethylsilyl)-1-[1′-(trimethylsilyl)cyclopropyl]-1,4,7,10-undecatetrayne. The reaction mixture obtained from **3**-Cl(SiMe$_3$) (3.9 g, 22.7 mmol) in diethyl ether (2 mL), a 2.3 M *n*-butyllithium solution in *n*-hexane (11.0 mL, 25.0 mmol), (phenylthio)copper (3.44 g, 20.0 mmol) in THF (100 mL), and **9**-SiMe$_3$(I) (2.4 g, 6.12 mmol) in THF (10 mL) according to GP2 was stirred at −55 °C for 3 h, then quenched with methanol (15 mL), and after having warmed to ambient temperature poured into saturated NH$_4$Cl solution (100 mL). After further workup, the orange oil was chromatographed over silica gel (130 g; column, 3 × 41 cm; elution with *n*-hexane and then gradually switched to diethyl ether).

Fraction I: R_f (*n*-hexane) = 0.14, elution with *n*-hexane; 610 mg (37%, based on **9**-SiMe$_3$(I)); **9**-SiMe$_3$(H).

Fraction II: R_f (*n*-hexane) = 0.05, elution with *n*-hexane/diethyl ether (2:1); 1.3 g (53%, based on **9**-SiMe$_3$(I)); 3,3:6,6:9,9-triethylene-11-(trimethylsilyl)-1-[1′-(trimethylsilyl)cyclopropyl]-1,4,7,10-undecatetrayne; colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.0 (s, 9 H), 0.13 (s, 9 H), 0.58 (m, 2 H), 0.80 (m, 2 H), 1.06 (mc, 4 H), 1.11 (br d, AA′BB′, 4 H), 1.17 (mc, 4 H); IR (film) 3080, 3005, 2955 (s), 2220, 2165 (s), 1420, 1370, 1245 (s), 1020 (br), 840 (br s), 760 cm^{-1}; MS (70 eV) *m/z* 402 (0.15, M$^+$), 387 (0.2, M − CH$_3$), 374 (0.3, M − C$_2$H$_4$), 359 (0.8, M − CH$_3$ − C$_2$H$_4$), 329 (2.5, M − SiMe$_3$), 313 (1.6), 299 (2.6), 285 (2.7), 271 (2.9), 255 (3.0), 241 (2.2), 97 (3.8), 73 (100). Anal. Calcd for C$_{26}$H$_{34}$Si$_2$: C, 77.54; H, 8.51. Found: C, 77.53; H, 8.63.

3,3:6,6:9,9-Triethylene-1-[1′-(trimethylsilyl)cyclopropyl]-1,4,7,10-undecatetrayne. The product obtained from 3,3:6,6:9,9-triethylene-11-(trimethylsilyl)-1-[1′-(trimethylsilyl)cyclopropyl]-1,4,7,10-undecatetrayne (1.3 g, 3.23 mmol) in methanol (10 mL) and potassium hydroxide (3.0 g, 50 mmol) in methanol (40 mL) was dried under reduced pressure: yield 1.02 g (95%); yellowish, viscous liquid; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.0 (s, 9 H), 0.58 (m, 2 H), 0.81 (m, 2 H), 1.05 (mc, 4 H), 1.10 (s, AA′BB′, 4 H), 1.17 (s, AA′BB′, 4 H), 1.93 (s, 1 H); IR (film) 3290 (s), 3080, 3005 (s), 2950 (s), 2890, 2230, 2120, 1425, 1370, 1250 (s), 1035, 990, 845 (br s), 755 cm^{-1}; MS (70 eV) *m/z* 330 (2.7, M$^+$), 329 (2.0, M − H), 315 (4.7, M − CH$_3$), 299 (13, M − H − (2 CH$_3$)), 285 (29, M − (3 CH$_3$)), 271 (33, M − H (2 CH$_3$) − C$_2$H$_4$), 257 (49, M − SiMe$_3$), 241 (61, M − H − CH$_3$ − SiMe$_3$), 227 (51, M − (2 CH$_3$) − SiMe$_3$), 215 (34, M − H − (2 CH$_3$) − (3 C$_2$H$_4$)), 202 (23), 189 (9.7), 179 (6.9), 165 (8.2), 155 (5.7), 115 (2.3), 97 (8.2), 83 (6.9), 73 (100). Anal. Calcd for C$_{23}$H$_{26}$Si: C, 83.58; H, 7.93. Found: C, 83.67; H, 7.90.

3,3:6,6:9,9-Triethylene-11-iodo-1-[1′-(trimethylsilyl)cyclopropyl]-1,4,7,10-undecatetrayne. The reaction mixture prepared according to GP1 from 3,3:6,6:9,9-triethylene-1-[1′-(trimethylsilyl)cyclopropyl]-1,4,7,10-undecatetrayne (1.02 g, 3.09 mmol) in ether (40 mL) and 1.2 M methyllithium solution (5.0 mL, 6.0 mmol) was treated at −78 °C with elemental iodine (1.8 g, 7.1 mmol), and after workup the crude product was freed from volatile components under reduced pressure: yield 1.35 g (96%); crude 3,3:6,6:9,9-triethylene-11-iodo-1-[1′-(trimethylsilyl)cyclopropyl]-1,4,7,10-undecatetrayne as a dark oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.0 (s, 9 H), 0.59 (m, 2 H), 0.83 (m, 2 H), 1.07 (mc, 4 H), 1.12 (s, AA′BB′, 4 H), 1.18 (mc, 4 H); IR (film) 3095, 3020, 2970 (s), 2905, 2235, 1430, 1380, 1260 (s), 1040, 995, 915, 850 (br s), 745 cm^{-1}; MS (70 eV) *m/z* 456 (0.81, M$^+$), 428 (1.3, M − C$_2$H$_4$), 413 (2.4, M − CH$_3$ − C$_2$H$_4$), 385 (2.0, M − CH$_3$ − (2 C$_2$H$_4$)), 372 (1.2), 355 (1.4), 329 (10, M − I), 313 (11), 299 (30), 285 (24), 271 (39), 255 (39), 241 (46), 227 (28), 215 (17), 202 (13), 97 (14), 73 (100).

3,3:6,6:9,9:12,12-Tetraethylene-14-(trimethylsilyl)-1-[1′-(trimethylsilyl)cyclopropyl]-1,4,7,10,13-tetradecapentayne (10-(SiMe$_3$)$_2$). The reaction mixture obtained according to GP2 from **3**-Cl(SiMe$_3$) (3.54 g, 20.6 mmol) in diethyl ether (2 mL), 1.5 M *n*-butyllithium solution in *n*-hexane (15.0 mL, 22.5 mmol), (phenylthio)copper (3.10 g, 18.0 mmol) in THF (80 mL), and 3,3:6,6:9,9-triethylene-11-iodo-1-[1′-(trimethylsilyl)cyclopropyl]-1,4,7,10-undecatetrayne (1.07 g, 2.35 mmol) in THF (5 mL) was stirred at −60 °C for 3.5 h, then quenched with methanol (10 mL), and after warming to ambient temperature poured into saturated NH$_4$Cl solution (100 mL). The crude orange oil was chromatographed over silica gel (120 g; column, 3 × 38 cm) eluting first with *n*-hexane and then gradually switching to diethyl ether. **10**-(SiMe$_3$) eluted with *n*-hexane/diethyl ether (2:1) (R_f (*n*-hexane) = 0.02) as a yellow oil (1.02 g) together with unreacted 3,3:6,6:9,9-triethylene-1-[1′-(trimethylsilyl)cyclopropyl]-1,4,7,10-undecatetrayne from the preceding step (relative amount 40%). Two consecutive recrystallizations from methanol at −30 °C yielded 250 mg (23%) of pure **10**-(SiMe$_3$) as a white solid: mp 215 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.0 (s, 9 H), 0.13 (s, 9 H), 0.59 (m, 2 H), 0.82 (m, 2 H), 1.06 (mc, 4 H), 1.10 (s, AA′BB′, 4 H), 1.11 (s, AA′BB′, 4 H), 1.18 (mc, 4 H); IR (film) 3090, 2965 (s), 2825, 2860, 2235, 2175 (s), 1420, 1380, 1255 (s), 1035, 845 (br s) cm^{-1}; MS (70 eV) *m/z* 466 (2.8 × 10^{-4}, M$^+$), 465 (3.4 × 10^{-4}, M − H), 438 (1.6 × 10^{-2}, M − C$_2$H$_4$), 437 (1.9 × 10^{-2}, M − H − C$_2$H$_4$), 423 (0.03, M − CH$_3$ − C$_2$H$_4$), 409 (0.03, M − H (2 C$_2$H$_4$)), 393 (0.12, M − SiMe$_3$), 377 (0.15, M − H − CH$_3$ − SiMe$_3$), 365 (0.42, M − C$_2$H$_4$ − SiMe$_3$), 349 (0.6), 335 (0.72), 319 (0.9), 305 (1.0), 291 (1.3), 277 (0.93), 265 (0.78), 253 (0.72), 239 (0.66), 155 (0.78), 97 (2.2), 83 (1.5), 73 (100). Anal. Calcd for C$_{31}$H$_{38}$Si$_2$: C, 79.76; H, 8.20. Found: C, 79.58; H, 8.19.

3,3:6,6:9,9:12,12-Tetraethylene-1-cyclopropyl-1,4,7,10,13-tetradecapentayne (10-H$_2$). To a solution of **10**-(SiMe$_3$)$_2$ (250 mg, 0.54 mmol) in dry THF (5 mL) was added dropwise at −10 °C a 0.63 M solution of tetrabutylammonium fluoride ((TBA)F) in THF (2 mL, 1.26 mmol), which had been dried by addition of 0.1 equiv of hexamethyldisilazane and partial evaporation of the solvent. The dark red solution was stirred at ambient temperature for 4 h and then hydrolyzed with 2 N HCl (10 mL), and the aqueous phase was extracted with three portions of ether (25 mL each). The combined organic layers were dried over magnesium sulfate, and the solvent was evaporated under reduced pressure. The crude product was chromatographed over silica gel (60 g; column, 3 × 20 cm) eluting with *n*-hexane/diethyl ether (1:1) and then dried under reduced pressure: yield 170 mg (98%); **10**-H$_2$; colorless oil; ^{1}H NMR

(270 MHz, $CDCl_3$) δ 0.55–0.72 (m, 4 H), 1.10 (m, 13 H), 1.17 (s, AA'BB', 4 H), 1.92 (s, 1 H); IR (film) 3150 (s), 3055, 3015 (s), 2970, 2940, 2260, 2130, 1425 (s), 1385 (s), 1070, 1040, 990, 915, 820, 740 cm^{-1}; MS (70 eV) *m/z* 319 (1.5), 305 (13), 291 (36), 276 (82), 263 (100), 252 (36), 239 (42), 226 (25), 215 (19), 209 (11), 202 (21), 189 (19), 182 (14), 165 (13), 152 (13), 138 (11), 126 (9.8), 115 (16), 99 (12), 87 (13), 77 (14), 63 (15), 51 (10).

3,3:6,6:9,9:12,12-Tetraethylene-1-cyclopropyl-14-[(2',3'-dimethyl-2'-butyl)dimethylsilyl]-1,4,7,10,13-tetradecapentayne (10-H($SiMe_2$Thex)). To a solution of **10**-H_2 (170 mg, 0.54 mmol) in dry THF (8 mL) was added dropwise at −78 °C a 1.2 M methyllithium solution (1.2 mL, 1.44 mmol). The reaction mixture was stirred at ambient temperature for 20 h, and then thexyldimethylsilyl chloride (400 mg, 2.2 mmol) was added at −10 °C. After having been stirred at ambient temperature for 14 h, the mixture was hydrolyzed with saturated NH_4Cl solution (10 mL), the aqueous phase was extracted with two portions of diethyl ether (15 mL each), and the combined organic phases were dried over $MgSO_4$. The solvents were removed under reduced pressure, and the residual oil was chromatographed over silica gel (32 g; column, 2 × 23 cm) eluting with diethyl ether/petroleum ether (60:80) (1:4): yield 185 mg (75%); **10**-H($SiMe_2$Thex); $R_f = 0.54$; colorless oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.09 (s, 6 H), 0.56–0.73 (m, 4 H), 0.84 (s, 6 H), 0.87 (d, 6 H), 1.03–1.12 (m, 13 H), 1.15 (br s, AA'BB', 4 H), 1.61 (sept, 1 H); IR (film) 3090, 3020, 2970 (s), 2870, 2240, 2170 (s), 1465, 1423, 1383 (s), 1255 (s), 1035, 840, 823 (s), 780 cm^{-1}; MS (70 eV) *m/z* 464 (0.07, M^+), 403 (0.21), 380 (1.5, $M - C_6H_{12}$), 379 (2.0, $M - C_6H_{13}$), 363 (4.0), 357 (6.7), 349 (6.8), 335 (9.8), 321 (13), 319 (12), 305 (27), 291 (62), 277 (94), 276 (93), 263 (100), 252 (41), 239 (45), 226 (29), 205 (33), 163 (28), 149 (55), 133 (28), 111 (19), 97 (23), 91 (25), 89 (65), 85 (41), 75 (52), 73 (89), 69 (49), 57 (94).

Deprotonation of 10-H($SiMe_2$Thex) with Butyllithium, Reaction with Iodine and Protiodesilylation of the Crude Product. To a solution of **10**-H($SiMe_2$Thex) (185 mg, 0.40 mmol) in dry THF (2 mL) was added at −78 °C a 1.5 M butyllithium solution in *n*-hexane (0.8 mL, 1.2 mmol); the mixture was stirred at ambient temperature for 1.5 h, then added to a cold (−78 °C) solution of elemental iodine (380 mg, 1.5 mmol) in dry THF (6 mL), and stirred for an additional 2.5 h at ambient temperature. The reaction mixture was hydrolyzed with saturated NH_4Cl solution (10 mL), and the organic phase was washed with saturated sodium sulfite solution, until no further decolorization could be observed. The organic phase was separated, the combined aqueous solutions were extracted with two portions of diethyl ether (15 mL each), and the combined organic phases were dried over $MgSO_4$. After evaporation of the solvents, there remained 225 mg of a brownish oil, which according to its TLC contained a new product differing from **10**-H($SiMe_2$Thex). The ^1H NMR spectrum of the crude product showed a decreased intensity of the multiplet between δ 0.56 and 0.73 and new signals in the region between δ 1.24 to 1.36.

Without purification, the crude product (225 mg) containing a mixture of **10**-H($SiMe_2$Thex) and **10**-I($SiMe_2$Thex) was dissolved in dry THF (6 mL), a commercially available 1.0 M (TBA)F solution in THF (0.8 mL) was added, and the mixture was stirred at ambient temperature for 1.5 h and then hydrolyzed with water (10 mL). After the aqueous phase had been extracted with two portions of diethyl ether (10 mL), the combined organic phases were dried over $MgSO_4$, the solvent was removed under reduced pressure, and the residue was filtered through a silica gel (30 g; column, 2 × 22 cm) eluting with diethyl ether/*n*-hexane (1:4), yielding 36 mg of a brownish oil, of which the ^1H NMR spectrum (270 MHz, $CDCl_3$) showed no signals of a $SiMe_2$Thex group, but a new absorption of an acetylenic proton at $\delta = 1.93$ ppm. According to the intensity of this signal with respect to those of the absorptions in the region δ 0.56–0.73 characteristic of the starting material **10**-H($SiMe_2$Thex) and the pentamer **10**-H_2, the new terminal acetylene **10**-I(H) amounted to 63%. The gas chromatogram of the mixture (column: 25-m capillary Oribond SE 54, 230 °C, then program 25 °C/min) indicated that, besides the pentayne **10**-H_2 (relative retention time 1.0, relative amount 33%), a new product, most probably **10**-I(H) (1.85, 67%). An attempted analysis in a GC/MS system failed, but a mass spectrum obtained after direct inlet of the mixture showed a characteristic molecular ion at *m/z* 448 (0.45) and further fragment ions at *m/z* 447 (0.9, M − H), 405 (3.1, $M - CH_3 - C_2H_4$), 390 (4.0, $M - C_2H_4 - (2\ CH_3)$).

Attempted Cyclization of 10-I(H) under Pd Catalysis. To a suspension of tetra-*n*-butylammonium bromide (67 mg, 0.21 mmol), anhydrous K_2CO_3 (98 mg, 0.71 mmol), and $Pd(OAc)_2$ (26 mg, 0.11 mmol) in dry and amine-free dimethylformamide (2 mL, distilled over calcium hydride and stirred with neutral alumina to remove dimethylamine, and then distilled again from phthalic anhydride) was added dropwise at ambient temperature over a period of 5–6 h the mixture of **10**-H_2 and **10**-I(H) (36 mg) in dry dimethylformamide (3.5 mL). After an additional 10 h, the mixture was diluted with diethyl ether (30 mL) and washed with three portions of water (30 mL each). The organic layer was dried over $MgSO_4$, the solvent evaporated under reduced pressure, and the residue tested by TLC (eluting with diethyl ether). Only polymeric material was detected by TLC. Nonetheless the crude material was filtered through silica gel (15 g; column, 2 × 10 cm) eluting with diethyl ether. Neither starting materials (**10**-H_2, **10**-I(H)) nor any other volatile components could be detected by GC.

Palladium-Catalyzed Coupling of 3-I($SiMe_3$) and 3-$SiMe_3$(H). To a mixture of **3**-I($SiMe_3$) (285 mg, 1.08 mmol), anhydrous K_2CO_3 (780 mg, 5.7 mmol), tetra-*n*-butylammonium bromide (650 mg, 2.05 mmol), and **3**-$SiMe_3$(H) (395 mg, 2.86 mmol) in dry and amine-free dimethylformamide was added palladium(II) acetate (35 mg, 0.16 mmol), and the mixture was stirred at ambient temperature for 14 h. The reaction mixture was diluted with diethyl ether (50 mL) and washed with three portions of water (150 mL each), and the organic phase was dried over $MgSO_4$. After the solution had been concentrated under reduced pressure (~40 Torr), the residue was filtered through silica gel (50 g; column, 2.5 × 22 cm) eluting with diethyl ether/hexane (1:1) and the resulting solution again concentrated under reduced pressure. The brownish residue was tested by GC (column: 25-m capillary Oribond SE 54, 40 °C, 6 min, then 20 °C/min) and by combination GC/MS. The components in the mixture were identified by comparison with authentic samples of **3**-$SiMe_3$(H) (relative retention time 1.0, relative amount 41%), **3**-H($SiMe_3$) (1.9, 5%), **3**-I($SiMe_3$) (3.9, 34%), **6**-$(SiMe_3)_2$ (4.9, 15%), and **4**-$(SiMe_3)_2$ (5.4, 5%).

1,1'-Bis[(trimethylsilyl)ethynyl]bicyclopropyl (5-$(SiMe_3)_2$). The reaction mixture obtained according to GP2 from **3**-Cl($SiMe_3$) (3.44 g, 20 mmol) in diethyl ether (2 mL), a 1.6 M *n*-butyllithium solution in *n*-hexane (14.0 mL, 22.4 mmol), (phenylthio)copper (2.46 g, 14.3 mmol) in THF (100 mL), and 1-iodo-1-[(trimethylsilyl)ethynyl]cyclopropane (**3**-I($SiMe_3$)) in THF (5 mL) was stirred at −75 °C for 1.5 h, quenched with methanol (5 mL), and after having warmed to ambient temperature added to saturated NH_4Cl solution (150 mL). The yellow oil obtained after workup was chromatographed over silica gel (260 g; column, 5 × 30 cm) eluting with *n*-pentane: yield 2.0 g (77%, based on **3**-I($SiMe_3$)); **5**-$(SiMe_3)_2$; white solid; mp 52 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 0.09 (s, 18 H), 0.89 (m, 4 H), 1.04 (m, 4 H); ^{13}C NMR (100.62 MHz, $CDCl_3$, broad-band decoupling and DEPT) δ 0.14 (+), 14.55 (−), 15.26 (ϕ), 81.92 (ϕ), 108.78 (ϕ); IR (KBr pellet) 3100, 3010, 2950 (s), 2890, 2160 (s), 1415, 1245 (s), 1155, 845 (br s), 760, 635, 560, 450 cm^{-1}; MS (70 eV) *m/z* 274 (0.15, M^+), 259 (4.3, $M - CH_3$), 231 (3.0), 201 (8.1, $M - SiMe_3$), 186 (14, $M - CH_3 - SiMe_3$), 171 (7.6, $M - (2\ CH_3) - SiMe_3$), 122 (9.0), 97 (10), 73 (100), 59 (13), 45 (11). Anal. Calcd for $C_{16}H_{26}Si_2$: C, 69.99; H, 9.54. Found: C, 70.09; H, 9.59.

1,1'-Diethynylbicyclopropyl (5-H_2). The reaction mixture obtained according to GP3 from **5**-$(SiMe_3)_2$ (3.5 g, 12.8 mmol) in methanol (10 mL) and potassium hydroxide (6.0 g, 0.1 mol) in methanol (40 mL) was worked up, and the solvents were distilled through a 40-cm column packed with glass turnings. The residue was fractionally distilled in a short-path still: yield 1.36 g (83%); **5**-$(SiMe_3)_2$ as a colorless liquid; ^1H NMR (270 MHz, C_6D_6) δ 0.88 (mc, AA'BB', 8 H), 1.59 (s, 2 H); IR (film) 3300 (s), 3100, 3040, 2960, 2940, 2810, 2120, 1425, 1410, 1160, 1060, 1025, 940, 850 cm^{-1}; MS (70 eV) *m/z* 130 (6.0, M^+), 129 (37, M − H), 128 (82, M − (2 × H)), 127 (38), 115 (100, $M - CH_3$), 102 (24, $M - C_2H_4$), 89 (17), 74 (46), 65 (24), 63 (31), 51 (39); HRMS exact mass for $C_{10}H_{10}$, calcd 130.0783, found 130.0778.

Hexaspiro[2,0,2,4,2,0,2,4,2,0,2,4]triaconta-7,9,17,19,27,29-hexayne (12). A solution of **5**-$(SiMe_3)_2$ (710 mg, 5.5 mmol) in anhydrous and oxygen-free pyridine (45 mL) was dropped under nitrogen at 0 °C into a mixture of copper(I) chloride (35.0 g, 0.35 mol) and copper(II) chloride in anhydrous and oxygen-free pyridine. The addition was finished after 3 days, and the reaction mixture was kept stirring at 0 °C for and additional 9 days and then poured into a mixture of water (500 mL) and benzene (200 mL). The aqueous phase was extracted with three portions of benzene (200 mL each), and the combined organic phases were washed with three portions of 10% hydrochloric acid (250 mL each) and two portions of 10% NH_4Cl solution (250 mL each). After having dried over $MgSO_4$, the solvents were evaporated and the residue was chromatographed over silica gel (130 g; column, 5.5 × 12 cm) eluting with *n*-hexane/toluene (1:2).

Fraction I: $R_f = 0.80$; 40 mg; unidentified material.

Fraction II: $R_f = 0.70$; 207 mg; unidentified material.

Fraction III: $R_f = 0.60$; 153 mg; brownish solid; showing a molecular ion peak at *m/z* 384 (9.8), second unidentified component with *m/z* 494 (4.5). Flash chromatography of fraction III over silica gel (35 g; column, 2 × 26 cm) eluting with *n*-hexane/toluene (1:1.25) gave the following.

Fraction III.1: $R_f - 0.63$; 21 mg; slightly yellow solid; identical with the higher molecular weight component in fraction III. Its ^1H NMR spectrum (270 MHz, $CDCl_3$) showed signals only around δ 0.26 and 0.62

J. Am. Chem. Soc. **1991**, *113*, 3941–3949

and in the region δ 1.18–1.38, which could not be assigned.

Fraction III.2: $R_f = 0.39$; 65 mg; slightly yellow solid, which was impure according to its ^{1}H NMR spectrum. Recrystallization from acid-free methylene chloride (stored over Na_2CO_3) and *n*-hexane gave pure **12**: yield 15 mg (2.1%); white solid; ^{1}H NMR (270 MHz, C_6D_6) δ 0.10 (m, 12 H), 0.58 (m, 12 H); ^{13}C NMR (67.93 MHz, [d_2]methylene chloride, broad-band decoupling and DEPT) δ 13.15 (–), 17.09 (ϕ), 63.15 (ϕ), 81.50 (ϕ); IR (KBr pellet) 3100, 3020, 2245, 2160 (s), 2125 (w), 2082 (w), 1630 (br), 1425, 1310, 1182 (s), 1062, 1038, 1028, 978 (s), 940, 84 cm^{-1}; UV (methanol) λ_{max} (10 g ϵ) 226.8 nm (3.53), 239.5 (3.60), 252.6 (3.64), 267.5 (3.46); MS (70 eV) *m/z* 384 (9.8, M^+), 367 (15), 353 (40), 339 (73), 324 (100), 300 (60), 287 (34), 276 (23), 263 (20), 250 (16), 226 (16), 213 (13), 162 (15), 150 (17), 135 (16), 123 (16), 111 (18), 99 (23), 87 (33), 75 (35), 63 (39), 51 (35), 39 (43); HRMS exact mass for $C_{30}H_{24}$, calcd 384.1878, found 384.1876.

1,4-Dicyclopropylbutadiyne (4-H_2). To a solution of anhydrous copper(II) acetate (6.0 g, 33.1 mmol) in dry methanol/pyridine (1:1 v/v) (80 mL) was added ethynylcyclopropane (3-H_2) (1.0 g, 15.1 mmol) in dry methanol (1.0 mL), and the mixture was stirred at ambient temperature for 3 days. The reaction mixture was then poured into ice-cold 18 N sulfuric acid (100 mL) and extracted with two portions of diethyl ether (30 mL each). The combined organic layers were dried over $MgSO_4$, the solvents were distilled over a 40-cm packed column, and the residue was purified by Kugelrohr distillation (100 °C (0.1 Torr)): yield 560 mg (57%); 4-H_2; colorless liquid; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.63–0.81 (m, 8 H), 1.19–1.30 (m, 2 H); ^{13}C NMR (67.93 MHz, $CDCl_3$, broad-band decoupling) δ 0.07, 8.56, 61.08, 79.92; IR (film) 3090, 3020, 2240, 2190, 2160 cm^{-1}; UV (methanol) λ_{max} (log ϵ) 228.4 nm (2.91), 240.0 (3.10), 253.2 (3.18), 268 (3.00); MS (70 eV) *m/z* 130 (M^+), 128 ($M - H_2$), 115 ($M - CH_3$), 102 ($M - C_2H_4$).

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Supplementary Material Available: Crystallographic data on **12**, a stereoscopic view of the unit cell, tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters as well as UV spectra of **12** and 1,4-dicyclopropylbuta-1,3-diyne (10 pages); a table of observed and calculated structure factors for **12** (9 pages). Ordering information is given on any current masthead page.

Concerted Mechanism for Alcoholysis of Esters: An Examination of the Requirements

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Abstract: The application of an extension of Marcus theory to exchange reactions of carboxylic esters leads to results in agreement with the conclusions, based on structure reactivity studies, reported by Williams and co-workers (*J. Am. Chem. Soc.* **1989**, *111*, 2647), namely, that, for strongly acidic phenols (p*K*a < 1), exchange will proceed by a limiting mechanism involving an acylium ion in a very "exploded" transition state and, for weakly acidic phenols (p*K*a > 11), exchange will proceed by the tetrahedral intermediate mechanism, while for p*K*a values between these limits the reaction will be concerted, with no intermediate and simultaneous formation of the bond to the nucleophile and breaking of the bond to the leaving group. Further we conclude that, in essentially all reactions of aryl acetates, the reactions have no intermediates of significant lifetimes because of the very small intrinsic barriers for making or breaking a bond to aryl oxide ion. For alkoxide ions, the intrinsic barriers are higher but p*K*a-dependent so that we can predict a concerted reaction for alcohols of low p*K*a, if such could be devised. Hydroxide ion has a uniquely high intrinsic barrier for attack on carbonyl.

Introduction

Several mechanisms have been found for base-catalyzed ester alcoholysis or hydrolysis, depending on the structure of the ester and the reaction conditions. The overwhelming majority of mechanistic studies have been interpreted in terms of the tetrahedral intermediate mechanisms described in the IUPAC system[1] as SuAC following an $A_N + D_N$ mechanism, although other mechanisms are known in special cases: elimination addition mechanisms,[2] $D_HA_H + D_N + A_N + D_HA_H$; S_N2 at the alkyl carbon of the ester,[3] SuAL following an A_ND_N mechanism; S_N1 with alkyl oxygen cleavage is known, although normally only in acid solution,[4] SuAL following a $D_N + A_N$ mechanism; S_N1 with acyl oxygen cleavage is also known, but for esters is only encountered in acid,[5] although for acid chlorides it has been proposed for uncatalyzed reactions,[6–13] SuAC following a $D_N + A_N$ mechanism. Recently there has been considerable interest in the question of whether ester alcoholyses can be concerted,[14–20] i.e., whether an SuAC reaction can follow an A_ND_N pathway. Williams has proposed[17] a theory predicting when ester alcoholysis will be concerted and when it will go by the limiting stepwise reactions, either $D_N + A_N$ through an acylium ion or $A_N + D_N$ through a tetrahedral intermediate. We thought it would be of interest to see what

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