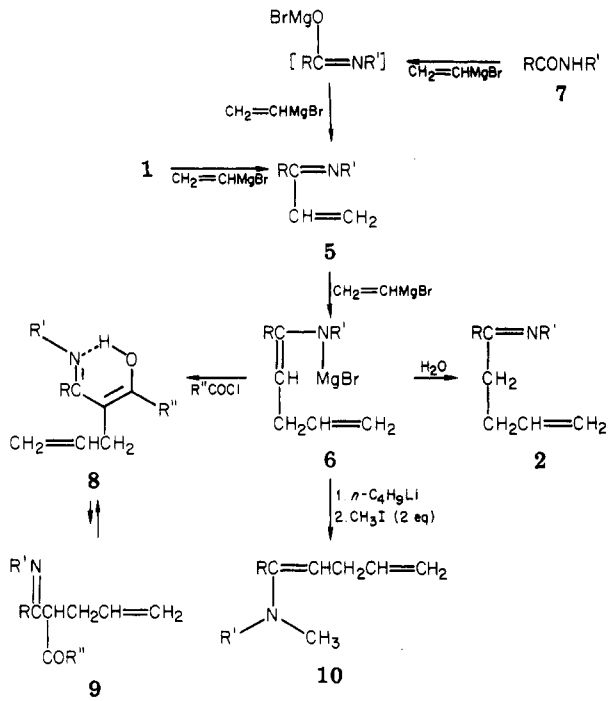
Scheme I



3 (R = Ph) and *p*-chloro-*N*-methylaniline. The formation of **10** is an exceptional case of N-alkylation of metallo enamines, since the latter generally experience C-alkylation.[5]

The following general procedure was used. To a vigorously stirred solution of **1** (1.70 mmol) in dry THF (15 mL) was added, in one portion, 3.50 mmol of vinylmagnesium bromide in 4 mL of THF. The reaction was exothermic, and the color of the solution became red-brown. After 30 min, the reaction mixture was poured into water and extracted with ether, and the ether extract was dried ($MgSO_4$) and concentrated. Analytically pure **2** was obtained by distillation or recrystallization. For the preparation of the enol imines **8**, an acid chloride was added to the red-brown solution, and the reaction mixture was stirred for 8–10 min and then poured into water. The methylated compound **10** was obtained by first adding 1.5 equiv of *n*-butyllithium to the red-brown solution (cooled to −78 °C), and then, after gradual warming to room temperature, methyl iodide (2 equiv) in THF (2 mL) was added dropwise. After being stirred for 30–60 min, the solution was worked up in the usual manner.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council for support of this work.

Registry No. 1 (R = Ph; R′ = *p*-ClC_6H_4), 34918-76-8; 1 (R = *p*-BrC_6H_4; R′ = Ph), 68695-50-1; 1 (R = R′ = *p*-ClC_6H_4), 29955-57-5; 2 (R = Ph; R′ = *p*-ClC_6H_4), 76173-06-3; 2 (R = *p*-BrC_6H_4; R′ = Ph), 76173-07-4; 3 (R = Ph), 3240-29-7; 3 (R = *p*-BrC_6H_4), 76173-08-5; 3 (R = *p*-ClC_6H_4), 35204-91-2; 4 (R = Ph; R′ = *p*-ClC_6H_4), 2866-82-2; 6 (R = Ph; R′ = *p*-ClC_6H_4), 76173-09-6; 7 (R″ = CH_3), 75-36-5; 7 (R″ = Ph), 98-88-4; 7 (R″ = $CH_3CH{=}CH$), 10487-71-5; 8 (R = Ph; R′ = *p*-ClC_6H_4; R″ = Ph), 76173-10-9; 8 (R = Ph; R′ = *p*-ClC_6H_4; R″ = $CH_3CH{=}CH$), 76173-11-0; 8 (R = Ph; R′ = *p*-ClC_6H_4; R″ = CH_3), 76173-12-1; 10 (R = Ph; R′ = *p*-ClC_6H_4), 76173-13-2; vinyl bromide, 593-60-2.

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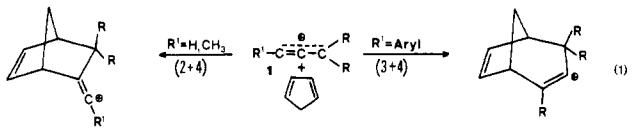
Stepwise [2 + 2] and [3 + 2] "Cycloaddition" Reactions of Allenyl Cations with Olefins

Summary: Propargyl halides $R^1C{\equiv}CCHalR^2R^3$ and olefins react under zinc halide catalysis to give α-halobenzylidenecyclobutanes (R^1 = phenyl) or 1-halocyclopentenes (R^1 = methyl).

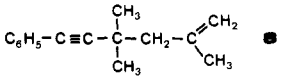
Sir: Allenyl cations (**1**) have been established as reactive intermediates in solvolysis reactions of allenyl and propargyl derivatives;[1] they can be observed as stable species in superacidic solutions.[2] Recently we demonstrated their ability to undergo [2 + 4] and [3 + 4] cycloadditions with cyclopentadiene (eq 1).[3] In this paper we report the Lewis



(1)

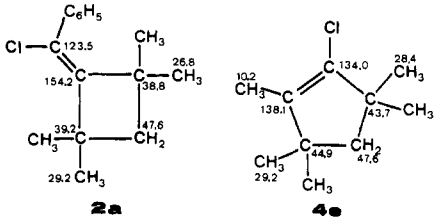
acid catalyzed formation of vinylcyclobutanes **2** and cyclopentenes **4** from propargyl halides **3** and olefins via stepwise [2 + 2] and [3 + 2] cycloadditions of intermediate allenyl cations **1** (Scheme I).

Vinyl halides **2** and **4** are accessible in moderate to good yields when equimolar mixtures of propargyl halides **3** and olefins are treated with the homogenous catalyst system 1:1.5 $ZnHal_2$–Et_2O in methylene chloride.[4] Best yields were usually obtained when **3** and 1–2 equiv of olefin in methylene chloride solution were added to the catalyst at −78 °C and subsequently warmed up to 0 °C (Table I). In addition to **2a** and **2b**, reactions a and b (Table I) yielded mixtures of enynes (~20%) from which **8** was isolated as the major component.[5]



8

Methylenecyclobutanes **2** and cyclopentenes **4** can be differentiated on the basis of their ^{13}C NMR spectra. As expected from increment calculations,[6] the vinylic resonances are very similar in the cyclopentenes (**4e**, Δ = 4.1 ppm) but differ considerably in the benzylidenecyclobutanes (**2a**, Δ = 30.7 ppm).



2a **4e**

In the mass spectra, the cyclobutanes **2** are characterized by strong peaks corresponding to ions **1**, whereas this type of fragmentation is not observed for cyclopentenes **4**. Treatment of **2b** with silver trifluoroacetate in ether and subsequent alkaline hydrolysis gave cyclobutyl phenyl ketone **9**;[7] the cyclopentene framework in compounds **4** was

(1) Schiavelli, M. D.; Germroth, T. C.; Stubbs, J. W. *J. Org. Chem.* **1976**, *41*, 681 and references cited therein.
(2) Richey, H. G., Jr.; Philips, J. C.; Rennick, L. E. *J. Am. Chem. Soc.* **1965**, *87*, 1382. Richey, H. G., Jr.; Rennick, L. E.; Kushner, A. S.; Richey, J. M.; Philips, J. C. *Ibid.* **1965**, *87*, 4017. Pittman, C. U., Jr.; Olah, G. A. *Ibid.* **1965**, *87*, 5632. Olah, G. A.; Spear, R. J.; Westerman, P. W.; Denis, J.-M. *Ibid.* **1974**, *96*, 5855.
(3) (a) Mayr, H.; Grubmüller, B. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 130. (b) Mayr, H.; Halberstadt, I. K. *Ibid.* **1980**, *19*, 814.
(4) For a description of the catalyst see ref 3b.
(5) For **8**: ^1H NMR (CCl_4) δ 1.30 (s, $C(CH_3)_2$), 1.98 (s, CH_3), 2.24 (s, CH_2), 4.82 and 4.91 (br s, $=CH_2$), 7.27 (mc, C_6H_5).
(6) Hesse, M.; Meier, H.; Zeeh, B. "Spektroskopische Methoden in der organischen Chemie"; Georg Thieme Verlag: Stuttgart, 1979; p 234.

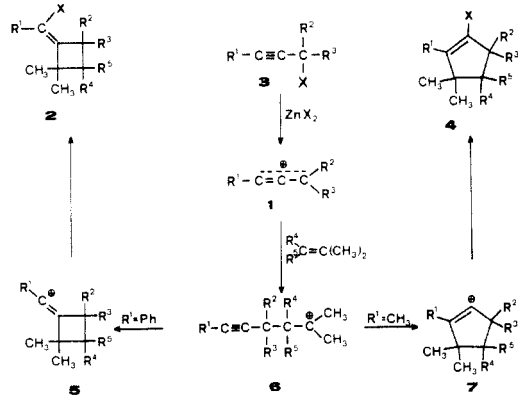
0022-3263/81/1946-1041$01.25/0

Table I. Cyclic Vinyl Halides from Propargyl Halides and Olefins

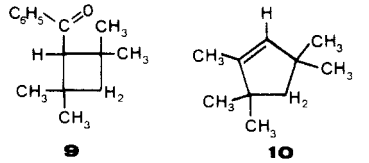
	R^1	R^2	R^3	R^4	R^5	X	yield, %[a] 2	yield, %[a] 4	bp (torr) or mp, °C	reaction conditions: time, h	reaction conditions: temp, °C	^{1}H NMR (CCl_4), δ
a	Ph	CH_3	CH_3	H	H	Cl	53	*c*	75-80[b] (0.05)	0.5 1	−50 −10	0.99 (s, 6 H), 1.42 (s, 6 H), 1.63 (s, 2 H), 7.22 (s, 5 H)
b	Ph	CH_3	CH_3	H	H	Br	26	*c*	40-41.5	15 7	−78 0	0.99 (s, 6 H), 1.43 (s, 6 H), 1.64 (s, 2 H), 7.23 (s, 5 H)
c	Ph	CH_3	CH_3	CH_3	H	Cl	62		90-95[b] (0.12)	7 3	−78 −45	0.87 (s, 3 H), 0.90 (d, 3 H), 0.93 (s, 3 H), 1.30 (s, 3 H), 1.42 (s, 3 H), 1.88 (q, 1 H), 7.26 (s, 5 H)
d	Ph	Ph	H	CH_3	CH_3	Cl	62		52-53.5	15 4	−78 0	0.67 (s, 3 H), 0.86 (s, 3 H), 1.05 (s, 3 H), 1.23 (s, 3 H), 3.97 (s, 1 H), 7.23 (s, 5 H), 7.3-7.5 (m, 5 H)
e	CH_3	CH_3	CH_3	H	H	Cl		38	53-56 (12)	24 15	−78 0	1.07 (s, 6 H), 1.10 (s, 6 H), 1.62 (s, 3 H), 1.73 (s, 2 H)
f	CH_3	CH_3	CH_3	CH_3	H	Cl		26	70-75 (12)	48 15	−78 20	0.75 (s, 3 H), 0.78 (s, 3 H), 0.87 (s, 3 H), 0.91 (s, 3 H), 0.81 (d, 3 H), 1.50 (s, 3 H), ~1.5 (q, 1 H)

[a] Isolated yield of pure material. [b] Bath temperature. [c] Side products 22% and 21% **8** (see text).

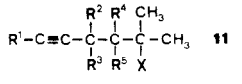
Scheme I



corroborated by Li–*t*-BuOH reduction of **2a** to give a compound (**10**) with a vinyl singlet in the ^{1}H NMR spectrum.[8]



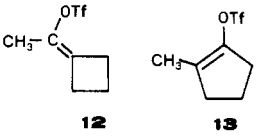
Vinyl cations **5** and **7**, from which **2** and **4** are deduced, may be formed via concerted or stepwise cycloaddition of **1** with olefins. The isolation of **8** as a side product indicates a stepwise mechanism with cation **6** as an intermediate. When the reactions were carried out at −78 °C and stopped by addition of aqueous ammonia before the temperature was raised, tertiary halides **11** were isolated as major products. Treatment of **11** with zinc halides at elevated temperatures yielded vinyl halides **2** and **4**.



11

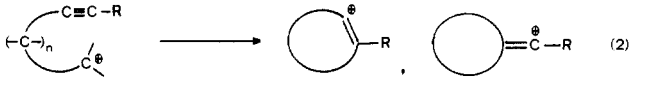
These experiments demonstrate that allenyl cations **1** initially add to olefins with formation of carbenium ions **6**, which are trapped by halide ions to yield the linear adducts **11**. The specific formation of 1:1 addition products from **3** and olefins is possible because the educts **3** ionize faster than the products **11**.[9]

Ionization of **11** regenerates cations **6** which undergo cyclization to **5** and **7** at elevated temperatures. For R^1 = phenyl, formation of **5** is preferred because phenyl is attached directly to the carbenium center. Systems with $R^1 = CH_3$ cyclize to *endo*-vinyl cations **7**,[10] since alkyl stabilization of the positive charge is not sufficient to overcome the cyclobutane ring strain in **5**. This result is in accord with a previous report that solvolysis of triflate **12** gives 50% ring-enlarged products whereas solvolysis of **13** yields 2-methylcyclopentanone exclusively.[11]



12 **13**

Rearrangements of **6** to either **5** or **7** fill a white spot on the map; whereas π cyclizations with attack at the triple bond (eq 2) are well-known for $n = 1$ (homopropargyl



(2)

rearrangement)[12] and $n \geq 3$,[13] to our knowledge these are the first examples for $n = 2$. This reaction type is probably

(7) For **9**: IR (neat) 1670 cm^{-1} (C=O); ^{1}H NMR (CCl_4) δ 1.22 (s, 2 CH_3), 1.29 (s, 2 CH_3), 1.69 (s, CH_2), 3.63 (s, CH), 7.32–7.97 (m, C_6H_5).

(8) For **10**: ^{1}H NMR (CCl_4) δ 1.04 (s, 2 $C(CH_3)_2$), 1.57 (br s, CH_3), 1.62 (s, CH_2), 4.97 (br s, CH).

(9) For rules for electrophilic alkylations of olefins see: Mayr, H. *Angew. Chem., Int. Ed. Engl.*, in press.

(10) Since 1-cyclopentenyl cations have been demonstrated to be highly unstable (see ref. 13, p 282), **7** may only exist in an ion pair.

(11) Hanack, M.; Schleyer, P. v. R.; Martinez, A. G. *An. Quim.*, **1974**, *70*, 941.

(12) Hanack, M.; Häffner, J.; Herterich, I. *Tetrahedron Lett.* **1965**, 875. Hanack, M.; Bocher, S.; Herterich, I.; Hummel, K.; Vött, V. *Justus Liebigs Ann. Chem.* **1970**, *733*, 5. Hanack, M.; Bässler, T.; Eymann, W.; Heyd, W. E.; Kopp, R. *J. Am. Chem. Soc.* **1974**, *96*, 6686. Stutz, H.; Hanack, M. *Tetrahedron Lett.* **1974**, 2457. Collins, C. J.; Benjamin, B. M.; Hanack, M.; Stutz, H. *J. Am. Chem. Soc.* **1977**, *99*, 1669.

(13) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979; p 123–147.

elusive under "normal" solvolytic conditions, because cyclization is slower than trapping of **6** by the nucleophilic solvent. In our system, however, the reaction of **6** with halide ions is a reversible process, and **11** can be converted to the thermodynamically more stable isomers **2** and **4**.

Acknowledgment. We thank Professor P. v. R. Schleyer for discussions and the Deutsche Forschungsgemeinschaft for financial support.

Registry No. 2a, 76173-69-8; **2b**, 76173-70-1; **2c**, 76173-71-2; **2d**, 76173-72-3; **3a**, 3355-29-1; **3b**, 75111-04-5; **3d**, 76173-73-4; **3e**, 999-79-1; **4e**, 76173-74-5; **4f**, 76173-75-6; **8**, 76173-76-7; **9**, 76173-77-8; **10**, 76173-78-9; 2-methyl-1-propene, 115-11-7; 2-methyl-2-butene, 513-35-9; 2,3-dimethyl-2-butene, 563-79-1.

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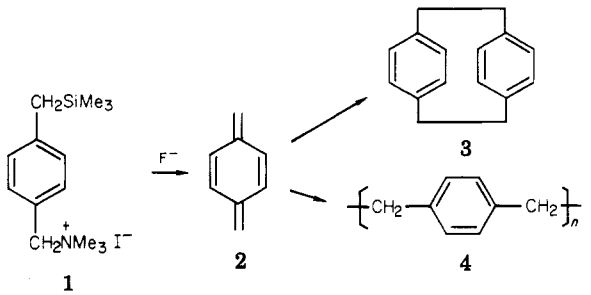
Fluoride-Induced 1,6-Elimination to *p*-Quinodimethane. A New Preparative Method for [2.2]Paracyclophane, [2.2](2.5)Furanophane and [2.2](2.5)Thiophenophane

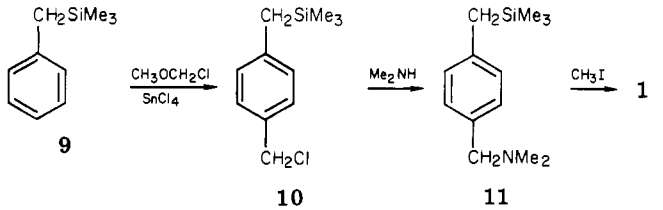
Summary: Fluoride anion induced 1,6-elimination of [*p*-[(trimethylsilyl)methyl]benzyl]trimethylammonium iodide provides a convenient method for preparation of [2.2]paracyclophane, [2.2](2.5)furanophane, and [2.2](2.5)thiophenophane.

Sir: In the pioneering studies on *p*-quinodimethane,[1] Fawcett[1a,b] and Errede[1c] reported that the Hofmann degradation of (*p*-methylbenzyl)trimethylammonium hydroxide and also the pyrolysis of *p*-xylene afforded [2.2]paracyclophane (**3**) in low yields together with poly-*p*-xylylene (**4**). Recently, we described[2] a novel and versatile method for the generation of *o*-quinodimethanes, in which [*o*-[(trimethylsilyl)methyl]benzyl]trimethylammonium iodide was treated with fluoride anion at room temperature.

We now report that 1,6-elimination of [*p*-[(trimethylsilyl)methyl]benzyl]trimethylammonium iodide (**1**)[3] was also induced by fluoride anion to furnish [2.2]paracyclophane (**3**) and poly-*p*-xylylene (**4**), either of which was



Scheme I



obtained as a major product under a choice of reaction conditions. An application of this methodology to [5-[(trimethylsilyl)methyl]furfuryl]trimethylammonium iodide (**5**) and [5-[(trimethylsilyl)methyl]thenyl]trimethylammonium iodide (**6**) also gave [2.2](2.5)furanophane (**7**)[1a] and [2.2](2.5)thiophenophane (**8**).[1a]

The simple and mild generation of *p*-quinodimethane resulting in the formation of [2.2]paracyclophane (**3**) and poly-*p*-xylylene (**4**) is illustrated as follows. To a refluxing solution of 155 mg (0.43 mmol) of [*p*-[(trimethylsilyl)-methyl]benzyl]trimethylammonium iodide (**1**)[3] in 10 mL of acetonitrile, was added dropwise a solution of 134 mg (0.51 mmol) of tetrabutylammonium fluoride in 10 mL of acetonitrile over 2 h. The reaction mixture was filtered to remove a small amount of insoluble poly-*p*-xylylene (**4**), and the filtrate was evaporated in vacuo. The residue was triturated with ether and filtered, and the filtrate was evaporated to give [2.2]paracyclophane (**3**) in 56% (25 mg) yield, which was identified by comparison of its spectral data with those of the authentic sample.[1] Similar treatment of [*p*-[(trimethylsilyl)methyl]benzyl]trimethylammonium iodide (**1**) with tetrabutylammonium fluoride at room temperature afforded 51% poly-*p*-xylylene (**4**)[1c] with ca. 6% **3**. Use of *p*-[(trimethylsilyl)methyl]benzyl chloride (**10**) instead of **1** in the reaction with tetrabutylammonium fluoride in acetonitrile at reflux gave [2.2]paracyclophane (**3**, 29%) and poly-*p*-xylylene (**4**, 20%).

The starting material **1**[3] can be readily prepared by starting with the para-selective chloromethylation of benzyltrimethylsilane (**9**)[4] followed by reaction with dimethylamine and quaternization with methyl iodide of the resulting [*p*-[(trimethylsilyl)methyl]benzyl]dimethylamine (**11**)[5] as shown in Scheme I.

The fluoride anion induced 1,6-elimination of [5-[(trimethylsilyl)methyl]furfuryl]trimethylammonium iodide (**5**)[6] and [5-[(trimethylsilyl)methyl]thenyl]trimethylammonium iodide (**6**)[6] also provided a simple and convenient method for the preparation of [2.2][(2.5)-furanophane (**7**)[1a] and [2.2](2.5)thiophenophane (**8**).[1a]

On treatment of **5** with tetrabutylammonium fluoride in refluxing acetonitrile according to the procedure mentioned above, [2.2](2.5)furanophane (**7**) was produced in a low yield. The NMR spectrum of the reaction mixture

(1) (a) Winberg, H. E.; Fawcett, F. S.; Mochel, W. E.; Theobald, C. W. *J. Am. Chem. Soc.* **1960**, *82*, 1428. (b) Winberg, H. E.; Fawcett, F. S. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 883. (c) Errede, L. A.; Gregorian, R. S.; Hovt, J. M. *J. Am. Chem. Soc.* **1960**, *82*, 5218. (d) Brown, G. W.; Sondheimer, F. *J. Am. Chem. Soc.* **1967**, *89*, 7116.

(2) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 863.

(3) **1**: mp 229–230 °C; NMR (CD_3CN, Me_4Si) δ 0.06 (s, 9 H), 2.10 (s, 2 H), 3.20 (s, 9 H), 4.85 (s, 2 H), 7.25 (AA'BB', 4 H).

(4) Hauser, C. R.; Hance, C. R. *J. Am. Chem. Soc.* **1951**, *73*, 5846.

(5) [*p*-[(Trimethylsilyl)methyl]benzyl]dimethylamine (**11**) was further elaborated by lithiation at the benzylic carbon bearing the silicon group (2 equiv of TMEDA and 2 equiv of *n*-BuLi in THF; 0 °C to room temperature; 3 h) and subsequent alkylation to yield [*p*-[(α-trimethylsilyl)-alkyl]benzyl]dimethylamine in good yield, of which quaternization with methyl iodide may provide a precursor of α-alkyl-*p*-quinodimethane. **11**: bp 110–111 °C (5 mmHg); NMR (CCl_4, Me_4Si) δ 0.00 (s, 9 H), 2.03 (s, 2 H), 2.16 (s, 6 H), 3.27 (s, 2 H), 6.93 (AA'BB', 4 H).

(6) **5** and **6** were prepared via (dimethylamino)methylation[7] of furfuryltrimethylsilane and thenyltrimethylsilane, which were synthesized by nickel-catalyzed coupling reaction[8] of 2-bromofurane and 2-bromothiophene with [(trimethylsilyl)methyl]magnesium chloride, respectively.

(7) Eliel, E. L.; Fisk, M. T. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 626.

(8) Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374.

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