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.

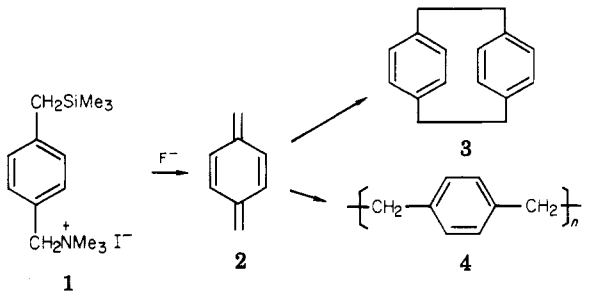
**Herbert Mayr,* Brigitte Seitz**
**Inge K. Halberstadt-Kausch**
*Institut für Organische Chemie der*
*Friedrich-Alexander-Universität*
*Erlangen-Nürnberg, Henkestr. 42, D-8520 Erlangen*
*West Germany*
*Received October 10, 1980*

## 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

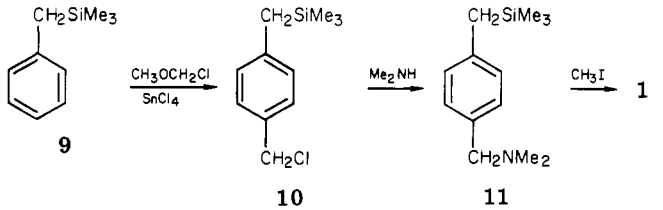
*Summary:* Fluoride anion induced 1,6-elimination of [*p*-[(trimethylsilyl)methyl]benzyl]trimethylammonium iodide provides a convenient method for preparation of [2.2]paracyclophane, [2.2](2.5)furanophane, and [2.2](2.5)thiophenophane.

*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 ($CD_3CN$, $Me_4Si$) $\delta$ 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 ($CCl_4$, $Me_4Si$) $\delta$ 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).

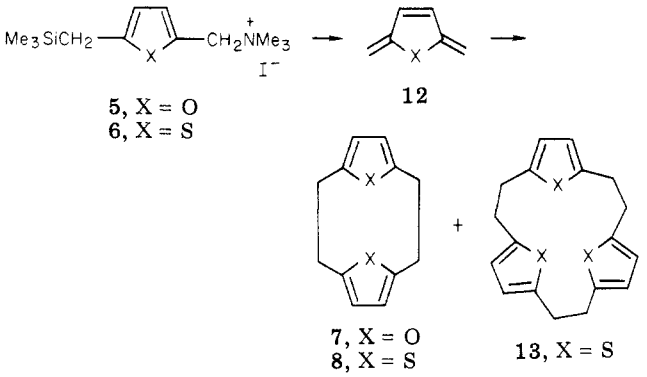
(6) **5** and **6** were prepared via (dimethylamino)methylation[7] of furfuryltrimethylsilane and thenyltrimethylsilane, which were synthesized by nickel-catalyzed coupling reaction[8] of 2-bromofurane and 2-bromothiophene with [(trimethylsilyl)methyl]magnesium chloride, respectively.

(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.

0022-3263/81/1946-1043$01.25/0 

indicated that 2,5-dimethylene-2,5-dihydrofuran intermediate (12, X = O)[9] was generated and existed in the mixture under the reaction conditions. When the mixture of 5 and tetrabutylammonium fluoride was heated at 110 °C for 4 h in a sealed tube, cyclodimerization of 12 (X = O) initially formed took place to give a 73% yield of [2.2](2.5)furanophane (7), whose structure was confirmed by comparison of NMR and IR spectra with those reported.[1a]



5, X = O
6, X = S

12

7, X = O
8, X = S

13, X = S

In the reaction of 6 with tetrabutylammonium fluoride[10] in acetonitrile at reflux, a mixture of [2.2](2.5)thiophenophane (8, 37%) and cyclic trimer (13,[12] 14%) of 2,5-dimethylene-2,5-dihydrothiophene (12, X = S) was produced, which was separable by preparative TLC. The former was identified by comparison of its spectral data with those reported[1a] and by its mass spectrum.[11] The latter was assigned by its NMR and mass spectra.[12]

Further work to prepare a variety of cyclophane derivatives by the present methodology is in progress.

**Registry No.** 1, 76233-23-3; 2, 502-86-3; 3, 1633-22-3; 4, 25722-33-2; 5, 76233-24-4; 6, 76233-25-5; 7, 5088-46-0; 8, 7075-88-9; 9, 770-09-2; 10, 18001-37-1; 11, 76233-26-6; 12 (X = O), 13314-90-4; 12 (X = S), 66806-34-6; 13, 65038-09-7; tetrabutylammonium fluoride, 429-41-4.

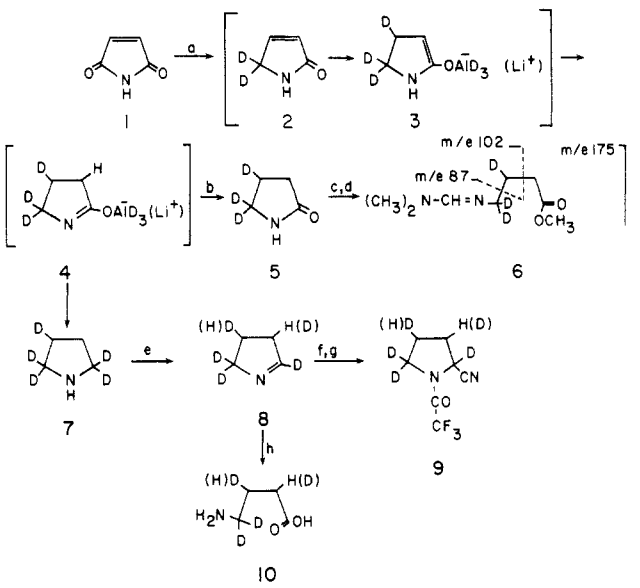
(9) Trahanovsky, W. S.; Park, M. G. *J. Org. Chem.* **1974**, *39*, 1448.
(10) Use of CsF in place of tetrabutylammonium fluoride in the reaction with 6 gave 8 and 13 in 43% and 17% yields, respectively.
(11) 8: white needles; TLC (silica gel, 3:1 hexane–$CHCl_3$) $R_f$ 0.44; mp 194–197 °C (lit.[1a] mp 194.5–196 °C); NMR ($CDCl_3$, $Me_4Si$) δ 3.04 (AA'BB' m, 8 H), 6.75 (s, 4 H); UV ($C_2H_5OH$) $\lambda_{max}$ 245 nm (ε 6.7 × $10^3$), 274 (5.0 × $10^3$); mass spectrum, *m/e* (relative intensity) 220 (24), 110 (100).
(12) 13: yellow solid; TLC (silica gel, 3:1 hexane–$CHCl_3$) $R_f$ 0.32; mp 126.5–127 °C; NMR ($CDCl_3$, $Me_4Si$) δ 3.01 (s, 12 H), 6.60 (s, 6 H); UV ($C_2H_5OH$) $\lambda_{max}$ 240 nm (ε 19.8 × $10^3$); mass spectrum, *m/e* (relative intensity) 330 (100), 220 (36), 110 (61).

**Yoshihiko Ito, Satoru Miyata**
**Masashi Nakatsuka, Takeo Saegusa***
*Department of Synthetic Chemistry*
*Faculty of Engineering*
*Kyoto University*
*Yoshida, Kyoto 606, Japan*
*Received September 22, 1980*

## Rearrangement of an Exchangeable Hydrogen during the Reduction of Maleimide with Lithium Aluminum Hydride

*Summary:* Reduction of maleimide with $LiAlD_4$ yields pyrrolidine containing five C–D bonds rather than the expected six. N-Deuterated maleimide results in pyrrolidine-*3-d*. These results are consistent with the migration of hydrogen from nitrogen to carbon. This is an example where reduction is favored over abstraction of an active hydrogen.

Scheme I



[a] (a) $LiAlD_4$; (b) $H_2O$; (c) 5 N HCl; (d) dimethylformamide dimethyl acetal; (e) $Na_2S_2O_8$, NaOH; (f) HCN; (g) $(CF_3CO)_2O$; (h) rabbit liver homogenate.

*Sir:* Attempted preparation of pyrrolidine-*2,2,3,4,5,5-d*$_6$ by the reduction of maleimide with lithium aluminum deuteride surprisingly resulted in pyrrolidine containing only 5 C–D bonds. Although it is generally accepted that the first step in the reaction of compounds containing active hydrogen atoms with metal hydrides is the liberation of $H_2$,[1] our findings indicate that the reduction of maleimide with $LiAlH_4$ does not take this course. The results are consistent with a hydrogen rearrangement from nitrogen to carbon and thus provide an example where reduction is favored over active proton abstraction.

Reduction was carried out in refluxing tetrahydrofuran with excess $LiAlD_4$ for 16 h. Quenching the reaction with either $H_2O$ or $D_2O$ resulted in the same product. GC–MS analysis of the *N*-trifluoroacetyl derivative of the pyrrolidine formed indicated that it contained 95% $d_5$ and 5% $d_6$ and the loss of deuterium from $M^+$. No significant $(M - H)^+$ could be observed, indicating the presence of four deuterium atoms in the α positions of 7.

Additional evidence that the positions α to the nitrogen were completely labeled was gained by the analysis of oxidation products. Thus, 1-pyrroline (8), prepared by the sodium persulfate oxidation[2,3] of the product, on treatment with cyanide[4] followed by trifluoroacetic anhydride yielded 9 which, by GC–MS analysis, showed the presence of four deuterium atoms. Further oxidation of 8 by a rabbit liver homogenate[3] resulted in the formation of labeled 4-aminobutanoic acid (10) containing three deuterium atoms. Analysis following derivatization with dimethylformamide dimethyl acetal to form labeled methyl 4-(*N,N*-dimethyl-*N'*-formamidino)butanoate[5] showed that 4 con-

(1) Brown, W. G. *Org. React.* **1951**, *6*, 469–509.
(2) Nomura, Y.; Ogawa, K.; Takenchi, Y.; Tomoda, S. *Chem. Lett.* **1977**, 693–696.
(3) Callery, P. S.; Nayar, M. S. B.; Geelhaar, L. A.; Stogniew, M.; Jakubowski, E. M. *Biomed. Mass Spectrom.*, in press.
(4) Bonnett, R.; Clark, V. M.; Giddey, A.; Todd, A. *J. Chem. Soc.* **1959**, 2087–2093.
(5) Callery, P. S.; Stogniew, M.; Geelhaar, L. A. *Biomed. Mass Spectrom.* **1979**, *6*, 23–26.

0022-3263/81/1946-1044$01.25/0 