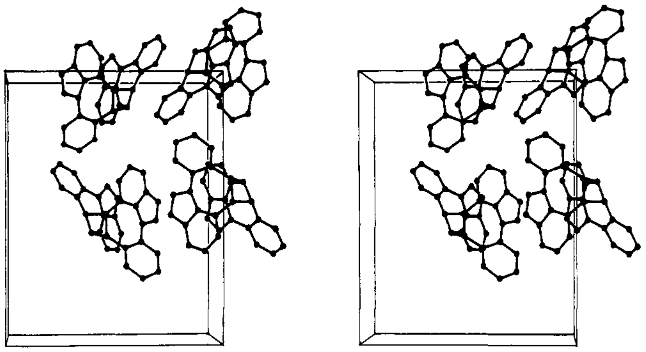

**Figure 3.** Stereoscopic views of a unit cell of **5**, with b axis horizontal and c axis vertical.

actually present. The spectrum of **5** is unfortunately insensitive to the four-bond couplings, since $J_{6,7}$ is sufficiently close in value to $J_{6,7'}$ that no lines other than those expected from an $A_2B_2$ spectrum were observed.[11]

The aromatic proton peaks of **4** and **5** (see Experimental Section) are almost all upfield of those in the spectrum of dihydro **1**,[12] which might have suggested that **4** and **5** are syn. Assignments on this basis were not considered safe in the absence of a good model for the anti dimers of **1**; **3** is not a good model as the electronic situation and geometry around the nitrogen are so different. Compared to those of **5**, the indole protons (on C1–C5) of **4** all absorb downfield and most of the other aromatic protons absorb upfield; this suggests that in solution, as in the crystals, the aromatic systems in each half of **4** are more nearly coplanar with one another than are the corresponding systems in **5**.

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**Registry No.** 1, 202-01-7; 4, 90669-98-0; 5, 90669-99-1.

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[11] Günther, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 861.

[12] Hallberg, A.; Dahlgren, T.; Martin, A.; Christensen, K. *J. Heterocycl. Chem.* **1983**, *20*, 37.

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# Reactions of 2,3-Dimethylenebutadiene Dianion with Electrophiles. Synthesis and Conformations of 2,3-Disubstituted-1,3-butadienes

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Reactions of 2,3-dimethylenebutadiene dianion **1** with monofunctional electrophiles were found to provide the best routes to symmetrically substituted 1,3-butadienes such as **2c**–**n**. Evidence that at least some of these reactions go by single electron-transfer mechanisms is presented. Possible mechanisms for the formation of some unusual byproducts are discussed. Reactions of **1** with dichlorides and dibromides were found to provide the best routes to most 1,2-dimethylenecycloalkanes **3**, the corresponding dimers **4** and trimers **5**, and 1,1-dimethyl-3,4-dimethylene-1-metallacyclopentanes **26**. From their UV spectra, the dienes **2** contain about 60% transoid conformations, except 2,3-dimethyl-1,3-butadiene (**2a**) which shows about 100% and 2,3-dineopentyl-1,3-butadiene (**2h**) which shows about 30%. 1,2-Dimethylenecycloalkanes **3** display cisoid conformations in rings smaller than 9-membered and transoid conformations in rings larger than 11. When the ring size exceeds 15, the homoallylic methylene groups on both sides are also anti coplanar. With rings larger than about 30, the next methylene group on each side is also anti coplanar, and when the ring size exceeds about 45, an additional methylene on each side is anti coplanar.

Dianion **1** (Chart I) has been prepared in 70–80% yield by metalating 2,3-dimethyl-1,3-butadiene (**2a**) as judged by the conversion of **1** to **2b** with $D_2O$ and to **2d** with diethyl sulfate.[2] We report that symmetrical 2,3-disubstituted 1,3-butadienes like **2**–**5** can be synthesized in two-step, one-pot reactions. The mechanisms by which these reactions occur, the byproducts which were found, and the preferred conformations of dienes **2**–**5** are discussed below.

## Reactions of Dianion 1 with Monofunctional Electrophiles

As can be seen from the first four entries in Table I, sulfates give higher yields than the corresponding halides; this is presumably because the sulfates go by an $S_N2$ mechanism, whereas the halides go at least partly by single electron transfer (SET) which can lead to other than

**Table I. Yields of Products from Dianion 1 and Monofunctional Electrophiles**

| electrophile | products (yield from **2a**) |
|---|---|
| MeI | **2c** (43) |
| $Me_2SO_4$ | **2c** (61) |
| EtBr | **2d** (43) |
| $Et_2SO_4$ | **2d** (71)[2] |
| *n*-PrBr | **2e** (34) |
| *n*-BuBr | **2f** (30) |
| *i*-PrBr | **2g** (41); **6a** (3); **7g** (2) |
| *t*-BuBr | **2h** (15); **6a** (12); **7h** (15); **4**, *n* = 4 (15) |
| *t*-BuI | **2h** (20); **6a** (14); **7h** (5); **4**, *n* = 4 (16) |
| allyl chloride | **2i** (70); **6i** (10) |
| $PhCH_2Cl$ | **2j** (53); $PhCH_2CH_2Ph$ (22) |
| $PhCH_2Br$ | **2j** (21), $PhCH_2CH_2Ph$ (30) |
| $Me_3SiCl$ | **2k** (47) |
| $Me_3GeBr$ | **2l** (54); **6l** (5); **8** (4) |
| $Me_3SnCl$ | **2m** (32); **6m** (6) |
| $Me_3PbCl$ | **2n** (30) |

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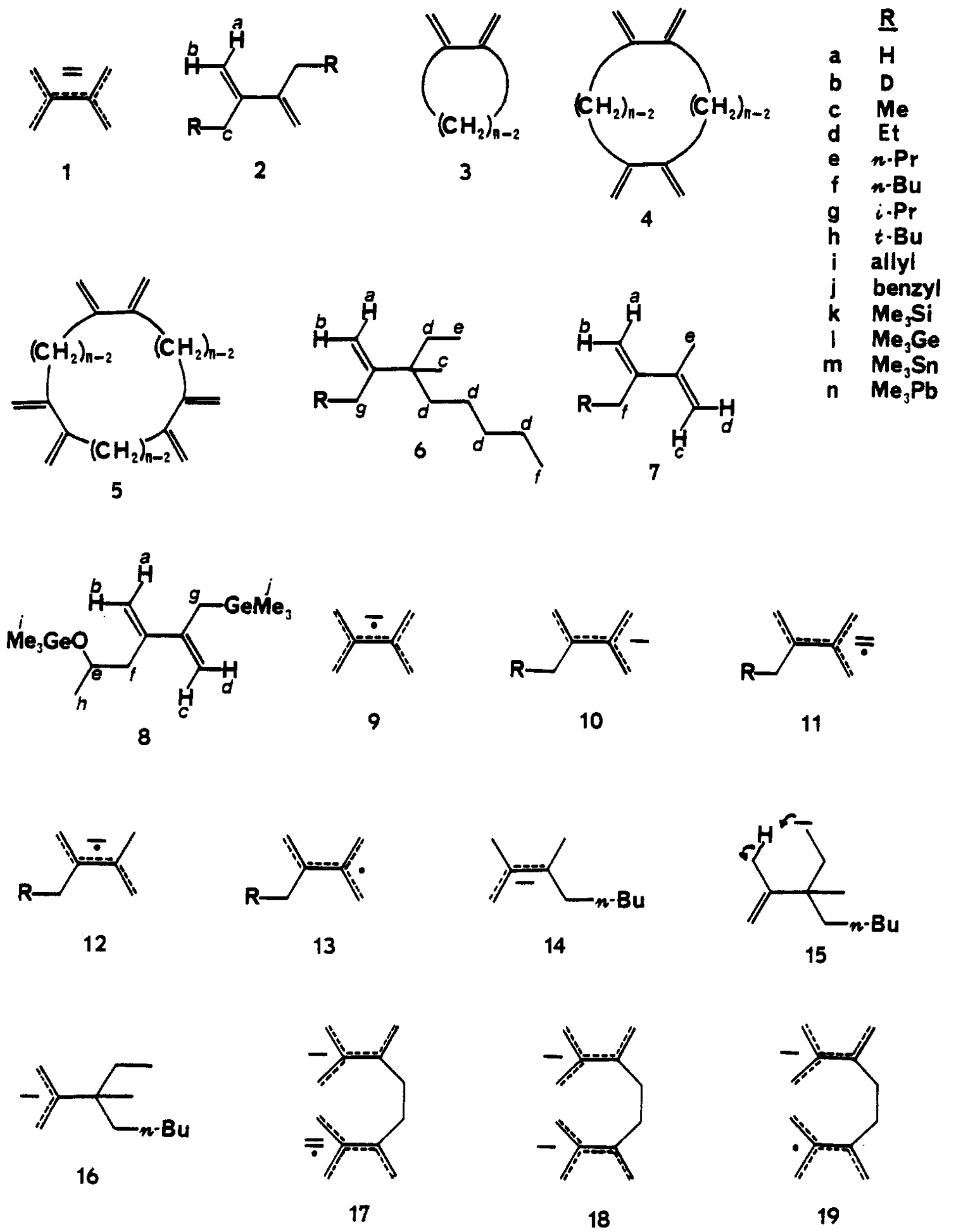
[1] Current address: Department of Materials Science, Pennsylvania State University, University Park, PA 16802.

[2] Bahl, J. J.; Bates, R. B.; Gordon, B., III *J. Org. Chem.* **1979**, *44*, 2290.

Chart I



|   | R |
|---|---|
| a | H |
| b | D |
| c | Me |
| d | Et |
| e | *n*-Pr |
| f | *n*-Bu |
| g | *i*-Pr |
| h | *t*-Bu |
| i | allyl |
| j | benzyl |
| k | $Me_3Si$ |
| l | $Me_3Ge$ |
| m | $Me_3Sn$ |
| n | $Me_3Pb$ |

substitution products.[3] The yields with *n*-PrBr and *n*-BuBr were slightly lower than those with EtBr.

Isopropyl bromide reacted as well as the primary halides used. This reaction, like that of allyllithium with 2-bromooctane (which gave 100% inversion of configuration), probably goes largely by an $S_N2$ mechanism.[4]

*tert*-Butyl bromide and iodide reacted to give dialkylation product 2,3-dineopentyl-1,3-butadiene (**2h**), monoalkylation product **7h**, and oxidative dimer 4 ($n = 4$); *tert*-butyl chloride gave none of these. A few other carbanions have been *tert*-butylated successfully with *tert*-butyl bromide.[5] $S_N2$ mechanisms are presumably ruled out by steric considerations, as are $S_N1$ mechanisms (at least in the present case) since *tert*-butyl halides should not ionize appreciably under the conditions used (below 25 °C, nonpolar solvent); thus SET mechanisms are indicated. The finding of oxidative dimer **4** ($n = 4$) shows that some SET is occurring from dianion to *tert*-butyl bromide and iodide; the resulting *tert*-butyl halide anion radicals would decompose very rapidly to halide ions and *tert*-butyl radicals,[4] which could couple with anion radical **9** to give **10h**,[6] precursor of **2h** and **7h**, or perhaps combine, with the much more abundant dianion **1** to give **11h**,[7] thereby initiating an $S_{RN}1$ generation of **10h**.[8] The conversion of **10h** into **2h** involves as an intermediate either

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[3] Primary alkyl iodides and bromides react with alkyllithiums to give coupling products which show CIDNP effects, showing these products to result at least partly from SET mechanisms: Lawler, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 5519. Ward, H. R.; Lawler, R. G.; Cooper, R. A. *Ibid.* **1969**, *91*, 746. Lepley, A. R.; Landau, R. L. *Ibid.*, **1969**, *91*, 748.

[4] Guthrie, R. D. In Buncel, E.; Durst, D. "Comprehensive Carbanion Chemistry", New York: Elsevier, 1980 p 197.

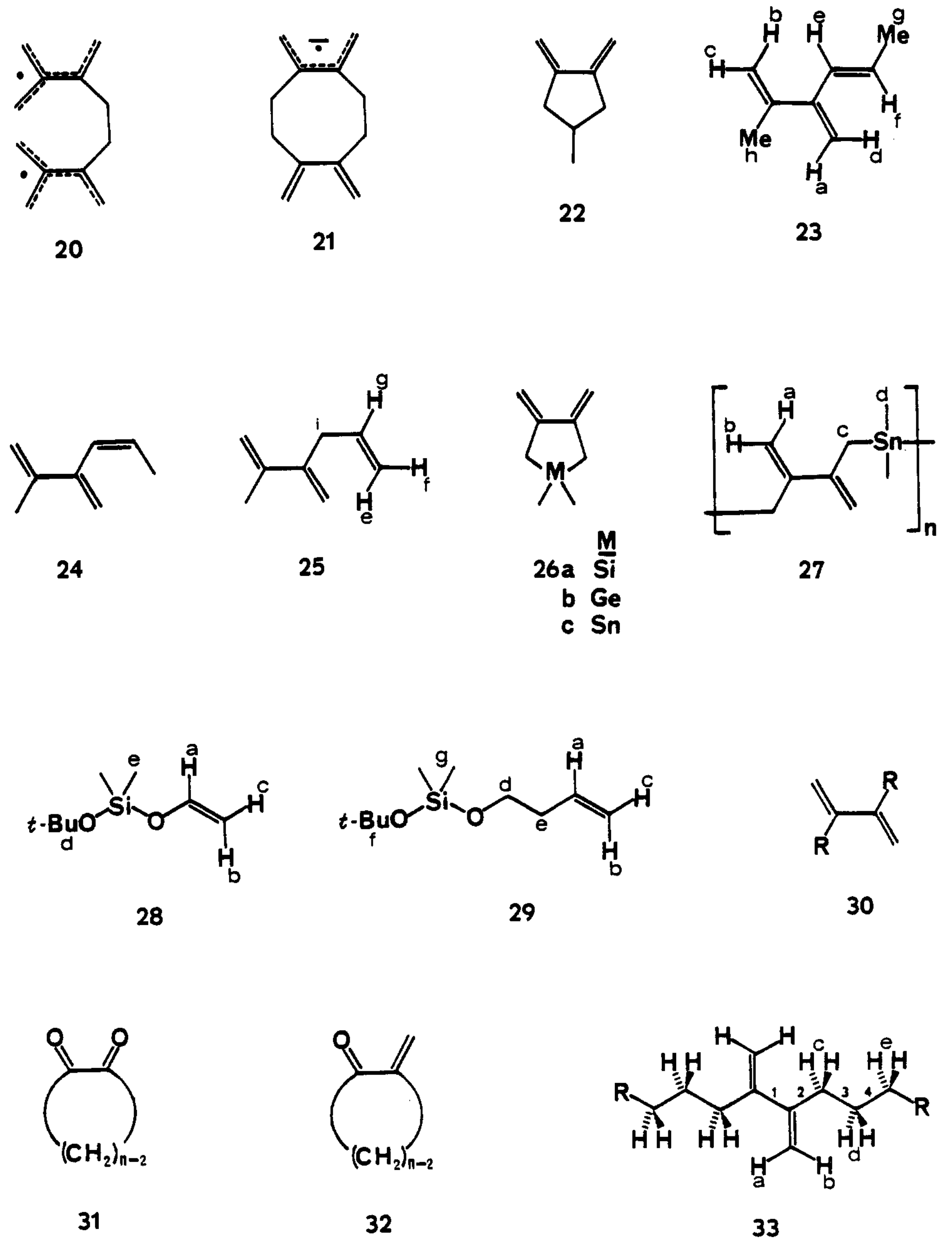
[5] (a) Cyclopentadienyl anion: Alder, K.; Ache, H. J. *Chem. Ber.* **1962**, *95*, 503. (b) Heteroatom-containing anions: Deuchert, K.; Hertenstein, U.; Hünig, S. *Synthesis* **1973**, 777. Kristensen, L. H.; Lund, H. *Acta Chem. Scand. Ser. B* **1979**, *B33*, 735. Ashe, A. J., III; Deiphouse, T. R.; El-Sheikh, M. Y. *J. Am. Chem. Soc.* **1982**, *104*, 5693.

[6] 2-Vinylallyl anions, intermediates in several reactions,[2] have been recently prepared in high concentration (Ogle, C. A., private communication).

[7] Dianion radicals generated by addition of an electron to an anion (Bauld, N. L.; Brown, M. S. *J. Am. Chem. Soc.* **1967**, *89*, 5417) and by removal of an electron from a trianion (Bahl, J. J.; Bates, R. B.; Beavers, W. A.; Launder, C. R. *J. Am. Chem. Soc.* **1977**, *99*, 6126) have been observed by ESR.

[8] Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413. Alder, R. W. *J. Chem. Soc., Chem. Commun.* **1980**, 1184.

Chart II



**12h** if the mechanism is $S_{RN}1$ or **13h** if it is radical–radical coupling. While we have no evidence to distinguish radical–radical couplings from $S_{RN}1$ paths, it should be noted that the latter should be more favorable in this case than in earlier cases involving less delocalized carbanions because this case involves a *diene* anion radical with resonance stabilization.

The coupling with allyl chloride to produce **2i** is virtually quantitative from dianion **1**.

Benzyl chloride gave much more dialkylation product **2j** than did benzyl bromide. The failure to find oxidative dimer **4** ($n = 4$) suggests that SET is not significant in these cases; we favor $S_N2$, accompanied by some halogen–metal exchange[9] to benzyl anion, which has a very high resonance energy.[10] More benzyl anion is expected from the bromide;[9] it can undergo $S_N2$ reactions with benzyl halide to give bibenzyl or with an allylic halide to give **2j**.

$Me_3SiCl$, $Me_3GeBr$, $Me_3SnCl$, and $Me_3PbCl$ all reacted in higher yield than $Me_3CX$, presumably by $S_N2$–Si mechanisms.[11]

Unexpected products **6a**, **6i**, **6l**, and **6m** were identified from the indicated reactions, and products of this type may have been present in the other reactions. We believe them to arise from initial *addition* of butyl anion to **2a**,[2] giving **14**, which adds to ethylene formed from cleavage of tetrahydrofuran (THF)[12] to give **15**. **15** undergoes intramolecular proton transfer to yield allyl anion **16**, which reacts with various electrophiles to give products **6**. An analogous radical pathway is also possible, but we favor the anion pathway depicted because there is precedent for an allyl anion with primary and tertiary end carbons reacting exclusively at the tertiary center.[13]

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[9] Winkler, H. J. S.; Winkler, H. *J. Am. Chem. Soc.* **1966**, *88*, 964, 969.

[10] Benzyl anion has a calculated resonance energy per atom (REPA) of 0.092 (B. A. Hess, Jr., private communication). The REPA of **1** is 0.062 (Bates, R. B.; Hess, B. A., Jr.; Ogle, C. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1981**, *103*, 5052).

[11] Corriu, R. J. P.; Lanneau, G. F. *J. Organomet. Chem.* **1974**, *67*, 243.

[12] Bates, R. B.; Kroposki, L. M.; Potter, D. E. *J. Org. Chem.* **1972**, *37*, 560.

**Table II. Yields of Products from Dianion 1 and Dihalides**

| dihalide | products (yield from 2,3-dimethyl-1,3-butadiene$^a$) |
|---|---|
| $ClCH_2Cl$ | **3**, $n = 5$ (12) |
| $BrCH_2Br^b$ | **3**, $n = 5$ (5); **4**, $n = 4$ (11) |
| $Cl(CH_2)_2Cl$ | **3**, $n = 6$ (19) |
| $Br(CH_2)_2Br$ | **3**, $n = 6$ (0); **4**, $n = 4$ (0), **6a** (12), **2f** (7) |
| $Br(CH_2)_3Br$ | **3**, $n = 7$ (18); **4**, $n = 4$ (1); **2i** (6) |
| $Br(CH_2)_4Br$ | **3**, $n = 8$ (18); **6a** (2) |
| $Br(CH_2)_5Br$ | **3**, $n = 9$ (15) |
| $Br(CH_2)_6Br^b$ | **3**, $n = 10$ (20) |
| $Br(CH_2)_7Br^b$ | **3**, $n = 11$ (2); **4**, $n = 11$ (2) |
| $Br(nCH_2)_8Br^b$ | **3**, $n = 12$ (2); **4**, $n = 12$ (7); **5**, $n = 12$ (3) |
| $Br(CH_2)_9Br^b$ | **3**, $n = 13$ (4); **4**, $n = 13$ (2); **5**, $n = 13$ (1) |
| $Br(CH_2)_{10}Br^b$ | **3**, $n = 14$ (5); **4**, $n = 14$ (3); **5**, $n = 14$ (1) |
| $Br(CH_2)_{12}Br^b$ | **3**, $n = 16$ (8); **4**, $n = 16$ (4); **5**, $n = 16$ (2) |
| $MeCHCl_2$ | **22** (6); **23** (7); **24** (1); **25** (2) |
| $Me_2SiCl_2$ | **26a** (30) |
| $Me_2GeCl_2$ | **26b** (32); **6a** (3) |
| $Me_2SnCl_2$ | **26c** (30) |

[a] Products were separated by GC or LC; the yields given here were estimated by $^1H$ NMR analysis of the crude reaction mixture after a known amount of benzene or dichloromethane had been added. [b] Simultaneous addition was used in these cases and inverse addition in the other cases.

Oxidative dimer **4** ($n = 4$) is probably formed by SET pathways. Anion radical **9** can combine with dianion **1** to give **17** or dimerize to give **18**; further oxidation gives **19**, which may cyclize to **21** or oxidize further to **20** (Chart II) which then cyclizes to **1**. Anion radical–anion radical coupling of **9** seems more likely for the first bond formation and $S_{RN}1$ coupling involving the sequence $18 \rightarrow 19 \rightarrow 21 \rightarrow 4$ ($n = 4$) appears better for the second bond formation.

Byproduct **8** may arise by the addition of **10l** to the oxygen-bearing carbon of $Me_3GeOCH{=}CH_2$, formed from enolate ion from the cleavage of THF.[12]

## Reactions of Dianion 1 with Dihalides

The yields of cyclic monomers **3** in Table II vary from 0% to 20%.[14] From the first and third entries, dichlorides give substantially better yields than dibromides; presumably the yields of **3** ($n = 7$–14, 16) would also be higher if the dichlorides were used. The preparations of **3** ($n = 5$–14, 16 were all carried out at least twice, and the 2% yield reported for **3** ($n = 12$) represents the best of many efforts; this was the only example in which dimer **4** ($n = 12$) and even trimer **5** ($n = 12$) were obtained in greater yield than monomer **3** ($n = 12$). Dimers and trimers, which, except for **4** ($n = 4$),[15] are new, were found when LC was used for isolation, and were probably formed but not detected in the cases where GC was used. The yield of cyclic monomer **3** drops dramatically when $n$ reaches 11, is similarly low for $n = 12$, and slowly increases as ring size increases further through $n = 16$. Though our yields are low, the availability of starting materials and shortness of the procedure probably make this the method of choice for the preparation of **3** ($n = 5$–16) except for $n = 6$[14d] and $n = 12$.[14e,16]

Byproducts identified are also given in Table II. Oxidative dimer **4** ($n = 4$), a byproduct observed in the reaction of **1** with *tert*-butyl bromide, was formed in significant amounts only with $BrCH_2Br$. With $Br(CH_2)_3Br$, **2i**, the product of **1** with allyl chloride, was obtained as a byproduct resulting from elimination. With $MeCHCl_2$, besides the desired product **22**, elimination products **23**–**25** were observed; these probably result from concerted intramolecular eliminations from the monoanion intermediate, with five- and seven-membered ring transition states.

The desired heterocyclic products **26a**–**c** were readily obtained from higher group IV dichlorides. The tin product **26c** rapidly underwent spontaneous ring opening to homopolymer **27** after GC purification.

Byproduct **6a** was observed in more than 3% yield only in the case of $Br(CH_2)_2Br$, which forms ethylene in addition to the ethylene formed by cleavage of THF.[12] An unexpected byproduct in the $Br(CH_2)_2Br$ reaction was **2f**.

When 30% excess KO-*t*-Bu was used in the reaction with $Me_2SiCl_2$, **28** (25%) and **29** (4%) were formed and the yield of **26a** dropped to 22%. **28** and **29** arise from $\alpha$- and $\beta$-cleavage products of THF,[12] respectively.

## Conformations of 2,3-Disubstituted-1,3-butadienes

From their UV and NMR parameters (Table III), dienes **2** all have largely transoid conformations except for **2h**, whose diene system is significantly twisted. All of the compounds in Table III have $\lambda_{max}$ values of about 228 nm except **2k**–**m**, whose heteroatoms cause bathochromic shifts, and **30h**, which does not attain a *transoid* conformation for steric reasons. The $\epsilon_{max}$ of 21 900 of **2a** indicates it to be transoid almost all of the time.[19] The $\epsilon_{max}$ values of **2c**–**d**,**g** of ~12 500 show roughly 60% transoid conformations. **2h**, with neopentyl groups, has $\epsilon_{max}$ 6500, which suggests it to be transoid only about 30% of the time; it either does not easily attain a cisoid conformation or reaches a sterically hindered one, since it did not make a maleic anhydride adduct under conditions where **7h** and **4** ($n = 4$) did. **30g** and **30h**, which have even more difficulty reaching the planar diene conformations, are included in Table III for comparison purposes. The heteroatom-containing compounds **2k**–**n** with their long heteroatom to carbon bonds should not be as sterically hindered as **2h** and thus should have higher percentages of transoid conformations, as indicated by their large extinction coefficients.

Of the NMR parameters, $\delta H_a$ and $\delta H_b$ are the most revealing. Their values are essentially constant for all structures **2** with R = *n*-alkyl groups larger than methyl. **2g**, with isobutyl groups, has values only slightly different from the *n*-alkyl compounds, but the parameters of the neopentyl compound **2h** differ greatly in the direction of those of the grossly twisted *tert*-butyl compound **30h**: $\delta H_a$ goes downfield and $\delta H_b$ goes upfield. $\delta H_b$ values for the

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[13] Seyferth, D.; Mammarella, R. E. *J. Organomet. Chem.* **1978**, *156*, 279.

[14] 1,2-Dimethylenecycloalkanes **3** have been prepared by a variety of methods, all involving numerous steps: (a) $n = 3$: Bloch, R.; LePerchec, P.; Conia, J. M. *Angew. Chem.* **1970**, *82*, 810. (b) $n = 4$: Blomquist, A. T.; Verdol, J. A. *J. Am. Chem. Soc.* **1959**, *84*, 1257. Hoover, F.; Lindsay, R. *J. Org. Chem.* **1969**, *34*, 3051. (c) $n = 4$–6: Blomquist, A. T.; Verdol, J. A. *J. Am. Chem. Soc.* **1955**, *77*, 1806. Blomquist, A. T.; Wolinsky, J.; Meinwald, Y. C.; Longone, D. T. *Ibid.* **1956**, *78*, 6057. Blomquist, A. T.; Longone, D. T. *Ibid.* **1957**, *79*, 3916. (d) $n = 6$: Baldwin, J. E.; Chang, G. E. C. *J. Org. Chem.* **1982**, *47*, 848. (e) $n = 6$–8, 12: van Straten, J. W.; van Norden, J. J.; van Schalk, T. A. M.; Franke, G. T.; de Wolf, W. H.; Bickelhaupt, F. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 105. (f) $n = 12$: Klein, E.; Thömel, F.; Roth, A.; Strume, H. *Liebigs Ann. Chem.* **1973**, *11*, 1797.

[15] **4** ($n = 4$) has been prepared in three steps from **3** ($n = 4$): Borden, W. T.; Sharpe, L.; Reich, I. L. *J. Chem. Soc., Chem. Commun.* **1970**, *8*, 461.

[16] Cyclododecanone, the starting material for Bickelhaupt's preparation of **3** ($n = 12$),[14e] is readily available and gave the *highest* yield of the cyclic ketones used.

[17] DeGroot, A.; Evenhuis, B.; Wynberg, H. *J. Org. Chem.* **1968**, *33*, 2214.

[18] Wynberg, H.; DeGroot, A.; Davies, D. W. *Tetrahedron Lett.* **1963**, *17*, 1083.

[19] Dienes constrained to transoid conformations by ring systems have $\epsilon_{max}$ ~20 000 (Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectroscopic Identification of Organic Compounds", 4th ed.; New York: Wiley 1981; p 313.

**Table III. UV and NMR Parameters for 2a, 2c–h, 2k–n, 30g, and 30h**

| | $\lambda_{max}$, nm | $\epsilon_{max}$ | $\delta H_a$ | $\delta H_b$ | $\delta H_c$ | $\delta H_d$ | $\delta H_e$ | others | $J_{ab}$, Hz | $J_{cd}$ | others |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **2a** | 228 | 21900 | 5.05 | 4.96 | 1.91 | | | | 1.0 | | |
| **2c** | 228 | 12800 | 5.07 | 4.94 | 2.27 | 1.07 | | | 1.0 | 7.4 | |
| **2d** | 228 | 12600 | 5.05 | 4.90 | 2.21 | 1.46 | 0.90 | | 1.0 | 7.2 | $J_{de} = 7.3$ |
| **2e** | 229 | 12000 | 5.05 | 4.91 | 2.23 | 1.43 | 1.33 | $\delta H_f = 0.91$ | 1.1 | 7.3 | $J_{ef} = 7.2$ |
| **2f** | | | 5.04 | 4.91 | 2.22 | 1.44 | 1.30 | $\delta H_f = 1.29$, $\delta H_g = 0.89$ | 0.9 | 7.5 | $J_{fg} = 6.8$ |
| **2g** | 231 | 11700 | 5.04 | 4.86 | 2.09 | 1.74 | 0.86 | | 0.9 | 6.7 | $J_{ac} = 0.5$, $J_{de} = 6.6$ |
| **2h** | 228 | 6500 | 5.14 | 4.73 | 2.15 | | 0.89 | | 2.6 | | |
| **2k** | 240 | 11700 | 4.91 | 4.72 | 1.74 | | −0.01 | | 1.1 | | |
| **2l** | 241 | 13800 | 4.85 | 4.74 | 1.88 | | 0.12 | | 1.0 | | |
| **2m** | 247 | 12700 | 4.75 | 4.75 | 1.95 | | 0.05 | | | | *a* |
| **2n** | | | 4.71 | 4.71 | 2.48 | | 0.72 | | | | |
| **30g**[17] | 223 | 6180 | 4.91 | 4.82 | 2.37 | 1.05 | | | 1.2 | 6.0 | |
| **30h**[18] | 185 | 6165 | 5.1 | 4.7 | | 1.1 | | | 1.5 | | |

[a] $J_{^{117}\mathrm{Sn-H_e}} = 52.9$, $J_{^{119}\mathrm{Sn-H_e}} = 51.2$, $J_{^{117,119}\mathrm{Sn-H_c}} = 63.5$, $J_{^{117,119}\mathrm{Sn-H_{ab}}} = 19.0$ Hz.

**Table IV. UV Data for 3 (*n* = 3–10, 12), 4 (*n* = 4, 14), 26b, and 2e**

| compd | $\lambda_{max}$, nm | $\epsilon_{max}$ | solvent | ref |
|---|---|---|---|---|
| **3**, *n* = 3 | 232 | 11000 | hexane | 14a |
| **3**, *n* = 4 | 248 | 10100 | EtOH | 22 |
| **3**, *n* = 5 | 248 | 10500 | isooctane | 14c |
| **3**, *n* = 6 | 220 | 5500 | hexane | 14c |
| | 220 | 6400 | EtOH | 22 |
| | 220 | 6375 | 95% EtOH | 23 |
| **3**, *n* = 7 | 235 | 5800 | EtOH | this work |
| **3**, *n* = 8 | 229 | 3700 | hexane | 14e |
| | 233 | 5800 | EtOH | this work |
| **3**, *n* = 9 | 225 | 7400 | EtOH | this work |
| **3**, *n* = 10 | 233 | 6950 | EtOH | this work |
| **3**, *n* = 12 | 230 | 7100 | hexane | 14e |
| **4**, *n* = 4 | 228 | 5000[a] | hexane | 15 |
| **4**, *n* = 14 | 228 | 12000[a] | hexane | this work |
| **26b** | 227 | 6400 | hexane | this work |
| **2e** | 228 | 12000 | hexane | this work |

[a] Per diene moiety.

series **2h,k–n** remain essentially constant, whereas $\delta H_a$ values for this series decrease unimformly; these trends probably result from a combination of inductive and through-space effects.

The preferred conformations of 1,2-cycloalkanediones **31**[20] and 2-methylenecycloalkanones **32**[21] have been studied as a function of ring size by using dipole moments. Diketones **31** are approximately cisoid up to *n* = 8 and approximately transoid with *n* ≥ 11, with *n* = 9 and 10 having intermediate conformations. Enones **32** are approximately cisoid up to *n* = 9 and approximately transoid with *n* ≥ 12; *n* = 10 was intermediate and *n* = 11 was not studied. The conformations of 1,2-dimethylenecycloalkanes **3** had not been systematically studied, though from UV and NMR data Bickelhaupt noted that the conformation of **3** (*n* = 12) was different from that of **3** (*n* = 6–8).[14e]

Table IV gives UV data for many 1,2-dimethylenecycloalkanes **3** and related compounds from the literature and from this work. **3** (*n* = 3) is probably very nearly coplanar cisoid, but the opening of the $CH_2{=}CC$ angles from 120° to about 150° makes it abnormal; similar opening of the corresponding angles in **3** (*n* = 4) to about 135° presumably lowers its $\lambda_{max}$ as well. **3** (*n* = 4, 5) have the highest $\lambda_{max}$ of the cisoid types; the $CH_2{=}CC$ angles are closer to 120° in the latter, but it is probably more twisted about the central diene bond. **3** (*n* = 6) is believed, based on its low $\lambda_{max}$ and low $\epsilon_{max}$ and its $^{13}C$ NMR parameters, to exist in a chair conformation with the central diene bond twisted about 55° from planar cisoid.[24] **26b**, with a germanium atom incorporated into a five-membered ring, has a ring size intermediate between **3** (*n* = 5) and **3** (*n* = 6) and intermediate values of $\lambda_{max}$ and $\epsilon_{max}$ as well. The $\lambda_{max}$ values of **3** (*n* = 7, 8) indicate them to be less twisted than **3** (*n* = 6). The $\lambda_{max}$ values of the medium-sized ring compounds **3** (*n* = 9, 10, 12) are not far from the 228 nm observed for acyclic model **2e** and 28-membered ring dimer **4** (*n* = 14), but the extinction coefficients of these medium-sized ring compounds are significantly lower, indicating that they do not spend as much time in planar transoid conformations. Eight-membered ring dimer **4** (*n* = 4) is similar to twisted cisoid monomers **3** (*n* = 6–8) in its UV absorption.

The $^1H$ NMR spectra of these compounds (Table V) were more informative regarding their conformations, especially for the larger ring sizes. The smaller ring compounds **3** (*n* = 3–10) show considerable variation in many of the NMR parameters as a function of ring size; in the cases of **3** (*n* = 3, 4 and perhaps 5) this is partly due to opening of the $CH_2{=}CC$ angle. In view of the smooth trends in $\delta H_a$ and $\delta H_b$ for the series **26a–c**, we have reversed the $\delta H_a$ and $\delta H_b$ values for **3** (*n* = 6) from the previously assigned values of δ 4.55 and 4.83, respectively,[21] to those in Table V. **26a–c**, with heteroatoms in the five-membered ring, can be considered to provide intermediate geometries between that of **3** (*n* = 5) and **3** (*n* = 6); $\delta H_a$ and $\delta H_b$ are strikingly similar for **3** (*n* = 6) and the tin compound **26c**, suggesting similar geometries for the diene systems in these compounds.

Since examination of molecular models rules out transoid conformations for **3** (*n* = 7, 8), these evidently have twisted cisoid conformations. The large change in $\delta H_a$ and $\delta H_b$ in going to **3** (*n* = 9) indicates a conformational change at this point, but a smooth trend of all of the NMR parameters to the clearly transoid values of the large rings is not observed until **3** (*n* = 13).

As the ring size increases, an exact match of all NMR parameters with the values of acyclic model **2e** is not reached until **5** (*n* = 16) with its 48-membered ring. This can be attributed to the requirement that the ring must be large enough to readily accommodate a segment **33**, rotated as shown about bonds 1–4, i.e., with 10 coplanar carbons in an extended chain. A study of space-filling models suggests that a 22-membered ring can adopt such

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**Table V.** $^1$H NMR Data for **3** ($n$ = 3–14, 16), **4** ($n$ = 4, 11–14, 16), **5** ($n$ = 12–14, 16), **26a–c**, and **2e**

| compd | ring size | $\delta H_a$[a] | $\delta H_b$ | $\delta H_c$ | $\delta H_d$ | other $\delta$H | $J_{ab}$[b] | "$J_{cd}$"[c] | other $J$'s |
|---|---|---|---|---|---|---|---|---|---|
| **3**, $n$ = 3[1a] | 3 | 5.50 | 5.27 | 1.56 | | | 0.9 | | $J_{ac}$ = 2.6, $J_{bc}$ = 1.7 |
| 4 | 4 | 5.15 | 4.71 | 2.63 | | | 0 | | |
| 5 | 5 | 5.35 | 4.89 | 2.43 | 1.67 | | 0 | 7.2 | $J_{ac} = J_{bc}$ = 2.1 |
| 6 | 6 | 4.92 | 4.63 | 2.25 | 1.62 | | 2.6 | ~5.7 | $J_{ac}$ = 1.3, $J_{bc}$ = 1.1 |
| 7 | 7 | 5.14 | 4.71 | 2.33 | 1.59 | 1.57 | 2.6 | ~3.5 | $J_{bc}$ = 1.1 |
| 8 | 8 | 5.09 | 4.76 | 2.32 | 1.59 | 1.57 | 2.4 | 5.5 | $J_{bc}$ = 0.7 |
| 9 | 9 | 4.95 | 4.95 | 2.30 | 1.52 | $H_e$ = 1.44, $H_f$ = 1.34 | 0 | 6.6 | $J_{bc}$ = 0.7 |
| 10 | 10 | 5.10 | 4.91 | 2.49 | 1.66 | $H_e$ = 1.45, $H_f$ = 1.36 | 1.5 | 6.1 | $J_{ab'}$ = 0.9 |
| 11 | 11 | 5.07 | 5.01 | 2.35 | 1.57 | 1.22–1.31 | 0.9 | 5.9 | |
| 12 | 12 | 5.08 | 4.98 | 2.36 | 1.38 | 1.23–1.34 | 1.1 | 5.6 | $J_{ab'}$ = 1.1 |
| 13 | 13 | 5.12 | 4.96 | 2.33 | 1.43 | ~1.28 | 1.0 | 6.2 | $J_{ab}'$ = 1.0 |
| 14 | 14 | 5.09 | 4.95 | 2.35 | 1.44 | 1.20–1.31 | 1.1 | 6.3 | $J_{ab'}$ = 1.1 |
| 16 | 16 | 5.03 | 4.93 | 2.29 | 1.44 | ~1.26 | 1.0 | 6.9 | |
| **4**, $n$ = 4 | 8 | 4.89 | 4.81 | 2.39 | | | 2.2 | | |
| 11 | 22 | 5.02 | 4.93 | 2.29 | 1.40 | 1.21–1.31 | 1.0 | 7.0 | |
| 12 | 21 | 5.01 | 4.91 | 2.27 | 1.40 | $H_e$ = 1.27, $H_{fg}$ = 1.21 | 1.0 | 6.8 | $J_{ab'}$ = 1.0 |
| 13 | 26 | 5.02 | 4.92 | 2.27 | 1.41 | ~1.23 | | 7.0 | |
| 14 | 28 | 5.02 | 4.91 | 2.26 | 1.41 | ~1.24 | 1.3 | 6.8 | $J_{ab'}$ = 1.3 |
| 16 | 32 | 5.01 | 4.89 | 2.23 | 1.42 | ~1.23 | | 7.2 | |
| **5**, $n$ = 12 | 36 | 5.03 | 4.90 | 2.23 | 1.41 | ~1.26 | | 7.3 | |
| 13 | 39 | 5.04 | 4.90 | 2.23 | 1.42 | ~1.26 | | 7.3 | |
| 14 | 42 | 5.04 | 4.90 | 2.23 | 1.42 | ~1.26 | | 7.3 | |
| 16 | 48 | 5.04 | 4.91 | 2.22 | 1.44 | ~1.26 | | 7.3 | |
| **26a** | 5 | 5.21 | 4.73 | 1.61 | | 0.14 | 1.8 | | $J_{ac}$ = 1.8, $J_{bc}$ = 1.6 |
| **26b** | 5 | 5.12 | 4.70 | 1.74 | | 0.32 | 2.1 | | $J_{ac}$ = 1.8, $J_{bc}$ = 1.8 |
| **26c** | 5 | 4.90 | 4.63 | 1.80 | | 0.30 | 1.6 | | $J_{ac}$ = 1.3, $J_{bc}$ = 1.9 |
| **2e** | ∞ | 5.05 | 4.91 | 2.23 | 1.43 | $H_e$ = 1.33, $H_f$ = 0.91 | 1.1 | 7.3 | $J_{ab'}$ = 1.1, $J_{ef}$ = 7.2 |

[a] See structure **33** for letter designations. [b] Coupling constants are in hertz. [c] These values were estimated from the approximate triplets observed for $H_c$.

a conformation, but the NMR evidence indicates that a much larger ring is necessary before such a conformation predominates to the extent that it does in acyclics.

$\delta H_d$ is the only parameter which changes between the 32-membered ring dimer **4** ($n$ = 16) and the acyclic model **2e**. Two further parameters, $\delta H_c$ and $J_{cd}$, change noticeably between the 28- and 32-membered rings, indicating significant deviation from the acyclic model involving rotation about bond 3 in **33**. Thus at a ring size of about 30, an extended chain two shorter than **33**, with 8 coplanar carbons, remains intact.

From the 16-membered ring monomer **3** ($n$ = 16) to larger ring sizes, little change occurs in $\delta H_a$, $\delta H_b$, and $\delta H_c$, suggesting that the conformations involving rotation about bonds 1 and 2 in **33** are similar to acyclic model **2e**, i.e., the intact extended chain now consists of six carbons.

Examination of molecular models indicates that these 6-carbon extended chains are unlikely to be maintained in rings smaller than 16, and the much larger changes in $\delta H_a$ and $\delta H_c$ which occur in **3** as n decreases from 16 to 12 suggest that this is the case. In **3** ($n$ = 12–14) the extended chain is now down to four carbons, i.e., rotation about bond 2 but not bond 1 in **33** is occurring.

Compounds **3** ($n$ = 9–11) have widely varying NMR parameters indicating conformational differences. $\delta H_d$ may be the best NMR parameter for distinguishing transoid from cisoid conformations: All of the compounds with $n \le 11$ have $\delta H_d \ge 1.52$, and all with $n \ge 12$ have $\delta H_d \le 1.44$. This parameter rules out appreciable amounts of transoid conformations for **3** ($n \le 11$); **3** ($n$ = 9–11) thus apparently have twisted cisoid conformations. **3** ($n$ = 9) from its low $\lambda_{max}$ as mentioned above is twisted more than most of the other compounds in the series but less than **3** ($n$ = 6); these UV results correlate well with these two compounds having by far the smallest values of $\delta H_a$. **3** ($n$ = 10) for some reason has unusually high values for $\delta H_c$ and $\delta H_d$.

In conclusion, the conformational preferences of the 1,2-dimethylenecycloalkanes **3–5** about bond 1 on **33** as a function of ring size as determined by UV and $^1$H NMR are similar to those determined for 1,2-cycloalkanediones **31** by dipole moment studies:[20] cisoid in rings smaller than 9-membered, and *transoid* in rings larger than 11. In addition, $^1$H NMR evidence indicates that as the ring size increases to 16, 30, and 45, rotational preferences about bonds 2, 3, and 4, respectively, in **3–5** become within experimental error of those in acyclic model **2e**.

## Experimental Section

NMR spectra were recorded in $CDCl_3$ on a Bruker WM-250 spectrometer. Mass spectra were run on a Finnigan 3300 Quadrupole GC/MS equipped with a column packed with 3% OV-17 on Chromosorb W-HP. UV spectra were measured on hexane solutions with a Varian Cary 219 spectrometer. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, or the University Analytical Center, Tucson. Melting points are uncorrected. GC was done on an Aerograph Model 700 using a column packed with 10% SE-30 on Chromosorb W-HP. For LC, a column peaked with LiChroprep Si60 was used with pentane as the solvent. THF was freshly distilled from Na/benzophenone. Pentane was washed with sulfuric acid and distilled from NaOH. Anion preparations and reactions were carried out under argon in oven-dried glassware. Anion transfers were done via syringe or cannula.

**Dianion 1** was prepared as previously described[2] except that LiO-*t*-Bu was removed by filtration and washing several times with pentane.

**Reactions of 1 with monofunctional electrophiles** were carried out by dropwise addition of a suspension of **1** prepared from 15 mmol of **2a** in 60 mL of THF at 0 °C to a stirred solution of electrophile (10% excess) in 200 mL of THF at 0 °C over 30 min. After warming to 25 °C, 100 mL of pentane was added and the solution was washed 5–10 times with water (or initially with NaCl or NaI solutions if emulsions formed) to remove salts and THF, dried over $MgSO_4$, filtered, and evaporated. Product yields were estimated from the NMR spectrum of the residue with the aid of an internal standard of $C_6H_6$, $CH_2Cl_2$, or dioxane. Volatile products were isolated and purified by GC after preliminary bulb-to-bulb distillation. Nonvolatile products were isolated and purified by LC.

**2c**,[25] **2d**,[2] **2e**,[26] **2k**,[27] and 4 ($n$ = 4)[15] have been prepared previously. UV and NMR parameters of **2a**, **2c–h**, **2k–n**, **30g**, and **30h** are given in Table III. Mass spectra consistent with the assigned structures were obtained on all new compounds.[28] All of the new compounds were liquids at 25 °C. Other properties of the new compounds are listed below.

**2f.** Anal. Calcd for C$_{14}$H$_{26}$: C, 86.52; H, 13.48. Found: C, 86.54; H, 13.46.

**2g.** Anal. Calcd for C$_{12}$H$_{22}$: C, 86.7; H, 13.3. Found: C, 86.8; H, 13.2.

**2h.**[29] Anal. Calcd for C$_{14}$H$_{26}$: C, 86.52; H, 13.48. Found: C, 86.44; H, 13.49.

**2i.** $^1$H NMR $\delta$H$_a$ = 5.09, H$_b$ = 4.95, H$_c$ = 2.34, H$_d$ = 2.21, H$_e$ = 5.83, H$_f$ = 5.02, H$_{f'}$ = 4.96; $J_{ab}$ = 0.7, $J_{cd}$ = 7.7, $J_{de}$ = 6.5, $J_{df}$ = 1.6, $J_{df'}$ = 1.2, $J_{ef}$ = 10.3, $J_{ef'}$ = 17.3 $J_{ff'}$ = 2.0 Hz. Anal. Calcd for C$_{12}$H$_{18}$: C, 88.82; H, 11.18. Found: C, 88.79; H, 11.20.

**2j**: $^1$H NMR $\delta$H$_a$ = 5.16, H$_b$ = 4.99, H$_c$ = 2.78, H$_d$ = 2.56, H$_{aryl}$ = 7.18–7.34; $J_{cd}$ = 8.0 Hz.

**2l.** Anal. Calcd for C$_{12}$H$_{26}$Ge$_2$: C, 45.68; H, 8.31. Found: C, 45.76; H, 8.35.

**2m**: mp −9 to −7 °C. Anal. Calcd for C$_{12}$H$_{26}$Sn$_2$: C, 35.35; H, 6.43. Found: C, 35.53; H, 6.45.

**6a**: $^1$H NMR $\delta$H$_a$ = 4.63, H$_b$ = 4.81, H$_c$ = 0.95, H$_d$ = 1.18–1.31, H$_e$ = 0.71, H$_f$ = 0.87, H$_g$ = 1.63; $J_{ab}$ = 0.9, $J_{ag}$ = 0.6, $J_{bg}$ = 1.6, $J_{de}$ = 6.9, $J_{df}$ = 7.5 Hz.

**6i**: $^1$H NMR $\delta$H$_a$ = 4.79, H$_b$ = 4.88, H$_c$ = 0.96, H$_d$ = 1.11–1.50, H$_e$ = 0.70, H$_f$ = 0.87, H$_g$ = 1.97, H$_h$ = 2.22, H$_i$ = 5.87, H$_j$ = 4.96, H$_{j'}$ = 4.99; $J_{ab}$ = 0.7, $J_{bg}$ = 1.3, $J_{de}$ = 6.9, $J_{df}$ = 7.0, $J_{gh}$ = 7.5, $J_{hi}$ = 6.5, $J_{hj}$ = 1.1, $J_{hj'}$ = 1.6, $J_{ij}$ = 10.1, $J_{ij'}$ = 17.2, $J_{jj'}$ = 2.0 Hz.

**6l**: $^1$H NMR $\delta$H$_a$ = H$_b$ = 4.64, H$_c$ = 0.91, H$_d$ = 1.14–1.34, H$_e$ = 0.69, H$_f$ = 0.85, H$_g$ = 1.54, H$_h$ = 0.15; $J_{de}$ = 6.9, $J_{df}$ = 7.5 Hz.

**6m**: $^1$H NMR $\delta$H$_a$ = H$_b$ = 4.57, H$_c$ = 0.92, H$_d$ = 1.12–1.38, H$_e$ = 0.70 H$_f$ = 0.85, H$_g$ = 1.67, H$_h$ = 0.08; $J_{de}$ = 6.8, $J_{df}$ = 7.5, $J_{^{117}\mathrm{Sn}-^{1}\mathrm{H}_h}$ = 53.0, $J_{^{119}\mathrm{Sn}-^{1}\mathrm{H}_h}$ = 51.2, $J_{^{117,119}\mathrm{Sn}-^{1}\mathrm{H}_g}$ = 70.0, $J_{^{117,119}\mathrm{Sn}-^{1}\mathrm{H}_{ab}}$ = 20.0 Hz.

**7g**: $^1$H NMR $\delta$H$_a$ = 5.09, H$_b$ = 4.90, H$_c$ = 5.04, H$_d$ = 4.96, H$_e$ = 1.90, H$_f$ = 2.13, H$_g$ = 1.78, H$_h$ = 0/.87, $J_{fg}$ = 6.8, $J_{gh}$ = 6.6 Hz.

**7h**: $^1$H NMR $\delta$H$_a$ = 5.19, H$_b$ = 4.85, H$_c$ = 5.08, H$_d$ = 4.94, H$_e$ = 1.91, H$_f$ = 2.21, H$_h$ = 0.89.

8: $^1$H NMR $\delta$H$_a$ = 5.12, H$_b$ = 5.01, H$_c$ = 4.94, H$_d$ = 4.78, H$_e$ = 3.86, H$_f$ = 2.57, H$_{f'}$ = 2.21, H$_g$ = 1.88, H$_h$ = 1.60, H$_i$ = 0.16, H$_j$ = 0.11; $J_{ef}$ = 2.9, $J_{ef'}$ = 9.2, $J_{ff'}$ = 13.8 Hz.

**Reactions of Danion 1 with Dihalides.** Inverse addition or simultaneous addition of dianion to dihalide was used; where both methods were tried, simultaneous addition gave equal or better yeilds of the desired products. A simultaneous addition procedure follows.

A suspension of dianion 1 (17.7 mmol) in THF (60/ mL) was added dropwise via syringe or cannula to stirring THF (200 mL) while dihalide (17.7 mmol) in THF (50 mL) was added simultaneously at 0 °C via an addition funnel over about 40 min. The best results were obtained when addition of dihalide was slightly ahead (mixture yellow rather than orange). The mixture was allowed to warm to 25 °C with stirring, pentane (200 mL) was added, and the mixture was extracted with 2 × 350 mL of 1 M NaCl (or NaI, in cases of severe emulsions) to remove salts and THF. After filtering over Celite to remove polymers, the pentane solution was washed with 6 × 350 mL of water to remove further THF. After drying (MgSO$_4$), filtering, and evaporating, the residue was separated by LC (**3**, $n$ = 11–16) or by evaorative distillation followed by GC.

**3**, **4**, and **5** for each value of $n > 6$ were cleanly separated from one another by LC. All of the monomers **3** ($n > 6$) had virtually the same LC retention time. The dimers **4** had the same (longer) retention time as one another; the same was true for trimers **5**. Dimers 4 ($n$ = 12, 14, 16) were all solids with mp 60–61 °C, and all of the other compounds were liquids. UV and $^1$H NMR data for **3–5**, **26**, and **2e** are given in Tables IV and V, respectively.[28,30]

**4-Methyl-1,2-dimethylenecyclopentane (22)** was purified by GC: $^1$H NMR $\delta$ 5.34 (2 H, s, H$_a$), 4.86 (2 H, s, H$_b$), ~2.04 (4 H, m, H$_c$), 1.06 (1 H, m, H$_d$), 0.99 (3 H, d, $J$ = 5.9 Hz, H$_e$); MS, calcd for C$_8$H$_{12}$ 108, found 108. **23–25** occurred together in a later GC fraction but could be identified by their $^1$H NMR spectra. **(*E*)-4-Methylene-5-methyl-2,5-hexadiene (23)**: $\delta$H$_a$ = 5.04, H$_b$ = 5.02, H$_c$ = 4.99, H$_d$ = 4.96, H$_e$ = 6.14, H$_f$ = 5.82, H$_g$ = 1.78, H$_h$ = 1.91, $J_{ef}$ = 15.4, $J_{eg}$ = 1.6, $J_{fg}$ = 6.6 Hz. *Z* isomer 24: $\delta$H$_g$ = 1.70, H$_h$ = 1.94,[31] $J_{eg}$ = 1.8, $J_{fg}$ = 6.9 Hz. **2-Methyl-3-methylene-1,5-hexadiene (25)**: $\delta$H$_a$ = 5.15, H$_b$ = 5.10, H$_c$ = H$_d$ = 5.00, H$_e$ = 5.07, H$_f$ = 5.05, H$_g$ = 5.90, H$_h$ = 1.92, H$_i$ = 3.03, $J_{ad}$ = 0.5, $J_{ai}$ = 1.3, $J_{eg}$ = 17.3, $J_{fg}$ = 10.4, $J_{gi}$ = 6.6 Hz; MS for mixture of **23–25**, calcd for C$_8$H$_{12}$ 108, found 108.

**1,1-Dimethyl-3,4-dimethylene-1-silacyclopentane (26a)** after GC had MS: calcd for C$_8$H$_{14}$Si 138, found 138.

Anal. Calcd for C$_8$H$_{14}$Si: C, 69.49; H, 10.20. Found: C, 69.26; H, 10.21.

**1,1-Dimethyl-3,4-dimethylene-1-germacyclopentane (26b)** purified by GC had MS, calcd for C$_8$H$_{14}$$^{74}$Ge 184, found 184.

Anal. Calcd for C$_8$H$_{14}$Ge: C, 52.57; H, 7.72. Found: C, 52.72; H, 7.74.

**1,1-Dimethyl-3,4-dimethylene-1-stannacyclopentane (26c)** decomposed to polymer **27** slowly before GC and rapidly after GC. **26c** and **27**, a white solid, were characterized by $^1$H NMR, the latter by its close similarity to the spectrum of **2m**. **27**: $^1$H NMR $\delta$H$_a$ = H$_b$ = 4.75, H$_c$ = 1.96, H$_d$ = 0.02.

**(*tert*-Butoxydimethylsiloxy)ethene (28)** was separated from **26a** and **29** by GC: $^1$H NMR $\delta$H$_a$ = 6.45, H$_b$ = 4.46, H$_c$ = 4.14, H$_d$ = 1.28, H$_e$ = 0.18, $J_{ab}$ = 13.6, $J_{ac}$ = 5.9, $J_{bc}$ = 0.7 Hz; MS, calcd for C$_8$H$_{18}$O$_2$Si 174, found 174. **4-(*tert*-Butoxydimethylsiloxy)-1-butene (29)**: $^1$H NMR $\delta$H$_a$ = 5.81, H$_b$ = 5.06, H$_c$ = 5.01, H$_d$ = 3.69, H$_e$ = 2.30, H$_f$ = 1.27, H$_g$ = 0.10, $J_{ab}$ = 17.5, $J_{ac}$ = 9.6, $J_{ae}$ = 6.9, $J_{bc}$ = 1.3, $J_{be}$ = 1.5 $J_{ce}$ = 1.1, $J_{de}$ = 6.9 Hz.

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**Registry No.** 1, 69780-62-7; **2a**, 513-81-5; **2b**, 52221-66-6; **2c**, 16356-05-1; **2d**, 16356-06-2; **2e**, 5731-93-1; **2f**, 84652-75-5; **2g**, 90822-62-1; **2h**, 90822-63-2; **2i**, 90822-64-3; **2j**, 90822-65-4; **2k**, 82167-48-4; **2l**, 90822-66-5; **2m**, 90837-92-6; **2n**, 90822-67-6; **3** ($n$ = 5), 20968-70-1; **3** ($n$ = 6), 2819-48-9; **3** ($n$ = 7), 58738-52-6; **3** ($n$ = 8), 64306-16-7; **3** ($n$ = 9), 90822-68-7; **3** ($n$ = 10), 90822-69-8; **3** ($n$ = 11), 90822-70-1; **3** ($n$ = 12), 41613-91-6; **3** ($n$ = 13), 90822-71-2; **3** ($n$ = 14), 90822-72-3; **3** ($n$ = 16), 90822-73-4; **4** ($n$ = 4), 27567-69-7; **4** ($n$ = 11), 90822-74-5; **4** ($n$ = 12), 90822-75-6; **4** ($n$ = 13), 90822-76-7; **4** ($n$ = 14), 90837-93-7; **4** ($n$ = 16), 90822-77-8; **5** ($n$ = 12), 90822-78-9; **5** ($n$ = 13), 90822-79-0; **5** ($n$ = 14), 90822-80-3; **5** ($n$ = 16), 90822-81-4; **6a**, 90822-82-5; **6i**, 90822-83-6; **6l**, 90822-84-7; **6m**, 90822-85-8; **7g**, 90822-86-9; **7h**, 90822-87-0; 8, 90822-88-1; **22**, 90822-89-2; **23**, 90822-90-5; **24**, 90822-91-6; **25**, 61786-10-5; **26a**, 90822-92-7; **26b**, 90822-93-8; **26c**, 90822-94-9; **28**, 90822-95-0; **29**, 90822-96-1; MeI, 74-88-4; Me$_2$SO$_4$, 77-78-1; EtBr, 74-96-4; Et$_2$SO$_4$, 64-67-5; $n$-PrBr, 106-94-5; $n$-BuBr, 109-65-9; $i$-PrBr, 75-26-3; $t$-BuBr, 507-19-7; $t$-BuI, 558-17-8; CH$_2$=CHCH$_2$Cl, 107-05-1; PhCH$_2$Cl, 100-44-7; PhCH$_2$Br, 100-39-0; Me$_3$SiCl, 75-77-4; Me$_3$GeBr, 1066-37-1; Me$_3$SnCl, 1066-45-1; Me$_3$PbCl, 1520-78-1; ClCH$_2$Cl, 75-09-2; BrCH$_2$Br, 74-95-3; Cl(CH$_2$)$_2$Cl, 107-06-2; Br(CH$_2$)$_2$Br, 106-93-4; Br(CH$_2$)$_3$Br, 109-64-8; Br(CH$_2$)$_4$Br, 110-52-1; Br(CH$_2$)$_5$Br, 111-24-0; Br(CH$_2$)$_6$Br, 629-03-8; Br(CH$_2$)$_7$Br, 4549-31-9; Br(CH$_2$)$_8$Br, 4549-32-0; Br(CH$_2$)$_9$Br, 4549-33-1; Br(CH$_2$)$_{10}$Br, 4101-68-2; Br(CH$_2$)$_{12}$Br, 3344-70-5; MeCHCl$_2$, 75-34-3; Me$_2$SiCl$_2$, 75-78-5; Me$_2$GeCl$_2$, 1529-48-2; Me$_2$SnCl$_2$, 753-73-1.

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(27) Trost, B. M.; Shimizu, M. *J. Am. Chem. Soc.* **1982**, *104*, 4299. No analysis was reported. We found: Anal. Calcd for C$_{12}$H$_{26}$Si$_2$: C, 66.63; H, 11.57. Found: C, 66.65; H, 11.58.

(28) Our extensive MS studies on 2,3-disubstituted-1,3-butadienes will be reported elsewhere.

(29) **2h** has the same GC retention time as **4** ($n$ = 4), but distillation of the mixture from maleic anhydride cleanly removed **4** ($n$ = 4).

(30) Elemental analyses were not obtained on the new members of the series as they would not distinguish between monomers **3**, dimers **4**, and trimers **5**; MS was used for this purpose.

(31) The vinyl hydrogen absorptions of **24** were obscured by those of **23** and **25**.