78828-52-1; **3a**, 78828-42-9; **3b**, 80581-36-8; **3c**, 78828-53-2; **4a**, 80533-34-2; **4b**, 78828-47-4; **4c**, 78828-54-3; **5a**, 2816-57-1; **5b**, 78828-48-5; **5c**, 78828-55-4; **6a**, 2408-37-9; **6b**, 80533-35-3; **6c**, 78828-56-5; **7a**, 108-94-1; **7b**, 80533-36-4; **7c**, 1122-25-4; **8a**, 1728-25-2; **8b**, 80533-37-5; **8c**, 80533-38-6; **8d**, 80540-34-7; **9a**, 1502-06-3; **9b**, 80533-39-7; **9c**, 80533-40-0; **10b**, 80533-41-1; **10c**, 58070-37-4; compound;, 80533-42-2; (phenylseleno)acetaldehyde, 71338-48-2; (methylseleno)acetaldehyde, 80533-43-3.

New Method for Coupling Allylic Halides: Use of Te^{2-} Species

Derrick L. J. Clive,* Paul C. Anderson,† Neil Moss,‡ and Alok Singh

Chemistry Department, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2

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A variety of allylic halides were treated with Te^{2-} (generated in situ) to afford coupled 1,5-dienes (average yield 78% for 11 examples). Mechanistic studies establish that bisallylic tellurides are produced, and these decompose into allylic radicals which then dimerize.

We report a new method for making carbon-carbon bonds that is based on special properties of tellurium not shared, at least in adequate degree, by selenium. The chemistry of selenium has, of course, made an important contribution[1] to synthetic methodology in recent years, but the exploration of tellurium chemistry in this respect is still at an early stage, and there are, as yet, few examples of the controlled manipulation of organic molecules involving the use of tellurium compounds.[2]

We have found that allylic halides[3] react with Te^{2-} to afford coupled products[4] (eq 1, X = Cl or Br). The results in Table I show that the method usually gives synthetically good yields and it is a convenient procedure which illustrates a new aspect of organotellurium chemistry.

(1)

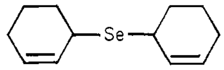
The species Te^{2-} is extremely sensitive to oxygen but it is easy to prepare (see Experimental Section[5]) provided that scrupulous attention is given to the exclusion of air. One simply injects a commercial solution of Super-Hydride[6] onto a stirred portion of powdered tellurium. The metal dissolves in the course of a few hours[7] and addition of the halide,[8] followed by a short period of heating, preferably near 110 °C, completes the sequence. The tellurium precipitates, and the dienes are isolable by chromatography and distillation. In our experience the optimum relative molar proportion is 2.6:1:2 Super-Hydride/tellurium/allylic halide.

The products were identified spectroscopically, although individual assignments of meso and *dl* stereochemistries were not made in most cases.[9] The structures of **14-19** followed from the close correspondence of their ^{13}C NMR spectra to those predicted by empirical methods.[10]

Mechanistic Considerations

Using 3-bromocyclohexene as a test case, we found that the triethylborane present in the reaction mixtures plays no critical role in the process: similar results were obtained by using commercial Na_2Te.[11]

The reaction is also one that is characteristic of tellurium. A comparable experiment with 3-bromocyclohexene and Se^{2-} afforded only the selenide **21**, as a mixture of diastereoisomers, and less than 2% (VPC) of 2,2′-bicyclohexenyl was formed even after the reaction period had



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† Natural Sciences and Engineering Research Council of Canada Postgraduate Scholar.

‡ NSERC Undergraduate Summer Research Award Recipient.

(1) Reviews: (a) Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049. (b) Reich, H. J. In "Oxidation in Organic Chemistry"; Trahanovsky, W. S., Ed.; Academic Press: New York, 1978; Part C, Chapter 1.

(2) Reviews of tellurium chemistry: (a) Irgolic, K. J. "The Organic Chemistry of Tellurium"; Gordon and Breach Science Publishers Inc.: New York, 1974. (b) Irgolic, K. J. *J. Organomet. Chem.* **1980**, *203*, 367. Synthetic methods based on tellurium chemistry: (c) Clive, D. L. J.; Menchen, S. M. *J. Org. Chem.* **1980**, *45*, 2347 (see also: Still, W. C.; Novack, V. J. *J. Am. Chem. Soc.* **1981**, *103*, 1283). (d) Ley, S. V.; Meerholz, C. A.; Barton, D. H. R. *Tetrahedron, Suppl.* **1981**, *No. 1*, 213. (e) Kambe, N.; Kondo, K.; Ishii, H.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 547. (f) Uemura, S.; Miyoshi, H.; Okano, M. *Chem. Lett.* **1979**, 1357. (g) Bäckvall, J. E.; Engman, L. *Tetrahedron Lett.* **1981**, 1919. Recent general studies on organotellurium compounds: (h) Clive, D. L. J.; Beaulieu, P. L. *J. Org. Chem.* **1982**, *47*, 1124. (i) Clive, D. L. J.; Chittattu, G. J.; Farina, V.; Kiel, W. A.; Menchen, S. M.; Russell, C. G.; Singh, A.; Wong, C. K.; Curtis, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 4438. (j) Uemura, S.; Fukuzawa, S. *J. Chem. Soc., Chem. Commun.* **1980**, 1033. (k) Kambe, N.; Kondo, K.; Morita, S.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1009. (l) Kambe, N.; Kondo, K.; Sonoda, N. *Ibid.* **1980**, *19*, 1009. (m) Bergman, J.; Engman, L. *Synthesis* **1980**, 569. (n) Yamashita, M.; Kato, Y.; Suemitsu, R. *Chem. Lett.* **1980**, 847. (o) Wiriyachitra, P.; Falcone, S. J.; Cava, M. P. *J. Org. Chem.* **1979**, *44*, 3957. (p) Lee, H.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1981**, 277. (q) Bergman, J.; Engman, L. *Tetrahedron Lett.* **1978**, 3279. (r) Bonilha, J. B. S.; Petragnani, N.; Toscano, V. G. *Chem. Ber.* **1978**, *111*, 2510. (s) Ramasamy, K.; Kalyanasundaram, S. K.; Shunmugam, P. *Synthesis* **1978**, 545. (t) Barrett, A. G. M.; Read, R. W.; Barton, D. H. R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2191. (u) Barrett, A. G. M.; Read, R. W.; Barton, D. H. R. *Ibid.* **1980**, 2184. (v) Bergman, J.; Engman, L. *J. Organomet. Chem.* **1980**, *201*, 377.

(3) We have used chlorides and bromides.

(4) For other methods of coupling allylic halides see, for example: (a) Wellmann, J.; Steckhan, E. *Synthesis* **1978**, 901. (b) Reijnders, P. J. M.; Blankert, J. P.; Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 30. (c) Olah, G. A.; Surya Prakash, G. K. *Synthesis* **1976**, 607. (d) Ho, T. L.; Olah, G. A. *Ibid.* **1977**, 170. (e) Kitagawa, Y.; Oshima, K.; Yamamoto, H.; Nozaki, H. *Tetrahedron Lett.* **1975**, 1859. (f) Semmelhack, M. F. *Org. React.* **1972**, *19*, 115. (g) Baker, R. *Chem. Rev.* **1973**, *73*, 487. (h) Benn, R.; Hoffmann, E. G.; Lehmkuhl, H.; Nehl, H. *J. Organomet. Chem.* **1978**, *146*, 103. (i) Okude, Y.; Hiyama, T.; Nozaki, H. *Tetrahedron Lett.* **1977**, 3829. (j) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693.

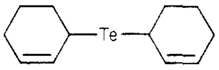
(5) For other preparations of Te^{2-} see ref 2a and: Gysling, H. J. Proceedings of the Third International Symposium on Organic Selenium and Tellurium Compounds, Metz, France, July 1979; Université de Metz: Metz, France, 1981, p 395.

(6) Aldrich trademark for a 1 M solution of lithium triethylborohydride in THF. See: Brown, H. C.; Kim, S. C.; Krishnamurthy, S. *J. Org. Chem.* **1980**, *45*, 1.

0022-3263/82/1947-1641$01.25/0

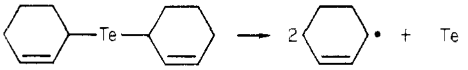
been extended from 1 to 3 h.[12]

The case of 3-bromocyclohexene was suitable for further study because the reaction proceeds at a convenient rate. When the halide was added to the reagent solution, the halide disappeared, but no 2,2′-bicyclohexenyl was formed. The ^{13}C NMR spectrum of the reaction mixture showed, in place of diagnostically characteristic signals (see Experimental Section) due to the allylic halide and 2,2′-bicyclohexenyl, new signals at δ 125.8, 125.9, 130.6, and 130.7. We attribute these to the sensitive[13] telluride **22** (meso and *dl* forms). The solution in which **22** was generated showed no ESR signal either at room temperature or at 100 °C. At the higher temperature tellurium was deposited. In a separate experiment, the mixture of halide and Te^{2-} (in THF) was kept at room temperature for 1 h (about twice the period that had elapsed before measuring the ^{13}C NMR spectrum), diluted with dioxane, and then refluxed for 1 h. The yield of isolated product was 82%. Clearly, an initial reaction period at room temperature[14] has no substantive effect on the final result. On the basis of these observations we conclude that bisallylic tellurides produced by ionic displacements are intermediates in the process and that the reaction does not proceed, at least as a main pathway, by an electron transfer between Te^{2-} and the halide.

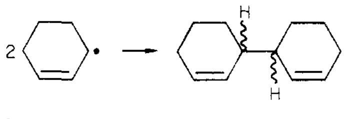


22

Thermal extrusion of tellurium probably occurs by fragmentation to radicals followed by recombination (eq 2 and 3), and, as expected on this basis, a cross-coupling product was obtained from the following experiment. Two THF solutions, one of 3-bromocyclohexene and Te^{2-} and the other of 3-bromocycloheptene and Te^{2-}, were prepared in the usual way and kept at room temperature for 0.5 h. Aliquots of the clear solutions were mixed, diluted with dioxane,[15] and refluxed for 1 h. Isolation of the 2,2′-bicycloalkenyls (67%[16] after distillation) gave pure (>98% by VPC) material consisting of three resolvable (VPC) compounds in the relative proportion 1:1.3:1.[17] Examination of the material by VPC/MS served to identify the compounds as 2,2′-bicyclohexenyl, 3-(2-cyclohexenyl)-cycloheptene, and 2,2′-bicycloheptenyl, respectively.

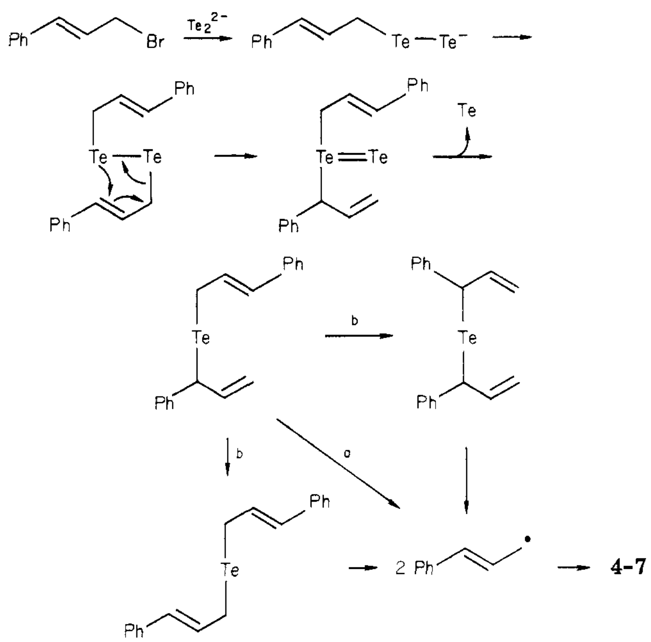


(2)



(3)

Scheme I[a]



[a] Incursion of 1,3-allylic shifts is shown (for convenience) only at stage b; they can, in principle, occur at an earlier stage. For simplicity S_N2' reactions have not been shown.

The reactions are not sensitive to double bond geometry (see Table I, entries 10 and 11), and, of course, allylic radicals are known to isomerize easily.[18] In all of the reactions two resonance structures A and B can be written for the radicals, and the ease of formation of such species would be expected to depend on the status (primary, secondary, or tertiary) of the radicals centered at C(1) and C(3) in A and B. Our qualitative observation is that reactions involving halides which would lead to secondary–secondary and primary–tertiary radicals proceed more easily than those that would involve primary–primary or primary–secondary systems. Also, cases in which especially stabilized radicals are possible (entries 5–7) undergo the reaction very readily. Besides the results shown in Table I we noted the fact that while bromomethylbenzene, perillyl chloride,[19] 1-chloro-2-methyl-2-propene, and 1-

A B

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(7) (a) From the known behavior[7b,c] of Super-Hydride with sulfur and selenium, from the stoichiometry we have used and the chemical behavior of the solution, it is obvious that the suspension contains Te^{2-}, but the degree of affiliation, if any, of the triethylborane that is also present, is not known. (b) Gladysz, J. A.; Wong, V. K.; Jick, B. S. *Tetrahedron* **1979**, *35*, 2329. (c) Gladysz, J. A.; Hornby, J. L.; Garbe, J. E. *J. Org. Chem.* **1978**, *43*, 1204.

(8) It is unnecessary to add *tert*-butyl alcohol (cf. ref 7c).

(9) See, however, the Experimental Section for Table entries 1, 2, 5, and 6.

(10) (a) Strothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972. (b) Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", 2nd ed.; Wiley: New York, 1980.

(11) The yields were lower, but we suspect that this merely reflects the poorer quality of the commercial product, which has, of course, been subjected to several transfer operations before reacting with the allylic halide. The commercial material is likely, also, to have a state of subdivision different from that of reagent generated in situ.

(12) The Se^{2-} species was made by the literature method (see ref 7c).

(13) Our impression is that bisallylic tellurides decompose on attempted examination by TLC (cf. ref 2i).

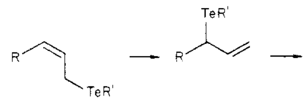
(14) These are the conditions under which the ESR signal was sought. In our preparative runs, we refluxed the mixture *soon after* mixing the reagents.

(15) The proportion of dioxane was the same as in the preparative runs.

(16) This is a calculated yield based on the size of the aliquots taken.

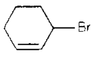
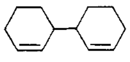
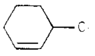
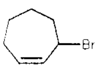
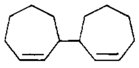
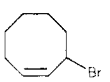
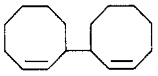
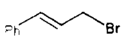
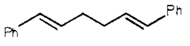
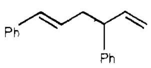
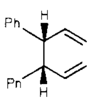
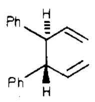
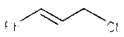
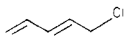
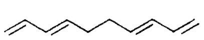
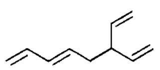
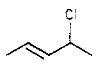
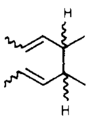
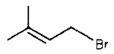
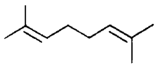
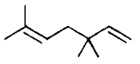
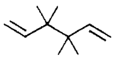
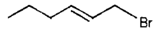
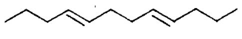
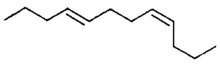
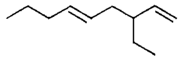
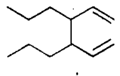
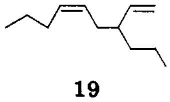
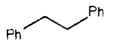
(17) Relative peak areas.

(18) (a) Denney, D. B.; Hoyte, R. M.; MacGregor, P. T. *Chem. Commun.* **1967**, 1241. (b) Crawford, R. J.; Hamelin, J.; Strehlke, B. *J. Am. Chem. Soc.* **1971**, *93*, 3810. (c) Klein, R.; Kelley, R. D. *J. Phys. Chem.* **1975**, *79*, 1780. (d) Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 4. Isomerization of the double bond can occur, in principle, also by a 1,3-tellura shift:



(19) Prepared by the method of: Stork, G.; Grieco, P. A.; Gregson, M. *Org. Synth.* **1974**, *54*, 68. It was characterized spectroscopically (IR, NMR, and mass spectroscopy).

Table I. Coupling of Allylic Halides Promoted by Te^{2-}

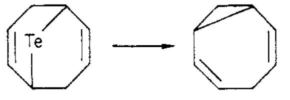
entry	allylic halide	reflux time, h[a]	products	% yield[b]
1		1	 1[c]	86
2		1	1	81
3		1	 2[d]	86
4		1	 3[c]	81
5		1	 4  5  6  7	91[e]
6		1	4-7	93[e]
7		1[f]	 8  9	82[g,h]
8		1	 10	82[g]
9		3	 11  12  13	73[g,i]
10		21	 14  15  16  17  18[j]  19	60[k]
11		21	14-19	53
12	$PhCH_2Br$	3[l]	 20	37

[a] Unless indicated to the contrary, reactions were run in a mixture of THF and dioxane (ca. 2:3 by volume), and the solution was heated in an oil bath set at 110 °C. [b] Except where indicated, yields refer to isolated products. [c] Meso/*dl* ratio of 1:1 (^{13}C NMR; isolation). [d] Meso and *dl*. [e] (6 + 7)/5/4 ratio of 1:3.9:3.0 (^1H NMR). [f] Reaction run in THF with an oil bath at 80 °C. [g] VPC yield. [h] 8/9 ratio of 1.3:1 (VPC). [i] 11/(12 + 13) ratio of 1.4:1 (VPC). [j] Meso and *dl* isomers were separated. [k] 18/17/19/14/15/16 ratio of 1:1.2:1.7:3.5:3.5:3.6 (determined by a combination of VPC and isolation). [l] Mixture heated in at sealed tube at 160 °C.

bromo-2-hexyne reacted with the tellurium reagent (TLC), extrusion of tellurium from the resultant species was very sluggish, and attempts to isolate hydrocarbon products were unpromising. The effect of using a higher temperature was examined in the case of bromomethylbenzene, and, when the reaction mixture was heated for 3 h in a sealed tube at 160 °C, the presumed intermediate dibenzyl telluride gave some bibenzyl (37%).

Because allylic sulfides[20] and selenides[21] are known to undergo 1,3 allylic shifts, we investigated briefly this aspect of allylic telluride chemistry. Treatment of (3-bromo-1-propenyl)benzene with Te_2^{2-}, prepared from the appropriate quantities of Super-Hydride and tellurium (see Experimental Section), produced an immediate precipitate of tellurium, and, after a brief heating period, another crop of tellurium was deposited, compounds 4–7 being produced in the same ratio as in the experiment using Te^{2-}. These observations can be interpreted, as shown in Scheme I, on the basis of an initial S_N2 displacement, but, as the product ratio is the same as that with Te^{2-}, the experiment is consistent with the radical path a (Scheme I) and also with path b involving 1,3 allylic shifts.

There are a few further points of a mechanistic nature. For the reaction to proceed under our comparatively mild conditions, *both* carbon–tellurium bonds should be allylic. For example, (2-propenyltelluro)benzene is a distillable liquid [bp 62 °C (0.3 mm)],[22] and the telluride **23**, in which the carbon–tellurium bonds are not coplanar with the p lobes of the double bonds, requires a high temperature (175 °C) for extrusion of tellurium (eq 4).[23] Our reaction does proceed in refluxing THF, but our impression in initial experiments is that the yields are less reproducible in this solvent, and we have routinely used a THF–dioxane mixture which gives a higher reflux temperature. The selenium analogue of **23** collapses[24] slowly to *o*-xylene and ethylbenzene at 200 °C.



23

(4)

Conclusion

The mild procedure reported here for coupling allylic halides generally affords good yields and is an example of a new application of organotellurium chemistry.

Experimental Section

Except where stated to the contrary, the following particulars apply. Experiments were performed under a slight static pressure of argon. Solvents for chromatography were distilled before use. Dry dioxane and THF were distilled immediately before use from sodium and benzophenone. Dry *tert*-butyl alcohol was distilled immediately before use from CaH_2. All apparatus was oven dried overnight (120 °C) and cooled in a desiccator over Drierite. During product isolation, solutions were dried (where necessary) over $MgSO_4$ and evaporated under water-pump vacuum at room temperature. In those cases where compounds were isolated by evaporation of their solutions (and not also by subsequent distillation) the residues were kept under oil pump vacuum and checked for constancy of weight. For yields evaluated by VPC, an internal standard was used. VPC measurements were made by using a column (6 ft × $^1/_8$ in.) packed with 10% w/w Apiezon L on Chromosorb W (80–100 mesh) at temperatures between 90 and 200 °C. Commercial TLC plates (silica gel Merck 60F-254) were used. Plates impregnated with silver nitrate were prepared from Merck silica gel 60PF-254. Silica gel for column chromatography was Merck type 60 (70–230 mesh). For silica gel impregnated with silver nitrate, the percent silver nitrate refers to (weight of $AgNO_3$)/(weight of silica gel). Boiling points given for products distilled in a Kugelrohr apparatus refer to the oven temperature. Mass spectra were run at an ionizing voltage of 70 eV. The following allylic halides were prepared by the methods described in the literature cited: 3-bromocyclohexene,[25] 3-bromocycloheptene,[25] 3-bromocyclooctene,[25] 3-chlorocyclohexene,[26] (3-bromo-1-propenyl)benzene,[27] (3-chloro-1-propenyl)benzene,[28] (*E*)-5-chloro-1,3-pentadiene,[29] (*E*)-4-chloro-2-pentene,[30] 1-bromo-3-methyl-2-butene,[31] (*E*)-1-bromo-2-hexene,[32] (*Z*)-1-bromo-2-hexene.[34] (Bromomethyl)benzene is commercially available (Aldrich). All allylic halides were stored at 0 °C and were distilled just prior to use. Super-Hydride[6] was purchased as a 1 M solution in THF and used at the stated concentration.

Preparation[35] of the Tellurium Reagent Te^{2-}. The apparatus consisted of a 25-mL round-bottomed flask to which were fused a condenser and side arm. The flask contained a Teflon-coated magnetic stirring bar, and the condenser was connected via a vacuum takeoff to a vacuum/argon line. The side arm was closed by using a rubber septum or, for those reactions which required long refluxing (>3 h), a stopcock fitted with a rubber septum. The apparatus was oven dried overnight (120 °C), assembled hot, charged immediately with commercial tellurium powder (ca. 200 mesh; 255 mg, 2.00 mmol), and evacuated (oil pump) while being allowed to cool. The apparatus was then filled with argon and purged of all air by three cycles of oil pump evacuation and refilling with argon. Super-Hydride (1 M, 5.2 mL, 5.2 mmol) was then added by syringe, and the mixture was stirred at room temperature for 5–7 h, during which time a gas was evolved and the tellurium dissolved. The mixture became purple and then slowly faded to a very pale pink or off-white suspension. At this point, the reagent was ready for use. In those cases where it was allowed to stand for longer periods, even under a positive pressure of argon, the reagent deteriorated, a crimson color developed, and lower yields of coupled products were obtained.

Coupling of 3-Bromocyclohexene. 3-Bromocyclohexene (322 mg, 2.00 mmol) in dry dioxane (2.0 mL plus a 2.0-mL rinse) was added by syringe to the tellurium reagent (1.00 mmol), prepared as described above. The mixture was lowered into an oil bath preheated to 110 °C and refluxed for 1 h. The mixture was then cooled to room temperature and filtered with the aid of CH_2Cl_2 (ca. 100 mL) through a pad (2 × 2.5 cm) of Celite. The filtrate was concentrated to an oil and partitioned between CH_2Cl_2 (50 mL) and water (50 mL). The aqueous phase was back-extracted with CH_2Cl_2 (2 × 25 mL), and the combined organic extracts were dried, filtered, and concentrated to an oil. Chromatography over silica gel (60 × 1 cm) with hexane, followed by Kugelrohr distillation [110 °C (15 mm)] gave **1**[36] (140 mg, 86%) as an apparently homogeneous (TLC, silica, hexane) oil of greater than 96% purity (VPC): NMR ($CDCl_3$, 100 MHz) δ 1.10–2.33 (m, 14 H), 5.40–5.86 (m, 4 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 22.3, 25.5, 26.1, 40.2, 127.7, 128.0, 130.5, 130.7; exact mass, *m/e* 162.1406 (calcd for $C_{12}H_{18}$, *m/e* 162.1408).

Examination of the material by TLC (silica gel impregnated with 5% $AgNO_3$, 3:1 hexane–ethyl acetate) resolved the two diastereoisomeric components. Chromatography of a portion of the mixture (127 mg) over silica gel impregnated with 5% $AgNO_3$ (60 × 1 cm) with 4:1 hexane–ethyl acetate gave the faster moving

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[32] Commercial (Aldrich) (*E*)-hex-2-en-1-ol was converted to the bromide by the method of ref 33.

[33] Truscheit, von E.; Eiter, K. *Justus Liebigs Ann. Chem.* **1962**, *658*, 65.

[34] Osbond, J. M. *J. Chem. Soc.* **1961**, 5270. The requisite alcohol was prepared by the method of ref 33.

[35] Although this procedure has been described for a 2.00-mmol scale, it was also successfully used to generate 1.00- and 4.00-mmol batches of the tellurium reagent. The reagent was generated at room temperature, but the reaction time can be shortened considerably by gentle heating.

[36] Berlande, A. *Bull. Soc. Chim. Fr.* **1942**, *9*, 641.

diastereoisomer (57 mg, 46% recovery) and the slower moving diastereoisomer (56 mg, 45% recovery). The more mobile material[37] had the following: NMR ($CDCl_3$, 100 MHz) δ 1.06–2.42 (m, 14 H), 5.40–5.92 (m, 4 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 22.4, 25.5, 26.1, 40.2, 128.0, 130.7; exact mass, *m/e* 162.1407 (calcd for $C_{12}H_{18}$, *m/e* 162.1408). The slower moving compound[37] had the following: NMR ($CDCl_3$, 100 MHz) δ 1.08–2.35 (m, 14 H), 5.40–5.88 (m, 4 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 22.2, 25.4, 26.1, 40.1, 127.7, 130.4; exact mass, *m/e* 162.1413 (calcd for $C_{12}H_{18}$, *m/e* 162.1408).

Coupling of 3-Chlorocyclohexene. The procedure for 3-bromocyclohexene was followed exactly by using 3-chlorocyclohexene (234 mg, 2.00 mmol) to give the same diastereoisomeric mixture of 1 (133 mg, 81%) of greater than 98% purity (VPC).

Coupling of 3-Bromocycloheptene. The procedure for 3-bromocyclohexene was followed exactly by using 3-bromocycloheptene (350 mg, 2.00 mmol) to give, after chromatography over silica gel (60 × 1 cm) with hexane and Kugelrohr distillation [165 °C (15 mm)], **2**[38] (165 mg, 86%) as an apparently homogeneous (TLC, silica, hexane) oil of greater than 98% purity (VPC). Examination of the product by TLC (silica gel impregnated with 5% $AgNO_3$, 3:1 hexane–ethyl acetate) partially resolved the two diastereoisomers. The mixture had the following: NMR ($CDCl_3$, 100 MHz) δ 1.00–2.47 (m, 18 H), 5.42–5.97 (m, 4 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 27.0, 28.8, 30.6, 31.0, 31.3, 31.5, 45.5, 46.0, 131.5, 131.8, 136.3, 136.6; exact mass, *m/e* 190.1726 (calcd for $C_{14}H_{22}$, *m/e* 190.1721).

Coupling of 3-Bromocyclooctene. The procedure for 3-bromocyclohexene was followed exactly by using 3-bromocyclooctene (379 mg, 2.00 mmol) to give, after chromatography over silica gel (60 × 1 cm) with hexane and Kugelrohr distillation [180 °C (15 mm)], **3**[38] (179 mg, 81%) as an apparently homogeneous (TLC, silica, hexane) oil of greater than 97% purity (VPC): NMR ($CDCl_3$, 100 MHz) δ 0.86–2.67 (m, 22 H), 5.14–5.86 (m, 4 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 26.0, 26.8, 27.2, 29.6, 29.8, 34.3, 40.8, 41.1, 129.3, 129.4, 133.3, 134.5; exact mass, *m/e* 218.2037 (calcd for $C_{16}H_{26}$, *m/e* 218.2034).

Examination of the material by TLC (silica gel impregnated with 5% $AgNO_3$, 3:1 hexane–ethyl acetate) resolved the two diastereoisomeric components. Chromatography of a portion of the mixture (107 mg) over silica gel impregnated with 5% $AgNO_3$ (60 × 1 cm) with 3:1 hexane–ethyl acetate gave, after Kugelrohr distillation [180 °C (15 mm)], the faster moving isomer (52 mg, 49% recovery) as a white solid (mp 53–56 °C) and the slower moving isomer (51 mg, 48% recovery) as a viscous oil of greater than 96% purity (VPC). The former had the following: NMR ($CDCl_3$, 100 MHz) δ 0.72–2.72 (m, 22 H), 5.08–5.92 (m, 4 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 26.0, 26.8, 27.2, 29.8, 34.3, 41.1, 129.2, 134.4; exact mass, *m/e* 218.2036 (calcd for $C_{16}H_{26}$, *m/e* 218.2034). The latter had the following: NMR ($CDCl_3$, 100 MHz) δ 0.76–2.80 (m, 22 H), 5.08–5.90 (m, 4 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 25.9, 26.8, 27.2, 29.6, 34.3, 40.7, 129.4, 133.3; exact mass, *m/e* 218.2038 (calcd for $C_{16}H_{26}$, *m/e* 218.2034).

Coupling of (3-Bromo-1-propenyl)benzene. The procedure for 3-bromocyclohexene was followed exactly by using (3-bromo-1-propenyl)benzene (394 mg, 2.00 mmol) to give, after chromatography over silica gel (60 × 1 cm) with 99:1 hexane–ethyl acetate, a mixture of **4**,[39] **5**,[39] **6**,[39] and **7**[39] (215 mg, 91%) as an apparently homogeneous (TLC, silica, 95:5 hexane–ethyl acetate), oily, white solid. Examination of the product by TLC (silica gel impregnated with 5% $AgNO_3$, 3:1 hexane–ethyl acetate) indicated a mixture of four isomers. A ^{1}H NMR spectrum (400 MHz) of the isomer mixture indicated that the products were present in the relative proportions 1:3.9:3.0 (**6** and **7**)/**5**/**4**.

A portion of the mixture (211 mg) was crystallized from hexane to afford a sample of **4** (28 mg). The material from the mother liquors was then chromatographed over silica gel impregnated with 5% $AgNO_3$ (100 × 2 cm) with 5:1 hexane–ethyl acetate to give a further portion of **4** (44 mg). The combined samples of **4** (72 mg, 34% recovery) were recrystallized twice from hexane (mp 77.5–79 °C, lit.[39] mp 79.0–79.5 °C). The chromatography also afforded **5** (77 mg, 36% recovery) as an oil, **6** (13 mg, 6% recovery) as a white solid [mp 77.5–86.5 °C (after recrystallization from hexane), lit.[39] mp 86–87 °C], and **7** (8 mg, 4% recovery) as an oil (lit.[39] mp 35–35.2 °C). Compound **4**: NMR ($CDCl_3$, 100 MHz) δ 2.16–2.58 (m, 4 H), 6.04–6.60 (m, 4 H), 6.92–7.52 (m, 10 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 32.9, 126.0, 126.9, 128.5, 129.9, 130.4, 137.7; exact mass, *m/e* 234.1411 (calcd for $C_{18}H_{18}$, *m/e* 234.1408). Compound **5**: NMR ($CDCl_3$, 100 MHz) δ 2.49–2.79 (m, 2 H), 3.26–3.58 (m, 1 H), 4.89–5.19 (m, 2 H), 5.80–6.50 (m, 3 H), 6.80–7.60 (m, 10 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 39.0, 50.0, 114.6, 126.0, 126.3, 126.9, 127.7, 128.4, 131.4, 137.7, 141.4, 143.7; exact mass, *m/e* 234.1412 (calcd for $C_{18}H_{18}$, *m/e* 234.1408. Compound **6**: NMR ($CDCl_3$, 100 MHz) δ 3.57–3.74 (m, 2 H), 4.65–4.98 (m, 4 H), 5.66–6.06 (m, 2 H), 7.00–7.44 (m, 10 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 55.6, 115.8, 126.5, 128.4, 128.7, 140.2, 142.7; exact mass, *m/e* 234.1405 (calcd for $C_{18}H_{18}$, *m/e* 234.1408). Compound **7**: NMR ($CDCl_3$, 100 MHz) δ 3.55–3.70 (m, 2 H), 4.86–5.16 (m, 4 H), 5.90–6.30 (m, 2 H), 6.87–7.22 (m, 10 H); ^{13}C NMR ($CDCl_3$, 50.33 MHz) δ 55.8, 115.8, 126.0, 128.1, 128.2, 140.5, 142.6; exact mass, *m/e* 234.1402 (calcd for $C_{18}H_{18}$, *m/e* 234.1408).

Coupling of (3-Chloro-1-propenyl)benzene. The procedure for (3-bromo-1-propenyl)benzene was followed exactly by using (3-chloro-1-propenyl)benzene (306 mg, 2.00 mmol) to give the same (^{1}H NMR, 400 MHz) isomer mixture of **4**–**7** (219 mg, 93%).

Coupling of (*E*)-5-Chloro-1,3-pentadiene. (*E*)-5-Chloro-1,3-pentadiene (205 mg, 2.00 mmol) in dry THF (2.0 mL plus 2.0 mL rinse) was added by syringe to the tellurium reagent (1.00 mmol) prepared as described previously. The mixture was lowered into an oil bath, preheated to 80 °C, and refluxed for 1 h. Analysis of the solution by VPC showed a mixture of **8**[38] (62 mg, 46%) and **9**[38] (48 mg, 36%).

For isolation of samples of each isomer for characterization, the reaction was repeated on a larger scale (4.00 mmol of the tellurium reagent). After being refluxed for 1 h, the reaction mixture was cooled to room temperature and filtered with the aid of CH_2Cl_2 (ca. 100 mL) through a pad (2 × 2.5 cm) of Celite. The filtrate was concentrated by distillation at atmospheric pressure through a Vigreux column (12 cm) to ca. 25 mL, was mixed with water (50 mL), and was extracted with pentane (3 × 50 mL). The combined organic extracts were dried, filtered, and concentrated (Vigreux column, 1 atm) to a volume of ca. 2 mL. Chromatography over silica gel (30 × 1 cm) with pentane, concentration (Vigreux column, 1 atm), and further chromatography over silica gel impregnated with 5% $AgNO_3$ (30 × 1 cm) by using 3:2 pentane–ether effected separation of **8** and **9**. Concentration (Vigreux column, 1 atm) and Kugelrohr distillation [100 °C (50 mm)] gave homogeneous (TLC, silica, hexane; TLC, silica gel impregnated with 5% $AgNO_3$, ether) samples of **8** of greater than 97% purity (VPC) and of **9** of greater than 93% purity (VPC), the major contaminant in the latter being **8** (4%). Compound **8**: NMR ($CDCl_3$, 100 MHz) δ 2.02–2.40 (m, 4 H), 4.81–5.30 (m, 4 H), 5.51–6.74 (m, 6 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 32.2, 115.0, 131.5, 134.2, 137.2; exact mass, *m/e* 134.1095 (calcd for $C_{10}H_{14}$, *m/e* 134.1096). Compound **9**: NMR ($CDCl_3$, 100 MHz) δ 2.10–2.45 (m, 2 H), 2.63–3.00 (m, 1 H), 4.86–5.28 (m, 6 H), 5.46–6.54 (m, 5 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 37.6, 47.6, 114.7, 115.2, 132.5, 137.1, 140.4; exact mass, *m/e* 134.1087 (calcd for $C_{10}H_{14}$, *m/e* 134.1096).

Coupling of (*E*)-4-Chloro-2-pentene. (*E*)-4-Chloro-2-pentene[40] (419 mg, 4.00 mmol) in dry dioxane (4.0 mL plus a 4.0-mL rinse) was added by syringe to the tellurium reagent (2.00 mmol) prepared as described previously. The mixture was lowered into an oil bath, preheated to 110 °C, and refluxed for 1 h. Analysis of the solution by VPC showed the presence of **10**[38] (228 mg, 82%).

In order to isolate a sample of the product, we repeated the reaction exactly as above. After being refluxed for 1 h, the mixture was cooled to room temperature and filtered with the aid of CH_2Cl_2 (ca. 100 mL) through a pad (2 × 2.5 cm) of Celite. The filtrate was concentrated by distillation at atmospheric pressure through a Vigreux column (12 cm) to ca. 5 mL and partitioned

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(37) By an argument used previously (van Tamelen, E. E.; Brauman, J. I.; Ellis, L. E. *J. Am. Chem. Soc.* **1971**, *93*, 6145) the more mobile material is assigned the *dl* stereochemistry.

(38) Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2036.

(39) Lutz, R. P.; Bernal, S.; Boggio, R. J.; Harris, R. O.; McNicholas, M. W. *J. Am. Chem. Soc.* **1971**, *93*, 3985.

(40) The compound contained ca. 10% of the other double bond isomer, as estimated by ^{13}C-NMR spectroscopy.

between pentane (50 mL) and water (50 mL). The aqueous phase was washed with pentane (2 × 25 mL), and the combined pentane extracts were dried, filtered, and concentrated (Vigreux column, 1 atm) to an oil. Chromatography over silica gel (60 × 1 cm) with pentane, concentration (Vigreux column, 1 atm), and Kugelrohr distillation [70 °C (12 mm)] gave **10** as an apparently homogeneous (TLC, silica, hexane) oil of greater than 99% purity (VPC). Analysis of the product by TLC (silica gel impregnated with 5% $AgNO_3$, 3:1 hexane–ethyl acetate) indicated a mixture of at least three isomers. The product had the following: IR (film) 965 (s), 720 cm^{-1} (weak); NMR ($CDCl_3$, 100 MHz) δ 0.72–1.14 (m, 6 H), 1.47–2.54 (m, 8 H), 5.03–5.62 (m, 4 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 13.1, 17.5, 18.0, 18.3, 18.6, 36.5, 41.9, 42.4, 42.8, 122.5, 122.8, 123.7, 123.9, 134.9, 135.1, 136.0; exact mass, *m/e* 138.1408 (calcd for $C_{10}H_{18}$, *m/e* 138.1408).

Coupling of 1-Bromo-3-methyl-2-butene. 1-Bromo-3-methyl-2-butene (596 mg, 4.00 mmol) in dry dioxane (2.0 mL plus a 2.0-mL rinse) was added by syringe to the tellurium reagent (2.00 mmol) prepared as described previously. The mixture was lowered into an oil bath, preheated to 110 °C, and refluxed for 3 h. Analysis of the solution by VPC showed a mixture of **11**[41] (120 mg, 43%) and **12**[41] plus **13**[41] (83 mg, 30%).

In order to isolate samples of each isomer for identification, we repeated the reaction on a larger scale (4.00 mmol of the tellurium reagent). After being refluxed for 3 h, the mixture was cooled to room temperature and filtered with the aid of CH_2Cl_2 (ca. 150 mL) through a pad (2 × 2.5 cm) of Celite. The filtrate was concentrated by distillation at atmospheric pressure through a Vigreux column (12 cm) to ca. 50 mL and partitioned between water (250 mL) and pentane (4 × 75 mL). The combined pentane extracts were dried, filtered, and concentrated (Vigreux column, 1 atm) to ca. 2 mL. Chromatography over silica gel (60 × 1 cm) with pentane and concentration (Vigreux column, 1 atm) gave an oil, which was further chromatographed over silica gel impregnated with 5% $AgNO_3$ (60 × 1 cm) by using 9:1 pentane–ether. Concentration (Vigreux column, 1 atm) and Kugelrohr distillation [120 °C (90 mm)] gave homogeneous (TLC, silica, hexane; TLC, silica gel impregnated with 5% $AgNO_3$, 9:1 pentane–ether) samples of **11** (100% pure by VPC), **12** (greater than 98% pure by VPC), and **13** (100% pure by VPC). Compound **11**: NMR ($CDCl_3$, 100 MHz) δ 1.61 (s, 6 H), 1.69 (s, 6 H), 1.86–2.12 (m, 4 H), 4.97–5.28 (m, 2 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 17.7, 25.7, 28.4, 124.5, 131.5; exact mass, *m/e* 138.1408 (calcd for $C_{10}H_{18}$, *m/e* 138.1408). Compound **12**: NMR ($CDCl_3$, 100 MHz) δ 0.99 (s, 6 H), 1.61 (s, 3 H), 1.73 (d, J = 1.4 Hz, 3 H), 1.98 (d, J = 7.4 Hz, 2 H), 4.78–5.02 (m, 2 H), 5.14 (t m, J = 7.4, 1.4 Hz, 1 H), 5.66–6.02 (m, 1 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 17.9, 25.9, 26.5, 37.4, 40.8, 110.0, 121.2, 132.8, 148.7; exact mass, *m/e* 138.1409 (calcd for $C_{10}H_{18}$, *m/e* 138.1408). Compound **13**: NMR ($CDCl_3$, 100 MHz) δ 0.99 (s, 12 H), 4.78–5.06 (m, 4 H), 5.78–6.14 (m, 2 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 22.5, 41.3, 111.7, 146.2; exact mass, *m/e* 138.1405 (calcd for $C_{10}H_{18}$, *m/e* 138.1408).

Coupling of (*E*)-1-Bromo-2-hexene. The procedure for 3-bromocyclohexene was followed by using (*E*)-1-bromo-2-hexene[40] (327 mg, 2.00 mmol) and a reflux period of 21 h. Chromatography over silica gel (60 × 1 cm) with hexane and Kugelrohr distillation [110 °C (13 mm)] gave an apparently homogeneous (TLC, silica, hexane) oil (100 mg, 60%), judged to be a mixture of isomers by VPC (three peaks: 5.94%, 39.49%, and 54.25%). TLC (silica gel impregnated with 5% $AgNO_3$, 9:1 hexane–ethyl acetate) resolved four components.

To obtain a sample of each component for characterization, we repeated the reaction on a larger scale (4.00 mmol of the tellurium reagent). Chromatography over silica gel (60 × 1 cm) with hexane afforded a homogeneous (TLC, silica, hexane) clear, colorless oil (433 mg, 65%). Chromatography of this isomer mixture over silica gel impregnated with 5% $AgNO_3$ [twice (70 × 2 cm) with 19:1 hexane–ethyl acetate, once (70 × 2 cm) with 97:3 hexane–ethyl acetate, and once (30 × 0.5 cm) with 97:3 hexane–ethyl acetate] gave four fractions which were each rechromatographed over silica gel (15 × 1.5 cm) with hexane. Kugelrohr distillation of each fraction gave material that was homogeneous by TLC (silica, hexane; silica gel impregnated with 5% $AgNO_3$, 9:1 hexane–ethyl acetate).

The least polar fraction [59.1 mg, 13% recovery; bp 120 °C (20 mm)] was **14**[42] of greater than 97% purity (VPC): IR (film) 970 cm^{-1} (s); NMR ($CDCl_3$, 100 MHz) δ 0.89 (t, J = 7 Hz, 6 H), 1.17–1.58 (m, 4 H), 1.80–2.16 (m, 8 H), 5.30–5.51 (m, 4 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 13.6, 22.7, 32.8, 34.7, 130.0, 130.5; exact mass, *m/e* 166.1723 (calcd for $C_{12}H_{22}$, *m/e* 166.1721).

The second fastest fraction [61.8 mg, 14% recovery; bp 130 °C (20 mm)] was **15**[42] of greater than 92% purity (VPC): IR (film) 970 (s), 720 cm^{-1} (w); NMR ($CDCl_3$, 100 MHz) δ 0.85 and 0.86 (2 overlapping t, J = 7 Hz, 6 H), 1.13–1.56 (m, 4 H), 1.78–2.20 (m, 8 H), 5.22–5.46 (m, 4 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 13.7, 22.7, 22.9, 27.5, 29.4, 32.8, 34.8, 129.4, 130.0, 130.6; exact mass, *m/e* 166.1720 (calcd for $C_{12}H_{22}$, *m/e* 166.1721).

The third fastest fraction [87.5 mg, 20% recovery; bp 130 °C (20 mm)] was made up of three components as judged by VPC: **16** (66.48%), **17**[42] (23.14%), and **18** (10.06%). The mixture had the following: IR (film) 1000 (m), 970 (s), 915 (s), 745 cm^{-1} (w); NMR ($CDCl_3$, 100 MHz) δ 0.73–1.04 (m, 5.8 H), 1.08–1.59 (m, 5.8 H), 1.78–2.20 (m, 5.4 H), 4.77–5.07 (m, 1.9 H), 5.26–5.79 (m, 3.2 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) displayed signals corresponding to **16** at δ 14.1, 20.2, 22.8, 34.8, 36.4, 38.3, 43.9, 113.8, 128.4, 131.6, and 143.1, signals corresponding to **17** at δ 13.6, 22.9, 27.5, 29.4, 129.4, and 130.1, and signals corresponding to **18** at δ 13.8, 20.5, 34.0, 48.6, 115.0, and 141.8; the mixture had exact mass, *m/e* 166.1721 (calcd for $C_{12}H_{22}$, *m/e* 166.1721).

The most polar fraction [35.4 mg, 8% recovery; bp 135 °C (20 mm)] was made up of two components as judged by VPC: **19** (78.48%) and **18** (21.05%). This mixture had the following: IR (film) 995 (m), 915 (s), 745 cm^{-1} (vw); NMR ($CDCl_3$, 100 MHz) δ 0.78–1.04 (m, 5.3 H), 1.15–1.62 (m, 6.8 H), 1.85–2.30 (m, 4.6 H), 4.80–5.14 (m, 2.3 H), 5.30–5.82 (m, 2.9 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) displayed signals corresponding to **19** at δ 14.2, 20.3, 22.9, 29.5, 32.7, 36.6, 44.0, 113.9, 128.0, 130.5, and 143.1 and signals corresponding to **18** at δ 13.8, 20.5, 35.0, 48.0, 115.3, and 140.3; the mixture had exact mass, *m/e* 166.1722 (calcd for $C_{12}H_{22}$, *m/e* 166.1721).

Coupling of (*Z*)-1-Bromo-2-hexene. The procedure for (*E*)-1-bromo-2-hexene was followed, except on a larger scale (2.00 mmol of the tellurium reagent), by using (*Z*)-1-bromo-2-hexene[40] (653 mg, 4.00 mmol). Chromatography over silica gel (60 × 1 cm) with hexane and Kugelrohr distillation [110 °C (13 mm)] gave the same product mixture (177 mg, 53%; VPC, TLC, and IR, ^1H NMR, ^{13}C NMR, and mass spectra) as that obtained from (*E*)-1-bromo-2-hexene.

Coupling of Bromomethylbenzene. A thick-walled ampule (volume ca. 25 mL) was oven dried overnight (120 °C), charged with tellurium powder (ca. 200 mesh; 255 mg, 2.00 mmol), closed with a rubber septum, and purged of all air by three cycles of oil pump evacuation and refilling with argon (by means of a needle passing through the septum). Super-Hydride (5.2 mL, 5.2 mmol) was injected, and the mixture was lowered into a sonic bath (used instead of magnetic stirring) and heated to ca. 70 °C. After 45 min, all of the tellurium had dissolved, and the mixture had become a milky white suspension. Bromomethylbenzene (685 mg, 4.00 mmol) in dry dioxane (4.0 mL plus a 4.0-mL rinse) was added. The ampule was sealed and heated in an oil bath at 160 °C for 3 h. The mixture was cooled to room temperature and filtered with the aid of CH_2Cl_2 (ca. 100 mL) through a pad (2 × 2.5 cm) of Celite. The filtrate was concentrated to an oil and partitioned between CH_2Cl_2 (50 mL) and water (50 mL). The aqueous phase was back-extracted with CH_2Cl_2 (2 × 25 mL), and the combined organic extracts were dried, filtered, and concentrated to an oil. Chromatography over silica gel (60 × 1 cm) with 49:1 hexane–ethyl acetate and again (60 × 1 cm) with hexane followed by Kugelrohr distillation [110 °C (0.25 mm)] gave **20**[43] (136 mg, 37%) as a white solid, homogeneous by TLC (silica, 49:1 hexane–ethyl acetate): mp 45–50 °C (lit.[43] mp 52 °C); NMR ($CDCl_3$, 100 MHz) δ 2.90 (s, 4 H), 7.02–7.38 (m, 10 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 37.9, 125.9, 128.4, 128.5, 141.8; exact mass, *m/e* 182.1093 (calcd for $C_{14}H_{14}$, *m/e* 182.1096).

Coupling of (3-Chloro-1-propenyl)benzene by Using Te_2^{2-}. The procedure used previously for the coupling of (3-chloro-1-

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[42] Pinazzi, C. P.; Guilmet, I.; Reyx, D. *Tetrahedron Lett.* **1976**, 989.

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propenyl)benzene was followed, except that the tellurium reagent was prepared with different proportions of Super-Hydride (1 M, 2.6 mL, 2.6 mmol) and tellurium powder (255 mg, 2.00 mmol). after the mixture was stirred at room temperature for 6 h all of the tellurium had dissolved, and the mixture was dark crimson. (3-Chloro-1-propenyl)benzene (306 mg, 2.00 mmol) in dry dioxane (2.0 mL plus a 2.0 mL rinse) was added, causing an immediate deposition of tellurium. The mixture was lowered into an oil bath, preheated to 110 °C, and refluxed for 1 h. A workup as before followed by chromatography over silica gel (60 × 1 cm) with 99:1 hexane–ethyl acetate gave the same (^{1}H NMR, 400 MHz) isomer ratio of 4–7 (207 mg, 88%) as obtained by the previous couplings of (3-chloro-1-propenyl)benzene and (3-bromo-1-propenyl)benzene.

Detection of Bis(2-cyclohexenyl) Telluride by ^{13}C NMR. 3-Bromocyclohexene (644 mg, 4.00 mmol) in dry THF (4.0 mL plus a 4.0-mL rinse) was added to the tellurium reagent (2.00 mmol) prepared in the usual manner in a septum-stoppered centrifuge tube. The tube contained a magnetic stirring bar and was filled with argon. The mixture was stirred at room temperature for 15 min and then centrifuged for 10 min to remove a small amount of particulate matter. A portion of the supernatant (2.0 mL) was transferred to a septum-stoppered, argon-filled ^{13}C NMR tube. THF-d_8 (1.0 mL) was added, and the ^{13}C NMR spectrum of the mixture was recorded (22.6 MHz). The diagnostically significant features of the spectrum were resonances at δ 125.8, 125.9, 130.6, and 130.7 and the absence of resonances between δ 30.0 and 65.0. The NMR sample remained unchanged on being allowed to stand under argon for longer than 10 days. However, upon exposure of air, the mixture rapidly deposited black tellurium. ^{13}C NMR spectra were also recorded for 3-bromocyclohexene and 2,2′-bicyclohexenyl (1) in the presence of 1 and 2 equiv, respectively, of triethylborane. The former had ^{13}C NMR (THF-d_8, 22.6 MHz) values of δ 19.5, 25.4, 33.7, 49.1, 130.0, and 131.2.[44] The latter had ^{13}C NMR (THF-d_8, 22.6 MHz) values of δ 23.2, 26.2, 26.8, 41.2, 128.2, 128.6, 131.2, and 131.3.[44]

Attempted Coupling of 3-Bromocyclohexene by Using Se^{2-}. A suspension of lithium selenide in THF was prepared by the literature procedure:[7c] Under argon, gray selenium powder (158 mg, 2.00 mmol) was added portionwise to Super-Hydride (1 M, 4.2 mL, 4.2 mmol) with magnetic stirring. The milky, white suspension was stirred for a further 20 min, and then 3-bromocyclohexene (645 mg, 4.00 mmol) and dry *tert*-butyl alcohol (0.37 mL, 0.29 g, 3.9 mmol) in dry dioxane (4.0 mL plus a 4.0-mL rinse) were added by syringe. Within 1 h, all of the halide had reacted (TLC). After a further 2.5 h at room temperature, the mixture was lowered into an oil bath (110 °C) and refluxed for 3.5 h. No metallic selenium was deposited, and VPC analysis of the reaction mixture indicated less than a 2% yield of the coupled product (1).

In a preparative experiment, gray selenium powder (154 mg, 1.95 mmol) was added portionwise under nitrogen to Super-Hydride (1 M, 4.0 mL, 4.0 mmol). After the mixture had been stirred for 20 min, 3-bromocyclohexene (647 mg, 4.02 mmol) and dry *tert*-butyl alcohol (0.37 mL, 0.29 g, 3.9 mmol) in dry THF (4.0 mL plus a 2.0-mL rinse) was added by syringe. After 3 h of stirring at room temperature, the reaction was complete (TLC), and the mixture was taken up in ether (40 mL) and washed with water (3 × 20 mL). The combined aqueous extracts were back-extracted with ether (30 mL). The combined ether extracts were dried (Na_2SO_4), filtered, and concentrated to an oily solid. The crude product was chromatographed over silica gel (40 × 1.5 cm) with 9:1 hexane–ethyl acetate and then again over silica gel (66 × 1.5 cm) with hexane to give **21** (306 mg, 65%) as a homogeneous (TLC, silica, 9:1 hexane–ethyl acetate) oil. Compound **21**: NMR ($CDCl_3$, 100 MHz) δ 1.31–2.31 (m, 12 H), 3.52–3.77 (m, 2 H), 5.52–5.96 (m, 4 H); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 20.0, 20.1, 24.9, 30.7, 31.0, 36.6, 128.4, 128.6, 128.9, 129.0; exact mass, *m/e* 242.0571 (calcd for $C_{12}H_{18}Se$, *m/e* 242.0574). A satisfactory combustion analysis could not be obtained for this compound.

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Registry No. 1 (isomer I), 42347-45-5; **1** (isomer II), 57705-09-6; **2**, 55759-30-3; **3** (isomer I), 80794-91-8; **3** (isomer II), 80794-92-9; **4**, 58463-02-8; **5**, 74120-63-1; **6**, 33788-14-6; **7**, 80754-12-7; **8**, 80754-13-8; **9**, 80754-14-9; **10**, 18476-57-8; **11**, 16736-42-8; **12**, 35387-63-4; **13**, 3047-21-0; **14**, 26907-85-7; **15**, 38926-02-2; **16**, 80754-15-0; **17**, 26907-84-6; **18** (isomer I), 80754-16-1; **18** (isomer II), 80754-17-2; **19**, 80754-18-3; **20**, 103-29-7; **21**, 80754-19-4; **22**, 80754-20-7; Te^{2-}, 22541-49-7; Te$_2^{2-}$, 25778-65-8; Se^{2-}, 22541-48-6; 3-bromocyclohexene, 1521-51-3; 3-chlorocyclohexene, 2441-97-6; 3-bromocycloheptene, 36291-49-3; 3-bromocyclooctene, 7422-06-2; (3-bromo-1-propenyl)benzene, 4392-24-9; (3-chloro-1-propenyl)benzene, 2687-12-9; (*E*)-5-chloro-1,3-pentadiene, 28070-18-0; (*E*)-4-chloro-2-pentene, 18610-33-8; 1-bromo-3-methyl-2-butene, 870-63-3; (*E*)-1-bromo-2-hexene, 73881-10-4; (*Z*)-1-bromo-2-hexene, 79930-19-1; (bromomethyl)benzene, 100-39-0.

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[44] Signals due to triethylborane are not reported here.

Indirect Electrooxidation (an Ex-Cell Method) of Alkylbenzenes by Recycle Use of $(NH_4)_2Ce(NO_3)_6$ in Various Solvent Systems

Sigeru Torii,* Hideo Tanaka, Tsutomu Inokuchi, Shoji Nakane, Mitsuo Akada, Norio Saito, and Tosifumi Sirakawa

Department of Industrial Chemistry, School of Engineering, Okayama University, Okayama 700, Japan

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Indirect electrooxidation (an ex-cell method) of the side chain of alkylbenzenes has been performed by recycle use of $(NH_4)_2Ce(NO_3)_6$ (CAN) in various solvent systems. The side-chain oxidation of *p*-methoxytoluene (1) with CAN in methanol proceeds smoothly, yielding anisaldehyde (3, 94%), while use of aqueous methanol or acetic acid resulted in a mixture of 3 and the dimeric product 4 (19–35%) along with complex products (28–47%). Electrooxidation of the recovered cerium(III) salts was performed smoothly in methanol by passing 1.1–1.2 F/mol of electricity to give a reddish methanol solution of CAN, which can be used for the next oxidation of 1. The repeated use of CAN over 10 times produced the desired 3 in over 90% yields. Similarly, the oxidation of alkylbenzenes, bearing a *p*-methoxy group, gave the corresponding side-chain-oxidized products. In contrast, *p-tert*-butyltoluene (**9e**) could be oxidized by heating with CAN in aqueous 50% acetic acid at 85–90 °C to give *p-tert*-butylbenzaldehyde in over 90% yield. The regeneration of CAN after the oxidation of **9e** was also accomplished by electrolysis in the aqueous 50% acetic acid system. The reaction mechanisms in connection with the nature of CAN in various solvent systems are discussed.

Recently, much attention has been paid to the four-electron oxidation of the side chain of alkylbenzenes. Among the various kinds of approaches, electrooxidation[1] seems attractive in view of its simple operation, nonpol-

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