Tellurolate-Induced 1,4-Elimination of 1,4-Dibromo 2-Enes. Syntheses of 1,3-Dienes

Lars Engman* and Styrbjörn E. Byström

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Received November 2, 1984

Sodium 2-thienyltellurolate, generated in catalytic amounts from sodium borohydride and bis(2-thienyl) ditelluride, was found to efficiently debrominate 1,4-dibromo-2-olefins to 1,3-dienes under very mild reaction conditions. The required 1,4-dibromo-2-olefins were usually synthesized by allylic α,α'-bromination of olefins. Terminal olefins yielded, via allylic rearrangement, a mixture of 1,4-dibromo-2-olefins and 1,2-dibromo-3-olefins. Both these isomers were converted to 1,3-dienes ($E/Z \approx 9/1$) by the tellurolate reagent. The synthetic utility of the tellurolate-induced debromination reaction was demonstrated in a two-step synthesis of the main component of the red bollworm moth sex pheromone.

The occurrence of conjugated dienic systems in a variety of insect pheromones[1,2] has stimulated a considerable research activity in the field of diene synthesis. Early methods[3] included 1,2- or 1,4-elimination reactions of allylic alcohols, esters, halides, ethers, and ammonium salts, isomerizations of nonconjugated olefins, reduction of polyenes, enynes or cumulenes, aldol condensations, Wittig reactions, and various coupling reactions. However, many of these methods have a poor regio- and/or stereospecificity and were unsuitable for the syntheses of insect pheromones of high isomeric purity. More recent methods for diene synthesis include stereospecific Wittig reactions,[4] reductions of 1,3-diynes and 1,3-enynes,[5] metal-catalyzed eliminations of allylic acetates[6] or 1,2-eliminations of compounds containing oxygen,[7] sulfur,[8] or silicon.[9] The recently developed palladium-catalyzed cross-coupling reaction[10] of vinylic compounds of copper,[11] aluminium,[12] boron,[13] magnesium,[14] and zirconium[15] with various vinylic halides represents one of the most useful methods for the stereocontrolled construction of dienic systems.

We have recently reported a catalytic procedure, based on organotellurium chemistry, for the 1,2-debromination of vicinal dibromides to olefins[16] and the reductive removal of electronegative α-substituents of carbonyl compounds.[17] In the following account we describe another synthetic application of organotellurium chemistry—the syntheses of 1,3-dienes with a tellurolate-induced 1,4-debromination of 1,4-dibromo-2-olefins.

Results

Conjugated dienes are available via three different dehalogenation pathways as shown in Figure 1. The 1,2-, 1,4-, and 1,2,3,4-elimination reactions have all been used for the preparation of 1,3-dienes.[18] Common dehalogenating agents include metals (Zn, Mg, Al), organometallic reagents (MeMgBr), as well as iodide ion.[18] However, as compared with other methods for diene synthesis, the dehalogenation reaction has received relatively little attention. This is due to the unavailability of the required halogenated starting materials and also problems associated with the dehalogenations. The dienic reaction products are often labile compounds not compatible with the rather harsh reaction conditions of the elimination. In fact, a majority of the dienes successfully prepared by dehalogenation reactions are halogen substituted.[18] This would certainly make them more stable toward, e.g., polymerization. Undesired coupling reactions might also be a problem, especially when organometallic dehalogenating agents are used.

We thought that sodium 2-thienyltellurolate (**1**), generated in situ by the sodium borohydride reduction of bis(2-thienyl) ditelluride (**2**), would be well suited to bring about all the different dehalogenation reations shown in Figure 1 under very mild conditions. Our results are summarized in Table I. The reactions were conveniently performed by titration of the bromo compounds in

---

(1) Rossi, R. *Synthesis* **1977**, 817.

(2) Henrick, C. A. *Tetrahedron* **1977**, *33*, 1845.

(3) von Brachtel, H.; Bahr, U. In Houben-Weil "Methoden der Organische Chemie"; Müller, E., Ed.; Georg Thieme Verlag: Stuttgart, 1970; Band 5/1C, p 1.

(4) Roelofs, W. L.; Comeau, A.; Hill, A.; Milicevic, G. *Science (Washington, D.C.)* 1971, *174*, 297. Goto, G.; Shima, T.; Masuya, H.; Masuoka, Y.; Hiraga, K. *Chem. Lett.* **1975**, 103. Bestmann, H. J.; Süß, J.; Vostrowsky, O. *Liebigs Ann. Chem.* **1981**, 2117.

(5) Silverstein, R. M.; Rodin, J. O.; Burkholder, W. E.; Gorman, J. E. *Science (Washington, D.C.)* **1967**, *157*, 85. Zweifel, G.; Polston, N. L. *J. Am. Chem. Soc.* **1970**, *92*, 4068. Negishi, E.; Lew, G.; Yoshida, T. *J. Chem. Soc., Chem. Commun.* **1973**, 874. Normant, J. F.; Commercon, A.; Villieras, J. *Tetrahedron Lett.* **1975**, 1465. Labovitz, J. N.; Henrick, C. A.; Corbin, V. L. *Tetrahedron Lett.* **1975**, 4209. Garanti, L.; Marchesini, A.; Pagnoni, U. M.; Trave, R. *Gazz. Chim. Ital.* **1976**, *106*, 187. Samain, D.; Descoins, C. *Bull. Soc. Chim. Fr.* **1979**, 71. Commercon, A.; Normant, J. F.; Villieras, J. *Tetrahedron* **1980**, *36*, 1215. Svirskaya, P. I.; Leznoff, C. C.; Roelofs, W. L. *Synth. Commun.* **1980**, *10*, 391. Ratovelomana, V.; Linstrumelle, G. *Synth. Commun.* **1981**, *11*, 917.

(6) Tsuji, J.; Yamakawa, T.; Kaito, M.; Mandai, T. *Tetrahedron Lett.* **1978**, 2075. Trost, B. M.; Verhoeven, T. R.; Fortunak, J. M. *Tetrahedron Lett.* **1979**, 2301. Trost, B. M.; Fortunak, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 2841. Matsushita, H.; Negishi, E. *J. Org. Chem.* **1982**, *47*, 4161. Trost, B. M.; Lautens, M.; Peterson, B. *Tetrahedron Lett.* **1983**, *24*, 4525. Suzuki, S.; Fujita, Y.; Nishida, T. *Tetrahedron Lett.* **1983**, *24*, 5737.

(7) Tanaka, S.; Yasuda, A.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1975**, *97*, 3252.

(8) Ochiai, M.; Tada, S.; Sumi, K.; Fujita, E. *Tetrahedron Lett.* **1982**, *23*, 2205. Reich, H. J.; Wollowitz, S. *J. Am. Chem. Soc.* **1982**, *104*, 7051. Block, E.; Aslam, M. *J. Am. Chem. Soc.* **1983**, *105*, 6164. Block, E.; Aslam, M.; Eswarakrishnan, V.; Wall, A. *Ibid.* **1983**, *105*, 6165.

(9) Chan, T.-H.; Li, J.-S. *J. Chem. Soc., Chem. Commun.* **1982**, 969. Yamamoto, Y.; Saito, Y.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1982**, 1326.

(10) For a review see: Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340. See also: Bäckvall, J.-E.; Byström, S. E.; Nordberg, R. E. *J. Org. Chem.* **1984**, *49*, 4619, ref 44.

(11) Jabri, N.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1981**, *22*, 959. Jabri, N.; Alexakis, A.; Normant, J. F. *Ibid.* **1982**, *23*, 1589. Jabri, N.; Alexakis, A.; Normant, J. F. *Bull. Soc. Chim. Fr.* **1983**, 321.

(12) Baba, S.; Negishi, E. *J. Am. Chem. Soc.* **1976**, *98*, 6729. Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *J. Am. Chem. Soc.* **1978**, *100*, 2254.

(13) Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Lett.* **1979**, 3437. Miyaura, N.; Suginome, H.; Suzuki, A. *Ibid.* **1981**, *22*, 127.

(14) Dang, H. P.; Linstrumelle, G. *Tetrahedron Lett.* **1978**, 191.

(15) Okukado, N.; Van Horn, D. E.; Klima, W. L.; Negishi, E. *Tetrahedron Lett.* **1978**, 1027.

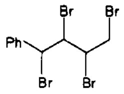
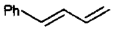
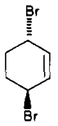
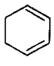
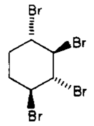
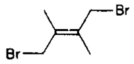
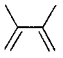
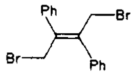
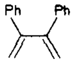
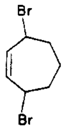
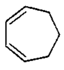
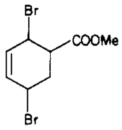
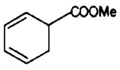
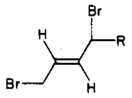
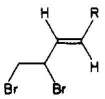
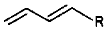
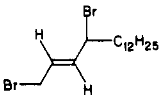
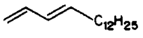
(16) Engman, L. *Tetrahedron Lett.* **1982**, *23*, 3601.

(17) Engman, L.; Cava, M. P. *J. Org. Chem.* **1982**, *47*, 3946.

(18) See ref 3, p 152, 292. For some recent examples see: Van Tamelen, E. E.; Pappas, B. C. T. *J. Am. Chem. Soc.* **1971**, *93*, 6111 (iodide- and zinc-induced 1,4-elimination of bromine from 1,4-dibromo-2-cyclohexene afforded cyclohexadiene in only 28% and 38% yield, respectively). Dowd, P.; Marwaha, L. K. *J. Org. Chem.* **1976**, *41*, 4035. Slupczynski, M.; Wolszczak, I.; Kosztolowicz, P. *Inorg. Chim. Acta* **1979**, *33*, L 97. Gaoni, Y.; Sadeh, S. *J. Org. Chem.* **1980**, *45*, 870.

0022-3263/85/1950-3170$01.50/0

Table I. 1,3-Dienes Obtained by Tellurolate-Induced Debromination Reactions

bromo compound		diene	yield[a]	*E*/*Z* ratio	solvent[b]
 3		 4	99	>95%*E*	B
 5		 6	(93)		A
 7		6	(92)		B
 8		 9	(82)		A
 10		 11	100		A
 12		 13	(79)		B
 14		 15	78[d]		A
 16	+  17	 18			
R	16/17 ratio				
a, C_2H_5	72/28		(71)[c]	87/13	B
b, C_4H_9	65/35		(88)	88/12	B
c, C_6H_{13}	64/36		73	88/12	B
d, $(CH_2)_7OAc$	74/26		60	93/7	B
e, $(CH_2)_8OAc$	62/38		60	88/12	B
 19		 20	90	>95%*E*	B

[a] Yields within brackets are GC yields. Other yields are isolated yield. [b] A = MeOH; B = THF. [c] The overall yield is probably better for this reaction. The GC analysis could not be performed until all the THF had been washed out of the pentane phase. Some diene was probably lost during this extraction process. [d] 10% of methyl benzoate was formed as a byproduct in this reaction.

methanol or tetrahydrofuran at ambient temperature with sodium borohydride, the ditelluride (in catalytic amount, 5–10%) serving as an indicator changing color from deep red to colorless when all the dibromide was consumed. At this point air was introduced into the system to oxidize the catalyst back to the ditelluride state.

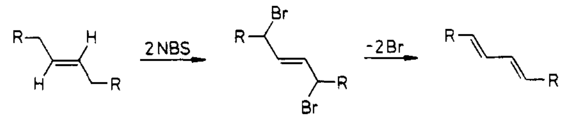
The bromo compounds used for the debromination reactions were in some cases prepared by 1,4-addition of bromine to the corresponding diene (compounds **3**, **8**, and **10**). The reformation of the diene is of course useful only for purification purposes in such cases. However, the majority of the dibromides were obtained via an α,α'-allylic bromination[19] of olefins. The allylic bromination–debromination sequence is synthetically equivalent to a dehydrogenation of an olefin to a diene as shown in eq 1.

The bromination of cyclic or nonterminal olefins with a 2-fold excess of *N*-bromosuccinimide is generally con-

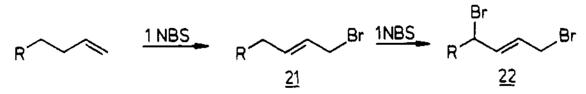
---

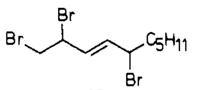
(19) Djerassi, C. *Chem. Rev.* **1948**, *43*, 271. Horner, L.; Winkelmann, E. H. *Angew. Chem.* **1959**, *71*, 349. Nechvatal, A. In Williams, G. H., Ed. "Advances in Free-Radical Chemistry"; Logos Press: London, 1972; Vol. IV, p. 175.

(1)



(2)





23

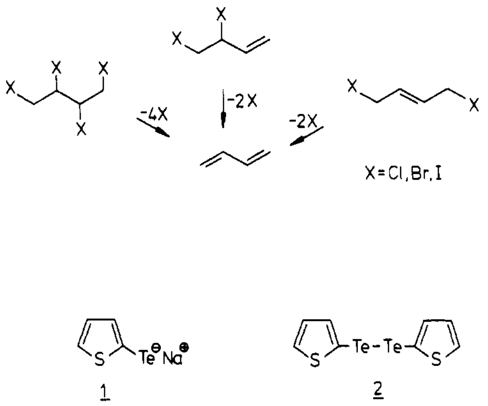


Figure 1.

sidered to give an α,α'-dibromo olefin[20-24] (compounds **5**, **12**, and **14**). Terminal olefins undergo an allylic rearrangement in the reaction with the first equivalent of *N*-bromosuccinimide.[25] The main product, a 1-bromo-2-olefin **21**, reacts further with the second equivalent of the halogenating agent to produce a 1,4-dibromo-2-olefin **22** (eq 2). However, the structures of the few dibromides **22** ever prepared[26,27] have never, to the best of our knowledge, been proven conclusively but were more or less based on assumption.

We prepared a series of 1,4-dibromo-2-olefins **22** by treatment of terminal olefins with 2 equiv of *N*-bromosuccinimide in refluxing carbon tetrachloride containing a small amount of benzoyl peroxide. The reactions were usually completed within 1 h as judged by the complete disappearance of the heavy *N*-bromosuccinimide from the bottom of the reaction flask. TLC analysis of the crude reaction mixture revealed the formation of several products. As a representative example, the product mixture obtained from 1-decene was analyzed in some detail. In addition to a small amount of monoallylic bromide (**21** R = C_6H_{13}), the two main products were identified as 1,4-dibromo-2-decene (**16c**) and 1,2-dibromo-3-decene (**17c**). On the basis of infrared data, both compounds predominantly have the E configuration (strong absorption at 965 cm^{-1} for both compounds). A fourth minor product was also isolated and identified as a tribromide **23**.

Distillation at low pressure of the crude reaction mixture obtained from 1-hexene, 1-octene, and 1-decene, respectively, separated the monobromo compound in the forefraction while the tribromide was left in the distillation residue. The mixture of 1,2- and 1,4-dibromoolefins was isolated in approximately 50% distilled yield and the 1,2/1,4-ratio determined by ^1H NMR spectroscopy (Table I). Both isomers could be converted to the same 1,3-diene in the tellurolate-induced debromination reaction as shown for the separated compounds **16c** and **17c**, which both yielded 1,3-decadiene.

The reaction mixture obtained from 1-hexadecene could not be distilled without serious decomposition. Fortunately, the 1,4-dibromoolefin **19** was isolated by crystallization of the crude bromination mixture from light petroleum. Some of the other dibromide mixtures (**16d**/**17d** and **16e**/**17e**) were purified by chromatography.

The yields of dienes reported in Table I are in some cases isolated yields obtained after chromatography, distillation, or recrystallization. In the case of highly volatile dienes, the GC yields are reported.

The yields of dienes in the tellurolate-induced debromination reaction were usually excellent, provided the di- or tetrabromides could be obtained in a pure state (compounds **3**, **5**, **7**, **8**, **10**, and **19** were easily purified by crystallization). After the completion of these reactions, bis(2-thienyl) ditelluride was usually reformed when air was introduced into the reaction vessel. When the dibromides were purified by other means (distillation, chromatography) the isolated yields were lower. Furthermore, the catalyst was often consumed in these reactions and no red color appeared during the oxidative workup. Instead, a white insolable material slowly precipitated on exposure to air. This consumption of the catalyst might be attributed to the presence of impurities, such as monoallylic bromides, in the starting materials (vide infra).

The isomeric composition of the terminal 1,3-dienes was determined by using ^1H NMR spectroscopy (Table I). All terminal dienes were highly enriched in the *E* isomer but contained approximately 10% of the *Z* isomer. However, (*E*)-1-phenyl-1,3-butadiene (**4**) and (*E*)-1,3-hexadecadiene (**20**) were obtained isomerically pure.

Discussion

The tellurolate-induced debromination reaction of 1,4-dibromo-2-olefins is a catalytic process easily performed under very mild reaction conditions. It should therefore be a useful method for the synthesis of sensitive conjugated dienes. However, the availability of the required brominated starting materials might impose some restrictions to the reaction.

The α,α'-allylic dibromination of olefins is not a very specific reaction. We have shown in this paper that terminal olefins afford two dibromo compounds on treatment with 2 equiv of *N*-bromosuccinimide. The major product, a 1,4-dibromo-2-olefin (**22**) is probably formed via a "normal" allylic bromination of a 1-bromo-2-olefin (**21**). The minor product, a 1,2-dibromo-3-olefin, might be formed either by rearrangement of dibromide **22** or by an allylic bromination of compound **21** accompanied by rearrangement (similar to the formation of compound **21** from the 1-olefin). Heasley and co-workers[28] have studied the addition of bromine to (*E*)- and (*Z*)-1,3-pentadiene in

---

(20) Maercker, A.; Geuβ, R. *Chem. Ber.* **1973**, *106*, 773.

(21) Hatch, L. F.; Bachmann, G. *Chem. Ber.* **1964**, *97*, 132.

(22) Hoare, J. H.; Policastro, P. P.; Berchtold, G. A. *J. Am. Chem. Soc.* **1983**, *105*, 6264.

(23) Gupta, S. C.; Kummerow, F. A. *J. Am. Oil Chem. Soc.* **1960**, *37*(1), 32.

(24) Ucciani, E.; Naudet, M. *Bull. Soc. Chim. Fr.* **1962**, 871.

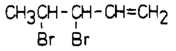
(25) Bateman, L.; Cunneen, J. I. *J. Chem. Soc.* **1950**, 941. Kharasch, M. S.; Malec, R.; Yang, N. C. *J. Org. Chem.* **1957**, *22*, 1443.

(26) Winkelmann, E. Dissertation, Mainz, 1957.

(27) Ziegler, K.; Späth, A.; Schaaf, E.; Schumann, W.; Winkelmann, E. *Liebigs Ann. Chem.* **1942**, *551*, 80.

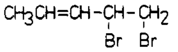
(28) Heasley, V. L.; Heasley, G. E.; Taylor, S. K.; Frye, C. L. *J. Org. Chem.* **1970**, *35*, 2967.

carbon tetrachloride at low temperature. They reported the formation of three different dibromides **24**–**26**. Depending on the geometry and concentration of the pentadiene, compounds **26** were obtained in 70–80% yield together with compounds **25** (20–30%) and trace amounts of compound **24**. Furthermore, when isolated amounts of each isomer were heated in sealed tubes for several days at 80 °C, identical mixtures were obtained in every case. This equilibrium mixture was shown to consist of 2% of **24**, 32% of **25**, and 66% of **26**. These results show that the 1,2- and 1,4-dibromo compounds are interrelated. In fact, it is possible that the product we obtained by using *N*-bromosuccinimide consisted of an equilibrium mixture, although we were unable to isolate compounds related to structure **24**. The formation of dibromoolefins was always accompanied by the formation of small amounts of monobromo and tribromo compounds. These compounds have to be separated before the debromination to avoid undesirable consumption of the catalyst. The nucleophilic tellurolate ion readily reacts (in a side reaction) with any monoallylic compound **21** to form a telluride **27**. A tribromide, such as compound **23**, is also a precursor of a monoallylic bromide (via 1,2- or 2,5-debromination). An attempt to debrominate the tetrabromide **28** resulted in rapid comsumption of the catalyst (probably due to nucleophilic substitution of the debromination product **29**).



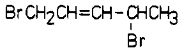
$\mathrm{CH_3\underset{Br}{CH}-\underset{Br}{CH}-CH{=}CH_2}$

24



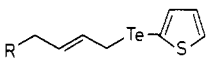
$\mathrm{CH_3CH{=}CH-\underset{Br}{CH}-\underset{Br}{CH_2}}$

25 (E+Z)

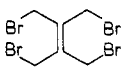


$\mathrm{BrCH_2CH{=}CH-\underset{Br}{CH}CH_3}$

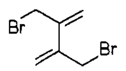
26 (E+Z)



27



28



29

We have previously shown that the tellurolate-induced 1,2-elimination of vicinal dibromides to olefins occurs with a high degree of anti specificity. This result was explained by assuming a nucleophilic attack of the tellurolate ion on bromine.[16]

The stereochemistry of 1,4-conjugate elimination reactions is a somewhat controversial issue.[29-31] *trans*-3,6-Dibromocyclohexene (**5**)[32] was the only 1,4-dibromo-2-olefin used in this study that would provide definite information concerning the stereochemistry of the tellurolate-induced 1,4-debromination reaction. Its facile elimination to 1,3-cyclohexadiene shows that it is possible to perform an overall anti elimination in a cyclic cisoid system. However, from a mechanistic point of view we can only speculate as to whether the reaction is concerted or not. The involvement of an electron-transfer process can certainly not be excluded.

The synthetic utility of the tellurolate-induced 1,2- and 1,4-dibromination reactions were demonstrated in a two-step synthesis of (*E*)-9,11-dodecadien-1-yl acetate (**18e**), a sex pheromone of the red bollworm moth, *Diparopsis castanea* Hmps. Our synthesis represents the shortest route available for this pheromone component although it does not allow the complete control of product stereochemistry (the product contained 12% of the *Z* isomer) that has been demonstrated in other syntheses.[33,41]

Experimental Section

Infrared spectra were recorded on a Pye Unicam SP 1000 instrument. NMR spectra were obtained with a Bruker WP 200 instrument at 200 MHz. They were recorded in $CDCl_3$ solutions containing Me_4Si as internal standard and are reported in δ units. GLC analyses were performed on a 6 ft × $^1/_8$ in. glass column packed with 10% SE-30 on Chromosorb W (60/80 mesh). All terminal olefins used were commercially available except for 11-dodecene-1-yl acetate which was kindly provided by Chemische Werke Hüls A.G. Bis(2-thienyl) ditelluride,[34] 1-phenyl-1,2,3,4-tetrabromobutane,[35] *trans*-3,6-dibromocyclohexene,[20] 1,2,3,4-tetrabromocyclohexane,[36] (*E*)-1,4-dibromo-2,3-dimethyl-2-butene,[37] (*E*)-1,4-dibromo-2,3-diphenyl-2-butene,[38] 3,7-dibromocycloheptene,[21] 4-carbomethoxy-3,6-dibromocyclohexene,[22] and 1,1,2,2-tetra(bromomethyl)ethylene[39] were prepared according to literature methods.

Bromination of 1-Decene. Typical Procedure. 1-Decene (3.0 g, 21.4 mmol), *N*-bromosuccinimide (8.0 g, 44.9 mmol), and dibenzoyl peroxide (0.4 g) were heated to reflux in CCl_4 (30 mL) for 45 min when all *N*-bromosuccinimide was consumed. The crude reaction product (7.2 g) obtained after cooling, filtration, and evaporation was then analyzed by TLC (light petroleum, bp 40–60 °C). In addition to a small spot corresponding to monobrominated 1-decene (R_f 0.51), two major products **17c** and **16c** (R_f 0.44 and 0.32, respectively) were isolated together with a minor one **23** (R_f 0.25). The three unknown products could be separated by column chromatography, but none of them was obtained completely pure.

17c: NMR 0.89 (t, 3 H), 1.20–1.43 (broad s, 8 H), 2.07 (m, 2 H), 3.63 (t, 1 H, J = 10.2 Hz), 3.83 (dd, 1 H, J = 4.6 Hz and 10.2 Hz), 4.68 (m, 1 H), 5.53 (dd, 1 H, J = 9.5 Hz and 15.1 Hz), 5.80 (m, 1 H); IR (neat) cm^{-1} 965.

16c: NMR 0.89 (t, 3 H), 1.28–1.47 (broad s, 8 H), 1.91 (m, 2 H), 3.94 (d, 2 H), 4.49 (m, 1 H), 5.86–5.93 (several peaks, 2 H); IR (neat) cm^{-1} 965.

23: NMR 0.89 (t, 3 H), 1.30–1.44 (several peaks, 6 H), 1.92 (m, 2 H), 3.65 (dd, 1 H, J = 10.3 Hz and 10.3 Hz), 3.84 (dd, 1 H, J = 4.6 Hz and 10.3 Hz), 4.49 (m, 1 H), 4.68 (m, 1 H), 5.75 (dd, 1 H, J = 9.0 Hz and 15.1 Hz), 5.98 (dd, 1 H, J = 8.8 Hz, and 15.1 Hz); IR (neat) cm^{-1} 965.

When the separated isomers **16c** and **17c** were submitted to the normal debromination conditions (10% catalyst), 1,3-decadiene (E/Z = 9/1) was isolated in 100% and 92% yield, respectively.

Distillation of the crude reaction product obtained from 1-decene and 2 equiv of *N*-bromosuccinimide afforded a mixture of compounds **16c** and **17c** in 50% yield, bp 82–88 °C (5 × 10^{-2} mm). The ratio **16c**/**17c** was determined with ^1H NMR spectroscopy and is shown in Table I.

The following dibromides were prepared according to the typical procedure: compound (bp, °C (mm Hg)), **12** (78–82 (5 × 10^{-2})), **16a**/**17a** (46–50 (5 × 10^{-1})), **16b**/**17b** (60–66 (5 × 10^{-2})). Compound **14** was Kugelrohr distilled before debromination.

---

(29) Tee, O. S.; Altmann, J. A.; Yates, K. *J. Am. Chem. Soc.* **1974**, *96*, 3141.

(30) Hill, R. K.; Bock, M. G. *J. Am. Chem. Soc.* **1978**, *100*, 637.

(31) Åkermark, B.; Nyström, J-E.; Rein, T.; Bäckvall, J.-E.; Helquist, P.; Aslanian, R. *Tetrahedron Lett.* **1984**, *25*, 5719.

(32) Heasley, G. E.; Heasley, V. L.; Manatt, S. L.; Day, H. A.; Hodges, R. V.; Kroon, P. A.; Redfield, D. A.; Rold, T. L.; Williamson, D. E. *J. Org. Chem.* **1973**, *38*, 4109.

(33) For other syntheses of compound **18e** see: Nesbitt, B. F.; Beevor, P. S.; Cole, R. A.; Lester, R.; Poppi, R. G. *Tetrahedron Lett.* **1973**, 4669. Mori, K. *Tetrahedron* **1974**, *30*, 3807. Babler, J. H.; Martin, M. J. *J. Org. Chem.* **1977**, *42*, 1799. Mandai, T.; Yasuda, H.; Kaito, M.; Tsuji, J.; Yamaoka, R.; Fukami, H. *Tetrahedron* **1979**, *35*, 309. Yasuda, A.; Tanaka, S.; Yamamoto, H.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1752. Babler, J. H.; Invergo, B. J. *J. Org. Chem.* **1979**, *44*, 3723. Wollenberg, R. H.; Peries, R. *Tetrahedron Lett.* **1979**, 297. Rossi, R.; Carpita, A.; Quirici, M. G. *Tetrahedron* **1981**, *37*, 2617. Knox, G. R.; Thom, I. G. *J. Chem. Soc., Chem. Commun.* **1981**, 373. Bloch, R.; Abecassis, J. *Tetrahedron Lett.* **1982**, *23*, 3277. Ochiai, M.; Ukita, T.; Fujita, E. *Chem. Pharm. Bull.* **1983**, *31*, 1641. Hayashi, T.; Yanagida, M.; Matsuda, Y.; Oishi, T. *Tetrahedron Lett.* **1983**, *24*, 2665.

(34) Engman, L.; Cava, M. P. *Organometallics* **1982**, *1*, 470.

(35) Muskat, I. E.; Herrman, M. *J. Am. Chem. Soc.* **1931**, *53*, 252.

(36) Hassel, O.; Lunde, K. *Acta Chem. Scand.* **1950**, *4*, 1597.

(37) Sweeting, O. J.; Johnson, J. R. *J. Am. Chem. Soc.* **1946**, *68*, 1057.

(38) Dodson, R. M.; Srinivasan, V.; Sharma, K. S.; Sauers, R. F. *J. Org. Chem.* **1972**, *37*, 2367.

(39) Cope, A. C.; Kagan, F. *J. Am. Chem. Soc.* **1958**, *80*, 5499.

Compounds **16d**/**17d** and **16e**/**17e** were isolated in 95% yield after filtration through a short silica pad (light petroleum bp 40–60 °C).

Compound **19** was obtained essentially pure in 18% yield as a low melting solid (mp 25–28 °C) after two recrystallizations (light petroleum, bp 40–60 °C) of the oily crude reaction product from 1-hexadecene and 2 equiv of *N*-bromosuccinimide (cooling to −15 °C and rapid filtration). On the basis of IR data (965 cm^{-1} s, 720 w) the product has been assigned the *E* configuration.

NMR 0.88 (t, 3 H), 1.26 (broad s, 20 H), 1.90 (m, 2 H), 3.95 (d, 2 H), 4.49 (m, 1 H), 5.86–5.93 (several peaks, 2 H).

General Procedure for the Preparation of Conjugated Dienes. Sodium borohydride (10% in 0.1% aqueous NaOH) was added dropwise under N_2 at ambient temperature to a solution of the appropriate allylic dibromide in methanol or tetrahydrofuran (1.5–2 mmol/15 mL solvent) containing bis(2-thienyl) ditelluride (5–10 mol %) until the orange-red color of the ditelluride disappeared. Two equivalents of $NaBH_4$ were usually required in the MeOH runs whereas the THF reactions required up to 3 equiv (due to formation of a two-phase system with incomplete phase transfer of the borohydride).

The reaction mixture was then poured into water and extracted with pentane. During this process the catalyst was usually reformed and extracted into the organic phase. In some cases (synthesis of terminal dienes) the catalyst was not reformed during the workup procedure. The formation of a white insoluble precipitate was observed in these cases. The combined organic extracts were washed several times with water, dried, and evaporated. The diene product was then purified by means of distillation or column chromatography and compared with authentic samples (compounds **4**, **6**, **9**, **11**, **13**, **15**, **18a**). Methanol was usually a good solvent for the debromination reactions. However, in the synthesis of terminal dienes methoxylated products were formed as undesired byproducts. Tetrahydrofuran was therefore the solvent of choice for these reactions.

In the synthesis of terminal olefins 10% of the catalyst was used in order to obtain good yields of product dienes.

The yields of C_6, C_7, and C_8 dienes were determined by GLC. The isomeric composition of the terminal olefins was determined by using ^1H NMR spectroscopy. In order to successfully isolate a sample of 1,3-hexadiene (**18a**), (preparative GLC was unsuitable) a slow stream of N_2 was passed through the reaction mixture (diluted with 6 volumes of H_2O after the completion of the borohydride addition) into a cold trap (−78 °C). The condensate was then dissolved in $CDCl_3$ and washed several times with water to remove most of the THF.

NMR data for terminal dienes.

18a: 1.01 (t, 3 H), 2.11 (m, 2 H), 4.95 (d, 1 H), 5.09 (d, 1 H), 5.75 (m, 1 H, $J_{\mathrm{H,H\ olefinic}}$ = 15.2 Hz), 6.04 (m, 1 H), 6.32 (m, 1 H).

18b: 0.90 (t, 3 H), 1.26–1.44 (several peaks, 4 H), 2.08 (m, 2 H), 4.95 (d, 1 H), 5.08 (d, 1 H), 5.71 (m, 1 H, $J_{\mathrm{H,H\ olefinic}}$ = 15.0 Hz), 6.04 (m, 1 H), 6.31 (m, 1 H).

18c: 0.88 (t, 3 H), 1.28 (broad s, 8 H), 2.08 (m, 2 H), 4.95 (d, 1 H), 5.08 (d, 1 H), 5.71 (m, 1 H, $J_{\mathrm{H,H\ olefinic}}$ = 15.1 Hz), 6.04 (m, 1 H), 6.29 (m, 1 H).

18d: 1.33 (broad s, 8 H), 1.60 (m, 2 H), 2.05 (s, 3 H), 2.07 (m, 2 H), 4.05 (t, 2 H), 4.95 (d, 1 H), 5.09 (d, 1 H), 5.70 (m, 1 H, $J_{\mathrm{H,H\ olefinic}}$ = 15.2 Hz), 6.05 (m, 1 H), 6.32 (m, 1 H).

20: 0.88 (t, 3 H), 1.26 (broad s, 20 H), 2.08 (m, 2 H), 4.95 (d, 1 H), 5.08 (d, 1 H), 5.71 (m, 1 H, $J_{\mathrm{H,H\ olefinic}}$ = 15.0 Hz), 6.04 (m, 1 H), 6.32 (m, 1 H).

The NMR data of compounds **14**[40] and **18e**[41] were in excellent agreement with published data.

Acknowledgment. We thank Chemische Werke Hüls A.G. for a generous gift of 11-dodecen-1-yl acetate. Financial support by the Swedish Natural Science Research Council is gratefully acknowledged.

Registry No. **1**, 82093-40-1; **2**, 66697-24-3; **3**, 97112-42-0; **4**, 16939-57-4; **5**, 42086-53-3; **6**, 592-57-4; **7**, 97102-18-6; **8**, 6044-73-1; **9**, 513-81-5; **10**, 34804-71-2; **11**, 2548-47-2; **12**, 97102-19-7; **13**, 4054-38-0; **14**, 97102-20-0; **15**, 54162-19-5; **16a**, 97102-21-1; **16b**, 97102-22-2; **16c**, 97102-23-3; **16d**, 97102-24-4; **16e**, 97102-25-5; **17a**, 97102-26-6; **17b**, 97102-27-7; **17c**, 97102-28-8; **17d**, 97102-29-9; **17e**, 97102-30-2; (*E*)-**18a**, 20237-34-7; (*Z*)-**18a**, 14596-92-0; (*E*)-**18b**, 39491-65-1; (*Z*)-**18b**, 39491-64-0; (*E*)-**18c**, 58396-45-5; (*Z*)-**18c**, 66717-33-7; (*E*)-**18d**, 97102-31-3; (*Z*)-**18d**, 97102-32-4; (*E*)-**18e**, 50767-78-7; (*Z*)-**18e**, 51760-35-1; **19**, 97102-33-5; **20**, 97102-34-6; **23**, 97102-35-7; **29**, 18214-55-6; $CH_2{=}CHCH_2CH_2CH_2CH_3$, 592-41-6; $CH_2{=}CH(CH_2)_5CH_3$, 111-66-0; $CH_2{=}CH(CH_2)_9OAc$, 112-19-6; 11-dodecen-1-yl acetate, 35153-10-7; 1,1,2,2-tetrakis(bromomethyl)ethylene, 30432-16-7; 1-decene, 872-05-9; 1-hexadecene, 629-73-2; methyl benzoate, 93-58-3.

---

[40] Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730.

[41] Schechter, H.; Hsiao, C.-N. *Tetrahedron Lett.* **1984**, *25*, 1219.

Computer-Assisted Mechanistic Evaluation of Organic Reactions. 10. Stereochemistry

Catherine E. Peishoff and William L. Jorgensen*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received December 11, 1984

The emphasis of CAMEO, an interactive computer synthesis program, is the application of mechanistic reasoning to the prediction of organic reaction products. In addition to intrinsic chemical reactivity, the question of stereochemical and physical limitations must be addressed in assessing overall reactivity. The program has been significantly improved in this area by the addition of algorithms which cover inversion of configuration, identification of stereorelationships, and steric-accessibility limits for intramolecular reactions. The paper begins with a review of stereoperception in CAMEO. Reactions from the base-catalyzed and nucleophilic module are then used to illustrate pertinent stereochemical and physical restrictions. Implementation of the algorithms is discussed, and reactions from a synthesis of longifolene are reviewed from a stereochemical perspective.

Introduction

CAMEO, an interactive computer synthesis program which predicts the products of organic reactions given starting materials and conditions, is under continued development.[1-7] In its initial stages, the predictive ability of the program focused on base-catalyzed and nucleophilic

---

[1] Salatin, T. D.; Jorgensen, W. L. *J. Org. Chem.* **1980**, *45*, 2043.