°C (0.02 Torr)) afforded 2.28 g (60%) of the aldehyde. The compound proved to be not very stable. Part of the material was directly used for the tandem-Knoevenagel-Diels-Alder reaction; a 2,4-dinitrophenylhydrazone was prepared for characterization: mp 141-143.5 °C (ethyl acetate); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.83 (d, J = 1.3 Hz, 3 H, CH_3 cis), 1.95 (d, J = 1.4 Hz, 3 H, CH_3 trans), 4.86 (d, J = 4.9 Hz, 2 H, CH_2), 6.36 (s, br, 1 H, =CH), 6.92-7.12 (m, 2 H, 4'-H, 6'-H), 7.20-7.28 (m, 2 H, 3'-H, 5'-H), 7.69 (td, J = 4.9 Hz, J = 0.8 Hz, 1 H, N=CH), 7.96 (d, J = 9.5 Hz, 1 H, 6'-H), 8.38 (ddd, J = 9.5 Hz, J = 2.5 Hz, J = 0.8 Hz, 1 H, 5''-H), 9.17(d, J = 2.5 Hz, 1 H, 3''-H), 11.16 (s, br, 1 H, NH). Anal. Calcd for $C_{18}H_{18}N_4O_4$: C, 58.37; H, 4.90; N, 15.13. Found: C, 58.49; H, 4.91; N, 15.27.

Reaction of 31 with *N*,*N*-Dimethylbarbituric Acid (32). To a stirred suspension of **32** (302 mg, 1.94 mmol) and EDDA (14 mg, 0.07 mmol) in dry acetonitrile (20 mL) was added a solution of aldehyde **31** (5.14 mg, 2.70 mmol) in acetonitrile (10 mL). The mixture was stirred for 22 h at room temperature, the solvent was then removed in vacuo, and the residue was flash chromatographed on silica gel (*tert*-butyl methyl ether/petroleum ether, 1:1).

Fraction 1. (3'*RS*,4'*RS*)-5-(4-Isopropenyl-3,4-dihydro-1*H*-[1]benzopyran-3-yl)-1,3-dimethyl-2,4,6(1*H*,3*H*,5*H*)-pyrimidinetrione (34): R_f 0.34; yield, 28%; UV 218 (4.09), 266 (3.86), 282 (sh); IR 1750, 1700-1670, 755; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.47 (d, J = 0.5 Hz, 3 H, =CCH_3), 3.10-3.24 (m, 1 H, 3'-H), 3.26 (s, 3 H, NCH_3), 3.35 (s, 3 H, NCH_3), 3.55 (d, J = 2.0 Hz, 1 H, 5-H), 3.83 (d, br, J = 11.0 Hz, 1 H, 4'-H), 4.20-4.30 (m, 2 H, 2'-H ax. and eq), 4.88-4.94 (m, 1 H, =CH), 4.98-5.06 (m, 1 H, =CH), 6.80-7.20 (m, 4 H, 5'-H to 8'-H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.33 (CH_3C=), 28.46 (NCH_3), 38.67 (C-3'), 47.24 (C-4'*), 49.29 (C-5*), 67.70 (C-2), 116.75 (C-8'), 116.99 (=CH_2), 120.93 (C-6'), 122.07 (C-4'a), 127.79, 128.69 (C-5', C-7') 144.93 (C=C_2), 151.19 (C-2), 154.44 (C-8'a), 166.69, 167.14 (C-4, C-6); some signals of the minor cis isomer **35** are seen, δ 21.27 (CH_3C=), 40.20 (C-3'), 44.67 (C-4'*), 48.95 (C-5*), 66.44 (C-2); ratio **34**:**35** = 5.2:1; MS, m/z 328 (6, M^+), 313 (0.2, M - CH_3), 285 (0.8, M - C_3H_7), 172 (100, $C_{12}H_{12}O$), 157 (69, $C_6H_9N_2O_3^+$). Anal. Calcd for $C_{18}H_{20}N_2O_4$: C, 65.84; H, 6.14; N, 8.53. Found: C, 65.78; H, 6.22; N, 8.55.

Fraction 2. (4b*RS*,10b*SR*)-1,2,3,4,4b,5,10b,11-Octahydro-1,3,11,11-tetramethyl[1]benzopyrano[3',4':4,5]pyrano[2,3-*d*]pyrimidine-2,4-dione (36): R_f 0.17-0.30; yield, 42%; mp 215-217 °C (methanol/water); UV 219 (4.16), 262 (3.99), 283 (3.36); IR 1705, 1640, 1230, 750; ^{1}H NMR (200 MHz, 50 °C, DMSO-d_6) δ 1.36 (s, 3 H, 11-CH_3 ax.), 1.95 (s, 3 H, 11-CH_3 eq), 2.78 (td, J = 11.0 Hz, J = 4.5 Hz, 1 H, 4b-H), 3.12 (d, br, J = 11.0 Hz, 1 H, 10b-H), 3.16 (s, 3 H, NCH_3), 3.21 (s, 3 H, NCH_3), 3.84 (dd, J = 11.0 Hz, J = 10.0 Hz, 1 H, 5-H ax.), 5.35 (dd, J = 10.0 Hz, J = 4.5 Hz, 1 H, 5-H eq), 6.84 (dd, J = 8.0 Hz, J = 1.5 Hz, 1 H, 7-H), 6.89 (td, J = 8.0 Hz, J = 1.5 Hz, 1 H, 9-H), 7.19 (tdd, J = 8.0 Hz, J = 1.8 Hz, J = 1.0 Hz, 1 H, 8-H), 7.37 (dt, J = 8.0 Hz, J = 1.0 Hz, 1 H, 10-H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 20.26 (11-CH_3 ax.), 27.84, 28.68 (NCH_3), 29.96 (11-CH_3 eq), 31.18 (C-4b*), 45.71 (C-10b*), 70.02 (C-5), 84.22, 85.59 (C-4a, C-11), 117.51 (C-7), 119.89 (C-9), 122.36 (C-10a), 125.01, 128.38 (C-8, C-10), 151.07 (C-2), 155.26, 155.43 (C-6a, C-12a), 162.18 (C-4); MS, m/z 328 (30, M^+), 313 (6, M - CH_3), 285 (24, M - C_3H_7), 181 (100, $C_8H_9N_2O_3^+$), 147 (8, $C_{10}H_{11}O^+$). Anal. Calcd for $C_{18}H_{20}N_2O_4$: C, 65.84; H, 6.14; N, 8.53. Found: C, 65.97; H, 6.22; N, 8.52.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. We are also indebted to Dr. Horst Meyer (Bayer AG) for a generous supply of chemicals.

Registry No. 1, 56074-73-8; **8a**, 876-92-6; **8b**, 89-25-8; **8c**, 4845-49-2; **8d**, 6631-89-6; **8e**, 10234-66-9; **8f**, 2749-59-9; **8g**, 41927-50-8; **8h**, 87031-30-9; (*E*)-**9a**, 112296-87-4; (*Z*)-**9a**, 112296-88-5; (*E*)-**9b**, 112296-89-6; (*Z*)-**9b**, 112296-90-9; (*Z*)-**9f**, 112296-91-0; (*Z*)-**9h**, 112296-79-4; **10a**, 112296-60-3; **10b**, 112296-62-5; **10c**, 112296-64-7; **10d**, 112296-66-9; **10e**, 112296-68-1; **10f**, 112296-70-5; **10g**, 112296-72-7; **10h**, 112296-74-9; **11a**, 112296-61-4; **11b**, 112296-63-6; **11c**, 112296-65-8; **11d**, 112296-67-0; **11e**, 112296-69-2; **11f**, 112296-71-6; **11g**, 112296-73-8; **11h**, 112296-75-0; **12**, 112296-59-0; **13**, 112296-76-1; **14**, 112296-77-2; **15**, 58758-47-7; **16**, 112296-78-3; **17**, 1076-59-1; **18**, 112296-80-7; **19**, 112296-81-8; **20**, 112296-82-9; **21**, 28752-82-1; (*E*)-**22a**, 112296-83-0; (*Z*)-**22a**, 112297-19-5; (*E*)-**22b**, 112297-20-8; (*Z*)-**22b**, 112296-84-1; **22c**, 112296-85-2; **22d**, 112296-86-3; **23a**, 112296-92-1; **23b**, 112296-94-3; **23c**, 112296-96-5; **23d**, 112296-98-7; **24a**, 112296-93-2; **24b**, 112296-95-4; **24c**, 112296-97-6; **24d**, 112296-99-8; **25**, 5392-40-5; **27a**, 112297-00-4; **27b**, 112319-73-0; **27c**, 112297-01-5; **27d**, 112297-02-6; **28a**, 112297-03-7; **28b**, 112297-06-0; **28c**, 112297-08-2; **29a**, 112297-04-8; **29b**, 112421-49-5; **29c**, 112421-50-8; **29d**, 112297-10-6; **30a**, 112297-05-9; **30b**, 112297-07-1; **30c**, 112297-09-3; **30d**, 112297-11-7; **31**, 112297-14-0; **31** (2,4-dinitrophenylhydrazone deriv), 112297-15-1; **32**, 769-42-6; **34**, 112297-16-2; **35**, 112297-17-3; **36**, 112297-18-4; 4,5-dihydro-1-methyl-5-oxo-1*H*-pyrazole-4-carboxylic acid methyl ester, 112296-58-9; dimethyl (methoxymethylene)malonate, 22398-14-7; methylhydrazine, 60-34-4; ethyl 4,4-dimethyl-3-oxopentanoate, 17094-34-7; 2-(2-methyl-1-propenyl)phenol, 6395-29-5; bromoacetic acid ethyl ester, 105-36-2; [2-(2-methyl-1-propenyl)phenoxy]acetic acid ethyl ester, 112297-12-8; 2-[2-(2-methyl-1-propenyl)phenoxy]ethanol, 112297-13-9.

Some Observations on the Stereochemical and Regiochemical Outcome of Hydrostannylation of Substituted Propargyl Alcohols

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Received April 23, 1987

A regio- and stereocontrolled hydrostannylation of substituted propargyl alcohols and derivatives has been performed. Tri-*n*-butylstannyl hydride reacts with different substituted propargyl alcohols to give a mixture of *Z*/*E* isomers of vinylstannane with the stannyl moiety bonded to the carbon closest to the OH or OR group. A careful study of the reaction conditions allowed the preparation and isolation of pure *Z* isomer for a wide set of compounds. The reaction products are unstable under the conditions of preparation. An outline of the possible mechanism of the reaction is described.

Hydrostannylation is a useful reaction for the preparation of carbon-functional organostannanes[1] and is the simplest and most direct route to transform alkynes into vinylstannanes.[1,2] This reaction, however, is not highly regio- and stereoselective, and analogously the mechanism does not appear to have been well established. The predominance of a free-radical mechanism or of a stepwise

(1) Davies, A. G.; Smith, P. J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Gordon, F., Stone, A., Abel, E. W., Eds.; Pergamon: London, 1982; Vol. 2, p 534.

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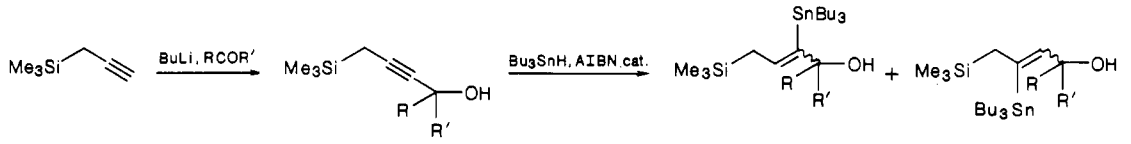
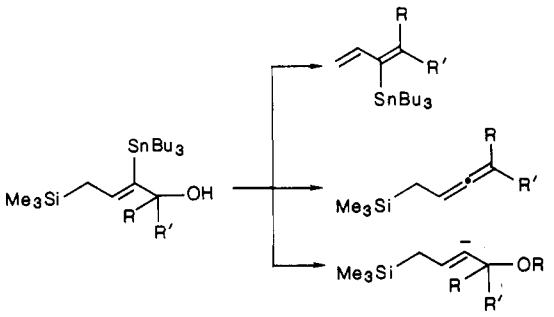
0022-3263/88/1953-0820$01.50/0

Scheme I



Scheme II



addition of hydride followed by triorganostannyl cation to the triple bond has been obtained for different substrates and reaction conditions.[2] Extensive studies have been carried out on 1-alkynes,[3-6] but the more intriguing reaction of internal alkynes has received little attention,[7,8] especially about the regiochemical characterization. In the first paper[3] dealing with the hydrostannylation, the formation of the *Z* product (the kinetically favored one) seemed to be well established; later reports[5,6] described the formation of different amounts of the *E* product under different reaction conditions.

We are interested in the regiospecific synthesis of 2-stannyl 1,3-dienes,[9] which require, in a key step, the hydrostannylation of propargyl alcohols in the presence of AIBN as reported in Scheme I.

The vinylstannanes obtained were prepared in high yields as a mixture of *Z*/*E* isomers ranging from 4:1 to 2:1 irrespective of the substituent R. Moreover, we always obtained the regioisomer with the stannyl moiety closest to the OH group; no traces of the other isomer are detectable by NMR analysis.

Due to the synthetic interest of such compounds (Scheme II), not only for the preparation of substituted 1,3-[9] and 2,3-dienes[10] but also for the preparation of differently functionalized allylsilanes as a convenient source of protected (*Z*)-3-lithioalkenols,[11] we decided to investigate this reaction more carefully, namely, to understand which parameters are responsible for the regio- and stereochemical outcome that is observed.

More extensively, we tried to find the best conditions for the hydrostannylation of substituted propargyl alcohols to give the corresponding vinylstannanes in a stereocontrolled way.

We now report the results obtained by performing this reaction under different conditions and on different substrates and attempts to interpret the results which will be of general use for people interested in synthesis of substituted *Z* alkenes.

Results and Discussion

The results of hydrostannylation of different alkynes with several substituents on the propargylic skeleton are reported in Table I.

The formation of the vinylstannane with the stannyl moiety closer to the OH group was not influenced by the reaction conditions. As reported later, in reactions performed in the presence or absence of AIBN, at different temperatures and with different ratios of tributylstannyl hydride, the product that would originate from attack of $Bu_3Sn^\bullet$ to the triple bond in a position remote from the OH group was never detected (detection limit, ^1H NMR, 90 MHz, ca. 1 M solution in CCl_4). It is clear that the uniqueness of the regiochemistry of this reaction is the presence of the oxygen on the carbon directly bonded to the triple bond.

As reported in entry 8, in the absence of the OR group, a mixture of the two regioisomers **30a/b** and **30c/d** was formed, with predominance of the product with the stannyl group at the less hindered side, e.g., the Me_3SiCH_2 side.

Protection of the OH did not affect the regiochemical pathway as observed in the case of the ethers **12–15** and the acetate **16**.

Reaction of a substrate where the site of the triple bond near the oxygen was too hindered (see entry 12) did not take place. When a CH_2 was interposed between the triple bond and the carbon bearing the OH, there was no regiochemical control and the mixture of isomers (**36a/b**) was once more obtained (see entry 15).

Finally, from entry 14 it is clear that the Me_3Si group has no effect on the regiochemistry of the reaction.[7]

Stereochemistry around the double bond of the products depends on the nature of the substituents as well as on the reaction conditions. As shown in Table I, increasing the bulk of R gives rise to an increase of the *Z*/*E* isomer ratio. The importance of substituent bulk is also demonstrated by the higher stereoselection obtained when the OH was replaced by the bulky OSi-*t*-BuMe_2 group.

Different conditions were studied on the model alcohol **3** to obtain a more complete overview of their effect on the fate of the reaction, and results are summarized in Table II. Table II demonstrates that longer reaction times caused a decrease of the *Z*:*E* ratio from 5:1 to 1:1. The longest period employed, 36 h (entry 5), suggests that thermodynamic equilibration between the two isomers has been achieved. On the other hand, acceptable yields of isomers **22a** and **22b** in a 5:1 ratio were obtained after about 1 h (entry 2).

The amount of tributylstannyl hydride is involved, too, in the stereochemical composition of the reaction mixture. Decreasing the amount gave an increase of the *Z*:*E* ratio to a limit of 50 mol % of the stannylating agents when appreciable amounts of vinylstannanes **22a/b** were not observed (see, for example, entries 6 and 7).

Temperature exerts a dramatic effect on the composition of the mixture. Performing the reaction at 60 °C gave a higher increment in the *Z*:*E* ratio (entry 11), whereas re-

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Table I. Hydrostannylation of Propargyl Alcohols and Derivatives

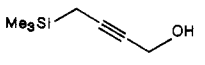
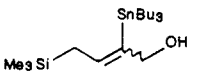
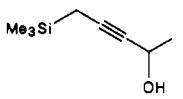
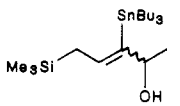
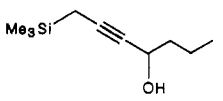
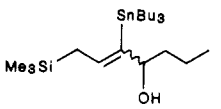
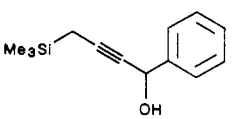
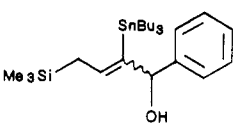
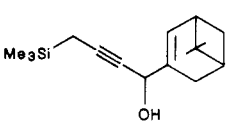
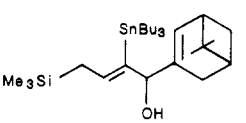
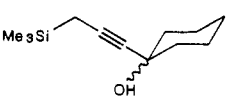
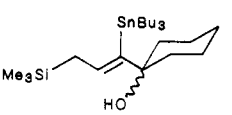
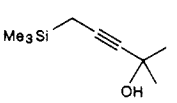
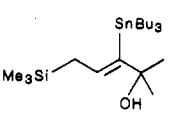
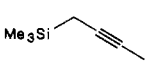
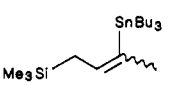
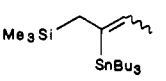
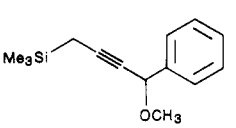
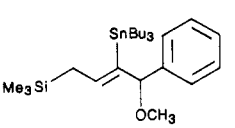
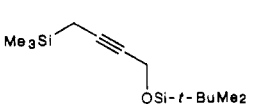
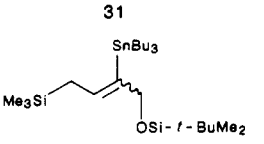
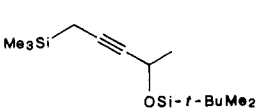
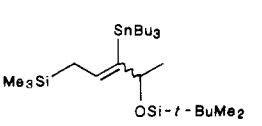
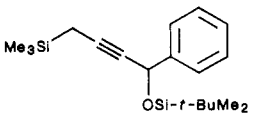
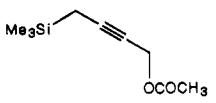
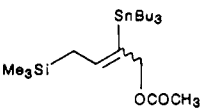
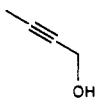
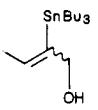
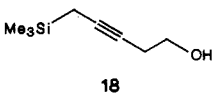
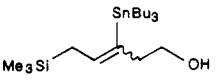
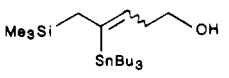
entry	starting material	products	yield,[a] %	Z:E ratio[b]
1	 **2**	 **21a/b**	71	1:1
2	 **3**	 **22a/b**	63	3:1
3	 **4**	 **23a/b**	76	4:1
4	 **5**	 **24a/b**	65	25:1
5	 **6**	 **25**	69	
6	 **7**	 **26**	61	
7	 **8**	 **27**	63	
8	 **11**	 **30a/b**	68	1:1
		 **30c/d**		1:1
9	 **12**	 **31**	73	
10	 **13**	 **32a/b**	80	3:1
11	 **14**	 **33a/b**	81	12:1

Table I (Continued)

entry	starting material	products	yield,[a] %	Z:E ratio[b]
12	 **15**	no reaction	–	–
13	 **16**	 **34a/b**	69	4:1
14	 **17**	 **35a/b**	86	10:1
15	 **18**	 **36a/b**	76	2:1
		 **36c/d**		2:1

[a] Yields of isolated and fully characterized products. [b] Ratio determined by NMR analysis. Satisfactory analytical data (±0.4% for C and H) were reported for all new compounds listed in the table.

Table II. Hydrostannylation of 3 under Different Reaction Conditions

entry	Bu_3SnH, equiv	temp, °C	AIBN, equiv	time, h	Z:E ratio	starting material left, %
1	1.5	120	0.2	0.2	5:1	20
2	1.5	120	0.2	1	4:1	20
3	1.5	120	0.2	4	2:1	0
4	1.5	120	0.2	8	2:1	0
5	1.5	120	0.2	36	1:1	0
6	0.1	120	0.2	8	5:1	90
7	0.5	120	0.2	8	4:1	50
8	1	120	0.2	8	3:1	10
9	2	120	0.2	8	2:1	0
10	1.5	rt[a]	0.2	8	–	100
11	1.5	60	0.2	8	8:1	10
12	1.5	80	0.2	8	2:1	0
13	1.5	200	0.2	8	1:1	5[b]
14	1.5	120	0.0	8	20:1	40
15	1.5	120	0.0	24	4:1	10

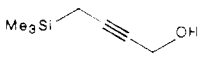
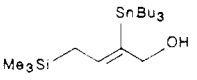
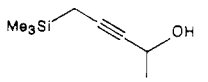
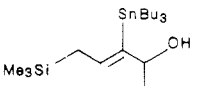
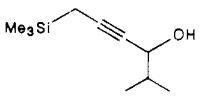
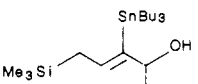
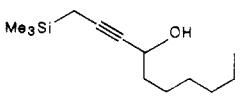
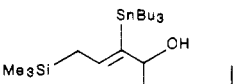
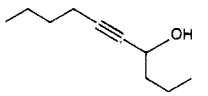
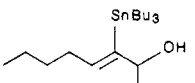
[a] Room temperature. [b] NMR analyses showed the presence of unidentified byproducts.

actions performed at higher temperatures exhibited no selectivity (entry 13).

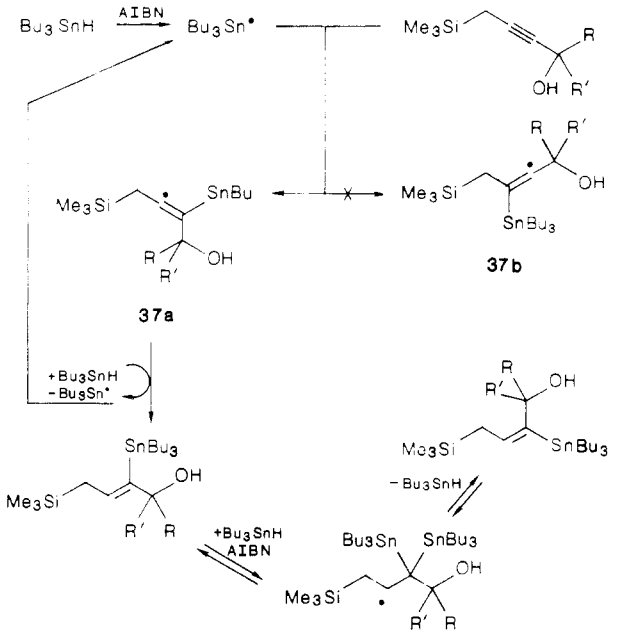
Finally, we found that in the absence of radical initiator (AIBN) reaction also took place to give higher *Z*:*E* ratios relative to the corresponding reaction in the presence of AIBN (entry 14). In this last case we obtained only **22a** but, unfortunately, in low yields, and attempts to improve them gave rise once more to the formation of the other isomer (entry 15). All these results show that temperature, time, and amounts of tributylstannly hydride have the same effect on the isomeric ratio for the hydrostannylation products. Stronger reaction conditions gave poor results in isomer distribution, but a lower limit exists under which reaction did not take place. This evidence suggests that the formation of the *Z* isomer has always been realized under "kinetic control" and that the forthcoming formation of the *E* isomer can be related to the observation that the *Z* isomer is stereochemically unstable under the free-radical conditions under which it is generated. In fact, we observed that previously purified *Z* isomer **22a** can be transformed into a 1:1 mixture of **22a** and **22b** at 120 °C in the presence of AIBN and Bu_3SnH. On the other hand, the same isomer is stereochemically stable at 120 °C alone or in the presence of AIBN *or* Bu_3SnH. This result suggests that at some higher temperature than that of the simple hydrostannylation of the triple bond the product undergoes free-radical isomerization. From all these observations we can propose a more accurate description of the reaction (Scheme III).

Assuming that the increase of yield due to the presence of AIBN means a predominantly free radical mechanism, we hypothesized that the generation of $Bu_3Sn^{\bullet}$ radical with coordination to the oxygen (interaction effective probably in the transition state) was followed by the formation of the C–Sn bond, explaining in this way the predominant formation of the intermediate **37a** instead of **37b**. The

Table III. Optimized Hydrostannylation of Propargyl Alcohols

entry	starting materials	products	rctn condns	yield, %
1	 2	 21a	1 equiv of Bu_3SnH, 0.01 equiv of AIBN, 60 °C, 1 h	80
2	 3	 22a	1 equiv of Bu_3SnH, 0.01 equiv of AIBN, 60 °C, 1 h	92
3	 9	 28	1 equiv of Bu_3SnH, 0.01 equiv of AIBN, 70 °C, 3 h	76
4	 10	 29	1 equiv of Bu_3SnH, 0.01 equiv of AIBN, 70 °C, 3 h	82
5	 19	 37	1 equiv of Bu_3SnH, 0.01 equiv of AIBN, 75 °C, 4 h	70

Scheme III



following quench of such intermediate with Bu_3SnH gave back $Bu_3Sn^•$ and the final product. This last attack of H• is kinetically controlled to give exclusively the *Z* isomer, which can undergo then, in the reaction mixture, a radical equilibration but only if the temperature is high enough. This interconversion can explain also the temperature effect (higher temperatures are generally needed to get addition of Bu_3Sn to a double bond[2]) and the effect of the hindrance of the substituent (larger R substituents should give an equilibration mixture richer in *Z* than smaller ones). We must also observe that the reaction of hydrostannylation is really selective because it runs under kinetic control but less selective when the reaction conditions partially transform the final product to a mixture of isomers with a composition determined only by the relative hindrance of the substituents. From such a mechanism we can conclude that to have a complete stereocontrolled hydrostannylation of propargylic alcohols we had to find the limiting conditions to prevent the transformation of the desired product in the reaction media.

Hydrostannylation of **3** at 60 °C with 1 equiv of tributylstannyl hydride and 0.02 equiv of AIBN for 1.5 h gave a very high *Z*:*E* ratio (up to 25:1 in the crude) so that pure **22a** was isolated in 92% yield.

As briefly reported in Table I, the presence of the Me_3Si group helps the reaction development in the sense that lower temperatures are needed to complete the hydrostannylation process. Nevertheless, we found that for any kind of substituted propargyl alcohols there is a lower limit of temperature for the reaction, and this limit allows the complete formation of the kinetic products, e.g., the *Z* product.

Table III reports examples of optimization for the wider application of the reaction conditions in the preparation of (*Z*)-vinylstannanes.

We can now conclude that the control of regiochemistry of hydrostannylation of propargyl alcohols to the *Z* isomer is possible when a CHOR group is close to a triple bond while at the lowest temperature (60–70 °C) for the shortest reaction times and with no excess of Bu_3SnH or AIBN (strong kinetic control). Finally we wish to stress the point that in the presence of these last reagents the final products should not be heated, which precludes purification by distillation as previously reported in some cases[7,11] and requires the use of column chromatography on silica gel or other nonthermic methods in the presence of radical initiators.

Experimental Section

All the solvents were appropriately dried before use and all reactions performed under strictly dry atmosphere. ^1H NMR spectra were obtained from a Varian EM 390 (90 MHz) instrument in CCl_4 solutions, and chemical shifts are quoted in ppm downfield

from TMS as internal standard. GLC analyses were performed with a HP 5970–5790 gas–mass system equipped with a 15-m SE30 capillary column. Elementary analyses were obtained on a Perkin-Elmer 240C instrument.

Preparation of (Trimethylsilyl)propargyl Alcohols. General Procedure. 1-(Trimethylsilyl)-2-butyn-4-ol (2). To a solution of **1** (11.2 g, 0.1 mol) in dry THF (60 mL) at −78 °C was added butyllithium (62.5 mL of a 1.6 M solution in diethyl ether, 0.1 mol) dropwise with a syringe. After 10 min at this temperature, gaseous formaldehyde, generated by depolymerization of trioxymethylene (90 g, 1 mol), at 180 °C, was carried over through a wide glass tube, into the mixture by a slow current of dry nitrogen. Then the mixture was allowed to warm to room temperature for 3 h, and it was treated with 30 mL of a saturated ammonium chloride solution and then poured into 50 mL of diethyl ether. The ethereal layer was separated and dried over anhydrous sodium sulfate. Evaporation of the solvent and final distillation gave the alcohol **2**: 7.3 g (51% yield); bp 170–172 °C (105 mmHg); ^{1}H NMR (CCl_4) 0.50 (s, 9 H, Me_3Si), 1.9 (m, 2 H, CH_2), 3.47 (s, 1 H, OH), 4.5 (m, 2 H, CH_2O) ppm. The resultant product is 98% pure according to GLC analysis.

1-(Trimethylsilyl)-2-pentyn-4-ol (3). Distillation gave **3**: 12 g (76% yield); bp 100–102 °C (25 mmHg); ^{1}H NMR (CCl_4) 0.43 (s, 9 H, Me_3Si), 1.7 (m, 5 H, CH_3CH_2), 2.97 (s, 1 H, OH), 4.7 (m, 1 H, CHO) ppm. The resultant product is 95% pure (GLC analysis).

1-(Trimethylsilyl)-2-heptyn-4-ol (4). Distillation gave **4**: 3.5 g (53% yield); bp 125–127 °C (55 mmHg); ^{1}H NMR (CCl_4) 0.43 (s, 9 H, Me_3Si), 1.2 (m, 5 H, CH_3 and CH_2), 1.8 (m, 4 H, CH_2Si and CH_2), 2.57 (s, 1 H, OH), 4.5 (m, 1 H, CH) ppm. The product is pure (GLC analysis).

1-(Trimethylsilyl)-4-phenyl-2-butyn-4-ol (5). Distillation gave **5**: 21.5 g (92% yield); bp 109–111 °C (0.04 mmHg); ^{1}H NMR (CCl_4) 0.20 (s, 9 H, Me_3Si), 1.57 (d, 2 H, J = 3 Hz, CH_2), 2.5 (s, 1 H, OH), 5.4 (m, 1 H, CHO), 7.3–7.6 (m, 5 H, arom) ppm. The resultant product is 98% pure (GLC analysis).

1-(6,6-Dimethylbicyclo[3.1.1]hept-2-enyl)-1-hydroxy-4-(trimethylsilyl)-2-butyne (6). Column chromatography on silica gel with eluant hexane/ethyl acetate, 10:1, gave **6**: 6.2 g (66% yield); ^{1}H NMR (CCl_4) 0.72 (s, 9 H, Me_3Si), 1.42 (s, 3 H, Me), 1.88 (s, 3 H, Me), 2.08 (d, 2 H, J = 3 Hz, CH_2), 2.5–2.7 (m, 1 H, OH), 2.8–3.1 (m, 3 H, CH_2 and CH), 5.40 (s, 1 H, CH), 6.20 (s, 1 H, CH=) ppm. The product is pure (GLC analysis).

1-[3-(Trimethylsilyl)-1-propynyl]cyclohexanol (7). Column chromatography on silica gel with hexane/ethyl acetate (6:1) as eluant gave **7**: 2.7 g (48% yield); ^{1}H NMR 0.15 (s, 9 H, Me_3Si), 1.2–2.4 (m, 13 H, cyclohexyl group, CH_2 and OH) ppm. The product is 98% pure (GLC analysis).

1-(Trimethylsilyl)-4-methyl-2-pentyn-4-ol (8). Column chromatography with hexane/ethyl acetate as eluant (6:1) gave **8**: 3.8 g (37% yield); ^{1}H NMR (CCl_4) 0.12 (s, 9 H, Me_3Si), 1.4 (m, 8 H, 2 Me and CH_2Si), 2.81 (s, 1 H, OH) ppm. The product is pure (GLC analysis).

1-(Trimethylsilyl)-5-methyl-2-hexyn-4-ol (9). Distillation gave **9**: 0.98 g (38% yield); bp 105–106 °C (1 mmHg); ^{1}H NMR (CCl_4) 0.2 (s, 9 H, Me_3Si), 1.0 (s, 6 H, 2 CH_3), 1.5–2.0 (m, 3 H, CH_2Si and $CHMe_2$), 2.9 (s, 1 H, OH), 4.05 (m, 1 H, CHO) ppm. The product is 96% pure (GLC analysis).

1-(Trimethylsilyl)-2-decyn-4-ol (10). Distillation gave **10**: 4.24 g (25% yield); bp 98–100 °C (1 mmHg); ^{1}H NMR (CCl_4) 0.15 (s, 9 H, Me_3Si), 0.8 (m, 3 H, CH_3), 1.1–1.4 (m, 10 H, 5 CH_2), 1.51 (d, 2 H, J = 2 Hz, CH_2Si), 2.3 (s, 1 H, OH), 4.2 (m, 1 H, CHO) ppm. The product is pure.

Preparation of 1-(Trimethylsilyl)-2-butyne (11). A solution of **1** (1 g, 9 mmol) in dry THF (8 mL) under nitrogen at −78 °C was treated with *n*-butyllithium (5.6 mL of a 1.6 M solution in hexane, 9 mmol). The yellow solution was stirred for 30 min at room temperature and cooled again to −78 °C. Methyl iodide (1.3 g, 9 mmol) in HMPA (8 mL) was added and the mixture allowed to warm to room temperature and then refluxed until GLC analysis showed the disappearance of **1** (ca. 4 h). The mixture was treated with saturated ammonium chloride solution (10 mL) and diluted with diethyl ether (35 mL). The ethereal layer was separated and dried on anhydrous sodium sulfate. The solvent was evaporated and the resulting oil distilled to give pure **11** (GLC analysis): 0.5 g (45% yield); bp 100–101 °C; ^{1}H NMR (CCl_4) 0.17 (s, 9 H, Me_3Si), 1.5 (m, 3 H, CH_3), 1.8 (m, 2 H, CH_2).

Table IV. Spectroscopical Characterization of Vinylstannanes 3

product	^{1}H NMR (CCl_4/TMS), ppm
21a	0.0 (s, 3 H, Me_3Si), 0.8–1.5 (m, 30 H, Bu_3Sn, CH_2Si, and OH), 3.97 (s, 2 H, CH_2O), 6.07 (t, 1 H, J = 7 Hz, CH=)
21b	5.4 (m, 1 H, CH=)
22a	0.0 (s, 9 H, Me_2Si), 0.7–1.7 (m, 33 H, Bu_3Sn, CH_3CH_2, and OH), 4.2 (m, 1 H, CHO), 6.08 (t, 1 H, J = 6 Hz, CH=)
22b	5.4 (m, 1 H, CH=)
23a	0.07 (s, 9 H, Me_3Si), 0.7 (m, 7 H, CH_3, CH_2, and CH_2Si), 1.4 (m, 28 H, Bu_3Sn and OH), 4.03 (s, 1 H, CHO), 6.06 (t, 1 H, J = 7 Hz, CH=)
23b	5.6 (m, 1 H, CH=)
24	0.08 (s, 9 H, Me_3Si), 0.6–1.7 (m, 30 H, Bu_3Sn, CH_2, and OH), 5.18 (s, 1 H, CHO), 6.18 (t, 1 H, J = 7 Hz, CH=), 7.3 (m, 5 H, arom)
25	0.50 (s, 9 H, Me_3Si), 0.9–2.2 (m, 35 H, CH_2Si, 2 CH_3 ring, and Bu_3Sn), 2.70 (s, 1 H, OH), 4.88 (s, 0.5 H, CHO), 5.00 (s, 0.5 H, CHO), 5.9 (m, 1 H, CH-ring), 6.6 (m, 1 H, CH=)
26	0.0 (s, 9 H, Me_3Si), 0.7–1.8 (m, 40 H, CH_2Si, cyclohex, and Bu_3Sn), 5.97 (t, 1 H, J = 7 Hz, CH=)
27	0.0 (s, 9 H, Me_3Si), 0.6–1.6 (m, 36 H, Bu_3Sn, 2 Me_3, CH_2Si, and OH), 5.97 (t, 1 H, J = 6 Hz, CH=)
28	0.15 (s, 9 H, Me_3Si), 0.6–1.0 (m, 30 H, Bu_3Sn, CH_2Si, and OH), 1.1–1.7 (m, 7 H, 2 CH_3 and CH), 3.59 (d, 1 H, J = 8 Hz, CHO), 6.08 (t, 1 H, J = 7 Hz, CH=)
29	0.0 (s, 9 H, Me_2Si), 0.8–1.6 (m, 42 H, Bu_3Sn, CH_2Si, CH_3, and 5 CH_2), 3.8–4.1 (m, 1 H, CHO), 6.05 (t, 1 H, J = 7 Hz, CH=)
30a–d	0.10 (s, 9 H, Me_3Si), 0.5–2.0 (m, 32 H, Bu_3Sn, CH_3, and CH_2Si), 5.60 (t, 1 H, J = 7 Hz, CH= **30a,b**), 6.00 (q, 1 H, J = 6 Hz, CH= **30c,d**)
31	0.20 (s, 9 H, Me_3Si), 0.6–2.4 (m, 29 H, Bu_3Sn and CH_2Si), 3.57 (s, 3 H, OMe), 4.3 (m, 1 H, CHO), 6.30 (t, 1 H, J = 6 Hz, CH=), 7.5 (m, 5 H, arom)
32a	0.23 (s, 9 H, Me_3Si), 0.28 (s, 6 H, Me_2Si), 0.4–2.2 (m, 38 H, Bu_3Sn, *t*-Bu, and CH_2Si) 4.33 (s, 2 H, CH_2O), 6.33 (t, 1 H, J = 9 Hz, CH=)
32b	4.50 (s, 2 H, CH_2O), 5.6 (t, 1 H, J = 9 Hz, CH=)
33	0.22 (s, 9 H, Me_3Si), 0.28 (s, 6 H, Me_2Si), 0.7–2.2 (m, 38 H, Bu_3Sn, *t*-Bu, and CH_2Si), 4.63 (q, 1 H, J = 6 Hz, CHO), 6.23 (t, 1 H, J = 7 Hz, CH=)
35a	0.9–1.6 (m, 27 H, Bu_3Sn), 1.71 (d, 3 H, J = 7 Hz, CH_3), 3.0 (s, 1 H, OH), 4.08 (s, 2 H, CH_2O), 6.2 (q, 1 H, J = 7 Hz, CH=)
35b	5.5 (m, 1 H, CH=)
36a	0.8–1.7 (m, 27 H, Bu_3Sn), 2.2 (m, 6 H, CH_2, CH_3, and OH), 3.6 (m, 2 H, CH_2O), 5.9 (m, 1 H, CH=)
36b	5.8 (m, 1 H, CH=)

Preparation of 1-(Trimethylsilyl)-4-phenyl-4-methoxy-2-butyne (12). Sodium hydride (55.2 mg of a 55% dispersion in mineral oil, 2.3 mmol) previously washed with hexane and dispersed in dry THF (5 mL) was heated under nitrogen atmosphere at 40 °C, and then a mixture of alcohol **5** (0.5 g, 2.3 mmol) and methyl iodide (0.42 g, 3 mmol) in THF (3 mL) was added. The mixture was refluxed for 1 h, then cooled, diluted with diethyl ether (30 mL), and treated with a saturated ammonium chloride solution (10 mL). The ethereal layer was separated, was dried on anhydrous sodium sulfate, and after evaporation of the solvent, provided pure **12** by column chromatography on silica gel with eluant hexane/ethyl acetate (10:1): 0.350 mg (65% yield); ^{1}H NMR 0.05 (s, 9 H, Me_3Si), 1.7 (m, 2 H, CH_2), 3.31 (s, 3 H, MeO), 5.1 (m, 1 H, CH), 7.2–7.7 (m, 5 H, arom) ppm.

Preparation of 1-(Trimethylsilyl)-4-(*tert*-butyldimethylsiloxy)-2-butyne (13). Compound **2** (224 mg, 2 mmol) was added to a stirred mixture of *tert*-butyldimethylsilyl chloride (320 mg, 2.2 mmol) and diazabicycloundecene (360 mg, 2.4 mmol) in dry dichloromethane (4 mL). After 1 h of stirring, the mixtue was diluted with diethyl ether (10 mL) and washed with 1 M HCl (4 mL), saturated sodium carbonate (2 × 5 mL), and brine. The ethereal layer was separated and dried on anhydrous sodium sulfate, and after evaporation of the solvent, pure **13** was isolated by column chromatography on silica gel, eluant hexane/ethyl

acetate (10:1): 300 mg (59% yield); ^{1}H NMR (CCl_4) 0.3 (m, 15 H, Me_3Si and Me_2Si), 1.1 (m, 9 H, *t*-Bu), 1.67 (t, 2 H, J = 3 Hz, CH_2), 4.37 (t, 2 H, J = 3 Hz, CH_2O) ppm.

1-(Trimethylsilyl)-4-(*tert*-butyldimethylsiloxy)-2-pentyne (14). Column chromatography on silica gel, eluant hexane/ethyl acetate (10:1), gave **14**: 300 mg (56% yield); ^{1}H NMR (CCl_4) 0.3 (m, 15 H, Me_3Si and Me_2Si), 1.1 (m, 9 H, *t*-Bu), 1.6 (m, 5 H, CH_3 and CH_2), 4.7 (t, 1 *H*, J = 3 Hz, CHO) ppm.

1-(Trimethylsilyl)-4-(*tert*-butyldimethylsiloxy)-4-phenyl-2-butyne (15). Column chromatography on silica gel, eluant hexane/ethyl acetate (10:1), gave **15**: 300 mg (45% yield); ^{1}H NMR (CCl_4) 0.3 (m, 15 H, Me_3Si and Me_2Si), 1.1 (m, 9 H, *t*-Bu), 1.7 (d, 2 H, J = 3 Hz, CH_2), 5.57 (t, 1 H, J = 3 Hz, CHO), 7.3-7.7 (m, 5 H, arom) ppm.

Preparation of 5-Decyn-4-ol (19). To a solution of 1-hexyne (1 g, 12 mmol) in dry THF (6 mL) at -78 °C was added butyllithium (7.5 mL of a 1.6 M solution in hexane, 12 mmol) slowly. After 30 min at this temperature, butyraldehyde (0.87 g, 12 mmol) in THF (3 mL) was added dropwise. The mixture was then stirred for 3 h at room temperature, diluted with diethyl ether (35 mL), and treated with water (5 mL), followed by a saturated ammonium chloride solution; the ethereal layer was separated and dried on anhydrous sodium sulfate. Evaporation and final distillation gave alcohol **19**: bp 85-89 °C (1 mmHg); ^{1}H NMR (CCl_4) 1.00 (m, 6 H, 2 CH_3), 1.5 (m, 8 H, 4 CH_2), 2.2 (m, 2 H, CH_2C), 3.2 (s, 1 H, OH), 4.3 (m, 1 H, CH) ppm.

Hydrostannylation of Propargyl Alcohols 2-19. General Procedure. (*Z*)-1-(Trimethylsilyl)-3-(tributylstannyl)-2-penten-4-ol (22a). The reaction was performed in a sealed tube. Tri-*n*-butylstannyl hydride (0.7 mmol), **3** (1.44 g, 9.2 mmol), and AIBN (3 mg, 0.02 mmol) were heated at 60 °C for 1 h. NMR analysis of the crude product mixture showed quantitative reduction of **3**. Vinylstannane **22a** was isolated by column chromatography on silica gel with hexane/ethyl acetate (11:1): 3 g (92% yield). The spectroscopic data are reported in Table IV as well as products obtained from **2**, **4**, and **19**.

Acknowledgment. NATO collaborative Grant No. 86/0535 is gratefully acknowledged.

Registry No. **1**, 13361-64-3; **2**, 90933-84-9; **3**, 108459-75-2; **4**, 111999-85-0; **5**, 108459-81-0; **6**, 111999-86-1; **7**, 111999-87-2; **8**, 108459-79-6; **9**, 108459-76-3; **10**, 111999-88-3; **11**, 18825-29-1; **12**, 111999-89-4; **13**, 111999-90-7; **14**, 111999-91-8; **15**, 111999-92-9; **16**, 111999-93-0; **17**, 764-01-2; **18**, 86486-02-4; **19**, 1817-52-3; **21a**, 111999-94-1; **21b**, 111999-95-2; **22a**, 111999-96-3; **22b**, 111999-97-4; **23a**, 111999-98-5; **23b**, 111999-99-6; **24a**, 112000-00-7; **24b**, 112000-01-8; **25**, 112000-02-9; **26**, 112021-15-5; **27**, 112000-03-0; **28**, 112000-19-8; **29**, 112000-20-1; **30a**, 112000-04-1; **30b**, 112000-05-2; **30c**, 112000-06-3; **30d**, 112000-07-4; **31**, 112000-08-5; **32a**, 112000-09-6; **32b**, 112000-10-9; **33a**, 112000-11-0; **33b**, 112000-12-1; **34a**, 112000-13-2; **34b**, 112000-14-3; **35a**, 79970-55-1; **35b**, 79970-54-0; **36a**, 112000-15-4; **36b**, 112000-16-5; **36c**, 112000-17-6; **36d**, 112000-18-7; **37**, 112000-21-2; Bu_3SnH, 688-73-3; H_2CO, 50-00-0; CH_3CHO, 75-07-0; $CH_3CH_2CH_2CHO$, 123-72-8; $CH_2C(O)CH_3$, 67-64-1; $(CH_2)_2CHCHO$, 78-84-2; $CH_3(CH_2)_5CHO$, 111-71-7; benzaldehyde, 100-52-7; 6,6-dimethyl-3-formylbicyclo[3.1.1]hept-2-ene, 80922-47-0; cyclohexanone, 108-94-1; methyl iodide, 74-88-4; *tert*-butyldimethylsilyl chloride, 18162-48-6; 1-hexyne, 693-02-7.

Correlation of the Circular Dichroic Spectra of 3-Arylphthalides with Absolute Configuration and Conformation

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Received August 19, 1987

The circular dichroic and ultraviolet absorption data for a series of configurationally established 3-naphthyl-substituted phthalide enantiomers belonging to three distinct classes are presented. A correlation is made between the observed circular dichroic spectra and absolute configuration, as well as the preferred solution conformations of these phthalide systems.

Introduction

The enantiomers of a series of 3-naphthylphthalides were separated by high-performance liquid chromatography on chiral stationary phases (CSPs) derived from (*S*)-*N*-(3,5-dinitrobenzoyl)leucine on (*R*)-*N*-(3,5-dinitrobenzoyl)phenylglycine. An a priori chiral recognition model was proposed to relate the absolute configuration of these phthalide enantiomers to their elution orders from the CSPs.[1] In an effort to establish the absolute configurations of these phthalides so as to ascertain the validity of the model, the circular dichroic (CD) spectra of representative enantiomers of the 3-naphthylphthalide series were recorded. Although it had been hoped that configurational assignments could be made through comparison of the CD spectra of the 3-naphthylphthalides with the CD spectra reported by Meyers and coworkers[2] for several asymmetrically synthesized 3-phenylphthalides of known absolution configuration, the clear difference in chromophoric properties between phenyl and α-naphthyl substituents prevented any such correlation of stereochemistry. Ultimately, the absolute configurations of several representative 3-naphthylphthalides were determined by independent chemical and spectroscopic techniques.[3]

Herein we report the CD characteristics obtained for the enantiomers of the various 3-naphthylphthalides investigated. A correlation is made between the CD curves observed for these configurationally established 3-naphthylphthalides and the absolute configuration and *conformation* of the phthalide's naphthyl substituent.

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