Table I. Asymmetric Reduction of Representative Ketones by *tert*-Butoxyisopinocampheylborane in THF at 0 °C

	tert-butoxyisopinocampheylborane[a]						$IpcBH_2$[b]	
$RCOCH_3$, R =	time, h	H^-/compd	yield,[c] %	$[\alpha]_D$ neat	ee, %	config[h]	ee, %	config
ethyl	3.0	1.5	86	-0.656	4.9[d]	*R*	22	*S*
isopropyl	3.0	1.5	82	-0.978	18.3[e]	*R*	46	*S*
tert-butyl	6.0	2.0	74	-1.850	22.8[f]	*R*	21	*S*
phenyl	3.0	1.5	71	+9.843	23.0[g]	*R*	15	*S*

[a] (+)-α-Pinene of 92% ee was used. [b] Reference 3, the results obtained by using $IpcBH_2$ of 100% ee, which was prepared from (+)-α-pinene of 94% ee. [c] Isolated yield. [d] Based on maximum rotation $[\alpha]_D$ -13.5° (neat): Leroux, P. J.; Lucas, H. J. *J. Am. Chem. Soc.* **1951**, *73*, 41. [e] Based on maximum rotation $[\alpha]_D$ +5.34° (neat): Pickard, R. H.; Kenyon, J. *J. Chem. Soc.* **1913**, *103*, 1957. [f] Based on maximum rotation $[\alpha]_D$ +8.1° (neat): Newman, P.; Lutkin, P.; Mislow, K. *J. Am. Chem. Soc.* **1958**, *80*, 465. [g] Based on maximum rotation $[\alpha]_D$ +42.85° (neat): Pickard, R. H.; Kenyon, J. *J. Chem. Soc.* **1911**, *99*, 45. [h] Absolute configurations from Klyne, W.; Buckingham, J. "Atlas of Stereochemistry"; Oxford University Press: New York, 1974.

As shown in Table I, 2-butanone is reduced to (*R*)-(-)-2-butanol in only 4.9% ee. However, the introduction of alkyl substituents in the α-position increases the asymmetric induction significantly. Thus, 3-methyl-2-butanone is reduced to (*R*)-(-)-3-methyl-2-butanol in 18.3% ee and 3,3-dimethyl-2-butanone is reduced to (*R*)-(-)-3,3-dimethyl-2-butanol in 22.8% ee. Acetophenone also yields the corresponding *R* alcohol in 23% ee. Thus, the *tert*-butoxyisopinocamphenylborane [from (+)-α-pinene] yields the product alcohols consistently enriched in the *R* enantiomer.

This is in sharp constrast to the earlier results[3] with $IpcBH_2$ [from (+)-α-pinene] in which the configuration of the reduced alcohols were consistently *S*. It is interesting that the introduction of the *tert*-butoxy group into the $IpcBH_2$ moiety has reversed the direction of reduction, presumably by reversing the orientation of the ketones in the transition states for these reductions.

A new chiral alkylalkoxyborane, *tert*-butoxyisopinocampheylborane, is prepared conveniently by merely adding 1 molar equiv of *tert*-butyl alcohol to $IpcBH_2$ in THF at 0 °C. In the reduction of four representative ketones, its asymmetric induction is consistently opposite to that realized in the reduction with $IpcBH_2$. Other applications of this reagent in asymmetric synthesis are under investigation.

Experimental Section

All operations were carried out under nitrogen, using oven-dried glassware. GC analyses were carried out on a Varian 3600 gas chromatograph using a 10% Carbowax 20M on Chromosorb W-HP 80/100 mesh size. The optical rotations were measured on a Rudolph Polarimeter Autopol III.

Materials. THF was treated with lithium aluminum hydride and distilled under nitrogen and stored over molecular sieves (Linde 5A, Ventron) under a slight positive nitrogen pressure. The borane-THF solution was standardized by hydrolyzing an aliquot of the solution with glycerine-water-THF mixture and measuring the hydrogen evolved.[7] The commercial ketones were purified by distillation and maintained under nitrogen. (+)-α-Pinene (Aldrich, 98%) was used without purification; it had an optical rotation of $[\alpha]^{22}_D$ +47.1°, indicating an optical purity of 92.0%.

Reduction of 3-Methyl-2-butanone. The following procedure for the asymmetric reduction of 3-methyl-2-butanone is representative. An oven-dried, 500-mL flask with a septum inlet, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler was cooled in an ice bath under a dry stream of nitrogen. The flask was charged with 126 mL of 1.19 M BH_3·THF solution (150 mmol) and then 24.3 mL of (+)-α-pinene (98%, 150 mmol) was introduced slowly with stirring. After the addition was completed, the reaction mixture was warmed up to room temperature and stirring was continued for 96 h.[8] The $IpcBH_2$ solution was cooled to 0 °C and 14.2 mL of *tert*-butyl alcohol (150 mmol) was slowly added. When the evolution of hydrogen gas had been completed, 10.7 mL of 3-methyl-2-butanone (100 mmol) was added to the reaction flask and the mixtrue was stirred for 3 h at 0 °C. Then 6 mL of water was added to destroy residual hydride. The oxidation of the boronic acid was effected by successive additions of 52.5 mL of 3 M NaOH and 17 mL of 30% aqueous H_2O_2 (1 h, 40 °C). The reaction mixture was then saturated with potassium carbonate, and the organic layer was separated and dried over anhydrous potassium carbonate. After the solvent was removed by distillation, the residue was fractionally distilled to provide 7.2 g (82%) of 3-methyl-2-butanol, bp 112-113 °C, 95% purity by GC. It was further purified by preparative GC, using a 20% DC-200 column: n^{25}_D 1.4056, $[\alpha]^{25}_D$ -0.978° (neat), an optical purity of 18.3% in *R* configuration.

Acknowledgment. We are grateful to the Ministry of Education, Republic of Korea, for financial support.

Registry No. 1, 91425-14-8; *t*-BuOH, 75-65-0; $IpcBH_2$, 83730-00-1; BH_3, 13283-31-3; $RCOCH_3$ (R = ethyl), 78-93-3; $RCOCH_3$ (R = isopropyl), 563-80-4; $RCOCH_3$ (R = *tert*-butyl), 75-97-8; $RCOCH_3$ (R = phenyl), 98-86-2; (*R*)-$RCH(OH)CH_3$ (R = ethyl), 14898-79-4; (*R*)-$RCH(OH)CH_3$ (R = isopropyl), 1572-93-6; (*R*)-$RCH(OH)CH_3$ (R = *tert*-butyl), 1572-96-9; (*R*)-$RCH(OH)CH_3$ (R = phenyl), 1517-69-7; 2,6-dimethylphenol, 576-26-1; (+)-α-pinene, 80-56-8; (2,6-dimethylphenoxy)monoisopinocampheylborane, 91425-15-9.

(7) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

(8) Pelter, A.; Ryder, D. J.; Sheppard, J. H.; Subrahmanyam, C.; Brown, H. C.; Mandal, A. K. *Tetrahedron Lett.* **1979**, 4777.

Direct Conversion of Allylic Selenides to Protected Allylic Amines

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Received February 28, 1984

We have recently reported that anhydrous chloramine T (**5**) in methanol is an effective reagent for the conversion of allylic phenyl selenides **1** to the corresponding rearranged *N*-allylic *p*-toluenesulfonamides **2**.[1] Reactions of this type hold promise as a stratagem for the formation of new carbon to nitrogen bonds with high regiochemical and stereochemical control.[2] The hazards associated with

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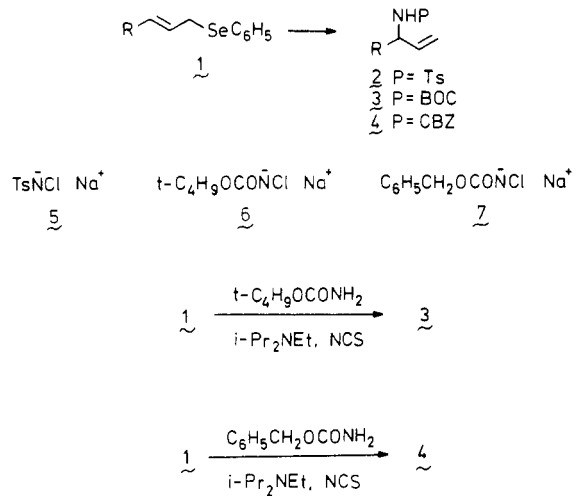
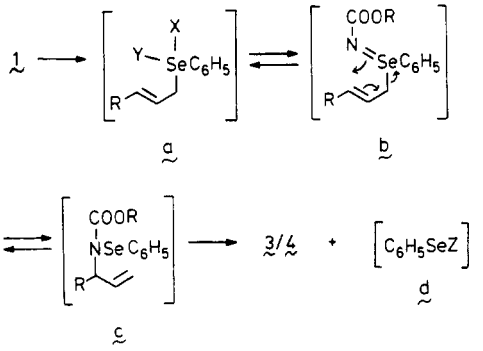
0022-3263/84/1949-3647$01.50/0



handling anhydrous chloramine T[1] and the limited number of procedures for the deprotection of an amine masked as a sulfonamide[3] prompted us to explore the use of chlorosodiocarbamate reagents **6** and **7**,[4] which were found to provide the more versatile carbamate-derived[5] *tert*-butoxycarbonyl-protected (BOC, **3**) and carbobenzyloxy-protected (CBZ, **4**) amines from allylic selenides.[6] Alternative approaches which eliminate the use of the potentially unstable chlorosodiocarbamate reagents have since been pursued. Herein is described an operationally simple, one-step procedure for the direct conversion of allylic phenyl selenides to BOC- or CBZ-protected primary allylic amines which utilizes inexpensive, stable, commercially available reagents.

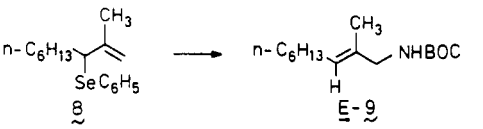
A methanolic solution of allylic selenide **1**[7] (R = *n*-C_3H_7, 1.0 equiv), *tert*-butyl carbamate (2.5 equiv), and diisopropylethylamine (5.0 equiv) stirred at 0 °C was treated with *N*-chlorosuccinimide (2.5 equiv). After being stirred for several minutes at 0 °C followed by several minutes at 25 °C, the mixture was concentrated and chromatographed on silica gel to afford the BOC-protected allylic amine **3** (*R* = *n*-C_3H_7)[8] in 81% yield. The substitution of benzyl carbamate for *tert*-butyl carbamate in this procedure resulted in the isolation of the CBZ-protected amine **4** in 86% isolated yield. The outcome of the exposure of a variety of selenides to these conditions is indicated in Table I. Although the reactant ratios have not been quantitatively optimized, we have observed that reduction of the quantity of any of the other three reagents relative to the selenide results in diminished yields.[10]

Scheme I



A well-precedented pathway which accounts for the observed products is proposed in Scheme I. Oxidation of the allylic selenide **1** by NCS provides an intermediate of type a, in which substituents X and Y represent two nucleophiles available in the reaction medium. Sharpless has previously proposed a similar intermediate in the NCS-promoted oxidation of allylic phenyl selenides in methylene chloride which ultimately provides a rearranged allylic chloride as the primary product.[11] In the presence of a carbamate, the intermediate a is presumably intercepted to afford selenimide b.[12] Analogy for this process is found in the known conversion of sulfides to sulfilimines by NCS and an amine.[13] [2,3]-Sigmatropic rearrangement of intermediate b then provides the carbalkoxy-substituted selenenamide c,[14] from which the selenium is removed by some nucleophile Z to afford the observed protected allylic amine **3** or **4** and the selenium-containing byproduct d.[15] The observation that yields of protected allylic amines are highest in the presence of several equivalents of NCS we attribute to the oxidative removal of the potentially electrophilic byproduct d, which is capable of initiating undesired side reactions.[15]

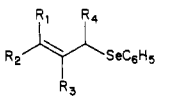
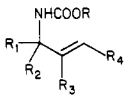
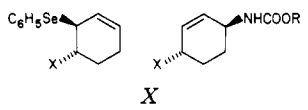
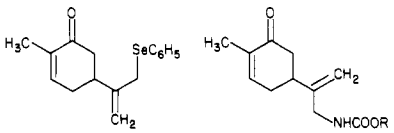
Of both mechanistic and synthetic interest is the rearrangement of selenide **8**[16] which under these conditions afforded the protected trisubstituted allylic amine **9** in



90% isolated yield. GLC analysis of **9** indicated an *E*:*Z* ratio of 97:3. This observation is fully consistent with the

(1) Fankhauser, J. E.; Peevey, R. M.; Hopkins, P. B. *Tetrahedron Lett.* **1984**, *25*, 15.
(2) Hoffman, R. W. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 563.
(3) Greene, T. W. "Protective Groups in Organic Synthesis"; Wiley: New York, 1981; pp 284–287.
(4) Review: Campbell, M. M.; Johnson, G. *Chem. Rev.* **1978**, *78*, 65.
(5) Reference 3, pp 223–249.
(6) Fitzner, J. N.; Shea, R. G.; Fankhauser, J. E.; Hopkins, P. B. *Synth. Commun.*, **1984**, *14*, 605.
(7) With the exception of **8** and Table I, entry 6, the allylic selenides were prepared by displacement of chloride, mesylate, or epoxide with sodium phenyl selenide in ethanol (see: Clive, D. J. *Tetrahedron* **1978**, *34*, 1049). The entry 6 selenide and **8** were prepared by the method of Reich (Reich, H. J. *J. Org. Chem.* **1975**, *40*, 2570). 10-Chlorocarvone was prepared by the method of Wolinsky: Hegde, S.; Wolinsky, J. *J. Org. Chem.* **1982**, *47*, 3148. We thank Stephen Hadley for a gift of the chloride.
(8) All of the protected amines provided NMR, IR, and low-resolution mass spectra in accord with the indicated structures. Key protected amines were further characterized by high-resolution MS. The BOC- and CBZ-protected amines in Table I, entries 1 and 5, and the CBZ derivative of entry 4 were compared with authentic samples prepared by protection of the authenic parent amines.[9]
(9) Overman, L. *J. Am. Chem. Soc.* **1976**, *98*, 2901.
(10) In one example (entry 2 selenide, CBZ derivative), the use of methylene chloride as reaction solvent resulted in a slower reaction which afforded a yield comparable to that obtained in methanol. Substitution of triethylamine for diisopropylethylamine had no discernible effect in one example (entry 2 selenide, CBZ derivative). Preliminary experiments indicate that pyridine and 2,6-lutidine are not satisfactory as the amine component. *Note added in revision*: We now use triethylamine exclusively as the amine component in these reactions.
(11) Hori, T.; Sharpless, K. B. *J. Org. Chem.* **1979**, *44*, 4204, 4208.
(12) Stable selenimides are known. For a recent example, see: David, F. A.; Billmers, J. M.; Stringer, O. D. *Tetrahedron Lett.* **1983**, *24*, 3191.
(13) Gilchrist, T. L.; Moody, C. *Chem. Rev.* **1977**, *77*, 409.
(14) Sharpless has previously proposed [2,3]-sigmatropic rearrangement of allylic imido selenium compounds: (a) Sharpless, K. B.; Singer, S. P. *J. Org. Chem.* **1976**, *41*, 2506; (b) Sharpless, K. B.; Hori, T.; Truesdale, L. K.; Kietrich, C. O. *J. Am. Chem. Soc.* **1976**, *98*, 269.
(15) Closely related observations have been made in the elimination of selenoxides and rearrangement of allylic selenoxides to allylic selenate esters, see: Reich, H. In "Oxidation in Organic Chemistry" Part C.; Trahanovsky, W. S.; Ed.; Academic Press: New York, 1978; pp 30–34, 102–107.
(16) See ref 7; **8** was contaminated with ca. 20% of the γ-alkylation product. Samples of **8** stored in $CDCl_3$ underwent [1,3]-allylic rearrangement. See: Di Giamberardino, T.; Halazy, S.; Dumont, W.; Krief, A. *Tetrahedron Lett.* **1983**, *24*, 3413.

Table I. NCS-Promoted Rearrangement of Allylic Selenides to Protected Allylic Amines

entry	selenide[a]	protected amine[b]	yield,[c] %	
			R = t-C_4H_9	R = $CH_2C_6H_5$
	R_1 R_2 R_3 R_4			
1	H H H H		67	82
2	H H CH_3 H		92	95
3	CH_3 CH_3 H H		71	72
4	H n-C_3H_7 H H		81	86
5	H C_6H_5 H H		95	71
6	H H H n-C_3H_7		63	63
				
	X			
7	H		50	77
8	OH		82	80
9			77	58

[a] See ref 7. [b] See ref 8. [c] Refers to isolated yield of purified material.

proposed concerted [2,3]-sigmatropic rearrangement mechanism[2,17] and recommends this reaction as a highly stereoselective method for trisubstituted olefin synthesis.

Relative to existing methods for allylic amine synthesis with allylic transposition,[18] the method disclosed herein seems especially well suited to applications in which mild reaction conditions are demanded. It is likely that carbamates carrying substituents other than *tert*-butyl and benzyl will function equally well in this procedure, allowing the convenient preparation of a wide variety of carbamate-protected primary allylic amines.[5] Efforts to exploit the stereochemical consequences of this [2,3]-sigmatropic reaction as a synthetic tool are underway and will be described in due course.

Experimental Section

Proton nuclear magnetic resonance (^{1}H NMR) spectra were determined on a Varian EM 360 (60 MHz) or Bruker WM 500 (500 MHz) spectrometer and are reported in parts per million (δ) downfield from internal tetramethylsilane (0.00 δ). Infrared spectra (IR) were recorded on a Beckman AccuLab 4 infrared spectrophotometer. Low-resolution mass spectra (MS) were measured on a Hewlett-Packard Model 5985 mass spectrometer. High-resolution mass spectra were determined on a VG 7070H double-focussing mass spectrometer. Gas–liquid chromatography (GLC) was performed on a Hewlett-Packard 5790A gas chromatograph.

Representative Experimental Procedure: *N*-(*tert*-Butoxycarbonyl)-2-methyl-2-propenylamine. A stirred solution of 88 mg (0.42 mmol) of 2-methyl-2-propenyl phenyl selenide,[7] 147 mg (1.25 mmol) of *tert*-butyl carbamate, and 324 mg (2.51 mmol) of diisopropylethylamine in 0.5 mL of methanol was cooled to 0 °C in an ice bath and treated with 167 mg (1.25 mmol) of *N*-chlorosuccinimide. The ice bath was removed and the reaction mixture was allowed to warm to room temperature. TLC analysis (SiO_2, 50% diethyl ether/pentane, visualized with basic aqueous potassium permanganate) after 10 min revealed the absence of starting selenide (R_f 0.71) and the presence of the desired carbamate (R_f 0.55). The reaction mixture was concentrated under a stream of argon and the residue was chromatographed on silica gel (eluant: 15% diethyl ether/pentane) to provide, after concentration under a stream of argon, 66 mg (92%) of *N*-(*Tert*-butoxycarbonyl)-2-methyl-2-propenylamine as a colorless oil: NMR ($CDCl_3$, 60 MHz) δ 1.46 (9 H, s, C_4H_9), 1.75 (bs, 3 H, vinyl CH_3), 3.68 (2 H, d, J = 6 Hz, -CH_2-), 4.85 (3 H, m, NH, =CH_2); IR ($CHCl_3$) 3460 (NH), 1710, 1510 (NHC=O), 1660 (C=C), 1400, 1375 (t-C_4H_9); MS (m/e, EI) 115 ($M^+ - C_4H_8$), 57 ($C_4H_9^+$). The lower molecular weight BOC derivatives showed appreciable volatility and traces of residual solvent were *not* removed in vacuo. Appreciable residual solvent was not, however, detected by ^{1}H NMR. An alternative workup for nonvolatile compounds (CBZ series) involved concentration in vacuo, addition of a small quantity of THF followed by silica gel, concentration in vacuo, and column chromatography on silica gel. Concentration in vacuo followed by exposure to 0.1 mm for ca 1 h afforded the CBZ derivatives generally as oils which did not show appreciable contamination by residual solvent (^{1}H NMR).

(*E*)-*N*-(*tert*-Butoxycarbonyl)-2-methyl-2-nonenylamine ((*E*)-9). 3-(Phenylseleno)-2-methyl-1-nonene (8) was converted to (*E*)-9 as described above in the representative procedure and was compared by GLC to authentic samples of (*E*)- and (*Z*)-9. Authentic samples of both (*E*)- and (*Z*)-9 were prepared from the corresponding alcohols (1, MsCl, Et_3N, CH_2Cl_2; 2, $C_6H_4(CO)_2$ NK, DMF; 3, H_2NNH_2, EtOH; 4, BOC-ON, EtOH). The *E* and *Z* alcohols were prepared by the methods of Sharpless[19] and Corey,[20] respectively. (*E*)- and (*Z*)-9 were clearly differentiated by ^{1}H NMR [($CDCl_3$, D_2O, 500 MHz, partial spectrum). (E)-9 δ 5.28 (1 H, t, C*H*=C(CH_3)), 3.62 (2 H, bs, CH_2NH), 1.99 (2 H, m, CH_2CH=C(CH_3)), 1.61 (3 H, bs, CH=C(CH_3)); *Z*-9 δ 5.28 (1 H, t, C*H*=C(CH_3) 3.73 (2 H, bs, CH_2NH) 2.03 (2 H, m, CH_2CH=C(CH_3)), 1.71 (3 H, bs, (CH=C(CH_3))].

Acknowledgment. We thank the Dreyfus Foundation, the donors of the Petroleum Research Fund, administered by the Americal Chemical Society, the Research Corporation, and Scripps Immunology Clinic for financial support of the work described herein. We thank Bradley J. Tenge for the preparation of several allylic selenides.

Registry No. 8, 91230-22-7; (*E*)-9, 91230-23-8; (*Z*)-9, 91230-24-9; CH_2=$CHCH_2SeC_6H_5$, 14370-82-2; CH_2=$C(CH_3)CH_2SeC_6H_5$,

(17) For example, Evans has observed an *E*:*Z* ratio of 96:4 in the corresponding allylic sulfoxide to allylic alcohol [2,3]-sigmatropic rearrangement: Evans, D. A.; Andrews, G. C.; Fujimoto, T. T.; Wells, D. *Tetrahedron Lett.* **1973**, 1389.

(18) See ref 9 and references cited therein.

(19) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 7154.

(20) Corey, E. J.; Yamamoto, H. *J. Am. Chem. Soc.* **1970**, *92*, 2261.

59085-70-0; $(CH_3)_2C{=}CHCH_2SeC_6H_5$, 69690-81-9; (*E*)-*n*-$C_3H_7CH{=}CHCH_2SeC_6H_5$, 90036-65-0; (*E*)-$PhCH{=}CHCH_2SeC_6H_5$, 69562-10-3; $CH_2{=}CHCH(SeC_6H_5)$-*n*-C_3H_7, 90036-67-2; BOC-$NHCH_2CH{=}CH_2$, 78888-18-3; CBZ-$NHCH_2CH{=}CH_2$, 5041-33-8; BOC-$NHCH_2C(CH_3){=}CH_2$, 91230-06-7; CBZ-$NHCH_2C(CH_3){=}CH_2$, 91230-07-8; BOC-$NHC(CH_3)_2CH{=}CH_2$, 91230-08-9; CBZ-$NHC(CH_3)_2CH{=}CH_2$, 91230-09-0; BOC-$NHCH(n\text{-}C_3H_7)CH{=}CH_2$, 91230-10-3; CBZ-$NHCH(n\text{-}C_3H_7)CH{=}CH_2$, 91230-11-4; BOC-$NHCH(C_6H_5)CH{=}CH_2$, 91230-12-5; CBZ-$NHCH(C_6H_5)CH{=}CH_2$, 91230-13-6; (*E*)-BOC-$NHCH_2CH{=}CH$-*n*-$C_3H_7$, 91230-14-7; (*E*)-CBZ-$NHCH_2CH{=}CH$-*n*-$C_3H_7$, 91230-15-8; (*E*)-*n*-$C_6H_{13}CH{=}C(CH_3)CH_2OH$, 43161-19-9; (*Z*)-*n*-$C_6H_{13}CH{=}C(CH_3)CH_2OH$, 3287-56-7; BOC-$NH_2$, 4248-19-5; CBZ-$NH_2$, 621-84-1; *i*-$Pr_2NEt$, 7087-68-5; NCS, 128-09-6; 3-(phenylseleno)cyclohexene, 83442-20-0; *trans*-2-(phenylseleno)-3-cyclohexen-1-ol, 91230-04-5; 10-(phenylseleno)carvone, 91230-05-6; *tert*-butyl *N*-(2-cyclohexen-1-yl)carbamate, 91230-16-9; benzyl *N*-(2-cyclohexen-1-yl)carbamate, 91230-17-0; *tert*-butyl *N*-(4-hydroxy-2-cyclohexen-1-yl)carbamate, 91230-18-1; benzyl *N*-(4-hydroxy-2-cyclohexen-1-yl)carbamate, 91230-19-2; *tert*-butyl *N*-(10-carvonyl)carbamate, 91230-20-5; benzyl *N*-(10-carvonyl)carbamate, 91230-21-6.

Crossover in π-Facial Stereoselection during [4 + 2] Cycloaddition of Triazolinediones to Isodicyclopentadiene and Its Dehydro Derivative[1]

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Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

Received March 9, 1984

The major thrust of our work involving cycloaddition reactions to norbornyl- and norbornenyl-fused cyclopentadiene systems such as **1** and **2** has been two-pronged.

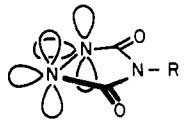
1

2

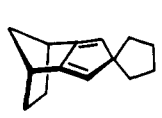
Elucidation of the extent and direction of π-facial stereoselectivity as a function of appendages grafted onto the diene or triene has been accorded considerable attention.[3,4] The directionality of electrophilic capture[5] and metal complexation[6] within the derived cyclopentadienide anions has comprised part of this effort. Companion activity directed at the development of synthetic applications based on this chemistry has resulted in the acquisition of *syn*-sesquinorbornene,[3a,b,7] a diazabishomocubane,[8] and [4]-peristylane.[9]

Detailed theoretical analysis of our findings has implicated strong σ/π coupling and resultant π lobe tilting as being chiefly responsible for the normally high stereoselectivity commonly observed.[4,10] Of necessity, the prevailing long-range interactions have been diagnosed in a static, time-independent mode. Ideally, an extended dynamic approach involving coupling between diene and dienophile as a function of changing internuclear distance would be more satisfying. At present, however, computer simulations of such pathways are too costly.

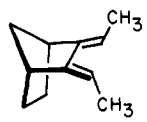
Notwithstanding, common dienophiles have not given evidence of ambiguity along the reaction profile except in those cases where an additional π orbital oriented orthogonal to that involved in bonding is present. In this connection, triazolinediones **3** have been proved most



3a, R = CH_3
b, R = C_6H_5



4



5

6

troublesome. For example, while **3a** adds to **4** with high above-plane stereoselectivity, the corresponding dehydro congener is transformed under analogous conditions to a 61:39 endo/exo mixture.[3e] Also, **3a** adds to **5** to give only the exo adduct in contradistinction to the stereochemical response of other dienophiles.[3g] Where **6** is concerned, [4 + 2] bonding to **3b** occurs at equal rates from both diene faces.[11]

For these reasons, we were prompted to examine the behavior of parent hydrocarbons **1** and **2** toward this pair of "maverick" dienophiles in some detail. *N*-Methyltriazolinedione addition to **2** in ether solution at −20 °C proceeded with rapid consumption of the dienophile as indicated by the almost instantaneous disappearance of its deep red color. Solvent evaporation provided in 84% isolated yield a single colorless solid having a melting point identical with that earlier reported.[8] Its 300-MHz ^1H NMR spectrum (in $CDCl_3$) consists of a pair of doublet of doublets centered at δ 6.50 and 5.17 due to the olefinic protons and those at the bridgehead α to nitrogen, respectively. The second set of bridgehead hydrogens appear upfield (δ 3.59) as a broadened singlet, well separated from the multiplet arising from the methano moieties (δ 2.32–2.04). Since this adduct has been converted in five

(1) Electronic Control of Stereoselectivity. 22. For Part 21, see: Hathaway, S. J.; Paquette, L. A. *Tetrahedron*, in press.

(2) Author to whom inquiries concerning the X-ray crystal structure analysis should be directed.

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