(−)-4-Demethoxy-7-deoxydaunomycinone (3). To an air-stirred solution of NaOH (240 mg, 6 mmol) and an excess of sodium dithionite (510 mg, 2.9 mmol) in H_2O (8 mL) was added 60 mg of the epoxy enone (−)-**20** under nitrogen. The dark mixture was stirred for 1 h at room temperature. Then, air was bubbled through for 10 min, the reaction mixture acidified with diluted HCl, and bubbling continued for another 10 min. The resulting red precipitate was separated by filtration and purified by silica gel chromatography. Elution with CH_2Cl_2 gave 8 mg of enone **11**, identified by direct comparation (TLC, NMR) with a sample obtained as described before. Further elution with 5% EtOAc in CH_2Cl_2 yielded (−)-**3** (23 mg, 47%): mp 201–202 °C; $[\alpha]_D$ −49° (*c* 0.55, $CHCl_3$) optical yield: 56%); identical with an authentic sample[12] (TLC, NMR, IR). A single trituration with EtOH–$CHCl_3$ gave an 82% optically pure sample of (−)-**3**: mp 201–203 °C; $[\alpha]_D$ −71° (*c* 0.15, $CHCl_3$) (literature value in ref 26).

Acknowledgment. We thank the Adria Laboratories for a grant in support of this work.

Registry No. (*R*)-(−)-**3**, 63229-48-1; (±)-**6**, 67122-26-3; (±)-**7**, 84498-97-5; (±)-**9**, 86309-10-6; (±)-**10**, 86323-10-6; (±)-**10** 6-demethyl, 86309-11-7; (±)-**10** 11-demethyl, 86309-12-8; **11**, 86309-13-9; **12**, 86309-14-0; **12** 6-demethyl, 86309-15-1; **12** 11-demethyl, 86309-16-2; **13**, 86309-17-3; **14**, 86309-18-4; (±)-**15**, 86309-19-5; (±)-**16**, 86309-20-8; (±)-**17**, 86309-21-9; (*R*)-(+)-**17**, 86362-06-3; (*S*)-(−)-**17**, 86362-07-4; (±)-**18**, 86309-22-0; (−)-**18**, 86362-08-5; (+)-**18**, 86362-09-6; (±)-**19**, 86362-10-9; (−)-**20**, 86309-23-1.

Cyclodehydration and Chlorination of Simple Diols with Triphenylphosphine and *tert*-Butyl Hypochlorite

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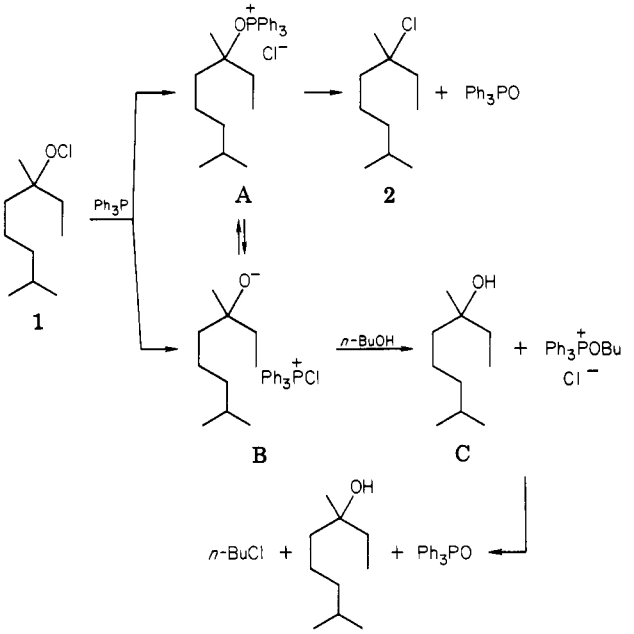
The reagent triphenylphosphine–*tert*-butyl hypochlorite converts 1,4-diols into the corresponding tetrahydrofurans and 1,2-diols into a mixture of the regioisomeric chlorohydrins and the epoxides at −78 °C followed by warming to ambient temperature (ca. 30 °C). Symmetrical diols give largely chlorohydrins and dichlorides.

Introduction

Various halogenating and cyclodehydrating reagents, consisting of phosphines and phosphites with halogens[1,2] and carbon tetrahalides,[3] have found useful preparative utility for primarily alkyl halides and, to a limited extent, cyclic ethers[4] from alcohols and diols, respectively.

It has been previously shown that triphenylphosphine (TPP) reacts with tetrahydrolinalyl hypochlorite (**1**) at −78 °C to afford oxyphosphonium chloride A, presumably through phosphonium ion B, which subsequently decomposes to tetrahydrolinalyl chloride (**2**) and triphenylphosphine oxide (TPPO), albeit in low yield.[5] However, in the presence of 1-butanol, trace amounts of 1-chlorobutane are obtained. A reasonable rationale for formation of 1-chlorobutane requires initial nucleophilic attack on the chlorine atom[6] of **1** to afford chlorophosphonium alkoxide B. Proton transfer between salt B and 1-butanol would ultimately lead to oxyphosphonium chloride C,

Chart I



which could decompose to 1-chlorobutane and TPPO[7] (Chart I).

These results strongly suggest that a potentially useful parallel may exist in the reactivity of triphenylphosphine (TPP)–tetrachloromethane (CCl_4) and triphenylphosphine–*tert*-alkyl hypochlorites in the chlorination of

(1) For a general review and recent references, see Cadogan, J. I. G., Ed. "Organophosphorus Reagents in Organic Synthesis"; Academic Press: New York, 1979.
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Table I. Product Distributions from Reactions of Diols with TPP-*t*-BHC

diol	equiv of TPP-*t*-BHC	unreacted diol, %	cyclic ether, %	chlorohydrin, %	dichloride, %
1,3-propanediol (3)	1.25[a]	4	0	76	20
1,4-butanediol (6)	1.1[b]	33	67	0	0
cis-1,2-butene-1,4-diol (7)	1.25[c]	39	61	0	0
cis-1,2-bis(hydroxymethyl)cyclohexane (8)	1.25[b]	<1	>99	0	0
1,5-pentanediol (5)	1.1[a]	12	8	38	42
1,6-hexanediol (4)	1.2[a]	15	0	44	41
trans-1,2-cyclohexanediol (9)	1.25[a]	25	35	40[d]	0

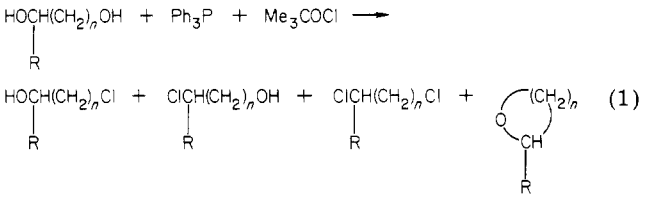
[a] Yield determined by GLC. [b] Yield determined by ^{13}C NMR. [c] Yield determined by ^{1}H NMR. [d] *trans*-2-Chlorocyclohexanol.

Table II. Product Distributions from Reactions of 1,2-Diols with TPP-*t*-BHC-K_2CO_3[a]

R	equiv of TPP-*t*-BHC	% HOCH(R)CH$_2$OH	%	% ClCH(R)CH$_2$OH	% HOCH(R)CH$_2$Cl	2-Cl/1-Cl
CH_3	2.0	17	3	40	6	6.7
Ph	1.5	24	22	16	19	0.9
i-C_4H_9	1.25	16	15	43	20	2.1
n-C_8H_{17}	1.25	25	18	37	5	7.3

[a] Some unidentified material was observed in the ^{13}C NMR spectra for all of these reactions.

alcohols. Furthermore, since diols react with the "TPP–CCl_4" and "TPP–CCl_4–K_2CO_3" reagents[8] to give cyclic ethers as well as chlorinated derivatives, one might anticipate that an appropriate combination of *tert*-butyl hypochlorite (*t*BHC), TPP, and diol would afford cyclic ethers as well. Here, we present our findings on the reaction of a variety of diols with TPP-*t*-BHC (eq 1).

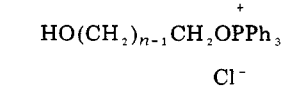


(1)

n = 1-4; R = alkyl, Ph

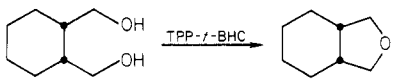
Results and Discussion

The general trends in the product distributions are very similar to those previously observed for the reactions of TPP–CCl_4 with these diols. For example, treatment of 1,3-propanediol (3) and 1,6-hexanediol (4) with TPP-*t*-BHC each gives a mixture of chlorohydrin and dichloride but no cyclic ether by GLC analysis. A small quantity (8%) of tetrahydropyran is obtained when 1,5-pentanediol (5) is treated with TPP-*t*-BHC; however, 5-chloro-1-pentanol (38%) and 1,5-dichloropentane (42%) are the predominant products. The chlorohydrins arise presumably from displacement of triphenylphosphine oxide (TPPO) from the oxyphosphonium chloride D by chloride ion



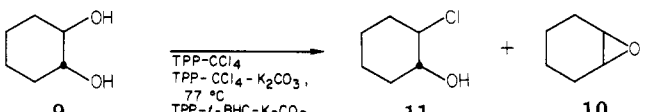
D

rather than by the alternative and less likely cyclic ether cleavage with hydrochloric acid (HCl). In a similar way, dichlorides are formed exclusively from the chlorohydrins. By contrast, 1,4-butanediol (6), *cis*-2-butene-1,4-diol (7), and *cis*-1,2-bis(hydroxymethyl)cyclohexane (8) react smoothly with TPP-*t*-BHC to afford tetrahydrofuran (67%), 2,5-dihydrofuran (61%), and *cis*-8-oxabicyclo[4.3.0]nonane (>99%), respectively. These cyclic ethers are the only products observed by ^{1}H and ^{13}C NMR analyses (see Table I).



8 >99%

When *trans*-1,2-cyclohexanediol (9) and 1.25 equiv of TPP-*t*-BHC are allowed to react in the presence of K_2CO_3,[4,8] 1,2-cyclohexene oxide (10), and *trans*-2-chlorocyclohexanol (11) are obtained in 35% and 40%, respectively. Presumably, chlorohydrin 11 comes from reaction of epoxide 10 with HCl. This result is particularly significant since cyclodehydration of diol 9 with the "TPP–CCl_4–K_2CO_3" reagent gives exclusively epoxide 10 (86%), while reaction of diol 9 with *only* the "TPP–CCl_4" reagent affords chlorohydrin 11 (88%).[4] In this latter case, K_2CO_3 reacts with the HCl formed in the reaction, thereby suppressing formation of chlorohydrin 11. However, in the



9	11	10
(12%)	88%	0%
(14%)	0%	86%
(25%)	40%	35%

TPP-*t*-BHC-promoted reaction with diol 9, K_2CO_3 is considerably less effective in preventing formation of chlorohydrin. The reason for this difference may lie in the change in polarity of the solvent in the latter reaction. The combination of $CHCl_3$–*t*-BuOH is probably more polar than CCl_4–$CHCl_3$ (from the TPP–CCl_4 reaction), which could promote a higher degree of HCl ionization and, perhaps, accelerate the conversion of epoxide to chlorohydrin.

Treatment of a series of monosubstituted ethylene glycols with TPP-*t*-BHC–K_2CO_3 gave mixtures consisting primarily of the regioisomeric chlorohydrins and the epoxide. The isomeric chlorohydrins apparently result from the reaction of HCl and epoxide and, with only one exception (R = Ph), the 2-chloro-1-hydroxy isomer predominates. The ratios of the isomeric chlorohydrins (2-Cl/1-Cl)

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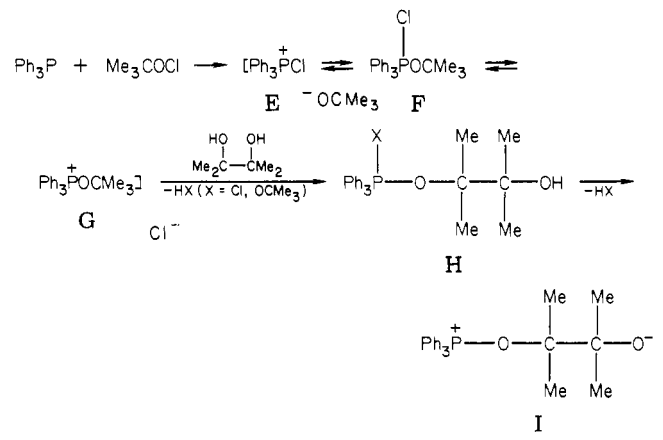
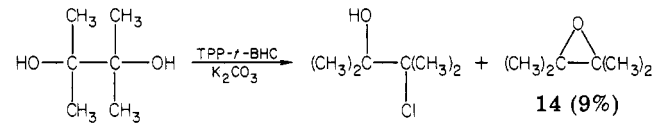
Chart II



suggest that the reaction of epoxide with HCl proceeds largely via an "A1" mechanism.[9] This seems reasonable since direct displacement of OP^+Ph_3 from Cl of monosubstituted diols by Cl^- is expected to give regioselective chlorination. This conclusion is based on previous observations with TPP–CCl_4 and other diols (Table II).[10]

The facility for ether ring formation (assuming that 1,2-chlorohydrins come from the reaction of HCl with previously formed epoxide) decreases in the following manner: 3 ~ 5 > 6 > 4 ~ 7. This qualitative trend in the propensity for ring closure of diols promoted by TPP–*t*-BHC–K_2CO_3 is essentially identical with that previously reported for TPP–CCl_4[4a] and diaryldialkoxysulfurane[11] reagents.

Reaction of 2,3-dimethyl-2,3-butanediol (12) with 1.25 equiv of TPP–*t*-BHC–K_2CO_3 affords a mixture of chlorohydrin 13 (6%), epoxide 14 (9%), and 85% unreacted diol 12. When these results are compared with those from



other reactions of 1,2-diols, where higher yields of epoxides and chlorohydrins are realized, they suggest that formation of the prerequisite oxyphosphonium salt I is apparently suppressed. Formation of phosphonium salts E and G through phosphorane F from the reaction of TPP and *t*-BHC allows diol 12 to become incorporated into the reaction. The reaction between phosphonium salts E and/or G and diol 12 to form phosphorane H and ultimately oxyphosphonium salt I is probably unfavorable because of severe steric interactions between the methyl groups and the phenyl rings (Chart II). 2,3-Dimethyl-2,3-epoxybutane (14) comes from the collapse of oxyphosphonium salt I, while chlorohydrin 13 probably arises from the reaction of 14 with HCl.

Experimental Section

Melting points were obtained with a Mel-Temp melting point apparatus with an open capillary tube and they are uncorrected.

Proton magnetic resonance (^1H NMR) spectra were recorded on Varian Model XL-100-12 and Perkin-Elmer Model R-24B NMR spectrometers. The ^{13}C NMR FT spectra were obtained at ambient temperature (ca. 30 °C) with noise decoupling. All ^1H and ^{13}C NMR chemical shifts of samples as 5–15% (wt/wt %) deuteriochloroform ($CDCl_3$) or perdeuteriodimethyl sulfoxide (Me_2SO-d_6) solutions are presented in parts per million (δ) downfield from internal tetramethylsilane (Me_4Si).

Gas chromatographic separations were obtained on a Hewlett Packard Model 5754B research gas chromatograph with a stainless steel column [0.125 in. i.d. × 6 ft packed with 20% Carbowax 20M on Chromosorb W-HP-AW-DMCS (100–125 mesh)]. Preparative gas chromatographic separations were performed on a GOW-MAC Series 550 research gas chromatograph with an aluminum column [0.375 in. i.d. × 5.5 ft packed with 15% Carbowax 20M (0.1% KOH) on Chromosorb A (20–30 mesh)].

Analytical high-performance liquid chromatography (HPLC) was performed on a Waters Model M-6000A research HPLC using a stainless steel column [4.60 mm i.d. × 250 mm packed with silica (Waters Partisil-10)]. Preparative HPLC was performed on a Waters LC-500A instrument with two Teflon columns [2.0 in. i.d. × 11.25 in., packed with silica (Waters Prepak-500/silica)].

The synthesis and characterization of all of the compounds in Table I have been previously described.

Triphenylphosphine [recrystallized from a solution containing methanol and petroleum ether (boiling range 30–60 °C)] was obtained from M & T Chemicals, Inc. and Aldrich Chemical Co. Potassium carbonate (Fisher Scientific Co.) was carefully ground and filtered through a 120 U.S. Standard Sieve (0.125-mm opening). The following compounds were obtained from the Aldrich Chemical Co.: 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, *cis*-2-butene-1,4-diol, tetrahydropyran, 1-decene, phenyl-1,2-ethanediol, and *m*-chloroperoxybenzoic acid (*m*-CPBA). Aqueous sodium hypochlorite (5.25%) was purchased from the Clorox Co.

General Procedure for the Reaction of Triphenylphosphine–*tert*-Butyl Hypochlorite with Diols. A mixture of the 1,2-diol (5 mmol), anhydrous potassium carbonate (2.38 g, 10 mmol), and triphenylphosphine (1.64 g, 6.25 mmol) in chloroform solvent (10 mL) was cooled to −70 °C (dry ice–acetone bath). *tert*-Butyl hypochlorite (679 mg, 6.25 mmol) was added dropwise to the cooled mixture and then the mixture was allowed to warm to ambient temperature. The resulting mixture was stirred at reflux for 24 h and the product composition was determined by ^1H and ^{13}C NMR analyses as well as GLC comparisons of components of the reaction mixture with retention times of authentic materials. The general preparative procedure for the other diols is essentially identical with that described above except that anhydrous potassium carbonate was omitted.

***tert*-Butyl Hypochlorite.** *tert*-Butyl hypochlorite was prepared in 75% yield by reaction of *tert*-butyl alcohol with 5.25% aqueous sodium hypochlorite in glacial acetic acid:[12] ^{13}C NMR ($CDCl_3$) δ 26.68 (CH_3), 83.86 [$C(CH_3)_3$].

2,3-Dimethyl-2,3-epoxybutane (14). 2,3-Dimethyl-2-butene was oxidized with *m*-CPBA in dichloromethane solvent to afford 2,3-dimethyl-2,3-epoxybutane in 30%: bp 83–93 °C (760 torr) [lit.[13] bp 90.2–91.4 °C (753 torr)]; ^1H NMR ($CDCl_3$) δ 1.31 (s, 12 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 21.15 (CH_3), 61.84 (C).

3-Chloro-2,3-dimethyl-2-butanol (13). The reaction of dry HCl with 2,3-dimethyl-2,3-epoxybutane gave 18% chlorohydrin 13 after distillation: bp 55–65 °C (30 torr) [lit.[14] bp 45–50 °C (15 torr)]; ^1H NMR ($CDCl_3$) δ 1.33 (s, 6 H, CH_3O), 1.64 (s, 6 H, CH_3Cl), 2.27 (s, 1 H, OH).

4-Methyl-1,2-pentanediol. 4-Methyl-1-pentene was oxidized with 30% hydrogen peroxide in formic acid, followed by hydrolysis of the formate ester with sodium hydroxide to afford 4-methyl-1,2-pentanediol (22%): bp 72–74 °C (torr) [lit.[15] bp 75 °C (2 torr)]; ^1H NMR ($CDCl_3$) δ 0.93 (d, 3 H, J = 6.5 Hz, CH_3), 0.95 (d, 3 H, J = 6.5 Hz, CH_3), 1.06–1.95 (m, 3 H $(CH_3)_2CHCH_2$), 3.23–3.89 (m, 3 H, $HOCH_2CH_2OH$), 4.00 (br, s, 2 H, OH); ^{13}C NMR ($CDCl_3$) δ 22.19 (CH_3), 23.34 (CH_3), 24.56 (CH_3CHCH_3), 42.06 (CH_2), 67.19 (CH_2OH), 70.59 (CH_2ChOH).

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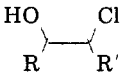
Table III. ^{13}C NMR Chemical Shifts (C1, C2) for Regioisomeric Chlorohydrins



R	R'	δC1	δC2
i-C_4H_9	H	69.7	50.1
H	i-C_4H_9	67.3	62.1
n-C_8H_{17}	H	71.4	49.6
H	n-C_8H_{17}	66.9	64.0

4-Methyl-1,2-epoxypentane. Oxidation of 4-methyl-1-pentene with 85% m-CPBA gave 1,2-epoxypentane (32%): bp 100–111 °C (760 torr) [lit.[16] bp 64–66 °C (150 torr)]; ^1H NMR ($CDCl_3$) δ 0.98 [d, 6 H, J = 7 Hz, $CH(CH_3)_2$], 1.42 (m, 2 H, $CH_2CH(CH_3)_2$], 1.63–2.07 (m, 1 H, $CH(CH_3)_2$], 2.44 (d,d, 1 H, J_{HaHb} = 5.5 Hz, J_{HaHc} = 3.0 Hz, CH_aH_bO), 2.76 (t, 1 H, J = 5 Hz, CH_aH_bO), 2.92 (m, 1 H, RCH_cO); ^{13}C NMR ($CDCl_3$) δ 22.50 (CH_3), 22.98 (CH_3), 26.53 (CH_3CHCH_3), 41.76 (CH_2), 47.06 (CH_2O), 51.16 [$CH_2CH(O)CH_2$].

1,2-Decanediol. Oxidation of 1-decane with 30% hydrogen peroxide and formic acid followed by hydrolysis of the formate ester with aqueous sodium hydroxide gave 42% 1,2-decanediol: mp 45–47 °C (lit.[17] mp 48–49 °C; ^1H NMR ($CDCl_3$) δ 0.89 (t, 3 H, J = 6 Hz, CH_3), 1.11–1.59 (m, 14 H, $(CH_2)_{14}$), 2.88 (brs, 2 H, OH), 3.30–3.87 (m, 3 H, $HOCHCH_2OH$); ^{13}C NMR ($CDCl_3$) δ 14.08 (CH_3), 22.71 (CH_2), 25.73 (CH_2), 29.36 (CH_2), 29.64 (CH_2), 29.81 (CH_2), 31.95 (CH_2), 33.23 (CH_2), 66.79 (CH_2OH), 72.46 (CH_2CHOH).

1,2-Epoxydecane. Oxidation of 1,2-decane with m-CPBA gave 1,2-epoxydecane in 61% yield: bp 85–91 °C (14 torr) [lit.[18] bp 88-90° (14 torr)]; ^{13}C NMR ($CDCl_3$) δ 14.09 (CH_3), 22.72 (CH_2), 26.05 (CH_2), 29.79 (CH_2), 29.54 (CH_2), 29.59 (CH_2), 31.93 (CH_2), 32.59 (CH_2), 47.02 (CH_2O), 52.34 [$CH_2CH(O)CH_2$].

The structures of the chlorohydrins in Table II were assigned by using ^{13}C NMR chemical shift data (Table III).

Acknowledgment is made to the National Science Foundation (CHE 78-05921) for support of this research, the National Science Foundation and the North Carolina Science and Technology Committee for grants to purchase the Waters LC-500A HPLC unit, and M & T Chemicals, Inc. for generous samples of triphenylphosphine.

Registry No. **3**, 504-63-2; **4**, 629-11-8; **5**, 30643-76-6; **6**, 110-63-4; **7**, 6117-80-2; **8**, 15753-50-1; **9**, 1460-57-7; **10**, 286-20-4; **11**, 6628-80-4; **12**, 76-09-5; **13**, 21326-63-6; **14**, 5076-20-0; 4-methyl-1,2-pentanediol, 72110-08-8; 4-methyl-1,2-epoxypentane, 23850-78-4; 1,2-decanediol, 1119-86-4; 1,2-epoxydecane, 2404-44-6; triphenylphosphine, 603-35-0; *tert*-butyl hypochlorite, 507-40-4; 2,3-dimethyl-2-butene, 563-79-1; 4-methyl-1-pentene, 691-37-2; 1-decene, 872-05-9; 1,2-propanediol, 57-55-6; 1-phenyl-1,2-ethanediol, 93-56-1; 1-chloro-4-methyl-2-pentanol, 84055-72-1; 2-chloro-4-methyl-1-pentanol, 86260-25-5; 1-chloro-2-decanol, 39579-73-2; 2-chloro-1-decanol, 39579-78-7.

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Ene Reaction Mechanisms. 1. Chirality Transfer to the Enophile 4-Methyl-*N*-sulfinylbenzenesulfonamide

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The ene reaction of (*S*)-(+)-3-phenyl-1-butene (**1**) with *N*-sulfinyl-*p*-toluenesulfonamide (**2**) leads to the optically active (*E*)-2-alkenesulfinamide **3**. This corresponds to a chirality transfer from the chiral carbon center in **1** to the sulfur atom of the product **3**. The enantiomeric excess of **3** as well as the absolute configuration of the predominant enantiomer have been determined. The formation of the major enantiomer of **3** is correlated with a preference for the endo orientation of the alkene and the *Z*-configurated enophile in the H-abstraction step. The results are in agreement with the formation of an orienting [2 + 2] complex between the reactants preceding the rate-determining H abstraction by the lone electron pair of the N atom.

We recently proposed a concerted "pseudopericyclic" mechanism for the ene reactions of *N*-sulfinyl compounds and sulfur diimides.[1] According to our proposal, in the rate-determining step of these reactions the allylic hydrogen is abstracted by the lone pair electrons of the nitrogen in a preformed [2 + 2] complex of the reactants.

One of the experiments which led us to the above conclusions was the investigation of the steric course of an ene reaction. These results are described here in detail.

With an RNSO compound as the educt and the allylic hydrogen bonded to a chiral carbon center, the possibility of chirality transfer to the developing sulfinyl S atom in concert with the loss of asymmetry at this carbon center can be envisaged.

Until now, there have been only a few examples for asymmetric inductions in ene reactions;[2] a case in point is the reaction of the azo dicarboxylic ester with (*S*)-(*Z*)-1-deuterio-4-methyl-1-phenyl-2-pentene, giving the ene product with 50% ee.[3] From this result as well as those obtained from H/D isotope effect measurements it was concluded that the process has to be regarded as a concerted reaction. In another example a favored endo transition state explains the diastereomeric ratio of the

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