l-2-Nitro-1,3-alkanediols by Stereoselective Addition of Nitroethanol to Aldehydes.[1] On the Asymmetric Electrophilic Addition to Double Bonds

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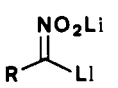
Abstract: Tetrahydropyranyl-protected nitroethanol and other vicinal nitro alcohols can be doubly deprotonated to lithium α-lithionitronates (cf. **2**,**27**). These are rather stable toward β-elimination of the pyranyloxy group. They combine in good yields with various electrophiles to give higher nitroalcohols, hydroxynitro ketones, and nitrodiols (**4–24**, **28**) after deprotection with an acidic ion-exchange resin in methanol (Scheme II, Tables I and II). Of the nitrodiols **9–18** and **28** obtained with aldehydes and a ketone in the presence of the cosolvent HMPT or DMPU, one diastereomer is formed preferentially (75 to >95%) and can be enriched in most cases by crystallization; additional centers of chirality in the reactands may (see **18**, **28**) or may not (see **19–24**) exert asymmetric induction on the process. The configuration of two of the nitrodiols (**13**, **14**) was established by chemical correlation to be *like*. The observed configuration results by diastereoselective nitronate protonation (relative topicity *unlike*, Schemes III and VI). The effects operating in such electrophilic additions to donor double bonds with 1,2-asymmetric induction are discussed more generally (Scheme IV), using the two-membered-ring or π-model for the double bond (Scheme V).

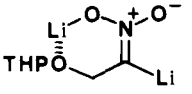
A. Introduction

Besides appropriate reaction conditions, such as very low temperature[3] and the use of stabilizing solvents, there are certain structural features by which β-elimination[4] from carbanionic systems with leaving groups may be prevented. These are demonstrated[5] by the reagents A–F, Scheme I, taken from the most recent literature, with emphasis on our own work. The leaving group may be forced in a position coplanar with the donor π-system (A),[6] it may be a dianion derivative such as LiO^- (B),[7] or it may be in an ideal position for chelation of a metal at the donor center (C);[8] furthermore, the carbanionic character may be reduced by the nature of the metal (D)[9] or by effective charge delocalization (E).[10] Finally, the elimination may not occur because a highly strained double bond would be formed (F).[11]

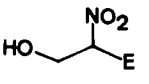
We describe here the remarkable case of a doubly lithiated nucleophilic reagent with a β-heterosubstituent; the lithium lithionitronate **2** generated from tetrahydropyranyl (THP) protected[12] nitroethanol is as stable as the previously described[10,13] nitroalkane derivatives **1** without the potential leaving group! The



1 (R = alkyl)



2



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stability of **2** does not rest upon the presence of the additional oxygen atom in the THP ring; the cyclohexyl ether of nitroethanol can be converted to an analogous reagent of comparable stability.[12] This is why we draw the *formula* of **2** with a chelation of the lithium atom on the nitronate group by the THP–O atom.[5] The stability and high nucleophilicity of the reagent **2** make nitro alcohols of type **3** readily available, and the diastereoselective preparation of 2-nitro-1,3-diols, and thus of 2-amino-1,3-diols from nitroethanol and aldehydes, becomes feasible. The products from **2** are also of interest in view of the recent studies on enzyme inhibition by nitro compounds.[14]

B. Results

The dilithio derivative **2** is generated by addition of a slight excess over 2 equiv of butyllithium to THP-protected nitroethanol[15] in tetrahydrofuran (THF)/hexamethylphosphoric acid triamide (HMPT) or dimethylpropyleneurea (DMPU)[16] at −90 °C.[3] The resulting yellow solution is slowly warmed[17] to −40 °C, cooled again, and combined with electrophiles such as alkyl halide, esters, ketones, and aldehydes. After quenching with acetic acid at low temperature (ca. −90 °C), and aqueous workup, the THP-protected nitro alcohol **4a**, β-hydroxy-α-nitrocarbonyl compounds **5a–7a**, and nitrodiols **8a–18a** were isolated in yields ranging from 44% to 90%; see the *formulae* in Scheme II and the numbers in

(1) Seebach, D. "Abstracts of Papers", National Meeting of the American Chemical Society, St. Louis, MO, 1984; American Chemical Society: Washington, DC, 1984.
(2) Eyer, M. Ph.D. Thesis, ETH Zürich, 1985.
(3) Review on the techniques of carrying out reactions at temperatures below −80 °C: Seebach, D.; Hidber, A. *Chimia* **1983**, *37*, 449.
(4) Many of the same features are also responsible for stabilizing systems which are capable of α elimination; see the NMR investigations of lithium halocarbenoids: Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308.
(5) Often, more than one of the effects are responsible for the observed stability.
(6) Seebach, D.; Aebi, J. D. *Tetrahedron Lett.* **1984**, *25*, 2545. Mulzer, J.; Kerkmann, T. *J. Am. Chem. Soc.* **1980**, *102*, 3620. Mulzer, J. *Nachr. Chem., Tech. Lab* **1981**, *29*, 614. These cases could be called trajectory-forbidden eliminations, or forbidden 4- or 5-*endo*-trigonal retrocycloadditions: Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.
(7) Nâjera, C.; Yus, M.; Seebach, D. *Helv. Chim. Acta* **1984**, *67*, 289.
(8) Yu, L.-C.; Helquist, P. *Tetrahedron Lett.* **1978**, *19*, 3423.
(9) Weidmann, B.; Widler, L.; Olivero, A. G.; Maycock, C. D.; Seebach, D. *Helv. Chim. Acta* **1981**, *64*, 357.
(10) Seebach, D.; Beck, A. K.; Lehr, F.; Weller, T.; Colvin, E. W. *Angew. Chem.* **1981**, *93*, 422; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 397. Seebach, D.; Beck, A. K.; Mukhopadhyay, T.; Thomas, E. *Helv. Chim. Acta* **1982**, *65*, 1101.
(11) Corey, E. J.; Ulrich, P. *Tetrahedron Lett.* **1975**, *16*, 3685.
(12) Doubly lithiated derivatives of type **2** were also generated with methoxymethyl (MOM), ethoxyethyl (EE), methoxyisopropyl (MIP), 4-methoxy-4-tetrahydropyranyl, and cyclohexyl instead of the THP group on oxygen. The yields/diastereoselectivities of addition of these reagents to benzaldehyde were 74/56%, 82/79%, 77/80%, 74/88%, and 88/80%, respectively.
(13) Seebach, D.; Lehr, F. *Angew. Chem.* **1976**, *88*, 540; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 505. Henning, R.; Lehr, F.; Seebach, D. *Helv. Chim. Acta* **1976**, *59*, 2213.
(14) Alston, T. A.; Porter, D. J. T.; Bright, H. J. *Acc. Chem. Res.* **1983**, *16*, 418.
(15) Kraus, G. A.; Frazier, K. *J. Org. Chem.* **1980**, *45*, 4820.
(16) With DMPU as a cosolvent [Mukhopadhyay, T.; Seebach, D. *Helv. Chim. Acta* **1982**, *65*, 385], the yields are comparable: **14a** is formed in 75% yield in the presence of 17% HMPT, in 69% yield with 25% DMPU, and in 75% without cosolvent. The ratios of diastereomeric nitrodiols **14b** in the three experiments are >95:5, 89:11, and 54:46, respectively. The yields given in the present paper were all obtained with HMPT.
(17) Even after the solutions were warmed to −30 °C for short periods of time, the yields of subsequent reactions were hardly reduced.

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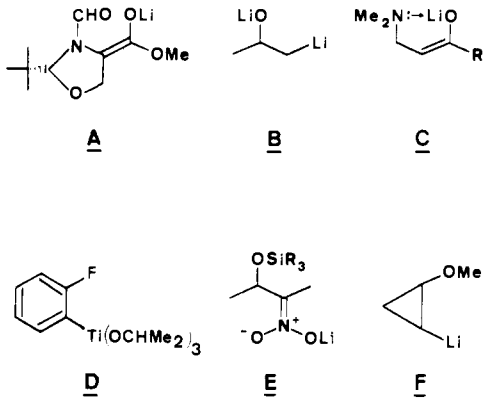
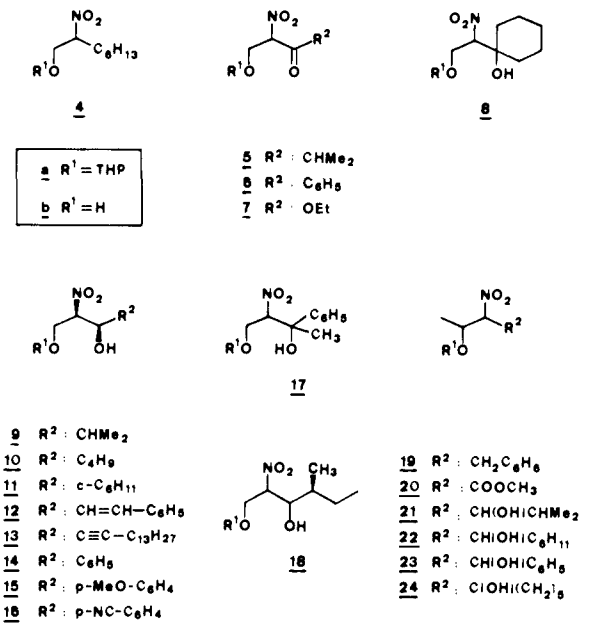
Scheme I



Scheme II



the second column of Table I. As is evident from their NMR spectra, all products **4a–17a** consist of mainly two diastereomers. Removal of the THP protecting group, and thus of one of the asymmetric carbon atoms from these primary products, was achieved by treatment in methanol with Amberlyst (acidic ion exchange resin). Under these conditions, no retro-nitroaldol reactions and/or dehydrations to nitroolefins occurred, and most[18] hydroxy derivatives **4b–17b** were isolated in essentially quantitative yields; see the fourth column in Table I. The samples of nitrodiols **9b–16b** thus obtained—formally products of a double nitroaldol addition of nitromethane to formaldehyde and another aldehyde—were all highly enriched in one diastereoisomer; see the sixth column of Table I. Since the nitrodiols crystallized eventually, pure samples of single diastereomers could easily be prepared.

For assignment of configuration to these products, a chemical correlation was possible in two cases, one aliphatic (**13b**), the other one aromatic (**14b**). The acetylenic nitrodiol **13b** was identical with a previously prepared[19] sample of *l* configuration[20] (threo after the Fischer convention); the compound was isolated as the

Table I. Yields of Flash-Chromatographed Products **4a–18a** and of the Corresponding Deprotected Nitro Alcohols **4b–18b** from Reagent **2** and Different Electrophiles

THP-protected prod **a**		free nitro alcohols **b**				
			% yield (purified)			
prod	% yield	prod	from **a** (hydrolysis)	overall from **2**	% ds[a]	mp, °C
4	44	**4**	92	41		
5	74	**5**	86	64		
6	85	**6**	83	70		
7	68	**7**	90	61		
8	73	**8**	>99	73		96–97
9	72	**9**	95	68	93	86–87
10	56	**10**	95	53	85	
11	64	**11**	>99	64	>95	90–91
12	80	**12**	92	74	91	94–95
13	57	**13**	95	54	>88	73–74
14	75	**14**	>99	75	>95	90–91
15	81	**15**	98	79	80	
16	90	**16**	98	88	75	86–87
17	54	**17**	96	52	73	90–91
18	64	**18**	>99	64	73	61–62

[a] The fraction of the major diastereoisomer (% ds) in the mixture of nitro alcohols was determined by ^{13}C NMR analysis before separation. For details, such as solvents for recrystallization, spectroscopic identification and elemental analysis of the pure nitro alcohols, see Experimental Section.

Table II. Products **19a–24a** and **19b–24b** from the Reactions of THP-Protected Nitropropanol with Different Electrophiles[a]

	THP-protected prod **a**		free nitro alcohols **b**		
				overall	ratio of
electrophile	prod	% yield	prod	% yield	diastereomers
benzyl bromide	**19**	62	**19**	61	
dimethyl carbonate	**20**	75	**20**	69	
2-methylpropanal	**21**	62	**21**	60	49:49:<1:<1
cyclohexanecarbaldehyde	**22**	58	**22**	57	49:49:<1:<1
benzaldehyde	**23**	66	**23**	66	49:49:<1:<1
cyclohexanone	**24**	55	**24**	53	

[a] In all cases, the crude mixture of diastereomeric THP-protected products was flash-chromatographed. Subsequent deprotection gives the nitro alcohols.

undesired epimer in a nonstereoselective synthesis of sphingosine, a component of gangliosides.[19] The configuration of the diol **14b** derived from benzaldehyde had been previously assigned[21] to be also *l*; it is an intermediate of an industrial synthesis of the antibiotic chloroamphenicol. Due to very similar NMR spectra, the diols (**15b**, **16b**) obtained with substituted benzaldehydes must have the same configuration as **14b**. In analogy, we assume that the other adducts (**9b–12b**) to aliphatic aldehydes also belong to the *l* series; see Discussion section. We do not dare to assign a configuration to the major product **17b** formed with acetophenone[22] (Table I).

To see whether there is a 1,2-asymmetric induction in the addition of the reagent **2** to α-branched aldehydes, we combined it with (*S*)-2-methylbutanal to find that of the four possible diastereoisomeric nitrodiols **18b**, only two were formed (64% yield), the major one (73% ds)[23] of which crystallized (Table I). If the reaction follows Cram's rule (open chain model[24]), and if we assume the *l* configuration of the two newly formed centers, the

(18) In the case of the nitro ketones and esters **5a–7a**, it is important that the removal of the THP group is carried out at room temperature. At higher temperature (ca. 45 °C), decomposition may take place (**7a**), or the α-nitro-β-methoxy ketones are formed in addition to or instead of the desired β-hydroxy ketones (as in the cases of **5a** and **6a**).

(19) Grob, C. A.; Gadient, F. *Helv. Chim. Acta* **1957**, *40*, 1145. For a recent paper on sphingosine: Wydila, J.; Thornton, E. R. *J. Org. Chem.* **1984**, *49*, 244 and references cited therein.

(20) Seebach, D.; Prelog, V. *Angew. Chem.* **1982**, *94*, 696; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 654.

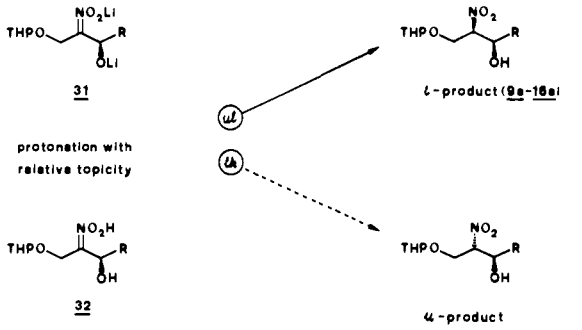
(21) Boehringer AG Patent (Mannheim, Germany). *Chem. Abstr. 86*, P16404*w*. We thank the Boehringer AG for supplying us with a generous sample of this compound.

(22) It may be that **17b** has also the *l* configuration, i.e., that the CH_3 group takes the position of the hydrogen of the aldehyde substrates in the proposed mechanism (section C).

(23) For discussions of the definition of % ds (percentage of a certain diastereomer in a mixture of diastereomers) see: Seebach, D.; Naef, R. *Helv. Chim. Acta* **1981**, *64*, 2704. Thaisrivongs, S.; Seebach, D. *J. Am. Chem. Soc.* **1983**, *105*, 7407.

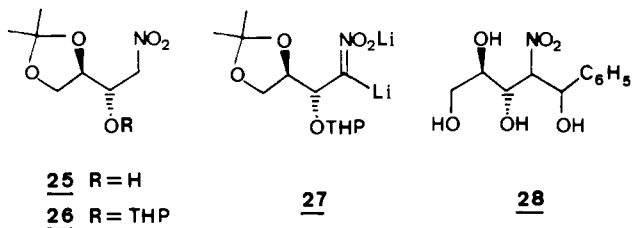
(24) Cram, D. J.; Abd Elhafez, F. A. *J. Am. Chem. Soc.* **1952**, *74*, 5828.

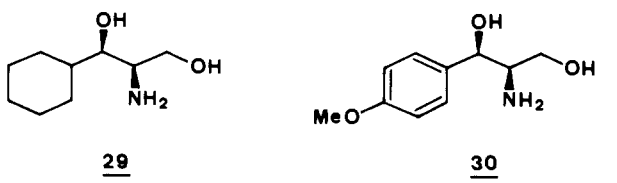
Scheme III



main product **18b** is the 2*R*,3*R*,4*S* stereoisomer.

No asymmetric induction is observed with the reagent generated from THP-protected 1-nitro-2-propanol. The corresponding dilithio derivative gives good yields of alkylated, acylated, and hydroxyalkylated products (**19a–24a**), but *all* deprotected nitro alcohols (**19b–24b**) are ca. 1:1 mixtures of diastereomers (Table II). For the nitrodiols **21b–23b** containing three asymmetric carbon atoms, this means that of the four possible diastereomers, only two have been formed. We assume that these have the same relative configuration (*l*) with respect to the two newly formed centers but are epimeric with respect to the carbinol center already present in the dilithiated nitropropanol derivative.[25] Again, in three of the six examples investigated, one of the diastereomers crystallized and could be isolated in analytically pure form (**21b, 22b,** and **24b**). In order to test whether a dilithionitronate of type **2** with an additional center of chirality bearing a heteroatom, capable of chelating with one of the lithium atoms, would add diastereoselectively to an aldehyde, we protected the known[26] acetonide **25** of (2*S*,3*R*)-1-nitro-2,3,4-butanetriol with a THP group (→**26**), generated the dilithio derivative **27**, and combined it with benzaldehyde. The usual workup and removal of the





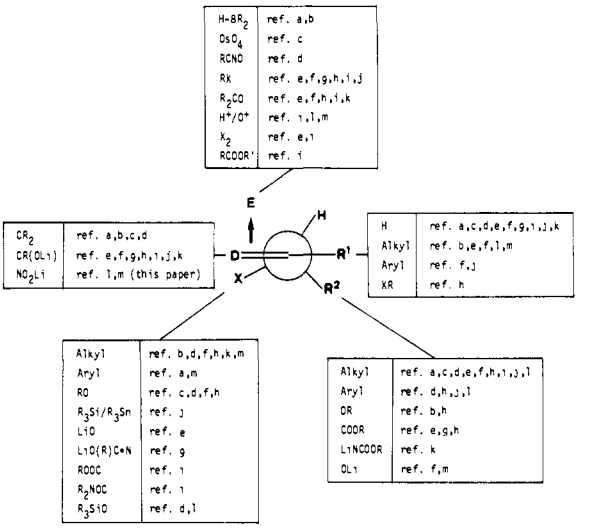
protecting group furnished a *single* (^{13}C NMR) crystalline diastereomer **28** of sharp melting point in 73% yield. We have no proof of the configuration at the two newly formed asymmetric carbon atoms, but—in analogy with the benzaldehyde adduct **14b**—we assume that **28** is either the (1*R*,2*S*) or the (1*S*,2*R*) diastereomer.

Two of the nitrodiols from nitroethanol were reduced to aminodiols (**29** from **11b**, **30** from **15b**) without loss of configurational purity.

C. Discussion

Obviously, the observed diastereoselective synthesis of nitrodiols is the result of selective protonation of the primary adducts to aldehydes in the presence of HMPT or DMPU cosolvent[16] (Scheme III). The alkoxide nitronates **31**, or the corresponding

Scheme IV



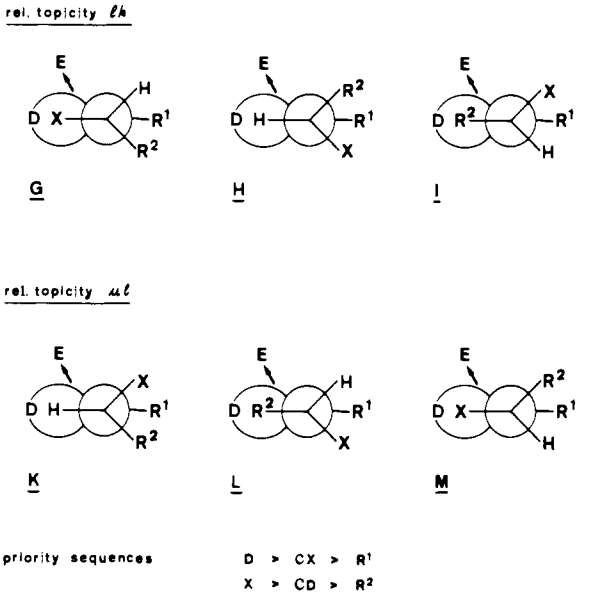
References. (a) Schmid, G.; Fukuyama, T.; Akasaka, K.; Kishi, Y. J. Am. Chem. Soc. 1979, 101, 259. (b) Still, W.C.; Barrish, J.C. J. Am. Chem. Soc. 1983, 105, 2487. (c) Cha, J.K.; Christ, W.J.; Kishi, Y. Tetrahedron Lett. 1983, 24, 3943. (d) Kozikowski, A.P.; Ghosh, A.K. J. Am. Chem. Soc. 1982, 104, 5788. Kozikowski, A.P.; Chen, Y.Y. Tetrahedron Lett. 1982, 23, 2081. Curran, D.P. J. Am. Chem. Soc. 1983, 105, 5826. Jager, V.; Grund, H.; Buss, V.; Schwab, W.; Müller, I.; Schohe, R.; Franz, R.; Ehrler, R. Bull. Soc. Chim. Belg. 1983, 92, 1039. Houk, K.N.; Moses, S.R.; Wu, Y.-D.; Rondan, N.G.; Jager, V.; Schohe, R.; Fronczek, F.R. J. Am. Chem. Soc. 1984, 106, 3880. (e) Kraus, G.A.; Taschner, M.J. Tetrahedron Lett. 1977, 18, 4575. Fráter, G. Helv. Chem. Acta 1979, 62, 2825. Seebach, D.; Wasmuth, D. Helv. Chim. Acta 1980, 63, 197. Wasmuth, D.; Arigoni, D.; Seebach, D. Helv. Chim. Acta 1982, 65, 344. Hoffmann, R.W.; Helbig, W. Chem. Ber. 1981, 114, 2802. Kramer, A.; Pfander, H. Helv. Chim. Acta 1982, 65, 293. (f) Chamberlin, A.R.; Dezube, M. Tetrahedron Lett. 1982, 23, 3055. Shieh, H.-M.; Prestwich, G.D. J. Org. Chem. 1981, 46, 4319. Shieh, H.-M.; Prestwich, G.D. Tetrahedron Lett. 1982, 23, 4643. Seebach, D.; Lawson, K.; Jakob, R. unpublished results, ETH Zürich. Mulzer, J. Nachr. Chem. Tech. Lab. 1981, 29, 614. (g) Seebach, D.; Wasmuth, D. Angew. Chem. 1981, 93, 1007, Int. Ed. Engl. 1981, 20, 971. (h) Naef, R.; Seebach, D. Angew. Chem. 1981, 93, 1113, Int. Ed. Engl. 1981, 20, 1030. Seebach, D. Aebi, J.D. Tetrahedron Lett. 1983, 24, 3311. Ladner, W. Chem. Ber. 1983, 116, 3413. (i) Mahalanabis, K.K.; Mumtaz, M.; Smieckus, V. Tetrahedron Lett. 1982, 23, 3971 and 3975. (j) Fleming, I.; Urch, C.J. Tetrahedron Lett. 1983, 24, 4591. Bernhard, W.; Fleming, I.; Waterson, D. J. Chem. Soc., Chem. Commun. 1984, 28. (k) Iimori, T.; Takahashi, Y.; Izawa, T.; Kobayashi, S.; Ohno, M. J. Am. Chem. Soc. 1983, 105, 1659. (l) Seebach, D.; Beck, A.K.; Lehr, F.; Weller, T.; Colvin, W. Angew. Chem. 1981, 93, 422, Int. Ed. Engl. 1981, 20, 397. Seebach, D.; Beck, A.K.; Mukhopadhyay, T.; Thomas, E. Helv. Chim. Acta 1982, 65, 1101. (m) Seebach, D.; Beck, A.K.; Mukhopadhyay, T.; Thomas E. Helv. Chim. Acta 1982, 65, 1101. Eyer, M.; Seebach, D. this publication.

nitronic acid derivatives **32**, are protonated with relative topicity[20] *ul* in a 1,2-asymmetric induction—while the asymmetric carbon atom in the 2-position of the tetrahydropran heterocycle does not exhibit a 1,4-induction. This is the same stereochemical course as previously observed[10] with simple alkoxide nitronates, not bearing additional functional groups. Thus, we are dealing with an asymmetric electrophilic addition with 1,2-induction. A number of such additions is documented in the references given in the accompanying Scheme IV. The conformation around the σ bond between the asymmetric carbon atom and the sp^2 carbon bearing the donor group is chosen arbitrarily for mapping purposes in Scheme IV. As with its counterpart, the nucleophilic addition to acceptor double bonds, different models will apply, depending on the particular structures of substrate and reagent, cf. the open-chain,[24] cyclic,[27] and dipolar[28] models of asymmetric addition to C=O bonds (Cram–Cornforth), their interpretations by Karabatsos[29] and Felkin,[30] and the more recent theoretical treatment by Anh.[31,32] The most rigorous calculations of the steric course of nucleophilic, radical, and electrophilic additions to double bonds

(25) Thus, the *u,l* and the *l,l* diastereoisomers should have been isolated.
(26) Kozikowski, A. P.; Kitagawa, Y.; Springer, J. P. *J. Chem. Soc., Chem. Commun.* **1983**, *1460*.

(27) Cram, D. J.; Wilson, D. R. *J. Am. Chem. Soc.* **1963**, *85*, 1245. Recently, it has become fashionable to refer to this type of induction as to "chelation control".
(28) Cornforth, J. W.; Cornforth, R. H.; Mathews, K. K. *J. Chem. Soc.* **1959**, 112.
(29) Karabatsos, G. J. *J. Am. Chem. Soc.* **1967**, *89*, 1367.
(30) Cherest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199, 2205.
(31) Anh, N. T.; Eisenstein, O. *Nouv. J. Chim.* **1977**, *1*, 61. Anh, N. T. *Top. Curr. Chem.* **1980**, *88*, 145.
(32) For a genreal discussion of Cram's rule, with numerous references, see: Mulzer, J. *Nachr. Chem., Tech. Lab.* **1984**, *32*, 16.

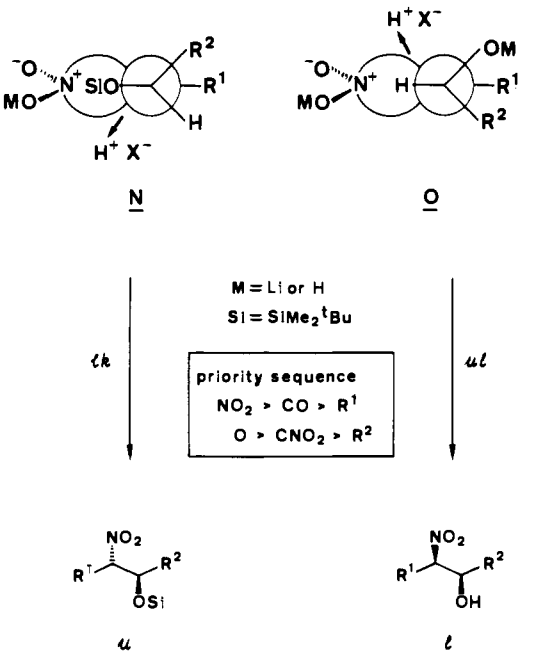
Scheme V



with adjacent asymmetric centers have been published by Houk and his collaborators.[33] While they find some generally applicable effects, they also confirm that there is no single model for any one of these three types of reactions. From the examples of electrophilic additions to donor double bonds listed in Scheme IV, it appears that—as a rule—polar substituents on the asymmetric carbon atom are more often than not in the position designated X. For the reaction described here, however, the oxygen atom of the former aldehyde carbonyl group has to be put in the position designated R^2, in order to denote the observed steric course of reaction.

Without further information about the structure of the species—especially intriguing is the role of the necessary cosolvent—we find it difficult to propose a definite mechanism for the selective protonation found. First, some general remarks about the expected effects seem to be appropriate. In Scheme V the six possible staggered conformations G–M are depicted, using the two-membered-ring or τ-model[34,35] for the donor double bond. For the sake of discussion and with the priority sequences given in Scheme V, the *formulae* G, H, and I describe a *lk*- (cf. Scheme IV) and the *formulae* K, L, and M a *ul*-1,2-induction (cf. Scheme III). Since one of the larger groups X or R^2, and not the hydrogen, will be preferentially in an antiperiplanar position with respect to the attacking reagent,[33] I and M are probably the least favorable modes for *steric reasons*. *Steric hindrance* may also favor H and K over G and L, to a degree which will depend on the size of the D group. The group X may exert an attractive interaction with the D group, favoring the *lk*-approach G, for instance, through a chelation of a metal by D and X. Finally,

Scheme VI



X may trap the electrophile by covalent binding, by forming a hydrogen bond, or by metal complexation, favoring the approach K with relative topicity *ul*. On the other hand, the following stereoelectronic effect[36] should be operative: (i) An electron-withdrawing substituent X (σ acceptor) on the asymmetric carbon atom will decrease the donor reactivity most strongly if antiperiplanar to the two-ring bond which is being attacked by the electrophile, such as in H and L. This makes the approach G the most favorable one for stereoelectronic reasons, as predicted by Eschenmoser[35] and as recently confirmed experimentally and computationally by Houk et al.[33] for the addition of nitril oxides to allylic ethers. (ii) By the same token, a strongly e-donating group X (cf. a metal) will on the contrary increase the reactivity toward an electrophile best if antiperiplanar with respect to the τ bond attacked, such as in H and L.

The opposite steric courses of the kinetically controlled[10] protonations of silyloxynitronates and of alkoxidonitronates might thus be rationalized by the mechanisms N (cf. G) and O (cf. K), respectively (Scheme VI).

D. Experimental Section

General Remarks. Flash chromatography was performed according to the method described by Still et al.[37] Nitroethanol[38] and nitropropanol[39] were synthesized according to the literature method. Nitro alcohol **25** has been described previously.[26] The THP protection of the OH group was performed by following a literature procedure.[15]

General Procedure. To a cooled (−90 °C) stirred solution of 50 mL of THF, 10 mL of HMPA—or 45 mL of THF and 15 ml of DMPU—and 10 mmol THP-protected nitro alcohol was added 15.2 mL (22 mmol) of *n*-butyllithium (1.45 M in hexane). The resulting yellow mixture was allowed to warm to −40 °C during 3 h, and at −90 °C the electrophile (10 mmol) was slowly added. After the reaction mixture had warmed to −60 °C within 90 min (aldehydes, ketones) or to −40 °C within 2 h (esters, alkylhalides), the mixture was cooled again to −90 °C and quenched with 3 mL (~50 mmol) of acetic acid. The clear cold reaction solution was combined with 100 mL of ether and washed successively with two 25-mL portions of cold saturated aqueous $NaHCO_3$. Each

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(34) For the use of this model of describing double bonds see: Baeyer, A. *Chem. Ber.* **1885**, *18*, 2269. Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 1367. Slater, S. C. *Phys. Rev.* **1931**, *37*, 481. Coulson, C. A.; Moffitt, W. E. *Philos. Mag.* **1949**, *40*, 1. Hall, G. G.; Lennard-Jones, J. *Proc. R. Soc. London, Ser. A* **1951**, *205*, 357. Pauling, L. "Kékulé and the Chemical Bond"; Butterworths: London, 1958; IUPAC Symp. Theoret. Cher., p 1. Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell Univeristy Press: Ithaca, NY 1960; p 136. Brown, K. L.; Damm, L.; Dunitz, J. D.; Eschenmoser, A.; Hobi, R.; Kratky, C. *Helv. Chim. Acta* **1978**, 61, 3108. Dale, J. "Stereochemistry and Conformational Analysis"; Veralg Chemie: Weinheim, New York, 1987. Bauer, W.; Laube, T.: Seebach, D. *Chem. Ber.* **1984**, *117*, 1.

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(36) For general discussions of stereoelectronic effects, see the books: Szarek, W. A.; Horton, D. "Anomeric Effect, Origin and Consequences"; American Chemical Society, Washington, DC, 1979; ACS Symp. Ser. No. 87. Kirby, A. J. "The Anomeric Effect and Related Stereoelectronic Effects at Oxygen"; Springer-Verlag: Berlin, Heidelberg, New York, 1983. Deslongchamps, P. "Stereoelectronic Effects in Organic Chemistry", Pergamon Press: Oxford, 1983.

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aqueous phase was extracted with one 100-mL portion of ether. The combined organic phases were washed 4 times with water and once with saturated aqueous NaCl, dried with anhydrous $MgSO_4$, filtered, and concentrated. Chromatography of the resulting residue on silica gel with ether/hexane afforded the pure nitro compound. The deprotonation of the THP group was carried out with 20 mL of MeOH and 0.3 g of Amberlyst at 45 °C for 2 h, except in the case of nitro ketones and nitro esters which were deprotected at room temperature.

Distillation or recrystallization provided analytically pure samples.

2-Nitro-1-octanol (4b). From **2** and 1-iodohexane; purification by distillation 100 °C/0.01 torr: IR (film) 3400, 1550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86–0.90 (m, 3 H, CH_3), 1.22–1.40 (m, 8 H, 4 CH_2), 1.68–1.79 (m, 1 H, C*H*–$CHNO_2$), 1.90–2.00 (m, 1 H, C*H*–$CH–NO_2$), 2.22 (br s, 1 H, OH), 3.89 (dd, J = 3.1, 12.2 Hz, 1 H, C*H*–OH), 4.03 (dxd, J = 8.2, 12.2 Hz, 1 H, C*H*–OH), 4.59 (dddd, J = 3.1, 5.6, 8.2, 13.8, Hz, 1 H, C*H*–NO_2); MS, m/e 175 (M^+, <1), 144 (4), 69 (100), 55 (88). Anal. Calcd for $C_8H_{17}NO_3$: C, 54.84; H, 9.78; N, 7.99. Found: C, 55.12; H, 9.76; N, 7.95.

Ethyl 3-Hydroxy-2-nitropropanoate (7b). From **2** and diethyl carbonate; purification by distillation 85 °C/0.06 torr: IR (film) 3540, 1745, 1565 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (t, J = 7.2 Hz, 3 H, CH_3), 2.73 (br t, 1 H, OH), 4.28–4.34 (m, 4 H, $COOCH_2CH_3$, CH_2OH), 5.29 (dd, J = 4.0, 6.3 Hz, 1 H, $CHNO_2$); MS, m/e 163 (M^+, <1), 88 (22), 71 (86), 29 (100). Anal. Calcd for $C_5H_9NO_5$: C, 36.81; H, 5.56; N, 8.59. Found: C, 36.92; H, 5.68; N, 8.36.

1-(2-Hydroxy-1-nitroethyl)-1-cyclohexanol (8b). From **2** and cyclohexanone; purification by recrystallization from ether/hexane: IR (KBr) 3370, 1560 cm^{-1}; ^1H NMR (acetone-d_6) δ 1.17–1.80 (m, 10 H, C_6H_{10}), 3.70 (br s, 2/3 H, OH), 3.81 (br s, 2/3 H, OH), 4.04 (dd, J = 3.0, 11.5 Hz, 1 H; CH_2OH), 4.18 (br s, 2/3 H, OH), 4.24 (dd, J = 10.0, 11.5 Hz, 1 H, CH_2OH), 4.64 (dd, J = 3.0, 10.0 Hz, 1 H, $CHNO_2$); MS, m/e 189 (M^+, <1), 99 (100), 81 (42), 55 (66), 43 (25). Anal. Calcd for $C_8H_{15}NO_4$: C, 50.78; H, 7.99; N, 7.40. Found: C, 51.04; H, 8.13; N, 7.49.

4-Methyl-2-nitro-1,3-pentanediol (9b). From **2** and 2-methylpropanal; purification by recrystallization from ether/hexane: IR (KBr) 3370, 1560 cm^{-1}; ^1H NMR (acetone-d_6) δ 0.93 (d, J = 6.8 Hz, 3 H, CH_3), 1.02 (d, J = 6.8 Hz, 3 H, CH_3), 1.72–1.82 (m, 1 H, $CH(CH_3)_2$), 3.70 (s, 1/2 H, OH), 3.82–4.07 (m, 3 H, $CHOH$, CH_2OH), 4.21–4.27 (m, 3/2 H, OH), 4.70 (ddd, J = 3.9, 7.9, 8.9 Hz, 1 H, $CHNO_2$); ^{13}C NMR (acetone-d_6) δ 14.99, 19.43, 30.17, 60.98, 73.88, 93.40; MS, m/e 163 (M^+ <1), 120 (9), 73 (49), 57 (47), 43 (100). Anal. Calcd for $C_6H_{13}NO_4$: C, 44.17; H, 8.03; N, 8.58. Found: C, 44.06; H, 7.83; N, 8.49.

1-Cyclohexyl-2-nitro-1,3-propanediol (11b). From **2** and cyclohexanecarbaldehyde; purification by recrystallization from ether/hexane: IR (KBr) 3270, 1560 cm^{-1}; ^1H NMR (acetone-d_6) δ 1.13–1.47 (m, 6 H, C_6H_{11}), 1.61–1.79 (m, 5 H, C_6H_{11}), 3.70 (s, 2/3 H, OH), 3.80–3.86 (m, 1 H, $CHOH$), 3.93 (ddd, J = 3.8, 4.9, 12.0 Hz, 1 H, CH_2OH), 4.04 (ddd, J = 6.5, 8.9, 12.0 Hz, 1 H, CH_2OH), 4.18 (d, J = 6.9, 2/3 H, OH), 4.23 (dd, J = 4.9, 6.5 Hz, 2/3 H, OH), 4.76 (ddd, J = 3.8, 7.7, 8.9 Hz, 1 H, $CHNO_2$); ^{13}C NMR (acetone-d_6) δ 25.98, 26.33, 30.02, 40.33, 61.11, 73.67, 92.91; MS, m/e 203 (M^+, <1), 112 (6), 95 (30), 83 (98), 55 (100), 41 (49). Anal. Calcd for $C_9H_{17}NO_4$: C, 53.19; H, 8.43; N, 6.89. Found: C, 53.34; H, 8.55; N, 7.06.

(*E*)-2-Nitro-5-phenyl-4-pentene-1,3-diol (12b). From **2** and *trans*-cinnamaldehyde; purification by recrystallization from ethyl acetate/pentane: IR (KBr) 3360, 1555, 975 cm^{-1}; ^1H NMR (acetone-d_6) δ 3.75 (br s, 1 H, OH), 3.90–4.13 (m, 2 H, CH_2OH, OH), 4.27–4.34 (m, 1 H, CH_2OH), 4.68–4.84 (m, 2 H, $CHOH$, $CHNO_2$), 6.32 (dd, J = 6.7, 15.9 Hz, 1 H, C*H*=CH), 6.78 (d, J = 15.9 Hz, 1 H, CH=C*H*), 7.23–7.47 (m, 5 H, C_6H_5); ^{13}C NMR (acetone-d_6) 61.00, 71.31, 94.50, 126.82, 127.16, 128.19, 128.78, 133.31; MS, m/e 223 (M^+, <1), 132 (100), 104 (58), 77 (44), 51 (31). Anal. Calcd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.27. Found: C, 59.28; H, 5.74; N, 6.40.

2-Nitro-4-octadecyne-1,3-diol (13b). From **2** and 2-pentadecyn-1-al; purification by recrystallization from ether/pentane: IR (KBr) 3420, 3350, 2240, 1562 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86–0.90 (m, 3 H, CH_3), 1.22–1.37 (m, 20 H, 10 CH_2), 1.46–1.53 (m, 2 H, CH_2), 2.12 (t, J = 6.5 Hz, 1 H, OH), 2.22 (dt, J = 2.0, 7.1 Hz, 2 H, $CH_2C{\equiv}C$), 2.52 (d, J = 6.7 Hz, 1 H, OH), 4.17–4.22 (m, 2 H, CH_2OH), 4.67 (ddd, J = 4.2, 6.3, 7.5 Hz, 1 H, $CHOH$), 4.90–4.95 (m, 1 H, $CHNO_2$); ^{13}C NMR ($CDCl_3$) δ 13.76, 18.35, 22.65, 28.27, 28.51, 28.83, 29.19, 29.39, 29.59, 29.72, 30.21, 31.19, 31.97, 60.88, 61.22, 76.94, 88.18, 94.47; MS, m/e 327 (M^+, <1), 137 (18), 110 (37), 95 (46), 70 (97), 43 (100).

2-Nitro-1-phenyl-1,3-propanediol (14b). From **2** and benzaldehyde; purification by recrystallization from ether/hexane: IR (KBr) 3370, 3020, 1555 cm^{-1}; ^1H NMR (acetone-d_6) δ 3.46 (ddd, J = 3.2, 7.9, 12.0 Hz, 1 H, CH_2OH), 3.70 (s, 2/3 H, OH), 3.90 (ddd, J = 6.5, 9.2, 12.0 Hz, 1 H, CH_2OH), 4.19–4.23 (m, 2/3 H, OH), 4.84 (ddd, J = 3.2, 9.2, 9.2 Hz, 1 H, C*H*–NO_2), 5.08 (d, J = 9.2 Hz, 1 H, C*H*–Ph), 5.03–5.11 (m, 2/3 H, OH), 7.31–7.48 (m, 5 H, C_6H_5); ^{13}C NMR (acetone-d_6) δ 61.15, 72.70, 95.74, 127.12, 128.76, 128.82, 140.32; MS, m/e 197 (M^+, <1), 106 (99), 77 (100), 51 (40), 45 (32).

1-(4-Cyanophenyl)-2-nitro-1,3-propanediol (16b). From **2** and 4-cyanobenzladehyde; purification by recrystallization from ether/hexane: IR (KBr) 3360, 2245, 1560 cm^{-1}; ^1H NMR (acetone-d_6) δ 3.59 (ddd, J = 3.3, 7.4, 12.1 Hz, 1 H, CH_2OH), 3.72 (s, 2/3 H, OH), 3.94 (ddd, J = 5.8, 8.7, 12.1 Hz, 1 H, CH_2OH), 4.32 (br t, J = 5.2 Hz, 2/3 H, OH), 4.87 (ddd, J = 3.3, 8.7, 8.7 Hz, 1 H, $CHNO_2$), 5.28 (dd, J = 4.4, 8.7 Hz, 1 H, C*H*Ph), 5.38 (br d, J = 4.8 Hz, 2/3 H, OH), 7.72 (d, J = 8.2 Hz, 2 H, C_6H_4), 7.81 (d, J = 8.6 Hz, 2 H, C_6H_4); ^{13}C NMR (acetone-d_6) δ 60.38, 71.18, 94.68, 127.70, 129.35, 132.10, 132.75, 144.85; MS, m/e 222 (M^+, <1), 130 (100), 102 (57), 76 (23), 45 (34). Anal. Calcd for $C_{10}H_{10}N_2O_4$: C, 54.05; H, 4.54; N, 12.61. Found: C, 54.21; H, 4.47; N, 12.39.

1-Methyl-2-nitro-1-phenyl-1,3-propanediol (17b). From **2** and acetophenone In this case the two diastereoisomers A and B could be separated; both of them were recrystallized from ether/pentane. A: IR (KBr) 3530, 3400, 1565 cm^{-1}; ^1H NMR (acetone-d_6) δ 1.63 (s, 3 H, CH_3), 3.59 (ddd, J = 2.8, 6.9, 12.0 Hz, 1 H, CH_2OH), 3.72 (s, 2/3 H, OH), 4.10–4.14 (m, 2/3 H, OH), 4.24 (ddd, J = 6.4, 10.0, 12.0 Hz, 1 H, CH_2OH) 4.74 (s, 2/3 H, OH), 4.96 (dd, J = 2.8, 10.0 Hz, 1 H, $CHNO_2$), 7.27–7.42 (m, 3 H, C_6H_5), 7.55–7.59 (m, 2 H, C_6H_5); ^{13}C NMR (acetone-d_6) δ 27.33, 60.08, 73.63, 98.48, 125.18, 127.58, 128.47, 144.19; MS, m/e 211 (M^+, <1), 121 (69), 105 (100), 77 (72), 43 (56). Anal. Calcd for $C_{10}H_{13}NO_4$: C, 56.87; H, 6.20; N, 6.63. Found: C, 56.92; H, 6.22; N, 6.50. B: ^1H NMR (acetone-d_6) δ 1.69 (s, 3 H, CH_3), 3.71 (s, 2/3 H, OH), 3.90–3.95 (m, 1 H, CH_2OH), 4.15–4.23 (m, 5/3 H, OH, CH_2OH), 4.70 (s, 2/3 H, OH), 5.01 (dd, J = 3.2, 9.9 Hz, 1 H, $CHNO_2$), 7.25–7.38 (m, 3 H, C_6H_5), 7.53–7.57 (m, 2 H, C_6H_5); ^{13}C NMR (acetone-d_6) δ 25.25, 60.55, 73.93, 98.20, 125.63, 127.73, 128.28, 144.69. Anal. Calcd for $C_{10}H_{13}NO_4$: C, 56.87; H, 6.20; N, 6.63. Found: C, 56.74; H, 6.24; N, 6.74.

(4*S*)-4-Methyl-2-nitro-1,3-hexanediol (18b). From **2** and (*S*)-2-methylbutanal; purification by recrystallization from ether/hexane: IR (KBr) 3350, 1560 cm^{-1}; ^1H NMR (acetone-d_6) 0.92 (t, J = 7.3 Hz, 3 H, CH_2CH_3), 0.92 (d, J = 6.6 Hz, 3 H, $CHCH_3$), 1.25–1.41 (m, 1 H, $CHCH_3$), 1.45–1.58 (m, 2 H, CH_2CH_3), 3.71 (br s, 2/3 H, OH), 3.85–3.97 (m, 2 H, CH_2OH), 4.02–4.07 (m, 1 H, $CHOH$), 4.22–4.27 (br m, 4/3 H, OH), 4.72 (ddd, J = 4.3, 8.5, 8.5 Hz, 1 H, $CHNO_2$); ^{13}C NMR (acetone-d_6) 11.21, 11.99, 26.64, 36.80, 60.87, 71.81, 93.99; MS, m/e 177 (M^+, <1), 74 (17), 57 (100), 45 (23). Anal. Calcd for $C_7H_{15}NO_4$: C, 47.45; H, 8.53; N, 7.90. Found: C, 47.38; H, 8.57; N, 7.94.

5-Methyl-3-nitro-2,4-hexanediol (21b). From the dilithio derivative of THP-protected nitropropanol and 2-methylpropanal; purification by recrystallization from ether/hexane (*one* diastereoisomer only crystallized): mp 82.0 °C; IR (KBr) 3390, 3310, 1550 cm^{-1}; ^1H NMR ($CDCl_3$) 0.98 (d, J = 6.6 Hz, 3 H, $CH(CH_3)_2$), 1.08 (d, J = 6.6 Hz, 3 H, $CH–(CH_3)_2$), 1.33 (d, J = 6.2 Hz, 3 H, $CHCH_3$), 1.68–1.75 (m, 1 H, C*H*–$(CH_3)_2$), 2.83 (d, J = 9.3 Hz, 1 H, OH), 2.98 (d, J = 4.9 Hz, 1 H, OH), 3.71 (ddd, J = 2.9, 9.3, 9.3 Hz, 1 H, $CHCH(CH_3)_2$), 4.46–4.52 (m, 1 H, $CHCH_3$), 4.56 (dd, J = 2.9, 6.6 Hz, 1 H, $CHNO_2$); ^{13}C NMR (acetone-d_6) δ 16.09, 18.33, 19.32, 30.06, 65.17, 73.86, 94.79; MS, m/e 178 (M^+ + 1, <1), 90 (45), 73 (36), 43 (100). Anal. Calcd for $C_7H_{15}NO_4$: C, 47.45; H, 8.53; N, 7.90. Found: C, 47.54; H, 8.41; N, 7.77.

1-Cyclohexyl-2-nitro-1,3-butanediol (22b). From the dilithio derivative of THP-protected nitropropanol and cyclohexanecarbaldehyde; purification by recrystallization from ether/hexane (*one* diastereoisomer only crystallized): mp 99.0–100.0 °C; IR (KBr) 3560, 3420, 1560 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98–1.44 (m, 6 H, C_6H_{11}), 1.32 (d, J = 6.2 Hz, 3 H, CH_3), 1.63–1.81 (m, 5 H, C_6H_{11}), 2.69 (br d, J = 8.6 Hz, 1 H, OH), 2.83 (br s, 1 H, OH), 3.77 (br m, 1 H, C*H*–C_6H_{11}), 4.50–4.57 (m, 1 H, $CHCH_3$), 4.55 (dd, J = 2.9, 6.5 Hz, 1 H, $CHNO_2$); ^{13}C NMR ($CDCl_3$) δ 19.63, 26.02, 26.17, 29.58, 40.79, 69.06, 76.80, 91.80; MS, m/e 217 (M^+, <1), 112 (5), 95 (43), 83 (92), 71 (37), 55 (100), 43 (41). Anal. Calcd for $C_{10}H_{19}NO_4$: C, 55.28; H, 8.81; N, 6.45. Found: C, 55.14; H, 8.84; N, 6.56.

1-(2-Hydroxy-1-nitropropyl)-1-cyclohexanol (24b). From the dilithio derivative of THP-protected nitropropanol and cyclohexanone; purification by recrystallization from ether/hexane (*one* diastereoisomer only crystallized): mp 75.0–76.0 °C; IR (KBr) 3380, 3340, 1550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17–1.90 (m, 10 H, C_6H_{10}), 1.33 (d, J = 6.1 Hz, 3 H, CH_3), 2.75 (d, J = 4.3, 1 H, OH), 2.97 (d, J = 1.1 Hz, 1 H, OH), 4.40 (d, J = 8.3 Hz, 1 H, C*H*–NO_2), 4.50–4.59 (m, 1 H, $CHOH$); ^{13}C NMR (acetone-d_6) δ 20.55, 21.11, 21.44, 25.45, 33.36, 34.17, 65.97, 72.27, 100.00; MS, m/e 203 (M^+, <1), 99 (100), 81 (33), 69 (26), 55 (54). Anal. Calcd for $C_9H_{17}NO_4$: C, 53.19; H, 8.43; N, 6.89. Found: C, 53.06; H, 8.40; N, 6.76.

2-Amino-1-cyclohexyl-1,3-propanediol (29). Nickel/aluminum alloy (3.35 g) in water (35 mL) was treated with NaOH (5.35 g) in small portions. The mixture was heated to 70 °C for 30 min. After cooling to 20 °C, the aqueous phase was decanted and the Raney nickel was washed with distilled water until completely neutral and then with ethanol (5 times).[10] The freshly prepared Raney nickel, the nitro compound (4 mmol), and the ethanol (45 mL) were shaken in a steel autoclave under 30 atm of H_2 for 20 h at 50 °C. The mixture was filtered through Celite and the filtrate evaporated to give the crude amino compound **29** which was recrystallized from methanol/ether; yield 0.64 g (3.68 mmol, 92%): mp 118.0 °C; IR (KBr) 3360, 3310, 1585 cm^{-1}; ^1H NMR (methanol-d_4) δ 1.01–1.54 (m, 6 H, C_6H_{11}), 1.64–1.80 (m, 4 H, C_6H_{11}), 1.89–1.95 (m, 1 H, $CH(CH_2)_5$), 2.85 (ddd, J = 4.0, 5.3, 6.7 Hz, 1 H, CH–NH_2), 3.23 (dd, J = 4.0, 7.0 Hz, 1 H, $CHOH$), 3.47 (dd, J = 6.7, 10.7 Hz, 1 H, CH_2OH), 3.58 (dd, J = 5.3, 10.7 Hz, 1 H, CH_2OH); ^{13}C NMR (methanol-d_4) 27.17, 27.30, 27.60, 29.56, 30.84, 41.22, 54.31, 65.62, 76.67; MS, m/e 174 ($M^+ + 1$, <1), 142 (16), 90 (13), 60 (100), 43 (22). Anal. Calcd for $C_9H_{19}NO_2$: C, 62.39; H, 11.05; N, 8.08. Found: C, 62.11; H, 10.92; N, 7.83.

(3*S*,4*R*)-2-Nitro-1-phenyl-1,3,4,5-pentanetetraol (28). To a cooled (−90 °C), stirred solution of 25 mL of THF, 5 mL of HMPA, and 1.39 g (5 mmol) nitro compound **26** was added 7.6 mL (11 mmol) of *n*-butyllithium (1.45 M in hexane). The resulting yellow mixture was allowed to warm to −40 °C during 3 h, and at −90 °C, 0.51 mL (5 mmol) of benzaldehyde was slowly added. After the reaction mixture had warmed to −60 °C within 90 min, the mixture was cooled again to −90 °C and quenched with 1.5 mL (~25 mmol) of acetic acid. The clear cold reaction solution was combined with 60 mL of ether and washed successively with two 15-mL portions of cold saturated aqueous $NaHCO_3$. Each aqueous phase was extracted with one 60-mL portion of ether. The combined organic phases were washed 4 times with water and once with saturated aqueous NaCl, dried with anhydrous $MgSO_4$, filtered, and concentrated. Chromatography of the resulting residue on silica gel with ethyl acetate/hexane (1:4) afforded the pure nitro compound. The deprotection of the THP and acetonide groups was carried out with 10 mL of methanol and 0.15 g of Amberlyst at 45 °C in 2 h. Recrystallization from methanol/ether provided 0.94 g (3.66 mmol, 73%): mp 141.0 °C; IR (KBr) 3525, 3390, 1540 cm^{-1}; ^1H NMR (CD_3OD) δ 2.96 (ddd, J = 3.6, 5.2, 8.8 Hz, 1 H, $CH(OH)CH_2OH$), 3.45 (dd, J = 5.2, 11.4 Hz, 1 H, CH_2OH), 3.57 (dd, J = 3.6, 11.4 Hz, 1 H, CH_2OH), 3.97 (dd, J = 3.2, 8.8 Hz, 1 H, $CH(OH)CHNO_2$, 5.12 (dd, J = 3.2, 7.7 Hz, 1 H, $CHNO_2$), 5.48 (d, J = 7.7 Hz, 1 H, $CHPh$), 7.25–7.48 (m, 5 H, C_6H_5); ^{13}C NMR (methanol-d_4) δ 64.14, 64.64, 72.45, 72.71, 95.53, 128.41, 129.28, 130.10, 141.42; MS, m/e 256 ($M^+ - 1$, <1), 105 (69), 77 (100), 61 (19), 51 (94). Anal. Calcd for $C_{11}H_{15}NO_6$: C, 51.36; H, 5.88; N, 5.44. Found: C, 51.30; H, 6.04; N, 5.17.

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Registry No. (±)-(*R**,*S**)-**4a**, 96039-96-2; (±)-(*R**,*R**)-**4a**, 96040-41-4; (±)-**4b**, 96039-95-1; (±)-(*R**,*S**)-**5a**, 96039-98-4; (±)-(*R**,*R**)-**5a**, 96040-42-5; (±)-**5b**, 96039-97-3; (±)-(*R**,*S**)-**6a**, 96040-00-5; (±)-(*R**,*R**)-**6a**, 96040-43-6; (±)-**6b**, 96039-99-5; (±)-(*R**,*S**)-**7a**, 96040-02-7; (±)-(*R**,*R**)-**7a**, 96055-49-1; (±)-**7b**, 96040-01-6; (±)-(*R**,*S**)-**8a**, 96040-04-9; (±)-(*R**,*R**)-**8a**, 96040-44-7; (±)-**8b**, 96040-03-8; (±)-**9a**, 96040-06-1; (±)-**9b**, 96040-05-0; (±)-**10a**, 96040-08-3; (±)-**10b**, 96040-07-2; (±)-**11a**, 96040-10-7; (±)-**11b**, 96040-09-4; (±)-**12a**, 96040-12-9; (±)-**12b**, 96040-11-8; (±)-**13a**, 96040-14-1; (±)-**13b**, 96040-13-0; (±)-**14a**, 96040-15-2; (±)-**14b**, 5285-85-8; (±)-**15a**, 96040-17-4; (±)-**15b**, 96040-16-3; (±)-**16a**, 96040-19-6; (±)-**16b**, 96040-18-5; (±)-*l*-**17a**, 96040-21-0; (±)-*u*-**17a**, 96094-33-6; (±)-*l*-**17b**, 96040-20-9; (±)-*u*-**17b**, 96040-40-3; (2*R*,3*R*,4*S*)-**18a**, 96040-23-2; (2*R*,3*R*,4*S*)-**18b**, 96040-22-1; (±)-*l*-**19a**, 96040-25-4; (±)-*u*-**19a**, 96094-34-7; (±)-*l*-**19b**, 96040-24-3; (±)-*u*-**19b**, 96040-37-8; (±)-*l*-**20a**, 96094-35-8; (±)-*u*-**20a**, 96040-27-6; (±)-*l*-**20b**, 96040-38-9; (±)-*u*-**20b**, 96040-26-5; (±)-**21a** (isomer 1), 96040-28-7; (±)-**21a** (isomer 2), 96094-38-1; (±)-**21b** (isomer 1), 96094-32-5; (±)-**21b** (isomer 2), 96094-37-0; (±)-**22a** (isomer 1), 96040-30-1; (±)-**22a** (isomer 2), 96040-46-9; (±)-**22b** (isomer 1), 96040-29-8; (±)-**22b** (isomer 2), 96040-45-8; (±)-**23a** (isomer 1), 96040-32-3; (±)-**23a** (isomer 2), 96094-40-5; (±)-**23b** (isomer 1), 96040-31-2; (±)-**23b** (isomer 2), 96094-39-2; (±)-*l*-**24a**, 96094-36-9; (±)-*u*-**24a**, 96040-34-5; (±)-*l*-**24b**, 96040-39-0; (±)-*u*-**24b**, 96040-33-4; **26**, 96040-35-6; **28**, 96040-36-7; (±)-**29**, 60204-66-2; $THPO(CH_2)_2NO_2$, 75233-61-3; *n*-$C_6H_{13}I$, 638-45-9; $(EtO)_2CO$, 105-58-8; Me_2CHCHO, 78-84-2; *trans*-$C_6H_5CH{=}CHCHO$, 14371-10-9; $C_{13}H_{27}C{\equiv}CCHO$, 51534-40-8; C_6H_5CHO, 100-52-7; *p*-NCC_6H_4CHO, 105-07-7; C_6H_5C-OCH_3, 98-86-2; (*S*)-$CH_3CH_2CH(CH_3)CHO$, 1730-97-8; $C_6H_5CH_2Br$, 100-39-0; $(CH_3O)_2CO$, 616-38-6; $CH_3CH(OTHP)CH_2NO_2$, 69386-03-4; cyclohexanone, 108-94-1; cyclohexanecarboxaldehyde, 2043-61-0.