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A Simple, CIP-Based Notation System for the Unambiguous Specification of Asymmetric Reactions#

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Abstract: A set of stereochemical rules based on the CIP configurational descriptors have been proposed for the specification of the stereochemical outcome of asymmetric transformations. This simple and unambiguous system denotes the steric approach involving prochiral faces and stereogenic centers of reactants, either in enantio- or diastereoselective synthesis. The descriptors form chiral codes of symbols and numbers, which are susceptible of computerization. A brief discussion and comparison with other terms currently employed in dynamic stereochemistry are also given.

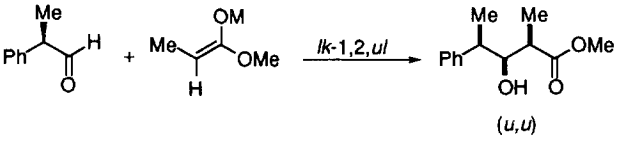
INTRODUCTION AND BACKGROUND

It is fair to say that the processes that have received the greatest attention of organic chemists are asymmetric reactions. The achievements in this field have certainly been impressive and there is no peace to beat Nature at her own game. Some chemical syntheses now proceed with almost complete steric control yielding enantioselectivities comparable to those provided by enzymes in living systems. If synthetic results are remarkable,[1] our efforts to denote the stereochemical outcome of asymmetric processes are still limited and not always satisfactory. An asymmetric reaction should be defined not only by the descriptors (*R*, *S*, *M*, *P*) at the stereogenic elements of products, but also by the stereoselective approach of reagents which will ultimately determine the steric course of the process.

The relative chirality of the new stereocenters (two centers in most cases) generated in a dynamic transformation may be defined by a combination of single words without specifying the configuration of each center, such as the pairs *erythro*/*threo*,[2] *syn*/*anti*,[3] *pref*/*parf*,[4] among others.[5] For cycloadditions, the descriptors *endo*/*exo* are also useful since the stereochemical course can be rationalized in terms of orbital symmetry rules.[6] All these terms have been misused as equivalents and there is quite ambiguity, particularly when extended to complex cases. The reason is that these classical terms were once established according to geometrical projections or by comparison with simple chiral models (*e.g.* sugars) and not based on unequivocal priority rules of ligands and substituents. One can of course associate these older nomenclatures with the unequivocal descriptors *Re* or *Si*, which emerge from the CIP sequence rules,[7,8] by assigning a hierarchical preference of the three substituents in each stereocenter of one diastereoisomer. For instance a pair *Re*/*Re* (or *Si*/*Si*) has been denoted as *threo*.[9] However, there is no always correspondence between the old *threo* with the

new *threo*. Moreover, these pairs cannot be applied to molecules bearing more than two stereocenters and, importantly, terms like *erythro/threo* or *syn/anti* are dependent on a conformational representation.[2,5]

Assuming that most asymmetric syntheses, which include a wide range of organic reactions,[1] usually involve a transformation of prochiral faces to chiral centers, Seebach and Prelog suggested a system[10] that takes into account the diastereofacial approach to the substrate, denoted by *lk* (*like*) or *ul* (*unlike*) as well as the resulting chirality of the stereocenters (or stereogenic elements) generated in products referred to as *l* (*like*) or *u* (*unlike*). For clarity, Scheme 1 outlines a typical aldol reaction consistent with the Cram rule for 1,2-inductions. The *lk*-1,2 selectivity indicates a) that the addition to the (*R*)-aldehyde occurs from the *Re*-face, and b) the relative topicity *ul* specifies that the new C-C bond results from a *Re*, *Si* combination of the trigonal centers. Finally, the relative configurations (*u*,*u*) indicate the *R*,*S* and *S*,*R* relationships among the descriptors.



Scheme 1

This system has also been employed for denoting the relative and absolute (if known) configurations of chiral molecules by referring each stereogenic center to the lowest numbered one which is arbitrarily assumed to be *l* (*like*) and not *R*.[11,12] There are some advantages associated with the *like/unlike* nomenclature: a) it agrees with the CIP sequence of substituents; b) it is quite unequivocal; c) it can be applied to multiple stereocenter-containing molecules. One additional feature of this nomenclature is the fact that the specification of relative topicities of reactants may reveal the different steric course of two similar reactions, even though the resulting diastereoisomers possess the same *like* or *unlike* configuration.

From an intuitive viewpoint, however, the correct application of *like* or *unlike* descriptors requires the previous assignment of the CIP descriptors, so that the above system has not been fully accepted by organic chemists.

For double stereodifferentiating reactions (double asymmetric induction), the steric preference may also be denoted by the terms *matched* and *mismatched*.[13] In the former case, the approach of a chiral reagent to a substrate with a preexisting chiral center maximizes the stereoselectivity (*e.g.* chiral consonance). The dissonance in the interaction of chiral centers is referred to as mismatching. These terms are useful for specifying the degree of stereocontrol, although they also add more confusion to the stereochemical puzzle.[14] If one considers a diastereoselective addition to the *Re*-face, the matching of chirality may occur with a stereocenter having either the *R* or *S* configurations, that is a reaction of the *like* or *unlike* type. Still, the relative configurations of products, in terms of *R*/*S* or *l*/*u* descriptors, should also be given.

It appears evident that nomenclature systems based on priority rules (*e.g.* CIP system) are unequivocal since they assign arbitrarily a hierarchical order to the different ligands of the simplest polyhedron (the simplex) in an n-dimensional space. Obviously, a stereochemical course based on precedence rules cannot be correlated with a particular mechanistic pathway as one might wish. Even if not completely unambiguous, *syn* or *anti* additions do define a stereochemical approach which is irrespective of the priority sequence of substituents. There is therefore a correspondence between topology and geometry. On the contrary, *like* or *unlike* denote, at least, two enantiomorphic or diastereomorphic relationships (*Re*,*Re* and *Si*,*Si*; *R*,*Re* and *S*,*Si*; *R*,*R* and *S*,*S*, etc.). On comparison of two reactions, *like* and *unlike* respectively, the steric approach to a trigonal center (*Re* for instance in both cases) will exclusively be dependent on the precedence of ligands,[15] thus hampering reaction correlations.

During the course of our own work on asymmetric transformations, we were faced with the task of

specifying the stereochemical outcome in an unequivocal fashion. Unfortunately, the use of standard terms discussed above constitute an indirect, often confusing, notation because all of them have to be ultimately associated with the CIP descriptors. It would be desirable an "at a glance" nomenclature in which chemists visualize the stereodescriptors as an integral part of the classification of stereochemical reactions.

With the advent and development of computer-assisted design, the logical approaches to more and more complex target molecules also requires the incorporation of the stereochemical information. Thus in the CIP system the pairs *R*, *S*; *M*, *P*; *seqcis*, *seqtrans* (*Z* and *E*, respectively) can be replaced by the numbers 0 and 1 in each case,[16] so that it is possible to obtain a binary code adaptable for computer use.[17] With a target molecule of known and well-defined stereochemistry, the computer should be able to write the myriad of possible steric approaches from different reactants and catalysts, and this accomplished solely in terms of descriptors of relative configuration and prochirality. The resulting notation is of course more extensive than we would have liked, but it is self-consistent, unambiguous and potentially readable by computers. In order to make it easier for the reader to cover the essential information, some general rules have been developed. The simplicity and logic of this proposal is demonstrated by means of a series of examples, including key steps of natural products syntheses, taken from the literature.

PROPOSED NOTATION

We have chosen a designation incorporating the configurations of reactants, the topicity of the two-dimensionally stereogenic trigonal atoms, and the relative distance between the inducing center of chirality and the reacting atom. A chiral code for the stereochemical approach includes the CIP descriptors in brackets (Figure 1).

Rule 1: Descriptors of relative configuration and relative topicity of each reactant involved in the asymmetric process, and in the same order indicated in the synthetic scheme, are included in brackets. This can also be extrapolated to the configurational notation (if possible) of chiral catalysts (*vide infra*). The notation of descriptors follows that of the CIP system.[7,8]

Rule 2: For descriptors in brackets, the notation of chiral elements (*R*, *S*, *M*, *P*) should be first specified and then the prochiral ones (*Re* or *Si*).

Rule 3: For chiral reactants containing heterotopic (prochiral) ligands or faces, the relative distance between the reactive two-dimensional unit and the inducing chiral center (either carbon or heteroatom) is denoted by the stereodescriptor of the latter and the number of connective bonds of separation in parentheses, disregarding their multiplicity, that is single, double, or triple bonds:

a) For 1,2-induction: 1 (one connective bond)

b) For 1,3-induction: 2 (two connective bonds)

c) For 1,4-induction: 3 (three connective bonds),

and so on.

This notation enables the easy incorporation of this connective parameter in a binary classification (see examples). As a corollary of this rule, only the nearest stereogenic center should be defined, even though the stereoselection can be provided by multiple chiral centers.

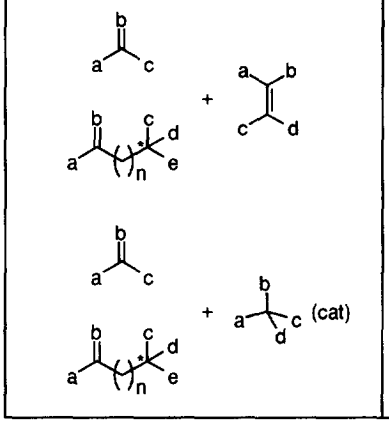
Rule 4: For cases in which two or more stereogenic centers are equidistant to one prochiral unit, both of them should be specified indicating their relative distances to the trigonal face. The ordering of chiral centers should be done according to their CIP sequence rules precedence (*e.g.*, *R* precedes *S*).

Rule 5: When two or more prochiral units are involved in the asymmetric transformation (*e.g.* hydrogenations, cycloadditions, etc.), all of them should be specified and their relative position referred to the nearest chiral center (if present) according to Rule 3. As a corollary: in the absence of chiral elements (*e.g.* achiral substrates), the prochiral face to be first specified is referred to the lowest numbered atom.

Rule 6: In catalytic asymmetric syntheses, the inherent chirality and topicity of the catalyst will be

denoted as we have already seen for reactants, though a subscript (c) after brackets, indicating the nature of a catalyst, appears to be convenient. Again, *R* precedes *S* and *M* precedes *P*.

Fig. 1. CIP-Based Configurational Notation of the Stereochemical Course



P_i : Descriptor(s) of prochiral units (*Re,Si*)

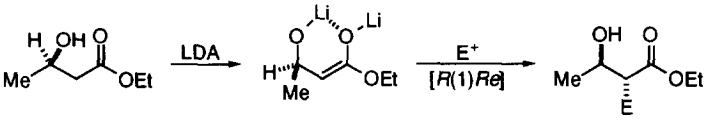
D^* : Descriptor(s) of relative configuration (*R,S,M,P*)

n+1 : Number of connective bonds between chiral and prochiral units

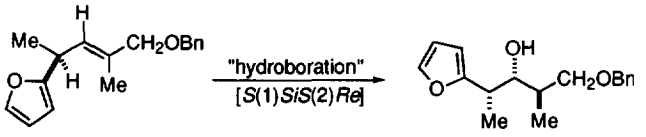
The following examples provide an illustration of the above rules in several cases of enantio- and diastereoselective syntheses in an unambiguous fashion. It is also worth mentioning that the broad concept of stereoselective reaction outlined through this article does not differentiate between substrate- or reagent-controlled reactions (often a elusive distinctive point between diastereoselective and enantioselective reactions).[1,18] The stereodescriptors are independent of the mechanism and derive simply from the structural relationships of substrate(s) and product(s).

In the reaction of Scheme 1 (*vide supra*) and according with the aforementioned rules, the relative topicity of reactants should be defined as [*R*(1)*Re*][*Si*]. This unequivocal notation discloses the 1,2-asymmetric induction provided by the contiguous (*R*)-chiral center to the aldehyde, while the *Re*-face of the latter reacts with the *Si*-face of the enolate. This is consistent with the relative configuration of the product as the (2*R*,3*S*,4*R*)-diastereoisomer.

Another well-known example of asymmetric induction involves the reaction of lithium enolates derived from chiral β-hydroxy esters with electrophiles.[19] The attack takes place preferentially on the *Re*-face (Scheme 2). Asymmetric hydroboration on a complex allyl ether (Scheme 3)[20] constitutes a good example of induction in which the presence of a chiral center influences the selectivity at two prochiral faces (Rules 3 and 5).

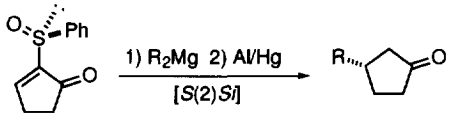


Scheme 2

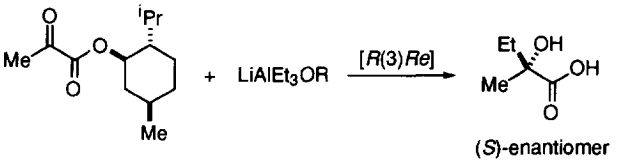


Scheme 3

The temporary incorporation of a chiral auxiliary which is ultimately cleaved by a conventional procedure, represents one of the most reliable strategies for achieving enantioselective synthesis. Likewise, it plays a crucial role by establishing a fixed stereochemical relationship between the stereocenter(s) and the reaction site. A typical example is the conjugate addition of nucleophiles to vinyl sulfoxides which occurs by attack to the less hindered *Si*-face (Scheme 4).[21] Remarkably, the steric course is opposite with a metal coordination to oxygen atoms favoring the attack from the upper *Re*-face, [*S*(2)*Re*]. Similarly, the presence of removable chiral auxiliaries derived from menthol and *N*-methylephedrine have been utilized in the asymmetric synthesis of 2-hydroxy-2-methylbutanoic acids by reaction with alkoxytrialkyl aluminates (Scheme 5).[22]

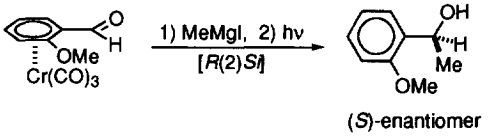


Scheme 4



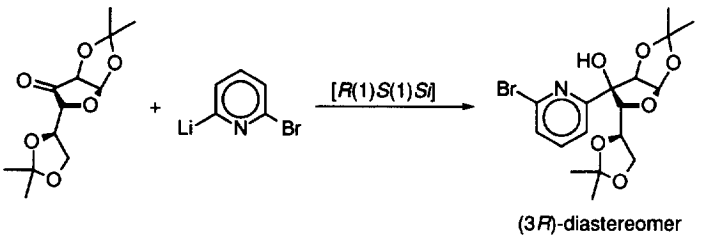
Scheme 5

Chiral organometallic complexes, especially those of iron and chromium which are easily separable in their enantiomers are excellent chiral auxiliaries.[23] Scheme 6 shows the steric course in the presence of a (*R*)-tricarbonyl(η^6-arene)chromium(0) complex,[24] whose inherent chirality arises from the enantiomeric coordination to one of the faces of the benzene ring. The attack of the Grignard reagent occurs from the opposite side of the $Cr(CO)_3$ ligand on the *Si*-face of the aldehyde.



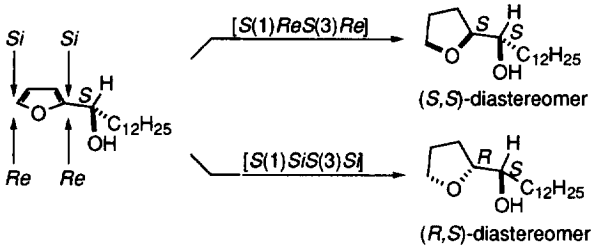
Scheme 6

Scheme 7 illustrates a direct application of Rule 4 in which a prochiral group is flanked by two equidistant stereogenic centers. Thus, the addition of 2-bromo-6-lithiopyridine to 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranos-3-ulose occurs with complete β-face selectivity to afford the (3*R*)-diastereoisomer only.[25] The stereochemical outcome arises from a *Si*-attack with the concomitant 1,2-induction of the stereocenters at C-2 and C-4 (Rule 3).



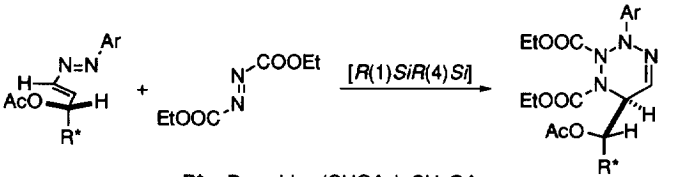
Scheme 7

The reactions depicted in Scheme 8 also serve for the application of Rule 5 in which two prochiral faces of a chiral furan are subjected to asymmetric hydrogenation owing to the influence of a preexisting (*S*)-chiral center.[26] The diastereoselective attack to the upper or lower faces was dependent on the solvent. Notably, authors do utilize the *like/unlike* nomenclature for denoting the steric approach, being one of the few papers on stereoselective synthesis with this useful custom.[27]

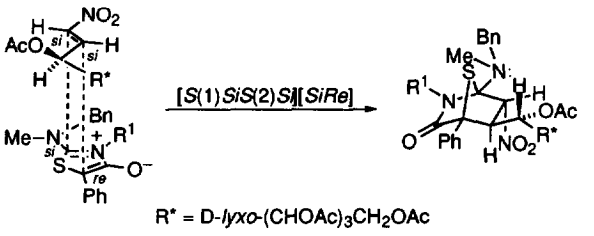


Scheme 8

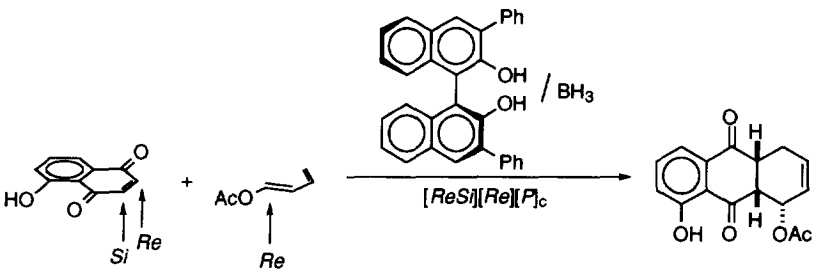
Schemes 9-11 provide examples of diastereoselective cycloadditions in which several prochiral faces are simultaneously involved. A notation of descriptors according with the above rules enables an easy computerization of the steric approach. The first case is a Diels-Alder reaction of chiral 1,2-diaza-1,3-butadienes with heterodienophiles. The process has been previously described as having arisen from an *unlike* attack on the heterodiene.[28] The dipolar cycloaddition of a chiral nitroalkene at their *Si-Si* faces with two faces of a heterocyclic ring is also depicted in Scheme 10.[29] In the latter case, there is also an application of the corollary of Rule 5 since the prochiral faces involved are *Si* and *Re* at C-2 and C-4 heterocyclic atoms, respectively. The third example (Scheme 11) constitutes a well-established cycloaddition of quinones in which the facial selectivity is provided by a chiral boron complex modified by a bis(aryl)binaphthol.[30] Even though the authors did utilize this substance in stoichiometric amounts, it is obviously serving as a chiral catalyst (Rule 6).



Scheme 9



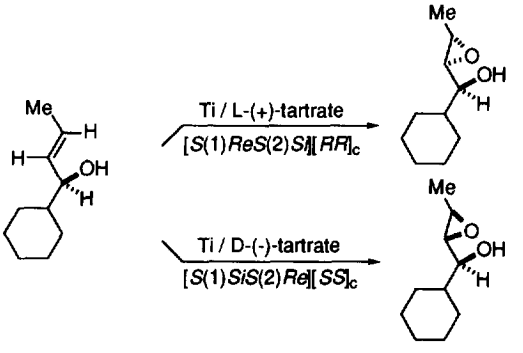
Scheme 10



Scheme 11

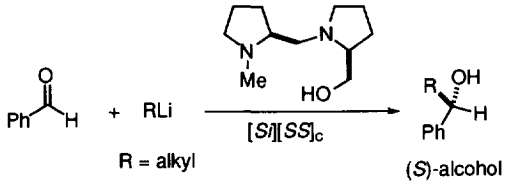
In relation with the latter, the challenge of specifying the steric control provided by a catalyst has not yet been pursued in detail by other nomenclature systems. This arises obviously from the fact that multiple chiral centers or elements are usually involved and the stereochemical outcome cannot be rationalized in terms of a "1,n-asymmetric induction", apart from the nonbonded interactions between reactant and catalyst. In a simplified approach, however, most chiral catalysts serve as chelating agents through two or more stereogenic centers of established and known configurations (*e.g.* the active site). The combination of these configurations with those of reactants provides a plausible idea of the way in which the stereocontrol is exerted.

One of the most relevant examples is the Katsuki-Sharpless asymmetric epoxidation of primary allylic alcohols.[31] Depending on the configuration of the titanium-tartrate complex, the epoxidation takes place high enantioface-differentiation leading to both enantiomers of the epoxy alcohols at will. Scheme 12 shows the propensity for the natural L-(+)-tartrate, the (2*R*,3*R*)-isomer, to give the product from the *Si,Si*-faces; whereas the unnatural D-(-)-tartrate, the (2*S*,3*S*)-isomer, gives the product from the *Re,Re*-faces. Note that the example provided also illustrates an interesting case of double stereodifferentiation.

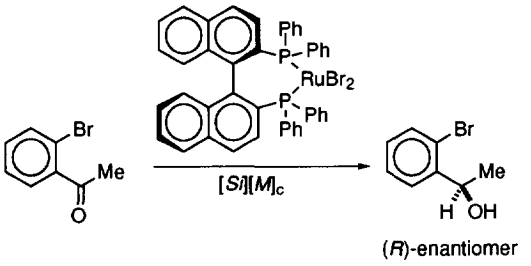


Scheme 12

Schemes 13 and 14 outline other cases of catalytic processes which can easily be specified. Mukaiyama's chiral pyrrolidine ligand, (2*S*,2'*S*)-(–)-hydroxymethyl-1-[(1-methylpyrrolidin-2-yl)-methyl]pyrrolidine, effects the enantioface-differentiating addition of organometallics to unsymmetrical, prochiral ketones leading to optically active secondary alcohols (Scheme 13).[32] Noyori's BINAP-Ru(II) complex catalysts lead to the stereoselective hydrogenation of a wide range of olefinic substrates as well as functionalized and unfunctionalized ketones (Scheme 14).[33]

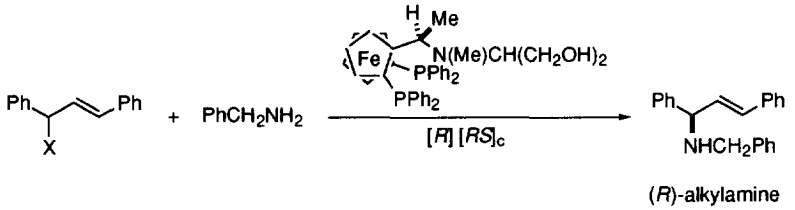


Scheme 13



Scheme 14

It is quite obvious that the above examples can be interpreted as catalytic kinetic resolutions, depending on the fact that the two enantiomers react at different rates with a chiral addend, in fact a good and economical method for the resolution of racemates.[34] Under this consideration, some catalytic processes not involving prochiral units could also be denoted according to Rule 6. Scheme 15 shows the asymmetric allylic amination catalyzed by a chiral ferrocenylphosphine complex.[35] The organometallic compound having a defined (*R*,1*S*)-configuration serves as "the resolving agent" by preferential attack with the (*R*)-isomer.



Scheme 15

The same notation may be applicable to resolution or derivatizing methods for the determination of configuration of chiral molecules such as the well-known Kato and Horeau's protocols.[36,37] Thus in the latter kinetic resolution, an (*R*)- or (*S*)-alcohol reacts preferentially with the (*R*)- or (*S*)-acylating agent, respectively. Thus, the notations [R][R] or [S][S] appear to be consistent with these processes, which follow clearly a *like*-approach.[10]

In summary, the present paper proposes a direct application of the CIP sequential system for the

specification of the steric approach of stereodifferentiating reactions. The main advantage of the above rules is that the stereodescriptors need not to be converted into those of the CIP system. The protocol is quite unambiguous and applicable to most stereochemical reactions whose selective paths can be identified by these simple codes of chiral descriptors and susceptible of computerization. Time will tell us the advantages and limitations provided by other examples. Last, but not least, *the aim of this work is to encourage organic chemist to utilize chiral descriptors*, including the *like/unlike* as well,[10] for the specification of asymmetric synthesis in addition to the synthetic and optical information provided. Efforts for computer implementation in organic synthesis programs are underway.

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To Vlado Prelog, with thanks and admiration over the years.

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