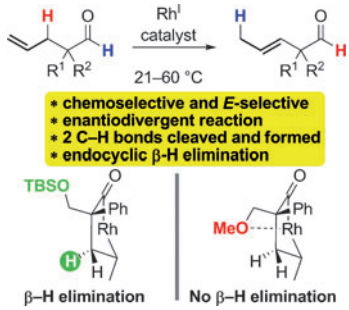
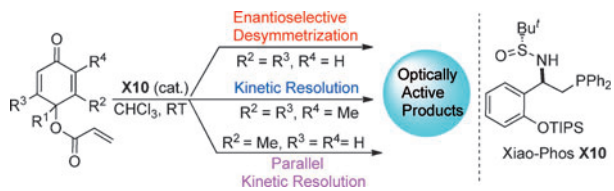
C–H Activation



Control of endocyclic β-H elimination of a pivotal five-membered metallacycle enables the rhodium-catalyzed isomerization of 4-pentenals into 3-pentenals without decarbonylation and leads to *trans* olefins with exquisite selectivity. Other sensitive olefins, even if prone to isomerization, remain intact. Endocyclic β-H elimination can also be prevented, in which case an enantiodivergent reaction on the racemic substrate was observed.

Organocatalysis



Xiao-Phos: A new class of chiral sulfinamide phosphine catalyst was developed. These Xiao-Phos catalysts can be prepared from inexpensive commercially available starting materials and show good performance in the enantioselective intramolecular Rauhut–Currier reaction under mild conditions. Moreover, kinetic resolution was also observed with the use of two different substituted racemic precursors.

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Flashback: 50 Years Ago . . .

Ivar Ugi is today best known for the multicomponent reaction that bears his name. In a Review, he summarized various routes for the synthesis of isonitriles (now known as isocyanides according to the IUPAC rules); the most efficient method for the preparation of large quantities of isonitriles was the reaction of phosgene with tertiary amines. In another Review, Hans Bock discussed the synthesis and spectroscopic characterization of azo compounds in order to establish the relationship between the color and constitution of the derivatives. It was found that varying the substituents caused shifts in the $n \rightarrow \pi^*$ transition. Interestingly, this was one of the first articles in *Angewandte Chemie* to contain color figures.

Hellmut Bredereck et al. published two Communications on the subject of acetals. The first report addressed the reactions of dimethylformamide acetals with isothiocyanates. Depending on the substituents, either 1,3-disubstituted 2,4-dithioxoparabanic O,N-acetals or α-substituted imino-α-(ethylthio)dimethylacetamides were formed. In the second Communication, the reactions of amide acetals with hydrocyanic acid were reported; O,N-acetals of α-ketonitriles were produced in good yields. Bredereck was President of the Gesellschaft Deutscher Chemiker (GDCh; German Chemical Society) in 1968/1969.

Christian Reichardt reported on the synthesis and spectroscopic properties of γ-phenylazopentamethinecyanine dyes. Introduction of the phenylazo group led to a hypsochromic shift of the long-wavelength bands. Reichardt is the author of *Solvent Effects in Organic Chemistry*, which was first published by Verlag Chemie in 1969, and the fourth edition of this truly classic text (published by Wiley-VCH and with Thomas Welton as co-author) appeared in 2011.

Read more in Issue 6/1965.