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[2,3]WITTIG REARRANGEMENT—PETERSON OLEFINATION SEQUENCE: A STEREOCONTROLLED APPROACH TO CONJUGATED DIENYNES

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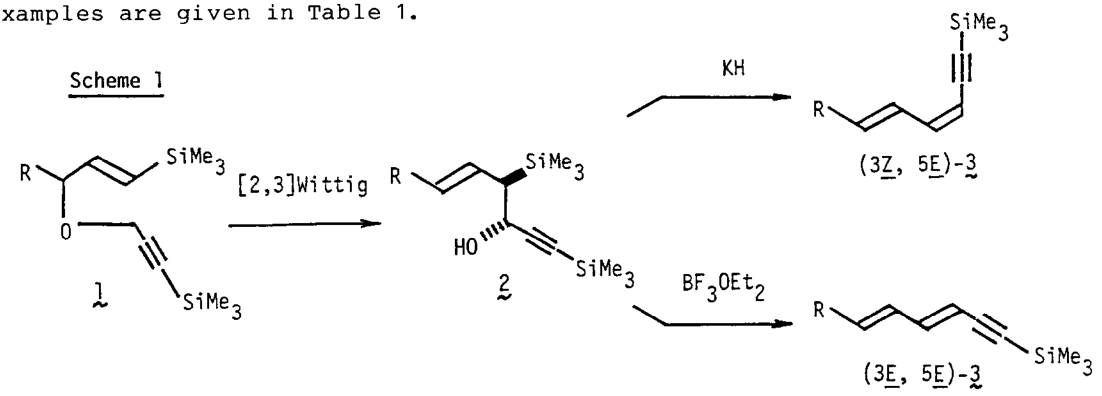
SUMMARY: A stereocontrolled entry to conjugated dienynes is described which relies upon the highly diastereoselective [2,3]Wittig variant followed by the Peterson olefination under an acidic or basic condition.

The stereocontrolled synthesis of conjugated dienynes (and trienes) is the subject of current synthetic efforts.[1] Herein we wish to report a new and stereocontrolled approach to conjugated dienynes which relies upon the highly diastereoselective [2,3]Wittig variant followed by the Peterson olefination reaction (Scheme 1). The key feature of this method is that the diene geometries are effectively controlled by sequentially combining the high (E)- and threo-selectivity in the [2,3]Wittig process with the well-established stereospecificity in the Peterson elimination process.[2] Representative examples are given in Table 1.

Scheme 1



The carbanion rearrangement of the bis-silylated ethers (1)[3] was carried out under the standard conditions (n-BuLi, THF, -85 °C).[4] The diastereomerically-defined β-silyl alcohols (2) thus obtained were subjected to either the syn- (KH, THF, 0 °C) or the anti-elimination conditions (BF_3OEt_2, CH_2Cl_2, -78 °C) to provide the (3Z, 5E)- or (3E, 5E)-dienynes (3), respectively.

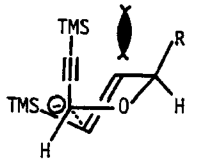
The diastereoselection observed in the present [2,3]Wittig variant deserves special comments. As seen in the table, the rearrangement of (E)-1a (R=H) shows a high erythro-selectivity,[5] while all the rest where R is an alkyl exhibit a high threo-selectivity, along with a high (E)-selectivity.[6]

Table 1. Preparation of Conjugated Dienynes via [2,3]Wittig-Peterson Sequence

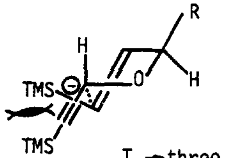
Substrate (**1**)	**1** → **2**			**2** → **3**		
	Yield, %	*E* : *Z*[a]	erythro : threo[a]	Additive	Yield, %	3*Z* : 3*E*[b]
1a, R=H (98%*E*)	91		97 : 3	BF_3OEt_2 KH[c]	85 54	>95 : 5 < 5 : 95
1b, $R=CH_3$ (95%*E*)	85	97 : 3	4 : 96	BF_3OEt_2 KH	85 96	< 5 : 95 >95 : 5
1c, $R=C_2H_5$ (100%*E*)	80	100 : 0	3 : 97	BF_3OEt_2 KH	88 97	6 : 94 92 : 8
1d, $R=n\text{-}C_4H_9$ (100%*E*)	61	100 : 0	11 : 89	KH	92	94 : 6

[a] Determined by ^{13}C NMR and HPLC analyses. [b] Determined by ^{1}H NMR and HPLC analyses: the $J_{3,4}$-values for the (3*Z*)- and (3*E*)-isomers are 10.2-10.8 Hz and 15.6-16.5 Hz, respectively. [c] The reaction was run after hydrogenation of **2a**.

The dramatic changeover in diastereoselection by the introduction of an α-alkyl group is explicable as follows. Of the two possible transition states T_1 and T_2, T_1 (R=H) should be sterically more favorable because T_2 (R=H) suffers a large gauche repulsion of TMS ↔ C≡C-TMS.[4] In the case where R=alkyl, however, T_1 should be greatly destabilized by an additional 1,3-repulsion of R ↔ C≡C-TMS which would prevail over the gauche repulsion in T_2.



$T_1 \rightarrow$ erythro



$T_2 \rightarrow$ threo

References

1) T. Mandai, T. Yanagi, K. Araki, Y. Morisaki, M. Kawada, and J. Otera, J. Am. Chem. Soc., 106, 3670 (1984), and references cited therein.

2) Review: D. J. Ager, Synthesis, 1984, 384.

3) Prepared via the etherification-silylation sequence (*cf*. ref 4) of the corresponding (*E*)-(γ-silyl)allylic alcohol which was easily obtainable by hydride reduction of the (γ-silyl)propargylic alcohol (*cf*. K. Mikami, T. Maeda, N. Kishi, and T. Nakai, Tetrahedron Lett., 25, 5151 (1984).

4) K. Mikami, K. Azuma, and T. Nakai, Tetrahedron, 40, 2303 (1984).

5) A similar but somewhat unusual (*E*→erythro)-selection has been reported for (*E*)-crotyl (γ-silyl)propargyl ether system, although the degree is much lower (*cf*. ref 4).

6) It is interesting to note that the high (*E*)-selectivity in the present variant is in stark contrast to the (*Z*)-selectivity reported for a similar variant involving (β-silyl)allylic moiety as the migrating group: A. D. Kaye and G. Pattenden, Tetrahedron Lett., 27, 2033 (1986); *cf*. K. Mikami, N. Kishi, and T. Nakai, Chem. Lett., 1982, 1643.

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