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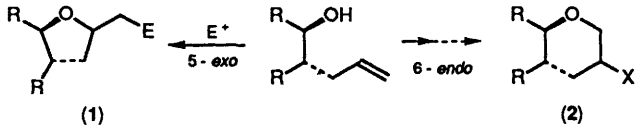
Iodonium-induced Cyclisations of 5-Silylalk-4-enols

Ernst Schaumann and Andreas Kirschning
Institut für Organische Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13, Federal Republic of Germany

In the presence of hypervalent iodine reagents, silyl-substituted δ,ε-unsaturated alcohols (**4a–f**) underwent ring-closure to give the pyran-3-ones (**5**) as well as tosyloxy substituted tetrahydropyrans (**6**) and (**7**).

Iodo- and phenylseleno-induced cyclisations of δ,ε-unsaturated alcohols are important tools for the generation of oxacycles in organic synthesis.[1] Formation of the tetrahydrofurans (**1**) *via* a 5-*exo*-*trig* pathway is usually favoured over the 6-*endo*-*trig* ring-closure leading to tetrahydropyrans (**2**) (Scheme 1).[2] Here



Scheme 1.

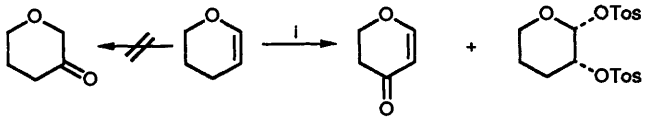
we report that switching of the regiochemistry of the intramolecular nucleophilic attack toward the 6-*endo* pathway can be achieved by hypervalent iodine reagents, which have found considerable interest in synthetic organic chemistry[3] and, in particular, are able to add to C=C bonds.[4] As substrates we used readily accessible[5] silyl-substituted olefins (**4**) and, using [hydroxy(tosyloxy)iodo]benzene (**3**), the Koser reagent,[6] observed efficient pyran formation. Thus, under our standard conditions, the reaction of vinylsilanes (**4a–f**) with (**3**) gave exclusively six-membered cyclisation products (**5a, b**), (**6b**), and (**7b**) (Scheme 2 and Table). The product ratios are independent of the substituent R^1 when $n = 4$ although the total yields drop with increasing size of R^1.

Quenching with a base such as imidazole is essential as otherwise polymerisation reactions prevented isolation of the desired products. Aqueous work-up should be avoided because the products are at least partially soluble in water. Further difficulties arose from separation of (**5**), (**6**), and (**7**) from iodobenzene which could be achieved by careful preparative column chromatography of the crude product.

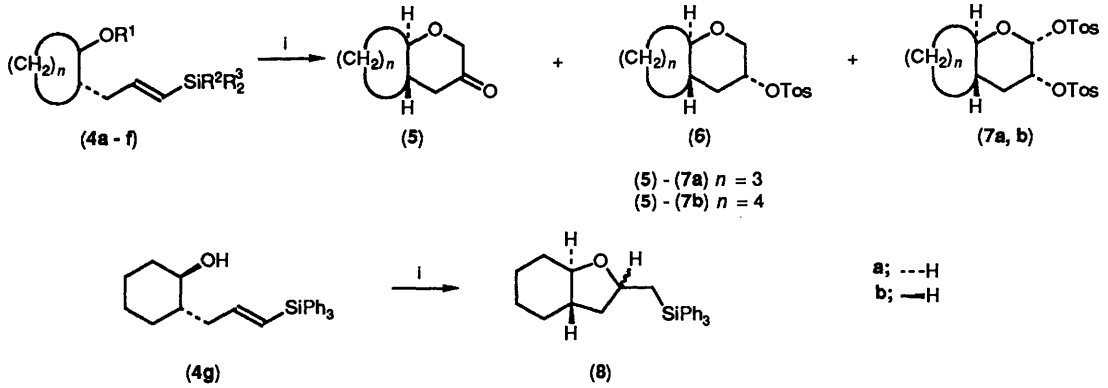
In alcohols (**4f, g**), phenyl substituents were used on silicon to assess the effect of electron-withdrawing substituents on the regiochemistry of the ring-closure. Here, the diphenylmethylsilyl group leads to the same products as the trimethylsilyl substituent in (**4a–e**), although now the preference for pyran-3-one (**5**) is more pronounced (see Table). In contrast, we observed exclusive formation of tetrahydrofurans (**8a, b**) from the triphenylsilyl-substituted alkenol (**4g**) (Scheme 2, Table). This outcome formally corresponds to a stereoselective proton-initiated cyclisation, in our case leading mainly to the 6,8-*cis*-isomer (**8a**).[7]

The stereochemistry of (**6b**), (**7b**) was deduced from the coupling pattern in the ^1H NMR spectra which could be fully analysed.[7] In particular, for (**6b**) an equatorial position for the tosyloxy group is suggested by large *trans* couplings of $J_{ax,ax}$ 10.6 Hz each between the C*H*OTos hydrogen and the neighbouring axial hydrogens 2-H and 4-H. Moreover, the *cis* arrangement of the tosyloxy groups in (**7b**) is obvious from $J_{ax,eq}$ 4.4 Hz of the C*H*OTos hydrogens.

An earlier report that (**3**) reacts with various olefins to give 1,2-bis(tosyloxy)alkanes[4] such as (**7**) suggested that a 3,4-dihydropyran derivative might be the key intermediate in the ring-closure giving (**5**)–(**7**). This prompted us to investigate the reaction of the 3,4-dihydropyran (**9**) with one equivalent of (**3**) under our standard conditions (Scheme 3). Instead of the expected pyran-3-one (**10**), we isolated 26% of 2,3-dihydropyran-



Scheme 3. *Reagents and conditions:* i, CH_2Cl_2, 0 °C, 1 equiv. PhI(OTos)OH (**3**), 4 h; then 2.2 equiv. imidazole.

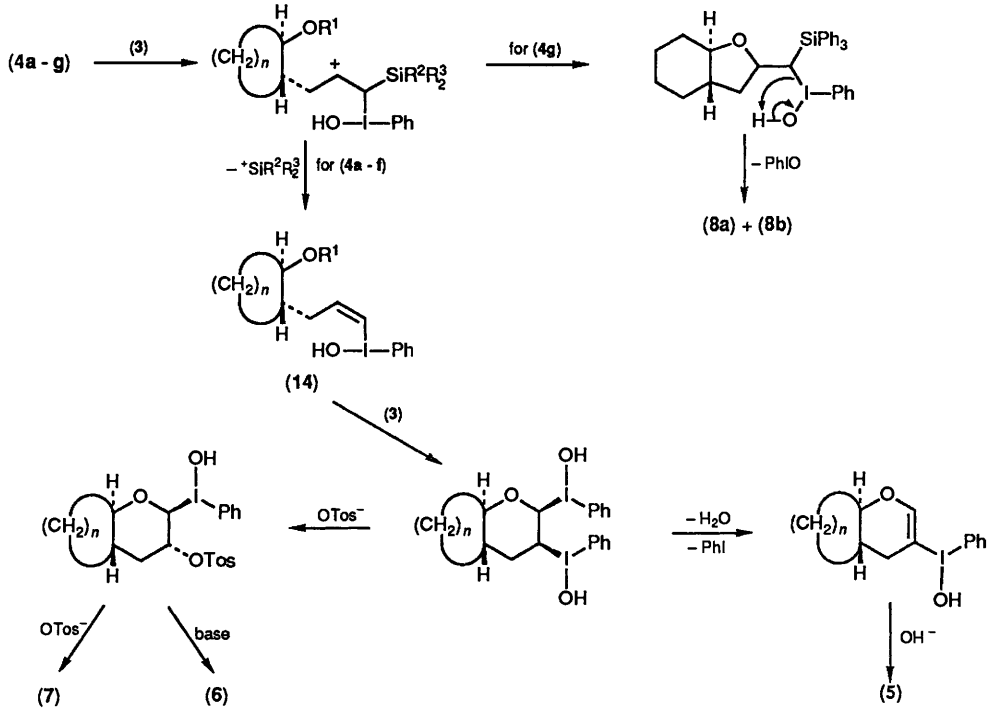


Scheme 2. *Reagents and conditions:* i, CH_2Cl_2, 0 °C, 2 equiv. PhI(OTos)OH (**3**), 2–4 h; then 2.2 equiv. imidazole. R^1, R^2, and R^3 refer to Table.

Table. Reactions of the Koser reagent (3) with (4).

Entry	Substrate	n	R^1	R^2	R^3	Product ratio (5)	(6)[a]	(7)[b]	Total yield[c] (%)
1	(4a)	3	H	Me	Me	>10	1	1[d]	15[e]
2	(4b)	4	H	Me	Me	3	1	0.5	87
3	(4c)	4	Me	Me	Me	3	1	0.5	68
4	(4d)	4	Bn	Me	Me	3	1	0.5	56
5	(4e)	4	$SiMe_2Thex$	Me	Me	3	1	0.6	51
6	(4f)	4	H	Me	Ph	>5	<0.4	0.4	51
7	(4g)	4	H	Ph	Ph	—	—	—	62[f]

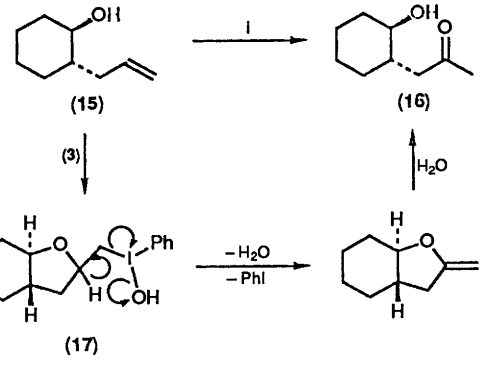
[a,b] Stereochemistry was deduced from ^1H coupling constants of all ring protons. [c] Isolated yields of pure products. [d] Compounds (6a) and (7a) were formed in trace amounts only, if any. [e] 48% of protodesilylated alcohol were isolated as main product. [f] Yield of(8a, b)(ratio 10:1).



Scheme 4. Suggested mechanism for the formation of compounds (5)–(8).

4-one (11) and 7% of the ditosylated tetrahydropyran (12). This rules out a dihydropyran as key intermediate in the formation of (5) and (6) and the well-known addition elimination mechanism (S_NV)[8,9] as the first step of ring-closure. Based on this experiment as well as on the stereochemistry of (6) and (7), we suggest that the *Z*-vinyliodonium species (13)[8] is the key intermediate in the formation of (5), (6), (7), and (8) (Scheme 4); the stereochemistry of (13) would be in line with the preferred inversion on addition of electrophiles with a soft counterion to vinylsilanes.[10]

In contrast to the silyl-substituted substrates, the silyl-free olefin (14) is inefficient in this type of cyclisation since only 22% (5b) and 11% (6b) are formed along with 43% of the ketone (15) (Scheme 5). In particular, formation of (15) shows that the ring-closure is not regiospecific. Species (15) results from intermediate (16) by a sequence of elimination and hydrolysis.



Scheme 5. *Reagents and conditions:* i, CH_2Cl_2, 0 °C, 2 equiv. PhI(OTos)OH (3), 4 h; then 2.2 equiv. imidazole.

Acknowledgements

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