Study of Bamford-Stevens Reaction on *α*-Oxy Tosylhydrazones

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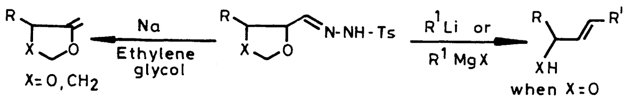
Exposure of tosyhydrazones of α–oxy carbonyl compounds obtainable from carbohydrates and tartaric acid furnishes exocylic vinylic ethers.

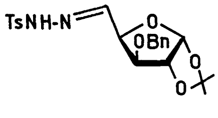
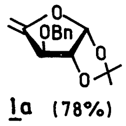
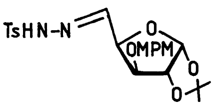
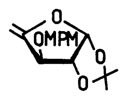
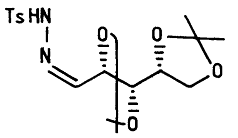
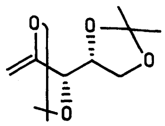
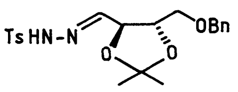
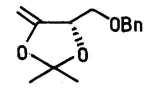
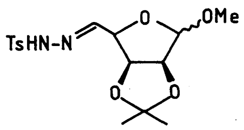
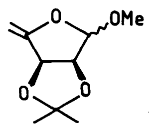
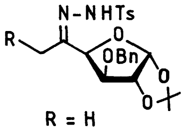
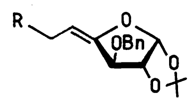
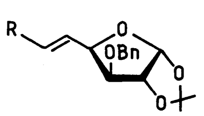
Olefin Synthesis by the Bamford -Stevens reaction (BSR)[1] is one of the very old methods and is totally eclipsed by the modifications made by Shapiro.[2] The limitations of the BSR may mainly be attributed to the poor regiochemistry of olefin formation and the relatively drastic reaction conditions. This poor regioselectivity is explained by the formation of a carbocation,[3] which is facilitated in a protic solvent such as ethylene glycol. As part of our continuing efforts on expanding the scope of carbonyltosylhydrazones, especially those derived from tartaric acid and carbohydrate sources,[4] we have observed a novel alkylation-fragmentation process mediated by alkyllithium and alkylmagnesium reagents. The hitherto unexploited Bamford-Stevens conditions on this class of compounds having α-oxyfunctionality prompted us to explore the possibility of formation of exocyclic vinylic ethers of the general type shown in Scheme 1, we now present our latest findings. The formation of this class of compounds may be due to the non-nucleophilicity of the base used (Na in ethylene glycol).

Scheme 1.



Accordingly, the hydrazone derivatives (Table 1, entry **1** and **2**) of the dialdofuranose obtained form D-glucose[5] when treated with preformed sodium alkoxide in ethylene glycol at 100^0 furnished the exocylic vinylic ethers (EVE) **1a** and **2a** in 78% and 72% yields respectively. This generalization is conveniently extrapolated to substrates derived from D-xylose[6] (entry **3**), L(+) tartaric acid[7] (entry **4**) and D-mannose[8] (entry **5**) which yielded the corresponding EVE **3a**, **4a** and **5a** in good yields (Table 1). For the structural authenticity, compound **4a** was also prepared from (4S, 5S) - 4 [(benzyloxy) methyl] - 5 iodomethyl 2,2-dimethyl - 1,3-dioxolane[9] with 2 equivalents of DBU in refluxing THF for 6 hrs. This product was identical with **4a** obtained under present reaction conditions including optical rotation { $[\alpha]_D = -32.9(c\ 1.0,\ CHCl_3)$}. Interestingly, the hydrazone of 5-ulofuranose[10] (entry **6**) underwent similar transformation smoothly and furnished olefin **6a** in 58% yield. It is interesting to note that not even a trace of the other regioisomer **6b** is formed under the reaction conditions. A plausible mechanism (Scheme 2) as proposed orginally[11] holds good for this reaction as well.

Table 1.

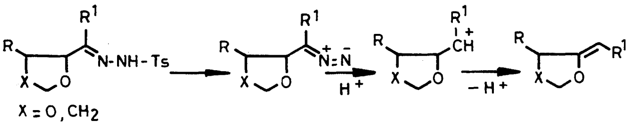
Entry	Tosyl hydrazone[a]	Product (yield)	$[\alpha]_D$ in $CHCl_3$
1		 1a (78%)	- 24 . 1 (C 1.5)
2		 2a (72%)	- 13 ·0 (C 1.2)
3		 3a (72%)	+ 9. 4 (C 1.1)
4		 4a (66%)	-32. 6 (C 1)
5		 5a (82%)	- 62. 5 (C 1)
6	 R = H	 6a (58%)	- 30. 5 (C 1.1)
		 6b (0 %)	—

a - Prepared by equimolar mixture of corresponding carbonyl compound and p-toluene sulfonylhydrazine in dry ether for 2 h.

In conclusion, an efficient and expeditious protocol has been developed for the preparation of EVE, which besides forming part structure of natural products such as obtsusilactone,[12] would also become crucial precursors in the preparation of substituted furans, β-oxa - γ - δ enones, α - hydroxy ketones[13] and prostaglandins[14] of high biological profile.

Representative experimental procedure is as follows (Table 1,

Scheme 2.



entry 5) : To anhydrous ethylene glycol (5 ml) was added freshly cut sodium metal (2 eq by weight) and the mixture was allowed to stir at room temperature until all of the sodium has reacted (approx. 1h). To this homogeneous solution is added the corresponding hydrazone (1 mmole) in ethylene glycol (1 ml) and heated at 100^0 for 2h. Reaction mixture was then poured into water (15ml) and extracted with ether (2 x 25 ml). The combined ethereal layer was washed with water and brine. After drying over Na_2SO_4, the solvent was evaporated *in vacuo* and residue filtered over SiO_2 to afford relatively low polar EVE **5a** in 82% yield.[15,16]

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References and Notes

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12 R. M. Adlington, and A. G. M. Barrett, *JCS Chem. Comm.*, **1979**, 1122.

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14 S. A. Mashhood, K. Ramesh, and R. T. Borchardt, *Tetrahedron Lett.*, **31**, 509 (1990).

15 a) Spectral data of **5a**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.10 (s, 1H), 4.95 (d, 1H, J=4.8 Hz), 4.50 (s,1H), 4.41 (d 1H, J=4.7 Hz), 4.30 (s, 1H), 3.35 (s, 3H), 1.41 (s, 3H), 1.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 144.8, 132.4, 128.3 127.7, 96.3, 72.3, 71.4, 70.2, 57.8. **6a** ^{1}H NMR : δ 7.20 - 7.41 (m, 5H), 6.05 (d, 1H, J = 4 Hz), 4.65 (d, 1H, J = 14 Hz), 4.55 - 4. 70 (m, 1H), 4.50 (d, 1H, J = 4 Hz), 4.45 (d, 1H, J = 14 Hz), 4.15 (s, 1H), 1.75 (d, 3H, J = 6 Hz), 1.45 (s, 3H), 1.39 (s, 3H). b) For the comparative spectral data of vinylic ethers, see Ref. 13.

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