

Study of Bamford-Stevens Reaction on α -Oxy Tosylhydrazones

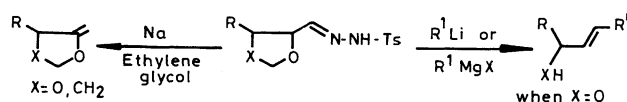
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Exposure of tosylhydrazones of α -oxy carbonyl compounds obtainable from carbohydrates and tartaric acid furnishes exocyclic vinylic ethers.

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 alkyl lithium and alkylmagnesium reagents. The hitherto unexploited Bamford-Stevens conditions on this class of compounds having α -oxy functionality 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 from D-glucose⁵ when treated with preformed sodium alkoxide in ethylene glycol at 100⁰ furnished the exocyclic vinylic ethers (EVE) **1a** and **2a** in 78% and 72% yields respectively. This generalization is conveniently extrapolated to substrates derived from D-xylose⁶ (entry 3), L(+) tartaric acid⁷ (entry 4) and D-mannose⁸ (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-dioxolane⁹ 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, CHCl₃) }. Interestingly, the hydrazone of 5-ulofuranose¹⁰ (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 originally¹¹ holds good for this reaction as well.

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

Table 1.

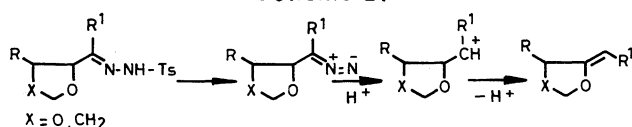
Entry	Tosyl hydrazone ^a	Product (yield)	$[\alpha]_D$ in CHCl ₃
1		 1a (78%)	- 24.1 (c 1.5)
2		 2a (72%)	- 13.0 (c 1.2)
3		 3a (72%)	+ 9.4 (c 1.1)
4		 4a (66%)	- 32.6 (c 1.1)
5		 5a (82%)	- 62.5 (c 1)
6		 6a (58%)	- 30.5 (c 1.1)
		 6b (0%)	—

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

become crucial precursors in the preparation of substituted furans, β -oxa - γ - δ enones, α - hydroxy ketones¹³ and prostaglandins¹⁴ 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 100⁰ 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 Na₂SO₄, the solvent was evaporated *in vacuo* and residue filtered over SiO₂ to afford relatively low polar EVE **5a** in 82% yield.^{15, 16}

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References and Notes

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- 15 a) Spectral data of **5a**: ¹H NMR (CDCl₃, 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). ¹³C NMR (CDCl₃, 50 MHz) δ 144.8, 132.4, 128.3 127.7, 96.3, 72.3, 71.4, 70.2, 57.8. **6a** ¹H 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.
- 16 IICT Communication No. 3507.