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SULFONYL CARBANIONS IN SYNTHESIS. III. A NEW METHOD FOR THE SYNTHESIS OF δ-LACTOLS.

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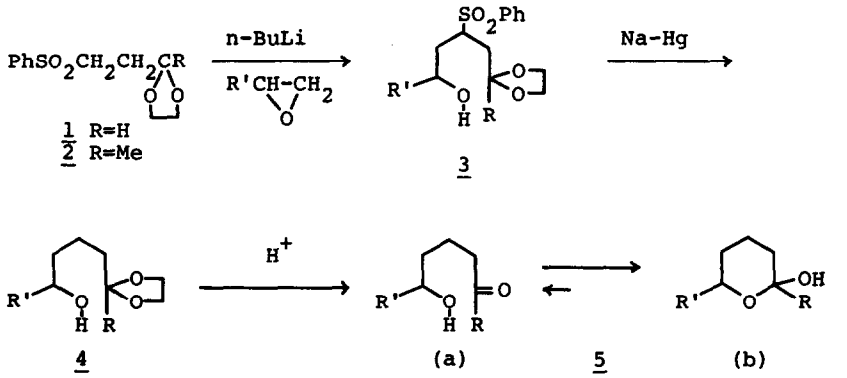
We have outlined in the preceeding communications the behavior of a sulfonyl carbanion bearing acetal or ketal function on the β-position. The carbanion acted as a masked β-acylvinyl anion when it was alkylated and as a masked β-acylethyl anion when acylated. Thus the synthetic application of the anion allowed us to construct α,β-unsaturated carbonyl compounds[1] as well as 1,4-dicarbonyl compounds.[2] In view of these results, we were encouraged to investigate the reaction of the anion with epoxides and wish to report herein a convenient method for the synthesis of δ-lactols.[3]

The sulfone acetal 1 and ketal 2 were prepared from acrolein and methyl vinyl ketone, respectively.[1] Treatment of the sulfone acetal 1 in anhydrous THF with 1 equivalent of n-butyllithium at -75° for 30 min and 0° for 1 hr gave a solution of the anion of 1, which was stable at 0°. The anion underwent smooth addition reaction with a variety of terminal epoxides. The reaction was generally carried out by adding a solution of 1.2 equivalents of the freshly distilled terminal epoxide in THF to a solution of the anion at -75° followed by stirring at the same temperature for 1 hr and then gradually warming up to room temperature. Purification of the crude products by column chromatography on silica gel afforded the addition products 3 (R=H) in moderate yields.[4] Nmr spectra revealed that the anion attacked from the less hindered side of the epoxide to produce the adduct having formula 3 as the sole product.[5]

Subsequent reductive elimination of benzenesulfonyl group was performed



by treating 3 (R=H) with 6% sodium amalgam in anhydrous ethanol for 3 hr at room temperature.[6] Hydrolysis of the resulting crude δ-hydroxy aldehyde ethylene acetals 4 in acetone:water (3:1) containing a catalytic amount of concentrated hydrochloric acid afforded the δ-hydroxy aldehydes 5 (R=H). The ir spectra of the products 5 (R=H), however, showed no carbonyl absorption. This means that the equilibrium between δ-hydroxy aldehyde (a) and δ-lactol (b) lies so far to the latter side. The nmr spectra ($CDCl_3$) of the products furthermore indicated that δ-lactols obtained were, in general, a mixture of two possible cis and trans isomers (ca. 2:1).[7]

Table I Yields of Addition Products 3 and δ-Lactols 5

Sulfone	Epoxide	3(%)[a]	5(%)[b]
1	EtCH-CH$_2$	77	77
1	Me(CH$_2$)$_5$CH-CH$_2$	72	79
1	PhCH-CH$_2$	61	79[c]
2	EtCH-CH$_2$	79	74

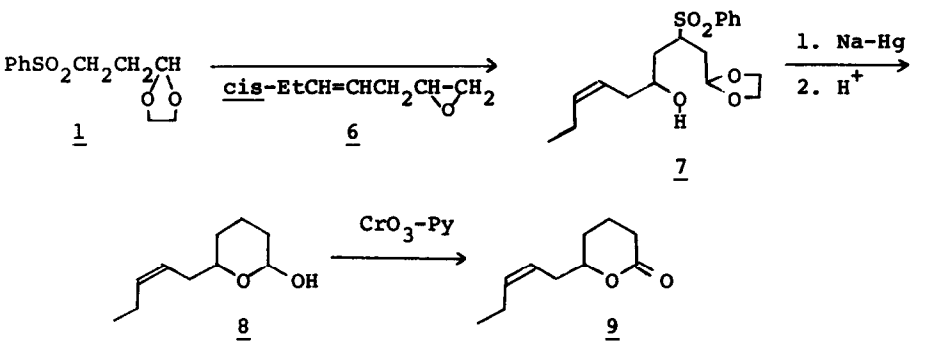
[a] Yields are based on sulfone acetal 1 or sulfone ketal 2 used.

[b] Yields are based on δ-hydroxy sulfones 3.

[c] Mp 69-69.5° (lit.,[3b] 68°).

Similarly, starting from sulfone ketal 2 and 1,2-epoxy-butane, the adduct 3 (R=Me, R'=Et) was obtained in good yield. Desulfonylation and hydrolysis of 3 as before afforded 5 (R=Me, R'=Et) as the final product. The nmr spectrum ($CDCl_3$) revealed that the product was an equilibrium mixture of cyclic hemiketal and δ-hydroxy ketone (ca. 1:2). Table I summarizes the yields of the typical examples investigated.

The sequence of reactions seems to be of preparative significance since δ-lactols can be easily transformed into δ-lactones.[8] As an example, we have now applied the reaction sequence to the synthesis of jasmine lactone, cis-5-(2-pentenyl)-5,1-pentanolide, which is a fragrant component of jasmine oil (Jasminum grandiflorum L.).[9]



1 6 7 8 9

Using the same procedure as described above, sulfone acetal 1 was reacted with 1,2-epoxy-cis-4-heptene 6,[10] to give the adduct 7 in 72% yield. Reductive desulfonylation of the adduct 7 followed by hydrolysis afforded the δ-lactol 8 [93% yield based on 7, ν_{max} 3450, 1035, 985 cm^{-1}, nmr ($CDCl_3$) δ 0.95 (t, J=7Hz, 3H, Me), 1.12-2.83 (m, 10H, CH_2), 3.17-4.40 (m, 2H, >CHO + OH), 4.67 (m, 0.65H, CH_{ax}(OH)), 5.10-5.75 (m, 2.35H, CH_{eq}(OH) + CH=CH)]. The synthesis was accomplished finally by oxidizing 8 with Collin's reagent to give (±)-jasmine lactone 9 [82%, nmr (CCl_4) δ 1.00 (t, J=7Hz, 3H, Me), 1.3-3.1 (m, 10H, CH_2), 4.03-4.63 (m, 1H, CHO), 5.10-5.95 (m, 2H, CH=CH)]. The ir spectrum (ν_{max} 1735, 730 cm^{-1}) of the synthetic product showed no absorption between 950-1000 cm^{-1} indicating the absence of trans isomer and thus was completely identical to that reported for the natural product.[9b]

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3. For the synthesis of δ-lactols, see, for examples: (a) M. Rosenberger, D. Andrews, F. DiMaria, A. J. Duggan, and G. Saucy, Helv. Chim. Acta, 55, 249 (1972); (b) J. Colonge, M. Costantini, and M. Ducloux, Bull. Soc. Chim. France, 2005 (1966); (c) G. Saucy and R. Borer, Helv. Chim. Acta, 54, 2121 (1971); (d) G. Saucy, R. Borer, and A. Fürst, ibid., 54, 2034 (1971): (e) L. A. Vlad, B. G. Kovalev, and A. A. Shamshurin, Zh. Org. Khim., 7, 664 (1971).
4. The yields given for all reactions are for isolated products. All new compounds exhibited satisfactory spectral and physical properties.
5. The addition product 3 is expected to be a mixture of two diastereomers. It was, however, impossible for us to isolate the each isomer by column chromatography.
6. R. E. Dabby, J. Kenyson, and R. F. Mason, J. Chem. Soc., 4881 (1952).
7. For the discussion of the tautomerism between δ-hydroxy aldehyde and δ-lactol and the equilibrium between the cis and trans isomers of δ-lactol, see ref. 3d and references cited therein.
8. For examples, see ref. 3a and references cited therein.
9. (a) M. Winter, G. Malet, M. Pfeiffer, and E. Demole, Helv. Chim. Acta, 45, 1250 (1962); (b) E. Demole and M. Winter, ibid., 45, 1256 (1962); (c) A. Ijima, H. Mizuno, and K. Takahashi, Chem. Pharm. Bull., 20, 197 (1972).
10. This epoxide was prepared by the following sequence; 1-hepten-4-yne [M. Winter and F. Gautschi, Helv. Chim. Acta, 45, 2567 (1962)] ⟶ 1,2-epoxy-4-heptyne (oxidation with m-chloroperbenzoic acid, bp 64-66°/20 mmHg, 35%) ⟶ 1,2-epoxy-cis-4-heptene (reduction using Lindlar catalyst, bp 45-46°/20 mmHg, 86%).