RETENTION OF OPTICAL ACTIVITY IN THE [3,3]-SIGMATROPIC REARRANGEMENT OF A VINYL FURFURYL ETHER

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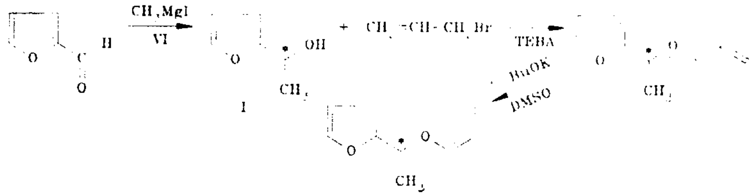
(−)-1-(2-Furyl)ethyl 2-propenyl ether undergoes a [3,3]-sigmatropic rearrangement with the formation of (+)-2-(2-ethyl-3-furyl)propanol, which indicates an at least partially concerted reaction mechanism.

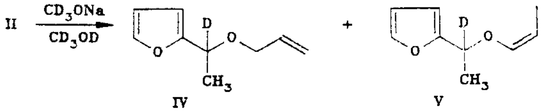
The retention of optical activity in [i, j]-sigmatropic rearrangements of allylic systems is one of the criteria for ascribing a concerted mechanism [1]. This may be illustrated by examples of [3,3]-sigmatropic rearrangements of allyl vinyl ethers [2] and pentenyl 2-thienyl sulfide [3].

The data on the effect of electron donor substituents in various positions of vinyl furfuryl ethers on the [3,3]-sigmatropic rearrangement indicates a concerted nature [4]. In order to confirm the mechanism of this reaction, we studied the [3,3]-sigmatropic rearrangement of optically active 1-(2-furyl)ethyl 2-propenyl ether (III), synthesized according to the following scheme:



Optically active 2-(1-hydroxyethyl)furan (I) was obtained initially by Duveen and Kenyon [5] by the cleavage of the acid phthalate of the racemic alcohol as a salt with natural quinone. An attempt to use (−)-α-phenylethylamine, as in the preparation of (−)-2-penten-4-ol [6], proved unsuccessful due to extensive polymerization in the preparation of the acid phthalate from alcohol (I) by the action of phthalic anhydride.

The asymmetric synthesis of alcohol (I) is possible since there have been reports of the preparation of optically active alcohols by the Grignard reaction with carbonyl compounds in optically active solvents or in the presence of an optically active additive [7]. Indeed, alcohol I is formed in the reaction of furfural with methylmagnesium iodide in ether in the presence of optically active 1,2,5,6-di-O-isopropylidene-α-D-glucofuranose (VI). Comparison of the $[\alpha]_D^{20}$ values of alcohol I (4.7°) and the sample obtained by the cleavage of the acid phthalate (−20.11°) [5] indicates a 23% optical yield. This is quite sufficient for obtaining optically active propenyl ether III assuming slight racemization in the alkylation and isomerization steps. Phase transfer catalysis conditions were employed in order to prevent racemization in the alkylation of alcohol I by allyl bromide (such racemization occurs upon carrying out this reaction by the Williamson procedure). The alkylation of alcohol I with subsequent isomerization of allyl furfuryl ether II by the action of potassium tert-butylate leads to the formation of optically active ether III. Partial racemization of ether II occurs in the isomerization step due to the rather high acidity of the methine hydrogen atom, as indicated by the data for the base-catalyzed H–D exchange in ether II at 65°C for 3 h.



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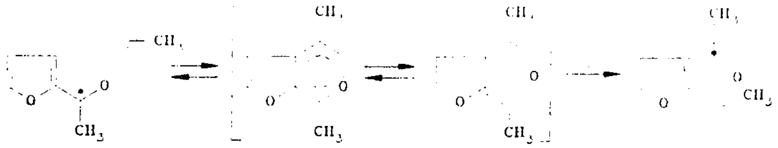
PMR spectroscopy indicated that the reaction products contain ethers IV and V. The extent of H–D exchange in the isomerization product, ether V, is 20%. Partial H–D exchange is also found in the furan ring.

Optically active aldehyde VII is formed in the rearrangement of ether III without solvent or in N,N-dimethylaniline:



III

VII

Hence, the [3,3]-sigmatropic rearrangement of ether III is at least achieved through a concerted mechanism involving a six-membered transition state with only slight charge separation.

EXPERIMENTAL

The PMR spectra were taken on a Varian T-60 spectrometer with HMDS as the internal standard. The IR spectra were taken on an IKS-22 spectrometer. The specific optical rotation was determined by a VNIÉKprodmash A-1 EPO polarimeter. The chromato-mass spectrometric analysis was carried out on a Finnigan MAT 112S instrument. The ionization voltage was 80 eV and the source temperature was 220°C.

1,2,5,6-Di-O-isopropylidene-α-D-glucofuranose (VI) was obtained according to Freudenberg and Smeykal [8] with additional recrystallization from 1:1 ether–pentane in 60% yield, mp 110-111°C, $[\alpha]_D^{20}$ −19° (c = 1, acetone) [7].

(+)-2-(1-Hydroxyethyl)furan (I) was synthesized according to Inch et al. [7] in 75% yield, bp 55-56°C (6 mm Hg), $[\alpha]_D^{20}$ 4.7° (c = 1, acetone). According to Duveen [5], $[\alpha]_D^{20}$ = −20.11°.

(+)-1-(2-Furyl)ethyl allyl ether (II) was obtained by a general method for the synthesis of ethers [9]. A sample of alcohol I was added to a mixture of DMSO, 50% KOH, and 3% TEBAC. Then, a slight excess of allyl bromide was added and the mixture was stirred for an additional 3 h at 60°C. After cooling, the mixture was extracted with ether, washed with water, and dried over $CaCl_2$. Ether was distilled off and the residue was distilled in vacuum to give a 63% yield, bp 52°C (6 mm Hg). PMR spectrum: 1.36 (3H, d, CH_3), 3.83 (2H, d.d, $-O-CH_2-$), 4.40 (1H, q, $>CH-O-$), 5.00-6.00 (3H, m, $-CH{=}CH_2$), 6.13 (2H, m, furan β-H), 7.20 ppm (1H, d, furan α-H). $[\alpha]_D^{20}$ 16.41° (c = 1, acetone).

(−)-1-(2-Furyl)ethyl 2-propenyl ether (III) was obtained by the isomerization of ether II in the presence of t-BuOK in DMSO [10] in 61% yield, bp 57-58°C (7 mm Hg). PMR spectrum: 1.53 (6H, d, $2CH_3$), 4.40 (1H, q, $>CH-$), 4.72 (1H, q, $-CH{=}CH-CH_3$), 6.06 (1H, d.d, $-CH_A{=}CH_B-CH_3$), 6.26 (2H, m, furan β-H), 7.36 ppm (1H, s, furan α-H), J_{AB} = 6 Hz. $[\alpha]_D^{20}$ −3.38° (c = 10, acetone).

The rearrangement of ether III was carried out at 150°C without solvent or in N,N-dimethylaniline over 3 h in an argon atmosphere in sealed ampules. The rearrangement product and starting ether II were separated plates with an unsupported layer of Silpearl adsorbent using 47:43:10 hexane–CCl_4–ether as the eluent.

(+)-2-(2-Ethyl-3-furyl)propanol (VII) was obtained in 40% yield, $[\alpha]_D^{20}$ 3.5° (c = 10, acetone). PMR spectrum: 1.10 (3H, t, CH_3), 1.30 (3H, d, CH_3), 2.63 (2H, q, $-CH_2-$), 3.46 (1H, q, $>CH-$), 6.23 (1H, d, furan β-H), 7.30 (1H, d, furan α-H), 9.43 ppm (1H, d, CHO). Mass spectrum, m/z (I, %): 55 (18), 95 (10), 108 (7), 123 (100), 152 (20). IR spectrum: 1735, 2720 cm^{-1}.

The H–D exchange was carried out in an argon atmosphere in sealed ampules for a solution of starting ether II in 0.3 N CD_3ONa in CD_3OD with toluene as the internal standard. The extent of the deuteration was determined by PMR spectroscopy.

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PHOTOCHEMICAL REACTIONS OF 7-AMINOCOUMARINS.

3.* REACTION OF 4-METHYL-7-DIETHYLAMINOCOUMARIN WITH OLEFINS AND ACETYLENES CONTAINING ELECTRON-WITHDRAWING SUBSTITUENTS

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The photochemical reactions of 4-methyl-7-diethylaminocoumarin with the dimethyl ester of acetylenedicarboxylic acid, diethyl ester of maleic acid, and N-phenylmaleimide in the presence of oxygen and acetophenone give products of the heterocyclization at $C_{(6)}$ and $C_{(8)}$ of coumarin fragment with participation of the diethylamino group. The stereochemical structure of the compounds synthesized was demonstrated using PMR spectroscopy. A mechanism was proposed for this reaction involving the formation of an α-amino radical and its addition to the acetylene or olefin, accompanied by attack on the aromatic ring with subsequent aromatization.

7-Aminocoumarins upon photoirradiation with olefins having not more than one electron-withdrawing substituent form [2 + 2]-cycloaddition adducts at the $C_{(3)}—C_{(4)}$ bond [1, 2]. In order to expand the scope of these reactions, we attempted to carry out the reaction of the dimethyl ester of acetylenedicarboxylic acid as well as olefins with two electron-withdrawing substituents, namely diethyl maleate and N-phenylmaleimide, with 4-methyl-7-diethylaminocoumarin (I). [2 + 2]-Cycloadducts are not formed under conditions described in our previous work [1, 2] in the absence of a sensitizer in an inert atmosphere. On the other hand, the irradiation of mixtures of reagents in acetonitrile upon saturation with air in the presence of a triplet sensitizer (acetophenone) gives heterocyclization products II-VI (see scheme on following page).

The yields of II-VI are 15-40% with the incomplete conversion of the starting coumarin (the conversion is 60-75%) (Table 1). The reaction should not be carried out with a greater conversion from a preparative viewpoint due to the formation of side-products. Saturation of the solution with pure oxygen or the addition of peroxides are also inefficient for the same reason.

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*See [1] for Communication 2.

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