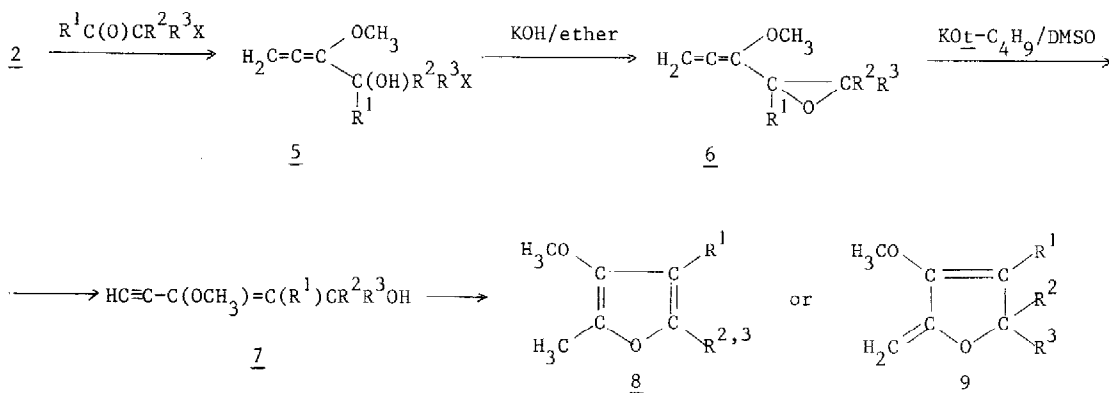




molecular ring closure leads (via intermediates) to the derivatives of furan or dihydrofuran.



X=Cl or Br

In support of the intermediate occurrence of compounds 7 is the detection of their Z-isomers (in mixtures with 8 or 9) when instead of  $KOT-C_4H_9$  potassium hydroxide is used. Under these milder conditions probably only E-7 can undergo the ring closure because the C-OH and  $C\equiv C$  are in a geometrically favourable position. When the mixtures of Z-7 and 8 or 9 were treated with  $KOT-C_4H_9$  in DMSO all Z-7 disappeared and a corresponding amount of 8 or 9 was produced in addition to the product which was already present. This remarkable cyclisation of Z-7 into E-7 (C-OH and  $C\equiv C$  in trans-position) under these conditions may be explained by assuming a preceding isomerisation of Z-7 into E-7 (or into another cyclisable isomer) via abstraction of a proton in  $R^1$  which is in the allylic position of the double bond. Such an isomerisation is not possible if  $R^1 = t-C_4H_9$ , thus upon treatment of 6, having  $R^1 = t-C_4H_9$ , with  $KOT-C_4H_9$  in DMSO both the corresponding Z-7 and 8 were isolated.

#### General procedure for the preparation of the allenic epoxides 6

To a solution of 0.25 mole of methoxyallene in 100 ml of dry THF cooled at  $-40^{\circ}$  was added dropwise 0.25 mole of butyllithium in 150 ml of ether. Ten minutes later 0.25 mole of the  $\alpha$ -haloketone was added at  $-30^{\circ}$  over a period of 30 minutes. After an additional period of 15 minutes the reaction mixture was poured into ice water. The ethereal extracts were dried over  $K_2CO_3$ . Finely powdered potassium hydroxide (0.50 mole) was then added in small portions to the stirred extract, keeping the temperature between  $0-5^{\circ}$ . After 30 minutes the mixture was poured into ice water. The usual work up afforded the epoxides 6. The yields varied between 50 and 75%

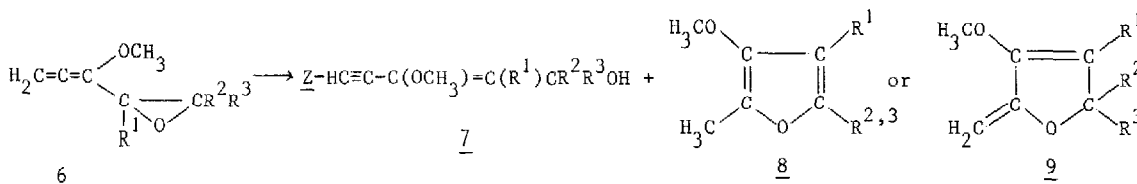
For further data see Table 1.

Conversion of 6 into the enyne alcohols 7, furan 8 or dihydrofuran 9

To a solution of 0.10 mole of potassium tert-butoxide in 120 ml of dimethyl sulfoxide was added in 15 minutes 0.10 mole of the allenic epoxide 6. The temperature of the mixture was kept between 20 and 30°. After an additional period of 30 minutes the reaction mixture was poured into 300 ml of ice water and the products were extracted with ether. The extracts were washed with water and dried over MgSO<sub>4</sub>. For further data see Table 1.

Table 1

Conversion of allenic epoxides 6 with KOt-C<sub>4</sub>H<sub>9</sub> in DMSO.

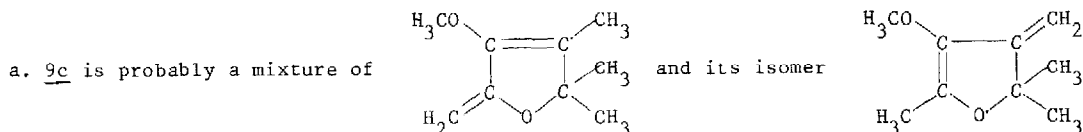


Starting compound

Reaction products

R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Nr	B.p. °C/mm Hg	n <sub>D</sub> <sup>20</sup>	Nr	B.p. °C/mm Hg	n <sub>D</sub> <sup>20</sup>	Yield%	Remarks
CH <sub>3</sub>	H	H	<u>6a</u>	57/17	1.4660	<u>8a</u>	42-3/17	1.4510	75	
CH <sub>3</sub>	CH <sub>3</sub>	H	<u>6b</u>	65-70/17	1.4680	<u>8b</u>	55-7/17	1.4580	76	
CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	<u>6c</u>	63-5/17	1.4600	<u>9c</u>	66-7/17	1.4762	87	a
C <sub>6</sub> H <sub>5</sub>	H	H	<u>6d</u>	88-9/0.001	1.5517	<u>8d</u>	83-5/0.001	1.5566	51	b
t-C <sub>4</sub> H <sub>9</sub>	H	H	<u>6e</u>	80-5/17	1.4640	<u>8e</u>	73-5/17	1.4557	56	
						<u>7d</u>	108-10/17	1.4895	35	

All compounds were shown to have a purity of at least 95% by PMR and GLC and elemental analyses were satisfactory.



b. The Z-enyne alcohol HC≡C-C(OCH<sub>3</sub>)=C(C<sub>6</sub>H<sub>5</sub>)CH<sub>2</sub>OH 7d could be detected in the crude reaction mixture by PMR. The low yield of 7d is probably caused by its polymerisation.

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