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THE SYNTHESIS OF α, β-UNSATURATED ALDEHYDES BY ONE-CARBON HOMOLOGATION OF CARBONYL COMPOUNDS

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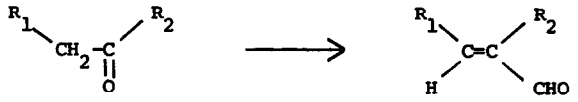
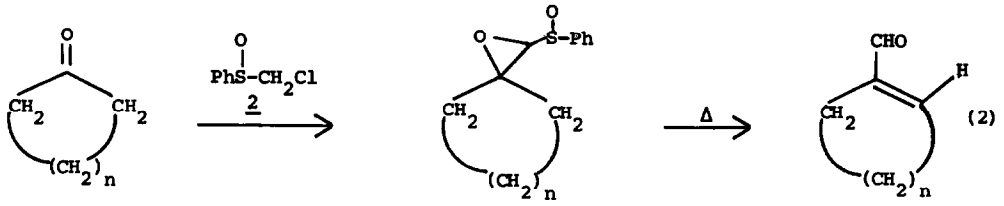
The synthesis of α, β-unsaturated aldehydes has been a focus of current interest[1]. However there are only few methods for the syntheses of α, β-unsaturated aldehydes by one-carbon homologation[2]. We wish to report a convenient synthesis of the 1-alkenecarboxaldehydes from the corresponding carbonyl compounds (equation 1).



(1)

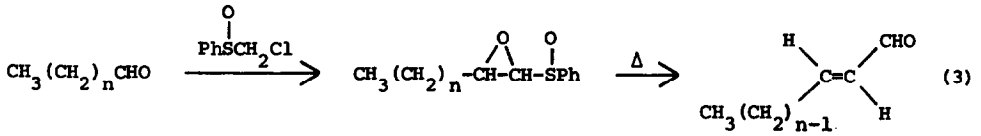
This process is based on the rearrangement, followed by the pyrolytic elimination of the derived sulfoxides, of the α-epoxysulfoxides as indicated in equations (2) and (3).



1 2 3 4

n = 1, 2, 3, 4, 5

(2)



5 6 7

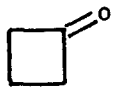
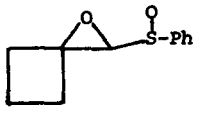
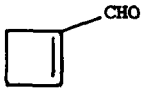
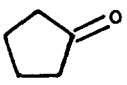
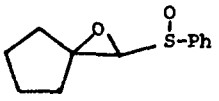
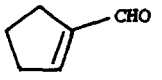
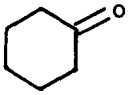
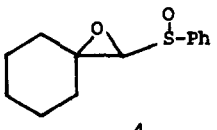
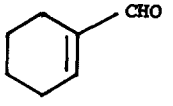
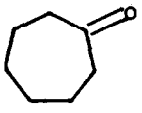
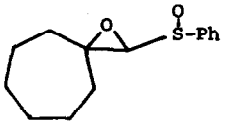
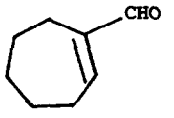
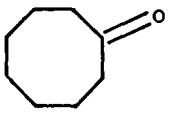
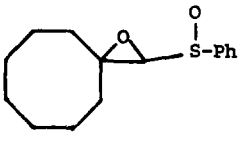
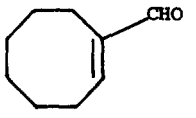
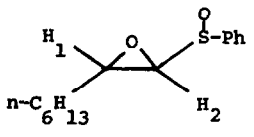
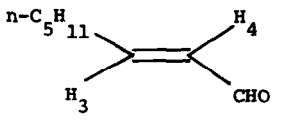
n = 5

(3)

The following procedure is representative: a solution of α-epoxysulfoxide 12 was heated in refluxing xylene under nitrogen for 1 hr. The product was purified by preparative thick layer

chromatography (PLC; on Merck PF_{254} silica gel; 1:9 ether-light petroleum; R_f = 0.45) to give 1-cyclooctenecarboxaldehyde in 90.0% yield. The results are summarized in Table 1.

Table 1

Carbonyl Compounds	α-Epoxysulfoxides	α, β-Unsaturated Aldehydes Yield %[a] (Method)[b]
	 **8**[3]	 40.0 (2)
	 **9**[3]	 42.0 (2)
	 **10**[4]	 53.6 (1) 71.9 (2) 75.5 (3)
	 **11**[4]	 57.3 (2) 76.9 (3)
	 **12**[4]	 90.0 (2) 88.8 (3)
$n\text{-}C_6H_{13}CHO$	 **13**[3]	 33.3 (2)

[a] Yields refer to isolated yields after chromatography (PLC).

[b] Method 1, Heat neat[5]

" 2, Heat in xylene

" 3, Heat in methanol/p-toluenesulfonic acid.

The stereochemistry of the epoxide 13 is exclusively trans (J_{12} = 2 Hz)[6], no cis isomer could be isolated. It is interesting to note that only trans-α, β-unsaturated aldehyde was obtained (J_{34} = 15 Hz) in the pyrolysis of 13.

The overall process represented by equation (1) involves the introduction of both an acyl, and a double bond at the original carbonyl carbon. The carbon of the chlorosulfoxide 2 functions as a masked nucleophilic acyl carbon[7].

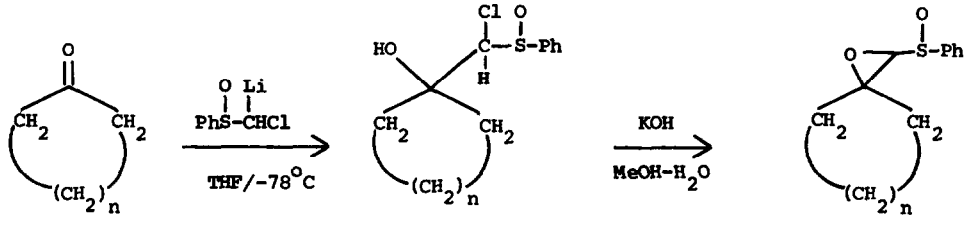
We are presently exploring the scope and limitation of this reaction.

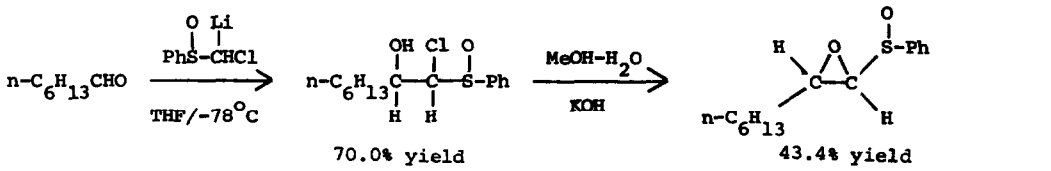
References and Notes

1. I.T. Harrison and S. Harrison, Compendium of Organic Synthetic Methods Vol. 2, John Wiley & Son, New York, 1974, p.328-335 and references therein; E.J. Corey and S. Terashima, Tetrahedron Lett., 1815 (1972); K. Hirai and Y. Kishida, ibid., 2743 (1972); T. Nakai, H. Shiono and M. Okawara, ibid., 3625 (1974); R.B. Erman, I.S. Aul'chenko, L.A. Kheifits, V.G. Dulova, Ju. N. Novikov and M.E. Vol' pin, ibid., 2981 (1976); E.J. Corey, D. Enders and M.G. Bock, ibid., 7 (1976) and references therein; E.J. Corey and A.P. Kozikowski, ibid., 925 (1975); H. Pauling, D.A. Andrews and N.C. Hindley, Helv. Chim. Acta., 59, 1233 (1976).

2. H. Taguchi, T. Tanaka, H. Yamamoto and H. Nozaki, Tetrahedron Lett., 2465 (1973); P.C. Traas, H. Boelens and H.J. Takken, ibid., 2287 (1976); T.L. Ho and C.M. Wong, Synthesis, 196 (1974); I. Hori, T. Hayashi and H. Midorikawa, ibid., 727 (1975).

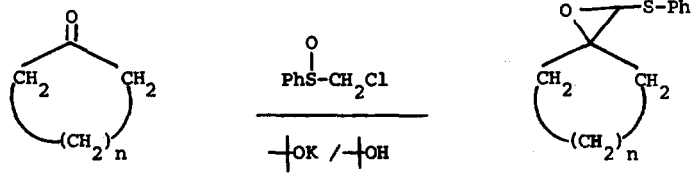
3. 8, 9 and 13 were prepared by a two-step procedure as shown.





Cf. T. Durst, J. Amer. Chem. Soc., 91, 1034 (1969).

4. 10, 11 and 12 were prepared by the reaction of the ketones with chloromethyl phenyl sulfoxide in the presence of potassium t-butoxide/t-butanol



n = 3 (74.0% yield)
n = 4 (65.0% yield)
n = 5 (95.0% yield)

Cf. P.F. Vogt and D.F. Tavares, Can. J. Chem., 47, 2875 (1969); G. Tsuchihashi and K. Ogura, Bull. Chem. Soc. Japan, 45, 2023 (1972).

5. Cf. T. Durst and K.C. Tin, Tetrahedron Lett., 2369 (1970).

6. G.G. Lyle and L.K. Keefer, J. Org. Chem., 31, 3921 (1966).

7. O.W. Lever, Jr., Tetrahedron, 32, 1943 (1976).