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THE SIMPLE SYNTHESIS OF ETHYL 2,4-DIENOATES FROM ALDEHYDES AND ETHYL 2-PHENYLSULFINYLACETATE

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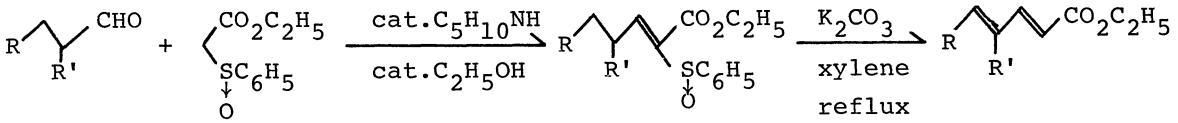
Treatment of aldehydes and ethyl 2-phenylsulfinylacetate (1) in the presence of piperidine gives Z-isomers (Z-2) of 2-phenylsulfinyl-2-alkylideneacetates (2). Thermolysis of Z-2 results in the formation of ethyl E,E-2,4-dienoates (3).

Thermolysis of sulfoxides constitutes a mild and general route to an α,β-unsaturated derivative from the corresponding saturated compound. Trost has developed the synthetic methods for E-isomers of α,β-unsaturated ketones and esters,[1] and Cookson briefly reported the formation of 2-methyl-1,3-nonadien-5-one from 2-methyl-4-phenylsulfinyl-2-nonen-5-one.[2] On the other hand, Okawara et al. found S-(2-substituted vinyl)-N-tosylsulfilimines rearranged to the corresponding N-allyltosylamides in the presence of sodium ethoxide via the migration of a carbon-carbon double-bond.[3]

On the basis of these results, the stereoselective synthesis of ethyl E,E-2,4-dienoates (3) was studied by the combination of the following two reactions; namely, (1) Knoevenagel condensation of ethyl 2-phenylsulfinylacetate (1) and aldehydes, and (2) thermolysis in the presence of a base.



1 Z-2 3

The preparation of ethyl E,E-2,4-hexadienoate (3a, R=CH_3, R'=H) is given here as a typical experiment. Butanal (15 mmol), 1 (10 mmol), piperidine (1 mmol), and ethanol (0.5 mmol) were stirred for 15 h at room temperature.[4] After purification by silica gel column chromatography, ethyl 2-phenylsulfinyl-Z-2-hexenoate (Z-2a) was obtained in 52% yield as a liquid, ^{1}H-NMR ($CDCl_3$) δ 0.98(t,3H), 1.4-1.8(m,2H), 2.73(q,2H), 7.12(t,J=7Hz,1H,CH=C), 1.14(t,3H), 4.06(q,2H), and 7.3-7.7 ppm(m,5H). Although aldol condensation competitively occurred, the corresponding E-isomer (E-2a) was not detected on TLC. The configuration of Z-2a was assigned by comparison with E-2a prepared by another method,[5] that is, (1) the chemical shift of the protons cis to the sulfinyl group was found in the lower field than those trans as reported,[6] and (2) the R_f value of Z-2a with a propyl group cis to the polar sulfinyl group was larger on silica gel TLC than that of E-2a.

Refluxing of Z-2a (10 mmol) and K_2CO_3 (12 mmol) in xylene (50 ml) for 4 h afforded 3a and ethyl 4-hydroxy-2-hexenoate (4a), but other isomers of 3a were scarcely detected by GC and TLC. After purification by silica gel TLC, 3a and 4a were obtained in 59% and 12% yields, respectively. The E,E structure of 3a was fully confirmed by its NMR and IR spectra with the authentic sample.

Other examples are summarized in Table 1.

Table 1. Synthesis of Z-2 and 3

			Condensation of 1 and Aldehydes			Thermolysis of Z-2		
				Z-2			3	
	R	R'	Time	Yield(%)[b]	Config.	Time	Yield(%)	Config.
a	CH_3	H	15 h	52	Z	4 h	59	E,E
b	n-C_3H_7	H	1 d	46	Z	4 h	55	(E,E)[d]
c	n-C_5H_{11}	H	1 d	44	Z	4 h	54	E,E[7,8]
d	H	CH_3	3 d	76	Z	15 h	17(43[c])	(E)[d]
e	-$(CH_2)_4$-		3 d	71	Z	15 h	46(68[c])	(E,E)[d]

a) All the products gave satisfactory analytical results and spectral data.
b) Yield was based on 1. c) Yield was based on the amount of Z-2 consumed.
d) GC and TLC revealed the presence of one isomer.

The present method has the following advantages; (1) the reagents are readily available and are inexpensive, and (2) the procedures are simple.

Interestingly, refluxing of E-2a for 1 h under the same condition yielded 3a in 61% yield. Further studies on the reaction mechanism are now in progress.

References and Notes

1) B.M.Trost, T.N.Salzmann, and K.Hiroi, J.Am.Chem.Soc., 98, 4887 (1976).
2) R.C.Cookson and P.J.Parsons, J.Chem.Soc.,Chem.Commun., 1978, 821.
3) M.Kakimoto, T.Yamamoto, and M.Okawara, Tetrahedron Lett., 1979, 623.
4) Knoevenagel condensation of ethyl acetoacetate and aldehydes likewise occurred; A.C.Cope and C.M.Hofmann, J.Am.Chem.Soc.,63,3456(1941). The similar results of the condensation of 1 and aldehydes were obtained, independently; M.Onaka and T. Mukaiyama, 41th National Meeting of the Chemical Society of Japan, Osaka, 1980.
5) Ethyl 2-phenylsulfinylhexanoate (10 mmol), $(CF_3CO)_2O$ (12 mmol), and CF_3CO_2H (1 mmol) in CH_2Cl_2 (70 ml) were stirred for 5 h at room temperature. An E;Z mixture of ethyl 2-phenylthio-2-hexenoate (5a) was obtained in 54% yield by distillation (E/Z = 80/20 by GC). After oxidation of the E:Z mixture of 5a with m-chloroperbenzoic acid and purification by silica gel column chromatogrphy, E-2a was obtained in 79% yield as a liquid, ^{1}H-NMR($CDCl_3$) δ 0.98(t,3H), 1.4-1.8(m,2H), 2.72(q,2H), 7.24(t,J=7Hz,1H), 1.13(t,3H), 4.03(q,2H), and 7.3-7.7 ppm(m,5H).
6) S.Yamagiwa, N.Hoshi, H.Sato, H.Kosugi, and H.Uda, J.Chem.Soc.,Perkin 1,1978,214.
7) J.Tsuji, H.Nagashima, T.Takahashi, and K.Masaoka, Tetrahedron Lett., 1977, 1917.
8) Perliminary thermolysis of 3c prepared through several steps was tried; J.Nokami, K.Ueta, and R.Okawara, 40th National Meeting of the Chemical Society of Japan, Fukuoka, 1979.

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