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PYROLYSIS OF SULFOXIDE. III.1) CONVERSION OF 2-(PHENYLSULFINYL)ENOATE TO 2,4-DIENOATE AND SYNTHESIS OF PELLITORINE2)

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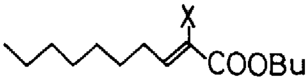
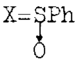
Summary: 2,4-Dienoate was prepared by pyrolysis of 2-(phenylsulfinyl)enoate. N-Isobutyl-E,E-2,4-decadieneamide (pellitorine) was synthesized from decanoic acid in a satisfactory yield.

We have been interested in the pyrolysis of various sulfoxides to obtain olefinic compounds, because this reaction proceeds smoothly by the elimination of sulfenic acid (RSOH).3) We describe here a new synthetic application of this pyrolysis reaction to prepare 2,4-dienoate derivative from 2-(phenylsulfinyl)-enoate which can be obtained from the corresponding saturated carboxylic acid involving electrolytic procedure found by us. For example, pellitorine (**9**)4) was synthesized from decanoic acid as follows. Butyl 2-bromodecanoate (**1**) which was derived by the usual bromination and esterification of decanoic acid was converted to butyl 2-(phenylthio)decanoate (**2**), bp 182°C/1.1 Torr; nmr5) δ 3.48 (t, 1 H, J=7.0 Hz, PhSC$\underline{\text{H}}$COOBu), by the treatment with thiophenol in hot acetone (50°C) in the presence of finely powdered potassium carbonate (ca. 1.5 equiv.). The ester **2** was electrolyzed in acetic acid with sodium acetate by 2.5 F/mol of electricity without cooling by using platinum electrodes to give butyl 2-acetoxy-2-(phenylthio)decanoate (**3**):6) nmr δ 1.97 (s, 3 H, $\text{CO}\underline{\text{CH}}_3$). The pyrolytic distillation of **3** afforded butyl 2-(phenylthio)-E-decanoate (**4**),7) nmr δ 2.45 (broad q, 2 H, J=7.4 Hz, $\text{C=C}\underline{\text{H}}_2$), 7.22 (t, 1 H, J=7.4 Hz, C$\underline{\text{H}}$=C), in a 70% yield based on **2**. Butyl 2-(phenylsulfinyl)-E-decenoate (E-**5**), nmr δ 2.5-3.0 (m, 2 H, $\text{C=CC}\underline{\text{H}}_2$), 7.20 (t, 1 H, J=8.0 Hz, C$\underline{\text{H}}$=C), was obtained by m-chloroperbenzoic acid oxidation of **4** in CH_2Cl_2 at 0°C, and Z-**5**, nmr δ 2.68 (q, 2 H, J=7.5 Hz, $\text{C=CC}\underline{\text{H}}_2$), 6.95 (t, 1 H, J=7.5 Hz, C$\underline{\text{H}}$=C), was obtained by sodium metaperiodate ($NaIO_4$) oxidation of **4** in an aqueous methanol at room temperature or by the treatment of E-**5** with refluxing methanol. Pyrolysis of Z-**5**8) to give 2,4-dienoate9) was carried out in refluxing xylene with suspended sodium bicarbonate (excess)10) for 6 hrs. Distillation of the reaction mixture after filtration gave a mixture of E,E and Z,E-**6** (85% yield, E,E/Z,E=4/1): bp 160°C/30 Torr.11) The ester **6** was hydrolyzed by sodium hydroxide in hot aqueous dioxane.12) Pure E,E-2,4-decadienoic acid (**7**), mp 49°C; nmr($CDCl_3$) δ 5.65 (d, 1 H, J=15.0 Hz, C=C$\underline{\text{H}}$CO), 6.0-6.3 (m, 2 H, C$\underline{\text{H}}$=C$\underline{\text{H}}$), 7.22 (ddd, 1 H, J=15.0 Hz, C$\underline{\text{H}}$=CCO), was isolated by recrystallization from pentane in an 80% yield. Pellitorine (**9**) was obtained via **8** in a 90% yield.

1, X=Br, Y=H
2, X=SPh, Y=H
3, X=SPh, Y=OAc



4, X=SPh
5, 
X=$\underset{\underset{O}{\downarrow}}{S}$Ph

6, Z=OBu
7, Z=OH, **8**, Z=Cl
9, Z=NHBu^i

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References and Notes

1) Part I, J.Nokami, N.Kunieda, and M.Kinoshita, Tetrahedron Lett., 2841(1975); Part II, J.Nokami, K.Ueta, and R.Okawara, ibid., 4903(1978).

2) J.Nokami, K.Ueta, and R.Okawara, 40th Anual Meeting of Chem.Soc.Jpn., Abstract II, 774(1979), Fukuoka.

3) For instance, we could list up the following reports; study on the reaction mechanism: C.A.Kingsbury et al., J.Am.Chem.Soc., 82, 1810(1960); D.W.Emerson et al., J.Org.Chem., 34, 4115(1969); synthetic application: J.Nokami et al., Chem.Lett., 715(1977); Tetrahedron Lett., 2841(1975), and references cited therein.

4) T.Mandai, J.Gotoh, J.Otera, and M.Kawada, Chem.Lett., 313(1980).

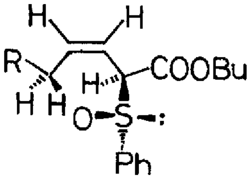
5) Measured in CCl_4 unless stated containing TMS as internal standard (δ 0 ppm) on a Hitachi R-24B (60 MHz) or Jeol FX-100 (100 MHz).

6) J.Nokami, M.Hatate, S.Wakabayashi, and R.Okawara, Tetrahedron Lett.,2557(1980)

7) **4** was also obtained from butyl 2-decenoate by the method reported by T.Fujisawa et al.$^{13)}$ or by the following method. Butyl 2-decenoate was treated with PhSCl to give the adduct, which was converted to **4** by the treatment with suspended K_2CO_3 in refluxing acetone(by the elimination of HCl).

8) The yield of **6** from Z-**5** is higher than that from E-**5**.

9) Here, we wish to propose an Ei mechanism passing through seven membered ring system as similar to the usual pyrolysis of sulfoxide to give olefin. The intermediate 2-(phenylsulfinyl)-3-enoate seems to be plausible because of the fact that the Evans type rearrengement occur to give 4-hydroxy-2-enoate(or -enone) from 2-(phenylsulfinyl)-2-enoate(or -enone).$^{13)\ 14)}$



10) Other acid scavenger such as Na_2CO_3 gave much amount of 4-hydroxy-2-enoate.

11) Rotary glass tube oven (SHIBATA CHEM.APP.MFG.CO.LTD.) was used.

12) An alcohol adduct of hydrolyzed product was observed by the reaction in hot alcoholic solvent.

13) T.Fujisawa, K.Sakai, 37th Anual Meeting of Chem.Soc.Jpn., Abstract II, 909 (1978).

14) H.Kosugi, H.Uda, and S.Yamagiwa, Chem.Comm., 192(1975).

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