*Russian Journal of Organic Chemistry, Vol. 37, No. 6, 2001, pp. 781–783. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 6, 2001, pp. 829–831.*


# Isomerization of Methyl (9*Z*)-12-Oxooctadec-9-enoate

**A. M. Davletbakova, N. Z. Baibulatova, V. A. Dokichev, S. G. Yunusova, and M. S. Yunusov**

*Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences, Ufa, Bashkortostan, 450054 Russia*

Received July 19, 2000

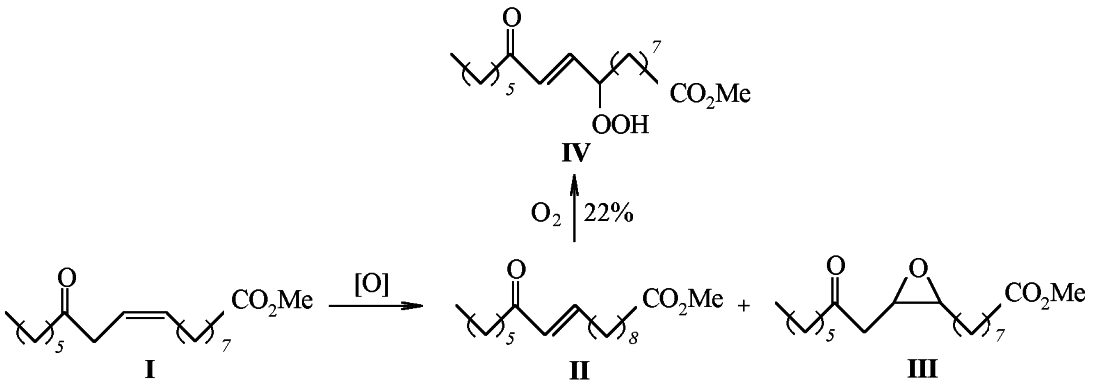
**Abstract**—Methyl (9*Z*)-12-oxooctadec-9-enoate isomerizes stereoselectively in 86% yield into methyl (10*E*)-12-octadec-10-enoate in the presence of a complex $H_2O_2$–$BF_3$–$Et_2O$.

The interest to chemical transformations of ricinoleic [(9*Z*), (12R)-12-hydroxyoctadec-9-enoic) acid has grown recently [1, 2]. Its derivatives possess antiviral, antiphlogistic, and antiallergic properties [3, 4]. It was shown formerly that the reaction of methyl (9Z)-12-oxooctadec-9-enoate (**I**) with peroxyacids resulted in epoxydation of the C=C bond [1, 3, 5].

In the present study during preparation of new derivatives of ricinoleic acid by oxydation of methyl (9*Z*)-12-oxooctadec-9-enoate (**I**) according to Bayer–Williger procedure we found that the compound suffered a stereoselective isomerization. Treating of ethereal solution of enone **I** with the reagent for ketone oxidation, a complex of 90% hydrogen peroxide and boron trifluoride etherate [6] [molar ratio ketone **I**–$H_2O_2$–$BF_3$–$Et_20$ 1 : 1 : 2], afforded methyl (10*E*)-12-octadec-10-enoate (**II**) in 86% yield. In the reaction under study alongside the displacement of the C=C bond from $C^9$ to $C^{10}$ occurred its selective *cis-trans* isomerization as showed the coupling constant of the vicinal protons attached to the $C^{10}$=$C^{11}$ bond of enone **II** (~16 Hz). Under similar conditions in the presence of only boron trifluoride etherate the ketoester **I** yielded just 58% of ester **II**.

The structure of compound **II** was confirmed by a known isomerization procedure for ketoester **I** isomerization [7]: refluxing of ether **I** in ethanol in the presence of oxalic acid under argon atmosphere.

A detailed investigation of ketoester **I** oxidation with a 5-foid excess of monoperoxyphthalic or *meta*-chloroperoxybenzoic acids revealed that alongside methyl 12-oxo-9,10-epoxyoctadecanoate **III** formed also ketoester **II**. The yields of compounds **III** and **II** amount respectively to 79 and 14% or 75 and 17%. No products resulting from oxidation of ketone **I** along Bayer–Williger reaction was detected.




| Reagent | Yield of compound **II** | Yield of compound **III** |
|---|---|---|
| 90% $H_2O_2$, $BF_3 \cdot Et_2O$ | 86 | – |
| $BF_3 \cdot Et_2O$ | 58 | – |
| $H_2C_2O_4$ | 41 | – |
| 2-$(HO_2C)C_6H_4CO_3H$ | 14 | 79 |
| 3-$ClC_6H_4CO_3H$ | 17 | 75 |

1070-4280/01/3706-0781$25.00 

Note that ketoester **II** stored in air readily undergoes autooxidation by air oxygen affording methyl (10*E*)-9-hydroperoxy-12-oxodec-10-enoate (**IV**) in 22% yield.

## EXPERIMENTAL

$^1$H and $^{13}$C NMR spectra were recorded on Bruker AM-300 spectrometer in $CDCl_3$. IR spectra were measured on Specord M-80 instrument from samples as thin films. Mass spectra were taken on spectrometer MKh-1300, injection source temperature 100°C, electron ionization energy 70 and 12 eV. The reaction products were analysed by GLC on Chrom-5 chromatograph, flame-ionization detector, column 1200×5 mm packed with 5% SE-30 on Inerton NAW DMCS carrier (0.125–0.165 μ), carrier gas helium.

**Methyl (9*Z*)-12-oxooctadec-9-enoate (I)** was prepared by oxidation of methyl (9*Z*),(12R)-12-hydroxyoctadec-9-enoate with the Collins reagent [3].

**Oxidation of ketone I with $H_2O_2$–$BF_3$–$Et_2O$ complex.** To a solution of 0.85 g (2.74 mmol) of ketone **I** in 0.24 ml of $Et_2O$ was added dropwise under argon at stirring while cooling to 0°C 0.11 g (2.88 mmol) of 90% $H_2O_2$ solution and 0.77 g (5.48 mmol) of $BF_3$–$Et_20$. The reaction mixture was maintained at 0°C for 2.5 h, then diluted with 5 ml of $Et_2O$, washed with saturated solutions of $Na_2SO_3$ (3×3 ml) and $K_2CO_3$ (3×3 ml), and dried with $MgSO_4$.

The solvent was removed in vacuo, and the residue was subjected to column chromatography on silica gel (L 100/250, eluent petroleum ether–$Et_2O$, 20:1). Ketone **II** was separated in 0.73 g amount (86%). IR spectrum ($cm^{-1}$): 1000 (*trans*-C=C), 1190 (C=O), 1650 (*trans*-C=C), 1690 (C=O), 3030 (*trans*-C=C), 1745 ($CO_2$). $^1$H NMR spectrum (δ, ppm, *J*, Hz): 0.80 t (3H, $C^{18}H_3$, 6.5), 1.13–1.42 m (16H, $CH_2$), 1.45–1.61 m (4H, $C^3H_2$, $C^{14}H_2$), 2.12 q (2H, $C^9H_2$, 7.2), 2.22 t (2 H, $C^2H_2$, 7.6), 2.45 t (2H, $C^{13}H_2$, 7.6), 3.60 s (3H, $CO_2CH_3$), 6.02 d (1H, $C^{11}H$, 16.2), 6.25 d.t (1H, $C^{10}H$, 15.9 and 6.9). $^{13}$C NMR spectrum ($\delta_C$, ppm): 14.06 ($C^{18}$), 22.54 ($C^{17}$), 24.33 ($C^3$), 24.91 ($C^{15}$), 28.11 ($C^{14}$), 29.01 ($C^4$), 29.12 ($C^5$, $C^6$, $C^7$), 29.72 ($C^8$), 31.66 ($C^{16}$), 32.44 ($C^9$), 34.08 ($C^2$), 40.13 ($C^{13}$), 51.48 ($OCH_3$), 130.36 ($C^{11}$), 147.34 ($C^{10}$), 173.33 ($C^1$), 201.12 ($C^{12}$). Mass spectrum, *m/z*: 310 $[M]^+$.

**Isomerization of ketone I.** (a) In the presence of $BF_3$–$Et_20$. From 0.3 g (0.97 mmol) of ketone **I** and 0.275 g (1.94 mmol) of $BF_3$–$Et_20$ along procedure described above was obtained 0.17 g (58%) of ketone **II**.

(b) In the presence of oxalic acid. A solution of 0.5 g (1.55 mmol) of ketone **I** and 0.05 g (0.55 mmol) of anhydrous oxalic acid in 20 ml of 95% ethanol was heated under argon for 2 h, then cooled to 20°C, and the solvent was evaporated in vacuo. The residue was diluted with 8 ml of $Et_2O$ and treated with saturated solution of $Na_2CO_3$ (3×5 ml)the reaction product was extracted with $Et_2O$, and extract was drid on $MgSO_4$. The solvent was evaporated in vacuo. We obtained 0.21 g (41%) of ketone **II**.

**Oxidation of ketone I with peroxyacids.** (a) To a solution of 0.46 g (1.5 mmol) of ketone **I** in 2 ml of $Et_2O$ at 0°C under argon while stirring was added dropwise a solution of 1.37 g (7.5 mmol) of monoperoxyphthalic acid in 7 ml of $Et_2O$, the mixture was maintained at 0°C for 4–5 h and left standing overnight at room temperature. The reaction mixture was filtered, washed with saturated solutions of $Na_2SO_3$ (3×5 ml) and $Na_2CO_3$ (3×5 ml), and dried with $MgSO_4$. The solvent was evaporated in vacuo. The residue was subjected to column chromatography on silica gel (L 100/250, eluent petroleum ether–$Et_2O$, 15:1). We separated 0.04 g (14%) of ketone **II** and 0.22 g (79%) of epoxide **III**.

(b) In a similar way 0.5 g (1.6 mmol) of ketone **I** dissolved in 2 ml of $CH_2Cl_2$ was oxidized with a solution of 1.4 g (8.1 mmol) of *meta*-chloroperoxybenzoic acid in 7 ml of $CH_2Cl_2$. Yield of ketone **II** 0.07 g (17%), of epoxide **III** 0.29 g (75%). IR and $^1$H NMR spectra are consistent with the published data [1, 3, 5]. $^{13}$C NMR spectrum ($\delta_C$, ppm): 14.06 ($C^{18}$), 22.51 ($C^{17}$), 23.58 ($C^3$), 24.91 ($C^{15}$), 26.43 ($C^8$), 28.00 ($C^{14}$), 28.84 ($C^4$), 29.04 ($C^5$), 29.17 ($C^6$), 29.29 ($C^7$), 31.61 ($C^{16}$), 34.06 ($C^2$), 41.63 ($C^{13}$), 43.36 ($C^{11}$), 51.51 ($CO_2CH_3$), 52.37 ($C^{10}$), 56.36 ($C^9$), 174.29 ($C^1$), 208.52 ($C^{12}$). Mass spectrum, *m/z*: 326 $[M]^+$.

**Methyl (10*E*)-9-hydroperoxy-12-oxooctadec-10-enoate (IV).** 4 g (1.3 mmol) of ketone **II** was stored in air at room temperature for 1 month. The resulting mixture was subjected to column chromatography on silica gel (L 100/250, eluent petroleum ether–$Et_2O$, 15:1). We separated 0.09 g (22%) of hydroperoxide **IV**. IR spectrum ($cm^{-1}$): 855 (C–O–O–H), 1050 (*trans*-C=C), 1190 ($CO_2$), 1645 (*trans*-C=C), 1690 (C=O), 1745 ($CO_2$), 3030 (*trans*-C=C), 3425 (C–O–O–H). $^1$H NMR spectrum (δ, ppm, *J*, Hz): 0.83 t (3H, $C^{18}H_3$, 6.6), 1.15–1.41 m (16H, $CH_2$), 1.42–1.65 m (4H, $C^3H_2$, $C^{14}H_2$), 2.23 t (2H, $C^2H_2$, 7.5),

2.52 t (2H, $C^{13}H_2$, 7.4), 3.6 s (3H, $CO_2CH_3$), 3.7 m (1H, OH), 4.43 m (1H, $C^9H$), 6.22 d (1H, $C^{11}H$, 16.2), 6.70 d.d (1H, $C^{10}H$, 15.9 and 6.6). $^{13}C$ NMR spectrum ($\delta_C$, ppm): 13.96 ($C^{18}$), 22.44 ($C^{17}$), 23.72 ($C^3$), 24.45 ($C^7$), 24.72 ($C^{14}$), 27.42 ($C^{15}$), 28.81 ($C^4$, $C^6$), 29.18 ($C^5$), 31.43 ($C^{16}$), 33.98 ($C^2$), 35.20 ($C^8$), 40.35 ($C^{13}$), 51.39 ($OCH_3$), 84.58 ($C^9$), 130.72 ($S^{11}$), 144.57 ($S^{10}$), 174.29 ($S^1$), 200.50 ($S^{12}$).

## REFERENCES


1. Foglia, T.A., Sonnet, P.E., Nunez, A., and Dudley, D.L., *J. Am. Oil Chem. Soc.*, 1998, vol. 75, no. 5, pp. 601–607.
2. Gunstone, F.D., *Acc. Chem. Res.*, 1976, vol. 9, no. 1, pp. 34–40.
3. Zabolotskii, D.A. and Myagkova, G.I., *Bioorg. khimiya*, 1991, vol. 17, no. 8, pp. 1129–1132.
4. Chakrabarti, P. and Khorana, H.G., *Biochemistry*. 1975, vol. 14, no. 23, pp. 5021–5023.
5. Lie Ken Jie, M.S.F. and Zheng, Y.F., *Synthesis*, 1988, no. 6, pp. 467–468.
6. McClure, J.D. and Williams, P.H., *J. Org. Chem.*, 1962, vol. 27, no. 1, pp. 24–26.
7. Fieser, L.F., *J. Am. Chem. Soc.*, 1953, vol. 75, no. 21, pp. 5421–5422.