The Stereoselective Synthesis of trans-Chrysanthemum Monocarboxylic Acid

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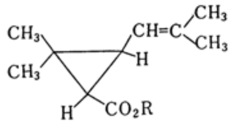
Chrysanthemum monocarboxylic acid ethyl ester (I) has been synthesized from ethyl diazoacetate and 2, 5-dimethyl-2, 4-hexadiene[1]. However, the product was a mixture of cis and trans esters in a ratio of about 1 : 1[2].



I $R=C_2H_5$
II $R=t\text{-}C_4H_9$
III $R=H$

The present authors wish to report a stereoselective formation of *trans*-chrysanthemum monocarboxylic acid *t*-butyl ester (II) achieved by treatment of the diene with *t*-butyl diazoacetate.

t-Butyl diazoacetate (1.42 g., 0.010 mol.)[3] was added slowly to a mixture of the diene 2.5 g., 0.022 mol.) and copper powder (0.05 g.) at 120∼130°C. The reaction product was distilled to yield 0.95 g. of II (b. p., 120∼125°C/14 mmHg; Found: C, 74.82; H, 10.81. Calcd. for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78%; ν_{max} 1720 cm^{-1}; δ (c. p. s.)'s are shown in Table I), the infrared spectrum of which was identical with that of the ester prepared form the silver salt of authentic trans acid III and *t*-butyl iodide. Complete hydrolysis of the ester II was effected in a 1 N hydrochloric acid solution at 100°C, affording a single crystalline acid whose infrared spectrum and m. p. (53∼54°C) were identical with those of *trans*-III.

Data of the NMR spectra of I, II and III are summarized in Table I. A quantitative analysis of the cis and trans ratio is especially possible by drawing a comparison between the intensity of the signals due to the olefin proton of each isomer. The fact that the synthetic II exhibited only one detectable

TABLE I. NMR SPECTRA OF CHRYSANTHEMUM MONOCARBOXYLIC ACID DERIVATIVES IN CARBON TETRACHLORIDE SOLUTION AT 56.4 Mc.

	cis-Acid III	*trans*-Acid III	*t*-Bu ester II
CH_3(ring)	0*(6H)	0*(3H) 8.6(3H)	0*(3H) 5.6(3H)
CH (side chain)	25(3H) 29(3H)	27(6H)	31(6H)
CH (olefin)	226 234 (1H)	200 208 (1H)	202.5 211.5 (1H)

* The chemical shifts (c. p. s. unit) were determined relative to the peak at the highest magnetic field.

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[1] H. Staudinger, O. Muntwyler, L. Ruzicka and S. Seibt, *Helv. Chim. Acta*, **7**, 390 (1924); I. G. M. Campbell and S. H. Harper, *J. Chem. Soc.*, **1945**, 283. The natural chrysathemum moncarboxylic acid has the trans configuration.

[2] The ratio of cis and trans isomers can be conveniently determined by measurement of the NMR spectum (cf. Table I).

[3] H. Reimlinger and L. Skatteböll, *Chem. Ber.*, **93**, 2116 (1960). In the present work, the *t*-butyl aceturate was prepared by the reaction of isobutylene with aceturic acid in the presence of sulfuric acid in a dioxane solution.

doublet peak in the low magnetic field confirmed the selective formation of the trans ester.

The steric course of this reaction seems to be controlled by the bulkiness of the *t*-butyl group.

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