BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 2866—2867 (1971)

Stereochemical Studies in Friedel-Crafts Reactions. IV. The Reactions of *cis*-1,2-Disubstituted 4-Cyclohexenes with Benzene

Kaichiro Sugita and Shuzi Tamura

Department of Chemistry, Ritsumeikan University, Kita-ku, Kyoto

(Received March 26, 1971)

In a previous paper,[1] we reported that the aluminum chloride-catalyzed reactions of benzene with *trans*-1,2-disubstituted 4-cyclohexenes, such as *trans*-2-benzoyl-4-cyclohexene-1-carboxylic acid and its methyl ester and methyl *trans*-2-chloroformyl-4-cyclohexene-1-carboxylate, give stereoselectively *r*-1, *c*-2, *t*-5-trisubstituted cyclohexane in all cases. The present paper will describe two reactions, those of benzene with methyl *cis*-2-chloroformyl-4-cyclohexene-1-carboxylate (**1**) and with *cis*-2-benzoyl-4-cyclohexene-1-carboxylic acid (**3**) in the presence of aluminum chloride.

The reaction of methyl *cis*-2-chloroformyl-4-cyclohexene-1-carboxylate (**1**) with benzene gave methyl *c*-2-benzoyl-*t*-5-phenylcyclohexane-*r*-1-carboxylate (**2**)[1,2] in a 54% yield. In the reaction of *cis*-2-benzoyl-4-cyclohexene-1-carboxylic acid (**3**) with benzene, a carboxylic acid (**4A**) was obtained in an 11% yield. The acid **4A** was converted to *c*-2-benzoyl-*t*-5-phenylcyclohexane-*r*-1-carboxylic acid (**4B**)[1,2] by treatment with sodium ethoxide in ethanol, followed by acidification. This epimerization indicates that the two acids, **4A** and **4B** are stereoisomeric with each other. When **4A** was treated with bromine in acetic acid, the bromine color disappeared, while in the case of **4B** the bromine color did not change under similar conditions.[2] Since the ease of bromination depends on the rates of enolization,[3] the difference in the behavior of **4A** and **4B** should be attributed to the presence of the axial benzoyl group in **4A**. These results support the **4A** structure.

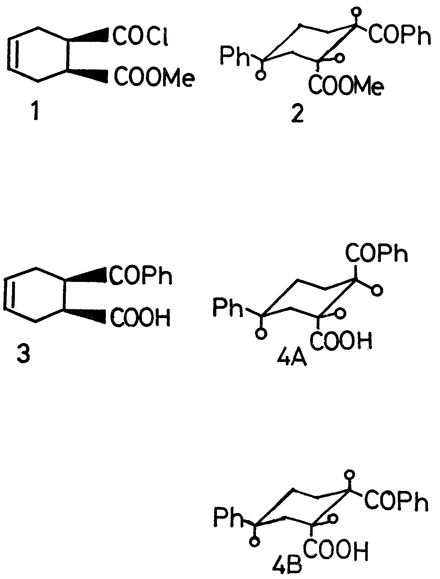

Fig. 1.

Experimental[4]

Material. The *cis*-methoxycarbonyl-4-cyclohexene-1-carboxylic acid was prepared by the procedure reported by Nazarov and Kucherov.[5] The *cis*-2-benzoyl-4-cyclohexene-1-carboxylic acid (**3**) was prepared by the procedure reported by Fieser and Nevello.[6]

Methyl cis-*Chloroformyl-4-cyclohexene-1-carboxylate (1).* A mixture of *cis*-2-methoxycarbonyl-4-cyclohexene-1-carboxylic acid (18 g) and thionyl chloride (18 g) was treated in a manner similar to that described previously. Methyl *cis*-2-chloroformyl-4-cyclohexene-1-carboxylate (**1**) was thus obtained quantitatively. The crude product was used without distillation. IR: (neat) 1795 (acid chloride), 1740 (ester), and 1655 cm^{-1} (olefin). NMR: δ ($CDCl_3$) 2.65—2.25 (m, 4H, $2CH_2$), 3.40—2.85 (m, 2H, 2CH), 3.72 (s, 3H, CH_3), and 5.70 ppm (m, 2H, CH=CH).

Reaction of Methyl cis-*2-Chloroformyl-4-cyclohexene-1-carboxylate (1) with Benzene.* Into a suspension of aluminum chloride (29 g) in dry benzene (90 m*l*) the ester chloride (**1**) (20 g) was vigorously stirred, drop by drop, below 10°C. The stirring was continued for one hour without further cooling and then for five additional hours reflux. Then the reaction mixture was poured onto ice-water. The resulting benzene solution was separated, washed with water, and dried over anhydrous magnesium sulfate. The benzene solution was finally evaporated to dryness. The distillation of the reaction residue gave **2** (17 g, 54%); bp 210—212°C/4 mmHg. The IR and NMR spectra of the ester **2** are identical with those of authentic methyl *c*-2-benzoyl-*t*-5-phenylcyclohexane-*r*-1-carboxylate. (Found: C, 78.59; H, 7.02%).

Reaction of cis-*2-Benzoyl-4-cyclohexene-1-carboxylic Acid (3) with Benzene.* Into a solution of the acid **3** (20 g) in dry benzene (90 m*l*) we stirred aluminum chloride (23 g) over a five-minute period below 10°C; the stirring was then continued for one hour without further cooling and for two hours under reflux. Then the reaction mixture was poured onto ice-water. The resulting benzene solution was separated, washed with water, and dried over anhydrous magnesium sulfate. The benzene solution was finally evaporated to dryness. A crystalline solid was thus obtained (25 g, 82%); mp 105—145°C. Recrystallization from 45% alcohol gave **4A** as colorless

---

[1] K. Sugita and S. Tamura, This Bulletin, Submitted.

[2] K. Sugita and S. Tamura, This Bulletin, in press.

[3] H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955).

[4] All the melting points and boiling points are uncorrected. The IR spectra were taken on a Hitachi EPI-S spectrometer. The NMR spectra were obtained on a Japan Electron Optics C-60-H spectrometer.

[5] I. N. Nazarov and V. F. Kucherov, *Ordel. Khim. Nauk*, **1954**, 329; *cf. Chem. Abstr.*, **49**, 5328 (1955). It is reported that methyl *cis*-2-chloroformyl-4-cyclohexene-1-carboxylate (**1**) was isomerized to a mixture of **1** and methyl *trans*-2-chloroformyl-4-cyclohexene-1-carboxylate under the conditions used for distillation (118—119°C/7 mmHg).

[6] L. F. Fieser and F. C. Nevello, *J. Amer. Chem. Soc.*, **64**, 802 (1942).

prisms (3.4 g, 11%); mp 156—157°C. The IR spectra of **4A** is different from that of *c*-2-benzoyl-*t*-5-phenyl-cyclohexane-*r*-1-carboxylic acid (**4B**).[1] The melting point of **4A** was depressed by mixing it with **4B**. IR: (KBr) 2800—2500 (-OH), 1700 (carboxyl), 1680 (ketone) and 1600 cm^{-1} (aromatic). Found: C, 77.83; H, 6.44%. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54%.

Conversion of 4A to 4B. To a sodium ethoxide solution prepared from absolute ethanol (50 m*l*) and sodium (100 mg), we added **4A** (500 mg). The solution was refluxed for five hours and then cooled. After the subsequent addition of water (100 m*l*) to the reaction mixture, the resulting mixture was acidified and filtered. The precipitates thus collected were washed with water and dried; 450 mg of a white product was thus yielded; 95%; mp 179—181°C. The IR spectrum of the product was identical with those of **4B**. The melting point of the product, without any purification, was not depressed by mixing it with **4B**.