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Catalytic Geometrical Isomerization of *cis*-Chrysanthemaldehyde and Related Ketones[1]

Tadashi Sasaki,* Shoji Eguchi, and Masatomi Ohno
Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464

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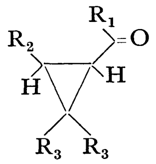
Synopsis. *cis*-Chrysanthemaldehyde isomerized cleanly to the *trans*-isomer catalyzed with methoxydimethylsulfonium iodide (**8**) at 25 °C. Zinc halides as well as silica gel were also demonstrated to be effective catalysts. Related aldehydes and ketones isomerized also with **8** at 80 °C but dihydrochrysanthemaldehyde did not isomerize at all.

Stereoisomerization of chrysanthemic acid **1** (2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylic acid) and its derivatives has drawn much interest for many years because the insecticidal activity of the ester derivative is specific for *d*- and *trans*-isomers.[2] These isomerizations were demonstrated in the nitrile derivative under anionic conditions,[3] the ester derivative under thermolytic and photolytic conditions,[4a,b] and the acid chloride derivative under Lewis acid catalytic conditions.[5]

We wish to report in this paper facile and convenient geometrical isomerization of *cis*-chrysanthemaldehyde **2** under catalytic conditions, where no competing structural isomerizations[6] were not observed.

cis-Aldehyde **2** was allowed to react at 25 °C in dimethyl sulfoxide containing a slight excess of methyl iodide to form *in situ* methoxydimethylsulfonium iodide **8**.[7] After 24 h, ^{1}H NMR inspection indicated the quantitative isomerization to the *trans*-isomer. This clean geometrical isomerization of **2** was also catalyzed with zinc halides.[8] The iodide, bromide, and chloride salts were all effective as far as used homogeneously in an appropriate solvent such as ether or dioxane. Interestingly, silica gel was found to be useful for this geometrical isomerization;[9] contact of **2** with silica-gel column (Mallinckrodt 100 mesh) at room temperature for 18 h produced quantitatively the *trans*-isomer.

Several comparative experiments were carried out to test the general applicability of this simple method. Firstly the choice of catalyst for **2** was shown to be critical. The catalyst coordinating much or less with the aldehyde carbonyl did not give satisfactory results; boron trifluoride catalysis led to the formation of an intractable mixture and lithium iodide catalysis resulted in no reaction. *p*-Toluenesulfonic acid catalysis caused undesired ring opening.[11] Secondly, reactivity of carbonyl compounds with the catalyst **8** was examined by using related aldehydes and ketones **3**—**7**: Chrysanthemyl methyl ketone **3** and phenyl ketone **4** were found to be less reactive than the aldehyde **2**, and thus underwent nearly quantitative isomerization on heating at 80 °C for 2 h and 7 h, respectively. Similarly, 2-phenylcyclopropanecarbaldehyde **5** and methyl ketone **6** isomerized to the corresponding *trans*-isomers in 83% and 46% yields, respectively, on heating as above for 7 h, although they were stable at 25 °C. However, dihydrochrysanthemaldehyde **7**, a saturated analogue of **2**, did not isomerize at all under the same catalytic conditions.



1	$R_1=OH$,	$R_2=CH{=}C(CH_3)_2$,	$R_3=CH_3$
2	$R_1=H$,	$R_2=CH{=}C(CH_3)_2$,	$R_3=CH_3$
3	$R_1=CH_3$,	$R_2=CH{=}C(CH_3)_2$,	$R_3=CH_3$
4	$R_1=C_6H_5$,	$R_2=CH{=}C(CH_3)_2$,	$R_3=CH_3$
5	$R_1=H$,	$R_2=C_6H_5$,	$R_3=H$
6	$R_1=CH_3$,	$R_2=C_6H_5$,	$R_3=H$
7	$R_1=H$,	$R_2=CH_2CH(CH_3)_2$,	$R_3=CH_3$

$$(CH_3)_2\overset{+}{S}OCH_3\ \ I^-$$

8

These experimental facts suggest that the geometrical isomerization is significantly affected by a substituent on the cyclopropane ring through conjugation and by the nature of coordination of carbonyl group with catalyst. The reactivity trend of the observed isomerization, *i.e.*, aldehyde>methyl ketone>phenyl ketone and isobutenyl>phenyl>isobutyl substituent[10] seems to reflect the ability to delocalize the positive charge to the cyclopropane ring. In addition, no deuterium incorporation was observed in the isomerization of **2** with **8** in 1:20 D_2O–DMSO (^{1}H NMR inspection) precluding an enolization pathway. Therefore, this stereoisomerization can be explained most reasonably as follows: The polarization of C=O double bond arising from the appropriate coordination of catalyst can generate a cyclopropylmethyl cation-like intermediate which caused the isomerization to thermally more stable *trans*-isomer. More activated intermediate carbonium ion may be responsible for the other reaction such as structural isomerization.[11]

Above clean geometrical isomerization of *cis*-alkenylcyclopropanecarbonyl derivative is unprecedented to the best of our knowledge, and may be useful for obtaining pure *trans* isomer from, for instance, *cis* and *trans* mixture of carbonylcarbene adduct with conjugated olefins.

Experimental

Materials. Aldehydes **2**, **5**, and **7** were prepared by oxidation of the corresponding alcohols with pyridine–chromium trioxide.[12a,b,c] Ketones **3**, **4**, and **6** were prepared from the corresponding carboxylic acids and methyl- or phenyllithium.[12a,d]

^{1}H NMR Analyses. ^{1}H NMR spectra were obtained with a JEOL JNM-C-60HL spectrometer in carbon tetrachlo-

ride with tetramethylsilane as an internal standard. *Cis* and *trans* ratio was determined by the integral ratio of key signals at δ 5.36 (*cis*) and 4.89 (*trans*) (CH=C) for **2**, 5.28 (*cis*) and 4.82 (*trans*) (CH=C) for **3**, 5.36 (*cis*) and 4.16 (*trans*) (CH=C) for **4**, 8.53 (*cis*) and 9.25 (*trans*) (CHO) for **5**, and 1.87 (*cis*) and 2.19 (*trans*) ($COCH_3$) for **6**, respecuvely.

Geometrical Isomerization. (*A*): The aldehyde or ketone (1 mmol) was dissolved in a solution of methyl iodide (150 mg, 1.06 mmol) in dimethyl sulfoxide (3 ml) and the resulted solution was left in the dark at 25 °C or 80 °C. After the reaction time described in the text, the solution was poured onto water and the isomerized aldehyde or ketone was recovered nearly quantitatively by extraction with hexane, followed by usual work up. The *cis* and *trans* ratio was then determined by ^1H NMR spectra.

(*B*): The aldehyde **2** (152 mg, 1 mmol) was added to a solution of zinc iodide (160 mg, 0.5 mmol) in ether (5 ml), and the solution was left at 25 °C for 24 h. The catalyst was removed by extraction with water and usual work up gave almost quantitatively the *trans*-aldehyde. The reaction with zinc bromide or chloride under the same conditions except for using dioxane as a solvent gave similar results, but a small amount of contaminants was produced in the case of zinc chloride.

(*C*): The aldehyde **2** (152 mg, 1 mmol) was adsorbed on the silica gel (Mallinckrodt 100 mesh) column with chloroform. After 18 h at room temperature, the isomerized aldehyde was recovered quantitatively by eluting out with chloroform.

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