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HIGH SELECTIVE CIS⇄TRANS ISOMERIZATION OF TRI-SUBSTITUTED DOUBLE BOND BY RUTHENIUM ACETYLACETONATE

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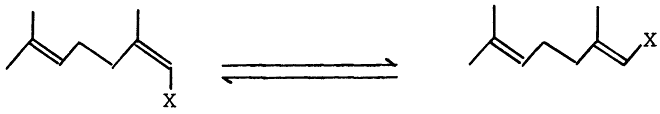
Ruthenium acetylacetonate was found to be effective for high selective cis⇄trans isomerization of tri-substituted double bond of geranylacetone, pseudoionone, ethyl geranylacetate etc., without any migration and hydrogenation of double bond.

Among the many noble metal catalysts for cis⇄trans isomerization of double bond$^{1)}$, attention was paid to ruthenium systems owing to the interesting activity in the absence of hydrogen. The use of hydrogen for activation of catalysts, which is generally employed in many cases, is not preferable because of the accompaniment of hydrogenation reaction. The increasing order of activity of the catalysts was reported to be $Pd < Rh < Ru$ in the absence of hydrogen$^{2a)}$ contrary to that of $Ru < Pt < Pd < Rh$ in the presence of hydrogen$^{2b)}$.

Recently, Henrick et al$^{3)}$ have reported the migration of double bond of $\Delta^{2,4}$-unsaturated ester with $RuCl_3\cdot 3H_2O$ (20 wt%) to yield $\Delta^{3,5}$-unsaturated isomer. However, treatment of cis-geranylacetone (1a) with small amount of $RuCl_3\cdot 3H_2O$ (1 wt%) at 150°C for 5 hr under nitrogen atmosphere afforded a cis/trans=69/31 mixture in ca. 75% selectivity [100 (1a + 2a)/changed olefin]. The use of ruthenium acetylacetonate [$Ru(AA)_3$] (0.1-0.3 wt% vs. 1 or 2) at the temperature range of 180-210°C in neat system was found to be more effective for isomerization to obtain the equilibrium mixture (see Fig.). Only a trace of polymer (ca. 3-5%) could be detected by G.P.C. analysis even after heating 1a at 200°C for 23 hr with 0.2 wt% of $Ru(AA)_3$.



1 a-e   2 a-e

As shown in Table, ethyl geranate (1c) or ethyl geranylacetate (1e) etc., also underwent geometrical isomerization in high selectivity.

In the case of Δ^3-trans, Δ^5-cis pseudoionone, double bond migration to $\Delta^{4,6}$-position could not be observed, and the stereochemistry of Δ^3-position was preserved in trans-form. Separation of the catalyst was easily carried out by flash distillation under reduced pressure.

In summary, the present results show that Ru(AA)$_3$ is an excellent catalyst for cis$\rightleftarrows$trans isomerization of tri-substituted olefins without any migration and hydrogenation of double bond.

Synthetic application of this procedure to all trans-geranyl farnesylacetate, having a potential anti-ulcer activity[4], will be reported in future communication[5].

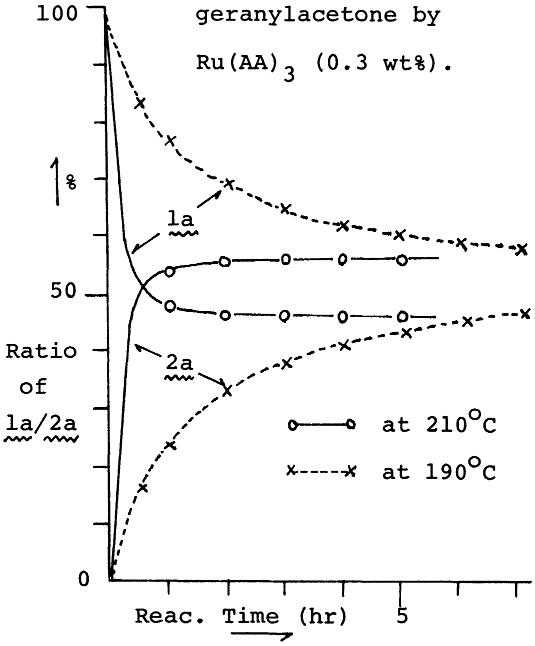


Fig. Isomerization of cis-geranylacetone by Ru(AA)$_3$ (0.3 wt%).

Table. Isomerization of $1 \rightleftarrows 2$ by Ru(AA)$_3$.

Starting Compds. [X=]	Ru(AA)$_3$ [wt%]	Reac. Conditions*	Ratio of 1/2**	Selectivity [%]**
1a [$-CH_2CH_2COCH_3$]	0.3	190°C, 6 hr	57/43	98***
1a	0.3	210°C, 1 hr	48/52	95
2a	0.2	200°C, 3.5 hr	30/70	95
1b [$-CH{=}CHCOCH_3$]	0.2	190°C, 5 hr	66/34	87
1c [$-CO_2C_2H_5$]	0.1	200°C, 3 hr	64/36	96
1d [-CN]	0.3	180°C, 7.5 hr	73/27	94
1e [$-CH_2CH_2CO_2C_2H_5$]	0.2	200°C, 3 hr	56/44	94***
2e	0.2	200°C, 4 hr	69/31	96

* Every treatment was carried out in nitrogen atmosphere without use of solvent.

** Determined by G.L.C. analyses; PEG 20M 10% on Chromosorb W (AW).

*** Recovery of the mixture after distillation was 93% (1a) and 90% (1e).

References and Notes

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2) G. Bellinzona and F. Bettinetti, Gazz. Chim. Ital., 90, 426 (1960): a) on the isomerization of cinnamic acid in refluxing ethanol. b) on the isomerization of stilbene in ethanol.
3) C. A. Henrick, W. E. Willy, J. W. Baum, T. A. Baer, B. A. Garcia, T. A. Mastre, and S. M. Chang, J. Org. Chem., 40, 1 (1975).
4) Recently the all four isomers were separated and identified by A. Didcmenico and D. Misiti, Chem. Scripta., 8, 84 (1975).
5) I would like to thank Mr. Yoshiaki Omura, Mr. Takashi Nishida, and Dr. Kazuo Itoi for their kind advices.

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