Acidity of Methine Hydrogen in Cyclopropyl Ketone—*Cis-Trans* Rearrangement of 1-Acetyl-2-phenylcyclopropane with Base

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Acidity of methine hydrogen in cyclopropyl ketone is of current interest. Dessy *et al.* reported that the base catalyzed isotopic exchange of the methine hydrogen in cyclopropyl phenyl ketone proceeded 14 times faster than the methine hydrogen in isobutyrophenone in D_2O-DMF solution because of the *s*-character of the carbon orbital of cyclopropane.[1] Recent reinvestigation of the same reaction, however, has shown that the exchange in D_2O-DMF containing NaOD (0.17 M) underwent resistance in 14 hr at 60°C,[2] and accordingly the above conclusion should be modified.

Rappe and Sachs reported also that the exchange of cyclopropyl methine proton is much slower than that of isopropyl methine proton in the same system.[3] Van der Maeden *et al.*, however, gave results which suggest that the opposite may be the case.[4] It is clear that further investigations are required on the acidity of cyclopropyl methine hydrogen. We wish to report our results on this question.

cis-1-Acetyl-2-phenylcyclopropane rearranges to *trans* isomer readily in 75% ethanol solution containing potassium hydroxide. The rates of the reaction were followed by gas chromatographical method. The results showed that the reaction follows first-order rate law at various base concentrations at 40 and 60°C. Constant values of k_1/[KOH] were obtained at both temperatures (Table 1).

TABLE 1. KINETICAL DATA OF REARRANGEMENT OF *cis*-1-ACETYL-2-PHENYLCYCLOPROPANE TO *trans*-ISOMER IN 75% ETHANOL

React. temp. °C	Initial concn. of *cis*-isomer (mol/*l*)	KOH concn. (mol/*l*)	$k_1 \cdot 10^5$ sec^{-1}	$\frac{k_1}{[KOH]} \cdot 10^4$
40.0	0.100	0.100	2.7	2.7
	0.100	0.196	5.2	2.7
	0.194	0.194	5.7	2.9
	0.200	0.388	10.8	2.8
60.0	0.0997	0.102	18	17
	0.0989	0.204	33	16
	0.194	0.204	32	16

Activation energy, 18 kcal/mol.

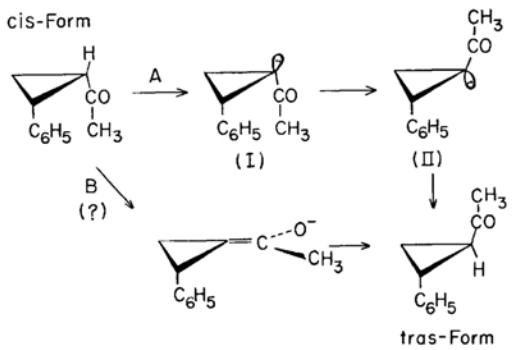

Fig. 1. Possible pathways for the rearrangement.

Two possible pathways of the reaction can be described (A and B in Fig. 1). Pathway B, however, appears to be unlikely, since enolization in this system is repressed because of steric inhibition.[2] The most probable mechanism A involves proton abstraction from cyclopropyl methine system to form carbanion. The rate determining step appears to be the proton abstraction, since no plausible reason for the stability of carbanion I can be found in this system. Large k_1 values obtained here make sharp contrast with those by isotopic exchange method. The reason for the disagreement might be found in the effect of the phenyl group attached to the cyclopropane ring. Assuming this to be the case, a pronounced effect through the ring is expected. Experiments along the line are under progress.

cis-1-Acetyl-2-phenylcyclopropane was prepared by alkaline deacetylation of 1,1-diacetyl-2-phenylcyclopropane[5] in 75% ethanol containing potassium hydroxide at 0°C. *Cis*- and *trans*-isomers were separated by column chromatography using WAKO GEL C-200 and hexane - ethyl acetate (90 : 10).

1) By R. Dessy, Y. Okuzumi and A. Chen in H. Shechter and M. J. Collins and R. Dessy, Y. Okuzumi and A. Chen, *J. Am. Chem. Soc.*, **84**, 2905 (1962).

2) H. W. Amburn, K. C. Kauffman and H. Shechter, *ibid.*, **91**, 530 (1969).

3) C. Rappe and W. H. Sachs, *Tetrahedron*, **24**, 6287 (1968).

4) F. P. B. van der Maeden, H. Steinberg and Th. J. de Boer, *Tetrahedron Letters*, **1967**, 4521.

5) To be published shortly.