Difference between the Acidities of *cis*- and *trans*-Hydrogens at a Cyclopropane Ring Carbon

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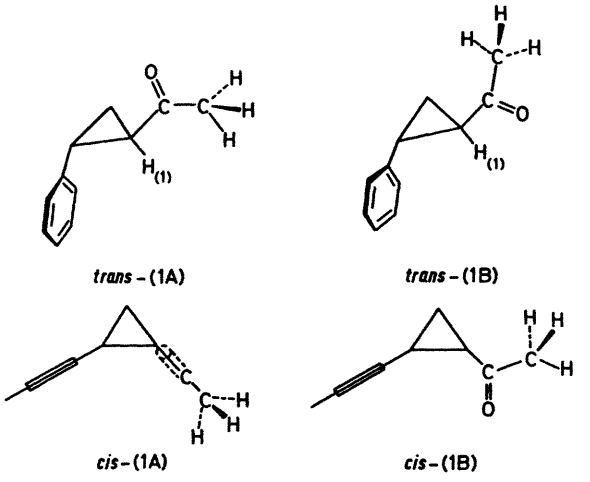
Summary Results from deuterium exchange experiments indicate that the acidity of 1-H of *cis*-1-acetyl-2-phenylcyclopropane is much higher than that of 1-H of the *trans*-isomer; this agrees with results of CNDO/2 calculations.

ACIDITIES of hydrogens at cyclopropane ring carbons have been extensively studied.[1] Seemingly, however, the difference in the acidity of such a hydrogen which is *cis* or *trans* with respect to the substituent at the other ring carbon has not been examined. Our results on the alkaline cleavage of 1,1-diacetyl-2-phenylcyclopropane at 0 °C showed that the *trans*-acetyl group was cleaved selectively to give *cis*-1-acetyl-2-phenylcyclopropane [*cis*-(**1**)] which is considered to be much more unstable than *trans*-(**1**). This suggests that the corresponding carbanion of *cis*-(**1**) was formed more readily than that of *trans*-(**1**).[2] Thus, the acidities of the hydrogens at the ring carbons bonded to the acetyl group of *cis*-(**1**) and *trans*-(**1**) should be different. To examine this, deuterium exchange of *cis*- and *trans*-(**1**) in the presence of base has been studied.†

† For preparation of *cis*- and *trans*-(**1**) see ref. 2.



The reactions were followed by determining the decrease in the proton signal of 1-H (*cis*-, δ 2·5; *trans*-, δ 2·3) which could be sufficiently resolved to permit valid integration of the individual resonances only by 220 MHz n.m.r. spectroscopy.

The reactions were run in CD_3OD–D_2O (75:25 v/v) as solvent containing NaOD at 40 °C. Upon adding a D_2O solution of NaOD to *trans*-(**1**) in CD_3OD–D_2O, the signals of the acetyl protons disappeared immediately, since the base-catalysed deuterium exchange proceeded rapidly, and then the intensities of those due to 1-H decreased gradually. With initial concentrations of 0·76 and 1·3 M for *trans*-(**1**) and NaOD, respectively, the pseudo-first order rate constant for the exchange of H was calculated to be 1×10^{-6} s^{-1} and the second-order rate constant $k_{ex.-trans}$ was found to be $0{\cdot}9 \times 10^{-6}$ l mol^{-1} s^{-1}.

Under similar conditions (initial concentrations of 0·42 and 1·40 M for *cis*-(**1**) and NaOD, respectively), the exchange of acetyl protons of *cis*-(**1**) was also very fast, followed by exchange of 1-H and rearrangement to *trans*-(**1**). The rate of exchange was much faster than that of the rearrangement. The second-order rate constant for the exchange $k_{ex.-cis}$ was calculated to be $0{\cdot}9 \times 10^{-4}$ l mol^{-1} s^{-1}, and that for the rearrangement $k_{rearr.-cis}$ was 3×10^{-5} l mol^{-1} s^{-1}, respectively.

Although these results are only qualitative, it is clear that $k_{ex\text{-}cis\text{-}(1)} > k_{rearr\text{-}cis\text{-}(1)} \gg k_{ex\text{-}trans\text{-}(1)}$. The exchange rate of 1-H of *cis*-(**1**) (kinetic acidity) is faster than that of 1-H of *trans*-(**1**) by a factor of 100.

TABLE. CNDO/2 results

	1-H electron density	C(1)–H(1) bond energy /eV	C(1) electron density	Total energy /eV
trans-(**1A**)	0·9912	−0·7538	3·9818	−105·7210
cis-(**1A**)	0·9896	−0·7540	3·9746	−105·5808
trans-(**1B**)	0·9731	−0·7453	3·9854	−105·7134
cis-(**1B**)	0·9743	−0·7454	3·9843	−105·7196

The results obtained here agree with those of the aforementioned acetyl cleavage. Explanation of these results is difficult and detailed discussion requires further experiments. One plausible explanation is that conjugation between the phenyl and acetyl groups through the cyclopropane ring can operate only in the case of *cis*-(**1**) since the three bonds phenyl–cyclopropyl, cyclopropane C–C_1, and cyclopropyl–acetyl are coplanar, but this is not possible for *trans*-(**1**). This may be reflected in the difference between the kinetic acidities of 1-H in the isomers.

The question as to whether a pyramidal ketonic carbanion can exist or not remains unresolved.[3] The observation that the exchange rate of 1-H in *cis*-(**1**) was greater than that of isomerization to *trans*-(**1**) shows that the kinetic acidity of *cis*-(**1**) is stronger than that of *trans*-(**1**) and that a pyramidal ketonic carbanion can possibly exist.

CNDO/2 calculations (by Fujimoto) of the thermodynamic acidities gave similar results. The calculations were made assuming the conformations *cis*-(**1A**), *cis*-(**1B**), *trans*-(**1A**), and *trans*-(**1B**) which are considered to be the most stable. For *cis*-(**1A**), both phenyl and acetyl planes are perpendicular to the cyclopropane, and for *cis*-(**1B**), the bond between the cyclopropane and the acetyl group in *cis*-(**1A**) is rotated by 90° towards the direction where the phenyl and acetyl groups are on opposite sides of the ring centre.

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[1] See, for example, 'Rodd's Chemistry of Carbon Compounds, IIA,' 2nd Edn., Elsevier, Amsterdam, 1967, p. 28; H. W. Amburn, K. C. Kauffman, and H. Shechter, *J. Amer. Chem. Soc.*, 1969, **91**, 530.
[2] O. Itoh, N. Yamamoto, K. Nakano, T. Sugita, and K. Ichikawa, *Bull. Chem. Soc. Japan*, 1975, **48**, 3698.
[3] See, for example, 'Isotopes in Organic Chemistry,' eds. E. Buncel and C. C. Lee, Vol. 2, Elsevier, Amsterdam, 1976, p. 58.