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-phenyl-cyclopropane 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.

trans - (1A)   *trans* - (1B)

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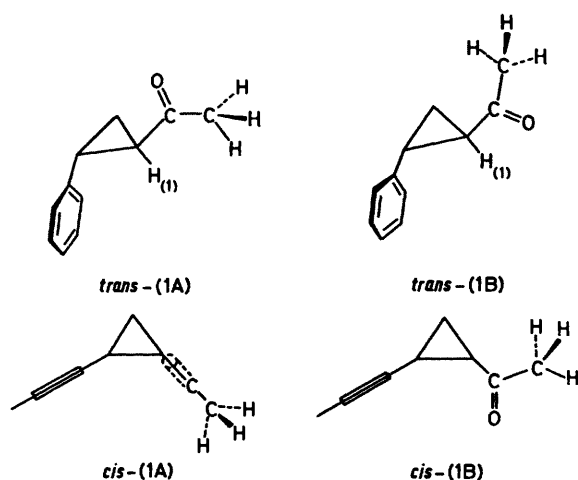
The reactions were followed by determining the decrease in the proton signal of 1-H (*cis*-, δ 2·5; *trans*-, δ 2·3) which could be sufficiently resolved to permit valid integration of the individual resonances only by 220 MHz n.m.r. spectroscopy.

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 $0·9 \times 10^{-6}$ 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 $0·9 \times 10^{-4}$ 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 $k_{ex-cis-(1)} > k_{rearr-cis-(1)} \gg k_{ex-trans-(1)}$. 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 afore-mentioned 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 cyclo-propane 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 thermo-dynamic 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.

[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.