The Addition of HCl and HBr to 1-Phenyl-4-t-butylcyclohexene. The Isolation of the Stereomers *cis*- and *trans*-1-Chloro-1-phenyl-4-t-butylcyclohexane and the Stereochemistry of the Addition Process

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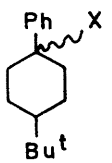
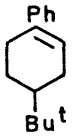
Summary Solid geometrical isomers have been isolated from the reaction of 1-phenyl-4-t-butylcyclohexene and HCl, which is shown to be a *syn*-addition process.

THE stereochemistry and mechanism of addition of HX to cyclic alkenes is an active and controversial subject.[1] We have actually isolated two geometrical isomers of (**1a**) from addition of HCl to (**2**). A thorough search of the literature[2] revealed only one publication[3] demonstrating the *isolation* of stereomers from additions of HCl and DCl to (**3**). Alkene (**2**) was selected for study because it should give Markovnikov addition.



(1)

a; X = Cl
b; X = Br



(2)

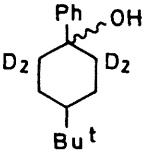
(3)

Treatment of (**2**) in n-pentane at −70° under N_2 with anhydrous HCl (g) with vigorous stirring gave, after 20 min., *cis*-(**1a**) (77·9%) and *trans*-(**1a**) (22·1%) [according to integration of the signals for t-butyl protons in the n.m.r. spectrum (*cis* and *trans* refer to relative positions of the t-butyl and phenyl groups)]. N.m.r. (**$CDCl_3$**) for *cis*-(**1a**): δ 0·74 (s, t-butyl 9H), 1·50 (m, ring protons 5H), 2·27 (d, 2,6-ax. 2H), 2·95 (d, 2,6-eq. 2H), and 7·35 (m, phenyl 5H); for *trans*-(**1a**): δ 0·92 (s, t-butyl 9H), 1·78 (m, ring protons 7H), 2·43 (d, 2,6-eq. 2H), and 7·35 (m, phenyl 5H). No signals for the t-butyl protons (δ 0·89) and =C–*H* (δ 5·95) proton in (**2**) were observable, indicating an essentially quantitative conversion.

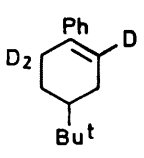
Isolation of pure *cis*-(**1a**) from the solid mixture obtained after evaporating n-pentane from the reaction mixture proved tedious. Two recrystallizations (n pentane at −15°) yielded *cis*-(**1a**) [7·6% based on (**2**)], m.p. 90—91°, free of both (**2**) and *trans*-(**1a**) according to n.m.r., i.r., and elemental analyses. In a separate experiment (same conditions), the solid mixture was dissolved in absolute ethanol and cooled to −70° causing *trans*-(**1a**) (44%, m.p. 64·5—65·5°; evac. tube) to precipitate, free of (**2**) and *cis*-(**1a**). Strong bands at 685 cm^{-1} for equatorial C–Cl stretch in *cis*-(**1a**) and at 647 cm^{-1} for axial C–Cl stretch in *trans*-(**1a**) were observed in the respective laser Raman spectra.[4]

An equimolar mixture of *cis*-(**1a**) and *trans*-(**1a**) treated under usual reaction conditions for 45 min. was altered to a ratio of 1 : 6·1. This result, plus the observation that over a 25-fold range of concentration for (**2**), *cis*-(**1a**) predominated over *trans*-(**1a**) in solution for the first 30 min., confirms that *cis*-(**1a**) is indeed the kinetic product. The highest ratio of *trans*-(**1a**) : *cis*-(**1a**) recorded starting from (**2**) was 5 : 1 after 1 hr., indicating *trans*-(**1a**) as the most stable stereomer. Heating a solid sample of *cis*-(**1a**) at its m.p. for a few seconds and cooling rapidly gave a mixture of (**2**) and *trans*-(**1a**). This is somewhat surprising in view of the Cl atom being axial in *trans*-(**1a**) and *anti* situated to the vicinal proton for potentially easy elimination.

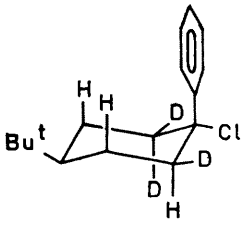
Addition of HBr (g) under almost identical conditions (at −78°) gave *cis*- (m.p. 84—4·5°, from di-isopropyl ether) and *trans*-(**1b**) (m.p. 73—75°, from n-hexane at −15°) but accurate elemental analysis was only possible on *trans*-(**1b**). Decomposition of *cis*-(**1b**) is rapid even when it is stored in highly evacuated containers. A fresh sample of *trans*-(**1b**) showed n.m.r. peaks (CCl_4) at δ 0·70 (s, t-butyl 9H), 1·67 (m, ring protons 7H), 2·60 (d, 2,6-eq. 2H), and 7·30 (m, phenyl 5H). Absorption occurred at 555 cm^{-1} in the Raman spectrum. Isolation of *trans*-(**1b**) was possible from the solid reaction product, but *cis*-(**1b**) required special techniques. The residue from recrystallizations (di-isopropyl ether) was dissolved in tetrahydrofuran, and treated with 2 equiv. of lithium (small pieces) under N_2 for 12 hr. Filtration (LiBr), evaporation of solvent, and recrystallization (di-isopropyl ether) gave *cis*-(**1b**). Raman absorptions were observed at 638 cm^{-1} [*cis*-(**1b**)] and 678 cm^{-1} [*trans*-(**1b**)]. Solutions of *cis*-(**1b**) began to show (n.m.r.) traces of *trans*-(**1b**) within a few minutes.



(4)



(5)



(6)

The stereochemistry of the addition of HCl (g) was elucidated by employing (**5**) made from (**4**).[5] After 15 min., the addition was terminated and (**6**) was isolated (24·8%), m.p. 90—91°. N.m.r. spectra of (**6**) and *cis*-(**1a**) were identical except at δ 2·95 which integrated for zero protons and at δ 2·21 (1H, doublet) in (**6**). This latter axial proton is strong evidence for an initial *syn*-addition since *cis*-(**1a**) is formed first. This result appears related to that of Dewar and Fahey[6] although they did not isolate geometrical isomers from reaction of indene or acenaphthalene with DCl. Recent results on the treatment of [1,3,3-$^2H_3$]cyclohexene in acetic acid indicate that more than one competing reaction occurs in their system to give both *syn*- and *anti*-addition products.[7] In our system both

rate of addition of HCl (g) and temperature affect the product ratio. A 10-fold decrease in rate of HCl (g) addition not only decreased the rate of reaction (at least 2 fold) but also resulted in a 1 : 1 ratio of *cis*-(**1a**) : *trans*-(**1a**) even after 100 min. at −70°. Obviously, the rate of formation of *trans*-(**1a**) from *cis*-(**1a**) is dependent upon the rate of addition of HCl (g). Similarly, the ratio of *cis*-(**1a**) : *trans*-(**1a**) also varied with temperature (1·17 : 1 at −78° and 1·36 : 1 at −54°).

It has been shown that shielding effects of a non-bonded phenyl group can influence the chemical shift of protons even at distances of 4 Å.[8] For the *cis*-isomers listed in the Table, Courtauld models demonstrate that the t-butyl protons can be 1·25 Å from the phenyl ring. The *trans*-isomers, however, are so structured that similar shielding effects would be negligible. Interestingly, resonances for t-butyl protons in solution for a series of substituted cyclohexane isomers are significantly separated, as shown in the Table. In all cases the *cis*-isomer had absorption for t-butyl protons at higher field. It is not unreasonable that the π-system of the phenyl group causes increased shielding of the t-butyl protons. This hypothesis is being investigated.

TABLE

Chemical shifts for t-butyl protons in a series of 1-substituted 1-phenyl-4-t-butylcyclohexane derivatives at 60 MHz

X at C-1	δ (p.p.m.)[a] *cis*	*trans*
Cl	0·73	0·95
Br	0·70	0·90
OH	0·77	0·89
H	0·80	0·88

[a] Equimolar solutions (CCl_4) with Me_4Si as internal standard.

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[1] For recent reviews, see R. C. Fahey, "The Stereochemistry of Electrophilic additions to Olefins and Acetylenes," in 'Topics in Stereochemistry,' eds. E. L. Eliel and N. L. Allinger, Vol. 3, Interscience, New York, 1965; P. B. D. de la Mare and R. Bolton, 'Electrophilic Additions to Unsaturated Systems,' Elsevier, New York, 1966; D. E. Gibbs, Ph.D. Thesis, Oklahoma State University, 1969.

[2] For examples of additions of HX to *simple* cyclic alkenes (both isomers not always isolated), see G. S. Hammond and C. H. Collins, *J. Amer. Chem. Soc.*, 1960, **82**, 4323; M. J. S. Dewar and R. C. Fahey, *ibid.*, 1963, **85**, 3645 and references therein; H. Kwart and J. L. Nyce, *ibid.*, 1964, **86**, 2601; and P. O. Readio and P. S. Skell, *J. Org. Chem.*, 1966, **31**, 753.

[3] P. K. Freeman, F. A. Raymond, and M. F. Grostic, *J. Org. Chem.*, 1967, **32**, 24.

[4] Stretching vibrations for C–Cl bonds in chlorocyclohexane at 684·5 (ax.) and 731 (eq.) cm^{-1} have been reported in the Raman spectrum; K. Kozima and K. Sakashita, *Bull. Chem. Soc. Japan*, 1958, **31**, 796.

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[6] M. J. S. Dewar and R. L. Fahey, *J. Amer. Chem. Soc.*, 1963, **85**, 2248; 3645.

[7] R. C. Fahey and M. W. Monaham, *J. Amer. Chem. Soc.*, 1970, **92**, 2816.

[8] L. M. Jackman and S. Sternhill, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, New York, 1969, pp. 94–98; and references therein.