Tetrahedron Letters No. 19, pp 1615 - 1616, 1976. Pergamon Press. Printed in Great Britain.

STEREOCHEMICAL STUDIES, XXVIII[1]; *t*-BUTYLCYCLOPENTANE DERIVATIVES, IV[2]

EFFECT OF THE *t*-BUTYL GROUP IN 1,2-DISUBSTITUED 4-*t*-BUTYLCYCLOPENTANES

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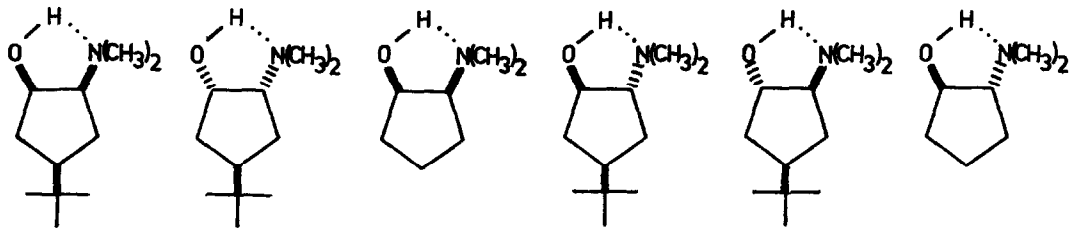
(Received in UK 16 March 1976; accepted for publication 29 March 1976)

In contrast to intensive investigations[3] on *t*-butylcyclohexane derivatives, *t*-butylcyclopentanes have been scarcely studied. This contrast may be explained by the fact that only negligible differences in the reactivity of *cis*- and *trans*-3-*t*-butylcyclopentane derivatives were found[4,5]. In this paper we wish to show that, in the case of 1,2-disubstituted-4-*t*-butylcyclopentanes[6], the effect of the *t*-butyl group is more pronounced.

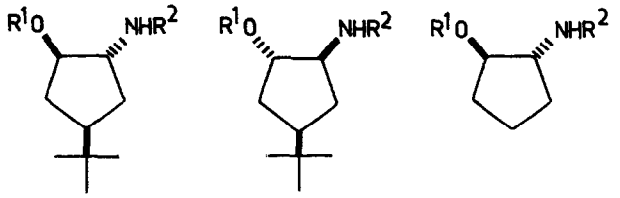
IR spectra of 1-6[7] were obtained in the region 3300-3700 cm^{-1} in tetrachloroethylene on a Unicam SP 100 spectrophotometer, with 6 cm^{-1} = 1 cm resolution; numerical separation of the bands was done with an Elliott 503 computer using the damped least squares method. The values $\Delta\nu = \nu(OH)_{free} - \nu(OH)_{bonded}$ obtained are as follows.



1 $\Delta\nu$ = 162 cm^{-1} | 2 135 cm^{-1} | 3 148 cm^{-1} | 4 40 cm^{-1} | 5 43 cm^{-1} | 6 37 cm^{-1}

Comparison of the $\Delta\nu$ values reveals a pronounced effect of the *t*-butyl group on the dihedral angle of the substituents in positions 1 and 2. The existence of intramolecular hydrogen bonding also in the *trans* isomers is remarkable, since in the case of cyclopentane-*trans*-1,2-diol no intramolecular hydrogen bond was observed[8].

The first order rate constants of the Δ^2-oxazoline formation[3] of *trans*--2-benzamido-*cis*- and *trans*-4-*t*-butylcyclopentylmethanesulphonate (7, 8) compared with *trans*-2-benzamidocyclopentylmethanesulphonate (9) were measured in abs. ethanol in the presence of NaOAc at 0°. The k_1 values were:

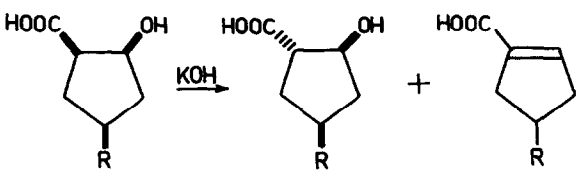


7 8 9

$R^1 = CH_3SO_2$; $R^2 = C_6H_5CO$

$k_1 = 2.25 \cdot 10^{-5}$, $4.25 \cdot 10^{-5}$ and $7.67 \cdot 10^{-5}$ for 7, 8 and 9, respectively. Since the Δ^2-oxazoline formation is favoured in the case of antiparallel arrangement of the reacting substituents, the results indicate that this arrangement is achieved to a lesser degree in the *t*-butyl-substituted system.

A more pronounced effect of the *t*-butyl group follows from the results obtained by alkaline isomerization of *cis*-2-hydroxycyclopentanecarboxylic acid (10) and *cis*-2-hydroxy-4-*t*-butylcyclopentanecarboxylic acid (13), the first order rate constants for the *cis* → *trans* isomerization determined in great excess of 6 M KOH at 100° being[9] $k_1 \cdot 10^3 = 7.33$ for 10 and $k_1 \cdot 10^3 = 2.42$ for 13. While the dehydration of 10 is known[10] to proceed very readily, we surprisingly found that this reaction of the *t*-butyl derivative 13 is significantly slower.



10: R= H 11: R= H 12: R= H

13: R= *t*-Bu 14: R= *t*-Bu 15: R= *t*-Bu

Under the above conditions of isomerization, 10 yields 34.7% of 1-cyclopentene-1-carboxylic acid (12) in 30 hrs, while 13 gives only 6% of 4-*t*-butylcyclopent-1,2-ene-1-carboxylic acid (15). *Antiperiplanar* position of the groups splitting out is considered to be the most advantageous for dehydration. This requirement is obviously less fulfilled in the case of the *t*-butyl derivative 13, than in the case of 10.

Acknowledgement. The authors are indebted to Dr. A. Vitek for the numerical separation of the IR spectra.

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