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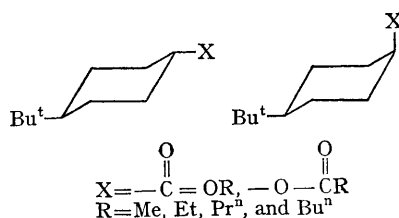
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Vapour Pressures of *cis*- and *trans*-Esters of 4-*t*-Butylcyclohexanecarboxylic Acid and 4-*t*-Butylcyclohexanol

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DURING the gas-liquid chromatographic study of the solution thermodynamics of isomeric cyclohexane derivatives, it became necessary to measure the vapour pressures of the esters of 4-*t*-butylcyclohexanecarboxylic acid and 4-*t*-butylcyclohexanol.



Pure *cis*- and *trans*-esters were obtained by preparative-scale gas-chromatographic separation of the appropriate isomeric pair, followed by trapping at liquid nitrogen temperatures. For the vapour pressure measurements, a semi-micro (0.1—0.3 ml.) modification of the Ramsey-Young¹ apparatus was constructed. For a given compound, vapour pressures above and below 176° were determined, and the value at 176° was then obtained from the straight line plot of $\log P^0$ vs. $1/T$. Several substances of known vapour pressure (and different polarities) were measured in this manner, and the results indicated that the experimental error was ± 0.15 mm.

Summarized in Tables 1 and 2 are the results obtained at 176°. In both series the *cis*-isomer always has a higher vapour pressure than the

corresponding *trans*-ester. This result is quite reasonable if one assumes that dipole-dipole forces are primarily responsible for intermolecular interactions. A polar functional group should be more accessible in the equatorial position than the axial position for intermolecular association. Consequently, the *trans*-isomer should associate with itself in the liquid state to a greater extent than the *cis*-isomer, and the vapour pressure of the *trans*- will thus be less than that of the *cis*-isomer at a given temperature.² Thus, for two isomers of

TABLE 1

Vapour pressure data for esters of 4-*t*-butylcyclohexanecarboxylic acid, $T = 176^\circ$

R	$P^0_{cis}(\text{mm.})^\dagger$	$P^0_{trans}(\text{mm.})$	(P^0_{cis}/P^0_{trans})
Me	133.3	97.7	1.32
Et	101.2	70.6	1.43
Pr ⁿ	59.9	40.5	1.48
Bu ⁿ	36.1	22.8	1.58

$^\dagger P^0$ = saturation vapour pressure at 176°.

roughly equivalent dipole moment, the one with the more accessible polar group will have the higher boiling point. (This statement may be considered a corollary of the dipole rule.³) Differential accessibility of the ester group is also suggested by the equatorial isomer of ethyl 4-*t*-butylcyclohexanecarboxylate being saponified about 20 times as fast as the axial isomer in 70% ethanolic sodium hydroxide at 25°.⁴

Comparison of the data shows that the P^0_{cis}/P^0_{trans} ratio for any ester of 4-t-butylcyclohexanecarboxylic acid exceeds the corresponding value for the ester of identical molecular weight of 4-t-butylcyclohexanol. This result can be explained if it is accepted that intermolecular interaction of the polar carbonyl group are stronger than those of the ethereal oxygen. As already stated, the sum of steric effects exerted by the cyclohexane ring render the axial carbonyl less accessible than the equatorial carbonyl. As the carbonyl interaction zone is removed from the cyclohexane ring, these steric effects will diminish in importance, with the resultant decrease in the differences in accessibility of the carbonyl group between the *cis*- and *trans*-esters. Since the ratio, P^0_{cis}/P^0_{trans} , reflects the differences in pure liquid *trans-trans* interactions as opposed to pure liquid *cis-cis* interactions, for any given R group,

TABLE 2

Vapour pressure data for esters of 4-t-butylcyclohexanol,
 $T = 176^\circ$

R	P^0_{cis} (mm.)	P^0_{trans} (mm.)	(P^0_{cis}/P^0_{trans})
Me	147.0	119.0	1.23
Et	104.0	80.5	1.29
Pr ^a	58.5	43.5	1.35
Bu ^a	36.2	26.5	1.42

the ratio would thus be expected to be less for the ester of 4-t-butylcyclohexanol than the ester of 4-t-butylcyclohexanecarboxylic acid. This same trend of relative accessibility of the carbonyl for the two ester series is observed when one compares the differences between the equatorial and axial rates of saponification for both types of esters. The ratio of rate constants, k_{trans}/k_{cis} , is found to be considerably smaller for the 4-t-butylcyclohexanol esters relative to the 4-t-butylcyclohexanecarboxylic acid esters.⁵

The results in Tables 1 and 2 also indicate for both series that as R increases in the straight chain series from methyl to n-butyl, the ratio P^0_{cis}/P^0_{trans} also increases. This surprising trend means that the *cis*-isomer is becoming relatively more volatile than the *trans*-isomer as the molecular weight is increased. Within the confines of this Communication, it is not possible to explore the reasons for this trend. However, an explanation involving the competing effects of dipole *vs.* dispersion forces on intermolecular association in the liquid state, as well as gas chromatographic solution thermodynamic results, will shortly be presented.

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⁴ E. L. Eliel, H. Haubenstock, and R. V. Acharya, *J. Amer. Chem. Soc.*, 1961, **83**, 2351.

⁵ Ref. 3, pp. 72-74.