

Gas Chromatographic Investigations of Cyclic Ketones.

Tore Ledaal

Universitetets Kjemiske Institutt, Blindern, Oslo 3, Norway.

(Received in U.K. 30 June 1967)

The carbonyl group is known to cause a lowering of the rotational barrier of neighbouring C-C single bonds¹. Its orientation may be important in determining the conformation of cyclic ketones. For each ring size such orientations should be preferred which result in the lowest Bayer and Pitzer strain and the minimum transannular hydrogen repulsion².

Interesting questions in this connection are, among others, the following: Do preferred distinct orientations of the carbonyl group really exist? Do the orientations change in a regular or an irregular manner within a homologous series? Experiments which may give an answer to these questions are in progress. The situation for small ring ketones are to some extent predictable and experimentally clarified. This, however, is not the case with the medium and large cyclic ketones. It has been suggested that conformers with the carbonyl oxygen located inside the

ring predominates for cyclodecanone and its higher homologues³. With 11 or more atoms in the ring Stuart molecular models of such "inside-carbonyl" conformers can easily be made.

Experimental indications which have been taken as a support of the "inside-carbonyl" conformation of cyclic ketones include differences in chemical reactivity⁴, spectroscopic properties⁵, and dipole moments⁶. It should be pointed out, however, that the existing experimental evidence is quite insufficient to allow any safe conclusions to be drawn about the carbonyl group orientation in medium-sized cyclic ketones.

The present investigation is based on the idea that differences in carbonyl group orientations in cyclic ketones in the gas phase might be reflected in their gas chromatographic retention times, particularly when using polar columns. The ratio between retention times on polar and nonpolar columns, R_p/R_{np} , was regarded as a function of the population of "carbonyl out" conformers.

As the carbonyl group becomes a gradually less dominating part of the molecule with increasing ring size, it was to be anticipated that the above ratio of retention times should decrease nearly linearly with increasing ring size, provided the carbonyl group orientations remain nearly the same. A corresponding graph of differences in retention times between neighbouring ketones should also

form a nearly straight line. The experimental results are given in Figs. 1 and 2.

As seen the graphs do not form straight lines. Fig. 1 shows plots of the ratio of retention times on polar and nonpolar columns, R_p/R_{np} , for the $C_5 - C_{12}$ membered cycloalkanones. Curve I is for temperature programmed columns, 80 - 190 °C, with a heating rate of 4 °C/min. Curves II and III are for constant column temperatures of 140 and 125 °C respectively. A rise in column temperature seems to give an increased negative slope of the first parts of the curves, but shows an opposite effect on their other ends. (High column temperatures gave as expected too low retention times for the lower ketones, while their higher homologues not could be run at too low temperatures.) Curve I may thus be regarded to represent the best values. Here only the values of the 5-, 6-, and 7- ring ketones and those of their 9-, 10-, and 11- ring homologues are seen to fall on two straight lines with different slopes. The 11- and the 12- ring ketone have the same R_p/R_{np} value. The curve seems to indicate different orientations of the carbonyl groups for the various ring sizes, except for the 11- and 12- membered rings, where the orientation may be the same.

In Fig. 2 the differences in retention times between a n+1- and a n-membered cycloalkanone are given as a function of n. For comparison a plot of C^{13} NMR chemical

Fig. 1.

Ratio between retention times on polar and nonpolar columns, R_p/R_{np} , for cycloalkanones.

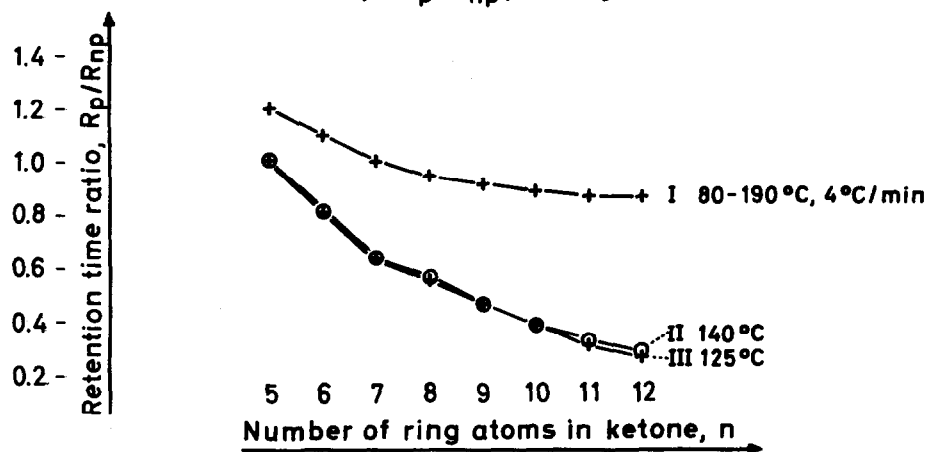
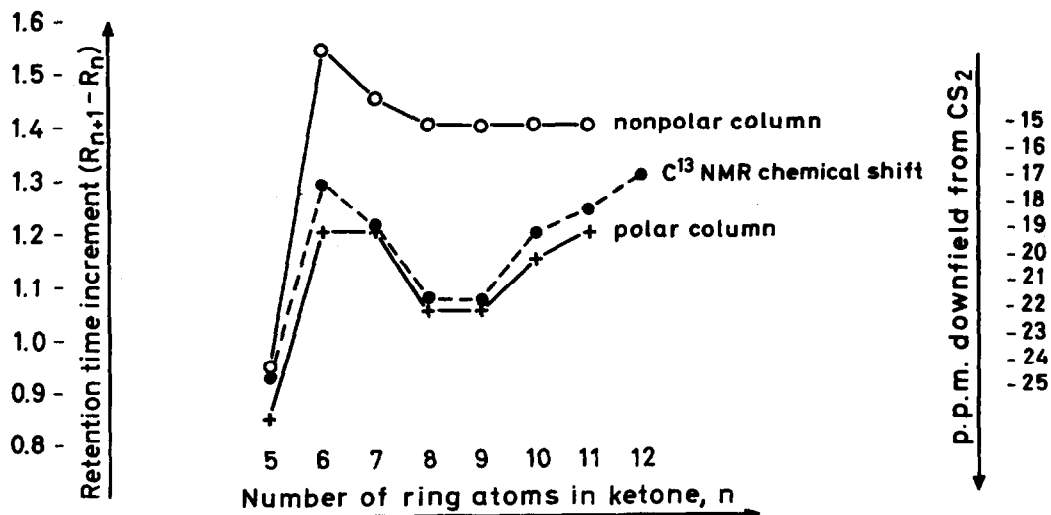


Fig. 2.

Differences in retention times between $C_{(n+1)}$ - and C_n -membered cycloalkanones and C^{13} NMR chemical shift of their carbonyl groups.



shift of the carbonyl group as measured by Stothers et al.⁷ is included.

As seen the curves for polar and nonpolar columns are quite different. On the nonpolar column the medium sized ring ketones come out equally spaced. This is markedly different from the polar column, where increments in retention time are seen to parallel closely the variations in the C¹³ NMR chemical shift of the carbonyl groups.

It has already been suggested in other connections that this chemical shift depends in fact of the orientation of the carbonyl group^{8,9}. It seems likely that the two parallel curves reflect one and the same physical reality, indicating that the cyclic ketones even at high temperature have dominating conformations with a characteristic orientation of the carbonyl group.

This study will be extended to open chain ketones and other cyclic ketones,

Experimental.

The ketones were of p.a. grade (Aldrich). Carbon tetrachloride solutions (10 %) were injected separately and in mixture in amounts of 0.5 μ l. The gas chromatograph was an Aerograph Wilkens 1520. Column dimension 4.5 ft x 1/8". The nonpolar column consisted of 20 % Apiezon L and the polar column of 10 % PEG 20 M both on Chromosorb WHMDS.

Acknowledgements.

I wish to thank Norges Almanvitenskapelige Forskningråd for a grant and Mr. J. Stubergh for performing the measurements.

References.

1. J. Dale, Tetrahedron 22 (1966) 3373.
2. J. Dale, Angew. Chem. 5 (1966) 1000.
3. V. Prelog, J. Chem. Soc. 1950 420.
4. V. Prelog, L. Ruzika et al., Helv. Chim. Acta 30 (1947) 1883.
5. V. Prelog, K. Wiesner, W. Ingold and O. Häflinger, Helv. Chim. Acta 31 (1948) 1325.
6. T. Bürer and Hs.H. Günthard, Helv. Chim. Acta 39 (1956) 356.
7. J.B. Stothers and P.C. Lauterbur, Cand. J. Chem 42 (1964) 1563.
8. K.S. Dahmi and J.B. Stothers, Cand. J. Chem. 43 (1965) 479.
9. J.B. Stothers, Quart. Rev. London 19 (1965) 144.