

CHROM. 4314

THIN-LAYER CHROMATOGRAPHIC SEPARATIONS OF CYCLOKETONE  
2,4-DINITROPHENYLHYDRAZONES\*

ROBERT D. SLENTZ

*Wheatland-Chili High School, Scottsville, N.Y. 14546 (U.S.A.)*

AND

ROBERT E. GILMAN AND K. THOMAS FINLEY\*\*

*Department of Chemistry, Rochester Institute of Technology, One Lomb Memorial Drive,  
Rochester, N.Y. 14623 (U.S.A.)*

(Received July 24th, 1969)

## SUMMARY

Ten cycloketone 2,4-dinitrophenylhydrazones have been chromatographed by thin-layer techniques using Eastman Chromagram sheets coated with silica gel and developed with benzene in Eastman sandwich apparatus. Good separations of all test compounds from binary mixtures with the standard cyclohexanone 2,4-dinitrophenylhydrazone are reported as well as good separations of more complex mixtures of the test compounds.

## INTRODUCTION

Many investigators have applied a variety of thin-layer chromatography techniques to a large group of carbonyl 2,4-dinitrophenylhydrazones (2,4-DNPHs). These compounds are particularly well suited to such studies because of the ease of their preparation and their intense orange-yellow color which makes visualization procedures unnecessary.

In all these works, only scattered reference is made to the separation of cycloketone 2,4-DNPHs. A most comprehensive study of TLC separations of carbonyl 2,4-DNPHs was made by BRÜMMER AND MÜLLER-PENNING<sup>1</sup>, in which they investigated nearly 250 compounds using a Kieselguhr G adsorbent with a developing solvent of petroleum ether-chloroform-ethyl acetate (30:3:1). Reported among the many  $R_B$  values ( $R_F$  relative to butter yellow) from this study were those of five cycloketone 2,4-DNPHs: cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone and cyclopentadecanone.

DENTI AND LUBOZ<sup>2</sup> have reported  $R_{for}$  values ( $R_F$  values relative to the  $R_F$  of formaldehyde) for the 2,4-DNPHs of cyclopentanone and cyclohexanone using ad-

\* Abstracted in part from the M.S. Thesis of R. D. SLENTZ.

\*\* Present address: Eastman Kodak Company, Research Laboratories, Rochester, N.Y. 14650, U.S.A.

sorbent layers of Silica Gel G and Alumina G (both alone and impregnated with silver nitrate) with four different solvent mixtures. ZAMOJSKI AND ZAMOJSKA<sup>3</sup> also determined  $R_{for}$  values for these two compounds in a study which included a large number of aliphatic aldehydes and ketones using silica gel with a benzene developer. Both groups obtained good separations for these two compounds. JART<sup>4</sup> included  $R_F$  values for cyclopentanone and cyclohexanone 2,4-DNPHs along with those for 70 other carbonyl compounds\*. SLOOT<sup>5</sup> used alumina impregnated with silver nitrate to separate several 2,4-DNPHs including those of cyclopentanone, cyclohexanone, 3-methylcyclopentanone and 2-methylcyclopentanone.

As far as can be determined, no other studies have included a homologous series of aliphatic cycloketone 2,4-DNPHs as does the study upon which this report is based\*\*.

## EXPERIMENTAL

### Materials

All of the cycloketone 2,4-DNPHs used in this experiment were prepared by the method of SHRINER *et al.*<sup>7</sup> and were recrystallized from methanol until the melting points agreed with those found in the literature<sup>7,8</sup>.

Solvents used for recrystallization, spotting, and developing were all "reagent grade".

Solutions of the test compounds were spotted on 20 × 20 cm Eastman Chromagram Sheets (Type 6061) with a stated silica gel coating thickness of 100  $\mu$ .

Benzene was used exclusively as the solvent for development.

### Procedure

Considerable effort was expended to insure standardization of procedure. The following steps were followed carefully in the collection of all data presented.

(1) Solutions of the 2,4-DNPHs used for spotting were made by dissolving 100 mg of the test compound in 100 ml of a chloroform-methanol (1:1) mixture. Since all the spotting solutions contained the same solvent mixture, the variable effect of different spotting solvents on spot mobility noted by KIDDER AND DEWEY<sup>9</sup> was avoided.

(2) All Chromagram sheets were activated for 60 min in a drying oven at 100–110° before spotting. Activated sheets were stored in a desiccator until spotted.

(3) Spots were applied to the 20 × 20 cm activated Chromagram sheets with a micropipet. Each spot contained 1.5–2.0  $\mu$ l of each compound in the spot. The spot diameter was kept below 3 mm.

(4) Spots were located 20 mm from the bottom edge of the sheet and 20 mm from each side. The distance between adjacent spots was 16 mm. Each sheet contained spots of nine binary mixtures (the 2,4-DNPHs of the standard cyclohexanone and another of the series), a spot of the standard alone, and a spot of one of two complex mixtures. The complex mixtures consisted of five compounds, the derivatives of all the odd-numbered cycloketones or the derivatives of all the even-numbered cycloketones. One such sheet is illustrated after development in Fig. 2.

\* *Editor's note.* There are ten to twenty other papers separating those two compounds.

\*\* *Editor's note.* For a similar separation by PC see ref. 6.

(5) Spotted sheets were heated for 5 min at 100–110° in a drying oven to insure complete evaporation of the spotting solvent. Spotted sheets not developed immediately were stored until used in a desiccator.

(6) The spotted sheets were developed in the Eastman Chromagram Developing Apparatus (6071). Since four such sandwich-type chambers were available, four sheets were developed simultaneously. All development was over a distance of  $150 \pm 4$  mm using benzene as the developing solvent.

## RESULTS AND DISCUSSION

Comparison of  $R_F$  values seems more meaningful when they are reported relative to an internal standard. Because cyclohexanone was available in largest amounts in our laboratory, its 2,4-DNPH was chosen as a standard. The  $R_F$  value of the standard ( $R_S$ ) was then defined as:

$$R_S = \frac{\text{migration distance of cycloketone 2,4-DNPH}}{\text{migration distance of cyclohexanone 2,4-DNPH}}$$

The mean  $R_F$  values and the mean  $R_S$  values for each of the ten cycloketone derivatives included in this study are reported in Table I with their standard deviations. Each of the values in the table represents the mean for twenty separate runs. Only those sheets on which the  $R_F$  value of the standard was 0.22 or less were included in this summary.

### Precision of results

Throughout the experimental procedure, Chromagram sheets were activated, spotted, and developed in groups of four. It was expected, therefore, that the precision within such a group should be very high. In fact, however, considerable deviations were found not only from group to group, but also from sheet to sheet within a group. On some sheets the adsorbent ability of the silica gel layer seemed high, and all the  $R_F$  values were low. On other sheets the adsorbent ability of the silica gel was apparently low and the  $R_F$  values of all compounds were relatively higher. The  $R_F$  value of the standard cyclohexanone 2,4-DNPH varied from 0.16 to 0.41 with 0.22 as the median value.

TABLE I  
 $R_F$  AND  $R_S$  VALUES FOR CYCLOKETONE 2,4-DNPHs

2,4-DNPH of	$R_F \pm \sigma$	$R_S \pm \sigma$
Cyclobutanone	0.13 $\pm$ 0.02	0.61 $\pm$ 0.02
Cyclopentanone	0.15 $\pm$ 0.01	0.73 $\pm$ 0.02
Cyclohexanone	0.20 $\pm$ 0.02	1.00
Cycloheptanone	0.28 $\pm$ 0.02	1.41 $\pm$ 0.04
Cyclooctanone	0.28 $\pm$ 0.02	1.43 $\pm$ 0.04
Cyclononanone	0.33 $\pm$ 0.02	1.71 $\pm$ 0.05
Cyclodecanone	0.40 $\pm$ 0.04	2.06 $\pm$ 0.08
Cycloundecanone	0.44 $\pm$ 0.04	2.23 $\pm$ 0.11
Cyclododecanone	0.49 $\pm$ 0.04	2.53 $\pm$ 0.12
Cyclopentadecanone	0.53 $\pm$ 0.04	2.70 $\pm$ 0.12

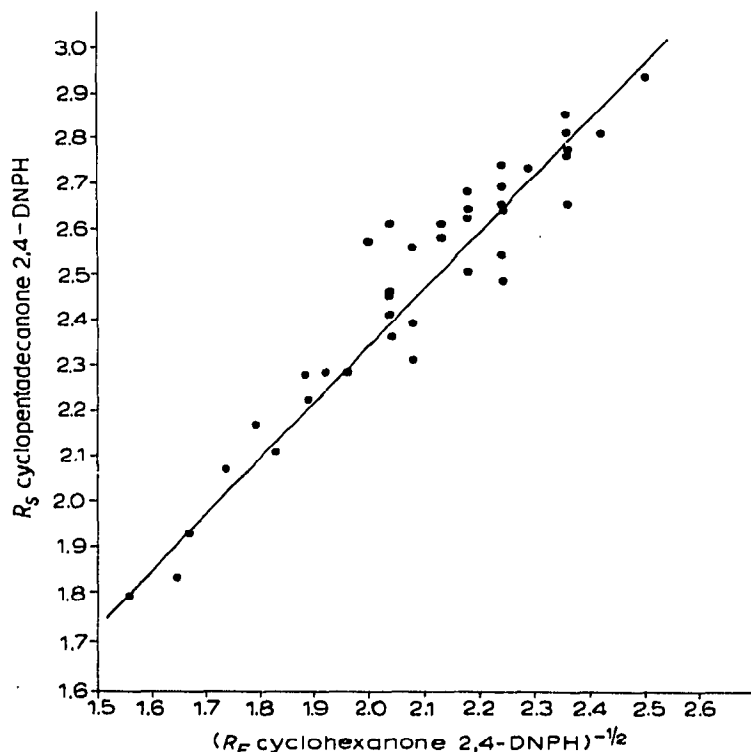


Fig. 1. Graph of the  $R_S$  value for cyclopentadecanone 2,4-DNPH plotted against the reciprocal of the square root of the  $R_F$  value of the standard.

On those sheets on which the  $R_F$  value of the standard was high, the  $R_S$  values of all test compounds were lowered with the exception of cyclobutanone and cyclopentanone 2,4-DNPHs, which increased slightly with increasing  $R_F$  value of the standard. Fig. 1 shows a graph of the  $R_S$  value for cyclopentadecanone 2,4-DNPH plotted against the reciprocal of the square root of the  $R_F$  value of the standard.

We conclude that despite the rigorous standardized procedure followed, differences in  $R_F$  and  $R_S$  values from sheet to sheet are caused by differences in the Chromagram sheets themselves. In a recent article, JOLLIFFE AND SHELLARD<sup>10</sup> also found a high variance ratio between the values taken from different Chromagram sheets from the same pack and suggested that the lack of reproducibility may be due to a lack of constancy in the pH of the silica gel layer which they report varies from 6.5 to 4.0.

Whatever the reason for variation in values, the  $R_F$  value of the standard seems to reflect rather accurately the adsorbent activity of the sheet. For these reasons, in compiling the data for Table I, only those sheets were considered on which the  $R_F$  value of the standard was at or below the arbitrary value of 0.22, which included the most active half of the forty sheets developed in this study.

### Separations

Each member of the series of compounds tested separated clearly from the standard. In addition, all compounds whose structure varied by two or more carbon atoms were separable. This was illustrated experimentally by the good separations of the complex mixtures composed of all the odd-numbered or of all the even-

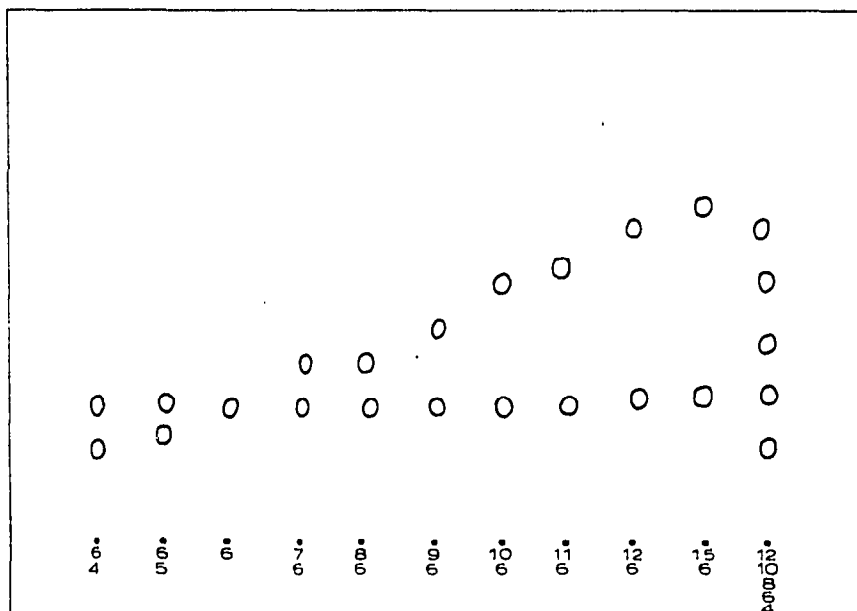


Fig. 2. Separation of mixtures of 2,4-DNPH derivatives of the following cycloketones: cyclobutanone (4); cyclopentanone (5); cyclohexanone (standard) (6); cycloheptanone (7); cyclooctanone (8); cyclononanone (9); cyclodecanone (10); cycloundecanone (11); cyclododecanone (12); cyclopentadecanone (15).

numbered cycloketone derivatives (see Fig. 2). Adjacent members of the series can be separated with the exception of the derivatives of cycloheptanone and cyclooctanone, cyclodecanone and cycloundecanone, and cycloundecanone and cyclododecanone.

Of special interest were the  $R_F$  and  $R_S$  values for the 2,4-DNPHs of cycloheptanone and cyclooctanone. Within experimental error these values were identical. It is noted that in their comprehensive study of TLC separations of carbonyl 2,4-DNPHs, BRÜMMER AND MÜLLER-PENNING<sup>1</sup> also obtained very similar  $R_B$  values for these two compounds (0.96 and 1.00). We are unable to suggest a reason for the apparent elevation of values for the cycloheptanone compound relative to the other members of the series.

#### ACKNOWLEDGEMENTS

The authors wish to express their appreciation to the following secondary school students who performed many of the experiments described in this communication: VIRGINIA BIRCH, JOHN FAY, LINDA PHAFF, TIMOTHY QUIGLEY, EDWARD RITZ, MARC ROBERTSON, JAMES THIRTLE, SHELLY WILLIAMS and WILLIAM VANDUSER.

This research was supported in part by the National Science Foundation under CCSS/PES Grant No. GW-729.

#### REFERENCES

- 1 J.-M. BRÜMMER AND T. J. MÜLLER-PENNING, *J. Chromatog.*, 27 (1967) 290.
- 2 E. DENTI AND M. P. LUBOZ, *J. Chromatog.*, 18 (1965) 325.
- 3 A. ZAMOJSKI AND F. ZAMOJSKA, *Chem. Anal. (Warsaw)*, 9 (1964) 589; *C. A.*, 62 (1965) 839in.
- 4 A. JART AND A. J. BIGLER, *J. Chromatog.*, 23 (1966) 261.

- 5 D. SLOOT, *J. Chromatog.*, 24 (1966) 451.
- 6 K. T. FINLEY, *J. Chromatog.*, 19 (1965) 443.
- 7 R. L. SHRINER, R. C. FUSON AND D. Y. CURTIN, *The Systematic Identification of Organic Compounds*, 5th Ed., Wiley, New York, 1965, p. 253.
- 8 E. MILLER AND M. BAUER, *Ann. Chem.*, 654 (1962) 92; *C. A.*, 57 (1962) 9681c.
- 9 G. W. KIDDER AND V. C. DEWEY, *J. Chromatog.*, 31 (1967) 234.
- 10 G. H. JOLLIFFE AND E. J. SHELLARD, *J. Chromatog.*, 33 (1968) 165.

*J. Chromatog.*, 44 (1969) 563-568