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# THIN-LAYER CHROMATOGRAPHY OF POLYCHLOROALICYCLIC KETONES

PETR ŠVEC* and MIROSLAV ZBIROVSKÝ
*Department of Organic Technology, Prague Institute of Chemical Technology, Suchbátarova 1905, Prague 6 (Czechoslovakia)*

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## SUMMARY

Thin-layer chromatography was applied in following the chlorination of some polychlorinated phenols in acetic acid and of metal salts of chlorinated phenols in inert solvents or reactions of organic hypochlorites with polychlorinated phenols.

Polychloroalicyclic ketones are both intermediates and products of these reactions. For comparative purposes a series of chromatographically pure polychloroalicyclic ketones was synthesised and the physicochemical constants of these compounds were determined. The chromatographic behaviours of polychloroalicyclic ketones on commercial Silufol foils and on poured thin layers of Silpearl are discussed.

## INTRODUCTION

Polychloroalicyclic ketones are a new class of non-peroxidic promoters for the cross-linking of polymers[1] and are weak vulcanizing agents for natural rubber[2]. These compounds are prepared mainly by the chlorination of chlorinated derivatives of phenol. The work described below arose from the need to find a rapid separation and identification method for the study of the course of chlorination of 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol and 2,3,4,5,6-pentachlorophenol in acetic acid. With the exception of a previous communication[3], where one- and two-dimensional thin-layer chromatographic (TLC) separations of tetrachloro- and hexachloro-2,5-cyclohexadiene-1-ones and some chlorinated phenols, quinones and hydroquinones are described, no work on the chromatography of polychloroalicyclic ketones appears to have been published to date.

## EXPERIMENTAL

### *Synthesis of pure compounds*

The chlorinated phenols used in this study were prepared according to the literature: 2,4,6-trichlorophenol[4] (compound 1), 2,3,4,6-tetrachlorophenol[5] (com-

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* To whom inquiries should be addressed.

pound 2), 2,3,4,5,6-pentachlorophenol[6] (compound 3) and purified until TLC and gas–liquid chromatographically (GLC) pure compounds were obtained[4]. Corrected melting points are, respectively, 67.5–68.5°, 65.0–66.0° and 190.8–191.3°. The polychloroalicyclic ketones were synthesised either by our procedures[7,8] or by methods described in the literature (Table I). On the basis of new synthetic methods[7,8] or preparative TLC, chromatographically pure compounds have been obtained. The purification methods used and IR and NMR data for the ketones are given in ref. 8.

TABLE I

POLYCHLOROALICYCLIC KETONES

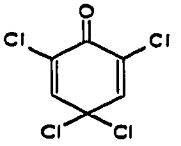
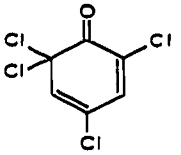
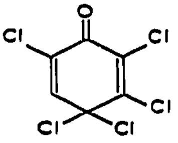
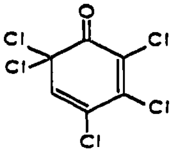
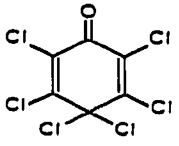
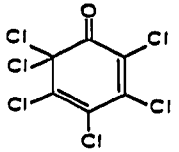
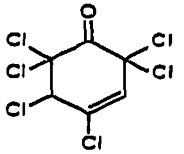
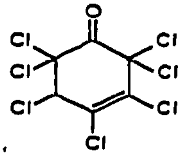
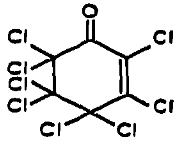
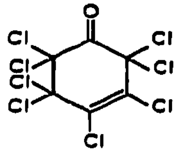
| *No.* | *Compound* (trivial name)* | *Structural formula* | *M.p. (°C)*** | *M.p. (°C)**** |
|---|---|---|---|---|
| 4 | 2,4,4,6-Tetrachloro-2,5-cyclohexadiene-1-one (trichlorophenol chlorine) |  | 122.0 (12) | 123.2 (7) |
| 5 | 2,4,6,6-Tetrachloro-2,4-cyclohexadiene-1-one |  | 105.0/0.2 torr (oil) (13) | 43.0/0.12 torr (oil) (8)§ |
| 6 | 2,3,4,4,6-Pentachloro-2,5-cyclohexadiene-1-one |  | 111.0–112.0 (14) | 112.0–113.0 (8)§ |
| 7 | 2,3,4,6,6-Pentachloro-2,4-cyclohexadiene-1-one |  | 110.0–112.0/0.2 torr (oil) (13) | 29.0–29.4 (8)§ |
| 8 | 2,3,4,4,5,6-Hexachloro-2,5-cyclohexadiene-1-one (hexachlorophenol or pentachlorophenolchlorine) |  | 106.0–107.0 (15) | 107.8–108.2 (9)§§ |
| 9 | 2,3,4,5,6,6-Hexachloro-2,4-cyclohexadiene-1-one |  | 51.0–52.0 (16) | 52.6–53.0 (10)§ |

TABLE I *(continued)*

| *No.* | *Compound* (trivial name)* | *Structural formula* | *M.p. (°C)*** | *M.p.(°C)**** |
|---|---|---|---|---|
| 10 | 2,2,4,5,6,6-Hexachloro-3-cyclohexen-1-one |  | —<br>oil (17, 18) | 44.0–44.3 (7) |
| 11 | 2,2,3,4,5,6,6-Heptachloro-3-cyclohexen-1-one (heptachlorophenol) |  | 97–99.0 (18) | 95.7–96.6 (8) |
| 12 | 2,3,4,4,5,5,6,6-Octachloro-2-cyclohexen-1-one (octachlorophenol *γ*) |  | 105–106.0 (5) | 104.4 (11)§§§ |
| 13 | 2,2,3,4,5,5,6,6-Octachloro-3-cyclohexen-1-one (octachlorophenol *δ*) |  | 85–88.0 (11) | 89.2 (11)§§§ |

* Using nomenclature of *Chemical Abstracts.*

** The highest (uncorrected) melting point known from literature data. The citing reference is noted in brackets.

*** The corrected melting points found for chromatographically pure compounds. The citing reference is noted in brackets.

§ Preparative TLC purification.

§§ Two-dimensional preparative TLC purification.

§§§ Column chromatographic purification (see Fig. 2).

### *Solvent systems*

All solvents were of analytical reagent purity and were distilled prior to use. All developing solutions were mixed immediately before being put into the developing chamber. The developing systems utilized in this work were (proportions being v/v) as follows:

$S_1$ = tetrachloromethane;
$S_2$ = *n*-hexane;
$S_3$ = cyclohexane;
$S_4$ = benzene–tetrachloromethane (5.45:1);
$S_5$ = benzene–*n*-heptane (1:1);
$S_6$ = chloroform–*n*-heptane (1:1);
$S_7$ = di-*n*-butyl ether–*n*-heptane (1:3).

### *Plate preparation*

The silica gel plates were prepared from a slurry of 45 g of silica gel Silpearl (UV 254)*, 5 g of gypsum and 70 ml of distilled water and spread on to 20 × 20-cm glass plates with a Camag applicator to give a thickness of 300 $\mu$m. The plates were dried for 60 min at room temperature and then heated for 120 min at 120° in an oven. The plates were then cooled and stored in a desiccator for at least 24 h before use.

Plates for preparative TLC with 1-mm layers were prepared from a slurry of 42.5 g of extracted Silpearl, 7.5 g of gypsum and 57 ml of distilled water using the procedure above (100 g of Silpearl were extracted for 10 h by 700 g of methanol in a Soxhlet apparatus). The use of starch as a binder for thicker layers was found to be inconvenient. Activation of these plates was carried out in accordance with requirements for 24 h within the range 90 to 120°. A Camag Chromatocharger was used to apply the samples in the form of bands. The bands were located under UV light at 254 nm.

In addition 15 × 15 cm reflex silica gel foils of Silufol UV 254 (Kavalier n.p.) were used. The layer thickness was 100 $\mu$m and 4% starch was used as binder.

### *Chromatography*

Standard compounds or samples from reaction mixtures were applied at the starting line, 1.5 cm from the base of the plate, in the form of solutions in glacial acetic acid or tetrachloromethane. The spotted samples were air-dried and the plate was placed in a developing chamber with walls lined with Whatman No. 1 paper. Saturation of the chamber atmosphere with solvent vapour was achieved overnight. The ascending technique was used until the solvent front had travelled 16 cm beyond the original spots. The precoated silica gel foils of Silufol® UV 254 were developed to a height of 12 cm.

### *Detection*

All spots were detected under UV light at 254 nm ($D_1$) as quenching spots. Solutions of 0.1 $N$ $AgNO_3$–5 $N$ $NH_4OH$ (1:1, $D_2$) or 25% aqueous ammonia ($D_3$) were used for chemical detection. Chemical detection gave coloured spots. The intensity of the colour decreased with increasing number of chlorine atoms in the molecule of ketone and decreasing amounts of the compounds were tested in order to find the detection limit (Table II).

## RESULTS AND DISCUSSION

Of the wide variety of solvent systems tested, the seven solvent systems mentioned in Table III gave the most satisfactory results. $R_F$ values represent the averages of at least six determinations.

It follows from Table III, that the $R_F$ value of the compound tested has been affected by the polarity of the solution in which the sample was applied. It is known from the literature[19] that the sample should be applied as a solution in a solvent as non-polar as possible, as the use of a polar solvent tends to cause the starting spot to

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* Silpearl (UV 254) is the trade name of a new silica gel with a UV indicator for TLC (Kavalier n.p., Czechoslovakia).

TABLE II

DETECTION LIMITS (g × $10^{-6}$) AND COLOURS OF POLYCHLOROALICYCLIC KETONES AND SOME CHLORINATED PHENOLS

| *Compound No.* | *Detection limit* | | *Colour*[*] | |
|---|---|---|---|---|
| | $D_1$ | $D_2$ | $D_2$ | $D_3$ |
| 1 | 10.0 | 2.0 | LY | W |
| 2 | 5.0 | 0.25 | LY | W |
| 3 | 1.5 | 0.10 | LY | W |
| 4 | 0.5 | 0.25 | B | DB |
| 5 | 3.1 | 1.6 | LB | DB |
| 6 | 1.2 | 0.75 | B | DB |
| 7 | 1.2 | 0.75 | LB | B |
| 8 | 1.0 | 1.5 | W | T |
| 9 | 0.75 | 0.05 | LB | DY |
| 10 | 30.0 | 0.5 | LB | B |
| 11 | 9.6 | 0.5 | RB | RB |
| 12 | 0.6 | 0.6 | W | W |
| 13 | 0.6 | 0.6 | W | W |

[*] LY = Light yellow, W = white, B = brown, LB = light brown, DB = dark brown, RB = red-brown, T = tan, DY = dark yellow.

spread out, especially when less polar solvents are used for development. We found that the resolution of the ketones was sharper when the samples were applied in acetic acid solution. When tetrachloromethane was used for spotting samples, compounds 10 and 11 tailed. Using acetic acid, tailing of compound 11 was completely eliminated and was lessened for compound 10. This phenomenon could be explained by the

TABLE III

$R_F$ VALUES OF POLYCHLOROALICYCLIC KETONES (SILUFOL)

Temperature: 19–21°. Relative humidity: 54–58%. $R_F$ values which have been obtained on Silpearl bound with gypsum are in good agreement[8] with $R_F$ values measured on Silufol.

| *Compound No.* | *Solvent systems* | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $S_1^{*}$ | $S_1^{**}$ | $S_2^{*,***}$ | $S_2^{**,***}$ | $S_3^{*,***}$ | $S_3^{**,***}$ | $S_4^{*}$ | $S_4^{**}$ | $S_5^{*}$ | $S_5^{**}$ | $S_6^{*}$ | $S_6^{**}$ | $S_7^{*}$ | $S_7^{**}$ |
| 1 | 0.15 | 0.17 | 0.07 | 0.11 | 0.08 | 0.11 | 0.26 | 0.29 | 0.22 | 0.25 | 0.32 | 0.33 | 0.43 | 0.47 |
| 2 | 0.13 | 0.16 | 0.05 | 0.10 | 0.06 | 0.09 | 0.24 | 0.26 | 0.19 | 0.21 | 0.26 | 0.28 | 0.41 | 0.44 |
| 3 | 0.10 | 0.15 | 0.04 | 0.09 | 0.03 | 0.08 | 0.21 | 0.26 | 0.16 | 0.22 | 0.22 | 0.27 | 0.41 | 0.43 |
| 4 | 0.22 | 0.30 | 0.10 | 0.17 | 0.11 | 0.18 | 0.40 | 0.42 | 0.34 | 0.40 | 0.48 | 0.48 | 0.64 | 0.62 |
| 6 | 0.27 | 0.34 | 0.12 | 0.18 | 0.13 | 0.19 | 0.45 | 0.44 | 0.39 | 0.44 | 0.52 | 0.50 | 0.65 | 0.65 |
| 8 | 0.37 | 0.42 | 0.19 | 0.24 | 0.21 | 0.24 | 0.54 | 0.56 | 0.45 | 0.52 | 0.59 | 0.57 | 0.78 | 0.80 |
| 5 | 0.28 | 0.37 | 0.16 | 0.21 | 0.18 | 0.21 | 0.48 | 0.50 | 0.42 | 0.46 | 0.52 | 0.53 | 0.70 | 0.67 |
| 7 | 0.35 | 0.41 | 0.19 | 0.24 | 0.21 | 0.25 | 0.53 | 0.55 | 0.46 | 0.52 | 0.56 | 0.56 | 0.74 | 0.71 |
| 9 | 0.43 | 0.47 | 0.23 | 0.29 | 0.25 | 0.29 | 0.59 | 0.61 | 0.52 | 0.57 | 0.61 | 0.59 | 0.78 | 0.81 |
| 10 | 0.34 | 0.34 | 0.17 | 0.26 | 0.18 | 0.27 | 0.49 | 0.60 | 0.46 | 0.58 | 0.60 | 0.60 | 0.48 | 0.56 |
| 11 | 0.43 | 0.47 | 0.29 | 0.33 | 0.32 | 0.33 | 0.62 | 0.67 | 0.57 | 0.62 | 0.66 | 0.64 | 0.64 | 0.68 |
| 12 | 0.56 | 0.59 | 0.44 | 0.47 | 0.49 | 0.51 | 0.65 | 0.68 | 0.59 | 0.66 | 0.68 | 0.67 | 0.75 | 0.85 |
| 13 | 0.63 | 0.67 | 0.62 | 0.64 | 0.65 | 0.67 | 0.71 | 0.74 | 0.61 | 0.79 | 0.72 | 0.71 | 0.80 | 0.87 |

[*] Compounds spotted in $CCl_4$.

[**] Compounds spotted in AcOH.

[***] Developed twice.

assumption that the active centres of the adsorbent are occupied by the molecules of highly polar acetic acid in preference to those of ketone. Subsequently the strength of the adsorbent–compound bond is reduced and the compound can be eluted more easily than in the case of a non-polar solvent such as tetrachloromethane. The behaviour of *n*-heptane-containing elution systems ($S_5$, $S_6$, $S_7$) on Silpearl bonded with a relatively high percentage of gypsum differed only little from the above[8].

TLC separations were succesfully applied:

(1) To follow the course of chlorination of chlorinated phenols in acetic acid solution. The samples from the reaction mixtures were applied directly to the thin layer together with an acetic acid solution of standard compounds. In connection with GLC[8] it was possible to correlate results from TLC and GLC as shown in Fig. 1. In this case the hexachlorocyclohexenone (10) was prepared by exhaustive chlorination of the trichlorophenol (1) in a mixture of acetic and hydrochloric acids at room temperature. The tetrachlorocyclohexadienone (5) was detected as an intermediate. This compound partially isomerises under these experimental conditions to compound 4.

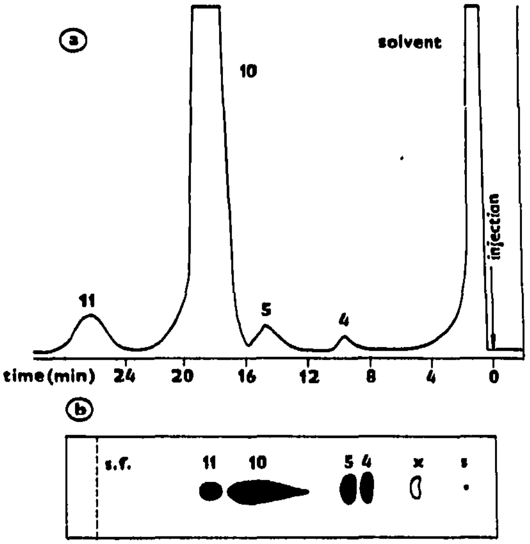

Fig. 1. GLC (a) and TLC (b) chromatograms of the crude reaction mixture resulting from the synthesis of hexachlorocyclohexenone. For identification of compounds see Table I. (a) GLC separation on a 165 cm × 3 mm I.D. spiral glass column packed with 5% QF-1 on 60–80 mesh Chromosorb W (HMDS) in a Chrom 31 chromatograph (Lab. Equip., Prague, Czechoslovakia); FID; nitrogen carrier gas at 10.1 ml/min, hydrogen at 42.5 ml/min; injection block, 125°, column, 120°. (b) TLC separation on Silufol foil; s = start, s.f. = solvent front; mobile phase, tetrachloromethane developed twice; x = 2,6-dichloroquinone (this compound is present in limiting concentration, not detectable using GLC).

In the reaction mixture heptachlorocyclohexenone (11) was detected on the basis of its $R_F$ value, colour reaction, elution time on GLC[8], and a trace amount of 2,6-dichloroquinone (Fig. 1b), on the basis of its $R_F$ value, colour reaction[20] and mass spectrum[21].

(2) To follow the course of chlorination of metal salts of chlorinated phenols in

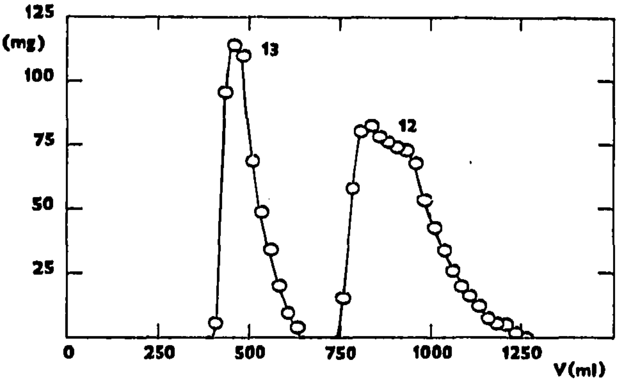

Fig. 2. Elution curves of octachlorocyclohexenones 12 and 13. The mixture of octachlorocyclohexenones was prepared according to ref. 11. Column, 610 × 25 mm I.D. Packing, 140 g of Silpearl UV 254 (for column chromatography). Sample size, 1.4169 g. Eluent, *n*-hexane. Temperature, 23°.

inert solvents and of reactions of chlorinated phenols with organic hypochlorites. The samples from the reaction mixtures were applied immediately to the thin layer together with standard compounds dissolved in tetrachloromethane.

(3) To follow the isomerisation of chlorinated 2,4-cyclohexadienones to more stable 2,5-cyclohexadienones. Chlorinated 2,4-cyclohexadienones are unstable compounds which could be identified with the unaided eye on a thin layer as intensely yellow spots. We have found that isomerization of these compounds proceeds very quickly even in non-polar solvents such as tetrachloromethane. Stability of these compounds decreases with decreasing number of chlorine atoms in the molecule (9 > 7 > 5). Although hexachloro-2,4-cyclohexadienone (9) could be prepared[10] almost chromatographically pure, pentachloro-2,4-cyclohexadienone (7) contained a small amount of its more stable isomer 6 as shown by TLC and NMR. For preparation of a pure compound we have used preparative TLC (see p. 538). Elution of the compound from the adsorbent was carried out with tetrachloromethane at room temperature. Silica gel was removed by centrifuging. The isomerization of tetrachloro-2,4-cyclohexadienone (5) to the more stable isomer 4 is very rapid. We were unable to obtain this compound completely pure even after purification by preparative TLC. Compound 4 obtained by this procedure isomerizes again. The use of column adsorption chromatography (column, 3.5 × 40 cm, 150 g of Silpearl UV 254; mobile phase, tetrachloromethane) was also found to be inconvenient. In this case tetrachloro-2,4-cyclohexadienone (5) isomerizes completely on account of the acidic properties of the adsorbent to tetrachloro-2,5-cyclohexadienone (4). An attempt has been made to purify pentachloro-2,4-cyclohexadienone (7) by column chromatography. The effluent contained pentachloro-2,5-cyclohexadienone (6) and tetrachlorophenol (2) as a decomposition product of 7 (ref. 8).

## CONCLUSIONS

All these observations are in agreement with previous conclusions[8,13], where some reasons for isomerization of this type of compound are discussed. The combination of TLC with quantitative GLC[8] is, in following these isomerization reactions, more rapid and exact than the spectrophotometric methods which have been proposed[13].

On the basis of TLC and GLC results, some reaction mechanisms for the chlorination of chlorinated phenols in acetic acid were proposed and some convenient procedures for the synthesis of chromatographically pure polychloroalicyclic ketones were found[8].

## ACKNOWLEDGEMENT

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