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On the Separation of Polychloro Acetones

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Separation of synthetic and authentic mixtures of polychloro acetones was attempted by distillation. 1,1-Di- and 1,1,1,-trichloroacetone could be separated from the other polychloro acetones due to their lower boiling points. It was not possible to separate 1,3-di-, 1,1,3-tri, 1,1,1,3-tetra-, and 1,1,3,3-tetrachloroacetone, whose boiling points all are within a 10°C range.

In connection with work on the Favorsky rearrangement of polyhalo ketones, it was necessary to prepare 1,1,3-trichloroacetone and to separate this compound from the other chloroacetones formed in the chlorination. According to the older literature the boiling points for 1,3-di-, 1,1,3-tri-, 1,1,3,3-tetra-, and 1,1,1,3-tetrachloro acetone are very close together (see Table 1 first column) and thus no separation by distillation seems to have been possible.[1–4]

Recently Wyman and Kaufman studied the chlorination of ketones using sulfuryl chloride.[5] In the case of acetone and two equivalents of sulfyrul chloride these authors found that the reaction products were 1,1-dichloroacetone, 1,3-dichloroacetone and 1,1,3-trichloroacetone. By the use of a 14-in (35 cm) Vigreux column the authors reported a complete and successful separation of all these components with a total yield of analytically pure chlorinated ketones as high as 98 %. The reported boiling points are given in Table 1, second column.

For the preparation of 1,1,3-trichloroacetone we treated 1,3-dichloroacetone with chlorine. In this way it was possible to avoid contamination with 1,1-di- and 1,1,1-trichloroacetone. The chlorination was followed by PMR and was interrupted at the stage when the concentration of starting 1,3-dichloroacetone was equal to the sum of the concentrations of the tetrachloroacetones, thus achieving the optimum yield of 1,1,3-trichloroacetone. The crude product consisted of unreacted 1,3-dichloroacetone (9 %), 1,1,3-trichloroacetone (82 %), 1,1,1,3-tetrachloroacetone (1 %), and 1,1,3,3-tetrachloroacetone (8 %). Using a 25 cm Widmer column, no separation was obtained; instead in the beginning of the distillation the starting ketone was enriched,

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Table 1. Boiling points of polychloroacetones.

Compound	b.p. °C/mm Hg [Ref.]	b.p. °C/mm Hg [Ref. 5]	b.p. °C/30 mm Hg
$CH_3COCHCl_2$	120/760 [1]	117–118/760	36
$CH_2ClCOCH_2Cl$	173.4/760 [1]	78– 80/30	83
CH_3COCCl_3	134/760 [1]	—	51.6
	60/54 [1]		
$CH_2ClCOCHCl_2$	172/760 [2]	91– 94/30	88
	76–78/19 [3]		
$CH_2ClCOCCl_3$	183/760 [1]	—	92
	71–72/13 [1]		
$CHCl_2COCHCl_2$	180–182/760 [1]	—	89
	78.5– 79/19 [4]	—	

while the tetrachloro isomers remained in the distillation residue. A Büchi spinning band distillation column with 30 theoretical plates was tried, but gave similar results – no separation. Thereafter we tried to distill a mixture consisting of 1,3-dichloroacetone (7 %), 1,1,3-trichloroacetone (72 %), 1,1,1,3-tetrachloroacetone (2 %), and 1,1,3,3-tetrachloroacetone (19 %) on a Nester-Faust spinning band distillation column with a reflux ratio of 1/100 (>100 plates). Seven fractions were collected and they were analyzed by PMR together with the residue, and the results are given in Table 2. All of the components were found in all fractions. Of special interest was the observation that in the beginning of the distillation the ratio 1,3-di-/1,1,3-trichloroacetone was 1/9, while at the end this ratio was about 1/30. Only in the residue, which consisted mainly of 1,1,3-tri and 1,1,3,3-tetrachloroacetone, was the starting dichloro ketone absent.

In order to establish whether it is possible (or not) to separate polychloroacetones by distillation, we tried to separate authentic mixtures prepared from pure samples of polychloroacetones.

1,1,3-Tri- and 1,1,1,3-tetrachloroacetones were prepared by Arndt-Eistert syntheses. This method appears to have been neglected as a possible means

Table 2. Results from the distillation with the Nester-Faust column.

Fraction No.	Amount g	B.p./30 mm °C	1,3-di- %	1,1,3-tri- %	1,1,1,3-tetra- %	1,1,3,3-tetra- %
1	1.8	80.0–82.0	9	85	2	4
2	2.1	82.0–82.5	7	81	3	9
3	9.5	83.2–84.5	5	80	3	12
4	8.3	84.2–84.5	3	80	3	14
5	3.5	84.0–84.3	2	79	2	17
6	2.0	84.2–84.6	2	78	2	18
7	5.8	84.5–85.0	2	70	3	25
Residue	5.0	—	0	38	5	57

for preparing these compounds. 1,1,1-Trichloroacetone was prepared from ethoxy magnesiomalonic ester and trichloroacetyl chloride according to a method described by Bowman *et al.*, [6,7] while 1,1-dichloroacetone could be prepared from the chlorination of acetone.[8] The boiling points of these four compounds and of distilled commercial samples of 1,3-di- and 1,1,3,3-tetrachloroacetone are given in Table 1, last column. Wyman and Kaufman found the difference in boiling points between 1,3- and 1,1,3- trichloroacetone to be 11 – 16°C at 30 mm.[5] However, we found the difference at the same pressure to be only 5°C and the boiling points of 1,1,3,3- and 1,1,1,3-tetrachloroacetone only a few degrees higher, so that these four chloroacetones all boil within a 10°C range. The purity of all compounds was checked by PMR.

Two authentic mixtures were prepared, one corresponding to the product distribution given by Wyman and Kaufman (Mixture A) and the other consisting of equal volumes of 1,3-di-, 1,1,1-tri-, 1,1,3-tri-, 1,1,1,3-tetra-, and 1,1,3,3-tetrachloroacetone, (Mixture B), see Table 3. These two mixtures were distilled on the Büchi spinning band column, each fraction was analyzed by PMR, and the results are given in Tables 4 and 5. With the exception of the pure fractions of 1,1-di- and 1,1,1-trichloroacetone, all the four other components were found in all fractions. In view of these observations we find it highly remarkable that Wyman and Kaufman [5] could successfully separate 1,3-di- and 1,1,3-trichloroacetone with a 14-in Vigreux column.

Experimental. 1,1,3-Trichloroacetone. A. A gentle stream of chlorine was passed into 98.5 g (0.78 mole) of commercial 1,3-dichloroacetone dissolved in 100 ml of aqueous hydrochloric acid (1:1 by volume). The temperature was kept at 50–60°C with external heating. The reaction was followed by running PMR-spectra every hour. After 4 h the yield of 1,1,3-trichloroacetone was optimized. The reaction mixture consisted of 1,3- (9 %), 1,1,3-tri- (82 %), 1,1,3,3-tetra- (8 %), and 1,1,1,3-tetrachloroacetone (1 %). This crude product was distilled through a 25 cm Widmer column yielding a main fraction boiling at 62–65°C at 10 mm consisting of 1,3-di- (7 %), 1,1,3-tri- (72 %), 1,1,3,3-tetra- (19 %) and 1,1,1,3-tetrachloroacetone (2 %). This fraction was redistilled using a Büchi and a Nester-Faust spinning band distillation column.

The results from the distillation on the Nester-Faust column are collected in Table 2.

B. To a solution of 15.6 (0.38 mole) of diazomethane in 550 ml ether (0°C) was added dropwise 20.0 g (0.13 mole) of dichloroacetyl chloride in 150 ml of ether. The mixture was kept overnight at room temperature before half of the ether was removed by distillation *in vacuo*. A gentle stream of hydrogen chloride gas was passed into the crude ether solution of the dichlorodiazoacetone until the evolution of nitrogen had ceased (4 h). The ether was removed and the product distilled through a Widmer column yielding 15.0 g (75 %) of 1,1,3-trichloroacetone, b.p. 68–70°C at 14 mm, $n_D^{20}=1.4900$. The product was redistilled on a Büchi spinning band column, b.p. 88°C at 30 mm, $n_D^{23}=1.4880$. The PMR analysis of the compound (in 10 % $CHCl_3$) gave two singlets at $\delta=4.58$ ppm and $\delta=6.14$ ppm with a signal ratio 2:1.

1,1,1,3-Tetrachloroacetone. This substance was prepared in a manner analogous to method B for 1,1,3-trichloroacetone above starting from trichloroacetyl chloride. The distillation through the Widmer column yielded 14.0 g (50 %) of 1,1,1,3-tetrachloroacetone, b.p. 70–71°C at 14 mm, $n_D^{25}=1.4920$. This compound was also redistilled through the Büchi column, b.p. 92°C at 30 mm, $n_D^{24}=1.4920$. The PMR spectrum (in 10 % $CHCl_3$) consisted of one singlet at $\delta=4.80$ ppm.

1,1,1-Trichloroacetone. This compound was prepared according to Bowman *et al.*,[6,7] b.p. 132–134°C at atmospheric pressure. Redistillation using the Büchi column gave b.p. 136°C at atmospheric pressure or 51.6°C at 30 mm, $n_D^{22}=1.4600$. The PMR spectrum (10 % chloroform) consisted of one singlet $\delta=2.62$ ppm.

Table 3. Composition of the authentic mixtures.

Mixture	1,1-di- %	1,3-di- %	1,1,1-tri- %	1,1,3-tri- %	1,1,1,3-tetra- %	1,1,3,3-tetra %
A	64	18	—	18	—	—
B	—	25	20	22	18	15

Table 4. Results from the distillation of mixture A.

Fraction No.	Volume ml	B.p./30 mm °C	1,1-di- %	1,3-di- %	1,1,3-tri- %
1	6.4	36	100	0	0
2	1.3	36—84.5	31	28	41
3	3.5	84.5—85	4	45	51

Table 5. Results from the distillation of mixture B.

Fraction No.	Volume ml	B.p./30 mm °C	1,3-di- %	1,1,1-tri- %	1,1,3-tri- %	1,1,1,3-tetra- %	1,1,3,3-tetra- %
1	2.8	51.6	0	100	0	0	0
2	1.6	50.4—86.0	44	24	16	12	4
3	5.1	86.0—86.6	51	3	25	14	7
4	4.8	86.6—89.8	24	2	41	21	12
5	1.7	89.8—90.2	2	2	31	34	31

Authentic mixtures. Two authentic mixtures (A and B) were prepared from the redistilled samples of polychloroacetones. The composition of these mixtures are given in Table 3 and the results from the distillations on the Büchi spinning band column in Tables 4 and 5.

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