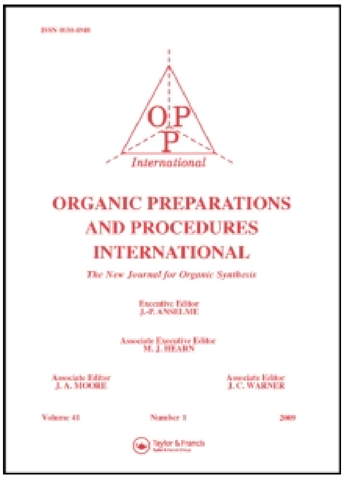


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

IMPROVED SYNTHESIS OF 2,4,4,6-TETRACHLORO-2,5-CYCLOHEXADIENONE AND OF 2,2,4,5,6,6-HEXACHLORO-3-CYCLOHEXENONE

P. Švec[a]; A. M. Sørensen[b]; M. Zbirovský[a]
[a] Department of Organic Technology, Prague Institute of Chemical Technology, Suchbátarova, CZECHOSLOVAKIA [b] Chemical Laboratory C, The Royal Danish School of Pharmacy, Copenhagen, DENMARK

To cite this Article Švec, P. , Sørensen, A. M. and Zbirovský, M.(1973) 'IMPROVED SYNTHESIS OF 2,4,4,6-TETRACHLORO-2,5-CYCLOHEXADIENONE AND OF 2,2,4,5,6,6-HEXACHLORO-3-CYCLOHEXENONE', Organic Preparations and Procedures International, 5: 5, 209 — 213

To link to this Article: DOI: 10.1080/00304947309356844

URL: http://dx.doi.org/10.1080/00304947309356844

ORGANIC PREPARATIONS AND PROCEDURES INT. 5(5), 209-213 (1973)

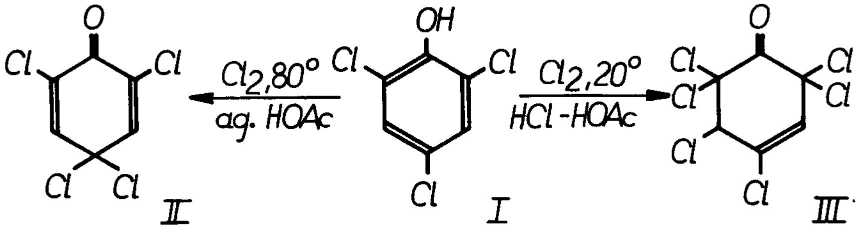
IMPROVED SYNTHESIS OF 2,4,4,6-TETRACHLORO-2,5-CYCLOHEXADIENONE AND OF 2,2,4,5,6,6-HEXACHLORO-3-CYCLOHEXENONE

P. Švec *[1], A. M. Sørensen ** and M. Zbirovský *

* Department of Organic Technology,
Prague Institute of Chemical Technology,
Prague 6,Suchbátarova 1905,CZECHOSLOVAKIA.

** Chemical Laboratory C,
The Royal Danish School of Pharmacy,
Copenhagen,DENMARK.

2,4,4,6-Tetrachloro-2,5-cyclohexadienone (II), with the trivial name "trichlorophenolchlorine" was obtained for the first time in the last century[2] by chlorination of 2,4,6-trichlorophenol (I) in hydrochloric acid. Although several authors[3,4] have tried to prepare II by modification of Benedikt´s method[2],no convenient procedure was found.



Non-crystallizable pastes or oils were obtained.[3] Zincke and Schaum[4] treated a solution of I in acetic acid with calcium hypochlorite. An oily product product was obtained,from which II precipitated after several months. Fort[3] used a procedure in which a 10 % solution of I in acetic acid was chlorinated in the presence of iodine.Experimental data were not given. Iodine most likely catalyses isomerization of 2,4,6,6-tetrachloro-2,4-cyclohexadienone to II.[3,5] Compound II was also detected as an intermediate in the chlorination of aqueous solutions of anisole- and phenetolesulphonic acid.[6]

We now report a modified procedure which gives a relatively high yield of chromatographically pure II.

In our procedure,II was prepared by the chlorination of I in aqueous acetic acid at 80°. 2,4,6,6-Tetrachloro-2,4-cyclohexadienone was identified as an unstable intermediate[7], which isomerizes quickly to II,the rate of isomerization being dependent upon the reaction temperature: react.temp./ % yield of II are given: 20°/23.2, 50°/38.7, 80°/50.7 /. Above 80°, chloranil could be isolated in about 5 % yield. The formation of chloranil could be attributed to partial hydrolysis of II followed by chlorination of the 2,6-dichloroquinone formed.

In connection with other work[7],it was desirable to have available reasonable amounts of chromatographically pure III. This compound was recently prepared by chlorination of phenol in acetic acid at 20 - 40°.[8] The oily product obtained could not be crystallized even after purification by column chromatography. Similarly chlorination of I in a mixture of acetic acid and hydrochloric acid at 50 - 60° gave only oily product (the yield not given).[9]

We have obtained III by chlorination of I in a mixture of acetic and hydrochloric acid at room temperature. The yield of crystalline product is excellent (91.2 %). The course of chlorination I ⟶ 2,4,6,6-tetrachloro-2,4-cyclohexadienone ⟶ III could be followed by TLC and GLC.[7]

EXPERIMENTAL[11]

2,4,4,6-Tetrachloro-2,5-cyclohexadienone (II).

A solution of 4.95 g (0.025 mole) of I in 50 ml of 75 % acetic acid, contained in a 100 ml 3-necked round bottomed flask fitted with a mechanical stirrer, thermometer and reflux condenser, was heated to 80° on a water bath. Gaseous chlorine (2.3 g, 0.032 mole) was introduced into the solution over 20 min. Upon cooling to 0°, II precipitated. Precipitation of the product by addition of water is not recommended since the precipitate then contains difficultly separable by-products. The precipitated crystals were washed with water and dried. TLC[10] of the product showed only one spot. Yield: 2.95 g, 50.7 %, mp. 118.5 - 122°. The analytical sample prepared by recrystallization from n-hexane (2.65 g, 45.5 % yield) had mp. 123.2° (corr.), lit. mp. 119° [2], 121 - 122° [5], 122° [4,6] (uncorr.).

Anal. Calcd. for $C_6H_2Cl_4O$: C 31.08 %, H 0.87 %, Cl 61.15 %

Found : C 31.14 %, H 0.87 %, Cl 61.03 %

IR (CCl_4) : $\nu_s(C-Cl_2)$ 692s, $\nu_{as}(C-Cl_2)$ 712s, $\nu(C=O)$ 1704s, $\nu(=C-H)$ 3062w cm^{-1}.

NMR ($CDCl_3$) : δ 7.12 s (p.p.m.).

2,2,4,5,6,6-Hexachloro-3-cyclohexenone (III).

2,4,6-Trichlorophenol (39.5 g, 0.2 mole) was dissolved in a mixture of 400 ml glacial acetic acid and 40 ml of conc. hydrochloric acid in a one liter 3-necked round bottomed flask equipped with a mechanical stirrer and reflux condenser. Gaseous chlorine (52.0 g, 0.73 mole) was introduced over 13 hrs. into the solution at 20°. After concentration of the reaction mixture to 75 ml on a rotatory evaporator under reduced pressure at or below 45°,the residue was added dropwise to 1000 ml of ice water. The light yellow oil which separated,solidified after 1 hr. to give 55.3 g of III,mp.37 - 38°. An additional portion of III (2.4 g,mp. 33 - 37°) was recovered from the water phase by extraction with chloroform. The total yield was 57.7 g (95.5 %). The mp. of colourless crystals (55.1 g,91.2 % yield) after crystallization from n-hexane is 44.0 - 44.3° (corr.).

<u>Anal.</u> Calcd. for $C_6H_2Cl_6O$: C 23.80 %, H 0.67 %, Cl 70.25 %
Found : C 23.82 %, H 0.74 %, Cl 70.19 %

IR (CCl_4) : $\nu_s(C-Cl_2)$ 694s, $\nu_{as}(C-Cl_2)$ 714s, $\nu(C=C)$ 1650s, $\nu(C=O)$ 1780s, $\nu(C-H)$ 2980m, $\nu(=C-H)$ 3060m cm^{-1}.

NMR ($CDCl_3$) : δ4.97 d, δ6.49 d (p.p.m.), J_{H-H} 1.5 Hz.

REFERENCES

1. To whom correspondence should be sent.
2. R. Benedikt, Monatsh., 4, 223 (1883).
3. R. Fort, Ann. Chim., 4, 203 (1959).
4. T. Zincke and C. Schaum, Ber., 27, 537 (1894).

5. G. King and H. Mc Combie, J. Chem. Soc. London , **103**, 220 (1913).

6. R. L. Datta and H. K. Mitter, J. Am. Chem. Soc., **41**, 2028 (1919).

7. P. Švec, A. Bradíková and M. Zbirovský, J. Chromatogr., (in press).

8. L. Vollbracht, W. G. B. Huysmans, W. J. Mijs and H. J. Hageman, Tetrahedron, **24**, 6265 (1968).

9. E. Morita and M. W. Dietrich, Can. J. Chem., **47**, 1943 (1969).

10. P. Švec and M. Zbirovský, Scientific Papers of the Prague Institute of Chemical Technology, C **17**, 95 (1972); C. A. **77**, 56178 w (1972).

11. The infrared spectra were obtained on a Perkin-Elmer model 325 spectrophotometer. Nuclear magnetic resonance spectra were determined on a Varian XL-100-15 spectrophotometer, TMS was used as internal standard. 2,4,6-Trichlorophenol was used in the purity mentioned previously[7].

(Received April 13, 1973; in revised form June 22, 1973)