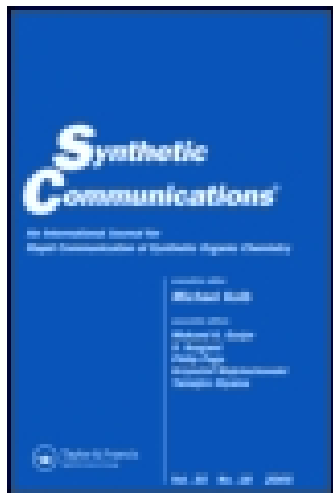


This article was downloaded by: [Tulane University]

On: 18 January 2015, At: 23:03

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH,
UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lcyc20>

Dechlorination Reactions of Hexachlorinated Polycyclic Compounds Using Ultra-Sound Radiation

Valentim Emilio Uberti Costa ^a, Maria E. S. Möllmann ^a & Valéria Belli Riatto ^a

^a Instituto de Química - Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500 Campus do Vale - 91501-970, Porto Alegre, Rio Grande do Sul, BRAZIL

Published online: 23 Sep 2006.

To cite this article: Valentim Emilio Uberti Costa, Maria E. S. Möllmann & Valéria Belli Riatto (1995) Dechlorination Reactions of Hexachlorinated Polycyclic Compounds Using Ultra-Sound Radiation, *Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry*, 25:14, 2091-2097, DOI: [10.1080/00397919508015890](https://doi.org/10.1080/00397919508015890)

To link to this article: <http://dx.doi.org/10.1080/00397919508015890>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness,

or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

DECHLORINATION REACTIONS OF HEXACHLORINATED POLYCYCLIC COMPOUNDS USING ULTRA-SOUND RADIATION

Valentim Emilio Uberti Costa*, Maria E.S. Möllmann and Valéria Belli Riatto.

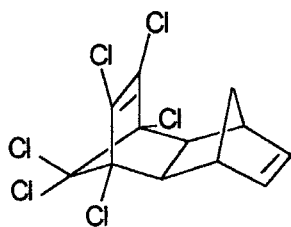
Instituto de Química - Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500
Campus do Vale - 91501-970 Porto Alegre, Rio Grande do Sul, BRAZIL.

ABSTRACT: Dechlorination reactions of exo-endo and endo-endo perhalogenated tetracyclic compounds with Li/t-BuOH/THF system, when subjected to simultaneous ultra-sound irradiation, led to exceptionally high yields (77-95%) of the corresponding hydrocarbons.

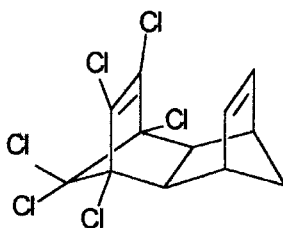
INTRODUCTION:

Several workers have published on the dechlorination reaction of hexachlorinated polycyclic systems. Winstein et al¹ utilized Li/t-BuOH/THF and heat to reach yields around 50% for "aldrin" derivatives. Gassmann and Pape² observed that this method could result in partial reduction of the double bond to give a mixture of saturated and unsaturated compounds; they replaced lithium by sodium. Paddon-Row et al³ observed that the method with sodium, when applied on large scale, required longer times and produced yields that were below 50%. So, they proposed the system Na/EtOH, which allowed shorter reaction times,

simpler separation procedures and yields better than those for previous dechlorinating agents; e.g., for aldrin close to 69%. Recently, Lightner et al⁴ observed that best result can be obtained with a Birch reduction with Na/NH₃(l), with yields about 70%. The first three methods^{1,2,3} have been tested in our laboratory on "aldrin" (1), "isodrin"(2) and their derivatives, and we have verified that normally intramolecular rearrangement, decomposition products, degradation by oxidative and retro-Diels-Alder reactions take place, decreasing the yield of pure products. Therefore, we decided to substitute the source of radiating energy from heat to ultrasound.



1

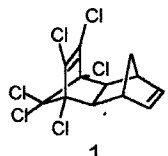
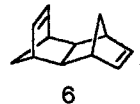
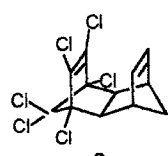
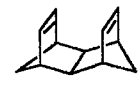
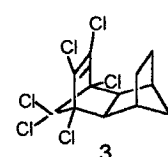
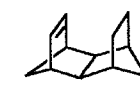
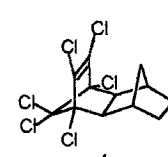
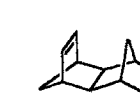
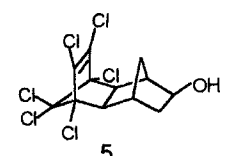
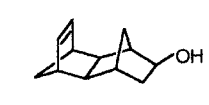


2

RESULTS AND DISCUSSION:

The ultra-sound apparatus was a Thornton T14 model, 40 kHz and 90 watt. We tested the following methods on "aldrin": Na/EtOH; Na/n-BuOH; Na/t-BuOH/THF; Li/EtOH; Zn/EtOH; Mg/EtOH; Li/t-BuOH/THF, ultra-sound bath temperature was kept between 30-50°C. However, with Li/EtOH it was impossible to control the temperature, and as the ultra-sound bath was turned on, a strong exothermic reaction is observed.

The Li/t-BuOH/THF/U-S system was the only one which worked and gave good yield. So, we decided to test this system on other hexachlorinated polycyclic molecules. Yields between 77-95% of the pure final product were obtained:

<u>Hexachlorinated Compounds</u>	<u>Pure Product</u>	<u>Yield (%)</u>
 1	 6	77 - 80
 2	 7	78 - 82
 3	 8	92 - 95
 4	 9	93 - 95
 5	 10	87 - 90

EXPERIMENTAL METHODS:

Into a 250 ml flask equipped with reflux condenser and under N₂ atmosphere were placed 88 ml of THF, and small pieces (wire) of lithium (2.25 g; 0.324 g - atoms) and tert-butyl alcohol (16 ml; 0.168 mol) were added. The apparatus was then immersed into the ultra-sound bath (45 kHz, 100 watt) the system was turned on, and a solution of 5 g (1.36.10⁻² mol) of hexachlorinated compound in 10 ml of THF was added during 20 min. The ultra-sound apparatus was turned off after 5 hours and the temperature of the bath oscillated between 30-50°C. A hundred grams of crushed ice was added under N₂ atmosphere. The aqueous layer was extracted with 3x80 ml of ethyl ether and the ethereal extracts were washed with 3x50 ml of water, dried over magnesium sulfate, filtered and the solvents were evaporated. After chromatography on a column of silica gel 60 (0.2-0.5mm) and elution with ethyl ether-petroleum ether gradients, the pure product was isolated.

The analytical data of the compounds are in good agreement with literature values. NMR spectra were recorded in CDCl₃ on a Varian VXR-200 spectrometer with TMS as reference set to 0.00 ppm to ¹H-NMR and CDCl₃ as reference set to 77.00 ppm to ¹³C-NMR. All NMR work was recorded at room temperature (22 °C). All melting points were recorded on Uniscience 498 Melting Point apparatus and are reported uncorrected. Elemental analysis were recorded on Perkin Elmer 2400 CHN Elemental Analyzer apparatus.

Compound 1 (lit⁵ mp 97 °C) ¹H-NMR δ 1.26 (1H,d), 1.50 (1H,d), 2.70 (2 H, br.s), 2.83 (2H,d), 6.26 (2H, d); ¹³C-NMR δ 40.73 (1C), 40.87 (2C), 54.55 (2C), 79.96 (2C), 105.35(1C) 141.00 (2C). Anal. Calcd. C:39.52 H:2.21 found C:39.70 H:2.03.

Compound 2 (lit⁶ mp 239-241 °C) ¹H-NMR δ 1.50 (1H,d), 1.70 (1H,d), 2.95 (2H, s), 3.30 (2H, s), 5.95 (2H,s); ¹³C-NMR δ 43.9 (2C), 52.6 (2C), 55.1 (1C), 80.3 (2C), 107.5 (1C), 129.2 (2C), 130.8 (2C).

Compound 3 (lit⁷ mp 218-219 °C) ¹H-NMR δ 1.4-1.7 (6H,m), 2.5 (2H,m), 3.1 (2H,m); ¹³C NMR δ 24.0 (2C), 38.7 (2C), 44.2 (1C), 55.0 (2C), 80.5 (2C), 110.0 (1C), 132.0 (2C). Anal. Calcd C:39.2 H:2.73 found C:39.4 H:2.70.

Compound 4 (lit⁵ mp 73 °C) ¹H-NMR δ 0.96 (1H,d), 1.11 (2H,dd), 1.39 (1H, dt), 1.52 (2H,m), 2.31 (2H,m), 2.59 (2H, br.s); ¹³C-NMR δ 30.45 (2C), 34.09 (1C), 35.50 (2C), 56.11 (2C), 80.87 (2C), 104.50 (1C), 130.28 (2C). Anal. Calcd C:39.30 H:2.75 found C:39.36 H:2.77.

Compound 5 (lit⁸ mp 115-117 °C) ¹H-NMR δ 1.25-1.40 (3H,m), 1.62 (1H,m), 2.24 (1H, br.s.), 2.35-2.42 (2H,m), 2.50 (1H,d), 3.72 (1H,d); ¹³C-NMR δ 30.30 (1C), 34.94 (1C), 43.28 (1C), 43.70 (1C), 51.81 (1C), 55.46 (1C), 74.33 (1C), 80.31 (1C), 80.61 (1C), 104.37 (1C), 130.37 (1C), 130.46 (1C).

Compound 6 (lit⁹ bp 108 °C 25mm n_D²⁶ 1.5324) ¹H-NMR δ 0.95 (1H,d), 1.50 (1H,d), 1.62 (1H,d), 2.19 (2H, br.s.), 2.47 (2H, br.s.), 2.55 (1H, d), 2.67 (2H, br.s.), 6.02 (2H, br.s.), 6.20 (2H, br.s.); ¹³C-NMR δ 40.49 (1C), 42.74 (2C), 44.48 (2C), 48.19 (2C), 55.72 (1C), 136.16 (2C), 141.28 (2C). Anal. Calcd C:91.08 H:8.92 found C:90.78 H:9.30.

Compound 7 (lit^{1,10} bp 100-101 °C C 17mm; n_D²⁵, 1.5285); ¹H-NMR δ 1.47 (4H,m), 2.59 (4H,m), 2.70 (2H,m), 5.22 (4H,m); ¹³C-NMR δ 42.93 (2C), 44.49 (4C), 55.50 (2C), 131.38 (4C).

Compound 8 (lit^{1,11} mp 64-65 °C); ¹H-NMR δ 0.9-1.8(8H,m), 2.0 (2H,br.s.), 2.4 (2H, br.s.), 2.6 (2H, br.s.), 6.03 (2H,br.s.); ¹³C-NMR δ 25.0 (2C), 39.7 (2C), 44.6 (2C), 47.1 (1C), 48.6 (2C), 59.1 (1C), 131.5 (2C); Anal. Calcd C:89.94 H:10.06 found C:90.01 H:9.95.

Compound 9 (lit¹² bp 90-93 °C 11mm; n_D²⁷ 1.5197) ¹H-NMR δ 0.52 (1H,d), 0.94-1.40 (6H,m), 1.93 (2H, br.s.), 2.00-2.07 (3H,m), 2.82 (2H,m), 5.93 (2H,d); ¹³C-NMR δ 31.89 (2C), 33.71 (1C), 37.81 (2C), 46.65 (2C), 48.59 (2C), 52.81 (1C), 135.17 (2C); Anal. Calcd. C:90.0 H:10.0 found C:89.8 H:10.0.

Compound 10 (lit¹³ mp 98-99 °C) ¹H-NMR δ 0.90 (1H,d), 1.09-1.21 (2H,m), 1.26 (1H,d), 1.52-1.54 (OH, 1H, m), 1.70 (1H,dd), 1.78 (1H,dd), 1.90-2.00 (3H,m), 2.76 (2H,br.s), 3.57 (1H,d), 5.90 (2H,br.s.); ¹³C-NMR δ 30.08 (1C), 37.12 (1C), 43.80 (1C), 45.14 (1C), 46.20 (1C), 46.38 (1C), 46.42 (1C), 48.09 (1C), 53.26(1C), 76.36 (1C), 135.37 (1C), 135.42 (1C); Anal. Calcd. C:81.79 H:9.15 found C:81.62 H:9.10.

ACKNOWLEDGEMENTS: V.E.U. Costa held CNPq research fellowship and M.E.S. Mollmann held CAPES M.Sc. fellowship. Financial support : FAPERGS and CNPq.

REFERENCES:

1. Bruck,P.; Thompson,D.; Winstein,S., *Chem. Ind.*, 9, 405 (1960).
2. Gassmann,P.G.; Pape,P.G., *J.Org. Chem.*, 29, 160 (1964).
3. Lap,B.V.; Paddow-Row,M.N., *J.Org. Chem.*, 44, 4979 (1979).
4. Robbins,T.A.; Toan,V.V.; Gewens,J.W., III, Lightner,D.A., *J. Am. Chem. S.*, 114, 10799 (1992).
5. (a) Parsons, A.M., Moore, D.J., *J.Chem.Soc.(C)*, 2026 (1966); (b) Soloway, B., U.S. Patent 2, 676, 131 (to Shell Development Co.), Apr. 20 (1954).
6. (a) Lidov, R.E., U.S.Patent 2, 717, 851 (to Shell Development Co.) Sept. 13 (1955); (b) Soloway, B., U.S. Patent 2, 676, 131 (to Shell Development Co.), Apr. 20 (1954).
7. Soloway, S.B.; Damiana, A.M.; Sims, J.W., Bluestone, H.; Lidov, R.E.; *J. Am. Chem. Soc.*, 20, 5377 (1960).
8. Cox, R.H.; Mckinney, J.D., *Org. Mag. Res.*, 11 (11), 541-61 (1978).

9. Stille, J.K., Frey, D.A., J. Am. Chem. Soc., 81, 4273 (1959).
10. Marchand, A.P.; Rose, J.E., J. Am. Chem. Soc., 90, 3724 (1968).
11. Stille, J.K.; Witherell, D.R., J. Am. Chem.Soc.,86, 2188 (1964).
12. Soloway, S.B., J.Am. Chem. Soc., 74, 1027 (1952).
13. Stille, J.K.; Kasper, P.R.; Witherell, D.R., J. Am. Chem. Soc., 28, 682 (1963).

(Received in the USA 01 December 1994)