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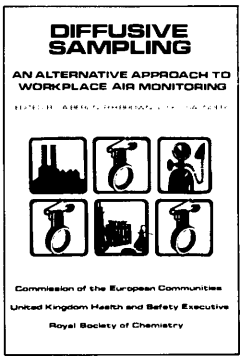
DIFFUSIVE SAMPLING
AN ALTERNATIVE APPROACH TO WORKPLACE AIR MONITORING



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Edited by: A. Berlin, Health & Safety Directorate
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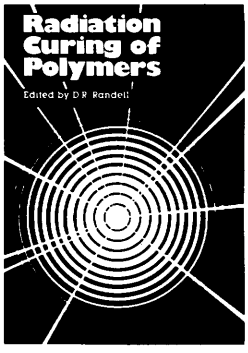
Diffusive Sampling is based on a symposium held in Luxembourg in September 1986 and organised jointly by the Commission of the European Communities and the United Kingdom Health and Safety Executive in cooperation with the World Health Organization and the Royal Society of Chemistry. This book:

- Reviews the state of the art of diffusive sampler techniques
- Stimulates the exchange of technical information
- Assesses the suitability and range of applications for workplace monitoring
- Promotes the further development of this technique and its wider use.

Brief contents: Introduction, Current Field Application, Role of Diffusive Sampler in Workplace Air Monitoring, Current Trends in Development of Diffusive Systems, Acceptability of Monitoring Data Based on Diffusive Sampling, Conclusions and Recommendations.

Radiation Curing of Polymers

EDITED BY D. R. RANDELL, CIBA-GEIGY INDUSTRIAL CHEMICALS



Throughout the 1970's and 1980's, there has been a growing interest in the use of radiation sources in the curing of polymers in surface coatings applications. This has arisen because the procedure presents a quick, clean and energy efficient means of achieving a hardened cross-linked polymer system. Initially ultraviolet was the sole radiation source used but more recently electron beam and laser energy sources have been introduced. Furthermore cationic as well as free radical initiators are now finding favour.

Industrial outlets now served by the technique include paper, metal, plastics and wood coatings, adhesives and printing. Consequently many workers in industry and academia are now involved in the varied aspects of developing new systems for the future.

This new book provides a timely review of progress in this rapidly developing and diverse subject area and offers useful and stimulating reading for practitioners of the radiation curing of polymers.

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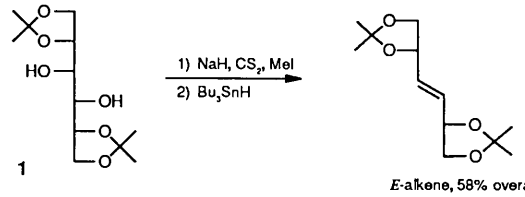
Radical Deoxygenation

The **tributyltin hydride**-mediated deoxygenation of thiocarbonyl derivatives of alcohols *via* a radical mechanism had its genesis in the work of Barton and co-workers.[1] Since the initial report, this and related reactions[2-5] have been used for the deoxygenation of steroidal and terpenoid alcohols, sugars, nucleosides, aminoglycosides, etc. The radical-deoxygenation method offers a number of advantages over the more conventional methods, *e.g.*, neutral conditions, less susceptibility to steric factors, compatibility with a wider variety of functionalities and less proclivity towards rearrangements.[2] Thus, this technique is rapidly growing in importance — particularly in carbohydrate chemistry. The following examples highlight some of the more recent work exploiting this methodology.

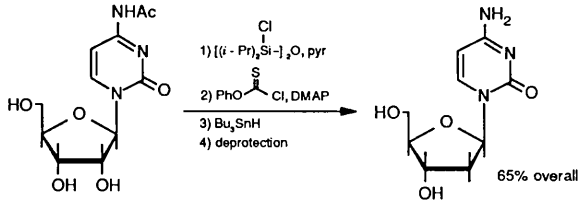
Formation of alkenes from vicinal diols:[6]

Treatment of the bis-xanthate derived from diisopropylidenemannitol (**1**) with **tributyltin hydride** in toluene resulted in the formation of the *E*-alkene in 65% yield.



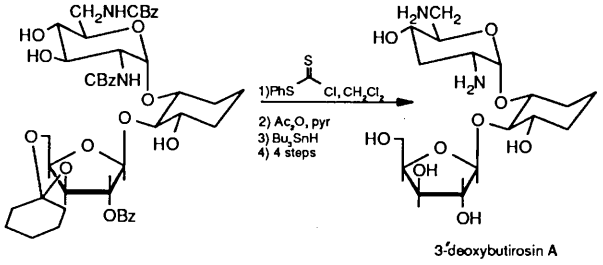
Conversion of ribonucleosides to 2′-deoxynucleosides:[7]

Robins and co-workers have developed a simple and efficient approach to the synthesis of 2′-deoxynucleosides from their ribo analogs using radical deoxygenation. Phenoxythiocarbonyl derivatives of the 2′-alcohols react with **tributyltin hydride** to give high overall yields (57-78%) of the 2′-deoxynucleosides.



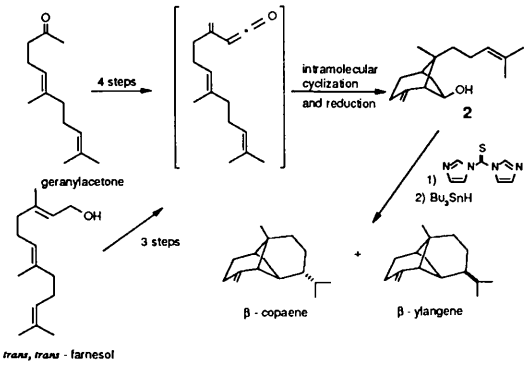
Aminoglycoside synthesis:[8]

Phenyl chlorodithioformate was utilized by Hayashi and coworkers in the synthesis of 3′-deoxybutirosin A, an aminoglycoside antibiotic. The deoxygenation step proceeded in 82% yield.



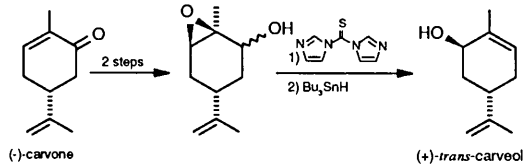
Radical deoxygenation-cyclization in terpene synthesis:[9]

A radical cyclization process was utilized by Snider and coworkers in the synthesis of the tricyclic sesquiterpenes β-copaene and β-ylangene. The radical intermediate required for this process was generated by the deoxygenation of alcohol **2**.



Radical-induced ring opening of epoxides:[10]

Barton and co-workers have utilized the radical-deoxygenation reaction in an interesting transformation of (-)-carvone into (+)-*trans*-carveol. This reaction serves as an alternative to the Wharton Rearrangement.



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(1) Barton, D.H.R.; McCombie, S.W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574. (2) Hartwig, W. *Tetrahedron* **1983**, *39*, 2609 (a review). (3) Kuivila, H.G.; Walsh, Jr., E.J. *J. Am. Chem. Soc.* **1966**, *88*, 571. (4) Pfenniger, J.; Heuberger, C.; Graf, W. *Helv. Chim. Acta* **1980**, *63*, 2238. (5) Khoo, L.E.; Lee, H.H. *Tetrahedron Lett.* **1968**, 4351. (6) Barton, D.H.R.; Barrett, A.G.M.; Bielski, R. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2378. (7) Robins, M.J.; Wilson, J.S.; Hansske, F. *J. Am. Chem. Soc.* **1983**, *105*, 4059. (8) Hayashi, T.; Iwaoka, T.; Takeda, N.; Ohki, E. *Chem. Pharm. Bull.* **1978**, *26*, 1786. (9) Snider, B.B.; Kulkarni, Y.S.; Niwa, M.; Ron, E. *J. Org. Chem.* **1987**, *52*, 1568. (10) Barton, D.H.R.; Motherwell, R.S.H.; Motherwell, W.B. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2363.

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