New Journal from The Royal Society of Chemistry

NATURAL PRODUCT REPORTS

Natural Product Reports is a new bimonthly review journal which will commence publication in February 1984. It will review recent developments in areas of natural product chemistry previously covered by the Specialist Periodical Reports (annual or biennial reviews) entitled "The Alkaloids", "Biosynthesis", "Terpenoids and Steroids" and "Aliphatic and Related Natural Product Chemistry". Publication in journal form will help to overcome the problem of overlap and enable reports to be published much faster than is possible in an annual volume. Furthermore, an annual subscription to Natural Product Reports will cost substantially less than a subscription to Specialist Periodical Reports.

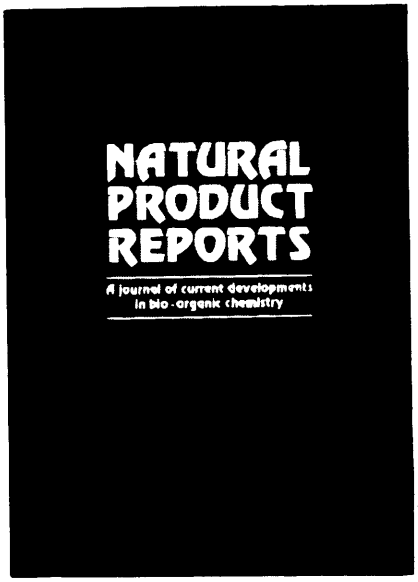
Natural Product Reports, however, is more than just a continuation of subjects covered by a number of SPR titles—it is planned that coverage should be expanded to include such areas as chemotaxonomy, enzymology and biosynthetic aspects of biotechnology, and also advances in physical techniques used for structure determination e.g. n.m.r., h.p.l.c., mass spectrometry, and chiroptical data.

Natural Product Reports will consist of critical reviews written by groups of leading authorities, many of whom have gained worldwide recognition for their contributions to the subject area. Each issue will contain approximately 120 pages covering six or seven articles; there will be an author index and a subject index (cumulated annually) to facilitate location of articles dealing with specific areas.

CONTENTS

It is expected that the first three issues will include the following reviews:

Issue 1 (February)	Rotenoids; Indole Alkaloids; Triterpenoids; Carotenoids and Polyterpenoids; Microbial Metabolites;
Issue 2 (April)	Alkaloid Biosynthesis; Aporphinoid Alkaloids; Quinoline, Quinazoline; and Acridone Alkaloids; Sesquiterpenoids; Diterpenoids;
Issue 3 (June)	Steroids; Insect Pheromones; Polyketides; plus several articles on alkaloids (details not yet available)



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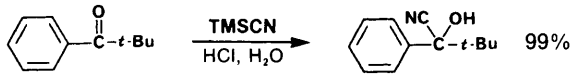
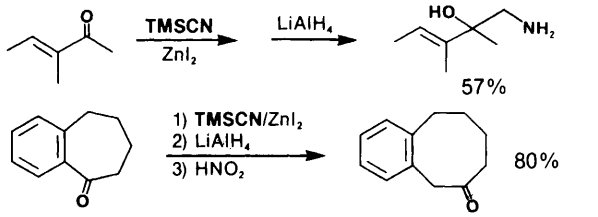
Trimethylsilyl Cyanide

Aldehydes and ketones react with **trimethylsilyl cyanide** (TMSCN) to give cyanohydrin trimethylsilyl ethers (**1**), useful intermediates in organic synthesis.[1]

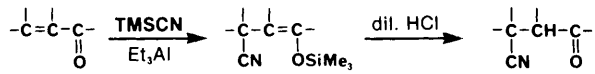
Even sterically hindered ketones react with **TMSCN** to give **1**, which in turn may be converted to the cyanohydrins in high yields with dilute HCl. This reaction works well with diaryl, dialkyl, and alkyl aryl ketones.[2]



Cyanohydrin TMS ethers (**1**) may be reduced with LAH to afford β-aminoethyl alcohols,[3] intermediates in the Tiffeneau-Demjanov ring-expansion reaction.[4]



Addition of **TMSCN** to α,β-unsaturated ketones normally gives the 1,2-product. However, in the presence of triethylaluminum, the 1,4-adduct is obtained.[5]



Other recent applications of **TMSCN** include the conversion of ketones to cyanoalkenes,[6] the preparation of thiocyanides,[7] and the conversion of pentanediol acetals to cyanohydrin ethers which can be readily transformed to cyanohydrins, β-amino alcohols, or α-hydroxy esters of optical purities greater than 90%.[8]

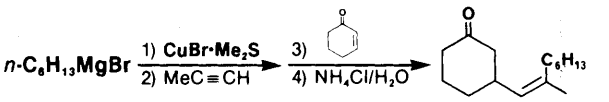
References:

1) Evans, D.A.; Truesdale, L.K.; Carroll, G.L. *Chem. Commun.* **1973**, 55.
2) Gassman, P.G.; Talley, J.J. *Tetrahedron Lett.* **1978**, 3773.
3) Evans, D.A.; Carroll, G.L.; Truesdale, L.K. *J. Org. Chem.* **1974**, *39*, 914.
4) Thies, R.W.; Seitz, E.P. *ibid.* **1978**, *43*, 1050.
5) Utimoto, K.; Obayashi, M.; Shishiyama, Y.; Inoue, M.; Nozaki, H. *Tetrahedron Lett.* **1980**, *21*, 3389.
6) Oda, M.; Yamamuro, A.; Watabe, T. *Chem. Lett.* **1979**, 1427.
7) Harpp, D.N.; Friedlander, B.T.; Smith, R.A. *Synthesis* **1979**, 181.
8) Elliott, J.D.; Choi, V.M.F.; Johnson, W.S. *J. Org. Chem.* **1983**, *48*, 2294.

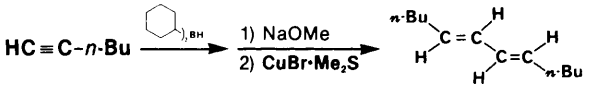
21,284-9 Trimethylsilyl cyanide, 98% **5g $13.85**
25g $46.20

Copper(I) Bromide - Dimethyl Sulfide Complex

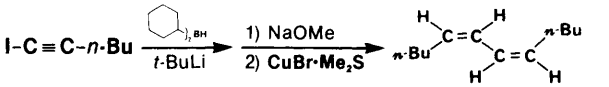
The reaction of **copper(I) bromide-dimethyl sulfide complex** with Grignard or alkyllithium reagents affords alkylcopper compounds (Gilman reagents) which are useful for the stereocontrolled synthesis of a variety of unsaturated compounds including trisubstituted olefins, dienes, substituted maleates and γ-alkyl-α,β-unsaturated carbonyl compounds.[1-5] **Complexed CuBr** is superior to the uncomplexed material in promoting clean, high-yield reactions, as evidenced by the following:



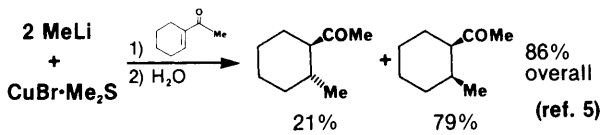
73% **(ref. 1)**
≥99.96% *Z*



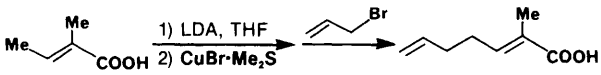
97% **(ref. 2)**
E,E exclusively



85% **(ref. 2)**
Z,Z exclusively



Coupling associated with alkenylcopper intermediates can be supressed by adjusting reaction conditions and treating with a suitable electrophile to give the alkylated product.[1,6]



88% yield **(ref. 3)**

Alkylcopper compounds derived from **copper(I) bromide-dimethyl sulfide complex** have provided a valuable synthetic strategy for a variety of natural product intermediates. To aid in the synthesis of organocopper compounds, Aldrich offers a wide selection of Grignard and organolithium reagents.

References:

1) Marfat, A.; McGuirk, P.R.; Helquist, P. *J. Org. Chem.* **1979**, *44*, 3888.
2) Campbell, J.B.; Brown, H.C. *ibid.* **1980**, *45*, 549.
3) Savu, P.M.; Katzenellenbogen, J.A. *ibid.* **1981**, *46*, 239.
4) Nishiyama, H.; Sasaki, M.; Itoh, K. *Chem. Lett.* **1981**, 905.
5) House, H.O.; Chu, C.-Y.; Wilkins, J.M.; Umen, M.J. *J. Org. Chem.* **1975**, *40*, 1460.
6) Brown, H.C.; Campbell, J.B. *ibid.* **1980**, *45*, 552.

23,050-2 Copper(I) bromide-dimethyl sulfide complex, 99% **10g $9.80; 50g $34.50**