



# COLOUR CHEMISTRY

THE DESIGN AND SYNTHESIS

OF ORGANIC DYES AND

PIGMENTS

EDITED BY

A.T. PETERS AND H.S. FREEMAN

ADVANCES IN COLOUR CHEMISTRY SERIES

ELSEVIER APPLIED SCIENCE

# COLOUR CHEMISTRY

## The Design and Synthesis of Organic Dyes and Pigments

*Edited by*

A. T. PETERS

*Department of Chemical Engineering (Chemistry and Chemical  
Technology), University of Bradford, UK*

H. S. FREEMAN

*Department of Textile Engineering, Chemistry and Science,  
College of Textiles, North Carolina State University,  
Raleigh, USA*



ELSEVIER APPLIED SCIENCE  
LONDON and NEW YORK

ELSEVIER SCIENCE PUBLISHERS LTD  
Crown House, Linton Road, Barking, Essex IG11 8JU, England

*Sole Distributor in the USA and Canada*  
ELSEVIER SCIENCE PUBLISHING CO., INC.  
655 Avenue of the Americas, New York, NY 10010, USA

WITH 34 TABLES AND 158 ILLUSTRATIONS

© 1991 ELSEVIER SCIENCE PUBLISHERS LTD

**British Library Cataloguing in Publication Data**

Colour chemistry

1. Colouring agents

I. Peters, A. T. (Anthony T.) II. Freeman H. S. III.  
Series

667.2

ISBN 1-85166-577-3

**Library of Congress Cataloging-in-Publication Data**

Colour chemistry/edited by A. T. Peters and H. S. Freeman.

p. cm.—(Advances in colour chemistry series)

Includes bibliographical references and index.

ISBN 1-85166-577-3

1. Dyes and dyeing—Chemistry. I. Peters, A. T. II. Freeman, H. S.

III. Title: Color chemistry. IV. Series.

TP910.C65 1991

667'.2—dc20

90-28875

CIP

No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein.

**Special regulations for readers in the USA**

This publication has been registered with the Copyright Clearance Center Inc. (CCC), Salem, Massachusetts. Information can be obtained from the CCC about conditions under which photocopies of parts of this publication may be made in the USA. All other copyright questions, including photocopying outside the USA, should be referred to the publisher.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the prior written permission of the publisher.

Typeset and printed by The Universities Press (Belfast) Ltd.

# **COLOUR CHEMISTRY**

**The Design and Synthesis of  
Organic Dyes and Pigments**

## **ADVANCES IN COLOUR CHEMISTRY SERIES**

## PREFACE

Taking a generalized historical viewpoint of the field of chemistry and chemical technology which can be broadly defined as colour chemistry, it could be concluded that at least four distinct developments have made a significant impact on the progression and expansion of this subject area. The initiation was, of course, the discovery of the first synthetic dye, mauveine, by W. H. Perkin in 1856. This historic event ultimately resulted in the commercial development of a vast range of synthetic colorants both for textile and non-textile applications, and which possessed a more favourable cost versus benefit ratio compared to the hitherto used naturally occurring colorants. The second factor was the development over the years of synthetic fibres, an innovation which led to vigorous new research and the addition of the disperse dyes and improved cationic dyes to the extensive volume of synthetic dyestuffs enjoying successful industrial exploitation. The introduction of the fibre reactive dyes, whilst presenting innovative ideas in both the chemistry and application of colorants, may be considered as a natural development from the first event.

The third development can be related to the recognition of the potential adverse effects of certain synthetic dye intermediates on human health. This resulted in the removal of most benzidine and 2-naphthylamine based dyestuffs from the manufacturing processes in a number of countries, and later to guidelines requiring dyestuff manufacturers to demonstrate safety aspects in all new and certain existing products, and also in the effluents released from manufacturing plants into local waters. Unlike the first two developments, both of which initiated new industrial dyestuff research, this third development did not provide an opportunity for the industry to expand. Indeed, it

presented, and continues to present, the challenge to manufacture colorants which do not pose potentially hazardous environmental or toxicological characteristics, but which also retain advantageous functional properties.

The fourth development, and one which has also resulted in new dyestuff research, has been in the application of synthetic colorants in high technology areas involving, for example, lasers, liquid crystalline displays, electro-optical devices and ink-jet printers. The research in these areas has been fruitful and has resulted in a large volume of innovative chemistry, but there exists, to some extent, a cost versus benefit consideration in the manufacture of such products.

This volume covers, in the broad sense, chapters pertinent to each of the above developments. The idea for the volume was conceived following the 1988 Symposium on Colour Chemistry, organized under the auspices of the American Chemical Society in Los Angeles, California. From that initial seed, the book was developed—using a combination of original research work and review material. The themes in the book have been selected to cover, as far as possible, some aspects of current activity pertinent to the four developments noted above. As a consequence, its chapters embrace the chemistry of traditional intermediates and colorants for textile and non-textile applications, structural analysis using the analytical technique of 2-dimensional nuclear magnetic resonance spectroscopy, aspects of the toxicological and environmental factors in the synthesis and evaluation of colorants and in the disposal of effluent liquors from their manufacture, and on the more recent developments pertaining to the use of colorants in high-technology applications.

This wide ranging theme of topics is indicative of how far the horizons of colour chemistry have broadened since Perkin first noted his purple impurity and unknowingly set the whole machinery of progress in colorants into motion. They are indicative of, and a reflection of, the ingenuity of mankind. They are also a very positive indication that, as we approach the 21st century, colour chemistry still has much to offer, to scientists, technologists, industry and to society.

A. T. PETERS  
H. S. FREEMAN

## LIST OF CONTRIBUTORS

- T. R. CHAMBERLAIN  
*Sun Chemicals Corporation, Pigments Division, Cincinnati, Ohio  
45232-1984, USA*
- R. M. CHRISTIE  
*Department of Technology, Scottish College of Textiles,  
Netherdale, Galashiels TD1 3HF, UK*
- L. D. CLAXTON  
*Genetic Toxicology Division, US Environmental Protection  
Agency, Research Triangle Park, North Carolina 27711, USA*
- M. DEZUBE  
*Office of Toxic Substances, US Environmental Protection Agency,  
401 Main Street SW Washington, DC 20460, USA, Present  
address: Glaxo Inc., 5 Moore Drive, Triangle Park, North  
Carolina 27709, USA*
- M. J. DOA  
*Office of Toxic Substances, US Environmental Protection Agency,  
401 Main Street, SW Washington, DC 20460, USA*
- R. EGLI  
*Sandoz Ltd, Chemicals Division, CH 4002 Basel, Switzerland*
- J. F. ESANCY  
*Department of Textile Engineering, Chemistry and Science, College  
of Textiles, North Carolina State University, Raleigh, North  
Carolina 27695-8302, USA*
- H. S. FREEMAN  
*Department of Textile Engineering, Chemistry and Science, College  
of Textiles, North Carolina State University Raleigh, North Carol-  
ina 27695-8302, USA*



- P. GREGORY  
*ICI Colours and Fine Chemicals, Blackley, Manchester M9 3DA, UK*
- J. HOUK  
*Office of Toxic Substances, US Environmental Protection Agency, 401 Main Street, SW Washington, DC 20460, USA. Present address: Keller and Heckman, Suite 1000, 1150 17th Street, NW Washington, DC 20036, USA*
- J. HU  
*Department of Fine Chemicals, Dalian University of Technology, Dalian 116012, People's Republic of China*
- J. JIRMAN  
*Research Institute of Organic Synthesis, 532 18 Pardubice-Rybitví, Czechoslovakia*
- Z. LI  
*Department of Fine Chemicals, Dalian University of Technology, Dalian 116012, People's Republic of China. Present address: Department of Colour Chemistry and Dyeing, Leeds University, Leeds LS2 9JT, UK*
- A. LYČKA  
*Research Institute of Organic Synthesis, 532 18 Pardubice-Rybitví, Czechoslovakia*
- M. MATSUOKA  
*Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai 591, Japan*
- C. O. OKAFOR  
*Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka, Nigeria*
- A. REIFE  
*CIBA-GEIGY Corporation, PO Box 71, Toms River, New Jersey, 08754, USA*
- J. M. ROVINSKI  
*Office of Toxic Substances, US Environmental Protection Agency, 401 Main Street, SW Washington, DC 20460, USA. Present address: US Food and Drug Administration (HFF-415), 200 C Street, SW Washington, DC 20204, USA*
- P. N. STANDRING  
*Department of Technology, Scottish College of Textiles, Netherdale, Galashiels TD1 3HF, UK*

# CONTENTS

<i>Preface</i> . . . . .	v
1. The Chemistry of Blue Disperse Dyes, Past and Present . . . . . R. EGLI	1
2. Molecular Modifications in the Development of Phenothiazine Dyes . . . . . C. O. OKAFOR	29
3. Molecular Orbital Design, Synthesis and Characteristics of Func- tional Dyes for Electro-optical Applications . . . . . M. MATSUOKA	61
4. An Approach to the Design of Nonmutagenic Azo Dyes: Ana- logues of the Mutagen 4-Amino-3-Methoxyazobenzene . . . . . H. S. FREEMAN, J. F. ESANCY and L. D. CLAXTON	85
5. Anthranilic Acid: A Versatile Pigment Intermediate . . . . . T. R. CHAMBERLAIN	115
6. Evaluation of Dyes Submitted Under the Toxic Substances Control Act New Chemicals Programme . . . . . J. HOUK, M. J. DOA, M. DEZUBE and J. M. ROVINSKI	135
7. Reduction of Toxic Wastewaters in Disperse Azo Dye Manufac- ture . . . . . A. REIFE	151
8. The Cyanation of <i>o</i> -Halogenated Azo Dyes using Phase Transfer Catalysis . . . . . Z. LI and J. HU	169
9. Colorants for High Technology . . . . . P. GREGORY	193
10. Two-Dimensional NMR Spectroscopy in the Analysis of Organic Dyes . . . . . A. LYČKA and J. JIRMAN	225
11. Colour and Constitution Relationships in Azoacetoacetanilide Pigments . . . . . R. M. CHRISTIE and P. N. STANDRING	253

## Chapter 1

# THE CHEMISTRY OF BLUE DISPERSE DYES, PAST AND PRESENT

R. EGLI

*Sandoz Products (Switzerland) Ltd, CH 4002 Basel, Switzerland*

### DEFINITION AND APPLICATIONS OF DISPERSE DYES

Disperse dyes are low molecular weight (approx. 300–700), virtually water-insoluble anthraquinone (AQ), azo or polymethine dyes suitable for colouring polyester (PES) fibres. The dyeing of partially acetylated cellulose, as well as nylon, is also possible with these dyes. Thus, red, as well as blue, AQ-dyes already used for the colouration of acetate silk were available for PES dyeing around 1950.

### MANUFACTURE AND FINISHING OF DISPERSE DYES

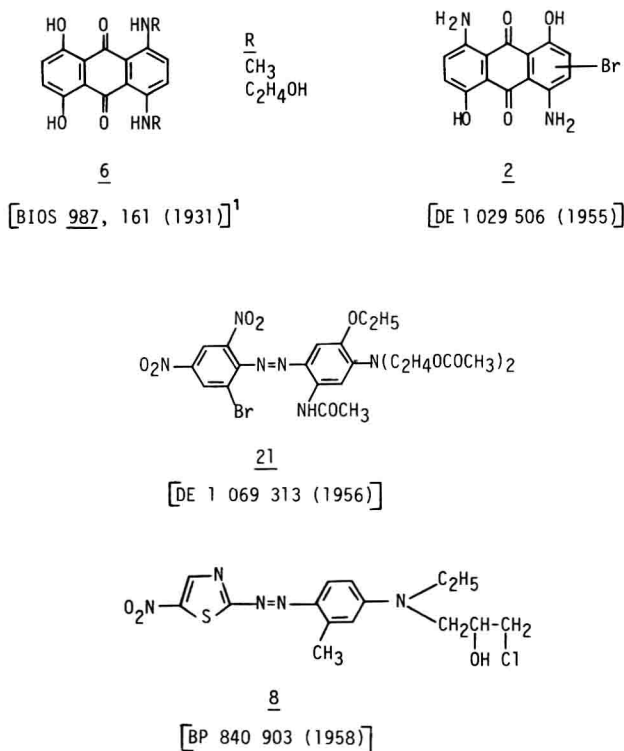
In the final stages of the laboratory synthesis, the water-insoluble disperse dye is filtered, washed, dried and analyzed. The dye then exists in the form of a so-called dye presscake. In this form, it is not suitable for dyeing purposes and must be further processed as follows.

In a typical laboratory procedure, the dye presscake is ground together with dispersants, mainly anionic lignin sulphonates. This grinding takes place in aqueous medium in a glass or steel beaker with glass beads using a two-plate steel mill at a speed of about 2000 rpm for several hours. When the grinding is complete, an aqueous dispersion is obtained which, when placed on a round filter paper, spreads out evenly, as with a solution, without forming a border at the edge. The dispersion is then filtered, dried on a rotary evaporator, and pulverized in a mortar into a so-called ultradisperse powder. Research preparations processed in this manner have a particle size of

approximately 1  $\mu\text{m}$ . These preparations are then subjected to various dyeing and fastness tests in the R&D test laboratories.

On a production scale the grinding is done in large mills and the drying process to obtain the final product is performed on special spray-drying equipment. The granulated form of the commercial product produced by this process conforms to practice conditions. The product has good flowing properties, is suitable for automatic dispensing and is non-dusting. The granules should also be capable of wetting out and dispersing quickly and completely so they can be further stirred into an aqueous dispersion that is stable for dyeing purposes.

Disperse dyes are sold also in liquid form for certain applications, e.g. printing.



**Fig. 1.** Blue disperse dyes—representative examples up to 1965.

## BLUE DISPERSE DYES AND INTERMEDIATE PRODUCTS

### Blue disperse dyes around 1965

With a selection of four types, Fig. 1 illustrates the situation with respect to blue disperse dyes available somewhat more than 20 years ago. Blue AQ dyes available for dyeing acetate silk are typified by **6** (strongly greenish) and dye **2** (neutral blue). Below these are shown typical azo dyes available at that time: compound **21** is the classic navy blue structure. The reddish blue and still somewhat dull 5-nitrothiazole-2-azo dye **8** indicates that the use of heterocyclic diazo components goes back well into the 1950s.

The hue and the brilliance of these commercial products is displayed in Fig. 2, which provides a colourimetric presentation of the hue ( $H^0$ ) as well as the brilliance ( $C^*$ ) of these four dye types. They are represented by the so-called CIELAB system.<sup>2</sup> In this system the brilliance and the shade of dyeings is recorded and plotted by reflectance measurement. The  $C^*$  value is a measure of the brilliance and is recorded on the ordinate. The  $H^0$  value given on the abscissa expresses the dyeing hue in numerical terms.

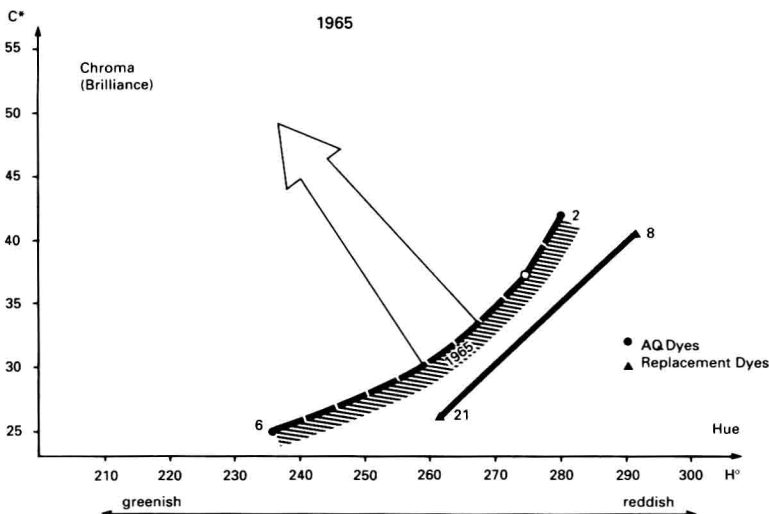


Fig. 2. Hue and chroma (brilliance) of blue disperse dyes in 1/1 standard depth (CIELAB).<sup>2</sup>

The direction of further research was therefore clear; the azo dyes, which were more economical than the AQs, needed to be improved with respect to their brilliance, and in addition the search for greener, more bathochromically absorbing dyes became a priority.

The following research results are not arranged according to strict chronology but principally from a structural standpoint. Relevant structures taken from the literature, including certain commercial dyes, are included.

### Blue disperse dyes based on azobenzene

Patent applications in the 1960s led to commercial products around 1970 with which PES could be dyed in a bright blue shade, at first a reddish blue and then, somewhat later, also a neutral to slightly greenish blue.

Figure 3 shows the azobenzene derivatives. These dyes are distinguished primarily by different substituent combinations in the diazo component; the coupling components differ only marginally. The influence of the substituent  $X$  on  $\lambda_{\max}$  is clearly apparent, and, accordingly, different blue tones could be expected on PES.

The reddish blue **11** ( $X = \text{Br}$ ) is prepared directly, i.e. by diazotization of the amine and coupling. The same procedure fails on a technical scale with more negatively substituted amines, e.g. as in the

	X	R	DMF $\lambda_{\max}$ [nm]
	Br	C <sub>2</sub> H <sub>5</sub>	591
	NO <sub>2</sub>	CH <sub>3</sub>	613
	CN	CH <sub>3</sub>	619
	SO <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	617

**18**

Fig. 3. Blue azobenzene disperse dyes—developments from 1965 to 1970.

case of dyes **14**, **15**, **17** and **18**. These are prepared in a two stage process by nucleophilic replacement of the 2-halogeno or the 2,6-dihalogeno intermediate dyes with cyanide (once in dyes **14** and **18**, twice in dye **17**) or with methylsulphinate as in dye **15**. By the additional introduction of an alkoxy residue into the 5'-position of the coupling component, a bathochromic shift then occurs into the strongly greenish blue region, thus making it possible to achieve the greenish AQ standard.

These azo dyes still represent the state of the art from a technical dyeing and fastness standpoint and cover the reddish to neutral blue region to the dyer's satisfaction.

Figure 4 shows the reddish blue (dye **11**) as well as the distinctly

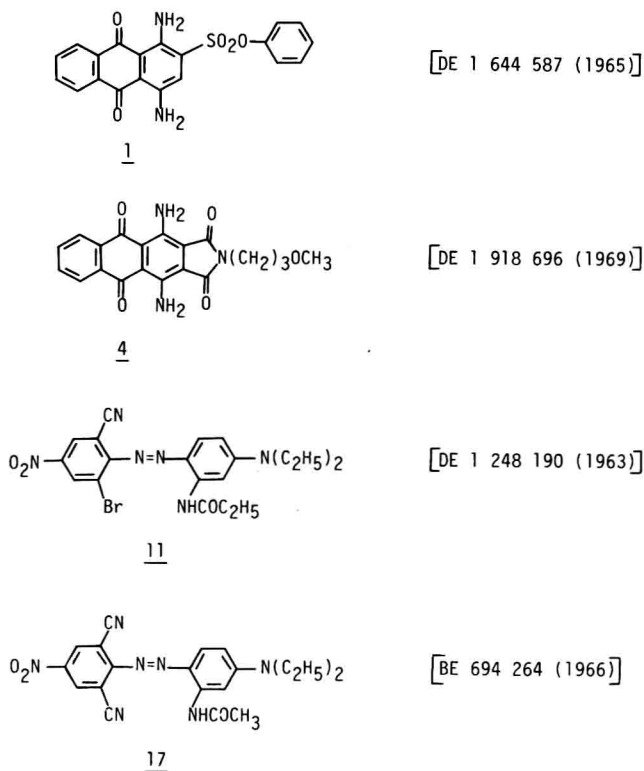
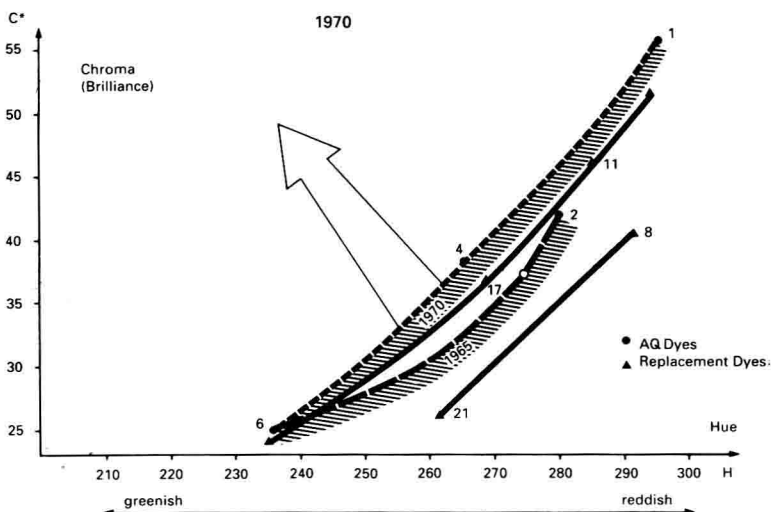


Fig. 4. Blue disperse dyes—representative examples from 1965 to 1970.



**Fig. 5.** Hue and chroma (brilliance) of blue disperse dyes in 1/1 standard depth (CIELAB).

greener neutral blue (dye 17) as two typical examples of the azobenzene type discussed above. In addition, two representative new developments in the AQ sector, which appeared between 1965 and 1970, are included, viz. the strongly reddish blue and brilliant dye 1, and the first representative of the extremely important turquoise elements of type 4. The shade and end-use fastness properties of these turquoises are still unequalled by any non-AQ based dye.

These four elements are also presented in the CIELAB diagram in Fig. 5. The two azobenzene derivatives 11 and 17 are shown in relation to the two AQ structures 1 (reddish blue) and 4 (turquoise).

In this figure it can be discerned that the newly accessible shade region has noticeably shifted within only a few years, to the direction of brighter ( $C^*$  values) and greener ( $H^0$  values) dyes.

### Thiazole intermediates and dyes

Three nitro substituted aminothiazoles (Fig. 6)<sup>3</sup> are primarily of interest; the 5-amino-4-nitroisothiazole and its benzoannellated derivative, the important 2-amino-5-nitrothiazole and the interesting structure 5-amino-2-nitrothiazole.



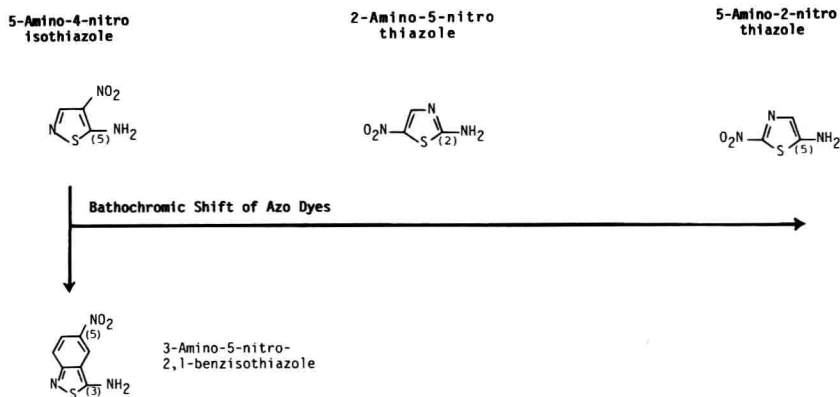


Fig. 6. Thiazole diazo components.<sup>3</sup>

### 5-Aminothiazoles

MO calculations indicate that azo dyes based on 5-aminothiazoles make worthwhile target molecules if maximum bathochromic shift is the goal. However, as far as is known, 5-amino-2-nitrothiazole has not yet been synthesized.

### 5-Aminoisothiazoles

These are, however, easily accessible and lead to excellent azo dyes from a dyeing and fastness standpoint, but mainly in the red-violet region. The principle of synthesis of 5-aminoisothiazoles is outlined in Fig. 7. Typical syntheses are

- (i) the 4-nitro-derivative: Acetonitrile dimer is treated with hydrogen sulphide to give the thioamide, which is then cyclized with hydrogen peroxide to the isothiazole with the 4-position free. Protected as the acetamide, it can now be nitrated and subsequently hydrolyzed to the free amine, 5-amino-3-methyl-4-nitroisothiazole.
- (ii) the 4-cyano-derivative: A synthesis based on the same principle of oxidative cyclization produces directly the 4-cyano derivative.<sup>4</sup> 2-Cyano-3-methoxycrotonic acid nitrile (readily obtainable from malodinitrile and orthoacetic acid esters) is converted into the thioamide; amino substitution of the methoxy group and cyclization with hydrogen peroxide leads to the final product. The three steps can be carried out in a one pot reaction.