

This article was downloaded by:

On: 27 January 2011

Access details: *Access Details: Free Access*

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



Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

AN EFFICIENT SYNTHESIS OF N-(2,4-DIFLUOROPHENYL)-N-METHYL-2,4-DINITRO-6-(TRIFLUOROMETHYL)ANILINE

E. V. P. Tao^a; H. A. Corbitt^a

^a The Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, IN

To cite this Article Tao, E. V. P. and Corbitt, H. A. (1985) 'AN EFFICIENT SYNTHESIS OF N-(2,4-DIFLUOROPHENYL)-N-METHYL-2,4-DINITRO-6-(TRIFLUOROMETHYL)ANILINE', *Organic Preparations and Procedures International*, 17: 3, 210 – 212

To link to this Article: DOI: 10.1080/00304948509355504

URL: <http://dx.doi.org/10.1080/00304948509355504>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

2-(p-Nitrobenzalazo)-4-(4'-hydroxycoumarin-3'-yl)-5-methylthiazol-2-one
(IIIh) in 85% yield as yellow crystals, mp. 305-308°. IR: 3420 (OH), 3000 (CH arom.), 2910 (CH₃), 1675 (CO), 1612 (C=C, arom.) cm⁻¹; nmr: δ 7.3-8.35 (m, 8H arom., NH, CH), 2.20 (s, CH₃); MS: M⁺ 422 (100).

Anal. Calcd for C₂₀H₁₄N₄O₅S: C, 56.86; H, 3.34; N, 13.26

Found: C, 57.45; H, 3.51; N, 13.27

Acknowledgement.- This investigation was supported financially by a grant in aid from the Republic's Association for Scientific Work of Bosnia and Hercegovina.

REFERENCES

1. G. P. Ellis and G. B. West, "Progress in Medicinal Chemistry", American Elsevier Inc., New York, N. Y., 1974, p. 85.
2. M. Trkovnik, N. Zivkovic, M. Kules and R. Djudjic, Org. Prep. Proced. Int., 10, 215 (1978).
3. I. Ya. Postovskii, A. P. Novikova, L. A. Chechulina and L. P. Sidorova, Khim. Geterotsikl. Soed., 8, 1051 (1976); C. A. 85, 177376 (1976).
4. V. D. Pfeiffer, E. Dick and E. Bulka, Z. Chem., 17, 218 (1977).

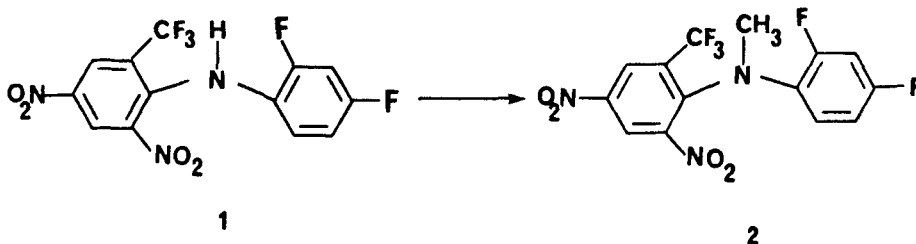
AN EFFICIENT SYNTHESIS OF N-(2,4-DIFLUOROPHENYL)- N-METHYL-2,4-DINITRO-6-(TRIFLUOROMETHYL)ANILINE

Submitted by E. V. P. Tao* and H. A. Corbitt
(11/05/84)

The Lilly Research Laboratories
Eli Lilly and Company
Indianapolis, IN 46285

N-(2,4-difluorophenyl)-N-methyl-2,4-dinitro-6-(trifluoromethyl)aniline
(2),¹ is a contact miticide which has demonstrated effective control of
phytophagus mites on cotton and tree fruits and nuts. Methyl bromide has

long been known as a methylating agent;² however, it is less known as a methylating agent to convert a secondary aromatic amine to the corresponding tertiary amine as shown below. Until recently there has not



been a satisfactory synthesis of 2; either the yield is not high or the process is not economically feasible for large-scale preparation. We now report an efficient synthesis of 2 which utilizes methyl bromide under pressure, gives good yields and is amenable to large scale production.

EXPERIMENTAL SECTION

N-(2,4-Difluorophenyl)-N-methyl-2,4-dinitro-6-(trifluoromethyl)aniline (2).-
 N-(2,4-Difluorophenyl)-2,4-dinitro-6-(trifluoromethyl)aniline (108.9 g, 64.4% pure, 0.193 mole), sodium carbonate (64 g), and dimethylformamide (150 ml) were placed in a 1 L Chemineer pressure reactor³ equipped with an air-driven agitator, a baffle, a pressure gauge, a relief port and a sample port. The reaction mixture was cooled to -15° , and methyl bromide (228 g, 2.47 moles) was added as a cold liquid; the reactor was sealed. The reaction mixture was then heated to 95° over a period of 30 min. and was maintained at that temperature for 2 hrs with agitation; the pressure was kept at 120 psig by occasional venting. The reaction mixture was allowed to cool to room temperature and the reactor purged with air in order to remove the remaining methyl bromide. The reaction mixture was poured into water and the product was collected and recrystallized from ethanol to afford 70.6 g, (97%) of 2, mp. $104.5-105.5^{\circ}$.

Anal. Calcd for $C_{14}H_8F_5N_3O_4$: C, 44.58; H, 2.14; F, 25.18; N, 11.14

Found: C, 44.67; H, 2.22; F, 25.26; N, 11.06

NMR (DMSO- d_6): δ 3.26 (s, 3, N-CH₃), 7.2 (m, 3, ArH), 8.65, 9.0 (d, 2 meta coupled ArH). Mass spectrum: M^+ 377.

REFERENCES

1. B. A. Dreikorn and K. E. Kramer, U. S. Patent 4407820 (1983); Chem. Abstr., 98, 71652y (1983).
2. N. Weiner, Org. Syn. Coll. Vol. 2, 279 (1943).
3. Chemineer, Inc., P. O. Box 1123, Dayton, Ohio 45401.

A CONVENIENT, TWO-STEP SYNTHESIS OF BICYCLO[3.3.0]OCT-1(5)-ENE

Submitted by Paul J. Okarma^o and Joseph J. Caringi
(2/1/85)

Department of Chemistry
Yale University
New Haven, Connecticut 06511

During the course of a collaborative effort on the study of the solid state NMR spectra of alkenes, a sample of bicyclo[3.3.0]oct-1(5)-ene (1) was desired.¹ Although 1 had been prepared by a variety of routes,² none of them were convenient. It appeared possible to obtain 1 via a reductive coupling of carbonyl groups.³ The use of the high dilution procedure of McMurry might allow the conversion of 1,5-cyclooctanedione (2) to 1.⁴

