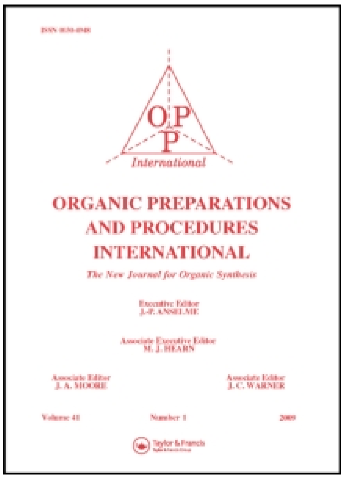
This article was downloaded by:
On: *27 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

DIAZEPINES. VIII. 3,8-DINITRO-11H-DIBENZO*[c, f] [1, 2]*-DIAZEPINE-5-OXIDE

A. Catala Casey[a]; F. D. Popp[a]
[a] Department of Chemistry, Clarkson College of Technology, Potsdam, New York

To cite this Article Casey, A. Catala and Popp, F. D.(1970) 'DIAZEPINES. VIII. 3,8-DINITRO-11H-DIBENZO*[c, f] [1, 2]*-DIAZEPINE-5-OXIDE', Organic Preparations and Procedures International, 2: 1, 29 — 31

To link to this Article: DOI: 10.1080/00304947009458414

URL: http://dx.doi.org/10.1080/00304947009458414

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.

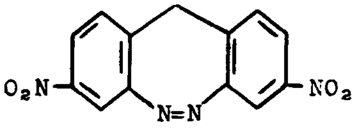
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any 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.

ORGANIC PREPARATIONS AND PROCEDURES 2(1), 29-31 (1970)

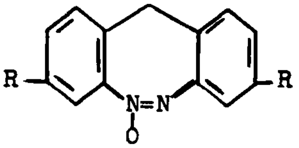
DIAZEPINES. VIII. 3,8-DINITRO-11H-DIBENZO[c,f][1,2]-DIAZEPINE-5-OXIDE[1]

A. Catala Casey[2] and F. D. Popp
Department of Chemistry, Clarkson College of Technology
Potsdam, New York 13676

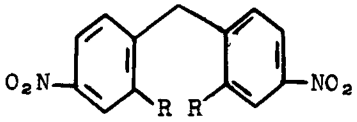
In connection with our studies of diazepines, we were interested in preparing I and II. It was hoped that an ammonium polysulfide reduction of the readily available tetranitro compound III might lead to some of the diamine IV which could then give I through an oxidative cyclization.[3] Reduction of III with ammonium polysulfide, however, led to 2,2'-dinitro-4,4'-diaminodiphenylmethane and a trinitroaminodiphenylmethane. The desired compound II was prepared, however, by decomposition of the diazonium fluoroborate of V in the presence of sodium nitrate and precipitated copper powder.



I



II R = NO_2
V R = NH_2



III R = NO_2 IV R = NH_2

Experimental

Reduction of 2,2′,4,4′-Tetranitrodiphenylmethane. - To a solution of 150 ml of ethanol and 50 ml of concentrated ammonium hydroxide was added 25 g (0.072 mole) of the tetranitro compound (III). The mixture was saturated with hydrogen sulfide and refluxed for 0.5 hr. This sequence was repeated 3 times. After 24 hr at room temperature, the mixture was filtered and the solid treated with 20% hydrochloric acid. Filtration and neutralization of the filtrate with ammonium hydroxide gave 7.3 g (35%) of 2,2′-dinitro-4,4′-diaminodiphenylmethane, m.p. 204-205° (reported[4] m.p. 205-206°), identical in all respects with an authentic sample. The residue from the above filtration was treated with hot ethanol and 3.6 g (16%) of an orange solid precipitated on cooling the ethanol. Recrystalization from ethanol gave a trinitroaminodiphenylmethane, m.p. 174-175°.

Anal. Calcd. for $C_{13}H_{10}N_4O_6$: C, 49.06; H, 3.17; N, 17.61. Found: C, 48.68; H, 3.55; N, 17.49.

Preparation of 3,8-Dinitro-11H-dibenzo[c,f][1,2]diazepine-5-oxide(II). - To a suspension of 3 g (0.0125 mole) of V[4] in 10 ml of concentrated hydrochloric acid and 3 ml of water with 8 g of sodium fluoroborate at 0° was added, with stirring, 2 g of sodium nitrite in 5 ml of water. After stirring at 0° for 0.5 hr, the mixture was filtered and the residue washed with a 5% solution of sodium fluoroborate, cold methanol, and cold ether. After drying over calcium chloride, a suspension of this diazonium fluoroborate in 30 ml of water was added to a suspension of 2 g of precipitated copper powder[5] and 10 g of sodium nitrite in 100 ml of water over a 15 min period. The mixture was stirred for 15 min., filtered, and the residue washed with water. Extraction of the residue with hot benzene and evaporation of the benzene gave 1.05 g (28%) of II, m.p. 212-214°. Recrystallization from glacial acetic acid or from ethanol did not change the m.p. IR (KBr): 1610, 1535, 1345 cm.$^{-1}$.

<u>Anal</u>. Calcd. for $C_{13}H_8N_4O_5$: C, 52.00; H, 2.68; N, 18.66. Found: C, 52.08; H, 2.80; N, 18.68.

References

1. For Part VII see: R. J. Dubois and F. D. Popp, Chem. Ind. (London), 620 (1969).

2. U.S.P.H.S. Predoctoral Fellow. Abstracted in part from the Ph.D. Thesis of Adria Catala, Clarkson College of Technology, 1964.

3. R. J. Dubois and F. D. Popp, J. Heterocyclic Chem., 6, 113 (1969).

4. H. Duval, Bull. Soc. Chim., (iv) 7, 532 (1910).

5. R. Q. Brewster and T. Groening, Org. Synth. II, 445 (1943).

(Received August 22, 1969)