Tetrahedron Letters No. 2, pp 141 - 142, 1977. Pergamon Press. Printed in Great Britain.

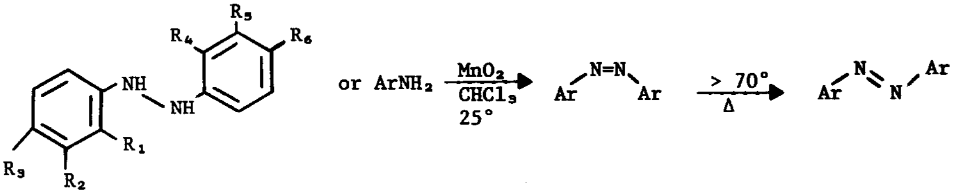
STEREOSPECIFIC SYNTHESIS OF *cis*-AZOBENZENES*

John A. Hyatt

Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company,
Kingsport, Tennessee 37662

(Received in USA 29 September 1976; received in UK for publication 30 November 1976)

To date the only method for preparing *cis*-azobenzenes has been *via* photochemical equilibration of *trans*-azobenzenes and chromatographic separation of the *cis* component.[1-3] We report that room-temperature oxidation by active manganese dioxide of substituted anilines or, more conveniently, hydrazobenzenes, produces the corresponding *cis*-azobenzenes in excellent yield and purity. The oxidation of *o*-chloroaniline with MnO_2 at 25° afforded a 20% yield of *cis*-2,2'-dichloroazobenzene (**2b**). Thermal isomerization to the *trans* isomer would account for the published results.[4,5]



3 **2** **1**

It was also found that 2,2'-dichlorohydrazobenzene **3b** affords *cis*-isomer **2b** in good yield and purity upon MnO_2 oxidation. The isomeric purity of the **2b** was increased to > 95% by argon-purging the MnO_2 slurry prior to the reaction and by excluding light. These measures prevent air oxidation of **3b** and photoisomerization of **2b**.

Pratt and McGovern[6] have reported *trans*-azobenzenes from the MnO_2 oxidation of hydrazobenzenes carried out at > 80°. As in the case of aniline oxidations under these conditions, thermal isomerization of initially formed *cis*-azobenzenes accounts for the results reported.

In view of the novelty of these results, the MnO_2 oxidation of a series of hydrazobenzenes, **3a**-**3i**, was carried out. As shown in Table 1, high yields of *cis*-azobenzenes were obtained except in those systems bearing strongly conjugating *para*-substituents.

---

*Dedicated to Prof. R. B. Woodward on the occasion of his sixtieth birthday.

Table 1. MnO_2 Oxidation of Hydrazobenzenes[a]

Starting Material							Product								
Compound	R_1	R_2	R_3	R_4	R_5	R_6	Compound	R_1	R_2	R_3	R_4	R_5	R_6	Mp	Yield, %
3a	H	H	H	H	H	H	**2a**	H	H	H	H	H	H	65-67°	89
3b	Cl	H	H	Cl	H	H	**2b**	Cl	H	H	Cl	H	H	91-92°	86
3c	H	Br	H	H	Br	H	**2c**	H	Br	H	H	Br	H	45-47°	98
3d	H	H	Cl	H	H	Cl	**2d**	H	H	Cl	H	H	Cl	66-68°	98
3e	OCH_3	H	H	OCH_3	H	H	**2e**	OCH_3	H	H	OCH_3	H	H	96-98°	96
3f	H	H	CH_3	H	H	CH_3	**2f**	H	H	CH_3	H	H	CH_3	96-98°	97
3g	H	H	H	H	H	OAc	*Trans*-isomer produced								
3h	H	H	H	H	H	OCH_3	*Trans*-isomer produced								
3i	H	H	H	H	H	NHAc	*Trans*-isomer produced								

[a] Compounds **3a**-**3i** were prepared by zinc-sodium hydroxide reduction of corresponding azo compounds[7]. Oxidations were carried out by adding the hydrazobenzene to an Ar-purged, darkened slurry of 5 to 10 parts by weight of activated MnO_2[8] in 10 parts by weight chloroform. Work-up by filtration, evaporation of solvent below 40° in the dark, and recrystallization afforded **2a**-**2f**. Products were characterized by IR, NMR, UV-VIS, and elemental analysis and by thermal isomerization (refluxing toluene) to the known *trans*-isomers.

References and Notes

1. G. S. Hartley, Nature, **140**, 281 (1937).
2. A. H. Cook, J. Chem. Soc., 876 (1938).
3. A. H. Cook and D. C. Jones, J. Chem. Soc., 1309 (1939).
4. M. Z. Barakat *et al.*, J. Chem. Soc., 4685 (1956).
5. O. H. Wheeler and D. Gonzalez, Tetrahedron, **20**, 189 (1964).
6. E. F. Pratt and T. McGovern, J. Org. Chem., **29**, 1540 (1964).
7. H. Snyder *et al.*, J. Am. Chem. Soc., **71**, 290 (1949).
8. Either commercial (Alfa Inorganics) or Attenburrow[9] MnO_2 may be used.
9. J. Attenburrow *et al.*, J. Chem. Soc., 1094 (1952).