EJ52-1998-835 Journal of the Chinese Chemical Society, 1998, 45, 835-837

832

Note

The Synthesis of New Type Bisazo Compounds Using 4-Hydroxy-2,2,6,6-Tetramethyl-1-Piperidinyloxyl as The Phase-Transfer Dehydrogenation Catalyst

Xiao-Yang Wang^{*}(王曉陽), Yu-Lu Wang^{*b}(王玉爐), Zi-Yi Zhang^{**}(張自義), Jian-Ping Li^b(李建平) and Cai-Lan Wang^b(王彩蘭) *Department of Chemistry, National Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, 730000, P. R. China *Department of Chemistry, Henan Normal University, Xinxiang, 453002, China

Using 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl as the phase-transfer dehydrogenation catalyst to prepare bisazo compounds is reported for the first time. Nine bisaryl carbodiazones were synthesized in high yields under mild conditions. This method was efficient, convenient and rapid. A possible mechanism was suggested by a nitroxide free radical which acted on aryl substituted carbazides to form azo compounds.

INTRODUCTION

It is well known that 4-hydroxy-2,2,6,6-tetramethyl-1piperidinyloxyl is a stable nitroxyl radical. It can be used as an antioxidant^{1,2} and spin labeled compounds to mark protein, biomembrance and nucleic acid.^{3,4} Furthermore, as an efficient inhibitor, it can prevent olefin from polymerization by free radicals.⁵ However, using 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl as the phase-transfer catalyst has not been reported before.

Azo compounds have been widely utilized as dyes and analytical reagents. Optical-switch and image storage can be made by azobenzene liquid crystal film.⁶ Generally, azo compounds are synthesized by diazo coupling or by hydrazine oxidization using N-bromosuccinimide (NBS)-pyridine, fuming nitric acid or nitrogen dioxide.^{7,8,9} From our experience, N-bromosuccinimide-pyridine is an efficient oxidant.¹⁰ The reaction using fuming nitric acid or nitrogen dioxide does not proceed to completion, and a side aromatic nitration reaction competes when the reactant contains a phenyl group.

RESULTS AND DISCUSSION

In this paper, we report a new phase-transfer catalyzed method for dehydrogenation of aryl substituted carbazides. Nine bisazo compounds of new type were synthesized in excellent yields (90.0-98.5%) under mild conditions.

When 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl was not added to the reaction system, there was no ob-

Scheme I



vious color change. Accordingly, a possible mechanism¹¹ was suggested: First, nitroxide free radical acted on aryl substituted carbazide compounds to give the corresponding bisaryl carbodiazones and hydroxyamine in dichloromethane phase. Second, the hydroxyamine yielded to the nitroxide anion in sodium hydroxide solution. Finally, the nitroxide anion became a nitroxyl free radical by passing an electron to potassium ferricyanide.

This paper provides a convenient and high-yielding method to prepare bisazo compounds. This method only requires a short reaction time (5-10 minutes). The structures of these bisazo compounds were established by UV, IR, ¹H NMR, mass spectral methods and elemental analysis.

Scheme II



EXPERIMENTAL SECTION

The melting points were determined with a Kofler micro melting apparatus and were uncorrected. Elemental analyses (C, H and N) were carried out on a Carlo-Erba 1102 elemental analyzer. UV-visible spectra were taken in CHCl₃ solution on a PE-LAMBDA spectrophotometer. IR spectra were recorded on a SP3-300 spectrophotometer as KBr film. ¹H NMR spectra were measured on a JEOL-Fx-90Q spectrometer using TMS as internal standard. Mass spectra were recorded on KRATOS-AEI-MS 50 (U.K.).

General Procedure for the Preparation of Bisazo Compounds 2a-2i from Aryl Substituted Carbazides 1a-1i¹²

The aryl substituted carbazides 1a-1i (1 mmol) and a trace amount of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl free radical (0.01 mmol) were dissolved in dichloromethane (50 mL) and shaken with a saturated solution of potassium ferricyanide in 2N aqueous sodium hydroxide (12 mL). After 5-10 minutes, the color in organic phase changed from white to yellow-orange or orange-red or deepred. The dichloromethane layer was separated, and the water layer was extracted with dichloromethane four times. The dichloromethane layers were combined and washed with water until the washing was neutral. The organic phase was dried over anhydrous sodium sulfate overnight, and dichloromethane was distilled on water-bath after removal sodium sulfate. The residue was recrystallized to give the desired products which were dried below 50 °C.

Bisphenyl carbodiazone 2a

Pale brown needle; Yield 90.0%; mp 173-175 °C; UV (CHCl₃): $\lambda_{max} = 354.5 \text{ nm}, \epsilon = 1.62 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$; IR

 v_{max} (KBr): 3055 (w, ArH), 1658 (s, C=O), 1630, 1590 (m, ArH), 1430 (m, N=N) cm⁻¹; ¹H NMR (CDCl₃): δ 7.32-7.82 (m, 10H, Ar-H); Anal. calcd for C₁₃H₁₀N₄O: C, 65.54; H, 4.23; N, 23.52; Found: C, 65.50; H, 4.18; N, 23.60.

Bis(2-methylphenyl)carbodiazone 2b

Pale-yellow plate; Yield 98.5%; mp 160-161 °C; UV (CHCl₃): $\lambda_{max} = 354.4$ nm, $\epsilon = 1.54 \times 10^4$ L·mol⁻¹·cm⁻¹; IR v_{max} (KBr): 3060 (w, ArH), 2965, 2865 (m, CH₃), 1655 (s, C=O), 1615, 1485 (m, ArH), 1455 (m, N=N) cm⁻¹; ¹H NMR (CDCl₃): δ 2.16 (s, 6H, 2 CH₃), 7.16-7.60 (m, 8H, ArH); Anal. calcd for C₁₅H₁₄N₄O: C, 67.65; H, 5.30; N, 21.04; Found: C, 67.57; H, 5.32; N, 21.01.

Bis(3-methylphenyl)carbodiazone 2c

Red needle; Yield 95.5%; mp 66-68 °C; UV (CHCl₃): $\lambda_{max} = 344.8 \text{ nm}, \epsilon = 1.51 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$; IR ν_{max} (KBr): 3073 (w, ArH), 2950, 2850 (m, CH₃), 1700 (s, C=O), 1595, 1575 (m, ArH), 1444 (m, N=N) cm⁻¹; 'H NMR (CDCl₃): δ 2.42 (s, 6H, 2 CH₃), 7.32-7.83 (m, 8H, ArH); Anal. calcd for C₁₅H₁₄N₄O: C, 67.65; H, 5.30; N, 21.04; Found: C, 67.55; H, 5.24; N, 21.10.

Bis(4-methylphenyl)carbodiazone 2d

Orange red needle; Yield 92.3%; mp 137-139 °C; UV (CHCl₃): $\lambda_{max} = 350.0 \text{ nm}, \epsilon = 1.52 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$; IR ν_{max} (KBr): 3065 (w, ArH), 2965, 2860 (m, CH₃), 1680 (s, C=O), 1595, 1500 (m, ArH), 1470 (m, N=N) cm⁻¹; ¹H NMR (CDCl₃): δ 2.40 (s, 6H, 2 CH₃), 7.25-7.88 (m, 8H, ArH); Anal. calcd for C₁₅H₁₄N₄O: C, 67.65; H, 5.30; N, 21.04; Found: C, 67.70; H, 5.28; N, 21.12.

Bis(4-ethyloxyphenyl)carbodiazone 2e

Orange red plate; Yield 94.5%; mp 157-158 °C; UV (CHCI₃): $\lambda_{max} = 351.5$ nm, $\epsilon = 1.56 \times 10^4$ L·mol⁻¹·cm⁻¹; IR ν_{max} (KBr): 3080 (w, ArH), 2975, 2885, 2925, 2850 (m, CH₃ or CH₂), 1700 (s, C=O), 1602, 1580 (m, ArH), 1450 (m, N=N) cm⁻¹; ¹H NMR (CDCI₃): δ 1.50 (t, 6H, 2 CH₃), 4.20 (q, 4H, 2 CH₂), 7.01-7.35 (m, 8H, ArH); Anal. calcd for C₁₇H₁₈N₄O₃: C, 62.55; H, 5.57; N, 17.17; Found: C, 62.59; H, 5.54; N, 17.42.

Bis(2,3-dimethylphenyl)carbodiazone 2f

Red plate; Yield 93.8%; mp 99-100 °C; UV (CHCl₃): $\lambda_{max} = 347.5 \text{ nm}, \epsilon = 1.23 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$; IR ν_{max} (KBr): 3058 (w, ArH), 2965, 2850 (m, CH₃), 1720 (s, C=O), 1602, 1490 (m, ArH), 1455 (m, N=N) cm⁻¹; ¹H NMR (CDCl₃): δ 2.39 (s, 6H, 2 CH₃), 2.63 (s, 6H, 2 CH₃), 7.08-7.60 (m, 6H, ArH); Anal. calcd for C₁₇H₁₈N₄O: C, 69.37; H, 6.16; N, 19.03; Found: C, 69.40; H, 6.15; N, 19.20.

Bis(2,5-dimethylphenyl)carbodiazone 2g

Yellow plate; Yield 90.4%; mp 159-160 °C; UV (CHCl₃): $\lambda_{max} = 341.5 \text{ nm}, \epsilon = 1.26 \times 10^4 \text{ L·mol}^{-1} \cdot \text{cm}^{-1}$; IR v_{max} (KBr): 3030 (w, ArH), 2965, 2860 (m, CH₃), 1710 (s, C=O), 1610, 1570 (m, ArH), 1450 (m, N=N) cm^{-1}; ¹H NMR (CDCl₃): δ 2.30 (s, 6H, 2 CH₃), 2.36 (s, 6H, 2 CH₃), 7.05-8.00 (m, 6H, ArH); MS *m*/z 294, 133, 105; Anal. calcd for C₁₇H₁₈N₄O: C, 69.37; H, 6.16; N, 19.03; Found: C, 69.35; H, 6.19; N, 19.23.

Bis(2,6-dimethylphenyl)carbodiazone 2h

Red needle; Yield 92.3%; mp 118-119 °C; UV (CHCl₃): $\lambda_{max} = 340.5$ nm, $\varepsilon = 1.30 \times 10^4$ L·mol⁻¹·cm⁻¹; IR ν_{max} (KBr): 3060 (w, ArH), 2964, 2850 (m, CH₃), 1700 (s, C=O), 1620, 1570 (m, ArH), 1445 (m, N=N) cm⁻¹; ¹H NMR (CDCl₃): δ 2.50 (s, 12H, 4 CH₃), 7.10-7.40 (m, 6H, ArH); Anal. calcd for C₁₇H₁₈N₄O: C, 69.37; H, 6.16; N, 19.03; Found: C, 69.38; H, 6.20; N, 19.09.

Bis(3,4-dimethylphenyl)carbodiazone 2i

Red plate; Yield 96.7%; mp 94-95 °C; UV (CHCl₃): $\lambda_{max} = 337.6 \text{ nm}, \epsilon = 1.27 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$; IR ν_{max} (KBr): 3050 (w, ArH), 2970, 2850 (m, CH₃), 1715 (s, C=O), 1610, 1570 (m, ArH), 1450 (m, N=N) cm^{-1}; ¹H NMR (CDCl₃): δ 2.30 (s, 6H, 2 CH₃), 2.36 (s, 6H, 2 CH₃), 7.05-8.00 (m, 6H, ArH); Anal. calcd for C₁₇H₁₈N₄O: C, 69.37; H, 6.16; N, 19.03; Found: C, 69.35; H, 6.19; N, 19.23.

ACKNOWLEDGMENT

We are grateful for the financial support of the Na-

tional Natural Science Foundation of the PRC.

Received May 27, 1998.

Key Words

4-Hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl; Aryl substituted carbazide; Bisaryl carbodiazone.

REFERENCES

- Krishna, M. C.; Russo, A.; Mitchell, J. B.; Goldstein, S.; Dafni, H.; Samuni, A. J. Biol. Chem. 1996, 271, 26026.
- 2. Rozantsev, E. G.; Sbolle, V. D. Synthesis 1971, 4, 190.
- 3. Smith, I. C. P. Biochemistry 1968, 7, 745.
- 4. Keana, J. F. W. Chem. Rev. 1978, 78, 37.
- Li, Z.-L.; Zhang, Z.-Y.; Liu, X.-B. Gao Fen Zi Xue Bao 1994, 2, 219.
- 6. Ikeda, T.; Tsutumi, O. Science 1995, 268, 1873.
- 7. Little, R. D.; Venegas, M. G. Org. Synth. 1983, 61, 17.
- Brimble, M. A.; Heathcock, C. H.; Nobin, G. N. Tetrahedron: Asymmetry 1996, 7, 2007.
- Loew, F. S.; Weiss, C. D. J. Heterocycl Chem. 1976, 13, 829.
- Wang, Y.-L.; Wang, X.-Y.; Li, J.-P.; Ma, D.-L.; Wang, H. Synth. Commun. 1997, 27, 1737.
- Sykes, P. A Guidebook to Mechanism in Organic Chemistry, Bath press: New York, 1986, p. 307.
- 12. Zuo, B.-L.; Xu, L.-R. Hua Xue Shi Ji 1983, 5, 164.