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TWO-PHASE DEHYDROGENATION OF ARYL SUBSTITUTED CARBAZIDE COMPOUNDS

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Abstract: Two-phase dehydrogenation, which is a new reaction of aryl substituted carbazide compounds, is described in this paper. Ten new azo compounds were synthesized by the reaction of aryl substituted carbazide compounds with a phenoxyl radical between two phases in good yields.

Substituted carbazide compounds have been described in many reactions¹, such as oxidation, reduction, condensation with carbonyl compounds, addition with iso (thio) cyanates, etc. yet, two-phase dehydrogenation of these compounds have not been

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reported so far. Azo compounds can be universally utlized as dyes and analytical reagents and can also be used in material of nonlinear optics, material of optics information storring in laser dish, and dyes with oil solubility in photochromy in modern technology^{2, 3}. The new reaction of phase-transfer-catalyzed dehydrogenation of aryl substituted carbazide compounds has been studied, and ten new azo compounds have been prepared in good yields under mild conditions. These compounds should have value of application in modern technology. Their structures were identified on the basis of Elemental Analyses, IR, UV, ¹HNMR, MS spectra.

Experimental

Melting points were determined with a Kofler micro melting point apparatus and were uncorrected. IR spectra were recorded on a SP3-300 spectraphotometer in KBr. UV-visible spectra in CHCl_a were taken on a PE-LAMBDA 17 spectro-photometer. ¹HNMR spectra were measured on a JEOL-Fx-90Q spectrometer using TMS or HMDS as internal standard and CDCl_a or DMSO-d_e as solvent. MS spectra were taken on a KRTOS-AEI-MS50 (U. K) spectrometer. Elementel Analyses were performed on a Carlo-Erba 1102 or a PE- 2400 elemental analyzer.

scheme I



Scheme I

$$\begin{array}{c} 2, 4, 6 - t - C_4 H_9 C_6 H_2 OH/K_3 Fe (CN) 6/NaOH\\ Ar NHNHCONHNHAr & 3_{a-1} \\ & 3_{a-1} \\ C_6 H_6 NHNHCONHC_6 H_6 & 2_3 & 4, 6 - t - C_4 H_9 C_6 H_2 OH/K_3 Fe (CN) 6/NaOH\\ & 2_3 & 3_3 \end{array}$$

General procedure

2b~i were synthesized according to Scheme 1^{4, 5}, they were recrystallized two times and their structures were confirmed by IR spectra. 2a is A.R., 2j is C.P..

The aryl substituted carbazide compounds 2a~j (3.5mmol) and a trace of a phenol (~0.035mmol) are dissolved in ethanol-free dichloromethane (150ml), and shaken with a saturated solution of potassium ferricyanide (35ml) in 2 normal aqueous sodium hydroxide. After 5~10 minutes, the organic phase changes its color from white to brown-yellow or orange-red or deep red with slight blue. The dichloromethane layer is separated, and the water layer İ₿ extracted with dichloromethane five times. The dichloromethane layers are mixed togather and washed with water for four times, dried with anhydrous sodium sulfate overnight. The dichloromethane is distilled in water-bath after sodium sulfate is removed. The products are washed with ethyl dther 3~4 times, dried at less than 50℃.

No.	Structure	M. P. (°C)	Yield (%)
88	C _@ H _{&} N=NCON=NC _@ H _{&}	174-6	79. 2
3b	o-CH3C6H4N=NCON=NC6H4CH8-0	159-60	97. 3
8 c	m-CH3C6H4N=NCON=NC6H4CH3-m	66. 5-68	89. 3
3d	p-CH3C6H4N=NCON=NC6H4CH3-p	138-39	86. 4
3e	2, 3-Me2C6H3N=NCON=NC6H3Me2-2, 3	98-100	97.4
3f	3, 4-MezCeH2N=NCON=NCeH2Me2-3, 4	93-95	95. 4
Зg	2, 5-Me 2C 6H 3N=NCON=NC 6H 3Me 2 - 2, 5	159-61	98.4
8h	2, 6-Me2C6H3N=NCON=NC6H3Me2-2, 6	118-19	92. 3
31	p-EtOC ₆ H ₄ N=NCON=NC ₆ H ₄ OEt-p	157-58	99. 0
8 j	C _s H _o N=NCONHC _s H _o	110-12	96. 9
		t.	

Table 1. M.P., Yield data of compounds 3a~j

¹HNMR (DMSO- d_6) δ : Bisphenyl carbodiazone 3a. Light brown needles, IR (KBr) v: 3055, 1656, 1628, 1589, 1488 7. 30-7. 82 (m, 10H, Ar-H); cm^{-1} ; UV (CHC1₃): λ max=354.4nm. Anal Caled. for C₁₃H₁₀N₂O: C, 65.53; H, 4. 24; N, 23. 52. Found: C, 65. 45; H, 4. 17; N, 23. 59. 1 HNMR Bis (2-methylphenyl) carbodiazone 3b. Light yellow tabular, $(DMSO-d_6)$ δ : 2.18 (s, 6H, 2×CH_a), 7.14-7.59 (m, 8H, Ar-H); IR (KBr) v: 3061, 2965, 2865, 1655, 1615, 1486, 1455, 1378cm⁻¹; UV (CHCl_a): λ_{max}=354, 4nm. Anai Caicd. for C15H14N4O: C, 67, 64; H, 5. 31; N, 21.04. Found: C, 67.07; H, 5.32; N, 21.01. Bis (3-methylphenyl) carbodiazone 3c. Red meedles, ¹HNMR (CDCl_a) δ: 2. 43 (8, 6H, $2 \times CH_B$), 7. 32-7. 83 (m, 8H, Ar-H); IR (KBr) \forall ; 3073, 2950,

2850, 1700, 1599, 1575, 1495, 1444, 1355 cm⁻¹; UV (CHCl₂); λ_{max}= 344. 8nm. Anal calcd. for C₁₅H₁₄N₄O: C, 67. 64; H, 5. 31; N, 21. 04. Found: C, 67. 35; H, 5. 24; N, 21. 20.

Bis (4-methylphenyl) carbodiazone 3d. Orange-red needles, ¹HNMR (CDCl_a) δ: 2.39 (s, 6H, 2×CH_a), 7.24-7.88 (m, 8H, Ar-H); IR (KBr) v: 3060, 2965, 2860, 1683, 1598, 1501, 1477, 1350 cm⁻¹; UV (CHCl_a); λ_{mex}=349.6nm. Anal calcd. for C₁₅H₁₄N₄O: C, 67.64; H. 5.31; N.21.04. Found: C, 67.74; H. 5.28; N, 21.32.

Bis (2, 3-dimethylphenyl) carbodiazone 3e. Red tabular, ¹HNMR (CDCl₂) δ : 2. 39 (s, 6H, 2×CH₂), 2. 63 (s, 6H, 2×CH₂), 7. 08-7. 58 (m, 6H, Ar-H); IR (KBr) v: 3058, 2965, 2860, 1729, 1603, 1490, 1455, 1345 cm⁻¹; UV (CHCl₃): λ_{max} =347. 2nm. Anal calcd. for C_{1.7}H_{1.8}N₄O: C, 69. 35; H, 6. 18; N, 19. 04. Found: C, 69. 54; H, 6. 15; N, 19. 21.

Bis (3, 4-dimethylphenyl) carbodiazone 3f. Red tabular, ¹HNMR (CDC1_a) δ : 2. 30 (s, 6H, 2×CH_a), 2. 36 (s, 6H, 2×CH_a), 7. 05-7. 81 (m, 6H, Ar-H); IR (KBr) v: 3053, 2973, 2880, 1714, 1608, 1575, 1495, 1450, 1337cm⁻¹; UV (CHC1_a): λ_{max} =336. 4nm. Anal calcd. for C_{1.7}H_{1.8}N₄O: C, 69. 35; H, 6. 18; N, 19. 04. Found: C, 69. 17; H, 6. 12; N, 19. 87.

Bis (2, 5-dimethylphenyl) carbodiazone 3g. yellow tabular, ¹HNMR (CDCl₃) δ: 2.16 (s, 6II, 2×CH₃), 2.22 (s, 6H, 2×CH₃), 6.72-7.43 (m, 6H, Ar-H); IR (KBr) v: 3030, 2965, 2868, 1645, 1615, 1575, 1502, 1453, 1364 cm⁻¹; UV (CHCl₃): λ_{max}=341.2nm; MS (m/z): 294 (M⁺), 133, 105. Anal calcd. for C₁₇H₁₈N₄ O: C, 69.35; H. 6.18; N. 19.04. Found: C, 69.16; H. 5.73; N. 20.35.

Bis (2, 6-dimethylphenyl) carbodiazone 3h. Red needles, ¹HNMR (CDC1_a) δ: 2. 49 (s, 12H, 4×CH_a), 7. 12-7. 42 (m, 6H, Ar-H); IR (KBr) v: 3070, 2965, 2870, 1695, 1590, 1502, 1437, 1358cm⁻¹; UV (CHC1_a): λ_{max}=340. 0nm. Anal calcd. for C₁₇H₁₈N₄O: C, 69. 35; H, 6. 18; N, 19. 04. Found: C, 69. 40; H, 6. 19; N, 19. 45. Bis (4-ethyloxyphenyl) carbodiazone 3i. Orange-red tabular, ¹HNMR (CDC1₃) δ : 1.50 (t, 6H, 2×CH₃), 4.20 (q, 4H, 2×CH₂), 7.01-7.36 (m, 8H, Ar -H); IR (KBr) v: 3080, 2975, 2885, 2925, 2850, 1700, 1602, 1580, 1500, 1255cm⁻¹; UV (CHC1₃): λ_{max} =451.6nm. Anal calcd for C_{1.7}H_{1.8}N₄O₃: C, 62.55; H, 5.57; N, 17.17. Found: C, 62.59; H, 5.54; N, 17.42. 1, 4-diphenylazourea 3j. Deep red tabular, ¹HNMR (CDC1₃) δ : 7.02-7.87 (m, 10H, Ar-H), 8.99 (s, 1H, NH); IR (KBr) v: 3230, 3060, 1690, 1595, 1545, 1488cm⁻¹; UV (CHC1₃): λ_{max} =445.6nm; MS (m/z): 225 (M⁺), 120, 105, 92, 91, 77. Anal calcd. for C_{1.2}H_{1.1}N₃O: C, 69.31; H, 4.93; N, 18. 66. Found: C, 69.16; H, 4.84; N, 19.07.

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References

- Frederick, K.; Michael, W. Chemical Review, 1970, 70 (1), 111 -150.
- 2. Nakazumi, H., J. Soc. Dyers and Colourists, 1988, 104 (3), 121.
- Peng, X. J., Yang, J. Z., Chin, Image Science and Practice, 1988, (<u>4</u>), 5.
- 4. Zuo, B.L., Xu, L.R., Huaxue Shiji, 1988, 5(3). 164-8.
- 5. U.S. 3, 366, 619 (C.A. 1968, 68: 96797t).

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