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PHASE TRANSFER CATALYZED DEHYDROGENATION SYNTHESIS OF AZO UREAS FROM ARYL SUBSTITUTED SEMICARBAZIDE

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ABSTRACT: Phase transfer catalyzed dehydrogenation synthesis azo Ureas Compounds have been studied. Ten of the compounds were Synthesized by the reaction of aryl Substituted Semicarbazied Compounds with phase transfer catalyst--"Galvinoxyl" radical between two phase under mild Conditions. The products are obtained in 90-99(%) yield. Their structure are identified by elemental analysis, IR, ^{1}HNMR, MS spectra. A possible mechanism is suggested by a "Galvinoxyl" radical act on aryl substituted semicarbazide formed azo compoumds.

Synthesis of bis (Substituted phenyl) Carbodiazone Compounds (ArN=NCON=NAr') have been reported[1], As another part of our studies, 1, 4-di-Substituted azo Compounds (ArNHCON=NAr') Were Synthesized by the reaction of Substituted Semicarbazide Compounds With a phase transfer Catalyst-"Galvinoxyl" radical. which has been acted as a radical Scavenger[2], yet, "Galvinoxyl" radical used as phase transfer Catalyst have not been reported so far. Azo Compounds have been widely utilized as dyes and analytical reagents. They can also be used as material of non-linear optics, optic information storring material in Laser dish and dyes with oil solubility in photochromy in modern technology[3,4]. Recently, many noteworthy Studies show that azobenzene derivative Possess Very good optic remembering and photoelectric properties[5], optical Switching and Image storege by means of Azobenzene Liquid-Crystal Films[6]. The preparation of the azo compounds which have the Connection of -N=N- and hydrocarbyl group have been described in many Literatures[7,8]. In this paper, a new reaction of phase transfer Catalyzed dehydrogenation of aryl Substituted Semicarbazide

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Compounds has been studied and ten of the new 1,4-disubstituted azo ureas have been Synthesized in good yield under mild Conditions. the Characteristic Structure of these new azo Compounds were the $-N=N-$ Connection with Carbonyl group in one side. these Compounds Should have Valuable application in modern technology.

EXPERIMENTAL SECTION

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. ^{1}HNMR Spectra were measured on a JEOl-Fx-90Q spectrometer using TMS or HMds as internal Standard and $CDCl_3$ as solvent. Ms spectra were taken on a KRTOS-AEI-MS50(U.K) spectrometer. Elemental Analyses were performed on a Carllo-Erba 1102 or a PE-2400 elemental analyzer.

$$ArNHCONHNHC_6H_5 \xrightarrow[CH_2Cl_2]{Galvinoxyl/Fe(CN)_6^{3-}/NaOH} ArNHCON=NC_6H_5$$

General Procedures for azo Ureas Compounds. Synthesis of 2a-j

The 1,4-disubstituted aryl Semicarbazide compounds 1a-j(3.5m mol) and a trace of "Galvinoxyl" radical (35 u mol) were dissolved in dichloromethane (150ml) and shaken with the Saturated Solution of potassium ferricyanide in a queous sodium hydroxide (35ml). After 5-10minutes, the Color in organic phase Changes from white to brown-yellow or orange-red or deep-red with slight blue. The dichloromethane Layer was separated, and the water Layer was extracted with dichloromethane five times. The dichloromethane Layers are mixed togather and washed with water until neutrality. then dried with anhydrous sodium sulfate overnigt. The dichloromethane is distilled in water-bath after sodium sulfate is removed. The products are washed with ethyl ether, dried at less then 50℃ , Their structures are identified by elemental analyses, IR, ^{1}HNMR, MS spectra.

Table M.P., Yield data of compounds 2a-j

No.	Structure	M. P. (℃)	Yield(%)
2a	$C_6H_5NHCON=NC_6H_5$	110-112	95.6
2b	$o-CH_3C_6H_4NHCON=NC_6H_5$	103-105	90.0
2c	$m-CH_3C_6H_4NHCON=NC_6H_5$	69-71	94.0
2d	$p-CH_3C_6H_4NHCON=NC_6H_5$	104-106	93.3
2c	$2,3-Me_2C_6H_3NHCON=NC_6H_5$	122-124	92.8
2f	$2,5-Me_2C_6H_3NHCON=NC_6H_5$	121-123	94.4
2g	$2,6-Me_2C_6H_3NHCON=NC_6H_5$	118-120	98.6
2h	$3,4-Me_2C_6H_3NHCON=NC_6H_5$	126-128	99.0
2i	$p-EtOC_6H_4NHCON=NC_6H_5$	127-129	96.1
2j	$1-C_{10}H_9NHCON=NC_6H_5$	132-134	98.2

2a: deep-red tabular, ^{1}H-NMR($CDCl_3$) δ_H 7.02-7.87(m,10H,ArH), 8.99(S,1H,NH): IR(KBr) ν: 3230, 3060, 1690, 1595, 1545cm^{-1}; MS(m/z) : 225(M^+) , 120, 105, 92, 91, 77; Anal. calcd for $C_{13}H_{11}N_3O$: C, 69.31; H, 4.93; N, 18.66; Found: C, 69.16; H, 4.84; N, 19.07.

2b: orange-red tabular, ^{1}H-NMR($CDCl_3$) δ_H 2.26(S, 3H,CH_3), 7.00-8.04(m, 9H, ArH), 8.91(S, 1H, NH); IR(KBr) ν: 3160, 3050, 2995, 1682, 1580, 1402, 928cm^{-1}; Anal. calcd for $C_{14}H_{13}N_3O$: C, 70.29; H, 5.44; N, 17.57; Found: C, 70.03; H, 5.63; N, 17.81.

2c: orange-red tabular, ^1H-NMR($CDCl_3$) δ_H 2.26 (S, 3H, CH_3), 6.86-8.02 (m, 9H, ArH), 8.25 (S, 1H, NH); IR(KBr) ν: 3360, 3048, 3000, 1686, 1588, 1048, 925cm^{-1}; Anal. calcd for $C_{14}H_{13}N_3O$: C, 70.29; H, 5.44; N, 17.57; Found: C, 70.14; H, 5.43; N, 17.91.

2d: orange-red tabular, ^1H-NMR($CDCl_3$) δ_H 2.26(S, 3H, CH_3), 7.08-8.03(m, 9H, ArH), 8.16 (S, 1H, NH); IR (KBr) ν: 3170, 3048, 2956, 1675, 1580, 1414, 924cm^{-1}; Anal. calcd for $C_{14}H_{13}N_3O$: C, 70.29; H, 5.44; N, 17.57; Found: C, 70.12; H, 5.31; N, 17.80.

2e: brown-red tabular, ^1H-NMR ($CDCl_3$) δ_H 2.22 (S, 6H, $2CH_3$), 7.02-8.02(m, 8H, ArH), 8.21 (S, NH); IR (KBr) ν: 3180, 3050, 2960, 2900, 1680, 1580, 1442, 922cm^{-1}; Anal. calcd for $C_{15}H_{15}N_3O$: C, 71.15; H, 5.93; N, 16.60; Found: C, 70.94; H, 5.60; N, 16.89.

2f: yellow tabular, ^1H-NMR ($CDCl_3$) δ_H 2.24 (S, 6H, $2CH_3$), 6.84-8.02(m, 8H, ArH), 8.22(S, 1H, NH); IR(KBr)ν: 3220, 3053, 2960, 2900, 1670, 1575, 1445, 922cm^{-1}, Anal. calcd for $C_{15}H_{15}N_3O$: C, 71.15; H, 5.93; N, 16.60; Found: C, 71.10; H, 5.70; N, 16.90.

2g: orange-yellow tabular, ^1H-NMR($CDCl_3$) δ_H 2.24(S, 6H, $2CH_3$), 7.40-8.02 (m, 8H, ArH), 7.66(S, 1H, NH): IR(KBr) ν: 3245, 3047, 2996, 2910, 1680, 1580, 1485, 922cm^{-1}, Anal. calcd for $C_{15}H_{15}N_3O$: C, 71.15; H, 5.93; N16.60; Found: C, 71.05; H, 5.73; N, 16.50.

2h: orange-red tabular, ^1H-NMR($CDCl_3$) δ_H 2.20(S, 6H, $2CH_3$), 7.03-8.02(m, 8H, ArH), 8.22 (S, 1H, NH); IR(KB) ν: 3250, 3060, 2960, 2900, 1690, 1590, 1440, 920cm^{-1}, Anal. calce for $C_{15}H_{15}N_3O$: C, 17.15; H, 5.93; N, 16.60; Found: C, 71.08; H, 5.28; N, 17.19.

2i: orange-red needles, ^1H-NMR($CDCl_3$) δ_H 1.28(t, 3H, CH_3), 3.90 (q, 2H, CH_2), 6.82-8.00(m, 9H, ArH), 8.22(S, 1H, NH); IR(KBr)ν: 3310, 3036, 2964, 2918, 1690, 1585, 1408, 916cm^{-1}; Anal. calcd for $C_{15}H_{11}N_3O_2$: C, 66.91; H, 5.58; N, 15.61; found: C, 67.00; H, 5.22; N, 15.40.

2j: orange-red needles, ^1H-NMR($CDCl_3$) δ_H 7.20-8.24 (m, 12 H, ArH), 8.83(S, 1H, NH); IR (KBr) ν: 3264, 3040, 1658, 1590, 1475, 1440, 920cm^{-1}; Anal. calcd for $C_{17}H_{13}N_3O$: C, 74.18; H, 4.73; N, 15.27; found: C, 74.36; H, 4.23; N, 15.46.

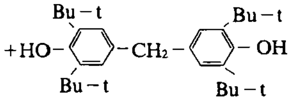
Results and Discussion

1. The System of the reaction of substituted semicarbazide compounds with "Galvinoxyl" radicae have been established, with mild reaction condition, short reaction time, single experiment instrument, High yield. Ten new azo ureas compounds were synthesized.

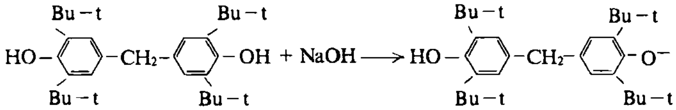
2. A possible mechanism of the reaction is suggested as following[9]:

1) " Galvinoxyl" radical in organic phase act on aryl substituted semicarbazide formed azo ureas compounds in dichloromethane.

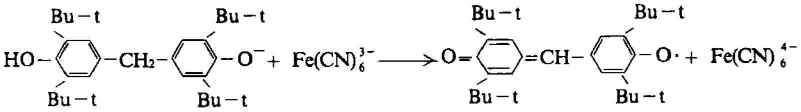
$$ArNHCONHNHC_6H_5 + \text{Galvinoxyl radical} \xrightarrow{CH_2Cl_2} ArNHCON=NC_6H_5$$



2)This "phenol" was Changed to "phenoxide anion" in sodium hyaroxide solution.



3) A stable "Galvinoxyl" radical was produced by passing an electron to potassium ferricyanide.



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