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Dimerization of Anilines and Benzylamines with Mercury(II) Oxide-Iodine Reagent

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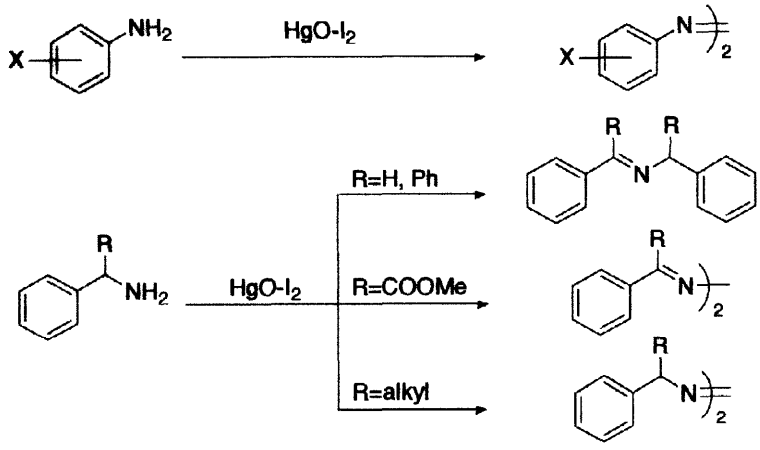
Abstract: By treatment with mercury(II) oxide-iodine reagent in dichloromethane at room temperature, substituted anilines were transformed to the corresponding azobenzenes. A similar treatment of benzylamines and benzhydrylamine gave N-benzylidenebenzylamines and N-benzhydrylidene-benzhydrylamine, respectively. α-Alkyl-substituted benzylamines gave diazenes and the corresponding phenyl ketones, competitively. An azine was obtained by interaction with the reagent of a benzylamine carrying an electron-withdrawing substituent at the α position, such as ethyl phenylglycinate.

INTRODUCTION

Recently, we reported convenient methods for iodination of alkoxy-substituted benzenes[1,2] and substituted anilines[3] and selective oxidation of sulfides to sulfoxides[4] with mercury(II) oxide-iodine reagent. Both reactions proceed smoothly in an electrophilic manner without acidic or alkaline additives and without liberation of HI. In contrast, most of the currently used reagents for iodination liberate acidic substances such as HI, HCl, H_2SO_4, HNO_3 or $HClO_4$, and some of them require acidic or basic additives and solvents.[3] Therefore, in this study we investigated the reaction with this reagent of amino compounds, such as anilines, benzylamines and alkylamines. Representative results of the present experiments are shown below.



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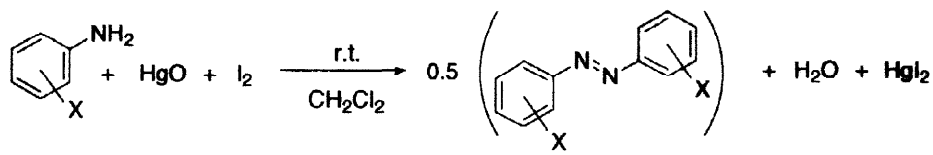
RESULTS AND DISCUSSION

Reactions of anilines with HgO-I_2 reagent

Treatment of aniline with HgO (0.5 molar equiv) and I_2 (1.0 molar equiv) in CH_2Cl_2 at room temperature was found to give 4-iodoaniline.[3] Use of excess reagents afforded a mixture of 4-iodoaniline and azobenzenes with or without the 4- and/or 4'-iodo group. As shown in Table 1 (entries 7~15), when 4-substituted anilines including 4-iodoaniline were similarly treated with HgO and I_2 (1.5 molar equiv each), 4,4'-disubstituted azobenzenes were obtained as the most mobile fraction by column chromatography on silica gel. Similarly, 2- and 3-substituted anilines were also converted to the corresponding azobenzenes in moderate yields (entries 1~6). Metal oxides [Ag_2CO_3,[5,6] Ag_2O,[7] $AgMnO_4$,[8] Ni peroxide,[9] MnO_2,[10~12] $NaBO_3$,[13~15] $Pb(OAc)_4$,[16,17] $BaMnO_4$,[18] $Ce(OH)_3O_2H$,[19] BBCP,[20] $Hg(OAc)_2$,[21] KO_2[22]], hypervalent iodine [Ph-$I(OAc)_2$[23]], aerial oxidation [O_2-KOtBu,[24] O_2-Cu_2Cl_2-pyridine,[25~27] O_2/Co_3O_4,[28] peroxidase-H_2O_2[29] and $K_3Fe(CN)_6$[30]] have been used as reagents for preparation of azobenzenes from anilines.[31] Some of these procedures are performed under undesirable acidic or basic conditions caused by their reagents, additives and/or solvents. The present method does not require any special solvents or conditions and can be achieved under neutral conditions, as described above. The reaction involves a nitrogen-nitrogen coupling of an initially formed cation radical (or aminyl radical) (like a in Scheme 1), which is probably produced by a one-

Table 1. Oxidation of Substituted Anilines to Azobenzenes with HgO-I_2 Reagent[a]



entry	X	yields of azobenzenes	entry	X	yields of azobenzenes
1	o-Cl	48%	9	p-I	50%
2	o-NO_2	50%	10	p-NO_2	90%
3	o-COOEt	41%	11	p-COOEt	87%
4	m-Cl	43%	12	p-$COCH_3$	83%
5	m-NO_2	56%	13	p-CH_3	88%
6	m-COOEt	49%	14	p-OCH_3	88%
7	p-Cl	88%	15	p-N=N-Ph	84%
8	p-Br	60%			

a. The appropriate aniline derivative was treated with HgO and I_2 (1.5 molar equiv each) in CH_2Cl_2 (0.2 M) at room temperature for 1 h.

electron transfer, followed by a two-electron oxidation of the resultant hydrazobenzene (like a→b→c), as described previously by Kinoshita[26] and Fetizon.[6] The latter reaction (b→c), which proceeds much faster than the former, can proceed with only HgO.[32] This dimerization was not observed in similar treatments of n-butylamine and β-phenethylamine, which were recovered unchanged.

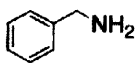
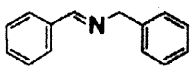
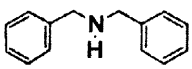
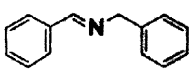
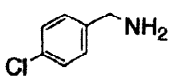
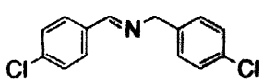
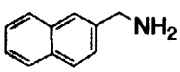
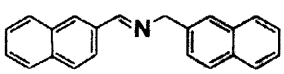
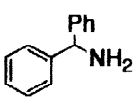
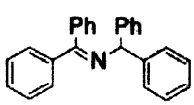
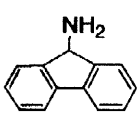
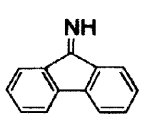
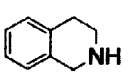
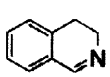
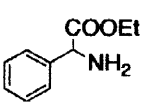
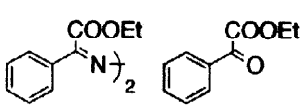
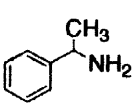
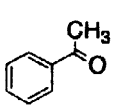
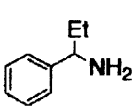
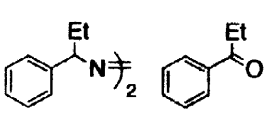
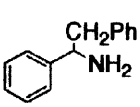
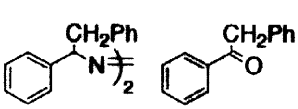
Reactions of benzylamines with HgO-I_2 reagent

A similar interaction of HgO-I_2 reagent with benzylamines and 1-naphthalenemethylamine gave N-benzylidenebenzylamines and the naphthylidene derivative almost quantitatively (entries 1, 3 and 4, Table 2). Under the same conditions, dibenzylamine gave N-benzylidene-benzylamine and tetrahydroisoquinoline gave dihydroisoquinoline in almost quantitative yields (entries 2 and 7). Even bulky aminodiphenylmethane (entry 5) dimerized to the corresponding N-benzylidenebenzylamine exclusively. It is notable that 9-aminofluorene gave fluoren-9-imine. A benzylamine derivative carrying a more electron-deficient substituent at the α position, such as ethyl 2-phenylglycinate, gave a phenyl ketone (ethyl benzoylformate) and its azine (4:5) (entry 8). In contrast, some benzylamines having an electron-donating substituent at the α-position, such as the α-alkyl group, gave neither the aforementioned dimeric imines nor azines. α-Phenethylamine gave acetophenone (entry 9), after the usual work-up using water. ^{1}H NMR analysis of its reaction mixture executed in CD_2Cl_2 revealed that the initial product was acetophenone imine [δ 2.71 (3H, s), 7.35 (3H, m), 7.68 (2H, dd, *J*=8.2, 1.3 Hz)]. Benzylamines carrying more bulky α-alkyl substituents appear to give a greater amount of azo compounds, diazenes (entries 10 and 11).

The reaction mechanisms

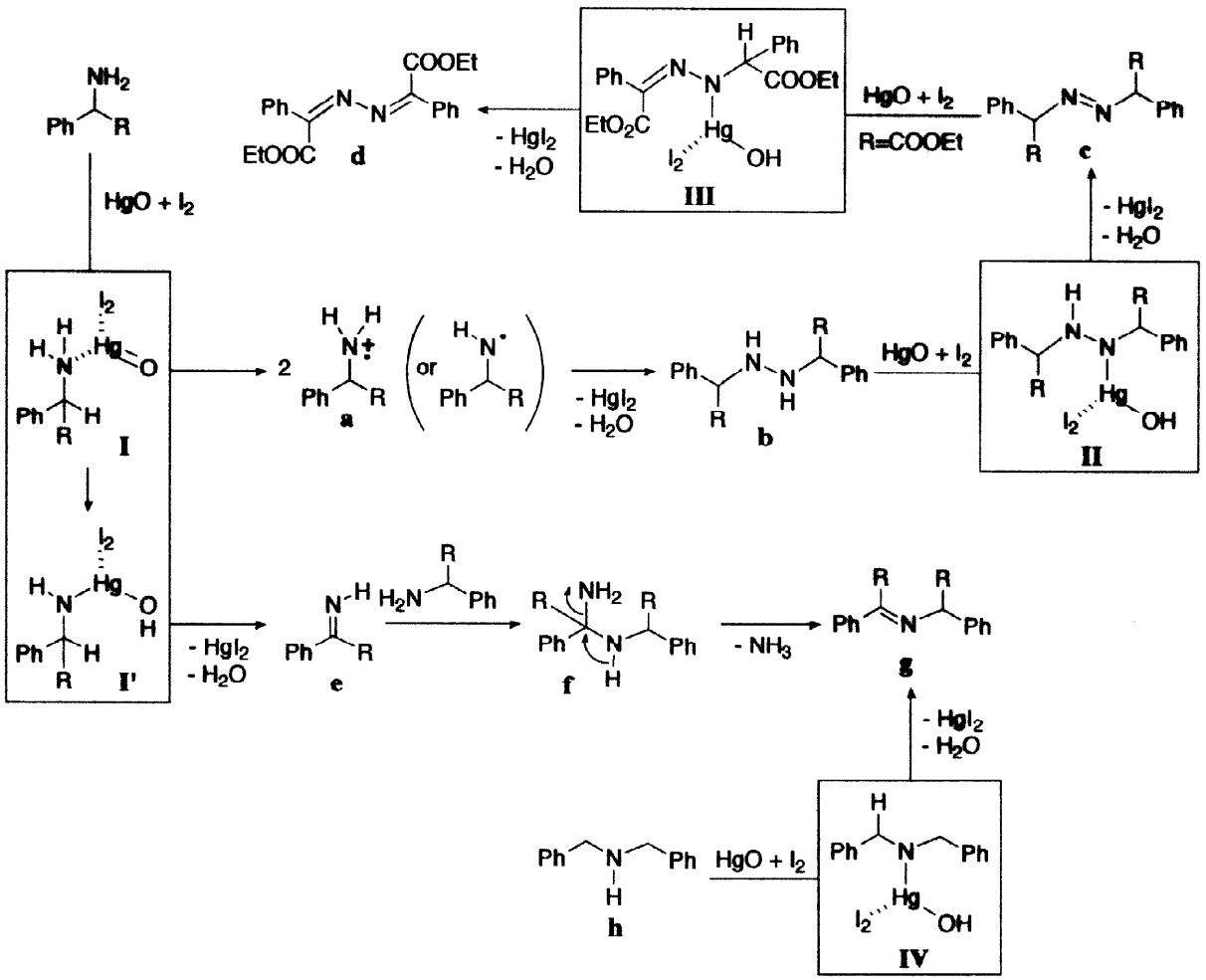
Oxidations of benzylamines and N-alkylbenzylamines with metal oxides produce benzaldehyde or phenylketones [Ni peroxide,[9] BBCP,[20] $Na_2S_2O_6/AgNO_2$,[33] $KMnO_4/CaSO_4$,[34] K_2FeO_4,[35,36] Ag_2O[37] $AgMnO_4$,[8] $BaMnO_4$,[18] MnO_2,[10] Fremy's salt,[38] $Na_5PMo_2V_2O_{40}$,[39] NaClO,[40] $Pb(OAc)_4$[41]], the corresponding imines [MnO_2,[42] K_2FeO_4,[35] $Na_5PMo_2V_2O_{40}$,[39] $Hg(OAc)_2$[43,44]], benzonitrile [Ni peroxide,[9] O_2/Co_3O_4,[28] Ag_2O,[37] Fremy's salt,[38] NaClO,[40] $Pb(OAc)_4$,[41,45] K_2RuO_4[46]], N-benzylidenebenzylamines [$Na_2S_2O_6/AgNO_2$,[33] $KMnO_4$,[34] Fremy's salt,[38] $Na_5PMo_2V_2O_{40}$,[39] $Pb(OAc)_4$,[41] $KMnO_4/ZnSO_4$,[47]], diazenes ($Na_2S_2O_6$/ $AgNO_2$,[33] O_2/Co_3O_4,[28] $AgMnO_4$[8]] and/or azines ($KMnO_4/ZnSO_4$[47]) (for other reagents, see ref. 31,48~50). The formation of N-benzylidenebenzylamine **g** has been reported to be the result of the addition of benzylamine to the imine intermediate **e**, followed by elimination of an ammonia molecule from **f**.[38,39,41] On the basis of these mechanistic aspects together with the behavior of anilines on anodic oxidation,[51,52] it was considered that this imine **e** was generated in situ by a two-electron oxidation through interaction of the N atom of benzylamine with HgO-I_2. Oxidation of dibenzylamine **h** to N-benzylidene-benzylamine **g** is also thought to proceed via a hydroxymercury amide **IV** with a two-electron oxidation. Diazenes **c** are produced in a sequence starting with a one-electron transfer of benzylamine (**I**→**a**→**b**→**II**→**c**), similar to that described above for azobenzene. A diazene **c** (R = COOEt) with an acidic benzylic proton is further transformed to the corresponding azine **d** through a similar two-electron oxidation. Pathways of the two-electron oxidations may involve the formation of a hydroxymercury amide, such as **I'**, following **I**. Thus, repeated interactions of the N atom with HgO-I_2 are thought to have caused one- or two- electron transfers, which induced the oxidative dimerization of anilines to azobenzenes, as well as those of benzylamines to N-benzylidenebenzylamines **g**, diazenes **c** and azines **d**. Phenyl ketones probably form owing to the interaction of the imine intermediates or the azine with water generated in the course of the reactions.

Table 2. Oxidation of Benzylamines with HgO-I_2 Reagent[a]

entry	benzylamines	yield	products
1		98%	
2		97%	
3		76%	
4		90%	
5		98%	
6		98%	
7		98%	
8		88% (5:4) [b]	
9		98%	
10		98% (13:12) [b]	
11		96% (47:1) [b]	

a. The appropriate benzylamine was treated with HgO and I_2 (1.5 molar equiv each) in CH_2Cl_2 (0.2 M) at room temperature for 1 h.

b. The ratio of products was obtained by ^1H NMR analysis.



Scheme 1. Dimerization of anilines and benzylamines with HgO-I_2 reagent

CONCLUSION

Thus, the reactions with mercury(II) oxide-iodine reagent of amines were found to proceed with the substrate specificity, depending mainly upon their electronic states and steric influences. The reagent has been used as a mild, efficient synthetic tool for iodination of alkyl aryl ethers,[1,2] aromatic amines,[3] and alcohols (for our recent results, see ref. 53~59), and oxidation of sulfides to sufoxides.[4] The present study led to the establishment of a new method with the reagent responsible for selective oxidation or dimerization of anilines and benzylamines to the corresponding azobenzenes, imines, diazenes, azines or ketones. Under neutral reaction conditions provided by this reagent, starting amines are not affected and the products remain unchanged. Therefore, this method is also promising for the reactions of substrates that are sensitive to acids or bases, compared with the above-described methods using metal oxides.[5~28,30,32~47]

EXPERIMENTAL

Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a JEOL JNM-EX270 FT high-resolution spectrometer. NMR samples were prepared using $CDCl_3$ (99.8 atom % D, containing 0.03% v/v TMS, Aldrich). Mass spectra were determined with a JEOL JMS-D 300 spectrometer. Mercury(II) oxide (red) was purchased from Kanto Chem. Co. Inc. Column chromatography was performed on Merck silica gel 60 (No.7739). Preparative thin-layer chromatography was carried out on Merck silica gel 60 PF_{254} (No. 7749).

General Procedure for Reaction of Anilines with Mercury(II) Oxide and Iodine. A suspension of the appropriate aniline derivative (0.5 mmol), mercury (II) oxide (red, 0.75 mmol) and iodine (0.75 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 1 h. The resultant precipitates (HgI_2) were removed by suction filtration. The filtrate and CH_2Cl_2 washings (5 mL) were combined, washed with diluted aq. 5% $Na_2S_2O_3$ solution (5 mL) and water (5 mL), dried (Na_2SO_4), and the solvent was evaporated. The crude product was flash-chromatographed on a silica gel column with petroleum ether and CH_2Cl_2 (2:1). The orange-colored, first fraction was concentrated and crystallized from the reported solvent, such as methanol or benzene. Physical and spectral data of the obtained azobenzenes were compared with the reported data.[5-29]

General Procedure for Reaction of Benzylamines with Mercury(II) Oxide and Iodine. Benzylamines (0.5 mmol) were treated with mercury (II) oxide (red, 0.75 mmol) and iodine (0.75 mmol) in CH_2Cl_2 (5 mL) at room temperature for 1 h and worked up as noted above. Without chromatographic purification, the crude products (entries 1~7, 9) were isolated by crystallization or distillation. In entries 8, 10 and 11, CD_2Cl_2 was used as a solvent, and one hour later, 0.2 mL of the decanted reaction solution was diluted with $CDCl_3$ (0.3 mL) to be subjected to ^1H NMR analysis. Physical and spectral data [N-(4-chlorobenzylidene)-4-chlorobenzylamine[60] (entry 3), N-benzhydrylidenebenzhydrylamine[61] (entry 5), fluoren-9-imine[62] (entry 6), dihydroisoquinoline[63] (entry 7), ethyl phenylglyoxylate azine[64] (entry 8)] were compared with the reported data.

N-Naphthylidene(2-naphthalene)methylamine (entry 4). mp 170-172°C (MeOH); IR (Nujol) 1638, 1599, 1507 cm^{-1}; ^1H NMR δ 5.05 (2H, s, CH_2), 7.43-8.10 (14H, m, Ar-H), 8.61 (1H, s, N=CH). FD-MS m/z (rel. int.) 295 (M^+, 53.6), 141 [$(M-NCHC_{10}H_7)^+$, 100%]. Anal. Calcd. for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74. Found: C, 89.62; H, 5.96; N, 5.00.

1,1'-Azobis(1-phenylpropane) (entry 10). The crude product was subjected to preparative thin-layer chromatography developed with a 1:1 mixture of CH_2Cl_2 and hexane. A band with Rf. 0.70 (propiophenone: Rf. 0.40) gave a 1 : 1 mixture of *meso*- and racemic forms of 1,1'-azobis(1-phenylpropane) as an oily material (47%) (cf. lit.[65] mp 55-56°C); IR (neat) 1603, 1585, 758, 698 cm^{-1}; ^1H NMR δ 0.71 (3H, t, J = 7.6 Hz), 0.87 (3H, t, J = 7.6 Hz), 1.92-2.14 (4H, m, 2 × CH_2), 4.31-4.38 (2H, m, 2 × CH), 7.25-7.50 (10H, m, Ar-H); FD-MS mz (rel. int.) 119 [1/2 $(M-N_2)^+$, 100%]. Anal. Calcd. for $C_{18}H_{22}N_2$: C, 86.16; H, 8.33; N,10.52. Found: C, 86.36; H, 8.56; N, 10.37.

1,1'-Azobis(1,2-diphenylethane) (entry 11). The reaction mixture contained a mixture of *meso*- and racemic 1,1'-azobis(1,2-diphenylethane) (1:1) and a small amount of deoxybenzoin (<2%). Fractional crystallizations from MeOH afforded both diazenes in pure form. *meso*-1,1'-azobis(1,2-diphenylethane): mp 134-135 °C

(MeOH) (17%) (lit.[66] mp 131.5-132.9 °C: [64] 134-5°C); IR (Nujol) 1602, 1584 cm^{-1}; ^1H NMR δ 3.21 (2H, dd, J = 13.9, 5.9 Hz, Ha of CH_2), 3.36 (2H, dd, J = 13.9, 8.6 Hz, Hb of CH_2), 4.70 (1H, dd, J = 13.9, 5.9 Hz, CHN), 6.85-6.90 (2H, m, Ar-H), 6.99-7.30 (3H, m, Ar-H), 7.10-7.20 (2H, m, Ar-H), 7.23-7.30 (3H, m, Ar-H); FD-MS mz (rel. int.) 362 [$(M-N_2)^+$, 32.3], 181 [1/2 $(M-N_2)^+$, 100%]. Anal. Calcd. for $C_{28}H_{26}N_2$: C, 86.11; H, 6.71; N, 7.17. Found: C, 86.19; H, 6.88; N, 7.07. Racemic 1,1'-azobis(1,2-diphenylethane): mp 101-102 °C (MeOH) (16%) (lit.[66] mp 102-102.8 °C); IR (Nujol) 1602, 1584 cm^{-1}; ^1H NMR δ 3.16 (2H, dd, J = 13.9, 7.6 Hz, Ha of CH_2), 3.22 (2H, dd, J = 13.9, 7.3 Hz, Hb of CH_2), 4.77 (1H, t, J = 7.3 Hz, CHN), 6.95-7.00 (2H, m, Ar-H), 7.10-7.26 (8H, m, Ar-H); FD-MS mz (rel. int.) 181 [1/2 $(M-N_2)^+$, 100%]. Anal. Calcd. for $C_{28}H_{26}N_2$: C, 86.11; H, 6.71; N, 7.17. Found: C, 86.06; H, 6.82; N, 7.21.

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