based on benzaldehyde) of **26**. A band at R_f 0.28 yielded 87 mg (36%) of mono adduct **27**, and a weak band at R_f 0.17 proved to be 26 mg of recovered **1**. Compound **27** exhibited the following properties: mp 126–129 °C; IR (CDCl$_3$) 1715 and 1630 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.95 (s, 3 H), 1.15 (s, 3 H), 1.4–3.4 (m, 8 H), 7.0–7.5 (m, 6 H); MS (70 eV), m/e (rel intensity) 268 (35), 253 (12), 116 (100), 115 (35); λ_{max} (EtOH) 294 nm (ϵ 25 000).

In a parallel experiment, a mixture of 90 mg of **1** (0.5 mmol), 214 mg of **26** (0.6 mmol), and 36 mg of sodium hydroxide in 25 mL of 2:3 water–glyme was refluxed for 42 h. Workup and separation as before gave 110 mg of **26** (0.3 mmol), 101 mg of **27** (0.4 mmol), and 20 mg of **1**.

Selective Catalytic Hydrogenation of Aromatic Nitro Groups in the Presence of Acetylenes. Synthesis of (3-Aminophenyl)acetylene via Hydrogenation of (3-Nitrophenyl)acetylene over Cobalt Polysulfide and Ruthenium Sulfide Catalysts

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Cobalt polysulfide (CoS$_x$, av x = 3) and ruthenium(IV) sulfide were found to be selective for the preferential hydrogenation of aromatic nitro groups in the presence of acetylenes. Thus, (3-nitrophenyl)acetylene, 2-methyl-4-(3-nitrophenyl)-3-butyn-2-ol, and the propargyl and 3-methyl-1-hexyn-3-yl benzoates were converted to the corresponding amines in 75–85% yield. Typical reactions were carried out in isopropyl alcohol solvent at temperatures around 100 °C and hydrogen pressures of 25–70 atm. With the activated and unprotected (3-nitrophenyl)acetylene, hydration of the acetylene bond competes with the nitro group hydrogenation. Hydrogenation is interpreted to involve a chemical reduction with hydrogen sulfide, which is catalytically generated under the reaction conditions. Highly reactive substrates interfere with the regenerative cycle of the catalyst by removing sulfur species from the system, which leads to low turnover frequency. Cobalt maintains the 2$^+$ valency throughout its regenerative cycle, while ruthenium changes from the 4$^+$ to the 2$^+$ valency state.

In view of the interest shown in (aminophenyl)acetylenes as end-capping agents for the preparation of polyimide resins stable at high temperatures,[1–3] we wish to report on the catalytic hydrogenation of (3-nitrophenyl)acetylene and related substrates to the corresponding amines over cobalt polysulfide and ruthenium sulfide catalysts.

(I/II = 98:2)
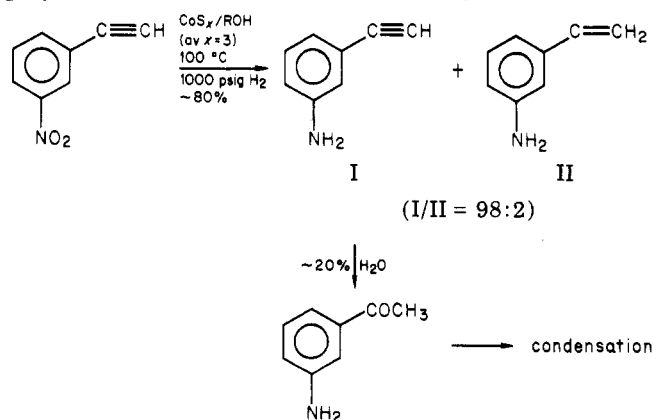
Earlier work was concerned with the hydrogenation of 2-methyl-4-(3-nitrophenyl)-3-butyn-2-ol over metallic ruthenium to give 2-methyl-4-(3-aminophenyl)-3-butyn-2-ol in essentially quantitative yields, which on treatment with caustic produced (3-aminophenyl)acetylene and acetone.[4] Direct hydrogenation of unprotected (3-nitrophenyl)acetylene over metallic ruthenium failed as this substrate was strongly adsorbed to the catalyst surface and led to poisoning. Recently, we succeeded in hydrogenating (3-nitrophenyl)acetylene to amine using a heterogeneous cobalt polysulfide or ruthenium sulfide catalysts.

Results and Discussion

Cobalt Polysulfide. Our work with sulfides was initiated when during catalyst screening it was observed that sulfided commercial 2.25% Ni, 1.25% Co, and 11.0% Mo on alumina catalyst reduced (3-nitrophenyl)acetylene selectively to the amine (100 °C, 1000 psig H$_2$) in 3% conversion. This result led us to investigate cobalt, nickel, molybdenum, and iron sulfides in more detail. On a 5–10-g scale, all of the above sulfides reduced the nitro group selectively, although conversions were less than ~12%. Spent catalysts were completely inactive on recycle. These results were rationalized by assuming that sulfides probably represent the inactive form of the catalyst and that the limited reaction observed came from impurities such as the polysulfides. A search of the literature indeed

(1) N. Bilow, A. L. Landis, and L. J. Miller, U.S. Patent 3 845 018 (1974).
(2) R. F. Kovar and F. E. Arnold, U.S. Patent 3 975 444 (1976).
(3) W. P. Barie, Jr., U.S. Patent 4 097 456 (1978).

(4) A. Onopchenko, E. T. Sabourin, and C. M. Selwitz, *J. Org. Chem.*, **44**, 1233 (1979).

Table I. Hydrogenation of (3-Nitrophenyl)acetylene (NPA) over CoS_x[a]

run no.	wt CoS_x paste, g (batch no.)[c]	wt NPA, g (I)	concn, % NPA in *i*-PrOH	wt ratio, NPA/ Co	temp, °C	pressure, psig H_2	time, h	NPA, % conv.	APA, % yield[b]	remarks (by difference)
1	2.0 (1)	2.0	2.0	10	50	50	1.75	0	0	no reaction
2	5.0 (1)	5.0	2.0	10	106	1000	0.75	100	81	19% unknowns + polymer
3	5.0 (1)	10.0	4.8	20	108	1000	0.75	100	86	14% unknowns + polymer
4	8.0 (2)	25.0	10.0	50	120	1000	1.0	90	90	10% polymeric
5	8.0 (2)	50.0	19.0	100	120	1000	2.1	72	79	21% polymeric
6	16.0 (2)	25.0	10.0[d]	25	120	1000	0.5	100	70	30% polymeric
7	16.0 (2)	50.0	19.0	50	120	1000	1.1	100	82	18% polymeric
8	100.0 (2)	600.0	22.0	100	88	1000	5.0			
					105	1000	1.5	100	79	21% polymeric
9	600.0 (3)	2600.0	20.0	62	120	1000	2.6	90	77	23% polymeric
10	300.0 (3)	1300.0	11.0	62	120	1000	1.3	97	85	15% polymeric
11	140.0 (4)	735.0	6.6	65	120	1000	1.4	82	82	18% polymeric

[a] Average composition CoS_3, based on elemental analysis. [b] Analytical (GLC, internal standard method). [c] Batches 1, 2, and 3 were prepared from $CoCl_2 \cdot 6H_2O$; batch 4 was prepared from $CoSO_4 \cdot 7H_2O$. [d] Methanol solvent.

Table II. Hydrogenation of Selected Acetylenic Nitro Compounds over CoS_x[a] Catalyst

expt no.	substrate, g	solvent, g	CoS_x paste, g (Co, g)	wt % CoS_x based on RH	temp, °C	pressure, psig H_2	react. time, min	yield of amine, g (%)	remarks
12	II,[b] 20	*i*-PrOH, 250	7.0 (0.43)	2.1	110	1000	73	13.1 (77)	mp 117–120 °C, from toluene
13	II, 18.4	*i*-PrOH, 250	7.0 (0.43)	2.3	110	400	106	12.8 (82)	mp 117.5–120 °C
14	III,[c] 40	EtOAc, 250	11.0 (0.67)	1.65	110	1000	220	27.2 (80)	mp 88–91 °C, from toluene
15	IV,[d] 45	EtOAc, 250	9.0 (0.55)	1.2	110	1000	106	33.9 (74)	oil, 87% amine (GLC)

[a] Average $x = 3$. [b] 2-Methyl-4-(3-nitrophenyl)-3-butyn-3-ol. [c] Propargyl *p*-nitrobenzoate. [d] 3-Methyl-1-hexyn-3-yl benzoate.

showed that polysulfides of cobalt, nickel, and iron have been suggested for hydrogenation of both acetylenes and nitro compounds, although neither reaction conditions nor specific substrates were mentioned.[5] Of the polysulfides prepared by us, cobalt, for reasons unknown, proved to be superior compared to nickel and iron. This may be due to the fact that compared to cobalt, iron and nickel tend to form a large number of relatively stable complexes.[6] While high selectivities to (3-aminophenyl)acetylene were obtained with all polysulfides, the reaction with cobalt required the least amount of catalyst.

While current work was in progress, a patent reference was found disclosing the use of polysulfides of group 7 of the periodic table of elements and rhenium to preferentially hydrogenate aromatic nitro compounds in the presence of double bonds.[7] While the attention was focused on the conversion of 4,4'-dinitrostilbene-2,2'-disulfonic acid to the corresponding diamine, one example reported on the hydrogenation of the propargyl ester of 2-acetylamino-4-nitrobenzoic acid to amine, indicating that an unactivated propargyl group survives hydrogenation over cobalt polysulfide catalyst. No examples of the hydrogenation of activated phenylacetylenes, however, highly susceptible to hydration reactions over inorganic sulfides,[8] in the presence of nitro groups were reported.

Some of the more representative experiments with (3-nitrophenyl)acetylene (I) are summarized in Table I. Optimum conditions for hydrogenation of (3-nitrophenyl)acetylene to amine comprise a temperature of 85–120 °C, a hydrogen pressure of 400–1000 psig, a

substrate concentration of up to 25%, and a substrate-to-catalyst ratio of 50–80:1 (grams of feed/gram of Co). As much as 125 g of (3-nitrophenyl)acetylene was converted to the desired amine for each gram of catalyst (as Co). Attempts to convert larger amounts of feed led only to incomplete conversions. Our data suggest the hydrogenation reaction to be catalytic, although turnover frequency of cobalt is low compared to those usually encountered with the noble metal catalysts. For reasons of safety, this reaction is best carried out in a solvent to moderate its exothermicity and to minimize competing side reactions by dilution. Among the solvents used were methanol, isopropyl alcohol, tetrahydrofuran, and ethyl acetate. Analysis of the total product by GLC (internal standard method), after filtration and stripping of solvent, showed that generally 80–85% of the product is visible on the chromatogram. The remainder consisted of higher boiling condensation products which do not elute off the column. Analysis of the residue by NMR, after distillation of (3-aminophenyl)acetylene, showed the presence of acetophenone structure (2.45 ppm, singlet, $ArCOCH_3$); this result was also confirmed by IR (1670 cm^{-1}). The NMR spectrum also contained a peak at 2.15 ppm, indicative of a Schiff base structure $ArC(CH_3)=NAr$.[9] These analyses indicate that hydration and condensation compete with the hydrogenation reaction.

Recovery of (3-aminophenyl)acetylene was most conveniently achieved by distillation. It is therefore important to take the reaction to complete conversion as it is difficult to separate unreacted feed from the amine product. During distillation, particularly in experiments where conversions are less than 90%, care must be exercised to keep the pot temperature below about 150 °C. Exceeding this limit resulted in an uncontrollable exotherm, ac-

(5) F. K. Signairo, U.S. Patent 2 402 684 (1946).
(6) J. Kleinberg, W. J. Artgersinger, and E. Griswold, "Inorganic Chemistry", D. C. Heath and Company, Boston, MA, 1960, pp 547, 560.
(7) R. Braden, H. Knupfer, and H. Zieman, U.S. Patent 4 051 177 (1977).
(8) M. L. Spector, G. L. M. Christopher, and E. L. Carpenter, U.S. Patent 2 784 236 (1957).

(9) J. Barluenga and F. Azner, *Synthesis*, 195 (1977).

Table III. Hydrogenation of Selected Substrates over Noble Metal Sulfides (Catalyst Screening)

expt no.	catalyst paste, g	feed, g	concn, wt %^{c}	temp, °C	pressure, psig H$_2$	time, min	feed conv., %	amine yield, %	remarks
16	Rh$_2$S$_3$, 3.4	I,^{a} 10	4.8	100	1000	20	100	40	3-aminostyrene (48% yield)
17	Rh$_2$S$_3$, 1.7	I, 15	7.0	100	1000	22	54	26	3-nitrostyrene (55% yield)
18	ReS$_2$, 1.1	I, 10	4.8	100	1000	72	15	15	reaction stopped (100% selectivity)
19	OsS$_2$, 1.6	I, 10	4.8	110	1000	45			
				130	1000	40	55	36	reaction very sluggish
20	RuS$_2$, 1.5	I, 5	2.5	110	1000	50	87	82	no high boilers
21	RuS$_2$, 2.5	I, 10	4.8	110	1000	93	99	80	15% polymeric
22	RuS$_2$, 4.4	I, 25	11.0	110	1000	23	78	33	65% polymeric
23	RuS$_2$, 2.2	I, 50	20.0	110	1000	230	100	9.5	90% polymeric
24	RuS$_2$, 1.8	II,^{b} 1.8	1.5	70	60	83	100	97	mp 115–118 °C (toluene)
25	RuS$_2$, 0.6	II, 22	15.6	63	60	9.6 h	16.4	16.4	mp 117–118 °C (toluene); 100% selectivity (by GLC)
26	RuS$_2$, 2.0	II, 2	16.8	60	60	180	100	83	

^{a} I = (3-nitrophenyl)acetylene. ^{b} II = 2-methyl-4-(3-nitrophenyl)-3-butyn-2-ol. ^{c} In *i*-PrOH.

companied by cracking, which led to the formation of foul-smelling contaminants, a loss of vacuum, and contamination of the distillate. While the reason for this occurrence is not clear, the amino group may possibly form thermally unstable complexes with the nitro group,[10] or residual (3-aminophenyl)acetylene may start to polymerize at 160 °C or above.

To extend the scope of the nitro group hydrogenation, several additional substrates, including 2-methyl-4-(3-nitrophenyl)-3-butyn-2-ol (II), the propargyl ester of 4-nitrobenzoic acid (III), and the 3-methyl-1-hexyn-3-yl ester of 4-nitrobenzoic acid (IV) were investigated (Table II). Each substrate afforded a good yield of the corresponding amine.

Mechanistically, hydrogenation over cobalt polysulfide is interpreted to involve (1) generation of hydrogen sulfide, (2) reduction of the aromatic nitro compound with hydrogen sulfide, and (3) regeneration of hydrogen sulfide. This mechanism is based on our observation that cobalt polysulfide reacts with hydrogen under reaction conditions to give hydrogen sulfide, which in turn is assumed to reduce nitro groups to amines (eq 1, 2). This is consistent
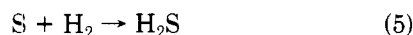
$$CoS_3 + H_2 \rightarrow CoS + H_2S \qquad (1)$$

$$ArNO_2 + 3H_2S \rightarrow ArNH_2 + 3S + 2H_2O \qquad (2)$$
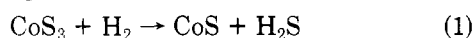
with a report that hydrogen sulfide in pyridine–water reduced nitrobenzene and related substrates to the corresponding amines at 0 °C.[11] Elemental sulfur, formed as the byproduct during reduction, is recycled to the system in the manner not clear as yet. One possibility involves direct reduction of the nitro group with sulfur (eq 3).[12] Such a reaction, however, requires a basic medium

$$2ArNO_2 + 6S + 6NaOH \rightarrow 2ArNH_2 + 3Na_2S_2O_3 \qquad (3)$$

and is not considered significant under relatively neutral conditions.[13,14] The reactions that we favor are the dissolution of sulfur to form polysulfide (eq 4) and the

$$CoS + nS \rightarrow CoS_x \qquad (4)$$

direct combination of sulfur and hydrogen to give hydrogen sulfide (eq 5), or both. While hydrogen sulfide formation

$$S + H_2 \rightarrow H_2S \qquad (5)$$

from elements is typically carried out in the vapor phase, it apparently also occurs in the liquid phase at 125 °C and elevated pressure.[15] According to the above mechanism, the loss of sulfur or hydrogen sulfide to side reactions leads to termination of the hydrogenation cycle. When this occurs, addition of sulfur or hydrogen sulfide in small amounts will reactivate the hydrogenation cycle. Of interest is a report on the hydrogenation of chloro- and bromonitrobenzenes over cobalt polysulfide and the platinum group sulfides.[16] The authors state that regardless of the ratio of catalyst to nitro compounds, and other variables, essentially quantitative yields of the corresponding anilines are obtained. This indicates that in our case with the acetylenic nitro compounds the low frequency numbers obtained with the cobalt must be linked to the loss of sulfur to interactions with the triple bond. Therefore, whenever cobalt polysulfide is reduced to the cobaltous sulfide (CoS) and all of the sulfur above the stoichiometric ratio has been consumed, reaction ceases.

Ruthenium(IV) Sulfide. We also screened the sulfide catalysts of rhodium, rhenium, osmium, and ruthenium for the conversion of (3-nitrophenyl)acetylene to (3-aminophenyl)acetylene (Table III). Of these catalysts, rhodium was nonselective; rhenium and osmium showed selectivity, but gave low conversions. Ruthenium was more promising and was investigated in more detail. Results with ruthenium(IV) sulfide indicated that (3-aminophenyl)acetylene can be prepared in good yields as long as the (3-nitrophenyl)acetylene concentration is kept low. Exceeding a 6% concentration level led predominantly to the formation of condensation products. It appears, then, that ruthenium sulfide is a more active hydration catalyst for phenylacetylenes than cobalt. Analysis of the condensation products (NMR, IR) indicated that the same type of materials are formed as with cobalt polysulfide. To assess the extent of hydration, a mixture of (3-aminophenyl)acetylene and propargyl 4-aminobenzoate (5 g each) was reacted in the presence of ruthenium(IV) sulfide in isopropyl alcohol–water (4:1) for 4 h (120 °C, 1000 psig N$_2$). Analysis showed that most of the ester had survived hydration, compared to only 60% in the case of phenylacetylene. (3-Aminophenyl)acetylene is therefore about 25 times more susceptible to hydration than the nonactivated propargyl ester.

Hydrogenation of dimethylcarbinol-substituted (3-nitrophenyl)acetylene (II) was achieved without difficulty,

(10) M. Freifelder, "Practical Catalytic Hydrogenation", Wiley, New York, 1971, p 207.

(11) S. Jozkiewicz, *Pr. Wroclaw. Tow. Nauk.*, Ser. B, No. 73, 48 (1956); *Chem. Abstr.*, **52**, 3711d (1958).

(12) N. Hirao, *J. Osaka Inst. Sci. Technol.*, 1, No. 2, 57 (1950); *Chem. Abstr.*, **48**, 2622h (1954).

(13) O. J. Cope and R. K. Brown, *J. Can. Chem.*, **41**, 1078 (1963).

(14) O. J. Cope and R. K. Brown, *J. Can. Chem.*, **40**, 2318 (1962).

(15) M. W. Farlow, M. Hunt, C. M. Langkammerer, W. A. Lazier, W. J. Pepper, and F. K. Signairo, *J. Am. Chem. Soc.*, **70**, 1392 (1948).

(16) F. S. Dovell and H. Greenfield, U.S. Patent 3 350 450 (1967).

although catalyst frequency numbers were still low.

Analysis of fresh ruthenium sulfide by ESCA showed ruthenium to be in the 4+ valency state, corresponding to RuS_2. The spent catalyst was divalent (2+), corresponding to RuS. Treatment of the latter with sodium sulfide solution restored its 4+ valence. Metallic ruthenium was never detected by ESCA in the hydrogenation work over ruthenium sulfides. This indicates that hydrogenations in the sulfide system are mechanistically different from those employing metallic ruthenium.

Finally, in hydrogenation of *m*-dinitrobenzene over cobalt polysulfide or ruthenium sulfide, both catalysts gave *m*-phenylenediamine exclusively (100 °C, 1000 psig H_2). This indicates that hydrogenations over transition metal sulfides in a neutral medium are mechanistically different from the conventional alkali metal sulfide reductions in basic medium, where only *m*-nitroaniline is formed.[18]

Experimental Section

All hydrogenations were carried out in a Parr low-pressure shaker (500-mL), or in 1-L, 1-gal, or 5-gal, 316-stainless steel, magnetically stirred autoclaves (Autoclave Engineers, Inc., Erie, PA), each equipped with cooling coils and heaters. Cobalt polysulfide catalysts were prepared from cobaltous chloride or cobaltous sulfate, sodium sulfide, and sulfur as reported.[5] The

propargyl and 3-methyl-1-hexyn-3-yl esters of 4-nitrobenzoic acid were prepared from the respective alcohols and 4-nitrobenzoic acid as reported.[17] NMR spectra were obtained on a Varian T-60 spectrometer. Shifts are quoted in δ units, parts per million, relative to Me_4Si. A typical procedure involved placing the substrate, catalyst, and solvent into a reactor and hydrogenating under given temperature until the theoretical amount of hydrogen had been consumed (monitored by pressure drop). After depressuring, the reaction mixture is filtered to recover the catalyst, and then solvent is removed on a rotary evaporator to give the product as the residue. (3-Aminophenyl)acetylene was recovered from the residue by vacuum distillation using a simple 6-in. Vigreux column: bp 78–80 °C (0.2 mmHg); n^{20}_D 1.6186; NMR (CCl_4) 3.0 (s, 1, C≡CH), 3.6 (s, 2, NH_2), 6.3–7.2 (m, 4, ring). 2-Methyl-4-(3-aminophenyl)-3-butyn-2-ol was obtained by crystallization from toluene: mp 117–120 °C; NMR ($CDCl_3$) 1.56 (s, 6, CH_3), 3.8–4.6 (s, 3, NH_2, OH, exchanges with D_2O), 6.6–7.2 (m, 4, ring); MS (*m/e*) 157 ($M - H_2O$)$^+$, 117 (M – acetone)$^+$, but no parent ion. Propargyl 4-aminobenzoate was recovered by crystallization from toluene: mp 88–91 °C; NMR (acetone-d_6) 2.95 (m, 1, C≡CH), 4.9 (d, 2, CH_2), 5.4 (s, 2, NH_2), 6.7 (d, 2, ring), 7.8 (d, 2, ring). 3-Methyl-1-hexyn-3-yl 4-aminobenzoate was obtained as an oil; NMR (acetone-d_6) 0.9 (t, 3, CH_3), 1.1–2.1 (m, 7, CH_2, CH_3), 2.95 (s, 1, C≡CH), 5.5 (s, 2, NH_2), 6.7 (d, 2, ring), 7.8 (d, 2, ring).

(17) G. F. Hennion and S. O. Barrett, *J. Am. Chem. Soc.*, 79, 2146 (1957).
(18) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry", Reinhold, New York, 1961, p 707.
(19) We thank one of the referees for pointing out that low frequency numbers could also be explained by gradual poisoning of cobalt sulfide catalyst.

Influence of the Cyano Group on Orientation of Nucleophiles to Aryne. 1. Reaction of Isomeric Halobenzonitriles with Alkali Amides in Liquid Ammonia[1a]

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The reaction of either *o*- or *m*-bromobenzonitrile with 2 equiv of lithium amide, sodium amide, or potassium amide yields aminobenzonitriles in a ratio of 95:5 meta/ortho, respectively. Similarly, *p*-bromobenzonitrile gives aminobenzonitriles in a ratio of 80:20 para/meta, respectively. These ratios are in a range which would be expected for the cyano group influencing amination orientation to aryne by the inductive mode. In the presence of 4 equiv of potassium amide, the meta/ortho and para/meta aminobenzonitrile ratios obtained from the corresponding bromobenzonitrile are 89:11 and 95:5, respectively. These altered ratios do not reflect a change in the orienting effect of the cyano group, but rather the instability of the aminobenzonitriles in highly basic medium. Similar results are observed for the reaction of the isomeric iodobenzonitrile with the exception of *o*-iodobenzonitrile, which is predominantly reduced by alkali amide. The reaction of the isomeric chloro- and fluorobenzonitriles yield aminobenzonitrile in very low yields, the predominant product being the corresponding chloro- or fluorobenzoamidine. An explanation in terms of the relative rates of formation of aryne and amidine is presented.

The direction of amination to arynes can be predicted usually by considering the nucleophile to add so as to provide, in the transition state, the most favorable location of the developing negative charge with respect to the inductive effect of the substituent.[2] For example, amination of 3-arynes possessing –I groups (electron withdrawing by induction), such as –OCH_3, –Cl, and –CF_3, occurs essentially at the 1-position to yield *m*-amino aromatics. Comparison of the transition states for 1- and 2-additions (**1** and **2**, respectively) indicates that the developing negative charge, being closer to the –I substituent