($CDCl_3$) δ 4.00–4.60 (m, 2 H), 3.47 (s, 4 H), 1.12, 1.13, 1.33, 1.35, 1.30–2.20 (4 s, m, 36 H); ^{13}C NMR ($CDCl_3$) δ 176.71, 78.43, 77.03, 75.60, 59.35, 51.78, 50.67, 48.46 (NCH_2), 42.06, 34.94, 33.28, 30.03, 18.82.

Anal. Calcd for $C_{22}H_{42}N_4O_2$: C, 66.96; H, 10.73; N, 14.20. Found: C, 67.19; H, 10.54; N, 14.40 (for the isomer with higher melting point). Found: C, 66.67; H, 10.47; N, 14.13 (for the isomer with lower melting point).

Acknowledgment. The authors thank W. Beears and D. Chasar for helpful discussions. The authors also acknowledge the instrumental analyses performed by R. Lattimer, K. Welch, and J. Westfahl.

Registry No. 1, 625-04-7; **2a**, 75812-95-2; **2b**, 75812-96-3; **2c**, 75812-97-4; **3a**, 71620-95-6; **3b**, 75812-98-5; **3c**, 75812-99-6; **3c'**, 75813-00-2; **3d**, 75813-01-3; **4a**, 75813-02-4; **4b**, 75813-03-5; **4c**, 75813-04-6; **4d**, 75813-05-7; **4e**, 75813-06-8; **4f**, 75813-07-9; **5a** (isomer 1), 75813-08-0; **5a** (isomer 2), 75813-09-1; **5b**, 75813-10-4; **5c** (isomer 1), 75813-11-5; **5c** (isomer 2), 75813-12-6; **5d**, 75813-13-7; **5e**, 75813-14-8; **5f**, 75813-15-9; **5g**, 75813-16-0; mesityl oxide, 141-79-7; *n*-butylamine, 109-73-9; 1,6-hexanediamine, 124-09-4; acetone, 67-64-1; acetone cyanohydrin, 75-86-5; *n*-dodecylamine, 124-22-1; ethanolamine, 141-43-5; ethylenediamine, 107-15-3; 1,3-diaminopropane, 109-76-2; 3,3'-diamino-*N*-methyldipropylamine, 105-83-9; *p*-xylene-α,α'-diamine, 539-48-0; *m*-xylene-α,α'-diamine, 1477-55-0; cyclohexanone, 108-94-1.

Supplementary Material Available: Elemental analyses and IR and ^1H NMR spectral data of compounds **2b,c**, **3a,c,d**, **4a,b,d–f**, and **5a–g** (8 pages). Ordering information is given on any current masthead page.

Schiff Bases as External and Internal Electrophiles in Reactions of Functionalized Organolithium Reagents. A New Route to Isoindoline Derivatives and 1,2,3,4-Tetrahydroisoquinolines[1]

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Received August 1, 1980

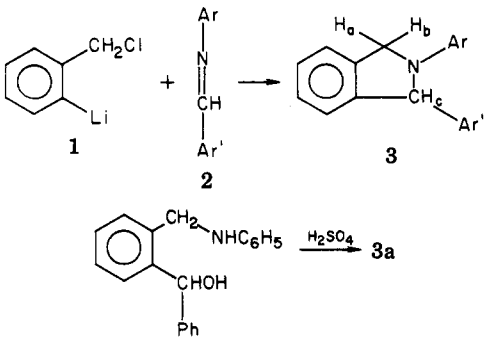
Reaction of Schiff bases with certain functionalized organolithium reagents is useful in the synthesis of 1,2-diarylisoindolines and 2,3-diarylphthalimidines. Schiff bases derived from 2-(2-bromophenyl)ethylamines on halogen–metal exchange with butyllithium undergo a Parham-type cyclization to yield 1-aryl-1,2,3,4-tetrahydroisoquinolines.

Parham et al.[2] discovered that at low temperatures certain aryl halides bearing electrophilic groups can be induced to undergo halogen–metal exchange selectively with butyllithium, affording synthetically useful functionalized organolithium reagents. When the organolithium reagents thus generated have the proper electrophilic group in the ortho position, cyclization reactions are possible. If the geometry of these functionalized organolithium reagents is correct, *direct* cyclization may occur through attack of the anionic center on the electrophilic substituent of the molecule.[3] The majority of the cyclizations studied have been *indirect* and involve the preliminary reaction of the anionic center with an added electrophile, followed by cyclization of the newly created anion.

Recently[2,4] it was shown that 3,4-dihydroisoquinolines could be prepared by the indirect method, through the addition of suitable nitriles to *o*-(2-bromoethyl)phenyllithium. One purpose of the present work was to investigate the possibility of forming dihydroisoindole derivatives by the indirect method using Schiff bases as the added electrophile.

The use of Schiff bases as electrophiles seemed promising since it is known[5] that in the presence of organolithium reagents N-substituted imines without hydrogens α to the imine carbon undergo simple addition at the imine double bond. When benzalaniline (**2a**) was added at −100 °C to the organolithium reagent (**1**) derived from *o*-bromobenzyl chloride and the mixture was allowed to warm to room temperature, 1,2-diphenylisoindoline (**3a**) was formed (Scheme I). The only known 1,2-diarylisoindoline was prepared earlier in this laboratory by Ludt and Hauser[6] through the acid-catalyzed cyclization of *o*-[(phenylamino)methyl]benzhydrol (**4**). Samples prepared

Scheme I[a]



[a] a, Ar = Ar' = Ph; b, Ar = 4-BrC_6H_4, Ar' = Ph; c, Ar = 2-Br-4-MeC_6H_3, Ar' = Ph; d, Ar = Ph, Ar' = 3,4-$(OCH_3)_2C_6H_3$.

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Table I. Reaction of Schiff Bases 2 with o-Lithiobenzyl Chloride (1) To Afford 1,2-Diarylisoindolines 3

for Schiff bases 2		for 1,2-diarylisoindolines 3								
					^{1}H NMR ($CDCl_3$)					
Ar	Ar'	mp, °C	yield, %[a]	mp, °C	H_a,[b] δ	H_b,[c] δ	H_x,[d] δ	J_{ab}, Hz	J_{ax}, Hz	J_{bx}, Hz
Ph	Ph	48.5-50[e]	69	149-150[f,g]	4.62	4.88	5.62	13	3	0.5-1.0
4-BrC_6H_4	Ph	65-66.5[h]	15	187-188[f,i]	5.10	5.36[j]	6.23[k]	14	<0.5	<0.5
2-Br,4MeC_6H_3	Ph	[l]	41	98-100[m]	4.23[n]	5.55	6.12	13	3	0.5-1.0
Ph	3,4-$(OCH_3)_2C_6H_3$	75-80[o]	57	112.5-114[p]	4.72	5.06	5.73	13	3	<0.5

[a] Satisfactory analytical data ±0.3% for C, H, N, and Br (when present) were reported. [b] Except as noted, observed as a broad asymmetric doublet. [c] Except as noted, appears as a doublet of doublets. [d] Except as noted, appears as a multiplet. [e] Lit.[14] mp 48 °C. [f] Colorless needles from benzene–hexane. [g] Lit.[6] mp 152-155 °C. An authentic sample prepared by the method of Ludt and Hauser[6] also melted at 149-150 °C alone or when mixed with our product: ^{13}C NMR ($CDCl_3$) δ 55.03, 69.00, 112.86, 116.56, 122.47, 123.25, 126.18, 127.35, 128.84, 128.91, 129.10, 129.17, 136.12, 142.55, 143.79, 146.45. [h] Lit.[15] mp 66-68 °C. [i] ^{13}C NMR ($CDCl_3$) δ 59.97, 65.88, 122.99, 123.97, 124.29, 124.49, 126.76, 128.71, 129.49, 130.21, 130.74, 133.97, 134.89, 138.78, 143.52, 145.54. [j] Broad unsymmetrical doublet. [k] Broad singlet. [l] Bp 130-133 °C (0.05 torr) [lit.[16] bp 170-175 °C (1.0 torr)]. [m] From methanol as pale yellow prisms: ^{13}C NMR ($CDCl_3$) δ 20.21, 57.18, 69.59, 119.03, 122.28, 123.06, 127.28, 127.41, 127.60, 127.80, 128.38, 128.58, 128.78, 133.98, 134.63, 138.14, 141.97, 143.14, 143.98. [n] Doublet of doublets. [o] The literature[17] gave no physical constants. [p] ^{13}C NMR ($CDCl_3$) δ 54.93, 55.10, 55.88, 69.00, 109.29, 111.56, 115.05, 116.69, 118.38, 122.47, 123.19, 127.28, 127.41, 129.10, 136.06, 136.58, 142.81, 146.77, 148.33, 149.57.

Table II. Reaction of Schiff Bases 2 with o-Lithiobenzonitrile (5) or Isopropyl o-Lithiobenzoate (7) as a Route to 2,3-Diarylphthalimidines 10

for Schiff base 2		for diarylphthalimidines 10						
		% yield from			IR (KBr),	^{1}H NMR ($CDCl_3$), δ		
Ar	Ar'	nitrile	ester	mp, °C	cm^{-1}	benzylic	aromatic	other
Ph	Ph	41	51	193-195[a,b]	1675[c]	6.06 (s)	7.04-8.06 (m)	
4-Br-C_6H_4	Ph	20	23	182-183.5[d,e]	1660	5.92 (s)	6.80-7.86 (m)	
Ph	3,4-$OCH_2OC_6H_3$	39	40	203-205[b,f]	1680	5.86 (s)	6.36-7.88 (m)	5.75 (s, 2, OCH_2O)

[a] Lit.[24] mp 192-193 °C. [b] Colorless needles. [c] Lit.[24] 1677 cm^{-1}. [d] Tan needles. [e] Analysis for C, H, Br, and N was ±0.21%. [f] Analysis for $C_{21}H_{15}NO_3 \cdot {}^1/_3H_2O$ for C, H, and N was ±0.21%; mass spectrum, m/e 329 (M^+), 301 (M^+ – CO), 208 ($M^+ - C_6H_3O_2CH_2$).

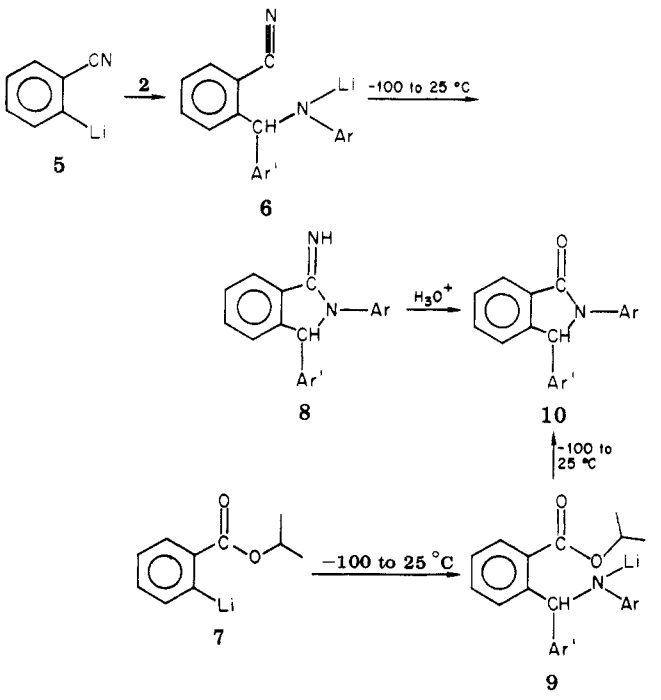
by either method are identical. When other diaryl Schiff bases were employed, good yields of 1,2-diarylisoindolines **3b-d** were obtained (Table I). Predictably, imines with α-hydrogens reacted as acids with the organolithium reagent **1**.

The ^{1}H NMR spectra of the diarylisoindolines exhibit an ABX coupling pattern in the aliphatic (benzylic) region, possibly due to a through-space coupling effect.[6]

Phthalimidines have been of interest as synthons in natural-product chemistry,[7,8] as isoindole intermediates,[9] and as antifungal agents,[10] and it appeared likely that 2,3-diarylphthalimidine (**10**) could be prepared by the reaction of Schiff bases with suitable Parham-type organolithium reagents. With o-lithiobenzonitrile (**5**, Scheme II)[11] the reaction at −78 °C with Schiff bases **2**, followed by warming of the mixture to −45 °C, presumably yielded the imine **8** (by cyclization of **6**), for on hydrolysis the product afforded diarylphthalimidines (**10**) in fair yield (Table II). A simpler and slightly more efficacious procedure involved the addition of Schiff bases **2** to isopropyl o-lithiobenzoate (**7**)[12] at −100 °C and allowing the salt (**9**) formed initially to warm to room temperature (Table II).

Despite the moderate yields obtained, this second procedure offers a simple one-pot preparation of 2,3-diarylphthalimidines which uses readily available starting materials. It has the advantage that it can be applied to the synthesis of phthalimidines having acid-sensitive groups.

Scheme II



As indicated in the introduction, Parham et al. discovered that selective halogen–metal exchange when carried out on an aryl halide having an appropriate electrophilic group on an ortho side chain can result in *direct* cycliza-

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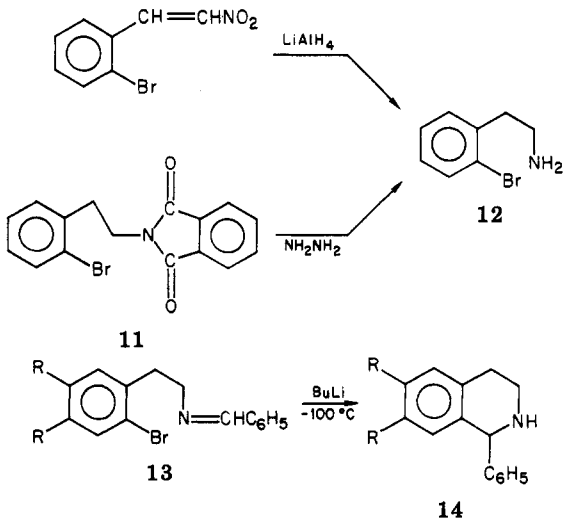
Scheme III[a]



[a] a, R = H; b, R = OCH_3.

tion. To date these Parham-type cyclizations have been carried out where the electrophilic group in the side chain was a carboxylate anion,[12] primary alkyl halide,[13] or epoxide[3] group. Characteristic of all three of these groups is a reactivity low enough toward butyllithium at −100 °C to permit lithium–metal exchange to occur with the aryl halogen (bromine or iodine) selectively and yet high enough to react with the newly generated aryllithium function before reaction with butyl bromide or the solvent can take place. An important goal of our research with Schiff bases was to determine whether the imine group would be effective in a Parham-type cyclization.

The benzylidene derivative (**13a**) of β-(2-bromophenyl)ethylamine (**12**) needed for the cyclization attempt was unknown as was the parent amine (**12**). The amine **12** was produced in good yield by reduction of 2-bromo-β-nitrostyrene[18] or from 2-bromophenethyl bromide[13] via the Gabriel synthesis (Scheme III). When the benzylidene derivative **13** was treated at −100 °C with 1 equiv of butyllithium, it afforded 1-phenyl-1,2,3,4-tetrahydroisoquinoline (**14a**) in 42% yield. Since 2-(2-bromo-3,4-dimethoxyphenyl)ethylamine can be prepared conveniently by bromination[19] of the parent amine, it was likewise converted to the benzylidene derivative **13b** and subjected to a Parham-type cyclization. The expected 1-phenyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline was isolated as the hydrochloride in 23% yield. The yields were disappointing in view of the fact that the cyclization is a favored process (6-endo-trig) according to Baldwin's rules.[20] This new synthesis of 1,2,3,4-tetrahydroisoquinoline appears to be of most promise in the synthesis of derivatives having acid-sensitive groups.

Experimental Section

All reactions involving organolithium reagents were conducted under an atmosphere of nitrogen. Tetrahydrofuran was distilled from lithium aluminum hydride or calcium hydride prior to use. Reaction temperatures of −100 °C were achieved with a diethyl ether–liquid nitrogen bath; reaction temperatures of −78 °C were achieved with an acetone–dry ice bath. All organic residues were dried over anhydrous magnesium sulfate. ^1H NMR data were obtained from a JEOL Model JNM-MH-100 100-MHz spectrometer employing 1–2% tetramethylsilane as an internal standard; ^{13}C NMR data were obtained from a JEOL Model FX-60 60-MHz Fourier transform spectrometer with a $CDCl_3$ lock and employing 1–2% tetramethylsilane as an internal standard. IR data were obtained from a Perkin-Elmer Model 297 spectrometer. GLC analyses were performed with a Varian Model 920 gas chromatograph (thermal-conductivity detector); mass spectra were obtained from a Bell and Howell Model 21-490 low-resolution mass spectrometer. Microanalyses were performed by M-H-W Laboratories. All melting points were determined in capillaries on a Mel-Temp heating block apparatus and are uncorrected.

Reaction of Schiff Bases 2a–d with *o*-Lithiobenzyl Chloride (1). Synthesis of 1,2-Diarylisoindolines 3. The Schiff base **2** (1 molar equiv) in dry tetrahydrofuran was added dropwise to the lithio derivative **1**[13] at −100 °C. The mixture was stirred at −100 °C for 3 h, after which it was allowed to warm to room temperature. Water was added, the organic layer separated, and the aqueous layer extracted three times with ether. The combined organic solutions were dried and concentrated under reduced pressure. The residue was purified by recrystallization. The results are summarized in Table I.

Synthesis of 2,3-Diarylphthalimidines (9). A. By Reaction of Schiff Bases with *o*-Lithiobenzonitrile (5). The Schiff base **2** (approximately 20 mmol) in dry tetrahydrofuran (50 mL) was added dropwise with stirring to 1 equiv of *o*-lithiobenzonitrile[11] at −78 °C, and after 4.5 h in the temperature was allowed to warm slowly to −45 °C. The reaction mixture was poured into water (200 mL) and the organic layer separated. The aqueous layer was extracted with chloroform (2 × 125 mL). The combined organic solutions were concentrated (rotary evaporation). To the residual oil was added 30 mL of 6 N hydrochloric acid, and the mixture was heated for 20 min on a steam bath. The mixture was diluted with water (100 mL) and extracted with chloroform (3 × 100 mL). The extracts, when dried and concentrated, yielded an oil which crystallized when triturated with ethanol. The resulting product was crystallized from ethanol (Table II).

B. By Reaction of Schiff Bases with Isopropyl *o*-Lithiobenzoate (7). The Schiff base **2** in tetrahydrofuran was added to isopropyl *o*-lithiobenzoate (**7**)[12] essentially as in part A except that the temperature was maintained at −100 °C during the addition and for 2–30 min thereafter before the mixture was allowed to warm to room temperature. After 4 h at room temperature, 100 mL of 5% hydrochloric acid was added to the reaction mixture. The organic layer was separated and later combined with the chloroform (2 × 100 mL) used to extract the aqueous layer. The organic solution was dried and concentrated (rotary evaporation) and the residue crystallized from ethanol (Table II).

***N*-[β-(2-Bromophenyl)ethyl]phthalimide[21] (11).** A mixture containing 90.65 g (343 mmol) of β-(2-bromophenyl)ethyl bromide,[13] 280 mL of *N*,*N*-dimethylformamide, and 66.64 g (360 mmol) of potassium phthalimide was stirred for 15 h at 90 °C. The mixture was cooled, diluted with chloroform (400 mL), and then transferred to a separatory funnel containing 300 mL of water. After the layers were mixed, the chloroform layer was removed and the aqueous layer extracted with chloroform (2 × 50 mL). The combined chloroform extracts were washed with 300 mL of 0.2 N sodium hydroxide and then with 300 mL of water. The chloroform solution was dried and concentrated (rotary evaporation) to yield 94.27 g (83%) of pale yellow solid which crystallized from 7:3 ligroin–methanol as fine colorless needles: mp 96.5–98 °C; IR (KBr) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.16 (t, J = 7 Hz, 2, CH_2), 4.02 (t, 2, benzylic CH_2), 7.00–7.96 (m, 8, Ar H).

Anal. Calcd for $C_{16}H_{12}BrNO_2$: C, 58.18; H, 3.64; Br, 24.24; N, 4.24. Found: C, 58.06; H, 3.60; Br, 24.43; N, 4.04.

β-(2-Bromophenyl)ethylamine (12). A. From 2-Bromo-β-nitrostyrene. Recrystallized 2-bromo-β-nitrostyrene[18] (10.71

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g, 86.1 mmol) was dissolved in anhydrous ether (500 mL) and added dropwise to a stirred slurry of lithium aluminum hydride (13.14 g, 346 mmol) in anhydrous ether (300 mL), and the mixture was stirred at 0–5 °C for 5 h, after which the mixture was hydrolyzed by addition of 28 mL of water, 28 mL of 20% sodium hydroxide, and finally 70 mL of water. The precipitate was filtered off and washed with ether, and the combined filtrates were dried, filtered, and concentrated (rotary evaporation) to yield 15.12 g (88%) of dark yellow oil which was purified by column chromatography on silica gel, eluting with benzene–ethyl acetate–methanol (1:2:3): IR (film) 3370, 3270, 1565, 1470 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.96 (br s, J = 5 Hz, 2, NH_2), 2.90 (overlapping t, 4, CH_2), 6.88–7.52 (m, 4, Ar H).

Anal. Calcd for $C_8H_{10}BrN$: C, 48.02; H, 5.04; Br, 39.94; N, 7.00. Found: C, 47.95; H, 4.85; Br, 40.23; N, 6.73.

B. From *N*-(β-(2-Bromophenyl)ethyl)phthalimide (11). The purified phthalimide (83.64 g, 253 mmol) was mixed with 250 mL of methanol and 30.43 mL (506 mmol) 85% hydrazine hydrate, and the mixture was refluxed and stirred for 1 h. The mixture, now containing a white voluminous solid, was allowed to cool to room temperature, and the methanol was removed by rotary evaporation. Concentrated hydrochloric acid (120 mL) was added to the solid and the mixture refluxed for 1.5 h with stirring. The mixture was cooled, the phthalimide removed by filtration, and the filtrate made basic to litmus with 2 N sodium hydroxide, followed by refrigeration for 3 h at 3 °C. The aqueous solution was extracted with ether (4 × 200 mL), and the ethereal solution was dried and concentrated (rotary evaporation) to yield 41.87 g (83%) of **12** as a yellow oil. Distillation afforded a colorless oil: bp 82–86 °C (0.3 torr); ^1H NMR and IR data as indicated in part A.

***n*-Benzylidene-β-(2-bromophenyl)ethylamine (13a).** The reaction of β-(2-bromophenyl)ethylamine (**12**; 13.11 g, 66 mmol) with benzaldehyde (6.95 g, 66 mmol) was carried out in refluxing benzene (250 mL), water being removed by the use of a Dean–Stark trap. Concentration of the benzene solution and distillation of the residue afforded 12.55 g (66%) of a yellow oil: bp 172–173 °C (0.25 torr); IR (film) 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.15 (t, J = 8 Hz, 2, CH_2), 3.88 (t, 2, benzylic CH_2), 6.93–7.88 (m, 9, Ar H), 8.17 (s, 1, azomethine CH).

Anal. Calcd $C_{15}H_{14}BrN$: C, 62.50; H, 4.86; N, 4.86. Found: C, 62.39; H, 4.74; N, 4.82.

***N*-Benzylidene-β-(2-bromo-4,5-dimethoxyphenyl)ethylamine (13b).** The reaction of β-(2-bromo-4,5-dimethoxyphenyl)ethylamine[19] (11.02 g, 42 mmol) with benzaldehyde (4.49 g, 42 mmol) was carried out as in the preparation of **13a**, affording 9.47 g (65%) of a viscous yellow oil: bp 205–207 °C (0.5 torr); IR (film) 1645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.07 (t, J = 6.5 Hz, 2, CH_2), 3.72 (s, 3, OCH_3), 3.82 (s, 3, OCH_3), 3.87 (partially observed t, 2, benzylic CH_2), 6.76 (s, 1, Ar H), 7.03 (s, 1, Ar H), 7.36–7.76 (m, 5, Ar H), 8.13 (s, 1, azomethine CH).

Anal. Calcd for $C_{17}H_{18}BrNO_2$: C, 58.62; H, 5.17; Br, 22.99; N, 4.02. Found: C, 58.74; H, 5.37; Br, 23.15; N, 3.87.

1-Phenyl-1,2,3,4-tetrahydroisoquinoline (14a). To a solution of 2.88 g (10 mmol) of **13a** in a mixture of dry tetrahydrofuran (125 mL) and dry hexane (30 mL) at −100 °C was added 10 mmol of butyllithium at such a rate as to maintain the temperature below −95 °C. ^1H NMR data from quenched samples showed that bromine–lithium exchange was complete within 15 min. The mixture was allowed to warm to room temperature and then quenched in 200 mL of 6 N hydrochloric acid. The organic layer was removed and the acid solution extracted with ether (3 × 100 mL) to remove any neutral compounds. The acid layer was then made basic to litmus by addition of 30% sodium hydroxide solution and extracted with ether (3 × 100 mL). The ether solution was dried and concentrated (rotary evaporation), affording 2.29 g of a brown oil which solidified on standing. Recrystallization of the solid afforded 0.88 g (42%) of colorless needles: mp 97–98 °C (lit.[22] mp 97 °C); IR (KBr) 3260 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.92 (br s, 1, NH), 2.94 (distorted t, 2, CH_2), 3.18 (distorted t, 2, benzylic CH_2), 5.10 (s, 1, benzylic CH), 6.68–7.57 (m, 9, Ar H).

1-Phenyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (14b). From 3.48 g (10 mmol) of **13b** was obtained 2.90 g of brown oil by following the procedure used in the preparation of **14a**. When this oil was dissolved in anhydrous ether and hydrogen chloride gas bubbled through it, 0.78 g of a brown precipitate formed. Recrystallization of the precipitate from methanol–ether afforded 0.69 g (23%) of colorless needles: mp 262–264 °C (lit.[23] mp 224–250 °C); IR (KBr) 2760, 2625, 2540, 1510 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.19 (t, J = 5.5 Hz, 2, CH_2), 3.46 (t, 2, benzylic CH_2), 3.73 (s, 3, OCH_3), 3.92 (s, 3, OCH_3), 5.79 (s, 1, benzylic CH), 6.23 (s, 1, Ar H), 6.75 (s, 1, Ar H), 7.08–7.52 (m, 5, Ar H), 7.70 (br s, 1, exchangeable H), 8.80 (br s, 1, exchangeable H).

Anal. Calcd for $C_{17}H_{19}NO_2$·HCl: C, 66.78; H, 6.55; Cl, 11.62; N, 4.58. Found: C, 66.59; H, 6.78; Cl, 11.94; N, 4.57.

Registry No. **1**, 74824-35-4; **2a**, 538-51-2; **2b**, 780-20-1; **2c**, 75767-88-3; **2d**, 27895-67-6; **3a**, 28519-59-7; **3b**, 75767-89-4; **3c**, 75767-90-7; **3d**, 75767-91-8; **5**, 59043-57-1; **7**, 75767-92-9; **10a**, 36149-34-5; **10b**, 75767-93-0; **10d**, 75767-94-1; **11**, 75767-95-2; **12**, 65185-58-2; **13a**, 75780-68-6; **13b**, 75767-96-3; **14a**, 22990-19-8; **14b**, 4118-36-9; β-(2-bromophenyl)ethyl bromide, 1074-15-3; benzaldehyde, 100-52-7; potassium phthalimide, 1074-82-4; 2-bromo-β-nitrostyrene, 65185-68-4; β-(2-bromo-4,5-dimethoxyphenyl)ethylamine, 63375-81-5.

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Reaction of Aromatic Sulfonyl Azides with Dienes

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Received July 8, 1980

The addition of aromatic sulfonyl azides to simple acyclic and cyclic dienes in a 1:2 molar ratio was investigated. In no case was the triazoline cycloaddition product isolated from the thermal cycloaddition. With the nonconjugated dienes 1,5-hexadiene and 1,7-octadiene, hydrogen migration occurred with nitrogen loss, affording sulfonimide products. No evidence for olefinic participation or alkyl group migration was obtained. Hydrolysis of the sulfonimides gave the corresponding unsaturated ketones 5-hexen-2-one and 7-octen-2-one, respectively. Conjugated dienes reacted with aromatic sulfonyl azides to give enamines rather than sulfonimides. The reaction of *p*-nitrobenzenesulfonyl azide with 1,3-cyclohexadiene followed by hydrolysis afforded only 2-cyclohexen-1-one resulting from hydrogen migration. Addition to either *cis,trans*- or *trans,trans*-2,4-hexadiene gave, after hydrolysis, *trans*-4-hexen-3-one and *trans*-2-methyl-2-pentenal arising from competitive hydrogen and vinyl group migration, respectively.

Although the reaction of organic azides with monoolefins has been widely investigated,[2-4] the addition to dienes has received less attention.[5] Scheiner[5] first suggested the addition of phenyl azide to conjugated dienes as a route

0022-3263/81/1946-0330$01.00/0