precipitated from the heterogeneous mixture.

***N,N'*-1,3-Phenylenebis(methanesulfonamide) (10).** The general procedure was followed except that the amounts of pyridine and methanesulfonyl chloride were increased (0.46 mol) as well as the amount of 6 N NaOH used in the workup (200 mL).

**General Procedure for the Preparation of [(Aminomethyl)phenyl]methanesulfonamides 11–20.** The amine (0.234 mol) was added to a room temperature solution of the methanesulfonamide (0.058 mol), 37% aqueous formaldehyde (0.299 mol), and ethanol (50 mL) in a pressure bottle. In some cases an exotherm was observed. The mixture was then stirred and heated at the temperature and time shown in Table II. The reaction mixture was concentrated in vacuo and the residue chromatographed on alumina (Fisher, neutral, activity II, 600 g).

Elution with hexane/EtOAc (3:2) afforded **11** as the free base. Treatment with ethanolic HCl gave the hydrochloride salt, which was recrystallized from EtOAc/EtOH (6:1): $^1$H NMR ($Me_2SO$-$d_6$) $\delta$ 1.87–1.99 (m, 4 H), 3.03 (s, 3 H), 3.33 (br s, 4 H), 4.27 (s, 2 H), 7.40 AB quartet, $J_{AB}$ = 8.0 Hz, $\Delta\nu_{AB}$ = 26.8 Hz, 4 H), 11.00 (br s, 1 H).

Elution with $CH_2Cl_2$/MeOH (97:3) afforded **12** as the free base. Treatment with ethanolic HCl gave the hydrochloride salt, which was recrystallized from EtOH: $^1$H NMR ($Me_2SO$-$d_6$) $\delta$ 1.24 (t, 6 H), 2.92–3.10 (m, 4 H), 3.04 (s, 3 H), 4.20 (s, 2 H), 7.42 (AB quartet, $J_{AB}$ = 8.6 Hz, $\Delta\nu_{AB}$ = 99.6 Hz, 4 H), 10.06 (s, 1 H), 10.68 (br s, 1 H).

Elution with $CH_2Cl_2$ afforded **13**. $^1$H NMR ($Me_2SO$-$d_6$) $\delta$ 1.39–1.50 (m, 6), 2.30 (m, 4), 2.96 (s, 3), 3.37 (s, 2), 7.19 (AB quartet, $J_{AB}$ = 8.0 Hz, $\Delta\nu_{AB}$ = 25.9 Hz, 4 H), 9.63 (br s, 1).

Elution with $CH_2Cl_2$ afforded recovered starting material **2** (77%) followed by **14**: $^1$H NMR ($CDCl_3$) $\delta$ 1.79 (m, 4 H), 2.50 (m, 4 H), 3.00 (s, 3 H), 3.57 (s, 2 H), 6.40 (br s, 1 H), 7.24 (dd, 1 H), 7.44 (d, 1 H), 7.57 (d, 1 H).

Elution with $CH_2Cl_2$/MeOH (19:1) afforded **15**: $^1$H NMR ($CDCl_3$) $\delta$ 1.82 (m, 4 H), 2.27 (s, 3 H), 2.29 (s, 3 H), 2.53 (m, 4 H), 3.01 (s, 3 H), 3.72 (s, 2 H), 6.72 (s, 1 H), 7.19 (s, 1 H).

Elution with $CH_2Cl_2$ afforded **16** as a yellow oil: $^1$H NMR ($CDCl_3$) $\delta$ 1.79–1.83 (m, 8 H), 2.53–2.58 (m, 8 H), 2.98 (s, 3 H), 3.61 (s, 2 H), 3.69 (s, 2 H), 3.82 (s, 3 H), 5.10 (br s, 1 H), 7.09 (s, 1 H), 7.11 (s, 1 H).

Elution with $CH_2Cl_2$ afforded recovered starting material **6** (73%) followed by **17**, which was recrystallized from hexane/EtOAc (9:1): $^1$H NMR ($CDCl_3$) $\delta$ 1.81–1.86 (m, 4 H), 2.52–2.56 (m, 4 H), 2.96 (s, 3 H), 3.71 (s, 2 H), 3.79 (s, 3 H), 6.69 (d, 1 H), 6.82 (dd, 1 H), 7.27 (s, 1 H), 7.44 (d, 1 H).

Elution with $CH_2Cl_2$/MeOH (24:1) afforded recovered starting material **7** (22%) followed by **18**: $^1$H NMR ($Me_2SO$-$d_6$) $\delta$ 1.71 (m, 4 H), 2.54 (m, 4 H), 2.82 (t, 2 H), 3.10 (s, 3 H), 3.16 (t, 2 H), 7.62 (AB quartet, $J_{AB}$ = 8.9 Hz, $\Delta\nu_{AB}$ = 205.8 Hz, 4 H).

Elution with $CH_2Cl_2$ afforded recovered starting material **8** (50%) followed by **19**: $^1$H NMR ($CDCl_3$) $\delta$ 1.83 (m, 4 H), 2.29 (s, 3 H), 2.54 (m, 4 H), 2.99 (s, 3 H), 3.70 (s, 2 H), 6.93 (br s, 1 H), 7.08 (d, 1 H), 7.40 (d, 1 H), 10.20 (br s, 1 H).

Elution with $CH_2Cl_2$/MeOH (19:1) afforded **20** as the free base. Treatment with ethanolic HCl gave the dihydrochloride salt, which was recrystallized from EtOH: $^1$H NMR ($Me_2SO$-$d_6$) $\delta$ 1.99 (m, 4 H), 2.03 (m, 4 H), 3.13 (s, 6 H), 3.38 (m, 4 H), 3.46 (m, 4 H), 4.45 (s, 4 H), 7.58 (s, 1 H), 8.25 (s, 1 H), 9.94 (s, 2 H), 10.96 (br s, 2 H).

**Acknowledgment.** We thank Dr. C. Anderson Evans and Mr. Joseph A. Traina for the proton NOE difference NMR spectra for adducts **14** and **17**.

**Registry No.** **1**, 1197-22-4; **2**, 7022-20-0; **3**, 66236-09-7; **4**, 66236-08-6; **5**, 7022-24-4; **6**, 4284-48-4; **7**, 5317-89-5; **8**, 4284-47-3; **9**, 50790-28-8; **10**, 6966-38-7; **11**, 108297-23-0; **11**·HCl, 108297-31-0; **12**, 100632-99-3; **12**·HCl, 108297-32-1; **13**, 108297-24-1; **14**, 108297-25-2; **15**, 108297-26-3; **16**, 108297-27-4; **17**, 108297-28-5; **18**, 76467-72-6; **19**, 108297-29-6; **20**, 108297-30-9; **20**·2HCl, 108297-33-2; $C_6H_5NH_2$, 62-53-3; 2-$ClC_6H_4NH_2$, 95-51-2; 2,6-$(CH_3)_2C_6H_3NH_2$, 87-62-7; 3,5-$(CH_3)_2C_6H_3NH_2$, 108-69-0; 3-$CH_3C_6H_4NH_2$, 536-90-3; 4-$CH_3OC_6H_4NH_2$, 104-94-9; 4-$CH_3COC_6H_4NH_2$, 99-92-3; 4-$CH_3C_6H_4NH_2$, 106-49-0; 4-$CH_3O_2CC_6H_4NH_2$, 619-45-4; 1,3-$C_6H_4(NH_2)_2$, 108-45-2; $(C_2H_5)_2NH$, 109-89-7; pyrrolidine, 123-75-1; piperidine, 110-89-4.

# Synthesis of 6-Phenylimidazo[1,2-*a*]pyrazin-8-one and 1-Methyl-6-phenylimidazo[1,5-*a*]pyrazin-8-one via Quaternary Intermediates

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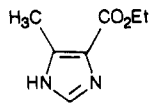
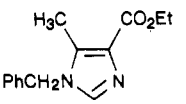
*Received January 12, 1987*

We were interested in 6-aryl-substituted imidazo[1,2-*a*]pyrazin-8-ones and imidazo[1,5-*a*]pyrazin-8-ones for evaluation as potential cardiovascular drugs.[1] While the most direct synthetic approach to these systems appeared to be reaction of an imidazole carboxamide with a 2-haloacetophenone, an important consideration for preparing the 1,5-*a* ring system is the site of alkylation, since only attack at the 3-position will lead to the desired target.

In this regard, we have previously prepared **2** from **1** in 71% isolated yield by a modification of a published procedure[2] in which an inseparable mixture of the 1- and 3-isomers was reported. Thus, we had an efficient means of protecting the 1-position with a group that could be removed by hydrogenolysis.




1




2

Reaction of **2** with concentrated ammonium hydroxide in a pressure reactor at 100 °C gave carboxamide **3** in 69% yield. Treatment of **3** with 2-bromoacetophenone in a mixture of DMF/acetonitrile at 90–100 °C afforded **4** in 87% yield. Several attempts to remove the benzyl group by hydrogenolysis resulted in the formation of **5** as the major product. Complete conversion to **5** could be accomplished by prolonging the reaction time.

Since reduction of the 5,6-double bond was occurring simultaneously with hydrogenolysis of the benzyl group, a different approach was sought. However, a major obstacle toward employing other known methods for debenzylation, i.e., nucleophilic displacement, was the poor solubility of **4** in both aqueous and organic media. From previous work,[3] we have demonstrated that neat imidazole at high temperature is an effective reagent for the demethylation of methoxyphenyl ketones. This method also has the benefict of dissolving the quaternary compounds. When **4** was treated with excess imidazole at 175 °C, debenzylation proceeded smoothly to afford **6** in 98% yield (Scheme I).

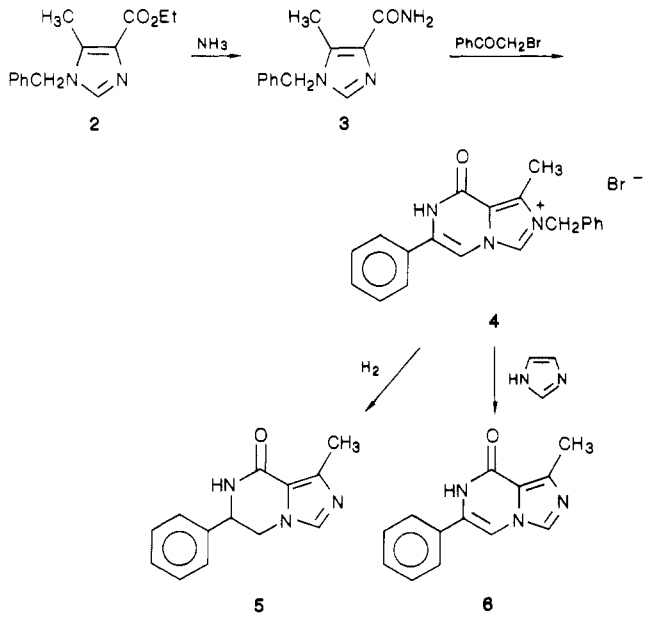
Compound **10** was prepared in an analogous manner. Treatment of 1-methylimidazole with ethyl chloroformate,[4] followed by reaction with aqueous ammonia, afforded carboxamide **7** in 65% overall yield. Treatment of **7** with 2-bromoacetophenone in acetonitrile resulted in a mixture of the desired imidazopyrazinium salt **8** and the uncyclized imidazolium salt **9**. Since these compounds could not be readily separated, the mixture was combined with excess imidazole and heated at 175 °C for 20 h. Workup afforded **10** in 89% yield (Scheme II).

During the course of this work a patent was issued to USV Corp.,[5] which described a series of substituted imi-

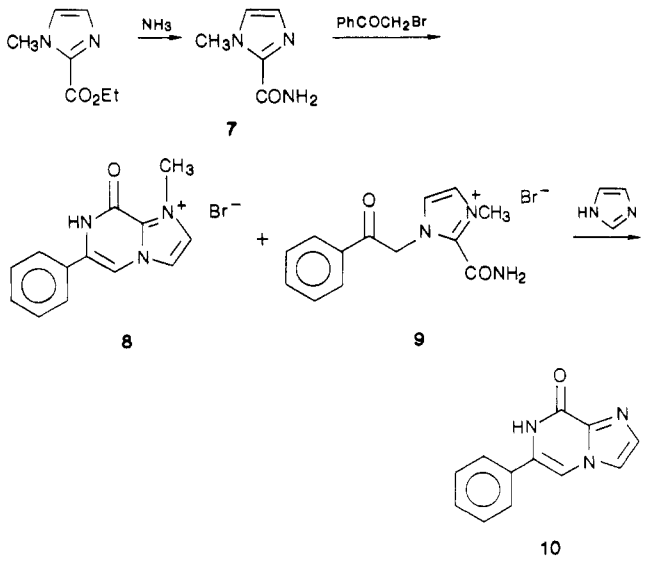
(1) Erhardt, P. W. *J. Med. Chem.* **1987**, *30*, 231.
(2) Bolhofer, W. A.; Cragoe, E. J.; Hoffman, J. M. U.S. Pat. 4 220 654, 1980.
(3) Davey, D. D. *J. Org. Chem.* **1987**, *52*, 1863–1867.
(4) Prepared by the method of Regel and Büchel: Regel, E.; Büchel, K. *Liebigs Ann. Chem.* **1977**, 145–158.
(5) Lee, T. D. U.S. Pat. 4 578 386, 1986.

0022-3263/87/1952-4379$01.50/0 

**Scheme I**



**Scheme II**



dazo[1,5-*a*]pyrazin-8-ones. Their synthesis involves reaction of **1** with an $\alpha$-halo carboxylic acid ester, followed by hydrolysis of the 3-substituted compound to the corresponding diacid. The diacid is then cyclized to the oxazine with an acid chloride, ring opened to the keto amide with ammonia, and finally cyclized by being heated to the imidazo[1,5-*a*]pyrazin-8-one in a five-step process and approximate 4% overall yield for the 6-pyridinyl derivative. By comparison, we prepared **6** in four steps with a 42% overall yield.

In conclusion, the preparation of compounds **6** and **10** via quaternization of an N-substituted imidazolecarboxamide represents a new and efficient method for the preparation of these two ring systems. Additionally, compound **10** represents the first reported example of a 6-aryl-substituted imidazo[1,2-*a*]pyrazin-8-one. The use of imidazole as a dealkylating agent for quaternary ammonium salts may be a useful alternative to existing methods, especially where solubility is a problem.

## Experimental Section

Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. IR spectra were obtained on a Sargent/Welch 3-300 spectrophotometer. $^1$H NMR spectra were recorded on a Varian XL-300 spectrometer. Elemental analyses were performed by the Berlex Analytical Department.

**5-Methyl-1-(phenylmethyl)-1*H*-imidazole-4-carboxylic Acid Ethyl Ester (2).** To a suspension of 70 g (1.75 mol) of sodium hydride (60% in oil) in 1.5 L of tetrahydrofuran at 0 °C under nitrogen was added 250 g (1.62 mol) of **1** over 1 h. The cooling bath was removed, and the reaction was allowed to warm to room temperature. After 2 h, 183 mL (1.54 mol) of benzyl brmide was added over 1 h, with the temperature rising to 35 °C. After stirring overnight, the solvent was removed under vacuum, the residue was slurried in 2 L of dichloromethane, washed with 2 x 2 L of water, dried over magnesium sulfate, and charcoal treated, and the solvent was removed under vacuum. The residue was crystallized from ether to provide 267 g (71%) of **2** as a white solid: mp 59–60 °C; NMR ($CDCl_3$) $\delta$ 1.37 (t, 3), 2.44 (s, 3), 4.33 (q, 2), 5.10 (s, 2), 7.04 (m, 2), 7.32 (m, 3), and 7.48 (s, 1).

**5-Methyl-1-(phenylmethyl)-1*H*-imidazole-4-carboxamide (3).** To 750 mL of concentrated ammonium hydroxide were added 90 g (0.37 mol) of **2** and 5 g of ammonium chloride. The mixture was heated at 100 °C for 7 h in a pressure reactor with good mixing. After cooling to room temperature, the resulting precipitate was filtered and washed with water and then ether to provide 55 g (69%) of a white solid: mp 232–234 °C; IR (KBr) 3090, 1670, 1500, 1450, and 1420 cm$^{-1}$; $^1$H NMR ($Me_2SO$-$d_6$) $\delta$ 2.33 (s, 3), 5.21 (s, 2), 6.96 (s, 1), 7.13 (d, 2), 7.20 (s, 1), 7.35 (m, 3), and 7.76 (s, 1). Anal. Calcd for $C_{12}H_{13}N_3O$: C, 66.96; H, 6.09; N, 19.52. Found: C, 66.98; H, 6.05; N, 19.52.

**7,8-Dihydro-1-methyl-8-oxo-6-phenyl-2-(phenylmethyl)-imidazo[1,5-*a*]pyrazinium Bromide (4).** A mixture of 23 g (0.11 mol) of **3** and 23 g (0.12 mol) of 2-bromoacetophenone in 700 mL of DMF/$CH_3CN$ (1:3) was heated at 90 °C for 20 h. After cooling to room temperature, the resulting precipitate was filtered and washed with acetonitrile to provide 37 g (87%) of an off-white solid: mp >300 °C; IR (Nujol) 1665, 1450, and 1355 cm$^{-1}$; $^1$H NMR ($Me_2SO$-$d_6$) $\delta$ 2.65 (s, 3), 5.70 (s, 2), 7.37 (m, 5), 7.54 (m, 3), 7.67 (m, 2), 7.96 (s, 1), and 9.59 (s, 1). Anal. Calcd for $C_{20}H_{18}BrN_3O$: C, 60.62; H, 4.58; N, 10.60. Found: C, 60.60; H, 4.52; N, 10.44.

**5,6-Dihydro-1-methyl-6-phenylimidazo[1,5-*a*]pyrazin-8-(7*H*)-one (5).** To 300 mL of methanol were added 3 g (7.6 mmol) of **4** and 0.5 g of 10% palladium on carbon, and the mixture was hydrogenated in a Parr reactor at 50 °C and 50 psi for 8 h. After cooling to room temperature, the catalyst was removed by filtration and the filtrate was concentrated under vacuum. The residue was crystallized from ether/dichloromethane (1:1) to provide 1.7 g (99%) of a white solid: mp 222–224 °C; IR ($CH_2Cl_2$) 1675, 1575, and 1420 cm$^{-1}$; $^1$H NMR ($Me_2SO$-$d_6$) $\delta$ 2.36 (s, 3), 4.22 (dd, 1), 4.36 (dd, 1), 4.89 (m, 1), 7.26 (m, 5), 7.60 (s, 1), and 8.21 (d, 1). Anal. Calcd for $C_{13}H_{13}N_3O$: C, 68.70; H, 5.77; N, 18.49. Found: C, 68.75; H, 5.77; N, 18.20.

**1-Methyl-6-phenylimidazo[1,5-*a*]pyrazin-8(7*H*)-one (6).** A mixture of 36 g (90 mmol) of **4** and 150 g (2.2 mol) of imidazole was heated at 175 °C under $N_2$ for 8 h. After being cooled to 100 °C, the reaction mixture was poured into 1 L of ice water with rapid stirring. The resulting precipitate was filtered and washed with water and ether to provide 20 g (98%) of an off-white solid: mp 281–282 °C; IR ($CH_2Cl_2$) 1680, 1430, and 1280 cm$^{-1}$; NMR ($Me_2SO$-$d_6$) $\delta$ 2.50 (s, 3), 7.43 (m, 3), 7.64 (m, 3), and 8.11 (s, 1). Anal. Calcd for $C_{13}H_{11}N_3O$: C, 69.32; H, 4.92; N, 18.65. Found: C, 69.15; H, 4.82; N, 18.62.

**1-Methyl-1*H*-imidazole-2-carboxamide (7).** To 300 mL of concentrated ammonium hydroxide were added 41 g (0.27 mol) of 1-methyl-1*H*-imidazole-2-carboxylic acid ethyl ester and 0.4 g of ammonium chloride, and the mixture was heated at 100 °C for 6 h in a pressure reactor with good mixing. After cooling to 0 °C, the resulting precipitate was filtered and washed with ice water and ether to provide 21 g (63%) of an off-white solid, mp 165–167 °C (lit.[6] mp 170 °C).

**6-Phenylimidazo[1,2-*a*]pyrazin-8(7*H*)-one (10).** A mixture of 10 g (80 mmol) of **7** and 19 g (95 mmol) of 2-bromoacetophenone in 300 mL of acetonitrile was refluxed for 20 h. After cooling to 20 °C, the precipitate was filtered and washed with ether. $^1$H NMR revealed the precipitate to be an approximate 1:5 mixture

(6) Fournari, P.; deCointet, P.; Laviron, E. *Bull. Soc. Chim. Fr.* **1968**, *6*, 2438–2446.

of compounds 8 and 9. The solids were combined with 120 g (1.76 mol) of imidazole and heated to 175 °C under nitrogen for 20 h. After being cooled to 100 °C, the reaction mixture was poured into 1 L of ice water with rapid stirring. The resulting precipitate was filtered and washed with water and then ether to provide 15.1 g (89% overall yield) of a white solid: mp 253–254 °C; IR (Nujol) 1670, 1420, and 1330 $cm^{-1}$; $^1H$ NMR ($Me_2SO$-$d_6$) δ 7.45 (m, 4), 7.69 (d, 2), 7.82 (s, 1), 7.89 (s, 1), and 11.52 (s, 1). Anal. Calcd for $C_{12}H_9N_3O$: C, 68.24; H, 4.29; N, 19.89. Found: C, 68.06; H, 4.24; N, 20.08

**Registry No.** 1, 51605-32-4; 2, 75815-53-1; 3, 108418-73-1; 4, 108418-74-2; 5, 108418-75-3; 6, 108418-76-4; 7, 20062-51-5; 8, 108418-77-5; 9, 108418-78-6; 10, 108418-79-7; ethyl 1-methyl-1*H*-imidazole-2-carboxylate, 30148-21-1; 2-bromoacetophenone, 70-11-1.

## Highly Chemoselective Addition of (*o*-Nitrobenzyl)silanes to Nonenolizable Aldehydes

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The use of silicon compounds in organic synthesis has been rapidly expanding[1] in recent years, and versatile methods of carbon–carbon bond formation have been developed, based on the ability of certain alkyl trimethylsilanes to act as carbanion synthetic equivalents in the presence of a fluoride ion source. In this way, for example, alkynyl,[2] benzyl,[3] propargyl,[4] and allyl[5] frameworks have been easily transferred to various electrophilic centres.

Recently, we reported[6] a general and highly chemoselective method of synthesis of functionalized nitrobenzyl silanes. In that work, as already suggested by Ricci and co-workers,[7] we tested the possibility of these compounds to act as nitrobenzyl carbanion equivalents by few preliminary examples of addition to benzaldehyde. If this reaction should have general application, it would be of great interest in organic chemistry as an efficient route to obtain (β-hydroxy alkyl)nitrobenzenes: an important class of intermediates for the synthesis of indoles.[8]

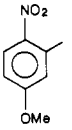
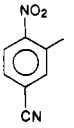
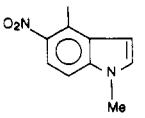
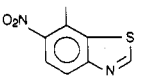
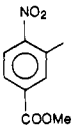
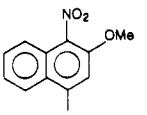
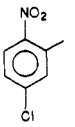
Previous attempts to utilize nitrobenzyl carbanions originated by base-promoted proton abstraction from nitrotoluenes generally gave unsatisfactory results[9] owing to the occurence of undesired electron-transfer and radical processes.[10,11] To our knowledge the only efficient example of this reaction is the sodium ethoxide promoted addition of nitrotoluenes to ethyl oxalate (Reissert reaction).[12]

Therefore, in this work we will report on our investigation on the reactivity of various (nitrobenzyl)trimethylsilanes with enolizable and nonenolizable aldehydes in the presence of stoichiometric or catalytic amounts of tetrabutylammonium fluoride (TBAF).

**Reaction with Nonenolizable Aldehydes.** As reported in Table I, in the case of nonenolizable aldehydes, the reaction proceeds smoothly at room temperature, giving the expected addition products in high yields with a large and significant variety of silyl substrates. In fact, the reaction can be successfully applied to homo- and bicyclic systems such as benzene and naphthalene as well

**Table I. Results of the Addition of [(Trimethylsilyl)methyl]nitroarenes to Aldehydes in the Presence of TBAF**

$$ArCH_2SiMe_3 + RCHO \xrightarrow{TBAF} ArCH_2CH(OH)R + ArCH_3$$

| Ar | R | TBAF | yield, % addn product | yield, % methyl deriv |
|---|---|---|---|---|
|  | Ph | 1 equiv | 34 | 20 |
| | Ph | 5% | 60 | traces |
| | 2-furyl | 5% | 73 | traces |
| | H | 5% | 74 | traces |
| | 4-nitrophenyl | 5% | 98 | traces |
| | $CCl_3$ | 5% | 78 | traces |
| | 2-bromophenyl | 5% | 82 | traces |
| | 4-cyanophenyl | 5% | 97 | traces |
| | MeCH=CH | 5% | 69 | traces |
|  | Ph | 5% | 68 | traces |
|  | Ph | 5% | 86 | traces |
| | 2-furyl | 5% | 97 | traces |
|  | 2-furyl | 5% | 94 | traces |
|  | Ph | 5% | 77 | traces |
|  | MeCH=CH | 5% | 94 | traces |
| | Ph | 5% | 80 | traces |
| | Ph | 1 equiv | 76 | 5[a] |
|  | Ph | 1 equiv | 67 | 15[a] |
| | Ph | 5% | 85 | traces |

[a] See ref 6.

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