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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Received January 26, 1987

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]

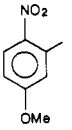
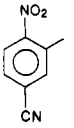
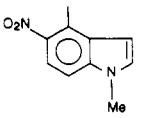
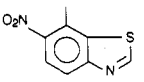
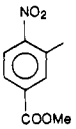
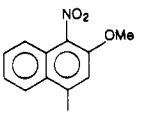
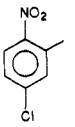
Previous attempts to utilize nitrobenzyl carbanions originated by base-promoted proton abstraction from nitrotoluenes generally gave unsatisfactory results[9] owing to the occurence of undesired electron-transfer and radical processes.[10,11] To our knowledge the only efficient example of this reaction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

(1) (a) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (b) Chan, T. H.; Fleming, I. *Synthesis*, **1979**, 761. (c) Habich, D., Effenberger, F. *Synthesis* **1979**, 841. (d) Magnus, P. D.; Sarkar, T.; Djuric, S. "*Organosilicon Compounds in Organic Synthesis*" *Comprehensive Organometallic Chemistry*, Wilkinson, G., Ed., Pergamon: New York, 1982; p 515.

(2) (a) Nakamura, E.; Kuwajima, I. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 498. (b) Holmes, A. B.; Jennings-White, C. L. D.; Schultess, A. H.; Akinde, B.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1979**, 840.

(3) (a) Ricci, A.; Fiorenza, M.; Grifagni, M. A.; Bartolini, G.; Seconi, G. *Tetrahedron Lett.* **1982**, *23*, 5079. (b) Bennetau, B.; Dunogues, J. *Tetrahedron Lett.* **1983**, *24*, 4217. (c) Bennetau, B.; Bordeau, M.; Dunogues, J. *Bull. Soc. Chim. Fr.* **1985**, II-90.

(4) Pornet, J.; Randrianoelina, B.; Miginiac, L. *Tetrahedron Lett.* **1984**, *25*, 651.

(5) (a) Hosomi, A.; Shirahata, A.; Sakurai, H. *Tetrahedron Lett.* **1978**, *19*, 3043. (b) Vorbruggen, H.; Krolikiewicz, K. *Tetrahedron Lett.* **1983**, *24*, 889. (c) DePuy, C. H.; Bierbaum, V. M.; Filippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5012.

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(7) Ricci, A.; Degl'Innocenti, A.; Fiorenza, M.; Taddei, M.; Spartera, M. A.; Walton, D. R. M. *Tetrahedron Lett.* **1982**, *23*, 577.

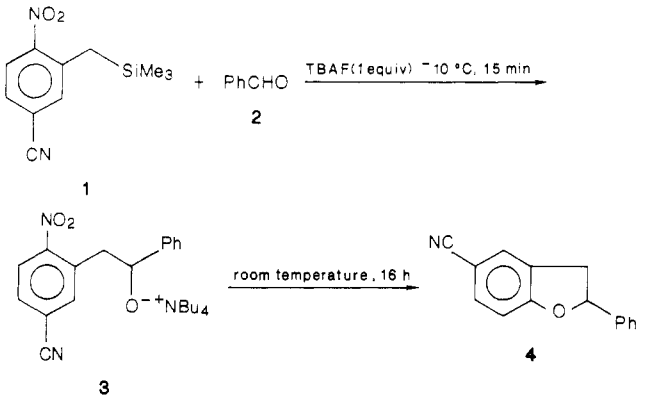
(8) Bakke J. *Acta Chem. Scand., Part B* **1974**, *B28*, 134.

(9) (a) Bakke, J. *Acta Chem. Scand.* **1967**, *21*, 1967. (b) Wesslen, B. *Acta Chem. Scand.* **1967**, *21*, 718.

† Università, Camerino (Mc).
‡ Università, Bologna.

0022-3263/87/1952-4381$01.50/0

Scheme I

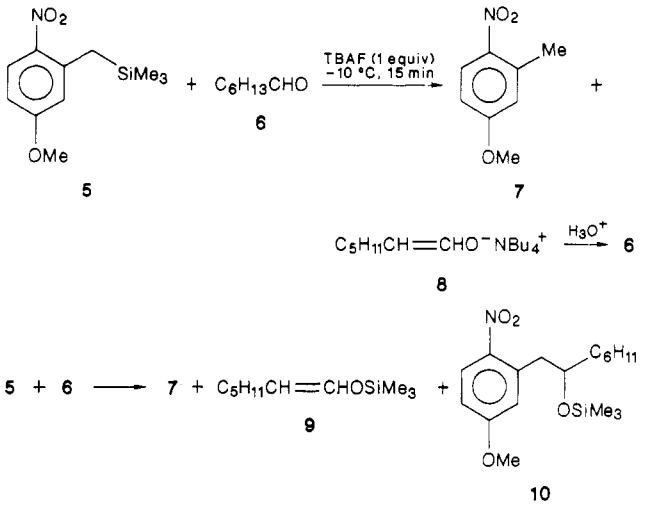


as to heterocyclic ones such as benzothiazole and indole. The last example is of particular interest as it represents an efficient route to the difficulty obtainable functionalization at 4-position of the biologically important indole nucleus.

The reaction proceeds with high chemoselectivity. For example, electrophilic functions (bromo, cyano, and ester) present both on the silyl reagent and on the aldehydes are unaffected. These findings are noteworthy, considering that classical carbanionic reagents (RLi andRMgX) are not able to selectively attack to aldehydes in the presence of the above-mentioned electrophilic groups.[13] Furthermore, products arising from self-addition of silyl substrates were never observed, even if the nitroarenic system is particularly activated toward nucleophilic attack, by the presence of a strong electron-withdrawing group such as a cyano function. The inertness of the nitroarenic system is confirmed by the reaction of 4-nitro-3-[(trimethylsilyl)-methyl]anisole with 4-nitrobenzaldehyde, in which the product arising from the attack on the carbonyl moiety was isolated in 98% yield. This trend is completely opposite to that exhibited by Grignard reagents which selectively react with nitroarenes in the presence of a carbonyl group,[6,14] under controlled experimental conditions. Finally, it must be mentioned that the observed nearly exclusive preferentiality of attack to the aldehydic function is obtained without resorting to particular experimental expedients (e.g., low temperature). TBAF can be used as a mere initiator (5%) without requiring a significant prolongation of the reaction times, moreover leading to an improvement in yield.

A possible explanation of this behavior is that TBAF cannot be completely dehydrated in practice. In addition during dehydration according to Cox's method,[15] some phenomena of TBAF decomposition may occur. As a consequence, the use of larger amounts of TBAF implies the presence of greater amounts of proton sources leading to the formation of methyl derivative instead of the addition product, as shown in Table I.

Scheme II



Finally, α,β-unsaturated aldehydes exclusively undergo 1,2-addition, as previously observed with unsubstituted benzylsylanes.[3b,c]

The reaction of 4-cyano-1-nitro-2-[(trimethylsilyl)-methyl]benzene with benzaldehyde in the presence of equimolar amounts of TBAF can give different final reaction products, depending on temperature and reaction times.

In fact, when the reaction was carried out at low temperature (−10 °C) and quenched a few minutes after mixing of the reagents, the expected addition product was recovered in high yield. When the reaction was allowed to stand overnight at room temperature, 5-cyano-2,3-dihydro-2-phenylbenzofuran (**4**) was exclusively isolated. Very likely, this product arises from an intramolecular nucleophilic attack of the alkoxide function to the nitro-substituted aromatic carbon in compound **3** (see Scheme I). The large difference in constant rate between formation of **3** and its subsequent monomolecular cyclization to **4** allows isolation of the intermediate **3** before the formation of appreciable amounts of **4** without employing high concentrations of the reactants and very low temperature conditions. The intramolecular nucleophilic displacement of a nitro group by an alkoxide is not surprising, since the nitro framework was demonstrated to behave as a good nucleofugic group in nucleophilic aromatic substitutions, when activated by an electron-withdrawing substituent in a conjugate position.[16]

Reaction with Enolizable Aldehydes and Ketones. The reaction with enolizable aldehydes or ketones follows a different course. The benzylic carbanionic species, originated from the attack of the fluoride at the silicon atom, preferentially acts as a base rather than as a nucleophile. For example the reaction of 3-[(trimethylsilyl)methyl]-4-nitroanisole (**5**) with heptanal (**6**) in the presence of equimolar amounts of TBAF gives 4-nitro-3-methylanisole (**7**) and the starting aldehyde after acidic quenching of the reaction mixture and after usual workup (see Scheme II). Using catalytic amounts of TBAF we followed the formation of the methyl derivative **7** of the silyl enol ether **9** and only of traces of the addition product **10** (3%), by monitoring the reaction by GLC–MS analysis (see Experimental Section).

Other enolizable aldehydes such as *n*- and isobutyraldehyde give analogous results. The use of higher reaction temperatures, or the change of the solvent (CH_3CN and

(10) Buncel, E.; Menon, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3499 and literature cited therein.

(11) Our attempts to prepare Grignard reagents from 2-(bromomethyl)nitrobenzenes failed due to the occurrence of electron-transfer from magnesium to the nitroarenic system (Bartoli, G.; Dalpozzo, R.; Grossi, L., unpublished results).

(12) Reissert, A. *Chem. Ber.* **1897**, *30*, 1030. For a recent application, see: Bergman, J.; Sand, P.; Tilstan, U. *Tetrahedron Lett.* **1983**, *24*, 3665.

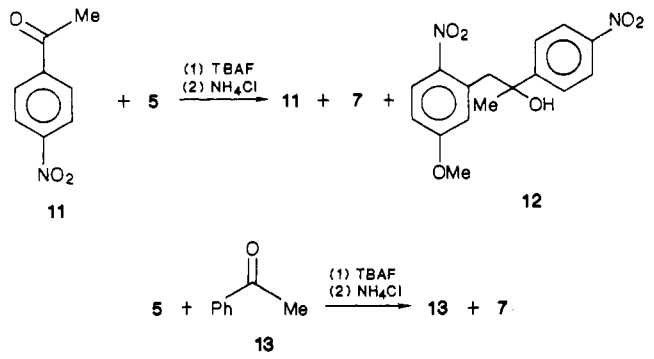
(13) (a) Weidmann, B.; Seebach, D. *Helv. Chim. Acta* **1980**, *63*, 2451. (b) Weidmann, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 31.

(14) Bartoli, G.; Bosco, M.; Dalpozzo, R. *Tetrahedron Lett.* **1985**, *26*, 115.

(15) Cox, D. P.; Terpinski, J.; Lawrynowicz, W. *J. Org. Chem.* **1984**, *49*, 3216.

(16) Bartoli, G.; Todesco, P. E. *Acc. Chem. Res.* *1977*, *10*, 125.

Scheme III



CH_3CN–THF or THF–HMPT mixtures) does not modify the reaction course.

Unsubstituted benzyl silanes are reported to add to enolizable aldehydes or ketones in fair to good yields under similar reaction conditions.[3b,c] Enolization vs. addition is favored by steric hindrance in either the carbonyl compound or the carbanionic reagent.[17] Thus, the complete enolization observed in the case of hindered (*o*-nitrobenzyl)silane **5** can be ascribed to steric factors due to the presence of the bulky nitro group near the reaction center.

This interpretation is supported by the difference in the product distribution observed in the reaction of **5** with 4-nitroacetophenone (**11**) with respect to that with unsubstituted acetophenone (**13**) (see Scheme III).

The presence of a strong electron-withdrawing substituent in a suitable position increases the electrophilicity of the carbonyl function of acetophenone system in a greater extent than the acidity of the hydrogen atoms of the methyl group, without varying the steric environment around the reaction center. As a consequence of this and on the basis of the above interpretation it may be expected that the relative proportion of addition vs. enolization increases on going from the unsubstituted to nitro-substituted compound. In fact, while in the case of **13** complete enolization was observed, in the case of **11**, the enolization competes with addition in about 1:1 ratio.

In conclusion, in this work an efficient method to obtain (β-hydroxyalkyl)nitroarenes from fluoride-mediated addition of (nitrobenzyl)silanes to nonenolizable aldehydes is reported. The most remarkable aspect of this method is the preferentiality to attack carbonyl functions showed by fluoride–silyl reagent carbanion system; highly reactive electrophilic functions such as nitro, cyano, bromo, and ester present both in the nucleophilic reagent and/or in the electrophilic substrate result to be unaffected. In addition should the above chemoselectivity be extended to other systems, it would open new prospects to application of silyl compounds in organic synthesis. Studies are in progress to verify this hypothesis.

Experimental Section

Melting points are uncorrected and were determined with a Buchi apparatus. NMR spectra were recorded at 60 MHz with a Varian EM-360-L instrument. IR spectra were recorded with a Perkin-Elmer 983 spectrometer. THF was dried by refluxing it over sodium wires until the blue color of benzophenone ketyl persisted and then distilling it into a dry receiver under a nitrogen atmosphere. [(Trimethylsilyl)methyl]nitroarenes were synthesized as previously reported.[6] Commercial aldehydes and ketones were distilled or recrystallized before use. Commercial TBAF·$3H_2O$ was dehydrated according to Cox's procedure[15] and then dissolved in dry THF to obtain a 1 M solution.

Reaction of [(Trimethylsilyl)methyl]nitroarenes with Aldehydes. General Procedure. Nitroarene (5 mmol) and aldehyde (6 mmol) were dissolved in 10 mL of dry THF under nitrogen atmosphere at room temperature in a three-necked round-bottomed flask equipped with a magnetic stirrer and a dropping funnel. The THF solution of TBAF (5 mmol or 0.25 mmol) was added dropwise to the mixture and stirring was continued for 15 min. About 5 mL of concentrated HCl was added, and the product was extracted with ether. Drying, concentration, and flash chromatography on silica gel yielded the 1,2-disubstituted ethanols. Yields are reported in Table I. Melting points and full NMR data follow.

2-(2-Nitro-5-methoxyphenyl)-1-phenylethanol: mp 65–68 °C; ^1H NMR ($CDCl_3$) δ 2.30 (br s, 1 H, OH), 3.13–3.47 (m, 2 H, CH_2), 3.77 (s, 3 H, OMe), 4.74–5.20 (m, 1 H, CH), 6.53–6.87, 7.07–7.50, and 7.83–8.10 (m, 2 H + 5 H + 1 H, Ar). Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 66.01; H, 5.50; N, 5.15.

2-(2-Nitro-5-methoxyphenyl)-1-fur-2-ylethanol: oil; ^1H NMR ($CDCl_3$) δ 3.00 (br s, 1 H, OH), 3.20–3.53 (m, 2 H, CH_2), 3.80 (s, 3 H, OMe), 4.80–5.17 (m, 1 H, CH), 6.17–6.37 (m, 2 H, H-3 and H-4 furyl), 6.50–6.80 (m, 2 H, H-5 and H-6 Ph) 7.20–7.43 (m, 1 H, H-5 furyl), 7.87–8.13 (m, 1 H, H-3 Ph). Anal. Calcd for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98; N, 5.32. Found: C, 59.39; H, 4.96; N, 5.31.

2-(2-Nitro-5-methoxyphenyl)ethanol:[18] oil; ^1H NMR ($CDCl_3$) δ 2.50 (br s, 1 H, OH), 3.20 (t, 2 H, J_{CH-CH} = 6.0 Hz, CH_2), 3.87 (s, 3 H, OMe), 3.97 (t, 2 H, CH_2OH), 6.77–7.07 and 8.00–8.30 (m, 2 H + 1 H, Ar). Anal. Calcd for $C_9H_{11}NO_4$: C, 54.81; H, 5.62; N, 7.10. Found: C, 54.77; H, 5.60; N, 7.15.

1-(2-Nitro-5-methoxyphenyl)-3,3,3-trichloropropan-2-ol: mp 92–94 °C; ^1H NMR ($CDCl_3$) δ 2.67 (br s, 1 H, OH), 2.97–3.73 (m, 2 H, CH_2), 4.00 (s, 3 H OMe), 4.27–4.53 (m, 1 H, CH), 6.63–6.97 and 7.90–8.13 (m, 2 H, + 1 H Ar). Anal. Calcd for $C_{10}H_{10}Cl_3NO_4$: C, 38.16; H, 3.18; N, 4.45; Cl, 33.86. Found: C, 38.20; H, 3.17; N, 4.46; Cl, 33.80.

2-(2-Nitro-5-methoxyphenyl)-1-(4-nitrophenyl)ethanol: mp 118–120 °C; ^1H NMR ($CDCl_3$) δ 2.50 (d, 1 H, J_{CH-OH} = 4.0 Hz, OH), 2.83–3.70 (m, 2 H, CH_2), 3.90 (s, 3 H, OMe), 5.00–5.33 (m, 1 H, CH), 6.67–7.00, 7.50–7.77, and 8.00–8.33 (m, 2 H + 2 H + 3 H, Ar). Anal. Calcd for $C_{15}H_{14}N_2O_6$: C, 56.60; H, 4.43; N, 8.80. Found: C, 56.55; H, 4.44; N, 8.76.

2-(2-Nitro-5-methoxyphenyl)-1-(2-bromophenyl)ethanol: 70–72 °C; ^1H NMR ($CDCl_3$) δ 3.00 (br s, 1 H, OH), 3.43 (d, 2 H, J_{CH-CH} = 6.0 Hz, CH_2), 3.83 (s, 3 H, OMe), 5.47 (t, 1 H, CH), 6.77–7.83 and 8.00–8.20 (m, 6 H + 1 H, Ar). Anal. Calcd for $C_{15}H_{14}BrNO_4$: C, 51.14; H, 3.98; N, 3.98; Br, 22.73. Found: C, 51.20; H, 3.96; N, 4.00; Br, 22.67.

2-(2-Nitro-5-methoxyphenyl)-1-(4-cyanophenyl)ethanol: mp 124–125 °C; ^1H NMR ($CDCl_3$) δ 2.63 (br s, 1 H, OH), 2.90–3.67 (m, 2 H, CH_2), 3.93 (s, 3 H, OMe), 5.00–5.40 (m, 1 H, CH), 6.77–7.13, 7.67–7.90, and 8.13–8.37 (m, 2 H + 4 H + 1 H, Ar). Anal. Calcd for $C_{16}H_{14}N_2O_4$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.45; H, 4.71; N, 9.41.

1-(2-Nitro-5-methoxyphenyl)pent-3-en-2-ol: oil; ^1H NMR ($CDCl_3$) δ 1.70 (d, 3 H, J_{CH-CH} = 5.0 Hz, CH_3), 2.00 (br s, 1 H, OH), 3.07–3.40 (m, 2 H, CH_2), 3.90 (s, 3 H, OMe), 4.23–4.57 (m, 1 H, CH), 5.57–5.83 (m, 2 H, CH=CH), 6.77–7.07 and 7.97–8.23 (m, 2 H + 1 H Ar). Anal. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.71; H, 6.36; N, 5.89.

2-(1-Methyl-5-nitroindol-4-yl)-1-phenylethanol: mp 107–108 °C; ^1H NMR ($CDCl_3$) δ 2.50 (br s, 1 H, OH), 3.53 (d, 2 H, J_{CH-CH} = 6.0 Hz, CH_2), 3.70 (s, 3 H, NMe), 5.00 (t, 1 H, CH), 6.60 (AB_d, 1 H, $J_{2,3}$ = 3.0 Hz, H-3 indolyl), 7.00–7.53 (m, 7 H Ar) 7.83 (AB_d, 1 H, $J_{6,7}$ = 9.0 Hz, H-6 indolyl). Anal. Calcd for $C_{17}H_{16}N_2O_3$: C, 68.90; H, 5.44; N, 9.45. Found: C, 69.01; H, 5.45; N, 9.41.

2-(1-Methyl-5-nitroindol-4-yl)-1-fur-2-ylethanol: mp 105–107 °C; ^1H NMR ($CDCl_3$) δ 2.60 (br s, 1 H, OH), 3.73 (d, 2 H, J_{CH-CH} = 7.0 Hz, CH_2), 3.80 (s, 3 H, NMe), 5.17 (t, 1 H, CH), 6.20–6.40 (m, 2 H, H-3 and H-4 furyl), 6.73 (AB_d, 1 H, $J_{2,3}$ = 3.0 Hz, H-3 indolyl), 7.30–7.50 (m, 3 H, Ar), 7.97 (AB_d, 1 H, $J_{6,7}$ =

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9.0 Hz, H-6 indolyl). Anal. Calcd for $C_{15}H_{14}N_2O_4$: C, 62.93; H, 4.93; N, 9.79. Found: C, 62.99; H, 4.92; N, 9.80.

2-(6-Nitrobenzothiazol-7-yl)-1-fur-2-ylethanol: mp 97–99 °C; ^{1}H NMR ($CDCl_3$) δ 3.13 (br s, 1 H, OH), 3.77 (d, 2 H, J_{CH-CH} = 7.0 Hz, CH_2), 5.30 (t, 1 H, CH), 6.27–6.47 (m, 2 H, H-3 and H-4 furyl), 7.43–7.57 (m, 1 H, H-5 furyl), 8.00–8.33 (m, 2 H, H-4 and H-5 benzothiazolyl), 9.33 (s, 1 H, H-2 benzothiazolyl). Anal. Calcd for $C_{13}H_{10}N_2O_4S$: C, 53.80; H, 3.47; N, 9.65; S, 11.03. Found: C, 53.81; H, 3.47; N, 9.63; S, 11.00.

2-(2-Nitro-5-carbomethoxyphenyl)-1-phenylethanol: mp 113–114 °C; ^{1}H NMR ($CDCl_3$) δ 2.93 (br s, 1 H, OH), 3.27 (d, 2 H, J_{CH-CH} = 6.0 Hz, CH_2), 3.90 (s, 3 H, OMe), 4.93 (t, 1 H, CH), 7.17–7.53 (m, 5 H, Ph), 7.87–8.13 (m, 3 H, Ar). Anal. Calcd for $C_{16}H_{15}NO_5$: C, 63.78; H, 5.02; N, 4.65. Found: C, 63.85; H, 5.00; N, 4.66.

1-(3-Methoxy-4-nitronaphthyl)pent-3-en-2-ol: oil; ^{1}H NMR ($CDCl_3$) δ 1.70 (d, 3 H, J_{CH-CH} = 4.0 Hz, CH_3), 1.93 (br s, 1 H, OH), 3.27 (d, 2 H, J_{CH-CH} = 6.0 Hz, CH_2), 4.00 (s, 3 H, OMe), 4.40 (t, 1 H, CH), 5.53–5.77 (m, 2 H, CH=CH), 7.23–8.23 (m, 5 H, Ar). Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.88; H, 5.96; N, 4.88. Found: C, 66.81; H, 5.95; N, 4.87.

Reaction of 4-Nitro-3-[(trimethylsilyl)methyl]benzonitrile with Benzaldehyde. The reaction was carried out as described above at −10 °C, and after flash chromatographic purification on silica gel (diethyl ether/light petroleum (bp 40–60 °C), 7:3, as eluant), 1-phenyl-2-(2-nitro-5-cyanophenyl)ethanol was recovered in 68% yield: oil, ^{1}H NMR ($CDCl_3$) δ 2.37 (br s, 1 H, OH), 3.13–3.41 (m, 2 H, CH_2), 4.77–5.17 (m, 1 H, CH), 7.20–8.13 (m, 8 H, Ar). Anal. Calcd for $C_{15}H_{12}N_2O_3$: C, 67.15; H, 4.51; N, 10.44. Found: C, 67.20; H, 4.50; N, 10.46.

When the reaction mixture was stirred overnight (16 h) at room temperature, 5-cyano-2,3-dihydro-2-phenylbenzo[*b*]furan was obtained in 70% yield after the usual workup: mp 86–88 °C; ^{1}H NMR ($CDCl_3$) δ 2.80–3.93 (m, 2 H, CH_2), 5.60–6.03 (m, 1 H, CH), 6.73–7.70 (m, 8 H, Ar); IR (KBr) 2223 (CN) and 1249 (C–O) cm^{-1}. Anal. Calcd for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33. Found: C, 81.51; H, 4.99; N, 6.35.

Reaction of 4-Nitro-3-[(trimethylsilyl)methyl]anisole (5) with *n*-Heptanal. When the reaction was carried out with equimolar amounts of TBAF after the usual workup, the starting aldehyde (95% yield) and 3-methyl-4-nitroanisole (85% yield) were recovered. Both compounds were identified by comparison with authentic samples.

The same results were obtained by using a 5% molar amount of TBAF. However, this reaction was followed by GLC-MS analysis using a Hewlett-Packard HP-59970 work station formed by an HP-5890 gas chromatograph equipped with a methyl silicone capillary column and by an HP-5970 mass detector. Reaction samples submitted to this analysis at various reaction times showed the disappearance of the reactants and the formation of 3-methyl-4-nitroanisole and of 1-[(trimethylsilyl)oxy]hept-1-ene as a mixture of the cis and trans isomers, two peaks being detected with similar fragmentation patterns.

3-[(Trimethylsilyl)methyl]-4-nitroanisole (5): *m/e* 224 ($M^+ - CH_3$), 150, 135, 122, 106, 95, 75, 73.

Heptanal (6): *m/e* 114 (M^+), 113, 96, 86, 81, 70, 57, 55, 44.

3-Methyl-4-nitroanisole (7): *m/e* 167 (M^+), 150, 122, 95, 91, 78, 77, 65.

1-[(Trimethylsilyl)oxy]hept-1-ene (9): *m/e* 186 (M^+), 171, 157, 143, 129, 99, 95, 76, 73.

The TLC analysis of the reaction showed the presence of the aldehyde from hydrolisis on silica of the silyl enol ether of the nitro compounds **5** and **7** and of traces of the addition product **10**.

Reaction of 5 with 4-Nitroacetophenone and Acetophenone. The reaction between **5** and acetophenone was carried out as described above by using a 5% molar of TBAF. After about 30 min, the quenching of the reaction mixture followed by the usual workup led to the methyl derivative **7** (80% yield) and to the starting acetophenone (recovered about 95%). The products were identified by comparison with authentic samples.

The reaction of **5** with 4-nitroacetophenone (**11**) was carried out with the same procedure described for aldehydes. After chromatography, with light petroleum (bp 40–60 °C)/diethyl ether (1:1) as eluant, the following products were isolated.

7: 54.4% yield; identified by comparison with a true sample.

11: 50% recovered unaltered; identified by comparison with a true sample.

1-(5-Methoxy-2-nitrophenyl)-2-(4-nitrophenyl)propan-2-ol: 37.4% yield; mp 132–134 °C; ^{1}H NMR ($CDCl_3$) δ 1.66 (s, 3 H, CH_3), 2.80 (s, 1 H, OH), 3.18–3.38 and 3.64–3.84 (AB system, 1 H + 1 H, CH_2), 3.70 (s, 3 H, OMe), 6.34 (d, 1 H, $J_{6,4}$ = 2.0 Hz, Ar), 6.80 (dd, 1 H, $J_{3,4}$ = 10 Hz, Ar), 7.50–7.70 and 8.12–8.28 (A_2B_2 system, 2 H + 2 H, Ar), 8.00 (d, 1 H, Ar). Anal. Calcd for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43. Found: C, 57.75; H, 4.84; N, 8.41.

1,3-Bis(4-nitrophenyl)-3-hydroxybutan-1-one: 7.3% yield; identified by comparison with a true sample.

Registry No. **5**, 109434-09-5; (*E*)-**9**, 52186-50-2; (*Z*)-**9**, 50300-19-1; 2-(2-nitro-5-methoxyphenyl)-1-phenylethanol, 109433-96-7; 2-(2-nitro-5-methoxyphenyl)-1-fur-2-ylethanol, 109433-97-8; 2-(2-nitro-5-methoxyphenyl)ethanol, 21857-42-1; 2-(2-nitro-5-methoxyphenyl)-1-(4-nitrophenyl)ethanol, 109433-98-9; 1-(2-nitro-5-methoxyphenyl)-3,3,3-trichloropropan-2-ol, 109433-99-0; 2-(2-nitro-5-methoxyphenyl)-1-(2-bromophenyl)-ethanol, 109434-00-6; 2-(2-nitro-5-methoxyphenyl)-1-(4-cyanophenyl)ethanol, 109434-01-7; 1-(2-nitro-5-methoxyphenyl)pent-3-en-2-ol, 109434-02-8; 2-(2-nitro-5-cyanophenyl)-1-phenylethanol, 109434-03-9; 2-(1-methyl-5-nitroindol-4-yl)-1-phenylethanol, 109434-04-0; 2-(1-methyl-5-nitroindol-4-yl)-1-fur-2-ylethanol, 109434-05-1; 2-(6-nitrobenzothiazol-7-yl)-1-fur-2-ylethanol, 109434-06-2; 2-(2-nitro-5-carbomethoxyphenyl)-1-phenylethanol, 109434-07-3; 1-(3-methoxy-4-nitronaphthyl)pent-3-en-2-ol, 109434-08-4; 2-(3-methoxy-4-nitronaphthyl)-1-phenylethanol, 103369-02-4; 2-(2-nitro-5-chlorophenyl)-1-phenylethanol, 103369-01-3; 4-nitro-3-[(trimethylsilyl)methyl]benzonitrile, 103368-89-4; 1-methyl-4-[(trimethylsilyl)methyl]-5-nitroindole, 103368-99-6; 6-nitro-7-[(trimethylsilyl)methyl]benzothiazole, 103368-98-5; methyl 4-nitro-3-[(trimethylsilyl)methyl]benzoate, 103368-91-8; 1-nitro-2-methoxy-4-[(trimethylsilyl)methyl]-naphthalene, 103368-96-3; 4-chloro-2-[(trimethylsilyl)methyl]-nitrobenzene, 103368-87-2; benzaldehyde, 100-52-7; 2-furancarboxaldehyde, 98-01-1; formaldehyde, 50-00-0; 4-nitrobenzaldehyde, 555-16-8; trichloroacetaldehyde, 75-87-6; 2-bromobenzaldehyde, 6630-33-7; 4-cyanobenzaldehyde, 105-07-7; crotonaldehyde, 4170-30-3; tetrabutylammonium fluoride, 429-41-4; 5-cyano-2,3-dihydro-2-phenylbenzo[*b*]furan, 109434-10-8; heptanal, 111-71-7; 2-methyl-4-methoxynitrobenzene, 5367-32-8; 4-nitroacetophenone, 100-19-6; acetophenone, 98-86-2; 1-(5-methoxy-2-nitrophenyl)-2-(4-nitrophenyl)propan-2-ol, 109434-11-9; 1,3-bis-(4-nitrophenyl)-3-hydroxybuten-1-one, 109434-12-0.

Functionalized Pyrazoles from Indazol-4-ols

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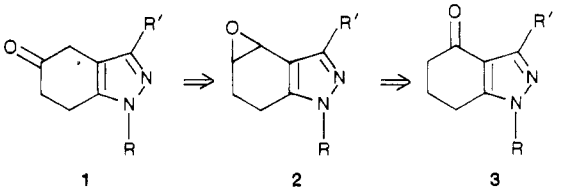
Received March 9, 1987

We recently required indazolones **1** as starting materials for the preparation of fused indazolones for biological evaluation. Retrosynthetically, it seemed attractive to envision 1,2-carbonyl transposition methodology[1] starting from indazolones **3**, which are available from 1,3-cyclohexanedione.[2] Since epoxides can be rearranged to ke-



1 **2** **3**

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