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The Preparation of 2-(1-Phenyl-5-Phenyl or 5-Substituted Phenyl-1H-Pyrazol-3-Yl)Phenols from Trilithiated 2′-Hydroxyacetophenone Phenylhydrazone and Aromatic Esters

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THE PREPARATION OF 2-(1-PHENYL-5-PHENYL OR 5-SUBSTITUTED PHENYL-1*H*-PYRAZOL-3-YL)PHENOLS FROM TRILITHIATED 2'-HYDROXYACETOPHENONE PHENYLHYDRAZONE AND AROMATIC ESTERS

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ABSTRACT: 2'-Hydroxyacetophenone phenylhydrazone was trilithiated with excess lithium diisopropylamide, and the resulting trianion-type intermediate was condensed with a variety of aromatic esters followed by acid cyclization to 2-(1-phenyl-5-phenyl or 5-substituted phenyl-1*H*-pyrazol-3-yl)phenols.

The preparations and uses of substituted 1*H*-pyrazoles and related materials are well documented, especially with regard to their biological potential and use in other syntheses[1,2]. Traditional preparations of these compounds using β–diketones involve the condensation/cyclization of symmetrical or unsymmetrical β-diketones with phenylhydrazine or related hydrazines[1], and the latter reactions usually afford a mixture of isomeric 1*H*-pyrazoles that can be separated by chromatographic techniques. While these separation methods are well developed,

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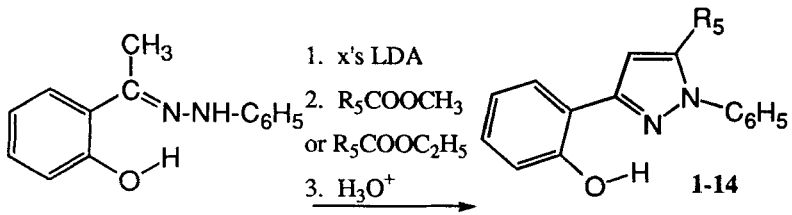
they can sometimes be time consuming. Also, very few unsymmetrical β–diketones are commercially available, and their preparation would involve additional synthetic procedures[3]. Recent reports[21,m] for the preparation of these materials include the oxidation of 4,5-dihydro-1*H*- pyrazoles (2-pyrazolines) to 1*H*-pyrazoles, which were prepared by a traditional condensation/cyclization of α,β-unsaturated carbonyl compounds with substituted hydrazines. Also, cycloaddition preparative methods[4], utilizing dipole precursors such as diphenylnitrile imine and α–azidostyrene, do not appear to be easily adaptable for the preparation of unsymmetrical 2-(1-phenyl-5-phenyl or 5-substituted phenyl-1*H*-pyrazol-3-yl)phenols, also referred to as *ortho*-hydroxyphenylpyrazoles.

In an earlier study[5], we trilithiated 2'-hydroxyacetophenone carboalkoxy-hydrazones with excess lithium diisopropylamide (LDA) followed by condensation/cyclization with lithiated methyl salicylates to afford substituted pyrazolobenzoxazinones[6]. While the trilithiation and reactions of 2'-hydroxy-acetophenone phenylhydrazone have not been undertaken, this polyanion-type system offers the potential for readily preparing a number of structurally placed *ortho*-hydroxyphenylpyrazoles, which have the additional potential of undergoing excited state proton transfer (ESPT)[7]. Many of the targeted *ortho*-hydroxyphenyl-



1-14

pyrazoles prepared in the current study are new, and those that have been reported earlier[21,m] were made by traditional methods.

During this investigation 2'-hydroxyacetophenone phenylhydrazone was rapidly prepared (see experimental section) by the condensation of phenylhydrazine with 2'-hydroxyacetophenone[8]. It was then treated with excess LDA (phenylhydrazone: LDA: ester - 1:4:1 or 1:5:1 for **4**, **8**, and **9** - see Table), and the trilithiated intermediate was condensed with a variety of substituted benzoate esters, such as methyl benzoate, ethyl 4-dimethylaminobenzoate, or methyl isonicotinate. After acid cyclization with aqueous hydrochloric acid, the desired *o*-hydroxyphenylpyrazoles **1-14** (Table) were isolated in 42-80% yield. *ortho*-Hydroxyphenylpyrazoles **1, 3-6, 8-10** and **12-14** are new, and they were characterized by absorption spectra with support from combustion analysis[9] (for C, H and N). Infrared spectra[10] were used primarily to indicate that the reaction had occurred, and that starting materials were not isolated. Phenolic OH in products **1-14** was observed at *ca.*, 3200 cm^{-1}. Proton magnetic resonance spectra[10] were most helpful for structure verification. The expected methoxy hydrogens in **2, 3,** and **5**, were noted as singlets with chemical shifts in the range of δ 3.67-3.93 ppm and methyl absorptions (tolyl type) in **1** and **10** were displayed as singlets δ 2.27-2.40 ppm. The *tert*-butyl methyl hydrogens (*tert*-butylphenyl) in **6** were located at δ 1.33 ppm and the 4-dimethyl-amino hydrogens in **9** were displayed at δ 2.98 ppm. In compounds **1, 3, 7, 8, 11, 12,** and **14** the C_4-H absorptions were readily identifiable as singlets absorbing in the range δ 6.80-7.10 ppm and were distinctive from the aromatic absorptions. The important 2-hydroxyphenyl hydrogen

absorption in all compounds were located at *ca.* δ 11 ppm (10.83-11.10), and they readily exchanged with deuterium oxide. Other phenolic hydrogens in **4** and **8** were noted at δ 9.73 and 9.53 ppm, respectively, and they also exchanged with deuterium oxide.

This is our first report of the condensation/cyclization of a polyanion-type system with ethyl 4-dimethylaminobenzoate. The success is attributed to the lithiation with excess LDA (phenylhydrazone: LDA - 1:5). In the past, we have experienced limited success with the condensation/cyclization of polylithiated intermediates with lithiated methyl 3-hydroxybenzoate. Of additional interest is the condensation and cyclization of the trianion-type intermediate with electron rich esters,[11] such as lithiated methyl 4-hydroxybenzoate, to afford *o*-hydroxyphenylpyrazole **4** (and related *o*-hydroxyphenylpyrazoles **2, 3, 5,** and **9**). The expected C-acylated intermediates, resulting from the condensation of the trianion-type intermediate with methyl isonicotinate or methyl 2-phenyl-4-quinolinecarboxylate, upon acid cyclization may have been initially envisioned as being more difficult to cyclize, due to the electron withdrawal of the heterocyclic nitrogen atom, which became part of the heteroaromatic pendant group in position 5 of the substituted pyrazoles, **13** and **14.** This did not prove to be a difficulty considering that these products were isolated in 55 and 71% yields, respectively. In general, the yields of products **1-14** may not be optimal for a particular compound, but the current general procedure readily affords multi-gram quantities of pure products resulting from recrystallization from routine solvents, which are in sufficient amounts for spectral characterization and other uses. The

experimental procedure is straightforward, so that someone not necessarily familiar with strong base procedures can be successful with the reactions, and the experimental set-up does not require elaborate apparatus (see experimental section).

Preliminary spectral studies of the *ortho*-hydroxyphenylpyrazoles **1-14** in *n*-heptane have shown UV/VIS [12] absorption maximum at *ca.* λ, 300 nm and a short wavelength emission maximum occurring in the region λ, 368-372 nm. Based on similarities in structure between these compounds and ESPT compounds cited in the literature [7], the *ortho*-hydroxyphenylpyrazoles also have the potential to undergo ESPT. If proton transfer is occurring in the excited state, a long wavelength emission maximum should be observed at *ca.* λ, 620 nm. As expected for such a large Stokes shift, our initial efforts have shown that a dominant radiationless pathway is greatly reducing the fluorescence quantum yield of the long wavelength band [7b, 13]. Efforts to limit the radiationless pathway and increase the quantum yield of the ESPT emission are currently underway.

Spectral studies have also shown that excited state charge transfer is causing a red shift in the emission maxima for the derivatives with electron donating substituents in resonance positions[14]. For example, the emission for the *o*-hydroxyphenylpyrazole **9** shifted from λ, 373 nm in *n*-heptane to λ, 428 nm in acetonitrile and also exhibited a phenomenal increase in the fluorescence quantum yield from 0.07 to 1.0. The latitude of making a vast number of *o*- hydroxphenyl-pyrazoles **1-14** varying in the position (*e.g.*, **2** and **5**), number (*e.g.*, **2** and **3**), and electron donating (*e.g.*, **2-4** and **9**) or withdrawing (*e.g.*, **13** and **14**) ability of

2-(1-Phenyl-5-Phenyl or 5-Substituted Phenyl-1*H*-Pyrazol-3-yl)Phenols

Compd. No.	R_5	Molecular Formula	% Yield	M.P., °C [a]
1	4-$CH_3C_6H_4$	$C_{22}H_{18}N_2O$	60	133-36[127-29] [b]
2	3,4-$(CH_3O)_2C_6H_3$	$C_{23}H_{20}N_2O_3$	80	161-63 [b, f]
3	3,4,5-$(CH_3O)_3C_6H_2$	$C_{24}H_{22}N_2O_4$	72	174-75 [b]
4	4-HOC_6H_4	$C_{21}H_{16}N_2O_2$	63	221-23 [c]
5	3,5-$(CH_3O)_2C_6H_3$	$C_{23}H_{20}N_2O_3$	58	159-60 [b]
6	4-$(CH_3)_3CC_6H_4$	$C_{25}H_{24}N_2O$	59	93-94 [c]
7	4-ClC_6H_4	$C_{21}H_{15}ClN_2O$	73	130-31 [c, g]
8	3-HOC_6H_4	$C_{21}H_{16}N_2O_2$	72	175-77 [d]
9	4-$(CH_3)_2NC_6H_4$	$C_{23}H_{21}N_3O$	42	137-39 [e]
10	3,5-$(CH_3)_2C_6H_3$	$C_{23}H_{20}N_2O$	48	80-82 [d]
11	C_6H_5	$C_{21}H_{16}N_2O$	63	115-16 [c, h]
12	C_5H_4N, 3-pyridinyl	$C_{20}H_{15}N_3O$	51	152-53 [c]
13	C_5H_4N, 4-pyridinyl	$C_{20}H_{15}N_3O$	55	157-59 [c]
14	$C_{15}H_{10}N$, 2-phenyl-quinolin-4-yl	$C_{30}H_{21}N_3O$	71	180-83 [c]

[a] Melting points were obtained with a Mel-Temp II melting point apparatus in open capillary tubes and are uncorrected. [b] recryst. from methanol/benzene. [c] recryst. from methanol. [c] recryst. from 95% ethanol or ethanol/water. [d] recryst. from methanol/water. [e] recryst. from ethanol/benzene. [f] see ref. 2n. [g] Lit. mp 131-33° and 138.5-39° ; see ref. 2 k, m. [h] Lit. mp, 114-15° and 117-19° ; see ref. 2 k, m..

substituents has created an opportunity to thoroughly investigate proton transfer and charge transfer for this series of compounds.

General Procedure for Preparation of *ortho*-Hydroxyphenyl Pyrazoles

In a typical reaction sequence, LDA (0.042 mol; 0.0525 mol for **4, 8,** and **9**) was prepared by the addition of 27 mL (or 31 mL for **4, 8,** and **9**) of 1.6 M *n*-butyllithium (0.042 mol or 0.0525 mol) to a three-neck round-bottomed flask (*ca.*, 500 mL) equipped with a nitrogen inlet tube, a side-arm addition funnel (*ca.*, 125 mL) , and a stir bar. The flask was cooled in an ice bath and 4.29 g (0.042 mol) [or 5.36 g (0.0525 mol) for **4, 8** and **9**] of diisopropylamine, dissolved in 35-45 mL of dry tetrahydrofuran (THF) (sodium/ benzophenone-ketyl) (0°, N_2), was added from the funnel at a fast dropwise rate over a period of 5 minutes. The solution was stirred for an additional 15-20 minutes, and then treated *via* the addition funnel with 2.26 g. (0.01 mol) of 2'-hydroxyacetophenone phenylhydrazone dissolved in 35-45 mL of THF. After 2 hours of polylithiation, 0.0105 mol of ester dissolved in 35-45 mL of THF, was added to the trilithiated intermediate, and the solution was stirred for 1-1.5 hours (0°, N_2). Finally, 100 mL of 3*N* hydrochloric acid was added, and the two-phase mixture was stirred and heated under reflux for approximately one hour. At the end of this period, the mixture was poured into a large flask containing ice (*ca.*, 100 g), followed by addition of 100 mL of solvent-grade ether. The mixture was then neutralized with solid sodium bicarbonate and the layers separated. The aqueous layer was extracted with ether or THF (2x75 mL), and the organic fractions were combined,

evaporated, and recrystallized. Recrystallization solvents are recorded in the footnote of the Table.

Preparation of 2'-Hydroxyacetophenone Phenylhydrazone[8]

The entry compound was prepared by heating under reflux a solution of 0.05 mol of ketone, 0.0525 mol of phenylhydrazine, 100-125 mL of ethanol and approximately 1 mL of glacial acetic acid. After 1.5 hrs, the solution was concentrated to 50-60 mL, cooled and crystallization occurred upon addition of a few ice crystals. The wet and finely divided solid was filtered through a Buchner funnel and rapidly recrystallized with benzene/hexanes to give dry crystalline material that was ready for immediate use.

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9. Combustion analyses were performed by Quantitative Technologies, Inc., P.O. Box 470, Salem Industrial Park, Bldg. 5, Whitehouse, NJ 08888. Molecular formulas are in the Table: Compd. No., *Anal.* Calcd./ Found [% C, H, and/or N]: **1.** C, 80.96/80.69; H, 5.56/5.70; N, 8.58/8.22. **2.** C, 74.18/74.06; H, 5.41/5.37; N, 7.52/7.40. **3.** C, 71.62/71.59; H, 5.51/5.54 ; N, 6.96/ 6.87. **4.** C, 76.81/ 76.59; H, 4.91/5.01; N, 8.53/8.41. **5.** C, 74.18/74.31; H, 5.41/5.46; N, 7.52/ 7.49. **6.** C, 81.49/ 81.56; H, 6.56/6.57; N, 7.60/7.56. **7.** N, 8.08/ 7.94. **8.** C, 76.81/76.58; H, 4.91/5.05; N, 8.53/8.32. **9.** C, 77.72/77.63; H, 5.95/6.05; N, 11.82/11.68. **10.** C, 81.15/81.52; H, 5.92/6.14; N, 8.23/8.12. **11.** N, 8.97/ 8.90. **12.** C, 76.66/76.39; H, 4.82/4.80; N, 13.41/13.23. **13.** C, 76.66/76.34; H, 4.82/4.76; N, 13.41/ 13.27. **14.** C, 81.98/81.93; H, 4.82/4.65; N, 9.56/ 9.38.

10. Fourier Transform infrared spectra were obtained on a Nicolet Impact 410 FT-IR. Proton magnetic resonance spectra were obtained with a Varian Associates EM-360L nuclear magnetic resonance spectrometer, and chemical shifts are recorded in δ ppm downfield from an internal tetramethylsilane standard. From Table: Compd. No., FT-IR data (paraffin oil - all compounds), ^{1}H NMR data (varied solvents - indicated). **1.** FT-IR, 3195 (OH) and 1584 (ArH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ ppm 2.40 (s, 3H, $ArCH_3$), 6.80 (s, IH, C_4-H) 7.67-8.67 (m, 13H, C_4-H and ArH) and 11.00 (s, 1H, ArOH, exch with D_2O). **2.** FT-IR, 3167 (OH) and 1584 (ArH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ ppm 3.67 and 3.90 (s, 3H and 3H, $ArOCH_3$), 6.73-7.83 (m, 13H, C_4-H and ArH) and 11.00 (s, 1H, ArOH exch. with D_2O). **3.** FT-IR, 3167 (OH) and 1584 (ArH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ ppm 3.70 (s, 6H, $ArOCH_3$), 3.93 (s, 3H, $ArOCH_3$), 6.53 (s, 2H, ArH), 6.93 (s, 1H, C_4-H) and 7.00 -7.80 (m, 9H, ArH), and 10.93 (s, 1H, ArOH, exch. with D_2O). **4.**

FT-IR, 3133-3381 (OH) cm^{-1}; ^1H NMR (DMSO-d_6) δ ppm 6.80-8.13 (m, 14H, C_4-H and ArH) and 9.73-10.80 (broad, 2H, ArOH, exch. with D_2O). **5.** FT-IR, 3181 (OH) and 1591 (ArH) cm^{-1}; ^1H NMR ($CDCl_3$) δ ppm, 3.70 (s, 6H, $ArOCH_3$), 6.47 and 6.80-7.87 (s and m, 13H, C_4-H and ArH) and 10.93 (s, 1H, ArOH exch. with D_2O). **6.** FT-IR, 3181 (OH) and 1591 (ArH) cm^{-1}; ^1H NMR ($CDCl_3$) δ ppm, 1.33 (s, 9H, $ArC(CH_3)_3$), 6.87-7.80 (m, 14H, C_4-H and ArH) and 11.00 (s, 1H, ArOH exch. with D_2O). **7.** FT-IR, 3181 (OH) and 1618, 1605 and 1598 (several ArH) cm^{-1}; ^1H NMR ($CDCl_3$) δ ppm 6.93 (s, 1H, C_4-H), 7.67-8.10 (m, 13H. ArH) and 10.90 (s, 1H, ArOH, exch. with D_2O). **8.** FT-IR, 3381, 3167-3188 (OH) and 1584 (ArH) cm^{-1}; ^1H NMR (DMSO-d_6 and $CDCl_3$) δ ppm, 6.87 (s, 1H, C_4-H), 7.00-7.93 (m, 13H, ArH), 9.53 (s-broad, 1H, ArOH exch. with D_2O) and 10.80 (s-sharp, 1H, ArOH exch. with th D_2O). **9.** FT-IR, 3174 (OH) and 1611 (ArH) cm^{-1}; ^1H NMR ($CDCl_3$) δ ppm, 2.98 (s, 6H, $N(CH_3)_2$), 6.77-7.90 (m, 14H, C_4-H and ArH) and 11.10 (s, 1H, ArOH exch. with D_2O). **10.** FT-IR, 3181 (OH) and 1605 (ArH) cm^{-1}; ^1H NMR ($CDCl_3$) δ ppm, 2.27 (s, 6H, $ArCH_3$), 6.90-7.83 (m, 13H, C_4-H and ArH), and 11.07 (s, 1H, ArOH exch. with D_2O). **11.** FT-IR, 3181 (OH) 1618 and 1584 (ArH) cm^{-1}; ^1H NMR ($CDCl_3$) δ ppm 6.90 (s, 1H, C_4-H) 7.07-7.80 (m, 14H, ArH) and 11.00 (s, 1H, ArOH exch. with D_2O). **12.** FT-IR, 3153-3195 (OH), 1611, 1597, and 1591 (several ArH) cm^{-1}; ^1H NMR ($CDCl_3$) δ ppm 7.00 (s, 1H, C_4H), 7.07- 8.00 (m. 12H, ArH), 8.73 (s, 1H, ArH), and 10.83 (s, 1H, ArOH exch. with D_2O). **13.** FT-IR, 3160-3188 (OH), 1611. 1598, 1591 (several ArH) cm^{-1}; ^1H NMR ($CDCl_3$) δ ppm 6.80-8.26 and 8.60 (m, 14H, C_4-H and ArH), and 11.00 (s, 1H, ArOH exch. with D_2O). **14.** FT-IR, 3174-3188 (OH) and 1618, 1584 with shoulder (several ArH) cm^{-1}; ^1H NMR ($CDCl_3$) δ ppm 7.10 (s, 1H, C_4-H), 7.20-8.60 (m, 19H, ArH), and 10.97 (s, 1H, ArOH exch. with D_2O).

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14. *ortho*-Hydroxyphenylpyrazoles **2-4**, and **9** have electron donating groups such as methoxy, hydroxy, or dimethylamino in the 4-position of the pendant 5-substituent, and they are capable of increasing the electron density of the pyrazole ring. By contrast, compounds **13** and **14** have electron withdrawing heterocyclic nitrogen atoms in the 4-position of the pendant-5 substituent.

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