B. Vallverdú for the pK_a measurement of imidazole-2-diazonium cation (starting from 2-aminoimidazole hydrochloride instead of its sulfate), which corroborated the formerly reported value.

Registry No. **1**, 59214-43-6; **1a**, 112298-51-8; **1b**, 112298-48-3; **1e**, 112298-52-9; **2**, 112298-50-7; **2a**, 112298-53-0; **2c**, 112298-56-3; **2e**, 112298-54-1; **3**, 57351-74-3; **3a**, 59105-03-2; **3b**, 112298-57-4; **3c**, 112298-58-5; **3e**, 112298-55-2; **4**, 2033-24-1; **5**, 112298-42-7; **6**, 112298-49-4; **7**, 112298-47-2; isopropylidene 3(5)-pyrazolylhydrazonomalonate, 112298-43-8; isopropylidene 1,2,4-triazol-3-ylhydrazonomalonate, 112298-44-9; isopropylidene 1-methylimidazol-2-ylhydrazonomalonate, 112298-45-0; isopropylidene 1-methylpyrazol-3-ylhydrazonomalonate, 112298-46-1; 2-aminoimidazolium sulfate, 36946-29-9; 3(5)-aminopyrazole, 1820-80-0; 2-amino-1-methylimidazole hydrochloride, 1450-94-8; 3-amino-1-methylpyrazole, 1904-31-0.

Supplementary Material Available: ^{1}H NMR, ^{13}C NMR, and ^{15}N NMR spectra of **1a** and **1e** labeled partially at N-2 (1 page). Ordering information is given on any current masthead page.

Quinone Methide *p*-Hydroxybenzylation of 1,3-Diketones

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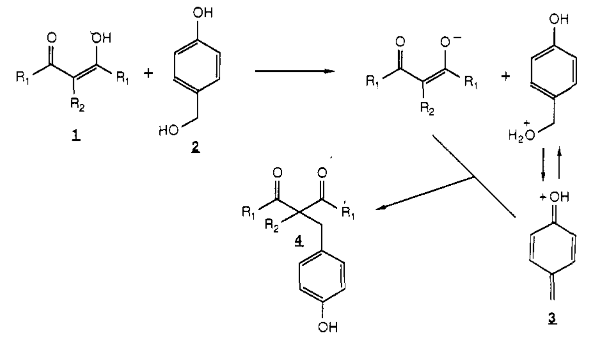
The Michael addition of 1,3-diketones to unsaturated compounds is well documented and has been extensively utilized in the preparation of natural products.[1] Quinone methides are conjugated homologues of vinyl ketones but are more reactive due to the additional driving force of aromatization after conjugate addition. The application of these highly conjugated intermediates to the formation of carbon–carbon bonds is limited by the stability of the quinone methide and the method for its generation.[2] Recently, the synthesis of delesserine has been achieved by the addition of 2-*O*-methylascorbic acid to the protonated methylene quinone derived from *p*-hydroxybenzyl alcohol.[3] Herein, we describe the application of this methodology to the C-2 benzylation of 1,3-diketones.

Treatment of cyclic and acyclic enolizable 1,3-diketones, **1**, with *p*-hydroxybenzyl alcohol, **2**, in water lead to carbon alkylation products, **3**.[4] These vinylogous acids are sufficiently acidic to facilitate generation of protonated quinone methides.[5] Consequently, the reaction proceeds by protonation of the benzylic alcohol, elimination of water to **4**, and finally addition of the conjugate base of **1** to yield **3**.[6] When ethyl acetoacetate or ethyl 2-oxocyclopentanecarboxylate was exposed to an aqueous solution of **2**, no addition product was observed.



R_1	R_2	Yield (%)
CH_3	H	78
$-CH_2-CH_2-$	H	18
$-CH_2-CH_2-CH_2-$	H	22
$-CH_2-C(CH_3)_2-CH_2-$	H	18
$-CH_2-CH_2-$	CH_3	97
$-CH_2-CH_2-CH_2-$	CH_3	73

Experimental Section

Typical Procedure. Preparation of 2-(4-Hydroxybenzyl)-2-methyl-1,3-cyclopentanedione. To 2-methyl-1,3-cyclopentanedione (111 mg, 1.0 mmol) in water (3 mL) was added *p*-hydroxybenzyl alcohol (62 mg, 0.5 mmol), and the solution was stirred at 80 °C for 12 h. The reaction mixture was evaporated and the residue chromatographed (1:1 EtOAc/hexanes) to give 105 mg (97%) of 2-(4-hydroxybenzyl)-2-methyl-1,3-cyclopentanedione: mp 146–147 °C; ^{1}H NMR ($CDCl_3$) δ 1.18 (s, 3 H), 1.8–2.8 (m, 4 H), 2.88 (s, 2 H), 5.8–6.2 (br s, 1 H), 6.6 (d, J = 14.5 Hz, 2 H), 6.85 (d, J = 14.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.7, 35.9, 42.5, 58.7, 115.5, 127.4, 130.8, 155.2, 218.6; IR ($CDCl_3$) ν 1730, 1619, 1522 cm^{-1}; MS (70 eV), *m/e* (relative intensity) 218 (9.7), 107 (100), 77 (7.4). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.40; H, 6.5.

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(6) Treatment of an aqueous solution of 2-methyl-1,3-cyclopentanedione with benzyl alcohol gave no addition product. Thus, the *p*-hydroxy group is necessary for reaction. See also: ref 3.

Thioanhydrides. 2. Synthesis of Phthalic Thiothionoanhydrides†

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Phthalic thioanhydride (**1**) has been a well-known compound since 1911,[1] but its unstable isomer, phthalic thionoanhydride (**2**), is the subject of only a single report.[2] The thione **2** readily isomerizes to **1**. Neither of the phthalic dithioanhydrides **4** or **5** has been reported previously, although both 1,8-naphthalic dithioanhydride and 1,8-naphthalic thiothionoanhydride have been made in these laboratories.[3] Phthalic thiothionoanhydride (**5**) has now been synthesized by the reaction of *tert*-butyl mer-

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† For Part 1, see ref 3.

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