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### SYNTHESIS OF PYRUVATE ESTERS BY THE REACTION OF SODIUM PYRUVATE WITH ORGANIC HALIDES IN DMSO

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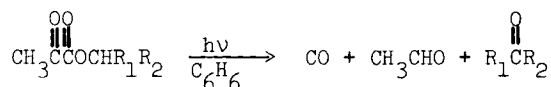
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SYNTHESIS OF PYRUVATE ESTERS BY THE REACTION OF  
SODIUM PYRUVATE WITH ORGANIC HALIDES IN DMSO

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The photolysis of pyruvate esters in benzene to give aldehydes and ketones,<sup>1</sup> has recently been shown by Binkley<sup>2</sup> to be a synthetically useful



one. The pyruvate esters used in Binkley's studies<sup>2</sup> were prepared by reaction of the alcohol with the now readily available pyruvyl chloride.<sup>3</sup> A convenient alternative procedure for preparing pyruvic acid esters, unlike earlier methods, utilizes an organic halide as the starting material rather than the corresponding alcohol. Thus, reaction of sodium pyruvate with *n*-octyl iodide or phenacyl bromide in dimethyl sulfoxide<sup>4</sup> for 3.5 hrs at 50° afforded *n*-octyl pyruvate and  $\alpha$ -pyruvyloxyacetophenone in 95% and 85% yield respectively.

EXPERIMENTAL

Sodium pyruvate was obtained from Aldrich Co. Dimethyl sulfoxide (DMSO) was freshly distilled from CaH<sub>2</sub> before use. NMR spectra were recorded in CDCl<sub>3</sub> on a Varian XL-100 spectrometer using the CHCl<sub>3</sub> absorption at  $\delta$  7.28 as a standard. Only diagnostic absorptions are reported. Elemental analysis was done by Dr. R. Wielesek at the University of Oregon. Low resolution mass spectra were recorded on a modified HP 5930-A spectrometer. Peak intensities are given in parentheses as a percentage of the base peak.

*n*-Octyl pyruvate.- 1-Iodoctane (500 mg, 2.08 mM) was added to a suspension of sodium pyruvate (241 mg, 2.19 mM) in 6 ml of DMSO. The mixture was heated for 3.5 hrs at 50°, resulting in a yellow solution. Addition of 10 ml of

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benzene caused sodium iodide to precipitate. The filtrate was diluted with 10 ml of benzene and washed with water to remove the DMSO. The benzene layer was dried and concentrated, affording 395 mg (95%) of *n*-octyl pyruvate (>95% pure by NMR). Evaporative distillation of a small sample (60°/1 mm) gave a pure specimen as a colorless oil.

NMR  $\delta$  4.19 (t, 2H), 2.38 (s, 3H); MS  $m/e$  200 (7), 157 (20), 113 (76), 87 (63), 73 (100), 43 (96).

$\alpha$ -Pyruvyloxyacetophenone.— Phenacyl bromide (200 mg, 1.00 mM) was added to a suspension of sodium pyruvate (116 mg, 1.05 mM) in 2 ml of DMSO and the mixture was stirred for 30 min. at 25°. The resulting yellow solution was diluted with 6 ml of benzene to precipitate sodium bromide. Filtration followed by evaporation of the filtrate at 0.5 mm gave a yellow solid. Crystallization from CCl<sub>4</sub> gave 175 mg (85%) of product as white stars, mp. 74.5–75.5°.

NMR  $\delta$  5.38 (s, 2H), 2.39 (s, 3H).

Anal. Calcd for C<sub>11</sub>H<sub>10</sub>O<sub>4</sub>: C, 64.08; H, 4.89. Found: C, 63.93; H, 4.81.

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2. R. W. Binkley, J. Org. Chem., 41, 3030 (1976); 42, 1216 (1977).
3. H. C. J. Ottenheijm and J. H. M. de Man, Synthesis, 163 (1975).
4. The known oxidation [N. Kornblum et al., J. Am. Chem. Soc., 79, 6562 (1957)] of phenacyl bromide by DMSO was not observed under these conditions. Such oxidations generally require longer reaction times.