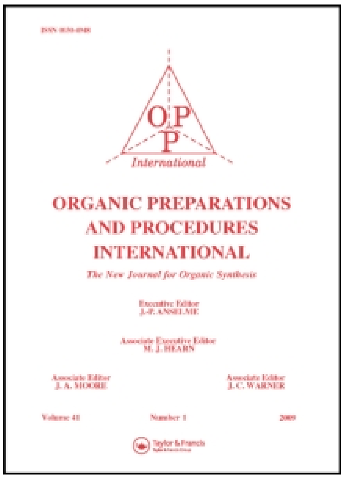


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

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

Patrick J. Boyle[a]; John F. W. Keana[a]
[a] Department of Chemistry, University of Oregon, Eugene, Oregon

To cite this Article Boyle, Patrick J. and Keana, John F. W.(1978) 'SYNTHESIS OF PYRUVATE ESTERS BY THE REACTION OF SODIUM PYRUVATE WITH ORGANIC HALIDES IN DMSO', Organic Preparations and Procedures International, 10: 2, 101 — 102

To link to this Article: DOI: 10.1080/00304947809355019

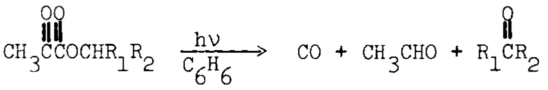
URL: http://dx.doi.org/10.1080/00304947809355019

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

Submitted by Patrick J. Boyle and John F. W. Keana*
(11/21/77)

Department of Chemistry
University of Oregon
Eugene, Oregon 97403

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



$$CH_3\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OCHR_1R_2 \xrightarrow[C_6H_6]{h\nu} CO + CH_3CHO + R_1\overset{O}{\overset{\|}{C}}R_2$$

one. The pyruvate esters used in Binkley's studies[2] were prepared by reaction of the alcohol with the now readily available pyruvyl chloride.[3] 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[4] for 3.5 hrs at 50° afforded n-octyl pyruvate and α-pyruvyloxyacetophenone in 95% and 85% yield respectively.

EXPERIMENTAL

Sodium pyruvate was obtained from Aldrich Co. Dimethyl sulfoxide (DMSO) was freshly distilled from CaH_2 before use. NMR spectra were recorded in $CDCl_3$ on a Varian XL-100 spectrometer using the $CHCl_3$ absorption at δ 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-Iodooctane (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 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 δ 4.19 (t, 2H), 2.38 (s, 3H); MS m/e 200 (7), 157 (20), 113 (76), 87 (63), 73 (100), 43 (96).

α-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_4 gave 175 mg (85%) of product as white stars, mp. 74.5-75.5°.

NMR δ 5.38 (s, 2H), 2.39 (s, 3H).

Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.08; H, 4.89. Found: C, 63.93; H, 4.81.

ACKNOWLEDGEMENT.- We thank the National Science Foundation (BNS 77-16952) for generous support of this research.

REFERENCES

1. See, inter alia, P. A. Leermakers, P. C. Warren and G. F. Vesley, J. Am. Chem. Soc., 86, 1968 (1964).
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.