Tetrahedron Letters No.7, pp. 741-742, 1966. Pergamon Press Ltd.
Printed in Great Britain.

C-METHYLATION OF β-DICARBONYL COMPOUNDS

R. Chong and P. S. Clezy
Department of Organic Chemistry,
University of New South Wales,
Kensington, N.S.W., Australia

(Received 20 December 1965)

Recent publications (1,2) referring to the O-alkylation of ethyl acetoacetate prompt us to report our own findings on this subject. We have successfully C-methylated acetylacetone and ethyl acetoacetate using methyl iodide in acetone in the presence of anhydrous potassium carbonate obtaining yields of the order of 70%. However attempts to replace methyl iodide with dimethyl sulphate have resulted in much lower yields of the C-methyl compound with the O-methyl isomer being the major product. Such a change in alkylation pattern is in accord with the findings of Brieger and Pelletier (2) who have reported that the type of alkylation achieved is profoundly influenced by the particular leaving group involved.

An acetone solution containing equimolar amounts of ethyl acetoacetate and dimethyl sulphate was heated under reflux in the presence of anhydrous potassium carbonate for 24 hr. Inorganic solids were filtered off and the filtrate and acetone washings were concentrated in vacuo and ether added. The C-methyl product (30%) was removed from the ethereal solution by extraction with ice-cold aqueous sodium

hydroxide solution. Removal of the ether then gave ethyl 3-methoxy-crotonate (36%) b.p. 67.5 - 70.5°/8.5 mm, n_D^{20} 1.4550 in good agreement with literature values (3). τ ($CDCl_3$) : 8.73 (3H, triplet, $\underline{CH_3}CH_2O-$), 7.71 (3H, $CH_3-\dot{C} = \dot{C}-$), 6.38 (3H, OCH_3), 5.88 (2H, quartet, $CH_3\underline{CH_2}O-$), 5.00 (1H, $-CH = \dot{C}-$).

In similar fashion 4-methoxypent-3-en-2-one, b.p. 54.5 - 56.5°/8 mm, n_D^{23} 1.4680 (4) was obtained in 31% yield by the methylation of acetylacetone. τ ($CDCl_3$) : 7.84, 7.72 (6H, $\underline{CH_3}-\dot{C} = \dot{C}-CO\underline{CH_3}$), 6.35 (3H, OCH_3), 4.51 (1H, $-CH = \dot{C}-$). This is accompanied by 26% of the C-methyl product.

All yields refer to isolated products.

References

1. S. T. Yoffe, K. V. Vatsuro, E. E. Kugutcheva, and M. I. Kabachnik, Tetrahedron Letters, 10, 593 (1965).
2. G. Brieger and W. M. Pelletier, Tetrahedron Letters, 40, 3555 (1965).
3. E. E. Smissman and A. N. Volding, J. Org. Chem. 29, 3164 (1964).
4. I. Heilbron, A. H. Cook, H. M. Bunburg, and D. H. Hey, "Dictionary of Organic Compounds", p. 15 (4th Ed. Eyre and Spottiswoode, London 1965).