A New Synthesis of 1,5-Dicarbonyl Compounds under Neutral Conditions

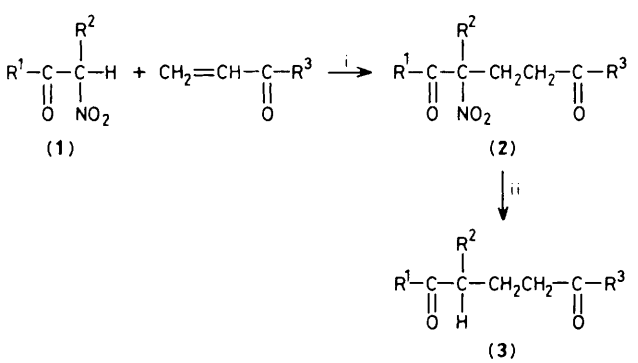
Noboru Ono,* Hideyoshi Miyake, and Aritsune Kaji*

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

Michael addition of α-nitroketones to methyl vinyl ketone or acrylaldehyde followed by denitration with Bu_3SnH affords 1,5-dicarbonyl compounds in good yields.

1,5-Dicarbonyl compounds (**3**) are an important class of compounds especially as intermediates for the preparation of cyclohexenones.[1] The available routes to (**3**) include 1,4-addition of enolates or enolate equivalents to α,β-unsaturated carbonyl compounds,[2] or alkylation of ketones with a 3-oxoalkyl halide equivalent.[3] Most of these routes are lengthy, require multistep preparation of a special reagent, or give low overall yields. These difficulties are serious in the preparation of δ-oxo-aldehydes owing to the instability of acrylaldehyde under basic conditions. We have found a short route using readily available starting materials which gives high yields of 1,5-dicarbonyl compounds including δ-oxo-aldehydes, as outlined in Scheme 1.

The requisite α-nitroketones (**1**) were prepared by acylation of nitroalkanes[4]† or by oxidation of β-nitroalcohols.[5] Michael addition of (**1**) to methyl vinyl ketone or acrylaldehyde proceeded in the presence of a catalytic amount (0.1 equiv.) of triphenylphosphine to give the adduct (**2**) in good yields.[6] Denitration of (**2**) was carried out by heating a stirred mixture of (**2**), Bu_3SnH (1.3 equiv.), and AIBN (0.3 equiv.) in benzene at 80 °C for 2 h to give the desired 1,5-dicarbonyl compounds



Scheme 1. Reagents: i, Ph_3P, THF, room temperature; ii, Bu_3SnH, AIBN, benzene, 80 °C. THF = tetrahydrofuran, AIBN = azoisobutyronitrile.

† Reaction of the potassium salt of nitroalkanes with *N*-acylimidazoles in dimethyl sulphoxide at room temperature gave (**1**) in 70—90% yields.

Table 1. Michael addition of α-nitroketones (**1**) to methyl vinyl ketone or acrylaldehyde, and preparation of 1,5-dicarbonyl compounds (**3**).

R^1	R^2	R^3	Time/h (**1**)→(**2**)	Yield/% (**2**)	Yield/% (**3**)
Ph	H	Me	24	81	78
n-C_7H_{15}	Me	Me	24	91	80
n-C_7H_{15}	H	Me	24	85	90
Pr^i	H	Me	24	77	82
$-[CH_2]_4-$		Me	24	94	90
Ph	Me	H	1	84	76
Pr^n	Et	H	1	87	71
n-C_7H_{15}	Me	H	1	87	87
n-C_4H_9	Et	H	1	90	76
$-[CH_2]_4-$		H	1	92	77

(**3**), where ketone and aldehyde functions were not affected under these conditions.[7] The results are summarized in Table 1. Thus, the present method consists of genuinely simple procedures and requires neither acidic nor basic conditions, so it affords some advantages over the conventional methods.[1]

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

Received, 3rd May 1983; Com. 558

References

1 È. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. React.*, 1959, **10**, 179; M. E. Jung, *Tetrahedron*, 1976, **32**, 3.
2 G. Stork and B. Ganem, *J. Am. Chem. Soc.*, 1973, **95**, 6152; J. Boyer, R. J. P. Corriu, R. Perz, and C. Reye, *J. Chem. Soc., Chem. Commun.*, 1981, 122; A. Hosomi, H. Kobayashi, and H. Sakurai, *Tetrahedron Lett.*, 1980, 955; S. Hara, K. Kishimura, and A. Suzuki, *Chem. Lett.*, 1980, 221; also ref. 1.
3 G. Stork and M. E. Jung, *J. Am. Chem. Soc.*, 1974, **96**, 3682 and references therein.
4 R. L. Crumbie, J. S. Nimitz, and H. S. Mosher, *J. Org. Chem.*, 1982, **47**, 4040 and references therein.
5 G. Rosini and R. Ballini, *Synthesis*, 1983, 137 and references therein.
6 K. Kostova, A. L. Riatsch, Y. Nakashita, and M. Hesse, *Helv. Chim. Acta*, 1982, **65**, 249; R. C. Cookson and P. S. Ray, *Tetrahedron Lett.*, 1982, 3521.
7 We have found that Bu_3SnH replaces an aliphatic nitro group by hydrogen without affecting oxo, cyano, sulphonyl, or sulphinyl groups; this is the basis of a new synthetic method; N. Ono, H. Miyake, R. Tamura, and A. Kaji, *Tetrahedron Lett.*, 1981, 1705; N. Ono, H. Miyake, R. Tamura, I. Hamamoto, and A. Kaji, *Chem. Lett.*, 1981, 1139; N. Ono, H. Miyake, and A. Kaji, *J. Chem. Soc., Chem. Commun.*, 1982, 33; N. Ono, I, Hamamoto, H. Miyake, and A. Kaji, *Chem. Lett.*, 1982, 1079; N. Ono, H. Miyake, A. Kamimura, N. Tsukui, and A. Kaji, *Tetrahedron Lett.*, 1982, 2957.