Methyl α-Bromocrotonate as a Biannelating Agent; Reactions with Cyclohex-2-enones

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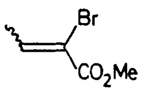
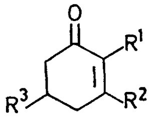
Summary With cyclohex-2-enones, methyl α-bromocrotonate undergoes double Michael additions and subsequent substitution yielding tricyclo[3.2.1.$0^{2,7}$]octan-6-ones in one-step.

Recent work by Cory and Chan[1] concerning the bicycloannulation reaction of vinyltriphenylphosphonium bromide with cyclohex-2-enones leading to tricyclo[3.2.1.$0^{2,7}$]octan-6-ones prompts us to report similar results of our independent work using methyl α-bromocrotonate (**1**) as an agent.[2,3]

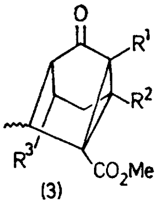
When a mixture of compound (**1**)† and the enolate of cyclohex-2-enone (**2a**), prepared by treatment of (**2a**) with 1 equiv. of lithium di-isopropylamide and then 1 equiv. of hexamethylphosphoric triamide in tetrahydrofuran, was stirred for 3 h at −19 °C to room temperature, a mixture of the stereoisomers of 1-methoxycarbonyl-8-methyltricyclo[3.2.1.$0^{2,7}$]octan-6-one (**3a**) was obtained in 30% yield. Similarly, the reaction of (**1**) with 3-methylcyclohex-2-enone (**2b**) (−12 to −2 °C for 1·5 h) gave (**3b**) (55% yield), (−)-carvone (**2c**) (−15 °C to room temperature for 1·5 h) gave (**3c**) (25%), and isophorone (**2d**) (lithium cyclohexylisopropylamide, −20 °C—room temp. for 4 h) gave (**3d**) (20%).‡ The products (**3**) showed a negative halogen test, and the analytical and spectral (mass, i.r., ^1H and ^{13}C n.m.r.) data are in accord with the assigned structures.§



(1)



(2)



(3)

a; $R^1 = R^2 = R^3 = H$
b; $R^1 = R^3 = H$, $R^2 = Me$
c; $R^1 = Me$, $R^2 = H$, $R^3 = CH(Me){=}CH_2$
d; $R^1 = H$, $R^2 = Me$, $R^3 = Me_2$

The use of (**1**) rather than the vinylphosphonium salt[1] provides a better method for the one-step synthesis of tricyclo[3.2.1.$0^{2,7}$]octane derivatives as it gives higher product yields.

(*Received*, 18*th March* 1976; *Com.* 279.)

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† Compound (**1**), which is an inseparable 2 : 1 mixture of the geometric isomers, was prepared by bromination of methyl crotonate in CCl_4, followed by dehydrobromination with quinoline.

‡ At present, no attempt has been made to optimise the yields.

§ *E.g.*, for (**3c**): ν_{max} (CCl_4) 3050, 1725, 1645, and 930 cm^{-1}; δ(CCl_4) 1·13 (3H, s) 1·21 (3H, d, *J* 7·0 Hz), 1·63 (3H, s), 1·70—3·00 (6H, m), 3·67 (3H, s) and 4·68 (2H, m).

[1] R. M. Cory and D. M. T. Chan, *Tetrahedron Letters*, 1975, 4441.

[2] The use of α-halogeno-α,β-unsaturated esters for Michael addition has so far been very limited. S. Ruhemann and C. G. L. Wolf, *J. Chem. Soc.*, 1896, **69**, 1383; A. R. Daniewski, and M. Kocor, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1972, **20**, 395; S. Ducher, J. P. Sudre, and R. Vessiere, *Compt. rend.* (*C*), 1974, **278**, 537.

[3] H. Kosugi, H. Uda, and S. Yamagiwa, *J.C.S. Chem. Comm.*, 1975, 192; 1976, 71; H. Hagiwara, K. Nakayama, and H. Uda, *Bull. Chem. Soc. Japan*, 1975, **48**, 3769.