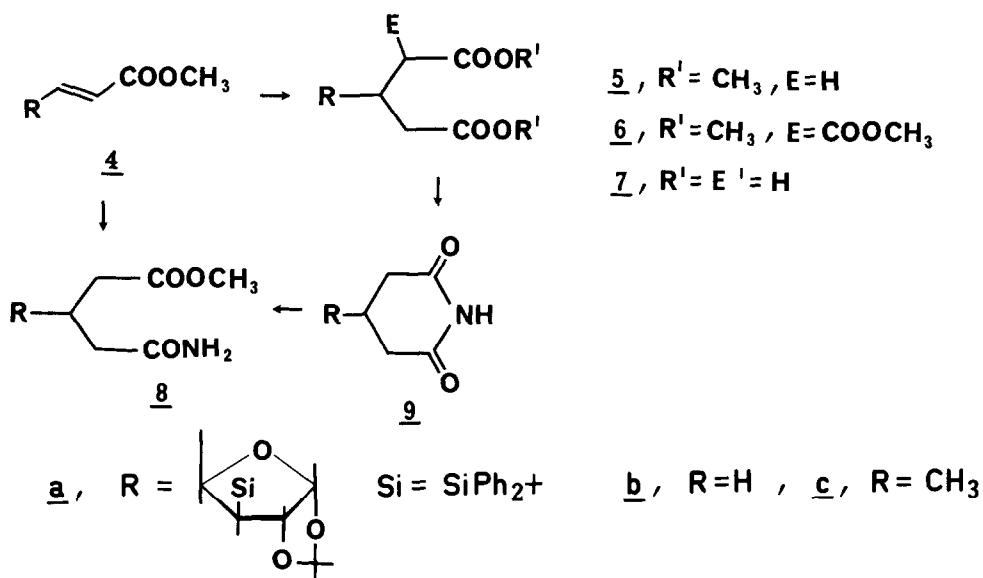


ful for the formation of 4-substituted glutarimides, we studied conditions for the addition of organic radicals generated in situ with tributyltin hydride, using α , β -unsaturated esters as substrates. Thus, when the α , β -unsaturated ester 4a and a twenty fold excess of methyl bromoacetate were heated at 80°C with catalytic amounts of azobisisobutyronitrile (AIBN) and slow addition of Bu_3SnH over a 15 h period (syringe pump), a 30% yield of glutarate 5a was obtained with recovery of over 60% starting material. Removal of the stannanes⁷ and recycling of the crude mixture employing the same conditions yielded 56% diester 5a and 8% starting material. It should be noted that with more rapid addition of Bu_3SnH , or dilution with solvent, the yield of 5a was vanishingly small.

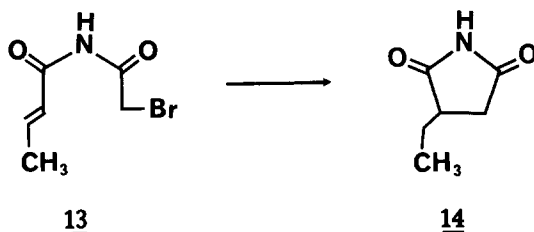
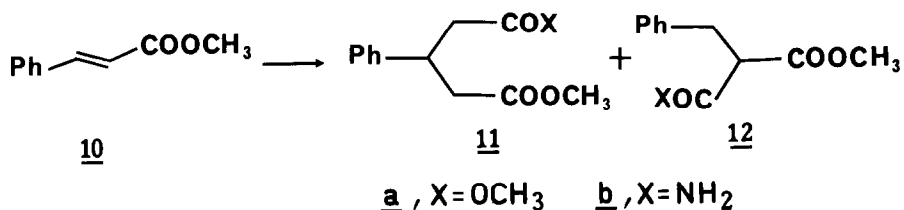


Addition of methyl bromoacetate to methyl acrylate 4b or methyl crotonate 4c, using the conditions described, gave 85 and 77% yield of glutarates 5b and 5c without recycling.

More interestingly, when the above reaction was carried out with excess iodoacetamide as the radical precursor, and 4a as the unsaturated ester component, and the mixture irradiated with a tungsten lamp at 80-90°C, a mixture of amido ester 8a and glutarimide 9a was obtained after recycling once. Further heating of this mixture at 120°C gave 64% of glutarimide, with a 5% recovery of 4a. Higher yields could be obtained by cyclising the isolated amido ester 8a by known methods⁸. A similar glutarimide has been converted to the A/B rings of sesbanimide^{2b}. The iodoacetamide addition to methyl acrylate and crotonate 4b, 4c gave similarly mixtures of amido esters 8b, 8c and glutarimide 9b, 9c in 87 and 85% combined yield respectively. Further heating provided glutarimide 9b, 9c in good yields without recycling. In

all of these reactions, no product of 1, 2-addition was detected.

When methyl cinnamate 10 was submitted to the action of methyl bromoacetate or iodoacetamide, an approximately 1:1 mixture of 11a and 12a or 11b and 12b was obtained, together, in the case of iodoacetamide, with some product of cyclisation.



Finally, the imide 13, derived from crotonamide and bromoacetic anhydride gave, not unexpectedly⁹, exclusively 2-ethyl succinimide 14 derived from a 5-exo-trig addition of the radical to the olefinic bond, with some product of reduction.

General Procedure (9a):

To 100 mg of ester 4a and 830 mg of iodoacetamide (20 eq) in 0.5 ml of absolute ethanol at 80-90°C under N₂ and irradiation (tungsten lamp), was added 1.3 g of Bu₃SnH over a 15 h period (syringe pump). After removal of the stannanes⁷, the crude mixture was dissolved in CH₂Cl₂, washed with water, dried, and concentrated by rotary evaporation. Recycling of this crude mixture employing the same conditions, followed by heating to 120°C in toluene, gave after the usual work-up and chromatographic separation, a 64% yield of glutarimide 9a and 5% starting material.

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