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INTRAMOLECULAR ALLYLATION OF CARBONYL COMPOUNDS. A NEW METHOD FOR FIVE AND SIX MEMBERED RING FORMATION

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By using metallic tin and aluminum in an aqueous medium, ketone having allylic-halides functionality can be cyclized to form five and six membered rings.

Various C-C bond forming reactions, which were found to occur intermolecularly, have been applied to an intramolecular reaction to prepare five or six membered ring.[1)] Here, we also propose a new method to prepare five and six membered ring by employing the allylation reaction of carbonyl compounds found by us.

We have reported[2)] a new reaction of a carbonyl compound (ketone or aldehyde) and allyl (or allylic) halide, with an aid of metallic tin and aluminum to give homoallyl (or homoallylic) alcohol in satisfactory yield. This reaction seems to be unique in the following point that the reaction proceeds in an aqueous medium by mixing all reagents at once. The fact suggests that the reaction may be applicable to intramolecular reaction associated with the ketone having an allylic-halide functionality in the molecule.

Namely, a bicyclo[4.3.0]nonane derivative **2** was prepared as follows. To a solution of a cyclohexanone derivative **1**[3)] (200 mg, 0.63 mmol) in aqueous THF (2 ml, 90% v/v), metallic tin (150 mg, 1.26 mmol), aluminum (34 mg, 1.26 mmol), and a catalytic amount of acetic acid were added, and the mixture was stirred at room temperature. The stirring was continued for 24 h (disappearance of the ketone was checked by TLC). The reaction mixture was filtrated to remove an insoluble material, and the precipitate was washed with ethyl acetate. The combined filtrate was washed with brine, dried, and concentrated *in vacuo*. The residue was column chromatographed on silica gel to give **2** in 81% yield. The typical results are listed in Table 1.

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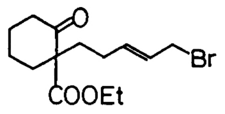
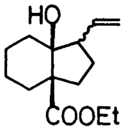
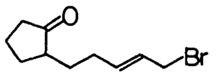
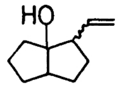
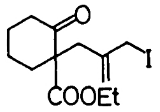
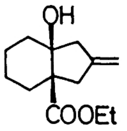
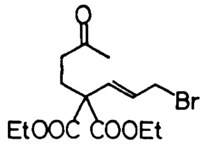
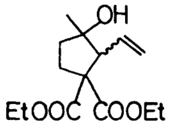
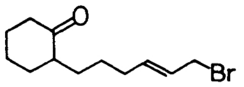
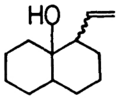
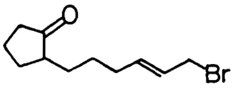
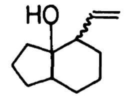
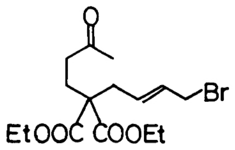
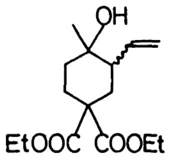
References

1) See reviews; M. Ono, Yuki Gosei Kagaku Kyokai Shi (J. Syn. Org. Chem. Jpn.), **39**, 872(1981); B. M. Trost, Chem. Soc. Rev., **11**, 141(1982).

2) J. Nokami, J. Otera, T. Sudo, and R. Okawara, Organometallics, **2**, 191(1983).

3) Allylic-bromide functionality(in **1**, **3**, **7**, **9**, **11**, and **13**) was formed by treatment of the corresponding 1-alkene with N-bromosuccinimide in refluxing CCl_4 in the presence of benzoyl peroxide (50-80% yield after column chromatography on silica gel). $+CH_2\text{-}CH\text{=}CH_2 \xrightarrow[\cdot Br]{} +CH\text{=}CH\text{-}CH_2Br$

Table 1.

Ketone[a]		Reaction method[b]	Reaction time/h	Product[c]		Yield/%
	1	A	24		2[d]	81
	3	B	14		4	71
	5[e]	A	6		6[f]	63
	7	C	7		8	45
	9	B	36		10	50
	11	B	24		12	61
	13	A	18		14	83

a) Ca. 1 mmol (E and Z mixture).

b) A: Described in the text. B: Aqueous dioxane (90% v/v) was used as a solvent. C: To a solution of 7 (1 mmol) in dry THF were added metallic tin (2 mmol), metallic aluminum (1.5 mmol), and catalytic amount of acetic acid. The mixture was stirred for 6 h at 40 °C, and then water (0.3 ml) was added to the reaction mixture and stirred for additional 1 h at r.t.

c) The stereochemical study is now in progress.

d) ^{1}H NMR δ 1.27(3H,t,J=7 Hz), 1.1-2.6(12H,m), 2.80(1H,q,J=9 Hz), 3.10(1H,br), 4.18(2H,q,J=7 Hz), 4.90-5.16(2H,m), 5.72-6.06(1H,m); ^{13}C NMR 14.1(q), 23.0(t), 23.2(t), 26.4(t), 32.1(t), 33.7(t), 34.5(t), 47.2(d), 56.2(s), 60.4(t), 81.6(s), 115.9(t), 137.9(d), 176.8(s); MS, m/e(relative intensity) 238(4), 220(4), 192(8), 170(100), 164(22), 147(41), 124(39), 123(44), 91(14), 81(22), 68(15), 67(15), 55(34), 41(30); IR (neat) 3560, 1710 cm^{-1}.

e) Prepared by treatment of 2-ethoxycarbonylcyclohexan-1-one (1 equiv.) with 3-chloro-2-chloromethyl-1-propene (2 equiv.), potassium carbonate (2 equiv.), and potassium iodide (4 equiv.) in acetone at 60 °C (ca. 60% yield).

f) ^{1}H NMR δ 1.27(3H,t,J=7 Hz), 1.2-3.1(12H,m), 3.8(1H,br), 4.18(2H,q,J=7 Hz), 4.96(2H,br); ^{13}C NMR 14.1(q), 22.3(t), 23.7(t), 33.2(t), 34.0(t), 41.8(t), 42.1(t), 55.1(s), 60.5(t), 80.2(s), 108.6(t), 146.1(s), 176.4(s); MS, m/e (relative intensity) 224(2), 206(22), 197(13), 168(42), 133(100), 132(46), 91(29), 79(25), 67(19), 55(25); IR (neat) 3540, 1715 cm^{-1}.

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