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SONOCHEMICALLY PREPARED ORGANOZINC REAGENTS[1].
CONJUGATE ADDITIONS TO α-β UNSATURATED ALDEHYDES

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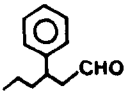
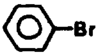
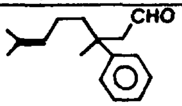
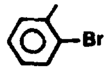
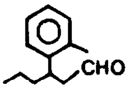
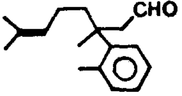
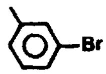
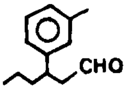
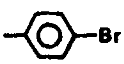
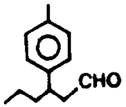
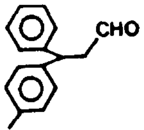
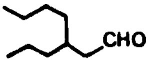
Summary : Organozinc reagents, prepared by sonication from organic halides, lithium and zinc bromide, add conjugatively to α-enals in the presence of nickel acetylacetonate. Satisfactory yields are obtained from arylbromides.

Conjugate additions to α,β-unsaturated ketones of various organometallic reagents are frequently used in synthesis[2]. In contrast, the same reactions with α,β-unsaturated aldehydes (α-enals) have been seldom investigated and appear to be less predictable. Alkylation, especially methylation and the addition of unsaturated groups (allyl, homoallyl, vinyl, alkynyl) can be obtained from several organocopper reagents[3]. In many instances, the 1-4 to 1-2 reactions ratio appears to be closely related to the substitution pattern of the substrate and the nature of the reagent[4].

We recently reported that ultrasonically prepared organozinc reagents (from an organic halide, lithium and zinc bromide) give rise to clean and selective 1-4 additions to α-enones[1] in the presence of nickel acetylacetonate [$Ni(acac)_2$]. We found of interest to investigate extensions of this process to α-enals. Thus, 2-hexenal (4.5 mmol) and $Ni(acac)_2$ (1.5 % of the stoichoimetry) in tetrahydrofurane (1 mL) solution is added dropwise over a few minutes period into sonochemically prepared diphenylzinc[5] (5 mmol) in 24 mL THF at -40°C followed by stirring with warming up to room temperature for 50 min. After quenching (sat. aq. NH_4Cl), extraction with diethylether and usual work up of the organic phase, the residue was purified by column chromatography, and a 67 % yield of the desired adduct was isolated. Generalization of the process was attempted and it was found that the addition of simple aromatic groups can be accomplished in a satisfactory manner. The reaction with citral, a β,β-disubstituted enal, requires 5 equiv. of the reagent for optimum yield. In other cases, only a modest excess is needed. In many cases, the selectivity is excellent, 1-4 addition being always largely favoured. The material balance consists in polymerized reaction products, due to the reactivity of the intermediate aldehyde enolate. Despite our efforts, addition of an alkyl group could not be accomplished in a satisfactory manner by this technique. As the conjugate arylation of α-enals has been but exceptionnaly described, the present method which uses free enals as starting material to yield free aldehydes should find synthetic applications.

Table

Halide	α-Enal	Reagent : Enal Ratio	Time min	Temp. °C	1-4 Adduct[a]		Isolated yield %
	2-Hexenal	1.1	50	-40		1	67 X=Cl 49 X=Br
	Citral	5	25	-40		2	69
	2-Hexenal	1.1	50	-40		3	57
	Citral	5	30	-40		4	49
	2-Hexenal	1.1	50	-40		5	73
	2-Hexenal	1.1	50	-40		6	61
	Cinnamaldehyde	1.1	60	-78		7	58[b]
	Hexenal	1.2	45	-40		8	15

[a] Adducts were obtained as air sensitive oils. Identification of the structures were made by the usual spectral methods (IR, ^{1}H and ^{13}C NMR, MS). Satisfactory microanalyses (CNRS, Lyon) were obtained for the cristalline derivatives : 2,4 DNP [1 : mp 87-8° (ethanol), 2 : mp 200-1° (methanol), 3 102-4° (ethanol), 4 mp 108-9° (methanol), 5 mp 90-1° (ethanol), 6 mp 111-2° (ethanol), 8 mp 69-70° (pentane)] and semicarbazone [7 mp 162-3° (ethanol)].

[b] In toluene : THF (5 : 1) solvent.

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Literature

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5. Luche, J.L. ; Pétrier, C. ; Lansard, J.P. ; Greene, A.E. J. Org. Chem. 1983 48 3837. For an improved sonication technique see ref 1.

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