The Reduction of Styrene Derivatives with the Commercial Sodium-Lead Alloy

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Recently a sodium-lead alloy was marketed as a drying agent of organic solvents.1) A sodium-lead alloy had previously been used in the reduction of multivalent metal ions, such as titanium(IV), vanadium(V), and chromium(III),2) but the alloy has not yet been used in organic reduction.

The present authors have tried the commercial sodium-lead alloy, "Drynap," as a reducing agent in place of sodium amalgam for the reduction of cinnamic acid in an aqueous sodium hydroxide solution according to the method of Erlenmeyer3); hydrocinnamic acid was thus obtained in a 87% yield. From this successful result, the Drynap reduction of several styrene derivatives was also attempted; a little of the information so obtained will be reported here.

The reduction was carried out in an ethanol solution by using the commercial sodium-lead alloy and acetic acid as in the method of amalgam reduction.4,5) Under these conditions, benzylideneacetone, dibenzylideneacetone, benzylideneacetophenone, piperonylideneacetone, and methyl-cinnamate were not reduced to the corresponding di- or tetra-hydrogenated compound, but were dimerized to 4, 5-diphenyl-2, 7-octanedione, 1, 5, 6, 10-tetraphenyl-1, 9-decadiene-3, 8-dione, 1, 3, 4, 6-tetraphenyl-1, 6-hexanedione, 4, 5-di-(3, 4-methylenedioxyphenyl)-2, 7-octanedione, and dimethyl 2, 4-diphenyladipate respectively. ω-Nitrostyrene was also reduced with Drynap and acetic acid in an ethanol solution to phenylacetaldoxime in about a 60% yield.

In the above reactions, the yield generally increased at higher temperatures, but decreased above 60°C because of the increase in polymerization. The yield also decreased in the reaction on a larger scale.

On the other hand, styrene, isosafrol, and cinnamyl alcohol were not affected by the sodium-lead alloy under the above conditions; the reaction then resulted in the recovery of the starting material. Cinnamaldehyde was also not reduced with sodium-lead alloy and acetic acid, and was easily polymerized, even at low temperatures.

On the basis of the above results, the authors recommend the use of sodium-lead alloy as the mild reducing agent; however, it has the disadvantage of being expensive.

Experimental

The Reduction of Cinnamic Acid with the Sodium-Lead Alloy.—Ten grams of cinnamic acid

Table I. The products of Drynap reduction

Material	Product	M. p., °C	Yield, %
$\mathrm{Ph\text{-}CH{=}CH\text{-}COCH_3}$	$[\mathrm{Ph\text{-}\underset{\vert}{C}H\text{-}CH_2\text{-}COCH_3}]_2$	116	10—35
$\mathrm{Ph\text{-}CH{=}CH\text{-}CO\text{-}CH{=}CH\text{-}Ph}$	$[\mathrm{Ph\text{-}\underset{\vert}{C}H\text{-}CH_2\text{-}CO\text{-}CH{=}CH\text{-}Ph}]_2$	210	58
$\mathrm{Ph\text{-}CH{=}CH\text{-}CO\text{-}Ph}$	$[\mathrm{Ph\text{-}\underset{\vert}{C}H\text{-}CH_2\text{-}CO\text{-}Ph}]_2$	193	45
$(\mathrm{H_2C}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{C_6H_3})\mathrm{\text{-}CH{=}CH\text{-}COCH_3}$*	$[(\mathrm{H_2C}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{C_6H_3})\mathrm{\text{-}\underset{\vert}{C}H\text{-}CH_2\text{-}COCH_3}]_2$	228	25—30
$\mathrm{Ph\text{-}CH{=}CH\text{-}COOCH_3}$	$[\mathrm{Ph\text{-}\underset{\vert}{C}H\text{-}CH_2\text{-}COOCH_3}]_2$	178	~5
$\mathrm{Ph\text{-}CH{=}CH\text{-}NO_2}$	$\mathrm{Ph\text{-}CH_2\text{-}CH{=}N\text{-}OH}$	103	~60

* $(\mathrm{H_2C}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{C_6H_3})$- is 3, 4-methylenedioxyphenyl group.

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2) R. A. Edge and G. W. Fowles, *Anal. Chim. Acta*, **32**, 191 (1965).

3) A. Erlenmeyer, *Ann.*, **121**, 375 (1862); **137**, 334 (1866).

4) L. Gattermann, Die Praxis des organischen Chemikers, 40 Aufl., 203 (1961).

5) C. Harries and G. Eschenbach, *Ber.*, **29**, 383 (1896); R. Kuhn and M. Hoffer, ibid., **65**, 170 (1932)

was dissolved in 70 ml. of a 5% sodium hydroxide solution. Into the solution, 50 g. of the commercial sodium-lead alloy "Drynap" (contains more than 9.5% of active sodium metal) was vigorously stirred in small portions at 55—60°C. After one hour, the alkaline mixture was acidified with hydrochloric acid; 9.0 g. of hydrocinnamic acid, m. p. 49°C, was thus obtained in a 87% yield.

The General Procedure of the Reduction with Drynap and Acetic Acid.—Into an ethanol solution of 0.02 mol. of material described in Table I, 20 g. of Drynap (corresponding to 0.08 atom of sodium metal) and 5 ml. of gracial acetic acid were vigorously stirred in small portions. The reaction temperature was maintained below 60°C.

After 1 or 1.5 hr., the reaction mixture was separated from the residual spongy lead, and the filtrate was evaporated in order to remove the solvent. The residue was extracted with benzene.

The extract was washed with 5% sodium hydrogen carbonate solution and water, and dried over sodium sulfate. The crude product was dissolved in benzene, passed through an alumina column, and recrystallized with benzene or ligroin.

The materials and reduced products are listed in Table I.

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