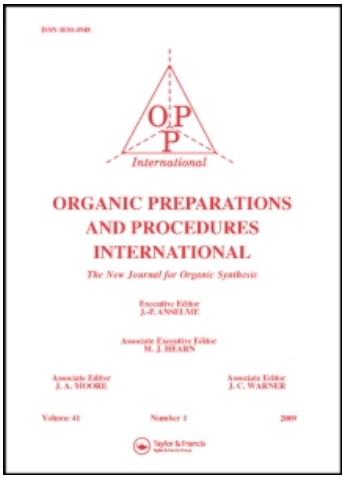

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ALDEHYDES FROM ACYLHYDRAZINES BY REDUCTION WITH SODIUM BOROHYDRIDE IN THE PRESENCE OF CUPRIC CHLORIDE

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ALDEHYDES FROM ACYLHYDRAZINES BY REDUCTION WITH SODIUM BOROHYDRIDE IN THE PRESENCE OF CUPRIC CHLORIDE†

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Acylhydrazines are useful intermediates and interesting products in organic chemistry; they are frequently prepared for the purification and characterization of carboxylic acids, or even for the protection of carboxylic groups.[1-4] Sodium borohydride easily reacts with several transition metal salts,[5] and particularly with copper salts,[6] to give transition metal-borohydride reagent systems normally generated in situ and used in the reduction of a variety of functional groups. Sometimes the production of such systems is preceded by the preparation of transition metal-triphenylphosphine complexes that are reacted with sodium borohydride to give bis(triphenylphosphine)-metal-borohydride complexes.[7] Considering these facts, we examined the reduction of some acylhydrazine-copper complexes with sodium borohydride as a possible route to the parent aldehydes.

$$RCONHNH_2 \xrightarrow[NaBH_4]{CuCl_2 \cdot 2H_2O} RCHO$$

R = C_6H_5, p-$NO_2C_6H_4$, m-ClC_6H_4, $C_6H_5CH_2$, $C_6H_5(CH_2)_2$, $C_6H_5(CH_2)_3$, 4-pyridine, 2-thiophene

TABLE. Aldehydes from Acylhydrazines

R	Yield[a] (%)	bp.(°C) (lit. bp.)	mp.(°C) (lit. mp.)	IR (CO) (cm^{-1})	2,4-DNP mp. (lit.) (°C)
C_6H_5	82	178-181 (178)[b]		1700	233-235 (235)[c]
p-$NO_2C_6H_4$	74		104-106 (106)[b]	1700	318-320 (320)[c]
m-ClC_6H_4	68	213-217 (213-214)[b]		1700	245-248 (248)[c]
$C_6H_5CH_2$	92	195-199 (195)[b]		1720	118-121 (121)[c]
$C_6H_5(CH_2)_2$	51		45-47 (47)[b]	1720	147-149 (149)[c]
$C_6H_5(CH_2)_3$	53		45-48 (46-48)[d]	1720	105-108 (106-107)[d]
4-pyridine	61	183-187 (185-187)[d]		1700	283-287 (287)[d]
2-thiophene	69	197-201 (197)[b]		1670	240-242 (242)[d]

a) Yield of pure isolated product. b) "Handbook of Chemistry and Physics", 67th Ed., The Chemical Rubber Co. Press, Cleveland, Ohio, 1986-1987. c) A. I. Vogel, "Practical Organic Chemistry", 3rd Ed., Longmans Green and Co. LTD, London, 1967. d) "Beilstein Handbook of Organic Chemistry", Springer-Verlag, Berlin.

The reaction readily proceeds under very mild conditions to afford aldehydes in good to excellent yields (Table). It is noteworthy that the reduction of acylhydrazines into parent aldehydes using bis(triphenylphosphine)copper(I) borohydride failed.

EXPERIMENTAL SECTION

General Procedure.- To a solution of acylhydrazine (1.0 mmol) in tetrahydrofuran (1.0 ml), under magnetic stirring and nitrogen atmosphere at

room temperature, was added a solution of copper(II) chloride dihydrate (1.1 mmol) in tetrahydrofuran (2.0 ml). The mixture was allowed to stand for 30 min and then was slowly (6 hrs) added dropwise to a suspension of sodium borohydride (4.5 mmol) in methanol (3.0 ml). The green solution at first became yellow, then rust colored, and finally black. The reaction was allowed to proceed for a further 12 hrs. The mixture was filtered and the solution was concentrated to a small volume under reduced pressure. The residue was extracted with ether (3x15 ml) and 10% aqueous sodium hydrogen carbonate (3x15 ml). The organic phase was washed with water (3x20 ml), dried over sodium sulfate and evaporated under reduced pressure to afford the crude aldehyde in good purity. Further purification was achieved by usual procedures. The isolated products were identified by comparison with authentic specimens and with the respective 2,4-dinitrophenylhydrazones, prepared by standard methods (see Table).

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SYNTHESIS OF UNUSUAL CONJUGATED AZOALKENES†

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Conjugated azoalkenes are interesting products and useful in C-functionalizations,[1,2] as well as for the preparation of a number of five- (i.e., pyrroles, pyrrolines)[1,3] and six-membered heterocycles (i.e.,