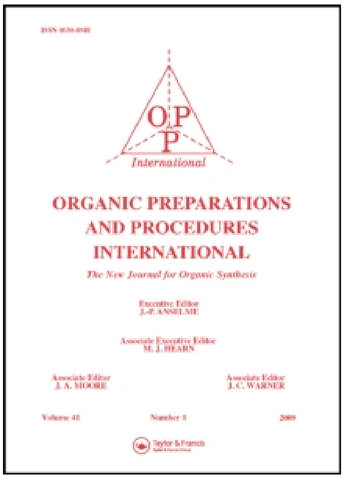


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

1,4-ADDITION TO CITRAL

Meyer Schwarz[a]; N. Wakabayashi[a]; Eric G. Thing[a]
[a] Dept. of Agriculture, Agricultural Environmental Quality, Institute, Agricultural Research Science and Education Administration U.S, Beltsville, Maryland

To cite this Article Schwarz, Meyer , Wakabayashi, N. and Thing, Eric G.(1979) '1,4-ADDITION TO CITRAL', Organic Preparations and Procedures International, 11: 2, 97 — 99

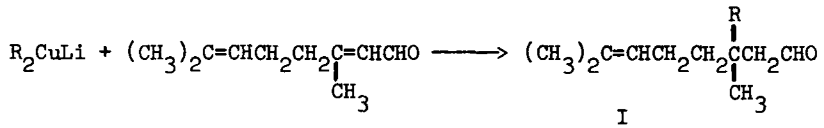
To link to this Article: DOI: 10.1080/00304947909354849

URL: http://dx.doi.org/10.1080/00304947909354849

1,4-ADDITION TO CITRAL

Submitted by Meyer Schwarz*, N. Wakabayashi and Eric G. Thing
(12/19/78)
Agricultural Environmental Quality Institute
Agricultural Research
Science and Education Administration
U.S. Dept. of Agriculture†
Beltsville, Maryland 20705

Lithium dialkyl- and diphenylcuprates[1,2] add very smoothly to citral at -70° in ether or hexane-ether mixtures to afford the corresponding 1,4-addition product in excellent yields. Less than 5% of the alcohols (derived from 1,2-addition) are formed and they can easily be separated by column chromatography.



$$R_2CuLi + (CH_3)_2C{=}CHCH_2CH_2\underset{CH_3}{C}{=}CHCHO \longrightarrow (CH_3)_2C{=}CHCH_2CH_2\overset{R}{\underset{CH_3}{C}}CH_2CHO$$

I

a) $R = CH_3$ b) $R = C_2H_5$ c) $R = \underline{n}\text{-}C_4H_9$ d) $R = Ph$

The same reaction with the unsubstituted α,β-unsaturated aldehydes, 2-hexenal and cinnamaldehyde was less successful. In the case of 2-hexenal and lithium di-n-butylcopper the desired product was isolated in 0-30% yield. In the case of cinnamaldehyde and lithium dimethylcopper, no aldehyde product could be isolated at all, even though the presence of 3-phenylbutyraldehyde in reasonable yields directly after work-up was evidenced by GLC and GLC-MS comparisons with an authentic sample (prepared by oxidation of 3-phenylbutanol).

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. NMR spectra were obtained with a Varian T-60 of CCl_4 solutions with TMS as the internal standard. Mass spectra were obtained with Hewlett-Packard 5992A GC/MS system. GLC analyses were performed with Tracor 550 gas chromatograph with a 6" x 1/4" glass column packed with 3% OV-1 on Chromosorb WHP (80/100 mesh), column temperature 120-150° and N_2 flow rate of 60 ml/min.

3,3,7-Trimethyl-6-octenal (Ia).- In a 500 ml 4-neck round bottom flask with mechanical stirrer, purged with nitrogen, cuprous iodide (6.5 g, 35 mmol; Fisher, used as received) was suspended in 100 ml anhydrous ether. Methyllithium (65 mmol, 40 ml of a 1.6 M solution[3] in ether) was slowly added by syringe, taking care to keep the reaction mixture below 10°. After completion of the addition of the methyllithium the resulting greenish-yellow solution of the $(CH_3)_2CuLi$ was cooled to -70°. Freshly distilled citral (4.5 g, 33 mmol) was then added dropwise over a 10-minute period. The reaction mixture was stirred at Dry Ice temperature for 30 min. and then allowed to warm to 0°, at which temperature the reaction mixture was decomposed by the cautious addition of saturated aqueous NH_4Cl. The reaction mixture was filtered through a pad of Hiflo Super Cel®, and the colorless organic layer was washed with dilute NH_4OH, water, satd. brine, and dried over Na_2SO_4. GLC analysis of this solution revealed the product of ca. 95% purity, contaminated by the 1,2-addition product, as evidenced by comparison with authentic samples. The ether solution was evaporated and the residue was chromatographed on 100 g of Florisil®. Elution with 400 ml of 5% ether in hexane gave a solution of pure I (GLC analysis). Evaporation of the solvents and distillation of the residue in a short path still gave 3.6 g (73%) of pure product, bp (bath temp) 110°/20 mm; IR (neat): 1725; nmr: δ 9.65 (t, J=3 Hz, 1 H, - C$\underline{H}$O), 2.2 (d, J=3 Hz, 2 H, $-C\underline{H}_2-CHO$), 1.0 (s, 6 H, $-C(C\underline{H}_3)_2-$); mass spectrum m/e 168 (M^+).

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98.

Found: C, 78.75; H, 11.94.

3-Ethyl-3,7-dimethyl-6-octenal (Ib) was prepared in the same manner as Ia (83%), except that the addition of ethyllithium to cuprous iodide was carried out at -30° and a black suspension resulted, bp (bath temp.) 125°/20 mm; IR: 1725; nmr: δ = 9.75 (t, J=3 Hz, 1 H, -C$\underline{H}$O), 2.2 (d, J=3 Hz, 2 H, -C$\underline{H}_2$ -CHO), δ = 1.0 (s, 3H, -C(C$\underline{H}_3$) (C_2H_5)-CH_2); mass spectrum m/e 182 (M^+).

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.06; H, 12.17.

Found: C, 79.34; H, 12.23.

3-n-Butyl-3,7-dimethyl-6-octenal (Ic) was prepared in the same manner as Ia (60%), using commercially available n-butyllithium in hexane, bp. (bath temp.) 110°/0.1 mm;IR: 1725; nmr: δ 9.8 (t, J=3 Hz, 1 H,-C$\underline{H}$O), 2.2 (d, J=3 Hz, 2 H, -C$\underline{H}_2$-CHO), 1.0 (s, 3 H, -C(C$\underline{H}_3$) (nBu)CH_2); mass spectrum m/e 210 (M^+).

Anal. Calcd. for $C_{14}H_{26}O$: C, 79.93; H, 12.46.

Found: C, 79.94; H, 12.30.

3,7-Dimethyl-3-phenyl-6-octenal (Id) was prepared in the same manner as Ia (90%) bp. 111°/0.01 mm;IR: 1725, nmr: δ 9.5 (t, J = 3 Hz, 1 H, -CHO), 7.3 (apparent s, 5 H, $C_6\underline{H}_5$), 2.5 and 2.6 (dd[diastereotopic H's], J = 3Hz; 2$\underline{H}$, -C$\underline{H}_2$-OHO), 1.45 (s, overlaps with terminal CH_3)-C(C_6H_5)(C$\underline{H}_3$)-CH_2); mass spectrum: m/e 230 (M^+).

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63.

Found: C, 83.42; H, 9.61.

REFERENCES

† Mention of a commercial or proprietary product in this paper does not constitute an endorsement of this product by the U. S. Department of Agriculture.

1. G. H. Posner, Org. Reactions, 19, 1 (1972).

2. B. M. Trost, J. M. Timeo and J. L. Stanton, Chem. Commun., 436 (1978).

3. W. G. Kofron and L. M. Baclawski, J. Org. Chem., 41, 1897 (1976).