1,2-Addition of Dilithium Trialkynylcuprates to αβ-Unsaturated Cyclic Ketones

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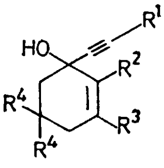
Summary Selective 1,2-addition of alkynyl groups to cyclic αβ-unsaturated ketones may be effected by dilithium trialkynylcuprates in the presence of hexamethyl phosphoric triamide.

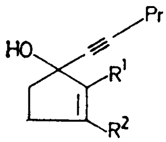
Whereas lithium (alkyl)(alkynyl)cuprates[1] were known to transfer alkyl groups selectively to αβ-unsaturated cyclic ketones *via* conjugated addition, dilithium trialkynylcuprates[2,3] failed to give either 1,2- or 1,4-addition with similar substrates.

We have found that the alkynyl groups (*e.g.*, pent-1-ynyl and hex-1-ynyl) of dilithium trialkynylcuprates were transferred regiospecifically to cyclic enones to afford (85—95%) the corresponding pure 1,2-adducts (**1a**—**e**) and (**2a,b**)‡ only in the presence of hexamethylphosphoric triamide (HMPA) as co-solvent (*ca.* 20%). Dilithium tris(pent-1-ynyl)cuprate was generated by stepwise addition of pent-1-ynyl-lithium (30 mmol; prepared *in situ* from Bu^{n}Li and pent-1-yne) to purified copper(I) iodide[4] (10·5 mmol).§ Treatment of this essentially homogeneous solution with cyclohex-2-enone in HMPA, first at −78 °C and then at room temperature (1 h), afforded (**1a**) (95%) as a colourless oil, > 98% pure by g.l.c.; ν_{max} (neat) 3368, 2242, and 1650 cm^{-1}; δ (CDCl$_3$) 0·93 (3H, t, *J* 7·5 Hz, Me), 2·75 (1H, br. s, D$_2$O exchangeable OH), 5·70 (2H, br. s, olefinic-H).

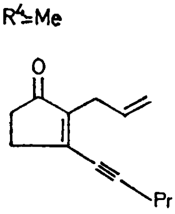
Because of its high regiospecificity and good yields, the reported procedure appears preferable to alternative methods[5] for the synthesis of unsaturated alkynyl methanols which may be valuable starting materials for modified prostaglandins. For example, acidic oxidative work-up[6] (Jones, −10 °C) of the crude product of reaction of dilithium tris(pent-1-ynyl)cuprate with 2-allylcyclopent-2-enone gave



(1) a; R^1=Pr^n, R^2=R^3=R^4=H
b; R^1=Pr^n, R^2=Me, R^3=R^4=H
c; R^1=Pr^n, R^2=H, R^3=R^4=Me
d; R^1=Bu^n, R^2=R^3=R^4=H
e; R^1=Bu^n, R^2=H, R^3=R^4=Me



(2) a; R^1=R^2=H
b, R^1=allyl, R^2=H



(3)

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‡ All new compounds have spectral and analytical data consistent with their assigned structures.

§ Appropriate controls were run to ensure that the observed addition was due to dilithium trialkynyl cuprate only. Pent-1-ynyl-lithium was estimated by the benzophenone method[1] and slight excess of Cu^I was added to ensure that excess of alkynyl-lithium was not present (see for example, E. Piers, W. deWaal, and R. W. Britton, *J. Amer. Chem. Soc.*, 1971, **93**, 5113).

a nearly quantitative yield of the rearranged ketone (**3**), as colourless oil, λ_{max} (MeOH) 268 nm (log ϵ 4·20); ν_{max} (neat) 2220, 1686, and 1605 cm^{-1}; δ ($CDCl_3$) 1·06 (3H, t, *J* 7·0 Hz, Me), 3·05 (2H, br. d, *J* 6·5 Hz, CH_2–C=), 4·8—6·2 (3H, m, CH_2=CH).

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