Tetrahedron Letters Vol. 22, pp 1041 - 1042 0040-4039/81/0308-1041$02.00/0

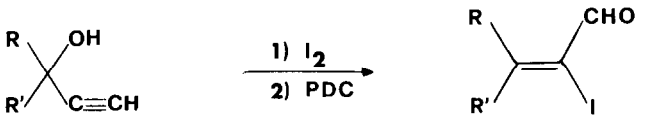
PYRIDINIUM DICHROMATE IN ORGANIC SYNTHESIS: A CONVENIENT OXIDATION OF α-YNOL-IODINE COMPLEXES TO α,β-UNSATURATED-α-IODO-ALDEHYDES

R. Antonioletti, M. D'Auria, G. Piancatelli*, A. Scettri

Centro CNR per lo Studio della Chimica delle Sostanze Organiche Naturali, c/o Istituto di Chimica Organica dell'Università, P.zza A. Moro 5, 00185 Roma, Italia

Summary - Under mild and simple conditions PDC oxidizes α-ynol-I_2 complexes to the title carbonyl compounds.

The nucleophilic properties of pyridinium dichromate (PDC) have been little investigated until now[1]; our recent interest accorded to the oxidant in this area prompts this report on the capability of PDC for the facile oxidation of ethynyl carbinol-iodine complexes to α,β-unsaturated-α-iodo-aldehydes.

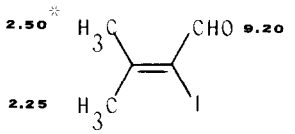
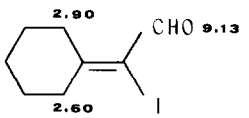
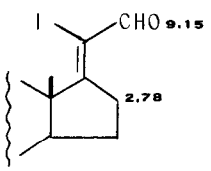
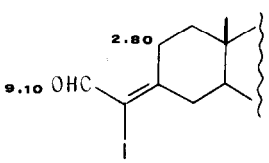
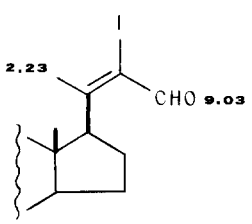


In a typical experiment procedure, I_2 (1 mmole) and 4 Å molecular sieves were added to a well stirred solution of α-ynols in anhydrous CH_2Cl_2 (5 ml), at 25°C under N_2. After 30 min., PDC (2.2 mmoles) was rapidly added and the mixture stirred for 24 h. The crude products, after the usual work up[1], were purified by column chromatography on neutral Al_2O_3 B III (Table).

The conversion points out an interesting regio- and stereospecific reactivity of the PDC; in fact only one geometrical isomer was obtained (Table). Further, the α-ynols were converted exclusively to the corresponding α,β-unsaturated-α-iodo-aldehydes (the Meyer-Schuster type products)[2].

Thus, our method describes the first one-step conversion of α-ynols to the title compounds, a class of compounds until now unknown; the mild conditions as

Table

Substrate	Product	I.R.	Yield(%)
2-Methyl-3-butyn-2-ol		1690 1595	40
1-Ethynyl-cyclohexanol		1690 1595	66
17-Ethynyl-3β-acethoxy-androstan-17-ol		1680 1580	65
3α-Ethynyl-cholestan-3β-ol		1690 1585	60
20-Ethynyl-3β-acethoxy-pregnan-20-ol		1670 1560	30**

(*) ^{1}H-NMR data (CCl_4, δ).

(**) The major product recovered (50%) was the 3β-acethoxy-pregnan-20-one, due to the loss of the acetylene, observed only in this case.

well as the above results make the present procedure useful for preparative purpose.

References

1) R. D'Ascoli, M. D'Auria, L. Nucciarelli, G. Piancatelli, A. Scettri, Tetrahedron Letters, 4521, 1980;

2) S. Swaminathan, K. V. Narayanan, Chem. Rev., 71, 429 (1971).

(Received in UK 6 January 1981)