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(5,5-DIETHOXY-2-(E)-PENTENYL) TRIPHENYLARSONIUM YLIDE : A NEW SYNTHETIC EQUIVALENT OF δ-FORMYL BUTADIENYLANION

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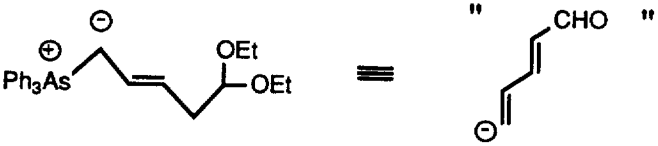
Summary : *The title arsonium ylide permits a five carbon homologation of aldehydes to the corresponding 6-hydroxy-2,4-(E)-dienals. This new reagent can be considered as a new δ-formyl butadienyl anion.*

We previously described[1] the functionalized arsonium ylide (3,3-diisopropoxypropyl) triphenylarsonium ylide which converts aldehydes to the corresponding γ-hydroxy-enals in a three steps sequence. Herein, we report the synthesis and the reactivity of a vinylog, (5,5-diethoxy-2-(E)-pentenyl) triphenylarsonium ylide **1**, which transforms under similar conditions aldehydes **2** into the corresponding 6-hydroxy-2,4-(E)-dienals **5**. To our knowledge, only one d^5 umpoled reagent has been described in the literature[2], although this fonctionality is commonly found in important fatty acids derivatives[3].

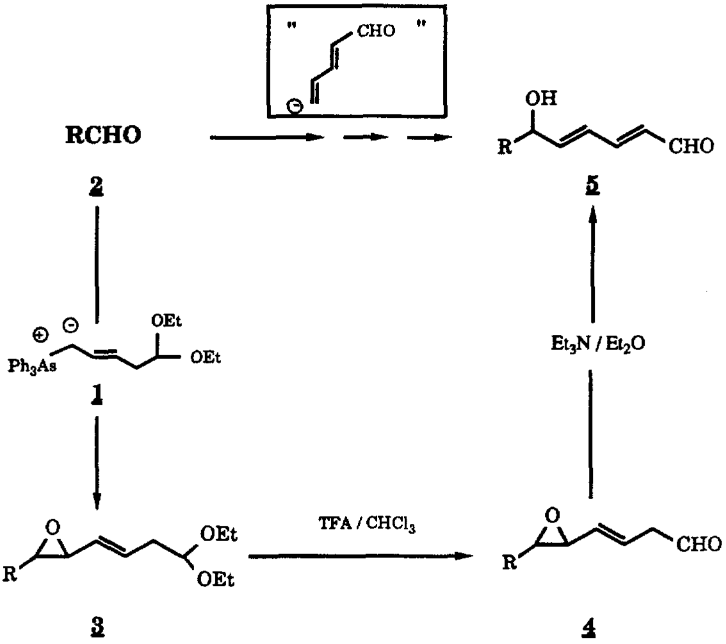


1

SCHEME 1

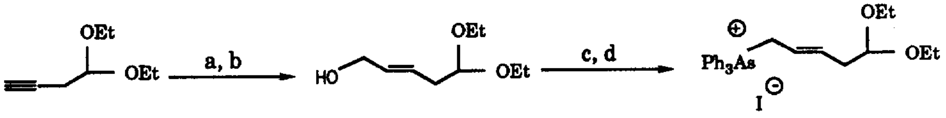
In THF at -70°C semi-stabilized arsonium ylide **1**, generated from the corresponding salt with LDA, reacts with aldehydes to give only epoxides[4] **3**. The acetal functions are selectively cleaved with trifluoroacetic acid in chloroform[5], to afford aldehydes **4** in moderate yields. Subsequent treatment of **4** with an excess of triethylamine leads to the 6-hydroxy-2,4-(E)-dienals **5**[6]. The final products are purified on silicagel by flash chromatography.

The three step sequence for the homologation of aldehydes is summarized in scheme 1.



SCHEME 2

Arsonium salt **8** is obtained from 4,4-diethoxybutyne **6**[7] which is converted to the allylic alcohol **7** by condensation of the corresponding Grignard derivative with formaldehyde, and subsequent reduction with lithium aluminium hydride. Treatment of the alcohol with mesyl chloride in the presence of triethylamine leads to the corresponding mesylate in 88 % yield[8]. Stirring equal amounts of mesylate, triphenylarsine, sodium iodide and potassium carbonate at room temperature in anhydrous acetonitrile, affords **8** in 57% yield[9] after purification by recristallization from methylene chloride / ether.

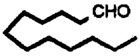
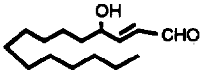
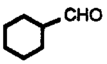
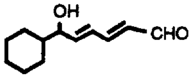
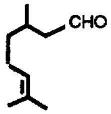
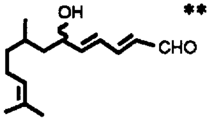
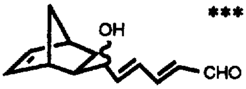
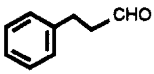
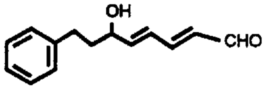


6 7 8

a- EtMgBr; b- CH_2O; c- MsCl / Et_3N; d- $AsPh_3$ / NaI / K_2CO_3

SCHEME 3

The conversion of aldehydes to the corresponding 6-hydroxy-2,4-(E)-dienals **5** is realized in overall moderate yields as shown in table 1.

Entry	Aldehyde **2**	Yield %*	Aldehyde **5**	Yield %**
a		45		46
b		57		62
c		41	 ***	58
d		46	 ***	40
e		42		70

* epoxidation ⟶ **3** ** deprotection + isomerization ⟶ **5**

*** mixture of diastereoisomers

TABLE 1

(5,5-Diethoxy-2-(E)-pentenyl) triphenylarsonium ylide is the first d^5 umpoled reagent who allows a five carbon homologation under very mild conditions through a three step sequence including epoxidation, acetal cleavage and isomerization reactions.[10]

References and notes:

1- P. Chabert, J.B. Ousset, C. Mioskowski, Tetrahedron Letters, **30**, 179 (1989)
P. Chabert, C. Mioskowski, J.R. Falck, Tetrahedron Letters, **30**, 2445 (1989)

2- T.A. Hase "Umpoled synthons" Wiley-Interscience, New-York (1987)
M. Pohmakotr, D. Seebach Tetrahedron Letters 2271 (1979)

3- E.J. Corey, A. Marfat, G. Goto, F. Brion, J. Am. Chem. Soc. , **102**, 7984 (1980)
K.C. Nicolaou, C. A. Veale, S.E. Weber, H. Katerinopoulos, C.N. Hamberg, J. Am. Chem. Soc., **107**, 7515 (1985)
K.C. Nicolaou, S.E. Weber, Synthesis 453 (1986)

4- No trace of olefin were detected by using the solvent and temperature conditions previously reported: J.B. Ousset, C. Mioskowski, G. Solladié, Synth. Comm., **13**, 1193 (1983)

5- Acetal cleavage: 10ml of a 0.15M solution of the diethyl acetals in chloroform is added to an aqueous solution of 50% trifluoroacetic acid (5ml) at room temperature. After 15 mn. the acid is neutralized with an aqueous solution of hydrogenocarbonate and the aldehyde is isolated by usual work-up.

6- Isomerization is conducted under anhydrous conditions, by addition of 10 equiv. of triethylamine to a 0.1M solution of epoxyaldehyde **4** in ether. The reaction mixture is stirred for two hours at room temperature, the solvent removed under reduced pressure and the product purified by flash chromatography on silicagel (ether-hexane 80:20).

7- F. Barbot, L. Poncini, B. Randrianoelina, P. Miginiac, J. Chem. Research (S), 343 (1981); J. Chem. Research (M), 4016 (1981)

8- Allylic alcohols **7** are obtained by stereospecific reduction of the corresponding propargylic alcohols by refluxing 0.4M etheral solutions with 1.1 equiv. of lithium aluminium hydride during 12 hours. Mesylations are performed by addition of 0.3M solution of allylic alcohols in methylene chloride to 2.0 equiv. of triethylamine and 1.5 equiv. of methane sulfonyl chloride at room temperature.

9- Physical data of (5,5-diethoxy-2-(E)-pentenyl) triphenylarsonium iodide **8**:
Mp: 123°C.
^{1}H NMR (200 MHz, CDCl$_3$): 7.80-7.65 (m,15H), 6.02-5.86 (m,1H), 5.64-5.48 (m,1H), 4.59(d,2H, J=7.5Hz), 4.34 (t,1H, J=5.5Hz), 3.60-3.30 (m,4H), 2.29 (t,2H,J=5.6Hz), 1.26 (t,6H, J=7.5Hz).
IR (CHCl$_3$): 1680(s), 1120(m), 1050(m) cm^{-1}.

10- all intermediates has been caracterized by ^{1}H, ^{13}C, and IR.

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