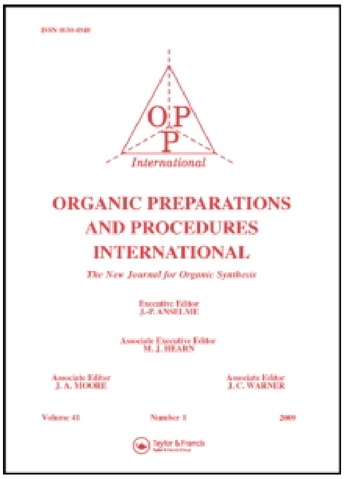

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SYNTHESIS OF α,α'-DIFUNCTIONAL CONJUGATED ENYNES

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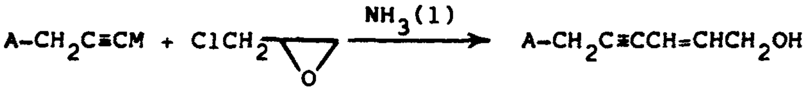
The reaction of metal acetylides (I, A = H, alkyl) with epichlorohydrin (II) has been reported[1] to give the corresponding alcohols (III), albeit in relatively low yields owing to the formation of by-products. We have now extended this reaction to α-functionalized metal acetylides (I, A = OH, CH_3O, $(CH_3)_2N$) which react with II to afford α,α'-difunctional conjugated enynes III. As far as we know, only one such reaction has been previously reported[2].



I II III

a) A = OH , b) A = CH_3O , c) A = $(CH_3)_2N$.

Though the yields are not very high (30-50%), this method is very useful to prepare rapidly α-alcohol-α'-functional enynes. Attemps to obtain the same conjugated enynes by other routes, mainly by the reaction of a metal derivative of pent-2-en-4-yn-1-ol with formaldehyde[1] or with chloromethyl methyl ether for IIIa and IIIb, and by the reaction of pent-2-en-4-yn-1-ol with formaldehyde and dimethylamine (Mannich reaction) for IIIc, were made ; the yields were uniformly low and these syntheses were much less direct than preparations from α-functional metal acetylides.

We also attempted to prepare IIIb from Ib and II, by using

Table 1. Reactions of α-Functional Metal Acetylides with II

$MC\equiv CCH_2$–A	Metal	Enyne	Yield	cis%	trans%
Ia	Li	IIIa	35%	50	50
	Na		10%	0	100
Ib	Li	IIIb	50%	50	50
	Na		30%	0	100
Ic	Li	IIIc	40%	55	45
	Na		28%	40	60

n-butyllithium with tetrahydrofuran and hexamethylphosphoric triamide as co-solvents; we obtained a quite similar result (yield = 48%, cis: trans = 45:55).

Enyne IIIb has been converted in good yields into α,α'-difunctional enynes IV, V and VI ; it would be very difficult to prepare these enynes via other routes.

$$CH_3OCH_2C\equiv CCH=CHCH_2OH \xrightarrow[CH_3I]{KOH} CH_3OCH_2C\equiv CCH=CHCH_2OCH_3 \quad (86\%)$$

IV

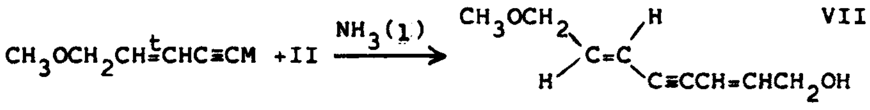
$$CH_3OCH_2C\equiv CCH=CHCH_2OH \xrightarrow{PBr_3} CH_3OCH_2C\equiv CCH=CHCH_2Br \quad (80\%)$$

V

$$CH_3OCH_2C\equiv CCH=CHCH_2Br \xrightarrow[benzene]{HN(CH_3)_2} CH_3OCH_2C\equiv CCH=CHCH_2N(CH_3)_2 (60\%)$$

VI

Finally, we observed that the reaction of epichlorhydrin with the metal derivative of an α-functional enyne leads to a conjugated α,α'-difunctional dienyne VII.



M= Li, Yield = 50% , <u>cis</u> : <u>trans</u> = 40:60 ,

M= Na, Yield = 30% , <u>cis</u> : <u>trans</u> = 0: 100.

EXPERIMENTAL

Epichlorhydrin and propargyl alcohol are commercial products and were purified by distillation prior to use. Methyl propargyl ether[1b] and dimethyl propargylamine[3] were obtained from propargyl alcohol in 80% and 62% yields respectively. The methyl ether of pent-4-en-2-yn-1-ol was prepared[1b] in 83 % yield, by warming a mixture of this alcohol, methyl iodide and potassium hydroxide to about 40°.

<u>Synthesis of α,α'-Difunctional Conjugated Enynes III. General Procedure</u>. -To a suspension of 0.65 mole of MNH_2 in 700 ml of liquid ammonia[1b], was added slowly 0.6 mole of the compound $HC{\equiv}CCH_2A$. After stirring for 15 min., an ethereal solution of 0.3 mole (28g.) of epichlorhydrin was added over a period of 15-20 min.. After stirring at -33° for 5h., ether (160 ml), powdered NH_4Cl (20g) and water (300 ml) were added. The ammonia was allowed to evaporate and the aqueous phase was extracted with 5 x 100 ml of ether. The combined extracts were dried over K_2CO_3. The ether was removed <u>in vacuo</u> (water pump) and the product was distilled under reduced pressure.

<u>Remark</u> : In the case of propargyl alcohol, only 0.3 mole of this alcohol and 0.15 mole of epichlorhydrin were used.

<u>Synthesis of Enynes IV, V and VI</u> - Enyne IV was obtained after[1b] by reacting at 40° 0.25 mole (31.5g) of enyne IIIb with 0.575 mole (82.5g) of methyl iodide and 0.9 mole (50g) of potassium hydroxide.
Enyne V was prepared after[4] by reacting at 0° 0.05 mole

Table 2. Physical Characteristics of α,α'-Difunctional Conjugated Enynes.

	Enyne[a]	bp./torr	n_D^{20}
IIIa *cis*	$HOCH_2C\equiv CCH=CHCH_2OH$	127–128°/0.1	1.5340
IIIa *trans*	$HOCH_2C\equiv CCH=CHCH_2OH$	129–130°/0.1	1.5405
IIIb *cis*	$CH_3OCH_2C\equiv CCH=CHCH_2OH$	90°/0.2	1.4932
IIIb *trans*	$CH_3OCH_2C\equiv CCH=CHCH_2OH$	132°/17	1.5046
IIIc *cis*	$(CH_3)_2NCH_2C\equiv CCH=CHCH_2OH$	94°/0.1	1.5085
IIIc *trans*	$(CH_3)_2NCH_2C\equiv CCH=CHCH_2OH$	139–140°/13	1.5145
IV *cis*	$CH_3OCH_2C\equiv CCH=CHCH_2OCH_3$	92°/13	1.4748
IV *trans*	$CH_3OCH_2C\equiv CCH=CHCH_2OCH_3$	95°/13	1.4805
V *cis*	$CH_3OCH_2C\equiv CCH=CHCH_2Br$	114°/17	
V *trans*	$CH_3OCH_2C\equiv CCH=CHCH_2Br$	117°/17	
VI *cis*	$CH_3OCH_2C\equiv CCH=CHCH_2N(CH_3)_2$	104°/17	1.4789
VI *trans*	$CH_3OCH_2C\equiv CCH=CHCH_2N(CH_3)_2$	106°/17	1.4838
VII *cis*	$CH_3OCH_2CH\overset{t}{=}CHC\equiv CCH=CHCH_2OH$	128°/0.3	1.5458
VII *trans*	$CH_3OCH_2CH\overset{t}{=}CHC\equiv CCH=CHCH_2OH$	130°/0.3	1.5496

a. Each isomer was purified by preparative g.l.c. (SE 30) after distillation.

Table 3. Elemental Analysis and Partial Spectra Data

	Elemental Analysis % Calculated (% Found)				
	C	H	N(ou Br)	NMR $^1H^a$	IR^b
IIIa *cis*	64.26 (64.30)	7.19 (7.15)		4.25(m,4H),4.80(s,2H), 5.85(m,2H,J=11 Hz)	3350,1630, 740
IIIa *trans*	64.26 (64.20)	7.19 (7.25)		4.15(m,4H),4.85(m,2H), 5.90(m,2H),J=16 Hz)	3350,1635, 960
IIIb *cis*	66.64 (66.60)	7.99 (7.90)		3.35(s,3H),3.60(s,1H), 4.25(m,4H),5.95(m,2H), J=10.7 Hz)	3350,1630, 740,1095
IIIb *trans*	66.64 (66.56)	7.99 (8.03)		3.30(s,3H),3.95(s,1H), 4.15(m,4H),6.00(m,2H), J=15.7 Hz)	3350,1635, 955,1100
IIIc *cis*	69.03 (68.93)	9.42 (9.48)	10.05 (10.10)	2.25(s,6H),3.35(s,2H), 4.25(d,2H),4.35(s,1H), 5.85(m,2H,J=11 Hz)	3350,1620, 740,1040
IIIc *trans*	69.03 (69.14)	9.42 (9.35)	10.05 (10.08)	2.20(s,6H),3.30(s,2H), 4.10(d,2H),4.65(s,1H), 6.00(m,2H,J=15.6 Hz)	3350,1630, 955,1025
IV *cis*	68.55 (68.43)	8.63 (8.69)		3.30(2s,6H),4.15(m,4H), 5.85(m,2H,J=11 Hz)	1625,740, 1115
IV *trans*	68.55 (68.60)	8.63 (8.59)		3.30(2s,6H),4.00(m,4H), 5.95(m,2H ,J=16 Hz)	1635,955, 1120
V *cis*	44.48 (44.55)	4.80 (4.76)	42.27 (42.10)	3.30(s,3H),4.15(m,4H), 5.95(m,2H,J=10.8 Hz)	1625,735, 1110
V *trans*	44.48 (44.38)	4.80 (4.86)	42.27 (42.35)	3.35(s,3H),4.00(m,4H), 6.05(m,2H,J=15.5 Hz)	1630,955, 1110
VI *cis*	70.55 (70.50)	9.87 (9.80)	9.14 (9.20)	2.20(s,6H),3.10(d,2H), 3.35(s,3H),4.15(d,2H), 5.90(m,2H,J=11 Hz)	1620,730, 1095,1040,
VI *trans*	70.55 (70.62)	9.87 (9.78)	9.14 (9.08)	2.10(s,6H),2.90(d,2H), 3.25(s,3H),4.05(d,2H), 5.90(m,2H),J=15.8 Hz)	1630,950, 1090,1045
VII *cis*	71.03 (70.94)	7.95 (7.99)		3.30(s,3H),3.55(s,1H), 3.90(d,2H),4.25(d,2H), 5.90(m,4H)	3350,1660, 1630,955, 740,1125
VII *trans*	71.03 (71.12)	7.95 (7.89)		3.30(s,3H),3.80(s,1H), 3.90(d,2H),4.10(d,2H), 6.0(m,4H)	3350,1665, 1640,960, 1120

a. Recorded on a Perkin-Elmer R 24 A spectrometer, expressed in δ relative to TMS.

b. Recorded on a Beckman IR 4240 spectrometer, expressed in cm^{-1} ; all these products show also one band of weak intensity at 2210 (C≡C).

(13.5 g) of PBr_3 with 0.12 mole (15.2g) of enyne IIIb, in solution in anhydrous ether (40 ml).

Enyne VI was obtained after[5] by reacting at 20° a solution of 0.06 mole (11.3 g) of enyne V in anhydrous benzene (15ml) with a solution of 0.12 mole (5.4g) of dimethylamine in anhydrous benzene (30 ml).

Synthesis of enyne VII.- This enyne was prepared in the same way as III from 0.6 mole (57.6g) of enyne IIIb *trans*.

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