A CONVENIENT METHOD FOR THE PREPARATION OF SYMMETRICAL POLYOLEFINS. _____ SYNTHESIS OF β -CAROTENE _____

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Various carbonyl compounds undergo the reductive dimerization to produce symmetrical olefins in high yields on treatment with low valent titanium compounds, formed in situ from TiCl_4 and LiAlH_4 , in the presence of a tertiary amine such as 1,8-bis(dimethylamino)naphthalene or tri-n-butylamine. This method is successfully applied to the direct synthesis of β -carotene(6) from retinal(5).

Recently, it was reported from our laboratory that the low valent titanium compound, formed from TiCl₄ and LiAlH₄¹⁾ or TiCl₄ and Zn²⁾, is a useful reagent for the preparation of pinacols²⁾, inner and terminal olefins^{3),4)}, and vinyl sulfides⁵⁾ by the reductive dimerization of carbonyl compounds or the reductive β -elimination of β -hydroxy sulfides and β -hydroxy thioacetal derivatives. Independently, Tyrlik and McMurry reported that the low valent titanium reagent, prepared from TiCl₃ and Mg⁶⁾, LiAlH₄⁷⁾ or K⁸⁾, is effective in the above reduction reactions.

Our interest in the TiCl₄ and LiAlH₄ reagent or the TiCl₄ and Zn reagent led us to study a convenient method for the preparation of symmetrical polyolefin and a one-step synthesis of β -carotene(6) from retinal(5)⁹⁾. β -Ionone(1) was used to determine the optimum experimental condition for the reductive dimerization using the low valent titanium compound. When β -ionone(1) was treated with TiCl₄ and Zn at -10°C for lhr under an argon atmosphere, pinacol(2)^{10),11)} was obtained in 94% yield. Pinacol(2) thus formed was found to be converted into a rearranged product (4)¹²⁾ on treatment with a small amount of Lewis acid^{2b)}.

Based on the above observation, the reductive coupling of β -ionone(1) to symmetrical polyolefin(3) was carried out in the presence of tertiary amines such as pyridine, triethylamine, tri-n-butylamine, 1,8-bis(dimethylamino)naphthalene (proton sponge), and 1,4-diazabicyclo[2.2.2]octane (DABCO) (See Table I).

As shown in Table I, it was found that, in the case of reductive coupling of β -ionone(1), symmetrical polyolefin(3) was obtained in optimum yield by using TiCl₄-LiAlH₄ in the presence of proton sponge, and other tertiary amines could be also effectively used in the present reaction to avoid the formation of undesirable rearranged products.



Coupling		tertiary	conditio	ons	Isolat	ed yie	eld(%)
reagent ^{a)}	n ^{b)}	amine ^{c)}	Temp. T	ime(hr)	(2)	(3)	(4)
A	1.5	-	-10°C	1.0	94		
в	2.5	-	refl.	1.0	8	44	25
в	2.5	n-Bu ₃ N	refl.	3.0		70	20
в	5.0	n-Bu ₃ N	refl.	3.0		91	
А	5.0	n-Bu ₃ N	refl.	3.0	20	63	
В	5.0	Pyridine	refl.	3.0		82	
В	5.0	(C ₂ H ₅) ₃ N	refl.	3.0		82	
В	5.0	Proton Sponge	refl.	3.0		94	
В	5.0	DABCO	refl.	3.0		72	

a) $A=TiCl_4-Zn$ (1 : 2), $B=TiCl_4-LiAlH_4$ (1.9 : 1)

b) Molar ratio of TiCl_4/β -ionone

c) Molar ratio of amine/ β -ionone is 1.0

The following experiment provides a typical procedure for the conversion of carbonyl compounds to symmetrical olefins: To a solution of TiCl₄ (10 mmol) in dry THF (20 ml) was added powdered LiAlH₄ (195 mg). The mixture was refluxed for 20 min under an argon atmosphere to give a deep black solution. To the metal complex solution thus obtained was added a solution of β -ionone (385 mg, 2.00 mmol) and proton sponge (428 mg, 2.00 mmol) in dry THF (7 ml) under refluxing. The mixture was refluxed for additional 3hr and quenched with 20% K₂CO₃ solution. After filtration, the filtrate was extracted with n-hexane. The extract was washed with water, and dried over anhydrous Na₂SO₄. Symmetrical polyolefin(3) (332 mg)¹³⁾ was obtained in 94% yield after separation by column chromatography on silica gel eluting with n-hexane.

Table I. The Conversion of β -Ionone to Olefin(3)

ert-amine ^{a)}	Yiel	1 (%)	Product
A	9	4 X	Kada X
В	9	ı Ç	
A	9	4	$\langle \gamma \rangle$
В	9) (
A	9	2	
В	9	2	^C 6 ^H 5∕∕ ^C 6 ^H 5
A	9)	C-H- C-H-
В	9)	с ₆ н ₅ с ₆ н ₅
	В А В А В В	B 91 A 94 B 90 A 92 B 92 A 90 B 90	B 91 A 94 B 90 A 92 B 92 A 92 B 90 B 90

Table II. Yields of Olefins

a) A=Proton Sponge. B=Tri-n-bytylamine

In a similar manner, various carbonyl compounds were successfully converted into the corresponding olefins in high yields as shown in Table II.



When retinal(5) was treated with TiCl₄ and LiAlH₄ in refluxing THF for 3hr under an argon atmosphere according to the above mentioned method, a crude β carotene was obtained in 90% yield. [$\lambda_{max}^{n-hexane} 272nm$ ($\epsilon 2.0 \times 10^4$), 449nm ($\epsilon 1.25 \times 10^5$), 477nm ($\epsilon 1.09 \times 10^5$)]. After recrystallization of the crude product from C_{H6}-CH₃OH, pure β -carotene(6) was obtained in 50% yield (mp 177-180°C, lit.¹⁵⁾ mp 180°C). The spectral data (ir, uv, and nmr) of β -carotene prepared by the present method were identical with those of the authentic natural β -carotene.

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- 11) (2): mp 56-58°C; ir (nujol): 3450, 1450, 1360, 980 cm⁻¹; nmr (CDCl₃): 8 6.25 (2H, d, J=16 HZ), 5.58 (2H, d, J=16 HZ), 2.29 (2H, br.s), 1.68 (6H, s), 1.35 (6H, s), 1.00 (12H, s), 1.00-2.10 (12H); Found: C, 80.08; H, 11.64%. Calcd. for C₂₆H₄₄O₂: C, 80.35; H, 11.41%.
- 12) (4): ir (neat): 1710, 1450, 1370, 1360, 980 cm⁻¹; nmr (CDCl₃): δ 6.00 (2H, d, J=16 HZ), 5.00 (2H, d, J=16 HZ), 2.12 (3H, s), 1.66 (6H, s), 1.34 (3H, s), 0.98 (12H, s), 1.00-2.10 (12H); mass: m/e 369 (M⁺), 325 (M⁺-44).
 2,4-Dinitrophenylhydrazone: mp 108-109°C; Found: C, 70.84; H, 8.20; N, 9.99%. Calcd: for C₃₂H₄₄N₄O₄: C, 71.04; H, 8.08; N, 10.21%.
- 13) (3): mp 109-110°C; ir (nujol): 1450, 1360, 960 cm⁻¹; UV: λ_{max}^{EtOH} 312nm (ϵ 1.97×10⁴); nmr (CCl₄): δ 6.60 (2H, d, J=16 HZ), 6.05 (2H, d, J=16 HZ), 1.95 (6H, s), 1.70 (6H, s), 1.02 (12H, s), 1.00-2.00 (12H); Found: C, 88.36; H, 11.29%. Calcd. for C₂₆H₄₀: C, 88.56; H, 11.44%.
- 14) mp 97-98°C; ir (nujol): 1460, 1360, 970 cm⁻¹; nmr (CCl₄): δ 5.83 (2H, s),
 1.75 (6H, s), 1.75 (6H, s), 1.02 (12H, s), 1.10-2.00 (12H); Found: C, 88.03;
 H, 11.94%. Calcd. for C₂₀H₃₂: C, 88.16; H, 11.84%.
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(Received September 4, 1976)