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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).

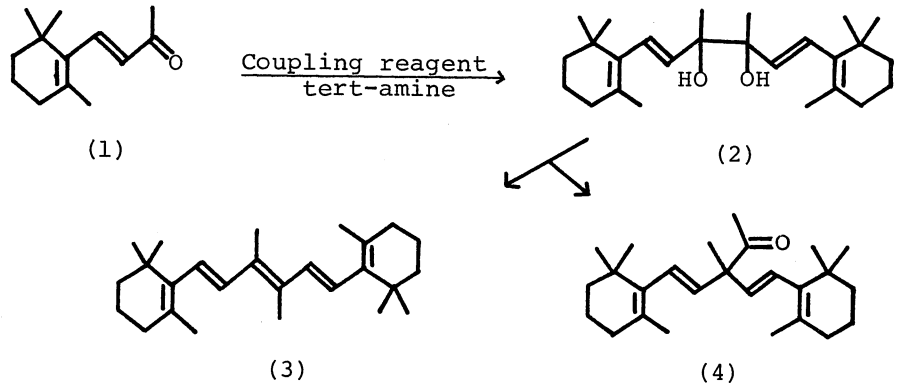
Recently, it was reported from our laboratory that the low valent titanium compound, formed from $TiCl_4$ and $LiAlH_4$[1] or $TiCl_4$ and Zn[2], is a useful reagent for the preparation of pinacols[2], inner and terminal olefins[3),4)], and vinyl sulfides[5] by the reductive dimerization of carbonyl 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 $TiCl_3$ and Mg[6], $LiAlH_4$[7] or K[8], is effective in the above reduction reactions.

Our interest in the $TiCl_4$ and $LiAlH_4$ reagent or the $TiCl_4$ 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 $TiCl_4$ and Zn at -10°C for 1hr 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 $TiCl_4$-$LiAlH_4$ 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.

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

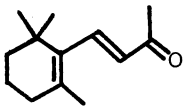
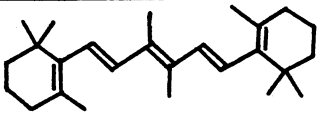
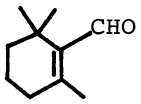
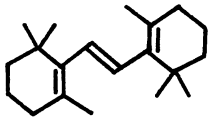
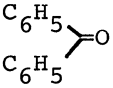
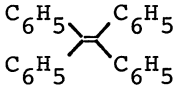


Coupling reagent[a]	n[b]	tertiary amine[c]	conditions Temp.	Time(hr)	Isolated yield(%) (2)	(3)	(4)
A	1.5	-	-10°C	1.0	94		
B	2.5	-	refl.	1.0	8	44	25
B	2.5	n-Bu_3N	refl.	3.0		70	20
B	5.0	n-Bu_3N	refl.	3.0		91	
A	5.0	n-Bu_3N	refl.	3.0	20	63	
B	5.0	Pyridine	refl.	3.0		82	
B	5.0	$(C_2H_5)_3N$	refl.	3.0		82	
B	5.0	Proton Sponge	refl.	3.0		94	
B	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

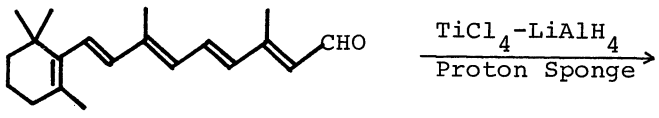
The following experiment provides a typical procedure for the conversion of carbonyl compounds to symmetrical olefins: To a solution of $TiCl_4$ (10 mmol) in dry THF (20 ml) was added powdered $LiAlH_4$ (195 mg). The mixture was refluxed for 20 min under an argon atmosphere to give a deep black solution. 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% K_2CO_3 solution. After filtration, the filtrate was extracted with n-hexane. The extract was washed with water, and dried over anhydrous Na_2SO_4. Symmetrical polyolefin(3) (332 mg)[13] was obtained in 94% yield after separation by column chromatography on silica gel eluting with n-hexane.

Table II. Yields of Olefins

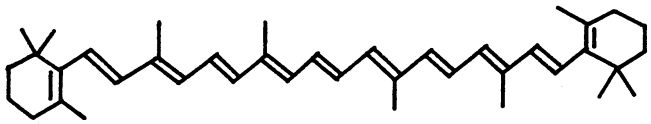
Starting material	tert-amine[a]	Yield (%)	Product
	A	94	
	B	91	
	A	94	
	B	90	
C_6H_5CHO	A	92	C_6H_5=C_6H_5
	B	92	
	A	90	
	B	90	

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.



(5)



(6)

When retinal(5) was treated with $TiCl_4$ and $LiAlH_4$ in refluxing THF for 3hr under an argon atmosphere according to the above mentioned method, a crude β-carotene was obtained in 90% yield. [$\lambda_{max}^{n\text{-hexane}}$ 272nm (ε 2.0×10^4), 449nm (ε 1.25×10^5), 477nm (ε 1.09×10^5)]. After recrystallization of the crude product from C_6H_6-CH_3OH, 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 ($CDCl_3$): δ 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 $C_{26}H_{44}O_2$: C, 80.35; H, 11.41%.

12) (4): ir (neat): 1710, 1450, 1370, 1360, 980 cm^{-1}; nmr ($CDCl_3$): 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 $C_{32}H_{44}N_4O_4$: 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 1.97×10^4); nmr (CCl_4): 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 $C_{26}H_{40}$: C, 88.56; H, 11.44%.

14) mp 97-98°C; ir (nujol): 1460, 1360, 970 cm^{-1}; nmr (CCl_4): 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 $C_{20}H_{32}$: C, 88.16; H, 11.84%.

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