Preparation of Conjugated Dienes and Ethylidenecycloalkanes by Double-Bond Shift Catalyzed by Titanocene Derivatives

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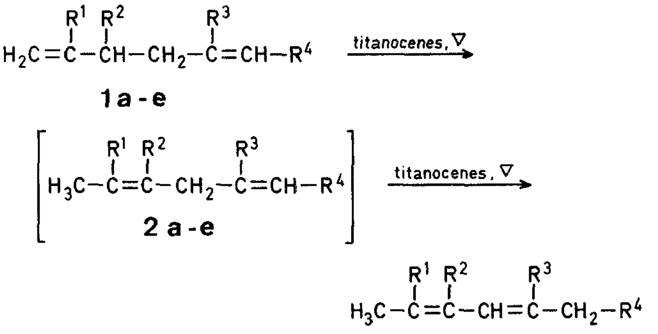
Syntheses of conjugated dienes are usually based on the Wittig reaction[1], coupling of alkenylcuprates[2], or elimination reactions[3]. Although the first two methods are generally applicable and can be conducted with high stereospecificity, difficulties may be encountered when scaling up the preparation. An alternative approach to conjugated dienes uses the isomerization of readily accessible 1,5-dienes which can be accomplished by bases[4,5] or, more effectively, by transition-metal organometallic catalysts, e.g., by nickel[6,7] and titanium compounds[8,9]. In this paper, the laboratory preparation of conjugated dienes from their 1,5-isomers is described, using two easily obtainable titanocene-derived catalysts. In the first case, the catalytically active species Cp_2TiR ($Cp = \eta^5$-C_5H_5, R = allyl, alkenyl, alkyl) is generated by reduction of Cp_2TiCl_2 with lithium alanate in the boiling olefin to be isomerized (Method A)[8]. In the second method, the catalyst is obtained by the decomposition of preformed ($\eta^5:\eta^5$-fulvalene)-di-μ-hydrido-bis[cyclopentadienyltitanium(III)], $(C_{10}H_8)(H)_2(CpTi)_2$, at 150-180°C (Method B). The latter compound is conveniently prepared by reducing Cp_2TiCl_2 with lithium alanate in mesitylene[10]. Both catalytic systems possess comparable isomerization selectivities in spite of marked differences in the reaction temperature required. The molar ratio catalyst : substrate depends mainly on the purity of the olefin since the catalysts are rapidly quenched by oxygen- or halogen-containing impurities. The ratio $1:10^3$ was chosen in Method A to effect a reasonably fast reduction of Cp_2TiCl_2. In Method B, a molar ratio as low as $1:10^4$ is sufficient to complete the isomerization. In both methods, the formation of the catalytically active compounds can be followed by E.S.R. spectroscopy[8,9]. The occurrence of the E.S.R. signal at $g = 1.993$ ($\Delta H_{pp} = 0.3$-0.6 mT) always coincides with the start of isomerization.



$$H_2C=\overset{R^1}{\overset{|}{C}}-\overset{R^2}{\overset{|}{C}}H-CH_2-\overset{R^3}{\overset{|}{C}}=CH-R^4 \xrightarrow{\text{titanocenes}, \nabla}$$

1a-e

$$\left[H_3C-\overset{R^1}{\overset{|}{C}}=\overset{R^2}{\overset{|}{C}}-CH_2-\overset{R^3}{\overset{|}{C}}=CH-R^4\right] \xrightarrow{\text{titanocenes}, \nabla}$$

2a-e

$$H_3C-\overset{R^1}{\overset{|}{C}}=\overset{R^2}{\overset{|}{C}}-CH=\overset{R^3}{\overset{|}{C}}-CH_2-R^4$$

(E,E)-**3a**, *(E,Z)*-**3a**, *(Z,Z)*-**3a**
(E)-**3b**, *(Z)*-**3b**
(E,E)-**3c**, *(Z,E)*-**3c**
3d
(E)-**3e**, *(Z)*-**3e**

1-3	R^1	R^2	R^3	R^4
a	H	H	H	H
b	H	H	CH_3	H
c	H	CH_3	H	CH_3
d	CH_3	H	CH_3	H
e	H	└ CH_2	H	┘

Both methods effect clean isomerization of the 1,5-dienes **1a-e** to the corresponding conjugated dienes **3** by a stepwise convergent shift of the double bonds via the intermediates **2**. The concentration of the intermediates **2** is relatively high in the beginning of the reaction. Compounds **2b, c, e** could be isolated by preparative G.L.C. after quenching the reaction mixture with air 10-30 min after beginning of the reaction. The structure of compounds **2** shows that the terminal C=C double bonds are more reactive than the disubstituted C=C double bonds. Compounds **2** are the main impurity in the final products **3**.

The product mixture obtained from the isomerization of 1,5-hexadiene (**1a**) consists of (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-2,4-hexadiene (**3a**); the composition of this mixture differs from that obtained by dehydration of 2-hexen-4-ol[11]. 2,5-Dimethyl-2,4-hexadiene (**3d**) is obtained as the only product from 2,5-dimethyl-1,5-hexadiene (**1d**). The analogous reaction of the 1,5-dienes **1b, c, e** affords the conjugated dienes **3b, c, e** as mix-

$$H_2C=CH-CH_2-CH_2-CH_2-CH_2-CH=CH_2 \xrightarrow{\text{titanocenes}, \nabla}$$

1f

$$H_3C-CH=CH-CH=CH-CH_2-CH_2-CH_3$$

3f

+

$$H_3C-CH_2-CH=CH-CH=CH-CH_2-CH_3$$

3f'

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tures of stereoisomers. The selectivity of the isomerization is lost with compounds such as 1,7-octadiene (**1f**) in which the distance between the two double bonds is too long. Thus, a 2 + 1 mixture of 2,4-octadienes (**3f**) and 3,5-octadienes (**3f′**) is obtained from **1f**.

The isomerization fails completely with 1-methyl-4-isopropenylcyclohexene (limonene), even under drastic conditions; this result shows that trisubstituted C=C double bonds exhibit only low reactivity towards titanium catalysts. We utilized this feature for the isomerization of vinylcyclohexane (**4a**) and vinylcyclooctane (**4b**) to pure ethylidenecyclohexane (**5a**) and ethylidenecyclooctane (**5b**), respectively. Both conversions proceed with nearly quantitative yield.

4a n = 5 **5a** n = 5
4b n = 7 **5b** n = 7

An extension of this method to the preparation of di- or poly(ethylidene)-cycloalkanes should present problems since *cis*- and *trans*-1,2-divinylcyclohexane yield ring-closure products[12] under similar conditions.

The yields of products **3a, b, d, e** obtained by our method are better than those reported for the calcium amide-[4] and potassium *t*-butoxide-promoted[5] isomerization. Compounds **1a, e** and **4a, b** have also been isomerized to the corresponding dienes **3** and **5**, respectively, using nickel catalysts[6]; experimental conditions and quantitative results were not reported, however.

The surface quality of the lithium alanate (lithium aluminum hydride) is crucial for rapid reduction; of the many samples tested, only those of Metallgesellschaft AG (Frankfurt/M) worked reliably. Lithium alanate and bis[cyclopentadienyl]-titanium dichloride (Cp_2TiCl_2; Schuchardt, München) were used as received.

Isomerization of Non-conjugated Dienes (1) to Conjugated Dienes (3); General Procedure:

Purification of Non-conjugated Dienes **1**: Commercial samples of the dienes **1** (Fluka) are refluxed over lithium alanate under an argon atmosphere and then heated repeatedly at 100 °C with fresh portions of (η^5,η^5-fulvalene)-di-μ-hydrido-bis[cyclopentadienyltitanium(III)] $[C_{10}H_8)(H)_2(CpTi)_2]$ in sealed ampoules until the solution remains green. Pure olefins were distilled under vacuum into ampoules for storage.

Method A: The purified diene **1** (30 ml) is added to lithium alanate (0.15 g, 4 mmol) and bis[cyclopentadienyl]-titanium dichloride (0.25 g, 1 mmol) under argon and the mixture is stirred and refluxed [the molar ratio Ti : Al = 1 : 4, which represents an excess over the stoichiometry of the reduction, is used to shorten the reaction time]. Hydrogen is evolved during the reduction. The exothermic isomerization starts when the green color of the mixture changes to blue or purple due to the formation of bis[cyclopentadienyl]-alkenyltitanium complexes. The mixture is refluxed for the time given in the Table and the product then distilled in vacuo. The pyrophoric residue is quenched with toluene/ethanol.

Method B: A solution of (η^5,η^5-fulvalene)di-μ-hydrido-bis[cyclopentadienyltitanium(III)] $[C_{10}H_8)(H)_2(CpTi)_2]$ is prepared by reducing bis[cyclopentadienyl]-titanium dichloride (Cp_2TiCl_2; 0.25 g, 1 mmol) with lithium alanate (0.15 g, 4 mmol) in mesitylene or xylene (30 ml) under the conditions described in Method A[10]. In boiling mesitylene, the reaction is complete within 20 min. The mixture is cooled to room temperature and the bright-green solution (λ_{max} = 828 nm, $\log\varepsilon \approx 3.0$) is decanted from the black sediment. The solution (2 ml containing

Table 1. Titanocene-Catalyzed Isomerization of Non-conjugated Dienes (**1**) and Vinylcycloalkanes (**4**)

Substrate	Reaction temperature and time [°C], [h]		Yield[a] [%]		Composition[b] [%] of products		b.p./torr [°C]	n_D^{20}	Literature data	
	Method A	Method B	Method A	Method B					b.p./torr [°C]	n_D^{20}
1a	60–70°, 10	160°, 4	94	96	(*E,E*)-**3a**	44[c]	80–82°	1.4540	81.5–82°[11]	1.4527–1.4548[11]
					(*E,Z*)-**3a**	36[c]				
					(*Z,Z*)-**3a**	16[c]				
1b	—	180°, 5	—	97	(*E*)-**3b**	60[d]	102–104°	1.4655	111.5°[4]	1.4680[4]
					(*Z*)-**3b**	34[d]				
					2b[h]	2				
1c	—	180°, 5	—	97	(*E,E*)-**3c**[h]	74[e]	132–133°	1.4725		
					(*Z,E*)-**3c**[h]	24				
					2c[h]	1				
1d	115–130°, 2	180°, 5	95	98	**3d**	99	132–134°	1.4780	134.5°[4]	1.4781[4]
1e	130°, 2	170°, 4	95	96	(*E*)-**3e**	57[f]	138–140°	1.5010		
					(*Z*)-**3e**	41[f]				
					2e[h]	2				
1f	117°, 3	170°, 5	90	94	**3f**	60[g]	130–135°	1.4535	133.5–134°[14]	n_D^{25}: 1.4542[14]
					3f′	30[g]				
4a	—	180°, 2	—	98	**5a**	98	136°	1.4616	136°[15]	1.4618–1.4631[15]
4b	—	180°, 2	—	98	**5b**	98	183–185°	1.4778	70–72°/50[16]	

[a] Yield of distilled product or product mixture.

[b] Determined by G.L.C. and G.L.C.-M.S. analyses for product mixtures or products obtained by Method B. Method A yielded very similar product compositions.

[c] Identified by G.L.C. comparison with a standard mixture (2.5 m, ECNSS-M 1% on Gaschrom Q).

[d] U.V. (hexane): λ_{max} = 237 nm.

[e] Lit.[13] gives no physical constants for (*E,E*)-**3c** and (*Z,E*)-**3c**. Adduct of (*E,E*)-**3c** with maleic anhydride, ¹H-N.M.R. ($CDCl_3$/TMS): δ = 5.50 (m, 1H, J = 3.3, 2.8 Hz); 3.34 (dd, 1H, J = 9.2, 6.0 Hz); 3.25 (dd, 1H, J = 9.2, 5.2 Hz); 2.5 (m, 1H, J = 7.4, 5.2, 2.8 Hz); 2.1 (m, 1H, J = 6.0, 3.3 Hz); 1.8 (m, 2H); 1.75 (m, 3H); 1.48 (d, 3H, J = 7.4 Hz); 1.06 ppm (t, 3H, J = 7.3 Hz).

[f] Determined from the ¹H-N.M.R. spectrum of the mixture.

[g] Determined from the ¹³C-N.M.R. spectrum (JEOL-FX-60 spectrometer, 15.036 MHz, FT-mode).

[h] These products were also isolated in pure form by preparative G.L.C. of the mixtures.

Table 2. I.R.- and ^{1}H-N.M.R.-spectral Data of Compounds **2** and **3**

Compound or compound mixtures	I.R. (neat) ν [cm^{-1}]	^{1}H-N.M.R. (CDCl$_3$/TMS) δ [ppm]
2b	3072, 3016, 1780, 1647, 1372, 958, 882, 687, 547	
2c	3074, 3020, 1666, 1382, 966, 822, 696	5.4 (m, 2 H); 5.2 (m, 1 H); 2.67 (dd, 2 H, J=11.6, 4.4 Hz); 1.67 (d, 3 H, J=5.2 Hz); 1.60 (s); 1.58 (dd, J=5.2 Hz)
2e	3026, 1654, 1623, 1395, 1386, 1172, 1040, 910, 817, 660	5.68 (s, 2 H); 5.3 (m, 1 H); 2.75 (m, 2 H); 2.2 (m, 4 H); 1.60 (d, 3 H, J=6.4 Hz). A non-distinguishable mixture of (E)- and (Z)-isomers cannot be excluded.
(E,E)-**3a** (44%) + (E,Z-**3a** (36%) + (Z,Z)-**3a** (16%)	3020, 1653, 1626, 1375, 988, 928, 818, 703, 596	
(E)-**3b** (60%) + (Z)-**3b** (34%) + **2b** (2%)	3016, 1658, 1622, 1607, 1034, 985, 953, 926, 865, 715, 453	
(E,E)-**3c** (74%) + (Z,E)-**3c** (24%) + **2c** (1%)	3020, 1650, 1640, 1622, 1606, 1382, 1032, 966, 910, 814, 795, 717	
(E,E)-**3c**		6.06 (d, 1 H, J=15.5 Hz); 5.6 (m, 1 H); 5.45 (m, 1 H); 1.72 (s, 3 H); 1.7 (m, 5 H); 1.01 (t, 3 H, J=7.5 Hz)
(Z,E)-**3c**		6.44 (d, 1 H, J=14.2 Hz); 5.75 (m, 1 H); 5.5 (m, 1 H); 1.8 (m, 2 H); 1.73 (s, 3 H); 1.71 (d, 3 H); 1.04 (t, 3 H, J=7.4 Hz)
3d	3024, 1649, 1621, 1387, 1373, 1168, 1053, 986, 840, 541, 447	
(E)-**3e** (57%) + (Z)-**3e** (41%) + **2e** (2%)	3026, 1647, 1608, 1387, 1342, 1260, 1008, 934, 870, 864, 835, 735, 727, 568	
(E)-**3e**		6.03 (ddd, 1 H, J=9.8, 2.2, 1.6 Hz); 5.67 (ddd, 1 H, J=9.8, 4.1, 4.0 Hz); 5.31 (q, 1 H, J=7.2 Hz); 2.3 (m, 4 H); 2.1 (m, 2 H); 1.69 (d, 3 H)
(Z)-**3e**		6.42 (ddd, 1 H, J=10.4, 3.0, 1.9 Hz); 5.82 (dddd, 1 H, J=10.4, 4.0, 4.0, 1.8 Hz); 5.17 (q, 1 H, J=6.9 Hz); 2.3 (m, 4 H); 2.1 (m, 2 H); 1.66 (d, 3 H)
3f (60%) + **3f′** (30%)	3021, 1653, 1630, 1380, 989, 980, 947, 927, 820, 728, 710	
5a	1673, 1387, 1344, 1237, 1012, 898, 857, 818, 622	5.20 (qdd, 1 H, J_q=6.6, J_{dd}=1.2 Hz); 1.9 (m, 4 H); 1.40 (d, 3 H, J=6.6 Hz); 1.4 (m, 6 H)
5b	1660, 1386, 1360, 1116, 1027, 874, 826, 789, 741, 571	5.25 (qdd, 1 H, J_q=6.9, J_{dd}=0.8 Hz); 2.2 (m, 4 H); 1.58 (d, 3 H, J=6.9 Hz); 1.5 (m, 10 H)

~0.03 mmol of the catalyst) is evaporated to dryness in vacuo in an ampoule, the diene **1** (30 ml) is distilled into the ampoule under vacuum, the ampoule is sealed, and heated as indicated in the Table. The ampoule is then opened and the product isolated by distillation in vacuo.

Isolation and Identification of Products: The composition of the product mixtures obtained was determined by G.L.C. analysis on a Perkin-Elmer F 21 preparative gas chromatograph using SE-30 (3%) and Carbowax 20 M (15%) columns (length 2.5 m). The identification of products obtained from **1a, b, d** was carried out by comparison of their G.L.C., G.L.C.-M.S. data and I.R. spectra with those of authentic samples. Compounds **2b, c,** (E,E)-**3c**, (Z,E)-**3c**, and **2e** were isolated by preparative G.L.C. on Carbowax 20 M (15% on Chromosorb W) column (length 2.5 m). Their structures and structures of final products obtained from **1e** and **4a, b** were determined by ^{1}H-N.M.R. spectrometry. Adduct formation of (E,E)-**3c** with maleic anhydride supported the ^{1}H-N.M.R. assignment. Compounds (E)-**3e** and (Z)-**3e** could not be separated by G.L.C. and therefore their percentages were determined by ^{1}H-N.M.R. spectrometry (which distinguishes clearly between both isomers). ^{1}H-N.M.R. spectra were measured on a Varian XL-200 superconducting instrument (200.05 MHz). The G.L.C.-M.S. spectra were obtained on a JEOL-JMS D-100 mass spectrometer coupled with a gas chromatograph (column SE 30, 3%, 2.5 m).

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