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The Homogeneous Hydrogenation of Acetylenes by Dicyclopentadienyltitaniumdicarbonyl[1]

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The homogeneous hydrogenation of acetylenes and olefins in the presence of dicyclopentadienyltitaniumdicarbonyl (I) was studied. The results of the hydrogenation varied with the acetylene substituent. The relative activating effects of the substituents on the hydrogenation of such acetylenes as RC≡CH and R'C≡CR' are as follows: R: Ph>*t*-butyl>*n*-alkyl, R' : Ph>*n*-alkyl. The order is the reverse of that observed with the usual metal catalysts of the VIII group. In order to elucidate the mechanism of hydrogenation, the reaction of the dicarbonyl (I) with various acetylenes was studied, and the structures of the products were discussed.

Previous works in this laboratory have elucidated the catalytic behaviors of various metallocenes and their analogues, such as dibenzenechromium,[2] nickelocene[3] and vanadocene.[4] During the course of an investigation of the catalytic actions of dicyclopentadienyltitaniumdicarbonyl (I) as a part of the above works, it was found that the compound I acts as a catalyst in a homogenous phase for the hydrogenation of 1-pentyne to 1-pentene under mild conditions.

The hydrogenations of other acetylenes and olefins by this catalyst have now been studied. The reductions were generally carried out in hydrocarbon solutions for 30 min. at 50—65°C under an initial hydrogen pressure of 50 atm. The results are summarized in Table I. The results of the catalytic reactions varied with the acetylene substituent. For example, 1-alkynes such as 1-pentyne and 1-hexyne were partially hydrogenated to 1-alkenes, while phenylacetylene was completely reduced to ethylbenzene and *t*-butylacetylene gave a mixture of partially and completely hydrogenated products. No hydrogenation was observed in the case of an alkyne without a terminal methylidyne group, 3-heptyne, although diphenylacetylene was completely hydrogenated to dibenzyl. On the basis of these results, the relative activating effects of the substituents of such acetylenes as RC≡CH and R'C≡CR' on the hydrogenation may be estimated as follows: R: Ph>*t*-butyl>*n*-alkyl, R': Ph>*n*-alkyl. It is interesting that the order is the reverse of that observed in the hydrogenations by the group VIII metal catalysts.

When the hydrogenation of phenylacetylene was carried out using a half quantity of hydrogen for complete reduction, 30% of ethylbenzene, 40% of styrene and 30% of recovered phenylacetylene were detected. The reduction must, therefore, involve a two-step process in which the phenylacetylene is first hydrogenated to styrene. In contrast with the complete hydrogenation of

1) Presented at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

2) H. Yamazaki, M. Yamaguchi and N. Hagihara, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **83**, 959 (1962); *Annual Reports of the Institute for Fibre Reserch*, **16**, 495 (1963).

3) H. Yamazaki, T. Nishido and N. Hagihara, Abstracts of the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April (1965), p. 448.

4) R. Tsumura and N. Hagihara, This Bulletin, **37**, 1889 (1964).

TABLE I. HYDROGENATION OF OLEFINS AND ACETYLENES WITH DICYCLOPENTADIENYLTITANIUMDICARBONYL[a]

Substrate	Catalyst solution[b]	Reaction temp. °C	Reaction time min.	Product (yield, %)	Recovery %	Remarks
Styrene	A	50—60	30	Ethylbenzene (15)	85	c
Styrene	A	50—65	120	Ethylbenzene (70)	30	c
trans-Stilbene	A	50—60	30	—	100	d
Butadiene	B	50—65	30	—	—	d
1, 3-Cyclooctadiene	A	50—65	30	—	—	d
Acetylene	B	50—60	30	—	—	d
1-Pentyne	A or B	50—60	30	1-Pentene (95)	0	c, e
1-Hexyne	A	50—60	30	1-Hexene (90)	10	c
t-Butylacetylene	A	50—60	30	3, 3-Dimethyl-1-butene (40) 2, 2-Dimethylbutane (60)	0	c
3-Heptyne	A or C	50—65	30	—	100	c
Phenylacetylene	A or B	50—60	30	Ethylbenzene (95)	5	c, e
Diphenylacetylene	A	50—60	30	Dibenzyl (90)	0	e

a) Reactions were generally carried out with 20 mmol. of substrate, dissolved in 20 ml. of the catalyst solution, in a 100 ml. autoclave under an initial hydrogen pressure of 50 atm.
b) The catalyst solutions A, B and C were prepared as follows. Freshly sublimed dicyclopentadienyl titaniumdicarbonyl was dissolved in benzene (catalyst A), in *n*-heptane (B) or in xylene (C) (the concentration 25 mmol./l.) and stocked in a Schlenk tube under argon.
c) Yield was determined by gas chromatography.
d) No absorption of hydrogen was observed.
e) Yield was determined by isolation.

TABLE II. NUCLEAR MAGNETIC RESONANCE DATA

Compound	Position of peak (τ)[a]	Relative intensity[b]	Multiplicity	Assignment
$(\pi\text{-}C_5H_5)_2Ti(C_6H_5C{\equiv}CC_6H_5)_2$ in CCl_4	3.8	10	Singlet	C_5H_5
	3.3	20	Multiplet	C_6H_5
$(\pi\text{-}C_5H_5)_2Ti(C_6H_5C{\equiv}CH)_2$ in CCl_4	3.8	12	Singlet	$C_5H_5 + {\equiv}CH$
	3.2	10	Multiplet	C_6H_5

a) Relative to $SiMe_4$ as internal standard.
b) Estimated to whole numbers by method of counting squares, relative to $C_5H_5=5$.

phenylacetylene, 1-alkynes were effectively subjected to partial hydrogenation to 1-alkenes. These facts also suggest that the kind of the substituent on acetylenes affects the type of hydrogenation.

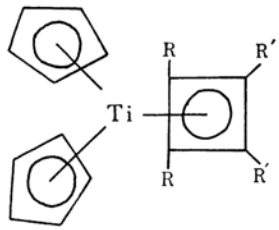
In the hydrogenation of olefins and butadiene, only very slow absorption, or no absorption at all, of hydrogen was observed.

On the other hand, it was reported by Breslow and his collaborators[5] that the soluble Ziegler-type catalysts activated hydrogen for the homogeneous hydrogenation of olefins. It has been suggested that the study of the cited soluble catalysts should shed some light on the mechanism of the heterogeneous hydrogenat·on of olefins. However, in order to explain the mechanism of the hydrogenation in terms of organometallic chemistry, it is more useful to study the simple organometallic complex catalyst than to study a combined one, such as the Ziegler-type catalyst, because such a simple complex will make more convenient the isolation of an intermediate of the reaction.

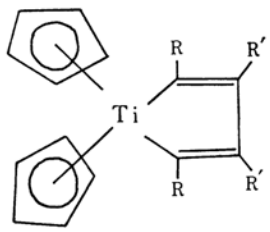
Thus, in the present study the isolation of the intermediate was attempted. The dicarbonyl complex (I) was heated to 60°C for 20 min. with diphenylacetylene in a benzene solution under an inert atmosphere. From the reaction mixture, by chromatography on alumina and recrystallization from *n*-hexane, air-stable green crystals (II) were obtained in a 15% yield. On the other hand, Volpin and his collaborators[6] reported the synthesis of the same complex (II) by the reaction of diphenylacetylene, sodium cyclopentadienide and titanium tetrachloride. On the basis of the products of the reaction with hydrochloric acid or potassium hydroxide, they proposed the structures A and B. The present authors also investigated the structure of the complex II by means of studies of the NMR, infrared and electronic absorption spectra. The infrared spectrum of the complex II is in accord with either structure, A or B, because it shows π-bonded cyclopentadienyl

5) M. F. Sloan, A. S. Matlack and D. S. Breslow, *J. Am. Chem. Soc.*, **85**, 4014 (1963).

6) M. E. Volpin, V. A. Dubovitskii, O. V. Nogina and D. N. Kursanov, *Dokl. Akad. Nauk SSSR*, **151**, 1100 (1963); *Chem. Abstr.*, **59**, 14012 (1963).



(A)



(B)

ligand absorptions and absorptions of sterically-hindered phenyl groups which are similar to that of π-cyclopentadienylcobalttetraphenylcyclobutadiene.[7] The data of NMR spectra are given in Table II, together with some assignments. The NMR spectrum of the complex II shows the aromatic multiplet at 3.2—3.65 τ and a sharp π-bonded cyclopentadienyl singlet at 3.8 τ. The phenyl/cyclopentadienyl proton ratio is 2.0 (calcd. 2.0).

The electronic absorption spectrum of the complex II is very similar to those of hexaphenylsilole, pentaphenylarsole and pentaphenylphosphole,[8] and it shows no characteristic absorption band of tetrasubstituted cyclobutadiene derivatives in the region of 320 mμ.[9,10] This fact supports the structure B, which has more sterrically-hindered phenyl groups than does the structure A.

The reaction of phenylacetylene with dicyclopentadienyltitaniumdicarbonyl was carried out under similar conditions. After the purification by chromatography on alumina, air-stable green needles (III) and a linear oligomer of phenylacetylene were obtained (yields, 7% and 25% respectively). The infrared spectrum of the complex III shows no acetylenic absorption bands, but it does show phenyl and π-bonded cyclopentadienyl absorptions. The NMR spectrum also shows phenyl and π-bonded cyclopentadienyl absorptions, where the ≡CH-proton band overlaps with the cyclopentadienyl band. The proton

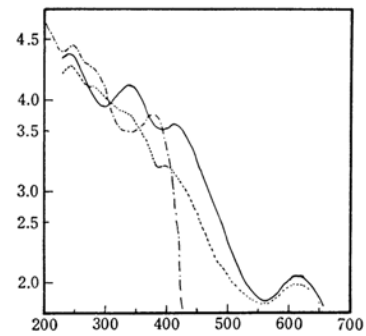
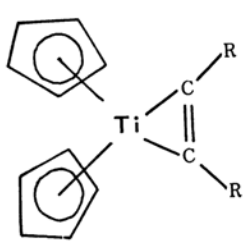


Fig. 1. The electronic absorption spectra of the complexes II and III and hexaphenylsilole.[8]
····· II in tetrahydrofuran
—— III in tetrahydrofuran
–·– hexaphenylsilole in cyclohexane

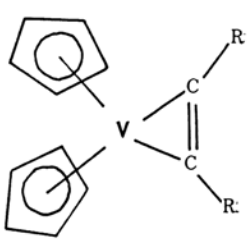
ratio of cyclopentadienyl (including methylidyne protons)/phenyl is 1.2 (calcd. 1.2). The electronic absorption spectrum of the complex III is given in Fig. 1. From the above consideration, it may be concluded that the complex III should have either the structure A or B. Of these structures, B seems more probable for the complex III as in the case of the complex II, since the complex III is even more stable than the complex II. However, we failed in an attempt to obtain structural proof by the direct synthesis of the complex III from the dicyclopentadienyltitanium dichloride and 1, 4-dilithiotetraphenylbutadiene by analogy with the synthesis of 1, 1-bis(π-cyclopentadienyl)-2, 3, 4, 5-tetraphenylzirconacyclopentadiene.[8]

When acetylene or pentyne is employed in a similar reaction with the dicarbonyl I, unstable green oils are obtained. Further investigation of these oils has been given up, however, because of their instability. Olefins and butadiene do not react with the dicarbonyl I. This finding agrees with the fact that the hydrogenation of olefins and butadiene is very slow.

Neither complex, II or III, catalyzes the hydrogenation of acetylenes. Therefore, the exact mechanism of the catalytic hydrogenation of acetylenes is not yet clear. However, it is possible at present to speculate that the active intermediate in the hydrogenation is a precursor of



(IV)



(V)

7) A. Nakamura and N. Hagihara, This Bulletin, **34**, 452 (1961).
8) E. H. Braye, W. Hübel and J. Caplier, *J. Am. Chem. Soc.*, **83**, 4406 (1961).
9) H. P. Fritz, *Z. Nautrforsch.*, **16b**, 415 (1961).
10) R. Huttel and H. J. Neugebauer, *Tetrahedron Letters*, **1964**, 3541.

the complex II or III, such as the complex IV, an analogue of the vanadium complex V which was reported on in a previous paper.[11]

Recently, the hydrogenation of olefins by dicyclopentadienyltitanium, which had been obtained by the decomposition of dicyclopentadienyldimethyltitanium with hydrogen,[12] was reported by Shikata and his collabolators.[13]

Experimental

The proton NMR data were obtained on a Varian A 60 spectrometer and a Japan Electron Optics Lab. JNM-4H-100 spectrometer, using tetramethylsilane as the internal standard. The infrared spectra were recorded on a Hitachi EPI-1 spectrometer. Gas chromatographic anaylses were carried out on Shimadzu GC-1 and GC-2B gas chromatographs. The melting and decomposition temperatures were observed by means of a hot-stage microscope and were not corrected.

The General Procedure of Hydrogenation.—The hydrogenation reactions were carried out in a 100-ml. autoclave. Since the catalyst was sensitive to air and moisture, all operations were carried out in an inert atmosphere. After the autoclave had been flushed with nitrogen, 20 ml. of the catalyst solution A, B or C (see below) was transferred from the stock tube by a syringe; then acetylene or olefin was charged in. The reduction was carried out under an initial hydrogen pressure of about 50 atm. and at 50—60°C for 30 min.. Although the hydrogenation of acetylenes did not proceed under 50°C, the rapid hydrogen uptake started at 50°C. In the case of olefins, no rapid reduction took place, even at 100°C. After the reaction, the hot solution was left standing in order to cool it. The products were analyzed and identified either by isolation or by gas chromatography. Several typical hydrogenation experiments are described below.

The Preparation of the Catalyst Solution.—Freshly-sublimed dicyclopentadienyltitaniumdicarbonyl was dissolved in benzene (catalyst A), in *n*-heptane (catalyst B) or in xylene (catalyst C), each concentration being 25 mmol./l., and stocked in a Schlenk tube under argon.

The Hydrogenation of 1-Pentyne.—A 100-ml. autoclave was charged with 2 ml. (20 mmol.) of 1-pentyne and 20 ml. of the catalyst solution A under nitrogen, and then with hydrogen up to a pressure of 50 atm. It was heated under shaking. A rapid hydrogen uptake started at 50°C, and the hydrogenation finished almost completely within 10 min. After it had been cooled with water, the reaction mixture was analyzed by gas chromatography. Found: 1-pentene 95%. Pentyne and pentane were not detected. (Dinonyl phthalate 3 m.; flow rate 32 ml./min. N_2; 55°C.) In a similar experiment, in which 5 g. of 1-pentyne, 0.5 g. of dicyclopentadienyltitaniumdicarbonyl and 20 ml. of benzene were used, 4.5 g. (90%) of 1-pentene was isolated by fractional distillation.

The Hydrogenation of Diphenylacetylene.—Into a 100-ml. autoclave, 3.4 g. of diphenylacetylene, 30 ml. of the catalyst solution A and 50 atm. of hydrogen were charged. The autoclave was shaken and heated. A rapid pressure drop took place at 50°C. After 30 min., the autocalve was cooled with water. The removal of the solvent yielded 3.6 g. of a pale yellow solid. It was purified by sublimation and recrystallization from methyl alcohol to give 3 g. of dibenzyl, m. p. 50—51°C (lit. 51.5—52.5°C). The infrared spectrum was identical with that of an authentic specimen.

The Partial Hydrogenation of Phenylacetylene. Into a 100-ml. autoclave, 2.7 g. (22 mmol.) of phenylacetylene, 20 ml. of the catalyst solution A and 6 atm. of hydrogen (22 mmol. of hydrogen) were charged. The autoclave was then shaken and heated. A rapid pressure drop took place at 50°C. After all the hydrogen had been absorbed, the autoclave was cooled with water. The reaction mixture was analyzed by gas chromatography, a study of its infrared spectrum, and the amount of the hydrogen absorption. Found: ethylbenzene 30%, styrene 40%, phenylacetylene 30%. (Thermol-2 3 m. and silicon-550 1.5 m.; flow rate 67 ml./min. N_2; 120°C; retention time: ethylbenzene 13 min.; styrene and phenylacetylene 16.5 min.) The styrene/phenylacetylene ratio was determined by the a amount of hydrogen absorption.

The Reaction of Diphenylacetylene with Dicyclopentadienyltitaniumdicarbonyl (I).—Dicylcopentadienyltitaniumdicarbonyl (I) (1.0 g., 4.3 mmol.) and diphenylacetylene (1.5 g., 8.6 mmol.) were heated in 20 ml. of benzene for 20 min. at 60°C. A violent evolution of gas took place, and the color of the reaction mixture changed to a greenish brown from red brown. After the mixture had cooled, the solvent was removed in vacuo and a green solid was obtained. Purification by chromatography on alumina and recrystallization from *n*-hexane yielded 0.3 g. of green crystals (II), m. p. 150°C in a sealed tube under nitrogen. A longer reaction time and a higher reaction temperature diminished the yield. Chromatographic purification must be carried out as quickly as possible because the green complex (II) slowly decomposes on alumina.

Found: C, 85.02; H, 5.59. Calcd. for $C_{38}H_{30}Ti$: C, 85.38; H, 5.66%.

An infrared spectrum in Nujol showed absorptions at 3080(w), 3040(w), 1590(m), 1495(sh), 1478(sh), 1442(m), 1362(w), 1257(s), 1175(w), 1152(w), 1145(w), 1095(sh), 1073(s), 1015(s), 940(vw), 905(vw), 835(w), 825(m), 803(vs), 796(vs), 772(m), 768(s), 750(m), 720(m), 697(vs), and 692(vs).

An electronic spectrum showed absorptions at 624 mμ (log ε, 1.90), 405 mμ (log ε, 3.16), 334 mμ (sh), 278 mμ(sh), and 240 mμ (logε, 4.24) in tetrahydrofuran.

The Reaction of Phenylacetylene with Dicyclopentadienyltitaniumdicarbonyl. — The dicarbonyl complex I (2.34 g., 10 mmol.) and phenylacetylene (2.0 g., 20 mmol.) were heated in 20 ml. of *n*-hexane for 20 min. at 60°C under nitrogen. A violent evolution of gas was observed, and the reaction mixture turned dark brown. The chromatography of the reaction mixture on alumina yielded 0.15 g. of an oxygenated product of the dicarbonyl complex I, 0.3 g. of a green solid (III), and 0.5 g. of a brown oligomer of phenylacetylene. After the recrystallization of the green solid (III) from *n*-hexane, 0.25 g. of green needles were obtained. M. p., 134—136°C in a sealed tube under nitrogen; yield, 7%.

11) R. Tsumura and N. Hagihara, This Bulletin, **38**, 861 (1965).
12) K. Caus and H. Bestian, *Ann.*, **654**, 8 (1962).
13) K. Shikata, K. Nishino and K. Azuma, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **68**, 358 (1965).

Found: C, 81.95; H, 5.84. Calcd. for $C_{26}H_{22}Ti$, C, 81.67; H, 5.82%.

An infrared spectrum in Nujol showed absorptions at 3080(w), 3055(w), 1590(s), 1568(w), 1482(s), 1443(m), 1437(m), 1300(vw), 1277(w), 1262(vw), 1200(vw), 1175(vw), 1150(vw), 1125(vw), 1070(m), 1020(s), 1010(s), 992(vw), 920(vw), 895(vw), 840(s), 820(vs) 810(vs), 802(sh), 750(vs), 745(sh), and 690(s).

An electronic absorption spectrum showed λ_{max} at 608 mμ (log ε, 2.14), 410 mμ (log ε, 3.55), 340 mμ (log ε, 4.16), and 238mμ (log ε, 4.32) in tetrahydrofuran.

The Attempted Reaction of Dicyclopentadienyltitanium Dichloride with 1, 4-Dilithiotetraphenylbutadiene.—A suspension of 1, 4-dilithiotetraphenylbutatriene, prepared from 2 g. of diphenylacetylene in 5 ml. of ether as described by Braye and his collaborators,[8] was added to a suspension of 2 g. of dicyclopentadienyltitanium dichloride in 100 ml. of ether. After the mixture had been refluxed for 3 hr., the formation of no product could be observed and the dichloride was recovered. A similar reaction was also attempted in tetrahydrofuran, but no reaction took place.

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