Inorganica Chimica Acta, 47 (1981) 197–199
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Action of Diphenylketene on Alkyltitanates Ti(OR)$_4$

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Received July 12, 1980

Insertion of diphenylketene into the titanium–oxygen bond of alkyltitanates $Ti(OR)_4$ (with $R = C_2H_5$, $i\text{-}C_3H_7$, C_6H_5.....) resulted in the unexpected generation of a titanium-carbon bond and a series of complexes $(RO)_{4-n}Ti(CPh_2C(O)OR)_n$ (with n = 1, 2) was obtained and characterized by spectroscopical data and hydrolysis products. Action of molecular oxygen changed Ti–C into Ti–O–C (autoxidation) and after hydrolysis α hydroxy esters (benzilates) were obtained.

Introduction

Reactions of heterocumulenes such as isocyanates RNCO, and ketenes R_2CCO with transition metal complexes are currently used as models for activation of the isoelectronic carbon dioxide CO_2 [1]. In fact, ketenes may be involved either in insertion reactions or adduct formation. Very little is known about insertion of ketenes on titanium derivatives but it is assumed to take place intermediately in the synthesis of β hydroxyesters by action of the ketene $H_2C{=}C{=}O$ on ketones using Ti(OR)$_4$ as catalyst [2].

More recently diphenylketene was found to react with $Cp_2Ti(CO)_2$ resulting in a η^2 bonded carbonyl in the 1:1 adduct and a new type of metallocycle in the 1:2 adduct [1].

We now report the action of diphenylketene on titanium alkoxides, leading, by an insertion process, to the unexpected formation of a titanium–carbon bond. By autoxidation and hydrolysis the corresponding α hydroxy ester is obtained.

Results and Discussion

When diphenyl ketene $(C_6H_5)_2C{=}C{=}O$ was reacted with alkyltitanates Ti(OR)$_4$ ($R{=}C_2H_5$, $i\text{-}C_3H_7$, C_6H_5, $p\text{-}CH_3O{-}C_6H_4$) in 1:1 or 2:1 molar ratio, new complexes were obtained and isolated in good yield as reddish liquids when $R{=}C_2H_5$, and as yellow microcrystalline solids in all other cases. Analytical data confirmed that one and two molecules of ketene are respectively added to the starting Ti(OR)$_4$ and the complexes were generally found to be monomeric in benzene except for the 1:1 molar ratio with $R = C_2H_5$ where the complex is trimeric owing probably to lower steric hindrance in this case. Attempts to react more than 2 equivalents of $Ph_2C{=}C{=}O$ on Ti(OR)$_4$ resulted in a mixture of complexes from which no pure products could be isolated.

The possibility that the complexes so obtained are 1:1 and 1:2 adducts of ketene with Ti(OR)$_4$ similarly to $Cp_2Ti(CO)_2$ is ruled out by IR spectra: the reaction can be followed by the total disappearance of the cumulene absorption at 2095 cm^{-1} and the appearance of an intense absorption near 1730 cm^{-1} which may be assigned to the ester group resulting from the insertion reaction:

$$Ti(OR)_4 + n(C_6H_5)_2C{=}C{=}O \rightarrow (RO)_{4-n}Ti[C(C_6H_5)_2C(O)OR]_n \qquad (1)$$

Ia, $n = 1$, $R = C_2H_5$
Ib, $n = 1$, $R = i\text{-}C_3H_7$
Ic, $n = 1$, $R = C_6H_5$
IIa, $n = 2$, $R = C_2H_5$
IIb, $n = 2$, $R = i\text{-}C_3H_7$

^{1}H NMR spectra showed two separate signals for the inequivalent OR groups, in the expected intensity ratio (1:3 for complexes Ia, Ib, Ic; 1:1 for complexes IIa, IIb), consistent with Scheme (1).

So the action of diphenyl ketene on Ti–OR bond appeared to proceed very similarly to the action of phenyl isocyanate resulting in urethanes [3]. An ester group is formed as a result of the insertion of the C=C= (or C=N–) group of the cumulene into the Ti–OR bond according to the Schemes

(2)

(3)

Reactions described by Scheme 3 result in replacing a metal-oxygen by a metal-carbon bond and are unprecedented and unexpected in titanium chemistry. In fact, all the previously reported insertions of ketenes (essentially H_2CCO) into M–OR bonds refer to metals having some B-character (Hg, Sn....) [4].

The reactivity of the titanium-carbon bond so generated in complexes (I) and (II) was explored.

Hydrolysis led to the expected diphenyl acetate $HCPh_2C(O)OR$ identified analytically and by comparison of physical and spectroscopical (NMR, IR) data with an authentic sample.

Action of molecular oxygen resulted in 'autoxidation' changing Ti–C into Ti–O–C–, as was previously observed for methyl [5] or benzyl [6] titanium derivatives. Here the reaction proceeded according to Scheme (4) leading to complexes (III) and (IV)and after hydrolysis of (III) or (IV) to the α hydroxyester (benzilate) $HOCPh_2C(O)OR$:

$$(RO)_{4-n}Ti\{CPh_2C(O)OR\}_n + n/2O_2 \rightarrow$$

$$(RO)_{4-n}Ti\{OCPh_2C(O)OR\}_n \xrightarrow{nH_2O}$$

$$nHOCPh_2C(O)OR \qquad (4)$$

IIIa, $n = 1$, $R{=}C_2H_5$
IVa, $n = 2$, $R{=}C_2H_5$
IVb, $n = 2$, $R{=}i\text{-}C_3H_7$

The reaction of fixation of gaseous oxygen was followed by volumetric measurements. Complexes were characterized analytically and spectroscopically and the benzilate was identified analytically and by comparison of physical and spectroscopical data (NMR, IR) with an authentic sample.

Polymerization of methyl methacrylate was obtained (but in low yield *ca.* 15%) using complex (Ia) as an initiator. This result is to be compared with $(RO)_3TiCH_3$ which gave 100% yield of polymer under similar experimental conditions [7] while $Ti(OR)_4$ is quite inactive. This supports the idea that Ti–C bond is necessary to initiate the polymerization but steric hindrance makes it less effective in complex (Ia) than in methyl derivatives.

Experimental

Alkyltitanates wery purified by distillation and diphenylketene was prepared by the method of Taylor [8]. Infrared data were obtained using a Perkin Elmer 577 spectrophotometer and KBr plates. ^1H NMR spectra were recorded on a Perkin Elmer R 12 at 60 MHz, using CCl_4 solutions with Me_4Si as internal standard. Molecular weight determinations were made cryoscopically in benzene solutions under argon. Elemental analyses were performed by the Service Central de Microanalyse du C.N.R.S.

Preparation of $(C_2H_5O)_3\ Ti–[C(Ph)_2C(O)OC_2H_5]$ *(Ia)*

Ph_2C_2O (0.80 g, 4.12 mmol) in 3 ml CCl_4 is added dropwise to a solution of $Ti(OC_2H_5)_4$ in equimolar ratio (0.94 g in 5 ml CCl_4) at room temperature. After three hours, the IR spectrum of the red solution shows a new band at 1735 cm^{-1} while the cumulene band (2095 cm^{-1}) has disappeared, and a new quartet signal in the NMR spectrum indicates that the insertion takes place.

After removing the solvent, the residue is dried for two hours *in vacuo*, as a reddish liquid. δ (in ppm): 7.23 (10H, m, C_6H_5), 4.34 (6H, q, CH_2CH_3), 3.88 (2H, q, CH_2CH_3), 1.21 (12H, t, CH_2CH_3). M (found: 1232; calcd. for trimer 1266).

Preparation of $(C_2H_5O)_2Ti–[C(Ph)_2C(O)OC_2H_5]_2$ *(IIa)*

The preparation of (IIa) is similar to the preparation of (Ia), 2:1 mole ratio of the reactants being used. $\nu_{C=O}$ 1735 cm^{-1} (in CCl_4). δ (in ppm): 7.23 (10H, m, C_6H_5), 4.23 (4H, q, CH_2CH_3), 3.81 (4H, q, CH_2CH_3), 1.21 (12H, t, CH_2CH_3).

Preparation of $(i\text{-}C_3H_7O)_3Ti–[C(Ph)_2C(O)Oi\text{-}C_3H_7]$ *(Ib)*

Ph_2C_2O (0.72 g, 3.73 mmol) in 3 ml pentane is added dropwise to a solution of $Ti(O\text{-}i\text{-}C_3H_7)_4$ in equimolar ratio (1.06 g in 5 ml pentane).

The yellow solid obtained is filtered off, washed with pentane and rapidly dried *in vacuo* (it becomes viscous). $\nu_{C=O}$ 1730 cm^{-1} (in nujol). δ (in ppm): 7.21 (10H, m, C_6H_5), 4.85 (4H, m, $CH(CH_3)_2$), 1.26 (18H, d, $CH(CH_3)_2$), 1.04 (6H, d, $CH(CH_3)_2$). *Anal.* Found: C, 64.19; H, 7.78; Ti, 9.94. M: 407. Calcd. for $C_{26}H_{38}O_5Ti$: C, 65.25; H, 7.95; Ti, 10.02%. M: 478.

Complexes (Ia) and (IIb) were prepared in a similar way from the appropriate solutions of alkoxy compounds in pentane and yellow solids were also obtained.

Hydrolysis of complex (Ia)

To 1.24 g of (Ia) in 10 ml pentane, an excess of water is added (2 ml) to obtain a white precipitate. The mixture is then stirred for 1 hour; the precipitate is filtered off and washed with ether.

After evaporation to dryness, the ethereal phase gives the expected ester $HC(Ph)_2COOC_2H_5$. δ (in ppm): 7.23 (10H, m, C_6H_5), 4.94 (1H, s, H), 4.07 (2H, q, CH_2CH_3), 1.10 (3H, t, CH_2CH_3). *Anal.* Found: C, 79.03; H, 6.73. Calcd. for $C_{16}H_{16}O_2$: C, 80.00; H, 6.67%.

Action of oxygen on complex (Ia)

Molecular oxygen is bubbled into a solution of (Ia), (1.24 g in 10 ml CCl_4) for ½ hour; the red mixture becomes yellow after 1 hour's stirring. Evaporation of the solution gives a viscous liquid (complex IIIa). δ (in ppm): 7.21–7.47 (10H, m, C_6H_5), 4.30 (8H, m, CH_2CH_3), 1.18 (12H, m, CH_2CH_3). $\nu_{C=O}$ 1735 cm^{-1} (in CCl_4).

Starting from complex (IIa) complex (IVa) is obtained in the same way. *Anal.* Found: C, 65.95; H, 5.94; Ti, 7.07. Calcd. for $C_{36}H_{40}O_8Ti$: C, 66.68; H, 6.17; Ti, 7.39%.

Starting from (Ib), complex (IIIb) is obtained in a similar way. δ (in ppm): 7.31–7.57 (10H, m, C_6H_5), 4.79 (4H, m, $CH(CH_3)_2$), 1.29 (18H, d, $CH(CH_3)_2$), 1.09 (6H, d, $CH(CH_3)_2$). $\nu_{C=O}$ 1730 cm^{-1} (in CCl_4).

Oxygen analysis: the amount of absorbed gaseous oxygen was volumetrically determinated. For 1.8 g of (IIa) in CCl_4, we measured an absorption corresponding to 62 ml of oxygen (expected volume 75 ml). O_2/Ti ratio measured: 0.83 (calcd.: 1).

Hydrolysis of complex (IVa)

By action of an excess of water, the expected ethyl benzilate $HOC(Ph)_2C(O)OC_2H_5$ is obtained as a very viscous white liquid. ν_{OH} 3480 cm^{-1}; $\nu_{C=O}$ 1725 cm^{-1} (in CCl_4). δ (in ppm): 7.22 (10H, m, C_6H_5), 4.13 (2H, q, CH_2CH_3), 1.11 (3H, t, CH_2CH_3). *Anal.* Found: C, 74.94; H, 6.28. Calcd. for $C_{16}H_{16}O_3$: C, 75.00; H, 6.25%.

Polymerization test

Freshly dried and distilled monomeric methylmethacrylate (5 g, 50 mmol) is added at room temperature to (Ia) (1.05 g, 2.5 mmol) in 5 ml CCl_4.

After 48 hours in daylight, some polymer characterized by ^1H NMR spectroscopy, is obtained in low yield (0.75 g, 15%).

References

1 G. Fachinetti, C. Biran, C. Floriani, A. C. Villa and C. Guastini, *Inorg. Chem.*, *17*, 2995 (1978).
2 L. Vuitel and A. Jacot-Guillarmod, *Helv. Chim. Acta*, *57*, 1713 (1974).
3 O. Meth-Cohn, D. Thorpe and H. J. Twitchett, *J. Chem. Soc.*, C132 (1970).
4 M. F. Lappert and B. Prokai, *Adv. Org. Chem.*, *5*, 225 (1967) and references therein.
5 C. Beermann and H. Bestian, *Angew. Chem.*, *71*, 618 (1959).
6 U. Zucchini, E. Albizzati and U. Giannini, *J. Organometal. Chem.*, *26*, 357 (1971).
7 C. Blandy and D. Gervais, *European Polymer. J.*, *15*, 949 (1979).
8 E. C. Taylor, A. McKillop and G. H. Hawks, *Org. Synth.*, *52*, 36 (1972).