dry (freshly distilled from P_2O_5) benzonitrile was added and the reaction mixture was refluxed for two days. The Raney Nickel was filtered and the filtrates were concentrated *in vacuo*, yielding 2.5 g of a yellow residue decomposing at about 265–270°. A maximum conversion of 9.0 g to the yellow complex was achieved after 10 days refluxing. (Found: Ni, 9.0–11.2. $C_{21}H_{15}N_3Ni$ calcd.: N, 15.95 %.)

This yellow residue was recrystallized from glacial acetic acid yielding long needles of triphenyltriazine, m.p. 228–230°. (Found: C, 81.80; H, 4.85; N, 13.62. $C_{21}H_{15}N_3$ calcd.: C, 81.53; H, 4.89; N, 13.58 %.) The infrared spectrum of this specimen was identical with that of triphenyltriazine and the sample did not depress the melting point of triphenyltriazine upon admixture.

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PRELIMINARY NOTES

A novel synthesis of allyldicyclopentadienyltitanium(III) complexes

Allyldicyclopentadienyltitanium(III)[1,2] and some methylallyl and dimethylallyl homologues[2] have previously been prepared by reaction of 1 mole of dicyclopentadienyltitanium(IV) dichloride with 2 moles of the (methyl)allyl Grignard reagent in ether or tetrahydrofuran solution:

$$(C_5H_5)_2TiCl_2 + 2\ \text{allyl-MgX} \longrightarrow (C_5H_5)_2\text{Ti-allyl} + 2\ \text{MgXCl} + [\text{allyl}^\bullet]. \qquad (1)$$

where allyl = C_3H_5, C_4H_7 or C_5H_9; and X = Cl or Br.

The extremely air-sensitive compounds $(C_5H_5)_2$Ti-allyl are monomeric; they have one unpaired electron per molecule. Evidence has been presented, indicating that the (methyl)allyl group is π-bonded to the metal, as are the cyclopentadienyl ligands[2].

We now wish to report an alternative, and sometimes more convenient way of preparation of allyldicyclopentadienyltitanium(III) complexes, namely by reaction of 1 mole of dicyclopentadienyltitanium(IV) dichloride with 2 moles of isopropylmagnesium bromide and an excess of a suitable 1,3-diene in ether solution:

$$(C_5H_5)_2TiCl_2 + 2\ \text{iso-}C_3H_7MgBr + \text{diene} \longrightarrow (C_5H_5)_2\text{Ti-allyl} + \text{gas} + 2\ MgClBr. \quad (2)$$

When taking pentadiene-1,3 as the diene we prepared 1,3-dimethylallyldicyclopentadienyltitanium in good yield. With butadiene-1,3 1-methylallyldicyclopentadienyltitanium was obtained, but the yield was much lower and the product very impure.

Experimental

All operations were carried out in an atmosphere of purified nitrogen.

Reaction with pentadiene-1,3. A solution of isopropylmagnesium bromide in ether (21.6 ml, 1.85 *M*) was dropwise added to a stirred mixture of 5 grams of powdered dicyclopentadienyltitanium dichloride and 10 ml of pentadiene-1,3 in 100 ml of ether, cooled at 0°C. Gas evolution set in immediately; initially, the reaction mixture became very dark, but after half of the Grignard solution was added the solution gradually turned blue. After the addition of the Grignard solution the mixture was stirred for three hours at room temperature, then refluxed for 30 minutes. The solvent was removed in vacuum and the product evaporated to complete dryness by sucking at an oil pump with a cold trap for 45 minutes. Pentane (350 ml) was added and the mixture stirred for 45 minutes at room temperature; the blue solution was filtered and slowly cooled to −80°. Crude 1,3-dimethylallyldicyclopentadienyltitanium(III) (3.6 grams, $\delta = 72\%$) separated as blue needles. M.p. 87–89° (dec.); $\lambda_{max} = 573$ mμ; found: 19.62% Ti; calcd. for $C_{15}H_{19}Ti$: 19.38% Ti.

For further purification the product was twice recrystallized from pentane (at −80°) in a Schlenk-type three-bulb vessel. M.p. 91–91.5° (dec.); $\lambda_{max} = 578$ mμ; found: 73.23, 72.91% C; 7.90, 7.88% H; 19.41% Ti; calcd. for $C_{15}H_{19}Ti$: 72.87% C; 7.75% H; 19.38% Ti. (Pure 1,3-dimethylallyl-dicyclopentadienyltitanium prepared by method (1) crystallizes in dark blue needles with m.p. 91–91.5° (dec.), $\lambda_{max} = 578$ mμ in cyclohexane[2].)

If an ethereal solution of tert.-butylmagnesium chloride was added to dicyclopentadienyltitanium dichloride and pentadiene-1,3 in the same way as described above, the reaction mixture turned to a clear green. After half of the Grignard solution was added the mixture coloured blue, but much slower than when isopropylmagnesium bromide was used. 1,3-Dimethylallyldicyclopentadienyltitanium was obtained in 45% yield.

Reaction with Butadiene-1,3. Butadiene-1,3 (10 ml) condensed in a cold trap was freed from air and dissolved in 100 ml of ether. If the reaction was carried out in the same way as described above, 21% of impure 1-methylallyldicyclopentadienyltitanium was obtained as a purple powder. A somewhat better yield (30%) was obtained, if the reaction mixture was not boiled, but worked up after standing at room temperature for 20 hours. The product started to melt at about 45° and decomposed under blowing up at 94°; $\lambda_{max} = 539$ mμ. (Pure 1-methylallyldicyclopentadienyltitanium crystallizes as violet platelets; m.p. 96.5–97° (dec.); $\lambda_{max} = 539$ mμ in cyclohexane[2].)

Discussion

The reaction described is somewhat similar to the reaction of isopropylmagnesium bromide with certain metal halides in the presence of cyclic olefines, studied by Fischer and Müller[3]. In crude approximation this reaction may be described as:

$$MCl_x + x\ \text{iso-}C_3H_7MgBr + n\ \text{olefine} \longrightarrow M(\text{olefine})_n + \frac{x}{2}C_3H_8 + \frac{x}{2}C_3H_6 + xMgClBr$$

$(M = Cr, Fe, Ru, Os)$,

but in some cases hydrogen is abstracted from the olefine, while in one case the ligand was hydrogenated. However, no allylic complexes were isolated by Fischer and Müller[3]. According to these authors the alkylmetal complexes originally formed from the metal halide and the Grignard reagent decompose to coordinatively unsaturated products, probably via hydride intermediates. The coordinatively unsaturated products are coordinated by the olefine to give the final products.

Similarly, we assume that in reaction (2) studied by us alkyltitanium complexes are initially formed (step a) which decompose to a titanium hydride complex (step b); the latter intermediate would react with the diene to form the final allylic complex (step c). Step b of the reaction would be similar to the decomposition of compounds $(C_5H_5)Fe(CO)_2R$ studied by Green and Nagy[4]. The stability of $(C_5H_5)Fe(CO)_2R$ decreases in the sequence R = n-propyl > isopropyl > tert-butyl; the latter compound could not be isolated but the hydride $(C_5H_5)Fe(CO)_2H$ and $(CH_3)_2C = CH_2$ were obtained; above 20° the hydride decomposes to $[(C_5H_5)Fe(CO)_2]_2$. Step c of our reaction scheme corresponds to the well-known reaction of some (stable) transition-metal hydride complexes with 1,3-dienes to form allylic complexes[5].

Whereas the allylic complex formed by reaction (2) with butadiene-1,3 must be 1-methylallyldicyclopentadienyltitanium, two complexes could *a priori* be formed in the reaction with pentadiene-1,3, *viz*. the 1,3-dimethlallyl complex actually isolated and the 1-ethylallyl complex. It does not seem unlikely that the crude reaction product contains some of the latter complex, since its absorption spectrum (in the visible range) has a maximum at 573 mμ, while that of the pure 1,3-dimethylallyl complex is at 578 mμ. The absorption maximum of the 1-ethylallyl complex would be expected at lower wave length (probably near 540 mμ). The very impure product of the reaction with butadiene-1,3 already has its absorption maximum at 539 mμ, the same as that of pure 1-methylallyldicyclopentadienyltitanium prepared by method (1).

The possibilities of the described synthetic method are further investigated.

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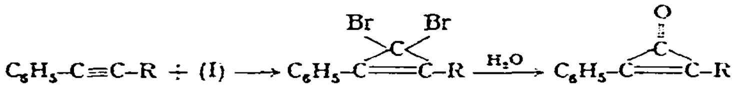
Die Umsetzung von Phenyl(tribrommethyl)-quecksilber mit Acetylenen

Seyferth und Mitarbeiter[1] haben in einer Serie von Arbeiten gezeigt, dass Phenyl(trihalomethyl)-quecksilberverbindungen lagerfähige Vorstufen von Dihalocarbenen (bzw. ihren Äquivalenten) sind. Beim Erhitzen mit Olefinen in inerten Lösungsmitteln entstehen Dihalocyclopropane. Im Rahmen unserer Untersuchungen über die Addition von Dihalocarbenen an Acetylene[2,3] haben wir die Umsetzung von Phenyl(tribrommethyl)-quecksilber (I) mit Alkinen untersucht.



$$\underset{(II)}{C_6H_5{-}C{\equiv}C{-}R} + (I) \longrightarrow \underset{(III)}{C_6H_5{-}\overset{\overset{Br\quad Br}{\diagdown C \diagup}}{C{=\!=}C}{-}R} \xrightarrow{H_2O} \underset{(IV)}{C_6H_5{-}\overset{\overset{O}{\|}}{\overset{C}{C{=\!=}C}}{-}R}$$

Die zunächst gebildeten Dibromcyclopropene (III) gehen beim Schütteln mit Wasser momentan in die relativ stabilen Cyclopropenone (IV) über, deren charakteristische IR-Absorptionen bei 1845–60 und 1630–50 cm^{-1} die Analyse erleichtern. Unter den gewählten Bedingungen (4 std. Kochen von äquimolaren Mengen (I) und (II) in Benzol unter Stickstoff) konnte die Bildung folgender, von uns schon auf anderem Wege[2,3] dargestellter Verbindungen beobachtet werden: IVa, R = C_6H_5; IVb R = C_2H_5; IVc, R = $C{\equiv}C{-}C_6H_5$; IVd, R = *trans*-$CH{=}CH{-}C_6H_5$. Die Ausbeute im Falle IVa lag bei 15 %. Ganz offenbar laufen neben der gewünschten Reaktion andere Prozesse ab. Das in fast quantitativer Menge abgeschiedene Phenylquecksilberbromid ist häufig von beträchtlichen Mengen dunkler Schmieren umschlossen. – Eine Anzahl verschiedenst substituierter rein aliphatischer Acetylene reagierte nicht mit (I).

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