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HYDROGENATION REACTIONS WITH HYDRIDOCOBALT TETRACARBONYL

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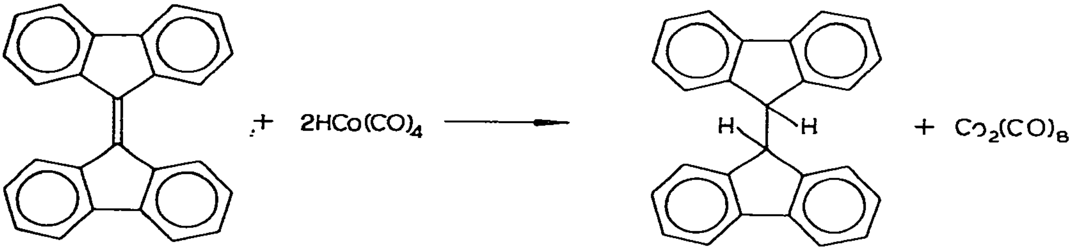
Summary

The tetrasubstituted ethylene, bifluorenylidene, reacts very rapidly (4.06×10^{-2} l mol^{-1} sec^{-1} at 0°C) with $HCo(CO)_4$ to give bifluorenyl. α-Phenylacrylonitrile (atroponitrile) reacts even more rapidly under the same conditions (6.0 l mol^{-1} sec^{-1}). Other highly substituted ethylenes react very slowly with $HCo(CO)_4$, indicating considerable steric effects. The data are consistent with radical type intermediates.

Introduction

The hydrogenation of 1,1-diphenylethylene with $HCo(CO)_4$ proceeds cleanly at 0°C in CH_2Cl_2 with $k_2 = 2.42 \times 10^{-2}$ l mol^{-1} sec^{-1} [1]. The same reaction with methylidenefluorene occurs more than 3500 times as fast [2]. In order to assess further the effect of structure on the rate and course of such hydrogenations we have determined the behavior of a variety of substituted olefins when treated with 2 moles of $HCo(CO)_4$. The results are shown in Table 1.

Several observations can be made concerning the data in Table 1. Clearly, there is a strong steric retardation of the rate as an increasing number of groups are substituted for the hydrogen atoms on the carbons of the olefinic bond. A striking exception is the unusually fast rate for the reaction:



(VI)

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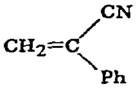
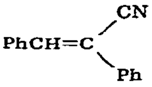
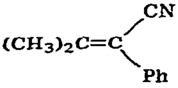
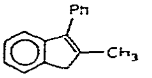
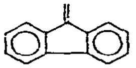
TABLE 1

RATES OF HYDROGENATION WITH $HCo(CO)_4$

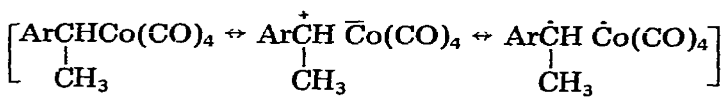
Compound		k_2 (l mol^{-1} s^{-1}) × 10^2 (0°C, CH_2Cl_2)	Relative rate
No.	Structure [a]		
I	$Ph_2C{=}CH_2$	2.42	1.00
II	$Fl{=}CH_2$	~8880	~3670
III	$Fl{=}CHCH_3$	6.06	2.50
IV	$Fl{=}CHPh$	2.17	0.90
V	$Fl{=}C(CH_3)_2$	0.64	0.26
VI	$Fl{=}Fl$	4.06	1.67
VII	$CH_2{=}CHCN$	~0.009 [b]	3 × 10^{-3}
VIII		200 [c]	80
IX		— [d]	1 × 10^{-5}
X		—	no reaction [e]
XI	$CH_3CH{=}CPh_2$	— [f]	<1 × 10^{-5}
XII		— [g]	<1 × 10^{-7}

[a] Fl= represents  , fluorenylidene. [b] 20% conversion after 5 h at 25°C. [c] Estimated from measured rate constant of 0.5 l mol^{-1} sec^{-1} at −23°C. [d] 30% conversion after 20 h at 25°C. [e] After 20 h. [f] 40% conversion after 20 h at 25°C. [g] 43% conversion after 5 days.

Although VI is a tetrasubstituted ethylene, it is known [3] to be non-planar in the ground state and accordingly possesses considerable biradical character. Because it appears probable that the $HCo(CO)_4$ hydrogenations of double bonds occur via intermediates with radical character, the rapid hydrogenation of VI is therefore not too surprising. The hydrogenation of α-phenylacrylonitrile (atroponitrile), VIII, is very fast; indeed it reacts faster than any other olefin that we have examined with the exception of II. The presence of both a phenyl and a cyano group on the same carbon atom of a disubstituted ethylene has a synergistic effect on the rate; both phenyl and cyano are known to enhance radical stability when bonded to the radical center [4].

With respect to the mechanism of the reaction the present data are consistent with a two step process suggested earlier [1] and involving a caged pair with radical character [5]:

$$ArCH{=}CH_2 + HCo(CO)_4 \overset{\text{slow}}{\rightleftharpoons} I$$



$$\left[\underset{\displaystyle CH_3}{ArCHCo(CO)_4} \leftrightarrow \underset{\displaystyle CH_3}{Ar\overset{+}{C}H}\ \overline{C}o(CO)_4 \leftrightarrow \underset{\displaystyle CH_3}{Ar\dot{C}H}\ \dot{C}o(CO)_4\right]$$

(I)

$$I + HCo(CO)_4 \xrightarrow{\text{fast}} ArCH_2CH_3 + Co_2(CO)_8$$

The exact nature of I remains to be elucidated.

Experimental

^1H NMR spectra were taken with a 60 MHz Varian T60 instrument. Gas chromatographic analyses were conducted with a F and M model 700.

2-Methyl-3-phenylindene, XII

To a solution of 28.0 g (0.2 mol) 2-methyl-3-phenylpropenal in 80 ml benzene was added 0.3 g $RhCl(PPh_3)$, 0.5 g NaOAc, and 0.5 g PPh_3 and the mixture treated at 2000 psi H_2 at 110°C for 24 h. Solvent was removed from the filtered product and the residue distilled to give 27 g (96% yield) of 2-methyl-3-phenylpropanal, b.p. 55—60°C (1 mmHg), as a clear, viscous oil. The aldehyde was oxidized with $KMnO_4$, using a known procedure [6]. The resulting acid (80% yield) was cyclized with polyphosphoric acid [7] to give 2-methylindanone as a red oil (85% yield) which was then treated with one equivalent of an ether solution of PhMgBr. The crude 1-hydroxy-2-methyl-1-phenylindane (91% yield) was dehydrated by treating a benzene solution of it with P_2O_5. Crude XII was recrystallized from hexane to give white crystals of XII, m.p. 57—58.5°C (Lit. [8] 56—57°C), in 52% yield.

Bifluorenylidene, VI

To a solution of 10 g (0.60 mol) fluorene in 250 ml of THF at —78°C there was added slowly 40 ml of 1.6 *M* n-butyllithium in hexane. The red solution was allowed to come to room temperature and was again cooled to —78°C, whereupon a solution of 10.8 g fluorenone in 35 ml of THF was added. The solution was allowed to come to room temperature and then stirred for 1 h. After decomposing with dil HCl, crude 9-hydroxy-9-fluorenylfluorene was isolated. Recrystallization from $CHCl_3$ gave 15.9 g (76%) white crystals, m.p. 196—196.5°C in agreement with the literature [9]. Dehydration of 4.0 g of this alcohol was achieved by refluxing its benzene solution with 4.0 g P_2O_5 for 1 h. Work up gave 2.9 g (76% yield) of VI, m.p. 193.5—194.5°C, from $CHCl_3$/hexane (Lit. [10] 194—195°C).

Isopropylidenefluorene, V

A solution of 18.3 g (0.10 mol) fluorenone in 60 ml of THF was added slowly to a solution of isopropylmagnesium chloride prepared from 8.0 g (0.10 mol) isopropyl chloride and 2.75 g (0.11 mol) magnesium turnings in 100 ml of ethyl ether. After complete addition, the solution was refluxed for an addition hour and then decomposed with a 10% aqueous HCl solution. The crude 9-hydroxy-9-isopropylfluorene was isolated and dehydrated by refluxing its solution in 150 ml of benzene with 15 g of P_2O_5. Recrystallization of the crude residue gave 5.20 g (28.7% yield) of 9,9'-bifluorenyl-9,9'-diol, m.p. 187.5—190°C (Lit. [11] 190—192°C) and not the desired V. The mother liquor was concentrated and passed through silica gel using hexanes as the eluent. The first yellow band was collected and concentrated and the crude product was recrystallized from hot hexanes to give 3.75 g (17.9% yield) of V, m.p. 114—115.2°C (Lit. [12] 113—116°C).

1,1-Diphenyl-1-propene, XI

Treatment of benzophenone with ethylmagnesium bromide followed by dehydration of the resulting alcohol with P_2O_5 as in the above procedures gave XI. Recrystallization from hexanes gave pure XI, m.p. 47.5—48.0°C (Lit. [13] 48.5—49.0°C).

α-Phenylacrylonitrile, VIII, and α,β-diphenylacrylonitrile, IX, were prepared according to the literature procedures [14,15].

Acrylonitrile was a commercial product (Aldrich) which was redistilled just prior to use.

β,β-Dimethyl-α-phenylacrylonitrile, X

To a solution of NaOEt (from 0.25 g Na in 15 ml absolute EtOH) was added 11.7 g of (0.1 mol) phenylacetonitrile and 10.0 ml (0.137 mol) of acetone. After refluxing for 2 h, 75 ml of CH_2Cl_2 was added and the solution extracted with water. The organic layer, after drying, was evaporated leaving an oil containing about 50% of the starting material. Chromatography on silica gel gave the desired product as the first fraction to be eluted with 1/1 $CHCl_3$/hexane. The product, XI, was obtained as a colorless oil. ^1H NMR (ppm, $CDCl_3$) δ 7.35 (s, 5, phenyl), 2.22 (s, 3, methyl); 1.87 (s, 3, methyl).

$Co_2(CO)_8$ was prepared according to the literature procedure [16].

$HCo(CO)_4$ was prepared by the pyridine/H_2SO_4 method [16] and was prepared fresh before each kinetic experiment. Its concentration in CH_2Cl_2 solution was determined by reaction with excess 0.1 *M* NaOH and back titration [17].

Rate studies

The rate of hydrogenation of α-phenylacrylonitrile was determined at —23°C (CCl_4/CO_2 slush) using napthalene as an internal standard. Sampling and work up was carried out as previously described [2]. The concentration of product was determined by gas chromatography. The rate with isopropylidenefluorene was determined by using ^1H NMR analysis and comparing the ratio of integrated areas of the methyl protons of product at δ 0.85 ppm (d, 6, methyl) and starting material at δ 2.52 ppm (s, 6, methyl). The integration values for the isopropylidenefluorene methyl protons were corrected for the contribution from the isopropylmethine proton in the product, δ 2.6 ppm (m, 1, methine). The rates of hydrogenation of acrylonitrile and bifluorenylidene were followed by titration of remaining $HCo(CO)_4$. In the reaction with VI, the yield of $Co_2(CO)_8$ was 97% of theory as determined by measuring CO evolution on treatment with pyridine. For characterization purposes all olefinic compounds were hydrogenated to completion. Compounds XI and XII were treated under catalytic conditions in order to secure the hydrogenated products for comparison purposes. With the exception of VII which gives some hydroformylated product [18], no other compounds gave either hydroformylated or isomerized prod product. The hydrogenated products were all isolated and then characterized in the usual way and gave properties consistent with those in the literature. The

^1H NMR spectrum of the product from XII has not been reported previously. 2,3-Dihydro-2-methyl-3-phenylindene, δ 6.8—7.5 (m, 9, phenyls), 4.38 (m, 1, methine), 2.6—3.2 (m,3, H's at positions 1 and 2), 0.7 (d, 3, methyl), 1.17 ppm (d, 3, methyl; ~6% relative to major doublet and probably due to *trans* isomer).

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