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THE STOICHIOMETRIC HYDROGENATION OF 9-METHYLIDENEFLUORENE AND RELATED COMPOUNDS WITH HYDRIDOCOBALT TETRACARBONYL

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Summary

9-Methylidenefluorene (IIa) reacts rapidly with $HCo(CO)_4$ at −67°C to give a quantitative yield of 9-methylfluorene (IIIa); $k_2 = (13.4 \pm 0.5) \times 10^{-2}$ l mol^{-1} s^{-1}. Although the internal olefin, 9-ethylidenefluorene (IIb) reacts more slowly than IIa, it is hydrogenated about 2.5 times as fast as the terminal olefin, 1,1-diphenylethylene (I). Measurement of the rate of the reaction of IIb with $DCo(CO)_4$ and comparison with $HCo(CO)_4$ shows a very large inverse isotope effect k_H/k_D of 0.43.

Introduction

We reported recently [1] that 1,1-diphenylethylene (I) undergoes facile hydrogenation in a stoichiometric reaction with $HCo(CO)_4$ (eq. 1). The reaction proceeds much faster than the stoichiometric hydroformylation of olefins and is first order in both reactants; at 0°C $k_2 = 2.42 \times 10^{-2}$ l mol^{-1} s^{-1}.

In the earlier paper [1] we pointed out that the hydrogenation of I with $HCo(CO)_4$ proceeded at the same rate regardless of whether the reaction was carried out under 1 atm of CO or under 1 atm of N_2. We also found that hydrogenation of I with $DCo(CO)_4$ proceeded faster than with $HCo(CO)_4$; k_H/k_D = 0.58. These results contrast sharply from those observed in the stoichiometric hydroformylation of other terminal olefins where the presence of 1 atm of CO has a marked inhibiting effect on the rate [2] and the k_H/k_D is approximately 1.12 [3]. Obviously the mechanism for the stoichiometric hydrogenation is different from that of the stoichiometric hydroformylation.

It has been shown previously [4] that certain hydrogenations with $HMn(CO)_5$ definitely proceed via a pathway involving a geminate radical pair. Our

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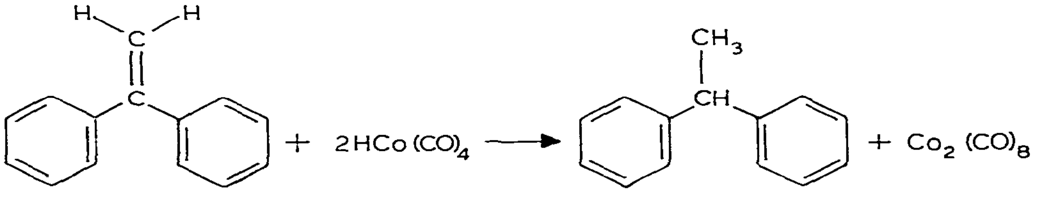
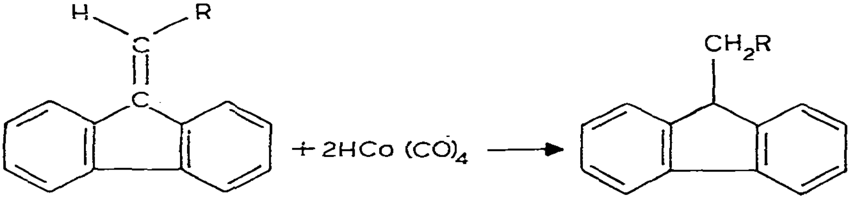
results with I and $HCo(CO)_4$ are consistent with this suggestion. It occurred to us that if stabilization of a transition state by electron or charge delocalization were critical, then forcing the diphenylethylene into a planar configuration would facilitate hydrogenation. We now wish to report that the hydrogenation at 0°C of 9-methylidenefluorene with $HCo(CO)_4$ (eq. 2), proceeds about 3600 times as fast as that of I (eq. 1).



(1)

(I)



(2)

(IIa, R = H;
IIb, R = CH_3;
IIc, R = Ph)

(IIIa, R = H;
IIIb, R = CH_3;
IIIc, R = Ph)

The rate shows no dependence on the atmosphere above the reaction, and a very large inverse isotope is observed.

Results and discussion

In order to compare the rate of reaction of I with IIa, the reaction of IIa with $HCo(CO)_4$ was attempted at 0°C. However, the reaction was so fast that measurements had to be performed at much lower temperatures. Second order rate constants were obtained at −67, −52, and −34°C, Table 1. Using these three results, a $\Delta H^{\neq}$ of 10 ± 2.1 kcal mol^{-1} was calculated, from which it was possible to extrapolate to a rate constant, k_2, at 0°C of about 88.8 l mol^{-1} s^{-1}. Thus IIa hydrogenates at least 3600 times as fast as I.

The rate of hydrogenation of IIb was also determined. IIb is an internal olefin and such olefins are known to undergo stoichiometric [5] as well as catalytic hydroformylation [6] at considerably slower rates than terminal olefins. Their rates of isomerization also are much slower [7]. The reasons for the slower rates is thought to be steric in nature; the internal olefin must overcome a higher energy barrier in forming the required complex with the cobalt hydrocarbonyl. However, the rate of hydrogenation of IIb, Table 1, was found to be about 2.5 times as fast as that of the terminal olefin I. Fig. 1 shows the rate curve for the reaction between IIb and $HCo(CO)_4$ at −10°C in the presence of CO and in the presence of N_2. These curves are essentially superimpossible. Also

TABLE 1

HYDROGENATION DATA

Compound	k_2 (l mol^{-1} s^{-1}) × 10^2						$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal deg^{-1} mol^{-1})	Relative rate (0°C)
	0°C	−10°C	−21°C	−34°C	−52°C	−67°C			
I [a]	2.42						17.0	−10.0	1.00
II a	8880			469	144	13.4	10.0 [b]	[c]	3670
IIb	6.06	2.10	0.51				15.7 [d]	−6.0 [e]	2.50
IIc	2.17						12.2 [f,g]	−21 [e]	0.90

[a] Ref. 1. [b] ±2.1. [c] Too uncertain. [d] ±1.2. [e] ±4. [f] The rates at 19 and 9.5°C were 10.2 × 10^{-2} and 4.6 × 10^{-2} l mol^{-1} s^{-1}, respectively. [g] ±1.2. The rate constants were determined with a precision of ±4%.

in Fig. 1 is shown the rate curve at 0°C and a rate curve at −10°C using DCo(CO)$_4$. From these rate curves it can be calculated that k_H/k_D = 0.43. A similar inverse isotope effect has been observed previously for HCo(CO)$_4$ hydrogenation [1] as well as for hydrogenation with HMn(CO)$_5$ [4]. Such results may be interpreted as signifying that in the transition state, the C—H(D) bond is largely formed. The curvature in the DCo(CO)$_4$ experiment shown in Fig. 1 is likely due to the observed H—D exchange (^{1}H NMR) and the resulting build-up of HCo(CO)$_4$ toward the end of the reaction.

Although definitive proof is still lacking, the intermediacy of a geminate radical pair remains the most likely possibility for explaining the mechanism of

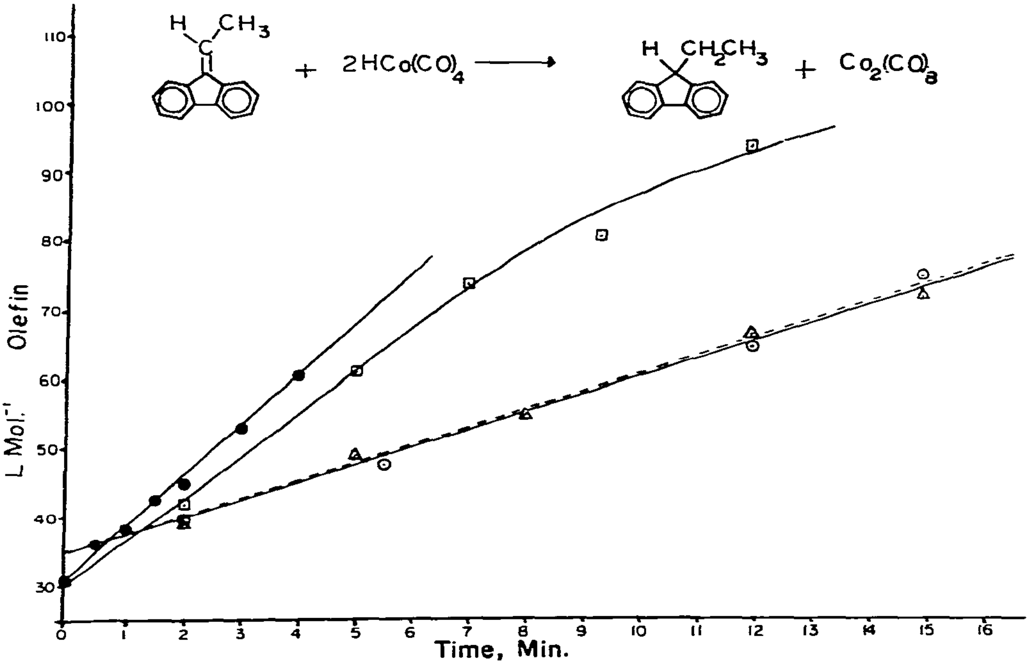


Fig. 1. Second order plot of conversion of 9-ethylidenefluorene (IIb): ● at 0°C under CO; ⊡ at −10°C under CO using DCo(CO)$_4$; △ at −10°C under N$_2$; ⊙ at −10°C under CO.

the reaction. The very extensive delocalization and hence stability of the 9-fluorenyl radical is thus assumed to account for the remarkably fast rate of reaction of 9-methylidenefluorene.

Experimental

9-Benzylidenefluorene was a commercial sample (J.T. Baker) and after recrystallization had m.p. 73—75° C.

9-Ethylidenefluorene was prepared by treating fluorene with EtMgBr and dehydrating the resulting carbinol by refluxing in benzene containing a small quantity of *p*-toluenesulfonic acid. The recrystallized material had m.p. 102—103° C.

9-Methylidenefluorene was prepared in accordance with the published report [8] and had m.p. 50—52°C.

Dicobalt octacarbonyl was prepared as previously described [9].

Gas chromatographic analyses were performed with an F and M model 700 having a katharometer detector. For the experiments with IIc, a 1/4" × 7' column filled with 3% SE-30 on Chromosorb W operating at 250° C under flowing He was used. In experiments with IIb at 1/4" × 20', 10% SE-30 on Chromosorb W operating at 225° C under He was used. In experiments with IIa, naphthalene was used as an internal standard and a 1/4" × 15' column containing 20% SE-30 on Chromosorb W at 200° C under He was used.

The rate of hydrogenation of 9-benzylidenefluorene

Because of its slow decomposition above 0° C, $HCo(CO)_4$ was prepared immediately prior to each kinetic run. The pyridine/H_2SO_4 method [10] usually was used and the gas phase $HCo(CO)_4$ was passed through a short column of P_2O_5 and then directly into about 13 ml of solvent at —78° C, under flowing CO (10 ml/min). Typically, 0.25 g $Co_2(CO)_8$ yields a 13 ml solution of about 0.06 *M*. The exact concentration was obtained by removing a 2.00 ml aliquot at 0° C, adding it to 5.00 ml of 0.1 *M* NaOH and back-titrating to the phenolphthalein end point with 0.01 HCl [10]. Of the remaining solution, 10.0 ml was removed by pipette and transferred to a 50 ml, CO purged round-bottomed flask immersed in constant temperature baths. The baths consisted of ice/water (0° C); t-amyl alcohol/CO_2 (—10° C); CCl_4/CO_2 (—21° C); $(CH_2Cl)_2/CO_2$ (—34° C); 1-hexanol/CO_2 (—52° C); and $CHCl_3/CO_2$ (—67° C). After the temperature of the $HCo(CO)_4/CH_2Cl_2$ solution had equilibrated with that of the desired bath, the reaction was commenced by injecting 1.0 ml of an approximately 0.33 *M* CH_2Cl_2 solution of the desired fluorene. This solution was cooled to bath temperatures before use and its exact concentration was adjusted to match the concentration of the $HCo(CO)_4$ solution. Sampling from the reaction flask was accomplished by inserting one end of a 6" double ended syringe into the reaction flask through a rubber septum and inserting the other end into a 10 ml erlenmeyer flask capped with a rubber septum and containing 2—3 ml of ethylenediamine as a quencher. The quencher flask was cooled to about 5° C. Samples (1—2 ml) were removed from the reaction flask by inserting a 20 ml syringe into the septum of the quencher, drawing up the barrel of the syringe and thus creating a small vacuum which sucks the sample into the quencher.

After all the samples had been collected, 3 ml of cold water was added to each of the quenched samples and the mixture stirred. The CH_2Cl_2 layer was removed, washed with H_2O several times until free of amine and dried with $MgSO_4$. The dry solution was concentrated to about 0.25 ml under argon and analyzed by GLC.

For experiments under nitrogen, the solvents and glassware were purged for 15—30 minutes at 0°C before commencing the reaction. For experiments with $DCo(CO)_4$, the $HCo(CO)_4$ solution was prepared in the usual way, then shaken twice with one ml D_2O; the mixture was cooled in dry-ice/acetone, and water-free $DCo(CO)_4$ solution removed and its concentration determined. Alternatively, hexane solutions of $DCo(CO)_4$ can be prepared directly with $Co_2(CO)_8$, DMF, and 20% DCl [11].

Rate of hydrogenation of 9-methylidenefluorene. Because of transfer problems at the low temperatures involved, sampling was eliminated and multiple experiments were conducted at the same temperature. Thus for example, five 15 ml round-bottomed flasks each equipped with a stirring bar and septum were purged with CO. About 5 ml of approximately 0.06 *M* $HCo(CO)_4$ in CH_2Cl_2 was pipetted into each and all five flasks cooled to the desired temperature. Five capped syringes, each containing 0.75 ml of 0.280 *M* IIa and CH_2Cl_2 in which was dissolved the naphthalene standard also were cooled to the temperature of the experiment. The reaction was started by removing the cap from one of the syringes, adjusting the sample to 0.50 ml and then injecting the solution into one of the flasks. After the desired elapsed time, cold ethylenediamine was injected to quench the reaction. Sample work-up and analyses was carried out as described above for the other fluorenylidene compounds.

Acknowledgements

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