

Preliminary communication

AROMATIC H–D EXCHANGE WITH $\text{HCo}(\text{CO})_4$

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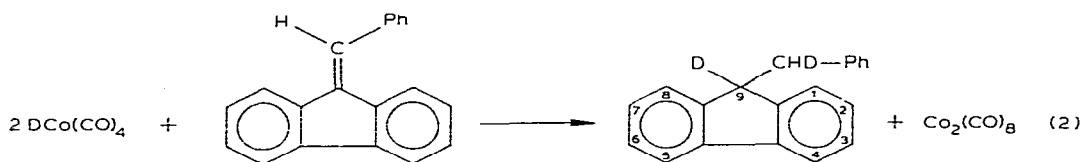
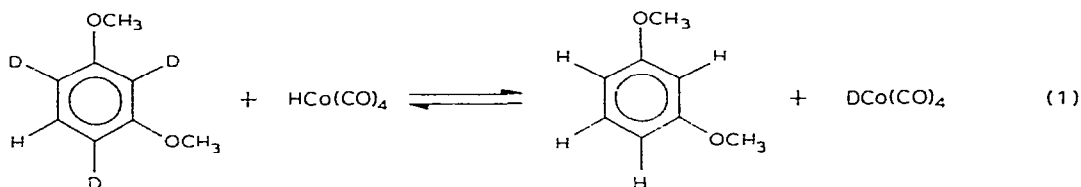
Summary

When 1,3-dimethoxybenzene-2,4,6- d_3 in methylene chloride is stirred at room temperature with $\text{HCo}(\text{CO})_4$ and then 9-benzylidene-fluorene added, the latter compound is hydrogenated to the corresponding 9-benzylfluorene- d_2 . The D–H exchange of the aromatic protons is ascribed to the electrophilic character of $\text{HCo}(\text{CO})_4$.

Although $\text{HCo}(\text{CO})_4$ is readily soluble in organic solvents it can readily be extracted into an aqueous phase with alkali. As a matter of fact, one commercial oxo process involves recycling $\text{HCo}(\text{CO})_4$ using this technique. In aqueous solution, $\text{HCo}(\text{CO})_4$ is reported [1] to have an acid strength between that of HNO_3 ($\text{p}K_a \sim 2.5$) and HCl ($\text{p}K_a \sim -5$) while other metal carbonyl hydrides are much weaker acids, e.g., $\text{HMn}(\text{CO})_5$, $\text{p}K_a \sim 7$; $\text{H}_2\text{Fe}(\text{CO})_4$, $\text{p}K_a \sim 4$. There is considerable indirect evidence that under catalytic oxo conditions, acid-catalyzed reactions occur. Such reactions involve formation and cleavage of acetals [2], the pinacol–pinacolone rearrangement [3] and the homologation of substituted benzyl alcohols [4]. More recently, an acid-catalyzed mechanism has been invoked to explain a cyclization reaction which accompanies the catalytic hydroformylation of saffrole [5].

We wish to report the success of the sequence of reactions shown in eq. 1 and 2 carried out successively in the same flask. The reaction was carried out in CH_2Cl_2 solution at room conditions. Previous work had shown [6] that benzylfluorene is cleanly and rapidly hydrogenated (eq. 2) to benzylfluorene by $\text{HCo}(\text{CO})_4$ in CH_2Cl_2 solution. The success of the exchange reaction (eq. 1) depends on the electrophilic attack by H^+ and thus demonstrates the protic character of $\text{HCo}(\text{CO})_4$ in organic solvents under mild conditions [7].

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Experimental

1,3-Dimethoxybenzene-2,4,6- d_3 . 1,3-Dimethoxybenzene (50 ml) was stirred with 75 ml of 33% $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$ in a sealed flask at room temperature for two days. The organic layer was separated and washed successively with saturated aqueous NaHSO_4 solution and saturated aqueous NaCl . After drying over MgSO_4 , the dimethoxybenzene was stirred with 2 g of NaH for 24 h, then distilled in vacuo from the NaH . Integration of the ^1H NMR signals of the distilled material with respect to the six methoxy protons (δ 3.85 ppm) showed that 88% of the hydrogens at positions 2, 4, and 6 (δ 6.55 ppm, m) had been exchanged by deuterium, and that there was no deuterium at positions 5 (δ 7.20 ppm, m).

H-D exchange and hydrogenation. Dry HCo(CO)_4 , generated in the usual way [8], was trapped in a solution consisting of 12 ml of the dimethoxybenzene- d_3 and 18 ml of CH_2Cl_2 held at -40°C . The solution was allowed to warm to room temperature and stirred under 1 atm CO for 24 h. A 2 ml sample was removed and titrated with alkali to determine the carbonyl concentration (total 1.23 mmol) and then 1 ml of CH_2Cl_2 solution containing 0.55 mmol of benzylidene-fluorene added and the mixture stirred under 1 atm of CO for 3 h. The benzylfluorene was isolated and its ^1H NMR spectrum determined. If pure DCo(CO)_4 were present for the hydrogenation, one of the two benzylic protons (δ 3.1 ppm, m, 2) would be D and the 9-fluorenyl proton (δ 4.22 ppm, m, 1) would be D. NMR analysis was based on the integration of the areas of the signals due to these three protons with respect to the integrated area of the signals due to the thirteen phenyl protons (δ 7.78 ppm, m, 2 (1, 8 protons); δ 7.2 ppm, m, 11 (remaining aromatic protons)). The ratios of the integrated areas indicated 1.8 protons of the maximum possible 3.0 (if zero D were present) corresponding to 60% deuteration. When the experiment was repeated using neat dimethoxybenzene- d_3 to trap the HCo(CO)_4 and allowing 5 h exchange time, the percent deuteration of the benzylfluorene corresponded to 70% of that expected had pure DCo(CO)_4 been present.

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References

- 1 W. Reppe, *Ann*, 582 (1952) 116.
- 2 B.I. Fleming and H.I. Bolker, *Can. J. Chem.*, 54 (1976) 685; L. Roos, R.W. Goetz, and M. Orchin, *J. Org. Chem.*, 30 (1965) 3023.
- 3 I. Wender, S. Metlin and M. Orchin, *J. Amer. Chem. Soc.*, 73 (1951) 5704.
- 4 H. Greenfield, S. Metlin and M. Orchin, *J. Amer. Chem. Soc.*, 74 (1952) 4079.
- 5 J. Palagyi, Z. Decsy, G. Palyi and L. Markó, *Hung. J. Ind. Chem. Ves.*, 1 (1973) 413.
- 6 T.E. Nalesnik and M. Orchin, *J. Organometal. Chem.*, 199 (1980) 265.
- 7 For a theoretical discussion of aromatic exchange with 1,3,5-trimethoxybenzene see e.g., A.J. Kresge, Y. Chiang, G.W. Koeppl, and R.A. MoreO'Ferral, *J. Amer. Chem. Soc.*, 99 (1977) 2245.
- 8 P.D. Taylor and M. Orchin, *J. Org. Chem.*, 37 (1972) 3913; H.W. Sternberg, I. Wender, R.A. Friedel, and M. Orchin, *J. Amer. Chem. Soc.*, 75 (1953) 2717.