Qrganometallic Phase Transfer Catalysis under Acidic Conditions. Cobalt Carbonyl Induced Hydrogenation of Activated Olefins

Howard Alper"? and Josef Heveling

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada KIN 9B4

Diarylethylenes and **9,9'-** bifluorenylidene are hydrogenated, in excellent yields, on treatment with cobalt carbonyl or bis(tri-n-buty1phosphine)dicobalt hexacarbonyl, benzene, **48--50%** aqueous tetrafluoroboric acid, and sodium 4-dodecylbenzenesulphonate.

Publications during the past five years have established that phase transfer catalysis is a valuable synthetic method in $organormalile chemistry^{1,2}$ Of the metal complexes employed as catalysts or stoicheiometric reagents, cobalt carbonyl has enjoyed the most widespread use thus far. Examples include the stoicheiometric synthesis of π -allylcobalt tricarbonyl complexes³ and the catalytic acylation of fulvenes.²

All of the previous chemistry with organometallic complexes, using phase transfer catalysis, has been effected under basic conditions. In this manner, for example, dicobalt octacarbonyl is efficiently converted into the cobalt tetracarbonyl anion. We thought that a cobalt carbonyl hydride might be generated under acidic conditions and now report the first examples of organometallic phase transfer catalysis under acidic conditions.

Reaction of 1,1-diphenylethylene $(1; R = R' = H)$ with bis(tri-n-butylphosphine)dicobalt hexacarbonyl (2),⁴ benzene as the organic phase, and $48-50\%$ aqueous tetrafluoroboric acid containing sodium **4-dodecylbenzenesulphonate** as the phase transfer agent,⁵ for 1 h at 55 °C (atmospheric pressure), afforded 1,1-diphenylethane **(4; R** = R' = H) in 52% yield (Scheme 1). The yield of $(4; R = R' = H)$ increased to 85% after 2 h, while **(4)** was obtained in 97 % yield when the reaction was effected for 4 h. Only 3% of $(4; R = R' = H)$ was produced when the latter reaction was run, for **4** h, in the absence of sodium **4-dodecylbenzenesulphonate [(4)** was not detected when a reaction time of 1 h was used]. In addition, olefin was recovered when the phase transfer catalysed reaction of **(1)** was attempted using water as the aqueous phase. In all cases, a *2:* 1 ratio of olefin: **(2)** was used. The hydrocarbon **(4;** $R = R' = H$) was not formed when the reaction of (1) was

Scheme 1. i, $C_{12}H_{25}C_6H_4SO_3-Na^+$, C_6H_6 , $48-50\%$ HBF₄, 4 h, *55 "C.*

t **E.** W. R. Steacie Fellow, 1980-1982.

repeated in the absence of the cobalt complex **(2)** but in the presence of sodium **4-dodecylbenzenesulphonate.**

Cobalt carbonyl(3) is as useful as the phosphine-substituted derivative for converting **(1)** into **(4; R** = R $=$ H) in quantitative yield. **A** series of other diarylethylenes were hydrogenated in nearly quantitative yield using cobalt carbonyl (Table I). In addition 9,9'-bifluorenylidene *(5)* afforded bifluorenyl **(6)** in 97% yield with $Co_2(CO)_8$ (Scheme 2). However, anthracene is inert under the reaction conditions.

We assume that a cobalt carbonyl hydride, *possibly* $HCo(CO)₃L$ (L = CO, PBu₃), is generated in these reactions. If such a hydride is indeed formed, it is much easier to handle compared with the manipulation of pure $HCo(CO)₃L$ (L = CO,PBu₃). The stoicheiometric hydrogenation of arylethylenes by hydridocobalt tetracarbonyl has been the subject of a series of excellent papers by Orchin and co-workers.⁶ The latter generate $HCo(CO)$, by disproportionation of $Co_2(CO)$ ₈ by pyridine giving an ionic complex, the anionic component $[Co(CO)₄]$ of which is subsequently acidified with sulphuric acid. Irrespective of the mechanistic details of the phase transfer reaction (a carbonium ion pathway is also possible), the results described above constitute the first examples of the application of phase transfer catalysis, under acidic conditions, to organometallic chemistry.

The following general procedure was used. **A** mixture of sodium **4-dodecylbenzenesulphonate** (0.50 mmol), tetrafluoroboric acid **(48-50%,** *25* ml), and benzene (25 ml) was stirred for 30 min under nitrogen. The olefinic substrate **(1)** or *(5)* (1.0 mmol) and **(2)** or (3) *(0.50* mmol) were added, and stirring was continued for **4** h at *55* "C. The phases were

Table 1. Reaction of olefins with $Co_2(CO)_8$, $48-50\%$ HBF₄, sodium **4-dodecylbenzenesulphonate,** and C,H, at *55 "C* for **4** h.

Reactant		Cobalt complex Product ^a (Yield, $\%$)
$(1; R = R' = H)$	(2)	(4) (97)
$(1: R = R' = H)$ $(1: R = R' = Me)$	(3) (3)	(4) (99) (4) (98)
$(1; R = MeO, R' = H)$	(3)	(4) (98)
$(1; R = R' = OMe)$ (5)	(3) (2)	(4) (95) (6) (96)
	(3)	(6) (97)

a Products were identified by comparison of physical and spectral data with those for authentic materials.

Scheme 2. i, C₁₂H₂₅C₆H₄SO₃⁻Na⁺, C₆H₆, 48-50% HBF₄, 4 h, *55 "C.*

separated, and the hydrogenated product **[(4)** or *(6)]* was isolated by rotary evaporation of benzene, followed by distillation or column chromatography of the residue.

We are grateful to the Natural Sciences and Engineering Research Council for support of this work.

Received, 22nd November 1982; Cam. 1341

References

1 H. Alper, *Adv. Organomet. Chern.,* **1981,19, 183,** and references cited therein; F. Francalanci and M. Foa, *J. Organomet. Chem.,* **1982,232,59; S.** Gambarotta and H. Alper, *J. Org. Chem.,* **1981, 46, 2142;** D. **H.** Gibson, F. **U.** Ahmed, and K. R. Phillips,

Organometallics, **1982, 1, 679;** J. J. Brunet, **C.** Sidot, and **P.** Caubere, *Tetrahedron Lett.,* **1981, 22, 1013; S.** Gambarotta and H. Alper, *J. Organomet. Chem.,* **1981, 212, C23;** H. Alper, **K.** Hashem, and **J.** Heveling, *Organometallics,* **1982, 1, 775.**

- **2 H.** Alper and D. **E.** Laycock, *Tetrahedron Lett.,* **1981,22,** *33.*
- *3* H. Alper, H. des Abbayes, and D. Des Roches, *J. Organomet. Chem.,* **1976, 121, C31.**
- 4 F. Piacenti, M. Bianchi, and E. Benedetti, *Chim. Ind.* (*Milan*), **1967, 49, 245.**
- **5 M.** Ellwood, J. Griffiths, and P. Gregory, *J. Chem. SOC., Chem. Commun.,* **1980, 181** ; **W.** Tagaki, N. Iwamoto, **K.** Suzuki, and **S.** Tamagaki, *Tetrahedron Lett.,* **1981, 22, 5213.**
- 6 T. **E.** Nalesnik and M. Orchin, *Organornetallics,* **1982, 1,** *222;* T. E. Nalesnik, **J.** H. Freudenberger, and M. Orchin, *J. Mol Catal.,* **1982, 16, 43,** and references cited therein.