Selective Reduction of Organic Compounds with Bis-(η-cyclopentadienyl)dihydridotungsten †

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Bis-(η-cyclopentadienyl)dihydrotungsten reduces carbon–halogen bonds to C–H in a wide variety of organic halogen compounds. The reactions can proceed in high yield with high selectivity.

IT is well known that transition metal hydrides react with halogenated hydrocarbons.[1] Generally the organic products of these reactions have been little studied although it has been shown that carbon tetrachloride can be converted into chloroform.[2]

Organotin monohydrides have been found to reduce organic halogen compounds and tributyltin hydride is a well known reagent for this reaction.[3] The corresponding reactions of tin dihydrides are relatively rare.

We thought it of interest to explore more widely the reduction of halogenated hydrocarbons with transition metal hydrides. We chose the readily available dihydride $(\eta\text{-}C_5H_5)_2WH_2$, since the expected metal-containing products, $(\eta\text{-}C_5H_5)_2WX_2$ (X = Cl, Br, or I), are known to be crystalline inert compounds of low solubility.[4] Also they are readily reduced to the dihydride.

Chemical Studies.—The general procedure was to treat the yellow dihydride with an excess of the purified halogen compound in a sealed tube. Dilute solutions in benzene were used for the more rapid reactions. The mixtures were heated when necessary and the extent of the reactions was indicated by the amounts of insoluble, crystalline dihalide products. The mother liquors were frequently colourless or pale in colour, and they were examined by g.l.c. and in some cases by i.r., ^{1}H n.m.r., or mass spectroscopy. In most reactions the total reduction products were isolated in high yield (80—100%). The reactants studied and the products are shown in the Table. The data show that in most cases one halogen atom is exchanged for hydrogen:

$$(\eta\text{-}C_5H_5)_2WH_2 + 2\,C\text{-}X \xrightarrow[\;X\,=\,Cl,\,Br,\,or\,I\;]{} (\eta\text{-}C_5H_5)_2WX_2 + 2\,C\text{-}H$$
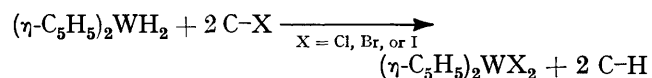
For a given radical R the rates of reduction of RX are in the order X = I > Br > Cl. This is also shown by the reduction of 1-bromo-2-chloroethane, which gives chloroethane cleanly; no bromoethane (<0·1%) is detected in the reduction products. ααα-Trifluorotoluene, a representative fluorocarbon, was not reduced by the tungsten dihydride.

The dihydride selectively reduces geminal polyhalides. The reductions of the chlorides CCl_nH_{4-n} (n = 4, 3, or 2) to CCl_mH_{3-m} (m = 3, 2, or 1, respectively) proceed smoothly under the conditions employed without giving any trace of secondary products; for example, carbon tetrachloride gives no dichloromethane.

Vicinal polychlorides are reduced at the carbon atom bonded to the most halogen atoms, e.g. pentachloroethane selectively forms 1,1,2,2-tetrachloroethane and no 1,1,1,2-isomer is detected. The same isomer is formed even when the reaction is carried out with a molar equivalent ratio of C_2HCl_5 to $(\eta\text{-}C_5H_5)_2WH_2$ of 2 : 1. In contrast, the vicinal dibromide $CH_2Br\cdot CHBr\cdot CH_3$ undergoes elimination giving propene and hydrogen.

It appears that reduction at sp^3 carbon is achieved more readily than at sp^2 carbon. Whereas carbon tetrachloride reacts rapidly at room temperature, tetrachloroethylene requires 12 h at 100° to achieve a similar yield of the tungsten dichloride. Also, 2,3-dichloropropene is selectively reduced to 2-chloropropene.

The reduction of the three isomeric dichloroethylenes is anomalous since they each give ethylene, and no vinyl chloride, which is itself only reduced slowly, is detected. Preliminary studies show that the reaction of β-bromostyrene gives styrene and ethylbenzene; this constitutes the only observed example of hydrogenation occurring as well as halogen exchange.

The polyfunctional chloro-compounds chloroacetone, chloroacetonitrile, and 2-chloroethanol are reduced; the other functional groups remain unchanged.

Reduction of benzoyl chloride in ether solution gives benzaldehyde in *ca.* 15% yield.

It appears that with respect to yield and reactivity the tungsten dihydride compares favourably to tri-n-butyltin hydride. The tungsten compound has advantages insofar as reaction may be carried out in most common solvents (it is only slightly soluble in light petroleum), reactions may be followed visually, and the air-stable, insoluble dihalide product $(\eta\text{-}C_5H_5)_2WX_2$ may be recovered and the hydride may be regenerated by reduction with sodium borohydride, or zinc amalgam in acid. The tungsten compounds are relatively involatile, unlike the volatile, toxic tri-n-butyltin derivatives. In the absence of a reaction the tungsten compound is readily removed by addition of chloroform. Alternatively the dihydride may be extracted by shaking with aqueous acid, which gives the water-soluble trihydride cation $[(\eta\text{-}C_5H_5)_2WH_3]^+$.

EXPERIMENTAL

All solvents were dried and deoxygenated. Reactions were carried out in glass tubes sealed under vacuum. All

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† This compound is named in accordance with the I.U.P.A.C. Rules for Nomenclature of Inorganic Chemistry, Second Edition, 1970, which prefer the term η-cyclopentadienyl to π-cyclopentadienyl.

[1] M. L. H. Green and D. J. Jones, *Adv. Inorg. Chem. Radiochem.,* 1965, **7,** 115.
[2] T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.,* 1956, **3,** 104.
[3] H. G. Kuivila, *Adv. Organometallic Chem.,* 1964, **1,** 47.
[4] R. L. Cooper and M. L. H. Green, *J. Chem. Soc. (A),* 1967, 1155; *Z. Naturforsch.,* 1964, **19b,** 652.

manipulations of the tungsten dihydride were carried out under nitrogen although the hydride may be handled for short periods in air. The volatile products were collected by distillation into side-arms attached to the reaction vessel. The products were examined by g.l.c. Three columns were

following modification of the previously reported method,[5] which gives improved reproducible yields.

Bis-(η-cyclopentadienyl)dihydridotungsten.—The preparation was carried out under nitrogen. A freshly prepared solution of sodium cyclopentadienide [from sodium (40 g)]

Reactions of the dihydride $(\eta\text{-}C_5H_5)_2WH_2$ with halogenocarbons

Halogenocarbon	Reaction temp. (°C)	Time [a]	Products [b] [relative yields (%)]
Saturated			
Carbon tetrachloride	20	1 min	Chloroform
Carbon tetrabromide	20	1 min	Bromoform
Chloroform	20	18 h	Dichloromethane
Iodoform [c]	20	1 min	Di-iodomethane
Dichloromethane	70	8 day	Chloromethane
Hexachloroethane [c]	20	15 min	Pentachloroethane
Pentachloroethane	20	20 min	1,1,2,2-Tetrachloroethane
1,1,2-Trichloroethane	102	18 h	1,2-Dichloroethane (94); chloroethane (6)
1,2-Dichloroethane	120	2 day	Chloroethane; ethane [d] (ca. 10)
1-Bromo-2-chloroethane	100	60 h	Chloroethane
1,2-Dibromopropane	100	2 h	Propene
Unsaturated			
Tetrachloroethylene	100	12 h	Trichloroethylene
Trichloroethylene	100	2 days	cis-1,2-Dichloroethylene (91); trans-1,2-dichloroethylene (6); 1,1-dichloroethylene (3)
cis-1,2-Dichloroethylene	120	2 day	Ethylene
trans-1,2-Dichloroethylene	120	2 day	Ethylene
1,1-Dichloroethylene	120	2 day	Ethylene
Vinyl chloride	120	3 day [e]	Ethylene
Vinyl bromide	120	12 h	Ethylene
Hexachloropropene	20	1 min	Pentachloropropene
2,3-Dichloropropene	100	18 h	2-Chloropropene
2-Chloropropene	120	18 h	Propene
Allyl chloride	100	12 h	Propene
3-Bromopropyne	20	1 min	Propyne
1-Chlorobut-2-ene [g]	100	12 h	trans-But-2-ene (61); cis-but-2-ene (21); but-1-ene (18)
3-Chlorobut-1-ene	100	12 h	trans-But-2-ene (53); cis-but-2-ene (28·5); but-1-ene (18·5)
Aromatic			
Chlorobenzene	140	7 day	No reaction [h]
Bromobenzene	100	7 day	Benzene
Iodobenzene	90	18 h	Benzene
o-Dichlorobenzene	140	5 day	No reaction
Hexachlorobenzene [c]	140	5 day	No reaction
Benzyl chloride	90	3 day	Toluene
ααα-Trifluorotoluene	120	4 day	No reaction
Miscellaneous			
Chloroacetone	90	4 h	Acetone
2-Chloroethanol	80	18 h	Ethanol
Chloroacetonitrile	120	6 day	Acetonitrile
Silicon tetrachloride	60	4 day	No reaction
Pentacarbonyltrichlorosilylmanganese [c]	120	4 day	No reaction
Benzoyl chloride–diethyl ether	20	12 h	Benzaldehyde (80); [i] benzyl benzoate (18)

[a] Time by which the reaction appeared complete; all reactions were carried out in the presence of excess of halogenocarbon (10—50 mol excess). [b] Products formed in >1% yield are reported. Except where stated, the dihalides $(\eta\text{-}C_5H_5)_2WX_2$ were the only involatile products; they were isolated and weighed and found to be present in essentially quantitative yield. In these circumstances the total yield of the reduced organic products is inferred, from the absence (except for traces) of other volatile or involatile products, to be >80%. *Relative* yields of reduced products are given in parentheses. [c] Reaction carried out in benzene solution. [d] Accurate assessment of relative yields not possible by g.l.c. owing to a large difference in volatilities (ethane ca. 10%). [e] Reaction incomplete. [f] Mass spectrum showed parent ion peaks (m/e 212, 214) for $C_3HCl_5^+$. A peak corresponding to $CHCl_2^+$ (m/e 83) was also observed. This suggests the product is the 1,1,2,3,3-isomer. [g] cis-trans-Mixture used. [h] In the presence of 18 mol % azobisisobutyronitrile; 0·5% benzene was obtained under these conditions. [i] Small amounts of toluene (<3%) were also detected. This reaction is complex and the total yield of benzaldehyde from benzoyl chloride is ca. 15%.

used: 10% Apiezon L–Embacel; 20% Carbowax,1500–Chromosorb P(60—80); 20% propylene carbonate–Embacel. Identity of peaks was confirmed by simultaneous injection of authentic samples and subsequent peak enhancement.

The dihydride $(\eta\text{-}C_5H_5)_2WH_2$ was prepared by the

containing a small excess of sodium sand (ca. 1 g) in *pure, dry* tetrahydrofuran (1400 ml) was cooled to ca. −100° in an ethanol slush bath. During the cooling the solution was stirred vigorously with a bushy Nichrome wire stirrer.

[5] M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1961, 4854.

This prevented the sodium cyclopentadienide, which crystallises from the solution, from accumulating in lumps or on the walls of the flask. To the cooled, vigorously stirred slurry were added commercial tungsten hexachloride (120 g) and powdered sodium borohydride (30 g). The tungsten hexachloride was added in portions (1—3 g) every few minutes and sodium borohydride was added in portions (5 g) at regular intervals. The alcohol bath was then packed with solid carbon dioxide; the mixture was stirred at −78° for *ca.* 6 h and then allowed to warm slowly (3 h) to room temperature. The alcohol bath was replaced by a hot-water bath (80°) and the mixture was stirred and refluxed for 1 h. The solvent was removed *in vacuo* (5 h); this was assisted by use of a hot-water bath (last traces at 80°). The residue, under a nitrogen stream, was treated with cold water (200 ml) and then, carefully, with 50% hydrochloric acid. It is better to keep the flask cooled in cold water during the addition of acid. The acid extracts the dihydride as the trihydride cation $[(\eta\text{-}C_5H_5)_2WH_3]^+$. The mixture was stirred vigorously, to break up and extract the insoluble residue. The aqueous extract was filtered through a glass sinter protected by a layer (2·5 cm) of 100—200 mesh silica gel. The residue was extracted again with *ca.* 50% hydrochloric acid (2 × 100 ml) and the extract was filtered. The filtrate was tested with a solution of silicotungstic acid

and extraction was judged to be effectively finished when only a slight precipitate formed. There is a slow reaction between the trihydride cation and chloride ion giving the water-insoluble dichloride, $(\eta\text{-}C_5H_5)_2WCl_2$. For this reason it is not profitable to keep the hydrochloric acid solution hot, or for a long time (several days). Excess of cooled, concentrated sodium hydroxide was added to the aqueous extract, with re-cooling. This precipitated the yellow dihydride. The precipitate was collected on a sintered glass filter which was covered by a layer (2·5 cm) of 100—200 mesh alumina. The filtrate was discarded and the residue washed with water (3 × 100 ml); then surplus water was allowed to drain off. The residue and filter-bed were extracted with acetone *in situ* (4 × 200 ml) and the extract was filtered and concentrated, giving yellow crystals of the dihydride $(\eta\text{-}C_5H_5)_2WH_2$. The acetone was removed in vacuum and the yellow residue was finally purified either by sublimation in vacuum (120° and 10^{-3} mmHg) or by recrystallisation from hot benzene or benzene–petroleum; yield *ca.* 46%. We do not know whether all these steps are necessary but this preparation gives reproducible yields. The preparation takes 4 days.