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Reactions of Uranium Hydride with some Organic and Organometallic Compounds

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Abstract

Uranium hydride reduces chloro-, bromo-, and iodo-benzene to benzene and biphenyl, nitrobenzene to azoxy- and azo-benzene, azoxybenzene to azobenzene, and triphenylarsine oxide to triphenylarsine in boiling tetrahydrofuran and/or in the absence of added solvent at 130–170 °C. In tetrahydrofuran, benzoyl chloride gives low yields of butyl benzoate and benzil. A wide range of substrates, e.g. PhF, p-$(O_2N)_2C_6H_4$, PhCHO, C_5H_5Tl, and Ph_3PO, fails to react with UH_3.

Introduction

Uranium hydride is important as a source of pure uranium and can be used to generate pure hydrogen [1]. Although the compound has been known for many years and its structural, thermodynamic, and physical properties have been extensively investigated [1–4], little is known of reactions with organic and organometallic substrates [1–4]*. Most information derives from the Manhattan project [4, 5]. Carbon tetrachloride was found to react explosively with UH_3 at room temperature [5]. There was evidence for reaction with chloroform and chlorobenzene at room temperature and with nitrobenzene and maleic anhydride on heating, but the products were not identified [5]. Most organic solvents were essentially unaffected at room temperature. Although UH_3 catalyses hydrogenation of benzene to cyclohexane at 180 °C/970 KPa, it is much less effective than MH_2 (M = Ti, Zr, or Hf) and NbH [6]. We now report a study of some reactions of UH_3 with organic and organometallic substrates.

Experimental

(a) Solvents and Reagents

Uranium hydride (99.5%; 100 mesh powder) was from CERAC. Nitrogen and argon were purified by passage through BASF R3/11 oxygen removal catalyst and molecular sieves. Tetrahydrofuran and toluene were distilled from sodium/benzophenone and from lithium aluminium hydride under nitrogen and were stored under nitrogen. Organic substrates were reagent grade and had satisfactory purity by GLC analysis. Triphenylphosphine oxide was from Koch-Light. Triphenylarsine oxide was prepared by a modification of the reported method [7], whilst thallous cyclopentadienide [8] and tris(η-cyclopentadienyl)tetrahydrofuransamarium(III) [9] were obtained by established procedures.

(b) Instrumentation

For analytical GLC, a Varian 3700 gas chromatograph equipped with a 52m SCOT column (OV101) was used. The injection port and F.I.D. temperatures were both 300 °C, and helium (average linear velocity 61 cm/s) was the carrier gas. Column temperatures were normally programmed to increase from 50 °C (initial) at 10 °C/min to 250 °C. For mixtures with low boiling products, isothermal conditions (40 °C) and an average linear velocity of 29 cm/s were used. Quantification was effected with this instrument using authentic samples and the internal standard method, except in the reaction with benzoyl chloride when the external standard method was used. GC/MS were obtained using a Finnigan 3000 series instrument fitted with a 25m SCOT OV101 capillary column. Helium (flow rate 4 ml/min) was the carrier gas, and the column temperature was initially at 40 °C (5 min) and increased at 15 °C/min to 210 °C. Electronic spectra were obtained with Hitachi 150.20 or Cary 17 instruments and IR spectra with a Jasco IRA1 spectrometer.

(c) Reactions with Uranium Hydride

Uranium hydride, a magnetic stirrer bead, and any solid reagent were placed in a Carius tube fitted with a Rotaflo tap under argon in a Vacuum Atmospheres HE43-2 dry box. The tube was then connected to an argon/vacuum manifold for addition

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*Systematic examination of *Chemical Abstracts* shows little on this topic in the past 20 years.

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TABLE I. Reactions of Uranium Hydride[a]

Substrate	Quantity (mmol)	Solvent	Quantity (ml)	Temperature (°C)	Time (h)	Products (% yield)
PhF	15	thf	10	67	60	no reaction
PhF	15	–	–	85	44	no reaction
PhCl	15	thf	5	67	60	no reaction
PhCl	15	–	–	132	44	PhH(44) Ph_2(6) ClC_6H_4Ph[b]
PhBr	15	thf	10	67	60	no reaction
PhBr	15	–	–	156	44	PhH(74) Ph_2(16) BrC_6H_4Ph[b]
PhI	15	thf	10	67	60	no reaction
PhI	15	–	–	170	44	PhH(20) Ph_2(4) IC_6H_4Ph[b]
$PhNO_2$	15	thf	10	67	54	PhN_2Ph(8) PhN(O)NPh(10)
$PhNO_2$	15	–	–	170	49	PhN_2Ph(7) PhN(O)NPh(12)
PhN(O)NPh	5	thf	10	67	49	PhN_2Ph(43)
p-$(O_2N)_2C_6H_4$	5	thf	10	67	48	no reaction
$O_2NC_6H_4CO_2H$[c]	5	thf	10	67	48	no reaction
cyclo-$C_6H_{11}NO_2$	5	thf	10	67	2	cyclo-$C_6H_{10}O$(3)[d]
cyclo-$C_6H_{11}NO_2$	5	–	–	170	0.5	C_6H_{14}, PhH, cyclo-C_6H_{12}, cyclo-C_6H_{10}, cyclo-$C_6H_{10}O$[e]
Ph_3AsO	5	thf	10	67	48	Ph_3As(56)
Ph_3AsO[f]	6.5	thf	10	67	60	Ph_3As(90)
Ph_3PO	5	thf	10	67	24	no reaction
Ph_3PO[f]	5	thf	10	67	88	no reaction
Ph_3PO	5	PhMe	5	111	72	no reaction
Ph_3PO	5	–	–	170	18	no reaction
$PhCH_2Cl$	5	–	–	170	64	PhMe[g], $(PhCH_2)_2$[g]
PhCOCl	5	thf	10	67	120	$PhCO_2Bu$(6), PhCOCOPh[g], BuCl[g]
PhCOCl	5	–	–	170	24	unstable, unidentified
PhCOMe	5	thf	5	67	48	no reaction
PhCHO	5	thf	5	67	48	no reaction
$PhCH{=}CH_2$	5	thf	5	67	48	no reaction
C_5H_5Tl	5	thf	10	67	48	no reaction
$(C_5H_5)_3Sm(thf)$	2.5	thf	10	67	48	no reaction

[a] 5.0 mmol in each case. [b] Traces of 3 isomers. [c] 3 isomers examined. [d] More volatile products not examined. [e] Products not quantified but in low yield. [f] Hg (6 mg at) added. [g] Trace amounts obtained.

of liquid reagents and/or any solvent by syringe. The tube was then sealed, and was stirred and heated in a thermostatically controlled oil bath either at reflux (solvent used) or at 130–170 °C. Amounts of reagents, reaction times and temperatures are given in Table I. After cooling, the reaction mixture was generally hydrolysed with 20% v/v hydrochloric acid under argon, and the organic or organometallic products were extracted with ether. The products from the reaction with nitrocyclohexane were extracted under argon without prior hydrolysis. After reaction with thallous cyclopentadienide, the solvent was evaporated under vacuum. Sublimation of the residue under vacuum gave the thallous reactant (90%). Following reaction with (η-$C_5H_5)_3Sm(thf)$, the solvent was evaporated and the residue transferred under argon to a Schlenk assembly. Extraction with tetrahydrofuran and evaporation gave the reactant (79%). Most products were identified by GLC and/or GC/MS and yields determined by GLC [section (b)]. The formation of cyclohexanone rather than cyclohexanol which had the same retention time was established by comparison of IR and UV spectra with those of authentic samples. Idenfification of triphenylarsine was confirmed by comparison of the IR spectrum with that of an authentic sample, obtained as reported [7]. Products from the reaction with benzoyl chloride without added solvent appeared to be unstable since the GLC behaviour varied with time.

After a reaction with bromobenzene, a solution of an excess of mercuric bromide in tetrahydrofuran was added by syringe under argon to the cooled products. A green solution with visible/near IR absorption (410, 432, 448, 464, 483, 506, 523, 549, 567, 606, 625, 766, 814, 897, 968, 1023, 1100, 1232, 1306 nm) indicative [10] of uranium(IV) and a grey-white precipitate containing (IR and MS) mercury and mercurous bromide but no phenylmercuric bromide, were obtained. Exposure of the green solution to the air saw the colour discharged and no absorption bands above 500 nm.

Results and Discussion

None of the phenyl halides was reduced by UH_3 in refluxing tetrahydrofuran nor was fluorobenzene reduced at the boiling point. However, chloro-, bromo-, and iodo-benzene underwent reaction at 130–170 °C giving benzene (major product), biphenyl, and traces of three monohalogenobiphenyl isomers (Table I). Recovery of aryl groups including unreacted halogenobenzene was *ca.* 85% (PhCl, PhI) and *ca.* 100% (PhBr). The high yield of benzene when a PhBr:UH_3 mole ratio of 3:1 was used, suggests the stoichiometry in reaction (1).

$$UH_3 + 3PhBr \longrightarrow UBr_3 + 3PhH \qquad (1)$$

Initial formation of a phenyluranium(IV) species which gives benzene on hydrolytic work up is inconsistent with the apparent stoichiometry, and with formation of mercurous bromide, mercury, and a uranium(IV) species (e.g. eqn. (2)) and not phenylmercuric bromide on treatment of the UH_3/PhBr reaction product with mercuric bromide in tetrahydrofuran.

$$2UBr_3 + 2HgBr_2 \longrightarrow Hg_2Br_2 + 2UBr_4 \qquad (2)$$

Although the behaviour of UH_3 towards halogenobenzenes can be represented as competition between hydride transfer giving benzene and electron transfer giving phenyl radicals, the former seems unlikely given the non-hydridic structure of UH_3 [11] and the lack of reactivity towards aldehydes and ketones (Table I). It is more probable that the products derive from charge transfer and free radical reactions (eqn. (3)–(7)).

$$UH_3 + PhX \rightleftharpoons [H_3UXPh]^{\bullet} \longrightarrow H_3UX + Ph^{\bullet} \qquad (3)$$

$$\downarrow$$

$$[H_3U^+]\,[PhX]^{\dot{-}} \longrightarrow PhH + UH_2X^* \qquad (4)$$

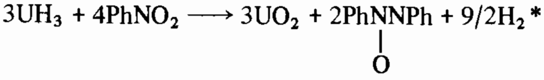
$$Ph^{\bullet} + PhX \longrightarrow Ph_2 + X^{\bullet} \qquad (5)$$

$$Ph^{\bullet} + PhX \longrightarrow PhC_6H_4X + H^{\bullet} \qquad (6)$$

$$2Ph^{\bullet} \longrightarrow Ph_2 \qquad . (7)$$

Dehalogenation of aryl halides has been achieved by a variety of other reagents, particularly metal hydrides [12], e.g. Ph_3SnH [13], $LiAlH_4$ [14], $NaBH_4$ with $PdCl_2$ [15], and NaH [16].

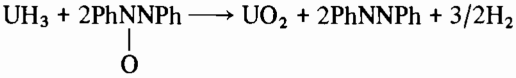
Reduction of nitrobenzene with UH_3 either in tetrahydrofuran or in the absence of a solvent gave azoxybenzene and azobenzene in low yield as the sole identifiable products (reactions (8) and (9)).



$$3UH_3 + 4PhNO_2 \longrightarrow 3UO_2 + 2\underset{\displaystyle O}{PhN\overset{}{N}Ph} + 9/2H_2^{**} \qquad (8)$$

$$2UH_3 + 2PhNO_2 \longrightarrow 2UO_2 + PhNNPh + 3H_2^{**} \qquad (9)$$

No aniline was formed in agreement with an earlier observation [5]. The low recovery of ary groups (35–50%, including unreacted $PhNO_2$) and the dark-brown appearance of the reaction mixtures suggested formation of polymeric or gross decomposition products. Azoxybenzene may be an intermediate in the formation of azobenzene, and it has been independently reduced to azobenzene in reasonable yield (Table I).



$$UH_3 + 2\underset{\displaystyle O}{PhNNPh} \longrightarrow UO_2 + 2PhNNPh + 3/2H_2 \qquad (10)$$

Reduction of nitrobenzene may involve initial formation of nitrosobenzene and phenylhydroxylamine, which are known to condense to give azoxybenzene [17, 18]. 1,1′-dibutyluranocene reduces a range of nitro compounds to azo compounds but the reactions do not involve azoxy intermediates [18]. Reduction of nitrobenzene by samarium diiodide yields aniline as well as azobenzene [19]. Attempted reduction of a range of other aromatic nitro compounds by UH_3 failed (Table I). Nitrocyclohexane at 170 °C gave a plethora of reduction products, including hexane, in low yield (Table I).

Triphenylarsine oxide was cleanly reduced to triphenylarsine by uranium hydride (eqn. (11)).

$$UH_3 + 2Ph_3AsO \longrightarrow UO_2 + 2Ph_3As + 3/2H_2 \qquad (11)$$

A near quantitative yield of the arsine was obtained using a UH_3 ‘quasi amalgam’ (actually a fine dispersion of UH_3 in mercury [20]). By contrast, triphenylphosphine oxide was recovered unchanged after attempted reaction with UH_3 under a variety of conditions including ‘quasi amalgamation’. The P=O stretching force constant in triphenylphosphine oxide [21, 22] is greater than the As=O force constant of the arsine oxide [22], and this difference in bond strength presumably accounts for the difference in reactivity.

In the reaction with benzyl chloride, the only identifiable products, toluene and bibenzyl, were obtained in trace amounts. Their formation by reactions analogous to eqns. (3)–(7) can readily be envisaged. From reaction with benzoyl chloride in tetrahydrofuran, the only identifiable products were butyl benzoate and traces of butyl chloride and benzil. The latter presumably arises from formation and coupling of benzoyl radicals. Butyl benzoate must result from cleavage of tetrahydrofuran since

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*Analogous sequences give UX_3.

**Although water may be an initial reaction product, this would be expected to hydrolyse UH_3 under conditions of prolonged heating [5].

it was not formed from $UH_3/PhCOCl$ in the absence of this solvent. It appears that $[PhCO]^{\bullet}$ radicals do not cause ring opening, as reduction of benzoyl chloride to benzil by samarium diiodide is not accompanied by formation of butyl benzoate [23]. Reaction of uranium tetrachloride with sodium metal and potassium cyclopentadienide in tetrahydrofuran gives tris(cyclopentadienyl)uranium butoxide [24], hence a hydridouranium species may open tetrahydrofuran in the $UH_3/PhCOCl$ system (reaction (12)), and the resulting butoxouranium species may react with benzoyl chloride to give butyl benzoate (reaction (13)).

$$-UH + thf \longrightarrow -UOBu \qquad (12)$$

$$-UOBu + PhCOCl \longrightarrow PhCO_2Bu + -UCl \qquad (13)$$

Uranium hydride failed to reduce keto, aldehyde, and terminal double bond functions (Table I). No reductive transmetallation to give cyclopentadienyluranium(IV) species and metallic thallium was observed with thallous cyclopentadienide, and tris(cyclopentadienyl)samarium could not be reduced to a divalent species.

Given the violent reaction of UH_3 with oxygen and with carbon tetrachloride [5], the low reactivity with a range of organic and organometallic substrates (Table I) is perhaps surprising and presumably arises from low solubility and the polymeric constitution [11]. The combination of this low reactivity and severe handling problems does not commend UH_3 as a synthetic reagent at present. If it could be dissolved, e.g. by complexation, considerably increased reactivity as a reductant could be expected.

Acknowledgement

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