Arene Hydrides, 4[1]

Reaction of Anthracene Hydride (Anion of 9,10-Dihydroanthracene) with Diaryl Ketones. Base-Induced Fragmentation of the Carbonyl Adduct

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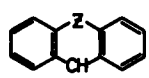
With benzophenone (**1a**) and fluorenone (**1b**) anthracene hydride (AH^-) rapidly forms the anions **3a,b** of the corresponding tertiary alcohols **4a,b**, the intense colour of the reaction mixture indicating the presence of the ketyls **2a,b**. Excess of AH^- converts **3a,b** into the diarylcarbinols. A mechanism is proposed for this ketone reduction.

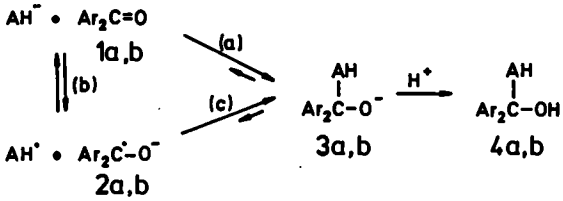
Anthracene hydride (AH^-) is a particularly interesting member of the arene hydride family which consists of carbanions formally constructed by addition of a hydride ion to an arene. Recently[1] it was reported that AH^- selectively reduces the C=C double bond of chalcone by a base-induced fragmentation of the intermediate Michael adduct of the two reagents. We present now a novel although similar base-induced fragmentation of a carbonyl adduct derived from AH^-. This finding may shed new light on the reported[2] intermediacy of a similar carbonyl adduct in the reductive opening of *N*-aroylaziridines by AH^-.

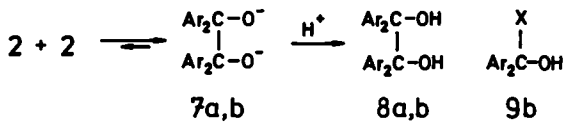
Scheme 1



A (anthracene) : Z = CH
AH : Z = CH_2
X : Z = O

	Ar_2C
a	Ph_2C
b	fluorenylidene





Addition of benzophenone (**1a**) or fluorenone (**1b**) to a dark red solution of AH^- in THF gives an instantaneous reaction: Each entering drop of the ketone solution (THF) takes immediately on the blue (green) colour of benzophenone (fluorenone) ketyl. This ketyl colour persists when the amount of ketone approaches equimolecularity. It did not disappear in the reactions of Table 1 until the reaction was quenched with glacial acetic acid.

After a short reaction time with one equivalent of AH^- (run 1) we isolated a high yield of the tertiary alcohol **4a**. The rest of **1a** was obtained unchanged in spite of the intense ketyl colour of the reaction mixture prior to quenching. At least two reactions had occurred in this run: classic nucleophilic addition (a) and single electron transfer (SET) (b) or SET (b) followed by radical combination (c). The latter alternative would be a pendant to the known[3] dimerization of **2a** with formation of **7a**. A SET mechanism has recently[4] been proven for the reaction of **1a** with carbanionic species. We assume that (a), (b), and (c) occur simultaneously and that they are reversible. The small amount of ketyl **2a** present prior to quenching may first be protonated to **5a** followed by an interradical hydrogen atom transfer with the dihydroanthryl radical $AH^\bullet$ forming **1a** and dihydroanthracene AH_2. The same reaction with fluorenone (run 2) provided a lesser amount of tertiary alcohol (**4b**), some fluorenol **6b** and the respective pinacol **8b**. Diol **8b** and probably also **6b** may be considered to arise from the ketyl **2b** present in the reaction mixture.

The main products of runs 1 and 2, the tertiary alcohols **4a,b**, disappeared completely after prolonged reaction with an excess of AH^- (runs 3 and 4). Thus, prior to quenching with acid the carbonyl adducts **3a,b** were converted to something else. Main product was now the respective diarylcarbinol **6a,b**. Pinacol (**8a,b**) and ketone (**1a,b**) were also isolated. These results of runs 3 and 4 point to an AH^--induced fragmentation of the carbonyl adducts **3a,b** similar to the reported fragmentation of the Michael adduct formed from AH^- and chalcone[1]. This fragmentation results in an over-all reduction of **1a,b** by AH_2. The driving force is certainly the aromatization of the AH moiety in **3a,b** forming anthracene A. A substantial part of A could be isolated by simple filtration in runs (3, 4, 6) with high yields of carbinol. A possible mechanism of the fragmentation is shown in Scheme 2.

3a,b is attacked (I) and deprotonated (II) by excess AH^- (exclusive 10-deprotonation of 9-alkyl-9,10-dihydroanthracenes is well known[5]).

Fragmentation (III), that may or may not occur concertedly with the deprotonation, yields A and the dianion of the ketone. This dianion abstracts a proton (IV) from AH_2 forming the alcoholate of **6a,b**. The required AH_2 molecule has been formed in this reaction sequence (in cage reaction) although protonation by the excess of free AH_2 cannot be excluded. Reaction of the dianion with uncharged ketone **1a,b** may yield pinacolate **7a,b** and ketyl.

To test the deprotonation step of this mechanism, we repeated run 4 substituting the xanthenyl anion (X^-) for AH^-. The oxa

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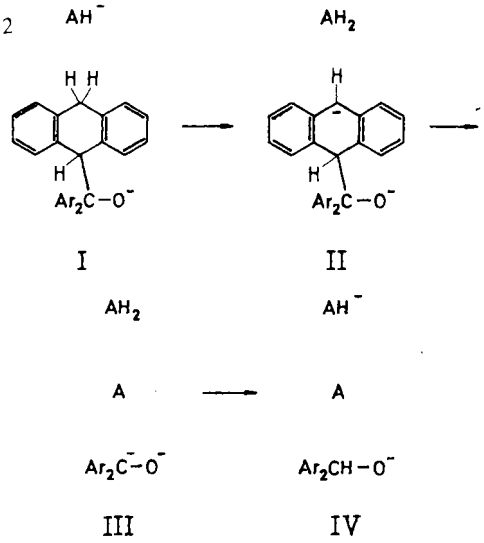
Table 1. Reactions of anthracene hydride (AH^-) with diaryl ketones **1a,b** at room temperature

run	mmol reagents					ml THF	time	products[a]
1	6.25 AH_2	5	BuLi	5	**1a**	50	3 min	84% **4a**, 13% **1a**
2	6.66 AH_2	5	BuLi	5	**1b**	60	10 min	63% **4b**, 20% **6b**, 9% **8b**
3	7.5 AH_2	5	BuLi	5	**1a**	70	3 d	73% **6a**, 8% **8a**, 12% **1a**, 64% **A**[b]
4	7.5 AH_2	5	BuLi	5	**1b**	70	6 d	48% **6b**, 40% **8b**, 12% **1b**, 34% **A**[b]
5	7.5 **XH**	6.25	BuLi	5	**1b**	70	6 d	66% **9b**, (14%) **6b**, (15%) **8b**
6	3.5 AH_2	2.25	BuLi	1.1	**4a**	40	4 d	95% **6a**, 71% **A**[b]
7	1.66 AH_2	1	BuLi	1.1	**4a**	30	5 min	(78%) **4a**, (21%) **1a**
8	1.66 AH_2	1	BuLi	1.1	**4a**	30	3 d	(50%) **4a**, (50%) **1a**

[a] Yields in parentheses from ^{1}H-NMR analysis. The amount of **A** obtained as mixture with unreacted AH_2 was not determined. — [b] Isolated by filtration.

Scheme 2



analogue of **3b** cannot form the stages II and III of Scheme 2. Indeed, as expected, the outcome of run 5 was quite similar to that of run 2, the tertiary alcohol **9b** being the main product despite the excess of carbanion.

We made cross-checks of the proposed mechanism by deprotonating the tertiary alcohol **4a** with AH^- thus entering the equilibria system (a)-(b)-(c) from the right side as evidenced by immediate development of the dark blue colour. In run 6 with great excess of AH^- and AH_2 the carbinol **6a** was the sole ketone-derived product. It was obtained in practically quantitative yield. Deprotonation of **4a** with an insufficient amount (90%) of AH^- gave no **6a** (runs 7 and 8). As expected, run 7 provided a result very similar to run 1. Run 8 ensured that even with a long reaction time no **6a** was obtained. The yield difference between run 7 and 8 is probably caused by a small leakage (allowing oxygen to enter) in run 8 as was indicated by the gradual disappearance of the ketyl colour in this run.

The ^{1}H-NMR doublet for the pseudo axial proton in position 10 of **4b** is shifted upfield from the usual value due to the ring-current effect of the fluorenyl moiety. In **4a**, the freely rotating two phenyl groups cannot exert a similar influence. Generally, the signals of pseudo axial protons are distinctly broader than those of their pseudo equatorial counterparts[1,2] owing to the angle-dependent long-range coupling.

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Experimental

IR spectrometer: Perkin-Elmer 283. — ^{1}H-NMR spectrometer: Bruker HX-90 E. — Column chromatography: Silica gel Merck 0.063–0.2 mm. Column dimensions (in cm) are given below.

All reactions were performed in dry THF under dry nitrogen and with continuous stirring.

General Method: THF solutions of AH^-Li^+ (X^-Li^+) were prepared from THF solutions of AH_2 (**XH**) and BuLi (solution in hexane) at −65°C (general technique as described in ref.[2]). A solution of the reactant (**1a,b**, **4a**) in THF (10 ml of the total amount given in Table 1) was added dropwise to the carbanion solution at room temperature. After the time given in Table 1, the reaction was quenched with glacial acetic acid. The mixture was evaporated to dryness (rotatory evaporator, bath temperature 40°C), the residue was taken up in dichloromethane, the solution washed with water and again evaporated. The residue was subjected to chromatography.

Run 1: Chromatography (2.2 × 60, toluene) provided 440 mg of AH_2, 1.52 g (84%) of **4a**, and 120 mg (13%) of **1a**.

α-(9,10-Dihydro-9-anthryl)benzhydrol (**4a**): M.p. 170–171°C (CCl_4). — IR (KBr): 3560 cm^{-1}, 1034 (C–O). — ^{1}H NMR ($CDCl_3$): δ = 2.26 (s, OH), 3.61 (d, J = 18.9 Hz, 10-H, pseudo eq), 3.86 (d, J = 18.9 Hz, 10-H, pseudo ax), 5.12 (s, 9-H, pseudo eq), 6.72–7.49 (m, 18H, aryl).

$C_{27}H_{22}O$ (362.5) Calcd. C 89.46 H 6.11
Found C 89.54 H 6.16

Run 2: Chromatography (2.2 × 60) with toluene provided 530 mg of AH_2 and 1.14 g (63%) of **4b** followed (ethyl acetate) by 260 mg of a mixture that was subjected to a second chromatography (3 × 25). Elution with dichloromethane yielded 180 mg (20%) of **6b**, elution with ethyl acetate gave 80 mg (9%) of **8b**.

9-(9,10-Dihydro-9-anthryl)-9-fluorenol (**4b**): M.p. 183°C (CCl_4). — IR (KBr): 3140–3520 cm^{-1} (OH), 1038 (C–O), 1030 (C–O). — ^{1}H NMR ($CDCl_3$): δ = 2.42 (s, OH), 3.14 (d, J = 19.2 Hz, 10-H, pseudo ax), 3.40 (d, J = 19.2 Hz, 10-H, pseudo eq), 4.67 (s, 9-H, pseudo eq), 6.88–7.31 (m, 16H, aryl).

$C_{27}H_{20}O$ (360.5) Calcd. C 89.96 H 5.59
Found C 90.09 H 5.60

6b: M.p. 153°C (ref.[6a] 153°C, 156°C). – IR (KBr): 3100–3480 cm^{-1}, 1036 sh (C–O). – ^1H NMR ($CDCl_3$): δ = 1.99 (s br, OH), 5.50 (s br, O–CH), 7.22–7.39 (m, 10H, aryl).

8b: M.p. 190°C (ref.[6b] 190–192°C). – IR (KBr): 3520 cm^{-1} (OH), 3400 (OH), 1047 (C–O). – ^1H NMR ($CDCl_3$): δ = 3.20 (s, OH), 7.10–7.35 (m, aryl).

Run 3: Prior to chromatography 570 mg of **A** (64%) was filtered off from the dichloromethane solution. Chromatography (3 × 25) with toluene provided 760 mg of hydrocarbons (**AH_2** and **A**) and 190 mg of a mixture consisting of **1a** and **8a**. Elution with dichloromethane/ethyl acetate (3:1) yielded 670 mg (73%) of **6a**. The above mixture was separated by preparative TLC (Merck silica gel 60 F_{254}, 2 mm thick, dichloromethane) into 72 mg (8%) of **8a** (upper zone) and 108 mg (12%) of **1a**.

6a: M.p. 66–67°C (ref.[6c] 67.5–68.5°C). – IR (KBr): 3160–3560 cm^{-1} (OH), 1039, 1033, 1020 (all C–O). – ^1H NMR ($CDCl_3$): δ = 2.32 (d, *J* = 3.3 Hz, OH), 5.80 (d, *J* = 3.3 Hz, O–CH), 7.22–7.39 (m, aryl).

8a: M.p. 185°C (ref.[6d] 185–186°C). – IR (KBr): 3580 cm^{-1} (OH), 3555 (OH), 1045 (C–O), 1028 (C–O). – ^1H NMR ($CDCl_3$): δ = 3.02 (s, OH), 7.10–7.35 (m, aryl).

Run 4: As in run 3, 300 mg (34%) of **A** was filtered off. Chromatography (3 × 25) with toluene provided 1.0 g of hydrocarbons (**AH_2** and **A**) and 110 mg (12%) of **1b**. Further elution yielded 430 mg (48%) of **6b** (dichloromethane) and 360 mg (40%) of **8b** (ethyl acetate).

Run 5: Chromatography (2.2 × 60) with toluene yielded 720 mg of **XH**. Further elution yielded 1.19 g (66%) of **9b** (dichloromethane) and 270 mg (ethyl acetate) of a mixture consisting (^1H-NMR analysis) of 131 mg (14%) of **6b** and 139 mg (15%) of **8b**.

9-(9-Xanthyl)-9-fluorenol (**9b**): M.p. 169–170°C. – IR (KBr): 3545 cm^{-1} (OH), 1258 (C–O–C), 1048 (C–O), 1034 (C–O). – ^1H NMR ($CDCl_3$): δ = 2.36 (s, OH), 4.63 (s, 9-H), 6.71–7.31 (m, aryl).

$C_{26}H_{20}O_2$ (364.4) Calcd. C 85.68 H 5.53
Found C 85.40 H 5.48

Run 6: As in run 3, 140 mg (71%) of **A** was filtered off. Chromatography (2.2 × 60) with dichloromethane provided 670 mg of hydrocarbons (**AH_2** and **A**). Elution with ethyl acetate yielded 190 mg (95%) of **6a**.

Run 7: Chromatography (3 × 25) with toluene provided 300 mg of **AH_2**. Elution with ethyl acetate yielded 350 mg of a mixture consisting (^1H NMR) of 310 mg (78%) of **4a** and 40 mg (21%) of **1a**.

Run 8: Work-up as in run 7 provided 300 mg of a mixture consisting (^1H NMR) of 200 mg (50%) of **4a** and 100 mg (50%) of **1a**.

CAS Registry Numbers

1a: 119-61-9 / **1b**: 486-25-9 / **2a**: 96179-06-5 / **4b**: 111410-41-4 / **6a**: 91-01-0 / **6b**: 1689-64-1 / **8a**: 464-72-2 / **8b**: 3073-51-6 / **9b**: 111410-42-5 / AH_2: 613-31-0 / HX: 92-83-1

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