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ARENE HYDRIDES - 7.[1]

REACTIONS OF ANTHRACENE HYDRIDE WITH STYRENE AND STILBENE OXIDE. REDUCTION IN BENZYLIC POSITION VIA NUCLEOPHILIC SUBSTITUTION

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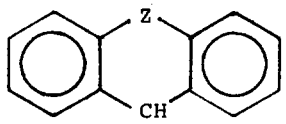
Abstract - Nucleophilic ring opening of oxiranes 1 and 2 by the carbanion AH^- ("anthracene hydride") proceeds rapidly giving rise to two isomeric products 3 and 5 from styrene oxide 1. In prolonged reactions, products with a 9-benzyl 9,10-dihydroanthracene structure (5, 6) are fragmented by an excess of carbanion to yield anthracene **A** and benzylic anions. The respective products 7 and 8 of reductive opening can be isolated in good yields with Na^+ as gegen ion; however, they are transformed into styrenes with Li^+. No fragmentation was observed in reactions of styrene oxide with xanthenyl anion Xan^-.

The reducing power of anthracene hydride AH^- has been demonstrated.[1-4] Conclusive arguments have been presented that the overall electron transfer proceeded mainly via an AH^- induced fragmentation of an intermediate carbonyl adduct[1-3] or Michael adduct[4]. We now describe the first examples of such a reduction of simple 9-benzyl 9,10-dihydroanthracene intermediates. This mild and novel reduction is restricted to a benzylic position sensitive to nucleophilic attack.

Styrene oxide 1 usually undergoes nucleophilic ring opening in both directions[5] with a preference for attack on the benzylic position by soft nucleophiles[6]. Therefore, the results obtained from AH^- and 1 in runs 1-3 of Table 1 (all reactions in THF) are not unexpected. Since one of the products (3a) was difficult to fully characterize, run 2 and 3 were quenched with acetic anhydride in order to obtain the ester 3b. It is worth mentioning,

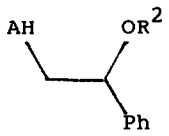
AH_2 = 9,10-dihydroanthracene
AH^- = anion of **AH_2** (anthracene hydride)
XanH = xanthene
Xan^- = xanthenyl anion
A = anthracene



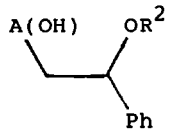
Z	
CH_2	9,10-dihydro-9-anthryl = **AH**
CHOH	10-hydroxydihydroanthryl = **A(OH)**
O	9-xanthenyl = **Xan**

	R^1
1	H
2	Ph

AH^-

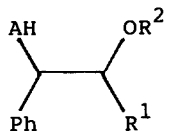


Ox.

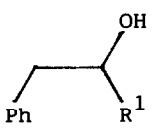


	R^2
3a	H
3b	Ac

	R^2
4a	H
4b	Ac

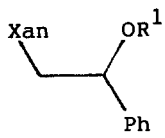


	R^1	R^2
5a	H	H
5b	H	Ac
6a	Ph	H



	R^1
7	H
8	Ph

1 **Xan^-**



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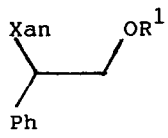


	R^1
9a	H
9b	Ac

	R^1
10a	H
10b	Ac

Table 1. Reactions of **1** and **2** (or **3a** and **5a**) with AH^- or Xan^-.

run	reactants (% excess of carbanions)	days	quenched with	yields (%) of products
1	**1** AH^-Li^+ (0)	.01	$MeCO_2H$	32 **3a**, 62 **5a**
2	**1** AH^-Li^+ (50)	.028	$(MeCO)_2O$	3 **3a**, 17 **3b**, 3 **5a**, 60 **5b**, trace **4b**
3	**1** AH^-Na^+ (60)	.01	$(MeCO)_2O$	3 **3a**, 12 **3b**, 66 **5b**, 3 **4b**
4	**1** AH^-Na^+ (50)	.21	-	27 **3a**, 42 **5a**[a], 20 **7**, trace **4a**
5	**1** AH^-Na^+ (100)	3	-	19 **3a**, 66 **7**
6	**1** AH^-Na^+ (120)	3	$MeCO_2H$	25 **3a**, 56 **7**
7	**1** AH^-Li^+ (25-50)	2-12	$MeCO_2H$	29-35 **3a**, 0 **5a**, 22-50 **7**, 34-68 **A**[b]
8	**5a** AH^-Li^+ (134)	11	$MeCO_2H$	0 **5a**, 24 **7**
9	**1** AH^-Li^+ (0)	3	-	16 **3a**, 50 **5a**
10	**3a** AH^-Li^+ (336)	7	$MeCO_2H$	92 **3a**
11	**1** X^-Li^+ (30)	4	-	16 **9a**, 68 **10a**
12	**1** X^-Li^+ (25)	1	$(MeCO)_2O$	1 **9a**, 14 **9b**, 2 **10a**, 69 **10b**
13	**2** AH^-Li^+ (0)	.007	$MeCO_2H$	72 **6a**, 3 **8**
14	**2** AH^-Li^+ (25)	5	$MeCO_2H$	12 **6a**, 18 **8**, 74 **A**, 52 stilbene
15	**2** AH^-Na^+ (23)	4	-	9 **6a**, 67 **8**
16	**6a** AH^-Li^+ (136)	6	$MeCO_2H$	0 **6a**, 24 **8**, 94 **A**, 67 stilbene

[a] Part of **5a** was converted into **5b** during chromatography with ethyl acetate.
[b] Usually only that part of **A** is given which remained undissolved in CH_2Cl_2.

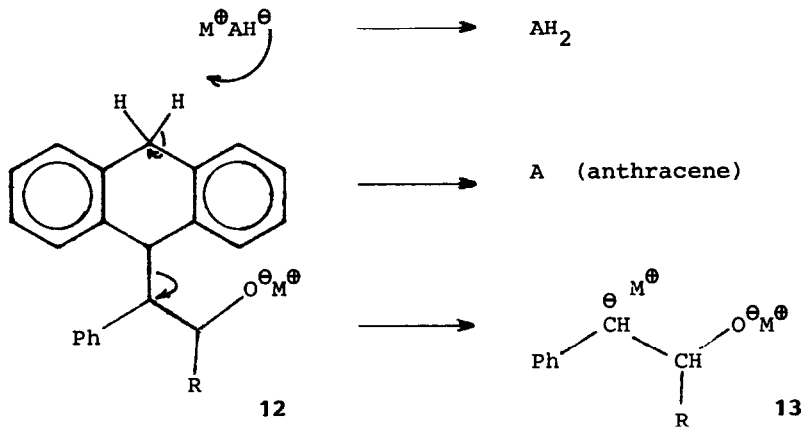
that **3a** or its anion was sensitive to air as the detection of small amounts of **4a,b** (hydroxylated **3a,b**) in runs 2-4 indicated. **4a,b** could not be isolated in a pure state but were characterized by their ^{1}H-NMR spectra.

Most remarkably, when an excess of AH^-Na^+ was allowed to react longer than in runs 1-3, the product **5a** disappeared slowly (run 4) but

completely (runs 5 and 6), being replaced by the new product **7**. Anthracene **A** had arisen in runs 4 and 5 but was not determined quantitatively. With AH^-Li^+ under similar conditions (several experiments are subsumed in run 7) a similar result was found except for lower yields of **7** despite complete disappearance of **5a** and formation of **A** in yields approaching those of **5a,b** in runs 1-3. This deficit in **7** is discussed later. These results demonstrate that **5a** is transformed into **A** and **7** which, or a precursor of which, respectively, undergoes further conversion when Li^+ is the counter ion. This is supported by run 8: long-time reaction of **5a** with an excess of AH^-Li^+ destroys **5a** completely but gives only a small yield of **7**. Run 9 shows that a long reaction time is insufficient for the conversion of **5a** when AH^- is not present in excess. In contrast, the isomer **3a** of **5a** was stable under the reaction conditions. This stability was separately confirmed in run 10. An analogous stability was observed when we obtained 86% 9-(2-hydroxy-2-methylpropyl)-9,10-dihydroanthracene (**11**) as sole product (not included in Table 1) from isobutylene oxide and an excess of AH^-Li^+ after 3 days (cf. also the stability of other 9-substituted dihydroanthracenes when the substituent is non-benzylic[7]).

Substituting xanthenyl anion X^- for AH^- led to simple nucleophilic ring opening with a regioselectivity similar to runs 1-3 but without reactions due to carbanion excess and long reaction time (runs 11 and 12).

trans Stilbene oxide **2** underwent nucleophilic ring opening by AH^- as expected (run 13-15). As above, subsequent reaction with an excess of AH^- led to reductive ring opening. The reduction product (**8**) could again be obtained in good yield (run 15) with Na^+ as gegen ion. The incomplete conversion **6a** → **8** in runs 14-15 indicates that the excess of AH^- was not high enough. The formation of trans stilbene in the AH^-Li^+ runs 14 and 16 accounts for the loss in **8** and allows conclusions concerning the diminished yield of **7** in the AH^-Li^+ runs.



$$\mathbf{13} \xrightarrow{M = Li} Li_2O + Ph\text{-}CH{=}CH\text{-}R \quad (R = H, Ph)$$

$$\mathbf{13} + AH_2 \xrightarrow{M = Na\ (Li)} Ph\text{-}CH_2\text{-}\underset{\displaystyle R}{\underset{|}{CH}}\text{-}O^{\ominus}M^{\oplus} \quad (+ H^{\oplus} \longrightarrow \mathbf{7, 8})$$

These results leave little doubt that the intermediates **12** form **A** and dianions **13** by deprotonation (through $\mathbf{AH}^-$). Important for this fragmentation is the charge stabilization by the phenyl group in **13**. This does not only follow from the present and previous[7] reports but also from the reversal of this fragmentation which is described and used[8] in the addition of alkyllithiums (without charge stabilization) to anthracene. Dianions of type **13** (including **13** itself with R = H and M = Li or K) have recently been generated and converted into substitution products at low temperatures[9]. At room temperature, the fate of **13** depends clearly on the counter ion: with Na^+ proton capture (from the acid $\mathbf{AH}_2$) occurs and with Li^+ mainly elimination of Li_2O takes place with formation of trans stilbene (R = Ph) or styrene (R = H) which cannot be expected to survive in the presence of $\mathbf{AH}^-$ and was therefore not found. The elimination of Li_2O from dianions of type **13** (M = Li) and the formation of alkenes has previously been described[10] as well as the absence

of such a reaction with M = Na.

Conclusion - There are no reasons why the preparation and subsequent fragmentation of 9-benzyl dihydroanthracenes should be restricted to the present cases[11]. Hence, this work may indicate a general route from Ar-C-(leaving group) to Ar-C-H. Benzylic positions without an appropriate leaving group should fail to form the respective benzyl dihydroanthracene intermediate.

EXPERIMENTAL

IR spectra (KBr tablets or film) were recorded on a Perkin-Elmer 283 spectrometer. ^{1}H-NMR spectra (90 MHz or 250 MHz, $CDCl_3$, internal TMS) were recorded on Bruker spectrometers HX 90-E or WM 250. Chemical shifts are given in ppm, coupling constants in Hz. Multiplicity abbreviations: s, d, t, m, mc (m centred at).

All runs were conducted at room temperature in dry THF under dry nitrogen with continuous stirring (for further details cf. ref.[2]). Column chromatography (column dimensions given in cm) was performed with silica gel Merck 0.063-0.2 mm.

Typical Procedure. (a) 6.25 mmol of butyllithium (solution in hexane) was added to a solution of 7.5 mmol of **AH_2** in 60-100 ml THF at or below -60°C (cf. ref.[2]) or (b) 20 mmol of sodium amide (50% dispersion in white oil) was heated to reflux for about 3 h in a solution of 25 mmol of **AH_2** in 200 ml THF. At room temperature, a solution of 5.0 mmol **1** (or the respective quantity of the respective reactant, see Table 1) in 10 ml THF was added drop-wise. Alternatively, in some runs undissolved **1** was added at once by means of a syringe. In several runs (cf. Table 1) the reaction was quenched with an excess of either glacial acetic acid or acetic acid anhydride. After evaporation of the reaction mixture under reduced pressure, the residue was taken up in CH_2Cl_2 and washed with water. On concentration, the organic layer separated **A** (only in runs with fragmentation of **5a** or **6a**) that was isolated by filtration in several runs. Chromatography (3 x 60) provided pure products or mixtures that were quantitatively analyzed by means of their weight and their ^{1}H-NMR spectra. Hydrocarbons (**AH_2**, **A**, trans stilbene) were eluted with toluene or CH_2Cl_2, other compounds were eluted with CH_2Cl_2 or ethyl acetate. The sequence of elution was **6a** > **8**, **XanH** >> **9b** > **10b** > **9a** > **10a**, **4b** ≈ **3b** > **5b** ≈ **4a** > **3a** ≈ **5a** > **7**. The hydrocarbon fraction was not always analyzed for **A**.

9-(2-Hydroxy-2-phenylethyl)-9,10-dihydroanthracene (**3a**). Oil; IR ν 3570, 3420, 1042/cm; H-NMR δ 1.61 (s br, 1 H, OH), 1.87 (ddd, 13.9 Hz, 10.0 Hz, 3.8 Hz, 1 H of O-C-CH_2), 2.07 (ddd, 14.0 Hz, 9.8 Hz, 5.5 Hz, 1 H of O-C-CH_2), 3.87 (d, 18.3 Hz, 1 H, 10-H pseudo eq), 4.09 (d, 18.3 Hz, 1 H, 10-H pseudo ax), 4.28 (dd, 9.9 Hz, 5.5 Hz, 1 H, 9-H pseudo eq), 4.56 (dd, 9.7 Hz, 3.7 Hz, 1 H, O-CH), 6.98-7.42 (m, 13 H, aromatic H). Anal. Cald. for $C_{44}H_{42}O_3$

corresponding to (**3a**)$_2$×H_2O: C, 85.38; H, 6.84; O, 7.78. Found (after drying at 80°C in vacuum): C, 85.46; H, 6.83; O, 7.75. Anal. Cald. for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found (after drying at 120°C in vacuum): C, 87.96; H, 6.83.

9-(2-Acetoxy-2-phenylethyl)-9,10-dihydroanthracene (**3b**). M.p. 104-105°C; IR ν 1740, 1732, 1233, 1022/cm; H-NMR δ 1.97 (ddd, 14.3 Hz, 9.0 Hz, 4.1 Hz, 1 H of O-C-CH_2), 2.05 (s, 3 H, Me), 2.27 (ddd, 14.3 Hz, 9.8 Hz, 5.9 Hz, 1 H of O-C-CH_2), 3.87 (d, 18.5 Hz, 1 H, 10-H pseudo eq), 4.04 (m_c, 1 H, 9-H pseudo eq), 4.09 (d, 18.5 Hz, 1 H, 10-H pseudo ax), 5.62 (dd, 9.8 Hz, 4.1 Hz, 1 H, O-CH), 7.15-7.31 (m, 13 H, aromatic H). Anal. Calcd. for $C_{24}H_{22}O_2$: C, 84.18; H, 6.47. Found: C, 84.11; H, 6.52.

9-(2-Hydroxy-2-phenylethyl)-10-hydroxy-9,10-dihydroanthracene (**4a**). Obtained as mixture with **3a**. H-NMR δ 2.08-2.19 (m, 1 H of CH_2), 2.26-2.38 (m, 1 H of CH_2), 4.35 (dd, 9.6 Hz, 5.8 Hz, 1 H, 9-H), 4.69 (dd, 9.6 Hz, 3.8 Hz, 1 H, O-CH), 5.90 (s, 1 H, 10-H), 7.15-7.60 (m, aromatic H together with those of **3a**).

9-(2-Acetoxy-2-phenylethyl)-10-hydroxy-9,10-dihydroanthracene (**4b**). Obtained as mixture with **3b**. H-NMR δ 2.01 (s, 3 H, Me), 2.33 (m_c, 1 H of CH_2), 2.55 (m_c, 1 H of CH_2), 4.38 (m_c, 1 H, 9-H), 5.71 (dd, 8.7 Hz, 5.1 Hz, 1 H, O-CH), 5.88 (s, 1 H, 10-H), 7.07-7.60 (m, aromatic together with those of **3b**).

9-(2-Hydroxy-1-phenylethyl)-9,10-dihydroanthracene (**5a**). M.p. 110-111°C; IR ν 3560, 3480, 1080, 1056, 1033, 1019/cm; H-NMR δ 1.87 (s br, 1 H, OH), 3.00 (d, 18.6 Hz, 1 H, 10-H pseudo ax), 3.08 (m_c, 1 H, O-C-CH) 3.47 (d, 18.6 Hz, 1 H, 10-H pseudo eq), 3.87 (m_c, 2 H, O-CH_2), 4.31 (d, 6.5 Hz, 1 H, 9-H pseudo eq), 6.54 (d, 7.8 Hz, 2 H, o-H of Ph), 6.74-7.34 (m, 11 H, aromatic H). Anal. Calcd. for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.85; H, 6.73.

9-(2-Acetoxy-1-phenylethyl)-9,10-dihydroanthracene (**5b**). M.p. 110-111°C; IR ν 1745, 1065, 1035/cm; H-NMR δ 2.00 (s, 3 H, Me), 2.83 (d, 18.7 Hz, 1 H, 10-H pseudo ax), 3.30 (m_c, 1 H, O-C-CH), 3.45 (d, 18.7 Hz, 1 H, 10-H pseudo eq), 4.31-4.47 (m, 3 H, O-CH_2, 9-H pseudo eq), 6.47 (d, 8.0 Hz, 2 H, 2 o-H of Ph), 6.97-7.25 (m, 10 H, aromatic H), 7.29-7.34 (m, 1 H, 1-H). Anal. Calcd. for $C_{24}H_{22}O_2$: C, 84.18; H, 6.47. Found: C, 84.24; H, 6.63.

9-(2-Hydroxy-1,2-diphenylethyl)-9,10-dihydroanthracene (**6a**). M.p. 163°C (CCl_4); IR ν 3595, 1054/cm; H-NMR δ 1.79 (d, 3.1 Hz, 1 H, OH), 2.83 (d, 18.5 Hz, 1 H, 10-H pseudo ax), 3.21-3.36 (m, 1 H, O-C-CH), 3.42 (d, 18.5 Hz, 1 H, 10-H pseudo eq), 4.31 (d, 5.7 Hz, 1 H, 9-H pseudo eq), 5.02 (dd, 7.7 Hz, 2.7 Hz, 1 H, O-CH), 6.62 (d, 7.7 Hz, 2 o-H of O-C-C-Ph), 6.89-7.41 (m, 16 H, aromatic H, s at 7.34 can be assigned to O-C-Ph). Anal. Calcd. for $C_{28}H_{24}O$: C, 89.32; H, 6.42. Found: C, 89.16; H, 6.32.

9-(2-Hydroxy-2-phenylethyl)-xanthene (**9a**). Oil; IR ν 3560, 3420, 1258, 1247, 1058/cm; H-NMR δ 1.89 (ddd, 14.0 Hz, 9.8 Hz, 3.5 Hz, 1 H of CH_2), 2.07 (ddd, 14.1 Hz, 10.1 Hz, 4.7 Hz, 1 H of CH_2), 2.38 (s br, 1 H, OH), 4.27 (dd, 9.8 Hz, 4.7 Hz, 1 H, 9-H), 4.59 (dd, 10.1 Hz, 3.5 Hz, 1 H, O-CH), 7.07-7.47 (m, 13 aromatic H). Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00; O, 10.58. Found: C, 83.75; H, 6.11; O, 10.66.

9-(2-Acetoxy-2-phenylethyl)-xanthene (**9b**). Oil; IR ν 1741, 1250, 1028/cm; H-NMR δ 1.98 (s, 3 H, Me), 2.05 (m_c, 1 H of CH_2), 2.34 (ddd, 14.4 Hz, 10.1 Hz, 4.8 Hz, 1 H of CH_2), 4.10 (dd, 8.2 Hz, 4.8 Hz, 1 H, 9-H), 5.66 (dd, 10.1 Hz, 3.7 Hz, 1 H, O-CH), 7.02-7.30 (m, 13 aromatic H). Anal. Calcd. for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85; O, 13.94. Found: C, 80.15; H, 5.94; O, 14.01.

9-(2-Hydroxy-1-phenylethyl)-xanthene (**10a**). M.p. 168-171°C; IR ν 3570, 3390, 1253, 1064, 1033/cm; H-NMR δ 1.76 (s br, 1 H, OH), 3.04 (m_c, 1 H, O-C-CH), 3.83 (m_c, 2 H, CH_2), 4.33 (d, 5.5 Hz, 1 H, 9-H), 6.55 (d, 7.7 Hz, 2 o-H of

Ph), 6.80-7.30 (m, 11 aromatic H). Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.26; H, 6.02.

9-(2-Acetoxy-1-phenylethyl)-xanthene (**10b**). M.p. 104-106°C; IR ν 1743, 1738, 1237, 1037, 1028; H-NMR δ 2.02 (s, 3 H, Me), 3.25 (m_c, 1 H, O-C-CH), 4.33 (m_c, 2 H, CH_2), 4.36 (d, 4.1 Hz, 1 H, 9-H), 6.49 (d_c, 7.7 Hz, 2 o-H of Ph), 6.92 (m_c, 2 aromatic H), 7.05-7.25 (m, 9 aromatic H). Anal. Calcd. for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 80.41; H, 5.91.

9-(2,2-Dimethyl-2-hydroxyethyl)-9,10-dihydroanthracene (**11**). 86% yield from 7.5 mmol of **AH**$_2$, 5 mmol of BuLi and 5 mmol of isobutylene oxide in 70 ml THF after 4 days; oil; IR ν 3140-3640, 1142/cm; H-NMR δ 1.21 (s, 6 H, Me, Me), 1.66 (s, 1H, OH), 1.81 (d, 7.1 Hz, 2 H, O-C-CH_2), 3.81 (d, 18.0 Hz, 1 H, 10-H pseudo eq), 4.11 (d, 18.0 Hz, 10-H pseudo ax), 4.24 (t, 7.1 Hz, 1 H, 9-H pseudo eq), 7.10-7.39 (m, 8 H, aromatic). Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.98. Found: C, 85.39; H, 7.74.

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