tetramethylammonium hydroxide of 1.1×10^{-2} mol dm^{-3} was contained in the measuring solvent to exclude the protonation of the nitrogen bridgehead. To 15 mL of 1×10^{-3} mol dm^{-3} alkali-metal perchlorate solution was added 0.3 mL of 5×10^{-3} mol dm^{-3} crown ether solution. Thereafter, 0.3 mL of the crown ether solution was added at each time until the total added volume was 6 mL. The emf readings were made after 4-min stirring of the solution at each addition. The microcomputer for the data processing was NEC PC-8801 mK II.

Acidity Constants. The pH-metric titration was carried out at 25 °C in methanol/water (90/10) under a nitrogen atmosphere, using a mV/pH meter (TOKO TP1000), a pH electrode (HORIBA 1026A), and a Ag/AgCl reference electrode (IWAKI IW 067). The ion strength was kept at 0.1 during the titration. The starting solutions contained 5×10^{-3} mol dm^{-3} crown ether, 7.75×10^{-2} mol dm^{-3} tetramethylammonium chloride, and 2.25×10^{-2} mol dm^{-3} HCl. To 10 mL of the solution was added the titrant containing 5.5×10^{-2} mol dm^{-3} tetramethylammonium hydroxide by 0.1-mL portions. The acidity constants, defined by the following equations, were calculated by using the microcomputer:

$$K_1 = [CrH^+][H^+]/[CrH_2^{2+}] \qquad K_2 = [Cr][H^+]/[CrH^+]$$

CrH_2^{2+}, CrH^+, and Cr stand for diprotonated, monoprotonated, deprotonated crown ethers, respectively.

Registry No. **1** (n = 0), 105040-36-6; **1** (n = 1), 102069-55-6; **1** (n = 2), 102069-56-7; **1** (n = 3), 102069-57-8; **2** (n = 0), 105040-37-7; **2** (n = 1), 105064-10-6; **2** (n = 2), 105040-38-8; **2** (n = 3), 105040-39-9; **3** (n = 1), 105040-40-2; **3** (n = 2), 105040-41-3; **3** (n = 3), 105040-42-4; **4** (n = 1), 102069-58-9; **4** (n = 2), 75006-56-3; **4** (n = 3), 75006-60-9; **5** (n = 1), 80403-59-4; **5** (n = 2), 87505-87-1; **5** (n = 3), 91787-47-2; **6** (n = 1), 102725-12-2; **6** (n = 2), 74649-89-1; **6** (n = 3), 83255-15-6; **7** (n = 0), 84761-08-0; **7** (n = 1), 84227-47-4; **7** (n = 2), 71089-11-7; **7** (n = 3), 63281-62-9; **8** (n = 1), 84227-48-5; **8** (n = 2), 81331-60-4; **8** (n = 3), 81331-61-5; **9** (n = 0), 7234-71-1; **9** (n = 1), 41775-76-2; **9** (n = 2), 66943-05-3; **9** (n = 3), 33941-15-0; **10**, 105040-45-7; Na, 7440-23-5; K, 7440-09-7; diethyl dodecylmalonate, 7252-87-1; 2-dodecylpropane-1,3-diol ditosylate, 71366-37-5; benzylamine, 100-46-9; dodecylamine, 124-22-1; ethanolamine, 141-43-5; 3,6-dioxaoctane-1,8-diol ditosylate, 36839-55-1; 1,11-diiodo-3,6,9-trioxaundecane, 37860-51-8; 1,14-diiodo-3,6,9,12-tetraoxatetradecane, 41024-91-3; 1,17-diiodo-3,6,9,12,15-pentaoxaheptadecane, 42749-27-9; 2-dodecylpropane-1,3-diol, 10395-09-2; ethyl diazoacetate, 623-73-4; diethyl 5-dodecyl-3,7-dioxanonan-1,9-oate, 105040-46-8; 5-dodecyl-3,7-dioxanonane-1,9-diol, 105040-47-9; tosyl chloride, 98-59-9; 2-dodecyl-2-methylmalonyl chloride, 87505-86-0.

Selective 1,4-Reduction of Chalcone with Anthracene Hydride via Base-Induced Fragmentation of Their Michael Adduct[1]

Helmut Stamm,* Andreas Sommer, Andreas Onistschenko, and Anton Woderer

Pharmazeutisch-Chemisches Institut der Universität Heidelberg, D-6900 Heidelberg, Federal Republic of Germany

Received May 1, 1986

Chalcone (1) and "anthracene hydride" (AH^-) form rapidly the anionic Michael adduct **2** in high yield along with the known dimerization product **5** of **1**. Prolonged reaction in the presence of an excess of AH^- converts **2** into anthracene A and the enolate **7** of the saturated ketone **8**. Reactions with other substrates show that the partial structure ArCCCO is necessary for this disproportionative fragmentation. This points to the intermediacy in the fragmentation of the enone dianion (e.g., 1^{2-}), with the β-aryl group stabilizing the second negative charge. The analogously formed Michael adduct of xanthene XH and **1** does not undergo fragmentation, indicating that a removable hydrogen in the proper position is necessary for the formation of the saturated carbonyl compound from its Michael adduct. Reduction of the carbonyl function could not be detected in any one of the reactions.

Anthracene hydride (AH^-; anion of 9,10-dihydroanthacene) is a conveniently prepared member of the so-called arene hydrides, formal adducts of an arene and a hydride ion.[2] It has been shown to be a strong reducing agent.[2] We report now on the selective reduction of the C=C double bond of chalcone (1) by AH^-. The mechanism involved may be considered to exclude any carbonyl reduction. This mechanism may perhaps also have some bearing on the mechanism of the reduction of carbonyl-conjugated C=C bonds by formate ion.[3] Selective reduction of the C=C double bond of chalcone and similar α,β-unsaturated monocarbonyl compounds has been described for special techniques[4] while the more familiar methods give usually product mixtures from competing reduction of C=C and C=O bonds.

Our experimental results are shown in Table I and Scheme I. AH^- and the other carbanionic reagents were generated in THF from 9,10-dihydroanthracene (AH_2) or from the respective precursors and butyllithium.[2] An excess of AH^- reduced **1** to 82% saturated ketone **8** and 17% **5** (entry 1). The formation of **8** is obviously coupled with an oxidation of AH^- to anthracene A that was found in more than 74% yield. **5** (mixture of two stereoisomers) is certainly formed by single-electron transfer from AH^- to **1**, followed by dimerization of the so-generated radical anion $1^{\bullet-}$. The dimer **4** undergoes cyclization to **5** that could be quantitatively dehydrated to **6** by dissolving in trifluoroacetic acid. A one-electron-reduction pathway[6] and the structures of **5**[6] and **6**[7] have been confirmed previously. Furthermore, we obtained 97% of **5** from **1** and the radical anion $A^{\bullet-}$ of anthracene in THF, probably the best method to prepare **5**.

When the reaction of **1** with an excess of AH^- was quenched with glacial acetic acid after 5 min (entry 2), roughly the same amount of **5** was isolated along with 78%

(1) Arene Hydrides. 3. Part 2: Woderer, A.; Stamm, H. *Chem. Ber.* **1986**, *119*, 2050.

(2) Stamm, H.; Sommer, A.; Woderer, A.; Wiesert, W.; Mall, T.; Assithianakis, P. *J. Org. Chem.* **1985**, *50*, 4946.

(3) Sekiya, M.; Suzuki, K. *Chem. Pharm. Bull. Jpn.* **1970**, *18*, 1530.

(4) With formic acid or formate ion: Bar, R.; Sasson, Y. *Tetrahedron Lett.* **1981**, *22*, 1709. Azran, J.; Buchman, O.; Orchin, M.; Blum, J. *J. Org. Chem.* **1984**, *49*, 1327. Catalytic hydrogen transfer: Alba, A.; Aramedia, A.; Borau, V.; Garcia-Raso, A.; Jimenez, C.; Marinas, J. M. *Can. J. Chem.* **1984**, *62*, 917. With tributyltin hydride: Four, P.; Guibe, F. *Tetrahedron Lett.* **1982**, *23*, 1825.

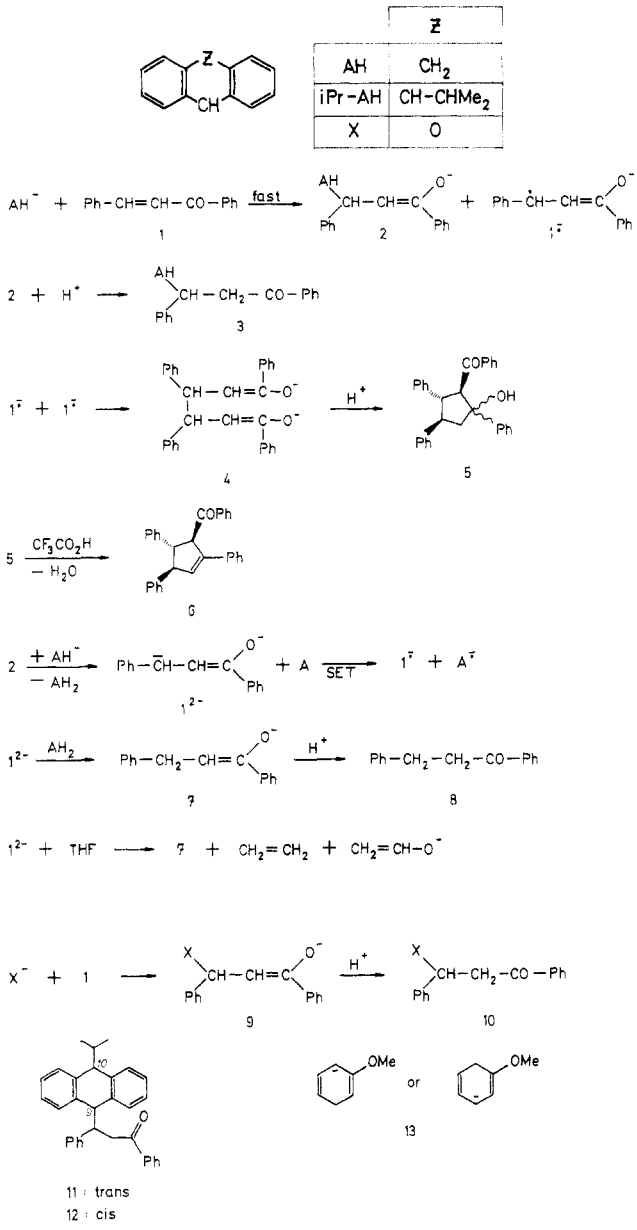
(5) See for instance the following references. With complex hydrides: Meyer, G. R. *J. Chem. Educ.* **1981**, *58*, 628. Nikles, J. A.; Sukenik, C. N. *Tetrahedron Lett.* **1982**, *23*, 4211. With copper hydride: Semmelhack, M. F.; Stauffer, R. D.; Yamashita, A. *J. Org. Chem.* **1977**, *42*, 3180.

(6) Simonet, J.; Albisson, A. *Bull. Chim. Fr.* **1971**, 1125 and the literature cited therein.

(7) Wawzonek, S.; Bennet, W. E. *Org. Magn. Reson.* **1972**, *4*, 73.

0022-3263/86/1951-4979$01.50/0

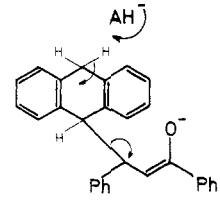
Scheme I



of the Michael adduct **3** but no **8**. A 1-day reaction (as in entry 1) of **1** with 1 equiv of AH^- (entry 3) led practically to the same result (80%, **3**; 15%, **5**; none, **8**) as the 5-min reaction (entry 2). Therefore, the reduction of **1** to **8** proceeds obviously by a novel base-induced fragmentation of the anion **2** of this Michael adduct. This slow fragmentation of the Michael adduct was directly proved in a separate experiment. The isolated Michael adduct **3** was practically quantitatively converted into **8** in a 1-day reaction with an excess of AH^- (entry 4). The importance of an excess of strong base, as indicated by entries 1, 3, and 4, was confirmed by two experiments with the anion X^- of xanthene. Addition of 1 equiv of **3** decolorized the red solution of X^--d_1 [X^- prepared from 9,9-dideuterioxanthene (XH-d_2)]. After 1 day no reaction had occurred (entry 5).[8] The ^1H NMR spectrum showed the expected amount of incorporation of protium into the starting XH-d_2. The same experiment with an excess of X^--d_1 (entry 6) gave

(8) The base for the fragmentation should not be a nonionic organometallic. *n*-Butyllithium adds to the carbonyl group of **3** as evidenced by the ^1H NMR spectrum of the product mixture. We did not try to isolate the products.

Scheme II



63% **8** (no incorporation of deuterium was detectable), 31% of **5**, 82% of A, and incorporation of protium into the starting XH-d_2. The proposed fragmentation finds further support from the reaction of **1** with X^- (entry 7) under the experimental conditions of entry 1. Only the Michael adduct **10** was isolated in high yield. This result shows that the methylene bridge is essential for the fragmentation, thus pointing to a deprotonation of this methylene group. The final products of this fragmentation are A, the enolate **7** of the saturated ketone **8**, and in one case (entry 6) the dimer **4**. **7** was identified by quenching with CF_3CO_2D (entry 8, incorporation of one deuterium into the α-position of the isolated **8** (structure **16d** of Scheme III) and by quenching with iodomethane that gave a quantitative yield of the methylated ketone (structure **16d** of Scheme III, entry 9).

Breaking the C–C bond between the anthracene moiety and the chalcone moiety of **2** might in principle occur by homolysis or by heterolysis. Several examples of the reverse reactions are reported in the literature: combination of $A^{\bullet-}$ with an alkyl radical[9] and addition of alkylometallics onto A.[10] We have reasons (see below) to suppose that the C–C bond cleavage in the fragmentation is heterolytic. The benzylic charge stabilization should favor this cleavage reaction, contrary to the reported cases of reverse reactions.[10] A simple picture of this fragmentation, that may be concerted or stepwise, is shown in Scheme II. The arising dianion 1^{2-} of chalcone will be very reactive as a proton acceptor, forming **7**, and as an electron source for the formation of $1^{\bullet-}$ and $A^{\bullet-}$, a process that would be favored by the close proximity of 1^{2-} and A at the end of the fragmentation. This latter reactivity could explain the formation of **5** in run 6. $1^{\bullet-}$ can obviously be formed either by SET subsequent to the fragmentation or initially and directly by SET from AH^- to **1** (entry 2). The variability in yields of the initially formed **5** (compare entries 1–3 with entries 7 and 9) is not yet understood. It seems to depend on unknown experimental details.

The proposed intermediate dianion 1^{2-} has to abstract a proton for the formation of the enolate **7**. In order to investigate the proton source, a special experiment with 9,9,10,10-tetradeuteriodihydroanthracene AH_2-d_4 was performed. In this experiment (entry 10) about 40% of the theoretical amount of deuterium for the formation of **7** from 1^{2-} and AH_2-d_4 was incorporated into **8**. Thus, the strongest acid present, i.e. AH_2, provides only a part of the required protons, probably more than 50% if one considers an isotope effect in entry 10. The rest of the required protons has to come from the solvent molecules (THF) whose deprotonation by very strong bases is well-known.[11] In sharp contrast to the marked and probably principal protonation by AH_2, entry 6 did not indicate a similar

(9) See e.g.: Malissard, M.; Mazabeyrat, J.-P.; Welvart, Z. *J. Am. Chem. Soc.* **1977**, *99*, 6933. Deschamps, E.; Mazaleyrat, J.-P. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1977**, 455.

(10) Brinkmann, A. W.; Gordon, M.; Harvey, R. G.; Rabideau, R. W.; Stothers, J. B.; Ternay, A. L., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 5912. Panek, E. J.; Rodgers, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 6921.

(11) Bates, R. B.; Kroposki, L. M.; Potter, D. E. *J. Org. Chem.* **1972**, *37*, 560.

Table I. Reactions of Carbanions with α,β-Unsaturated Carbonyl Compounds

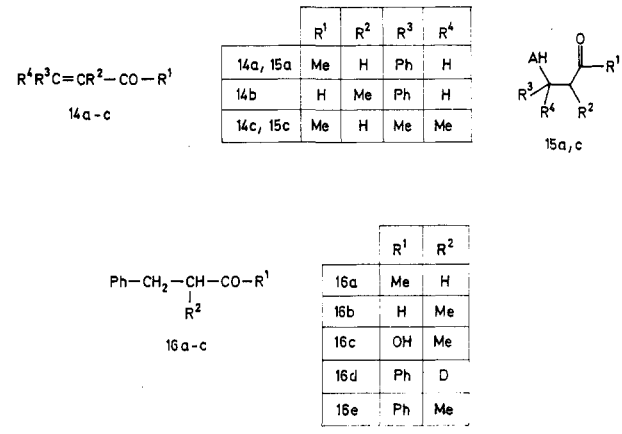
run	mmol (reactant)			THF, mL (time)	yield, % (products)
1[a]	7.5 AH_2	6.25 BuLi	4.8 **1**	70, (1 day)	17 (**5**), 82 (**8**), >74 (A)
2	3.9 AH_2	2.4 BuLi	1.9 **1**	40, (5 min)	20 (**5**), 78 (**3**)
3	6.25 AH_2	5.0 BuLi	5.0 **1**	70, (1 day)	15 (**5**), 80 (**3**)
4	1.11 AH_2	0.31 BuLi	0.25 **3**	30, (1 day)	95 (**8**)
5	1.68 XH-d_2	1.0 BuLi	1.0 **3**	80, (1 day)	ca. 93 (**3**), O (A)[b]
6	6.0 XH-d_2	3.0 BuLi	2.0 **3**	80, (1 day)	31 (**5**), 63 (**8**),[c] 82 (A)[d]
7	7.25 XH	6.25 BuLi	5.0 **1**	70, (1 day)	>90 (**10**)
8	6.0 AH_2	3.0 BuLi	2.0 **3**	80, (1 day)[e]	18 (**3**), 74 [**16d** (=8-α-d_1)][f]
9	7.5 AH_2	6.25 BuLi	4.8 **1**	70, (1 day)	
			21 MeI	(1 day)	100 (**16e**)
10	3.0 AH_2-d_4	2.88 BuLi	1.0 **3**	80, (1 day)	94 (**8**)[g]
11	4.5 *i*-PrAH_2	4.0 BuLi	2.4 **1**	70, (5 min)	46 (**5**), 41 (**11**), 12 (**12**)
12	7.5 **13**	6.25 BuLi	3.17 **1**	40, (1 day)	15 (**8**)[h]
13	7.5 AH_2	6.25 BuLi	5.0 **14a**	70, (1 day)	4 (**15a**), 81 (**16a**), >47 (A)
14	3.9 AH_2	3.0 BuLi	2.74 **14a**	40, (5 min)	83 (**15a**)
15	7.5 AH_2	6.25 BuLi	4.1 **14b**	70, (1 day)	78 (**16b**), >72 (A)
16	7.5 AH_2	6.25 BuLi	5.1 **14c**	70, (1 day)	87 (**15c**)

[a] A similar amount of **3** was obtained from the sodium salt of AH_2 generated with sodium amide.[2] [b] Ca. 93% of the starting XH-d_2 was recovered. About 1 mmol of protium was incorporated into this XH-d_2 (exchange of H for D). [c] No incorporation of deuterium could be detected by ^{1}H NMR (90 MHz). [d] 79% of the starting XH-d_2 was recovered (^{1}H NMR, 250 MHz); 3 mmol of protium was incorporated into this XH-d_2 (exchange of H for D). [e] Quenching with CF_3CO_2D in place of glacial acetic acid. [f] 64% of the theoretical amount of deuterium for the acidification of **7** with CF_3CO_2D was incorporated. CF_3CO_2D had been taken from an often-opened stock bottle. The acid was therefore probably contaminated with H_2O accounting for the low degree of deuterium incorporation. [g] About 20% deuterium was incorporated into the benzylic position corresponding to about 40% of the theoretical amount for a deuterium transfer from AH_2-d_4 or AH_2-d_3. [h] Many unidentified products are formed according to TLC.

proton transfer from XH to 1^{2-}. We have no explanation for this different behavior apart from the possibility that in a cage process the topology of the attacking 9-lithio-9,10-dihydroanthracene (AH^-Li^+) and the leaving 1^{2-} relative to one another is such that the proton is provided by the methylene group in position 10 which in X^- and XH would by replaced by the oxygen atom. At the moment it is difficult to make substantiated proposals to explain the discrepancies between the fragmentation of **3** induced by AH^- and that one induced by X^-, although we are tempted to correlate the two anomalies of X^- induction with one another, i.e. to correlate the formation of **5** with the absence of protonation of 1^{2-} by XH.

A further question remains, namely whether **2** is formed by the classical Michael addition mechanism or by the combination of $1^{\bullet-}$ and $AH^\bullet$ subsequent to an initial SET step. The classical mechanism cannot be taken for granted in this case. Fluorene, structurally closely related to AH_2, is a bad Michael donor.[12] On the other hand, the SET alternative is not as unusual as perhaps might be thought, since, e.g., the addition of organocuprates to Michael acceptors is supposed to proceed via electron transfer.[13,14] An experiment with *i*-PrAH^- did not prove helpful to distinguish between the two alternatives. Literature reports[15] give strong evidence that 9-isopropyl-9,10-dihydroanthracene (*i*-PrAH_2) is deprotonated practically exclusively at position 10 to from *i*-PrAH^-. A 5-min reaction of this arene hydride with **1** (entry 11) gave only 53% Michael adduct as a mixture of 41% trans (**11**) and 12% cis (**12**, not pure) isomer. The decreased Michael addition was compensated by a markedly increased dimerization of **1** (46% **5**) pointing to a steric hindrance of the Michael addition. This steric hindrance is compatible with both mechanisms in question. Steric deceleration of

Scheme III



the classic ionic addition could lead to more SET and therefore to more dimerization. Alternatively, supposing a common first SET step both for Michael addition and for dimerization one would expect a retarded combination of the radicals *i*-Pr$AH^\bullet$ and $1^{\bullet-}$, resulting in more time for $1^{\bullet-}$ to diffuse away from the solvent cage.

Substituting an excess of anisole hydride **13** for AH^- (entry 12) gave only 15% **8** in a 1-day reaction along with many unidentified products. The ability of **13** to reduce the carbonyl function of some benzoyl derivatives has recently been reported.[16]

In order to stabilize the dianion of type 1^{2-}, the benzylidene phenyl of **1** is necessary for the fragmentation step, whereas the benzoyl phenyl is not. This is shown by entries 13–16. Benzylideneacetone (**14a**) and an excess of AH^- gave 83% Michael adduct **15a** after 5 min (entry 14) but after 1 day only 14% **15a** and 81% of the saturated ketone **16a** (entry 13). Likewise, an excess of AH^- reduced 2-methylcinnamaldehyde (**14b**; entry 15) in 78% yield to the saturated aldehyde **16b**, identified by its ^{1}H NMR spectrum and by its known[17] spontaneous oxidation to the acid **16c**. On the other hand, mesityl oxide (**14c**) gave only

(12) Taylor, R. S.; Connor, R. *J. Org. Chem.* **1941**, *6*, 696.
(13) House, H. O.; Respess, W. L.; Whitesides, G. M. *J. Org. Chem.* **1966**, *31*, 3128. House, H. O.; Fischer, W. F., Jr. *J. Org. Chem.* **1968**, *33*, 949. House, H. O.; Umen, M. J. *J. Org. Chem.* **1973**, *38*, 3893.
(14) Reduction potential of **1**: House, H. O.; Huber, L. E.; Umen, M. J. *J. Am. Chem. Soc.* **1972**, *94*, 8471.
(15) Zieger, H. E.; Gelbaum, L. T. *J. Org. Chem.* **1972**, *37*, 1012; Zieger, H. E.; Schaeffer, D.; Padronaggio, R. M. *Tetrahedron Lett.* **1969**, 5027. Compare also: Bank, S.; Bank, J.; Daney, M.; Labrande, B.; Bouas-Laurent, H. *J. Org. Chem.* **1977**, *25*, 4058.
(16) Hiramatsu, M.; Fujinami, T.; Sakai, S. *Chem. Lett.* **1982**, 7.
(17) v. Miller, W.; Rohde, G. *Chem. Ber.* **1890**, *23*, 1080.

the Michael adduct **15c** (87%, entry 16) under the experimental conditions (excess AH^-, 1 day) that produced high yields of the saturated carbonyl compounds in entries 1, 13, and 15. This result can be considered evidence for the intermediacy of a dianion of type 1^{2-} in the fragmentation.

The Michael adducts **3**, **10**, and **15a** of the β-phenyl enones are characterized by an unusual upfield chemical shift for the two ortho protons of the phenyl group (near 6.6 ppm), due to a ring current effect of the aromatic parts in the AH_2 moiety. Further insight into this effect is obtained from the cis–trans pair **12** and **11**. Although only the major product **11** could be isolated in a pure state, there is no doubt about the correct recognition of the **12** signals within a chromatographically obtained 4:1 mixture of **12** and **11**. The discussed upfield chemical shift is much weaker (about 6.9 ppm) for **11** than for the other adducts quite in accord with a very flat boat conformation forced by the trans disubstitution. On the other hand, the upfield shift for the pseudoaxially sited benzyl group of the normal boat conformation is much more pronounced (6.16 ppm) in the cis isomer **12**, but here for one ortho proton only due to a frozen conformation of the two pseudoaxially sited bulky substituents. Therefore, the shift near 6.6 ppm is an average between about 6.1 ppm and a normal phenyl shift greater than 7 ppm, indicating a free rotation of the respective phenyl ring in **3**, **10**, and **15a**. The frozen conformation in **12** is also indicated by the anisochrony of its two methyls (1.06, 1.08 ppm), while the two methyls in **11** are isochronous (0.91 ppm). All these conclusions are reasonable, if the stereochemical assignment for **11** and **12** is correct. This assignment is strongly supported by comparison with the published NMR data for *cis*- and *trans*-9,10-diisopropyl-9,10-dihydroanthracene.[18] In both cis–trans pairs the methyl signals for the trans isomers are upfield from the signals of the cis isomers, while the signals of the isopropyl CH for trans are downfield from those of cis. Even more important may be considered the congruence in coupling between isopropyl CH and meso H: 5.0 and 5.5 Hz for trans; 10.0 Hz for cis in both cases. Signal assignment for 9-H and 10-H of **11** and **12** was unequivocally confirmed by decoupling.

Experimental Section

General Methods and Materials. These are described in ref 2, e.g. spectroscopy, chromatography, preparation of 9,9,10,10-tetradeuterio-9,10-dihydroanthracene (AH_2-d_4), etc. 9,9-Dideuterioxanthene (XH-d_2, degree of deuteriation better than 96% according to the ^1H NMR spectrum at 90 MHz) was prepared analogously to AH_2-d_4.

Reactions with 9-Lithio-9,10-dihydroanthracene, 9-Lithioxanthene, 9-Lithio-10-isopropyl-9,10-dihydroanthracene, or Lithio-2,5-dihydroanisole. The THF solutions of AH^-, X^-, *i*-$PrAH^-$, and **13** were prepared as described for AH^- and X^- in ref 2. The enone, respectively **3** in entries 4–6, 8, and 10 or **14b** in entry 15, dissolved in 10 mL of THF, was added dropwise while stirring the carbanion solution. The reactions were quenched under nitrogen by neutralization with glacial acetic acid (CF_3CO_2D in entry 8). The solvent was removed under reduced pressure and the residue taken up in CH_2Cl_2 and washed with water. On concentration of the dried CH_2Cl_2 solution, anthracene **A** or the major product crystallized sometimes and was isolated by filtration by vacuum. Except entry 5, further workup was done with column chromatography according to the details noted for the specific reaction (dimensions in centimeters of the column given in parentheses). All products were identified by ^1H NMR.

Table I, Entry 1. A 630-mg (74%) portion of **A** was removed by filtration. The filtrate was chromatographed (2.2 × 60). Elution with toluene afforded a mixture of A and AH_2 followed by 820 mg (82%) of **8**, mp 69 °C (lit.[19] mp 72–73 °C). Elution with CH_2Cl_2 provided 170 mg (17%) of **5**, mp 180–190 °C. A 100-mg portion of **5** dissolved in about 1 mL of CF_3CO_2H gave upon addition of water and extraction with CH_2Cl_2 95 mg (100%) of **6**: mp 178 °C (lit.[7] mp 182 °C); ^1H NMR spectrum consistent with the published[7] data.

Separate Preparation of 5. A 1.33-g (7.5-mmol) sample of A, 350 mg (7.5 mmol) of sodium dispersion (50%), and 60 mL of THF were stirred for 3 h. A 950-mg (4.56-mmol) sample of **1** dissolved in 10 mL THF was added dropwise whereupon the dark blue solution brightened somewhat. Quenching and workup were as in the other experiments. Filtration of the CH_2Cl_2 solution provided 930 mg of A. Chromatography (2.2 × 60) with CH_2Cl_2 gave a mixture of hydrocarbons (A and paraffin) and then 920 mg (97%) of **5**.

Table I, Entry 2. A total of 180 mg of **3** was obtained by filtration. Chromatography (2.2 × 60) with toluene gave 460 mg of AH_2 and 400 mg [i.e. total 580 mg (78%)] of **3**. Elution with CH_2Cl_2 provided 80 mg (20%) of **5**.

3-(9,10-Dihydroanthr-9-yl)-1,3-diphenylpropan-1-one (3): mp 204–205 °C; ^1H NMR ($CDCl_3$, 250 MHz) δ 3.01 (d br, J = 19.0 Hz, 10-H pseudo ax), 3.36 (dd, ^3J = 7.0 Hz, ^2J = 17.2 Hz, COCH), 3.51 (d, J = 19.0 Hz, 10-H pseudo eq), 3.58 (dd, ^3J = 7.0 Hz, ^2J = 17.2 Hz, COCH), 3.77 (m, q-like, COCH), 4.27 (d, J = 6.0 Hz, 9-H pseudo eq), 6.60 (d, J = 7.5 Hz, ortho H of Ph at saturated C), 6.91 (d, J = 8.1 Hz, 1 H, 1-H of AH), 7.02–7.57 (m, 13 H, aryl H except 4 ortho H and 1-H of AH), 7.86 (d, J = 7.5 Hz, 2 ortho H of benzoyl); IR (KBr) 1684 cm^{-1} (C=O). Anal. Calcd for $C_{29}H_{24}O$: C, 89.65; H, 6.22. Found: C, 89.84; H, 6.18.

Table I, Entry 3. Isolation of products was as in Entry 2.

Table I, Entry 4. Chromatography (3 × 25) with toluene provided a mixture of A and AH_2 followed by 50 mg (95%) of **8**.

Table I, Entry 5. Workup without Chromatography. Evaporation of the water-washed dichloromethane solution gave 650 mg (50-mg material deficit) of residue that according to the ^1H NMR spectrum (250 MHz) consisted of **3** (about 93% yield) and XH-d_2 (about 93% of the starting material recovered). Protium was incorporated at position 9 of the latter, amounting to 1 mmol as was shown by a triplet (J = 2 Hz) at 4.03 ppm.

Table I, Entry 6. Chromatography (1.5 × 45) with toluene provided first 1.170 g of a mixture consisting (^1H NMR at 90 MHz) of 292 mg (82%) of A and 877 mg (79% of the starting material recovered) of xanthene as a mixture of 324 mg of XH-d_2 and 553 mg (corresponding to 100% of the theoretical amount) of XH-d_1. Toluene gave a second fraction (265 mg) and a third fraction (190 mg). Elution with dichloromethane provided a forth fraction (126 mg). The second fraction consisted of **8** (63%, no deuterium incorporated according to the ^1H NMR spectrum at 90 MHz). The third and the forth fraction were made of **5** and unknown aromatic compounds. The yield of **5** (31%) was determined from the ^1H NMR spectra (90 MHz) by calibration of the integral with an internal standard (4-chlorobenzaldehyde).

Table I, Entry 7. Evaporating the CH_2Cl_2 solution gave a residue that on washing with toluene left 1.75 g (90%) of **10** undissolved.

1,3-Diphenyl-3-xanth-9-ylpropan-1-one (10): mp 183–184 °C; ^1H NMR ($CDCl_3$, 250 MHz) δ 3.26 (dd, ^3J = 8.1 Hz, ^2J = 17.2 Hz, COCH), 3.39 (dd, ^3J = 6.5 Hz, ^2J = 17.2 Hz, COCH), 3.71–3.79 (m, COCCH), 4.32 (d, J = 4.6 Hz, 9-H pseudo eq), 6.65 (d, J = 7.5 Hz, 2 ortho H of Ph at saturated C), 6.92–ca. 7.02 (m, 3 H, 1-H, 4-H and 5-H of X), 7.02–7.56 (m, 11 H, aryl H except 4 ortho H and 3 H of X), 7.81 (d, J = 7.8 Hz, 2 ortho H of benzoyl); IR (KBr) 1682 (C=O), 1256 cm^{-1} (CO). Anal. Calcd for $C_{28}H_{22}O_2$: C, 86.12; H, 5.67. Found: C, 85.79; H, 5.55.

Table I, Entry 8. Subsequent to quenching the reaction with CF_3CO_2D the usual workup followed. Chromatography (1.5 × 45) with toluene provided (subsequent to the hydrocarbons) 450 mg of a mixture. ^1H NMR (250 MHz) showed the latter to consist of 140 mg (18%) of **3** and 310 mg (74%) of **16d** with a deuterium content in the α-position of about 64% of the theoretical amount (i.e., a 64:36 mixture of **16d** and **8**).

(18) Ahmad, N.; Cloke, C.; Hatton, I. K.; Lewis, N. J.; MacMillan, J. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1849.

(19) Schneidewind, W. *Chem. Ber.* **1888**, *21*, 1325.

Table I, Entry 9. The reaction was quenched with 3 g (21 mmol) of iodomethane. The usual workup followed after standing for another day. Chromatography (3 × 60) with toluene provided (subsequent to the hydrocarbons) 1.07 g (100%) of **16e** as oil, identified by ^{1}H NMR comparison with an authentic sample prepared from propiophenone and benzyl chloride according to ref 20: ^{1}H NMR (90 MHz) δ 1.15 (d, J = 6.5 Hz, Me), 2.64 (dd, ^3J = 7.8 Hz, ^2J = 13.6 Hz, 1 benzylic H), 3.15 (dd, ^3J = 6.3 Hz, ^2J = 13.6 Hz, 1 benzylic H), 3.67 (mc, CHCO), 7.07–7.50 (m, Ph, meta and para H of benzoyl), 7.83–7.94 (m, ortho H of benzoyl); IR (film) 1682 cm^{-1}.

Table I, Entry 10. Chromatography (1.5 × 45) with toluene provided (subsequent to the hydrocarbons) 197 mg (94%) of **8** whose benzylic methylene group contained (^{1}H NMR at 250 MHz) about 60% of the theoretical protium content for a deuterium transfer from AH_2-d_4 to 1^{2-}: ^{1}H NMR (250 MHz) δ 3.07 (mc, t-like with apparent $J \sim 8$ Hz, benzylic CH_2), 3.30 (mc, t-like with apparent $J \approx 8$ Hz, benzoylic CH_2), 7.16–1.34 (m, benzylic Ph), 7.40–7.48 (m, meta H of benzoyl), 7.50–7.58 (m, para H of benzoyl), 7.92–7.98 (m, ortho H of benzoyl).

Table I, Entry 11. Chromatography (2.2 × 60) with toluene provided i-PrAH_2, 390 mg (38%) of **11**, and a mixture of (^{1}H NMR) 31 mg (3%) of **11** and 129 mg (12%) of **12**. Elution with ethyl acetate provided 230 mg (46%) of **5**.

***trans*-1,3-Diphenyl-3-(10-isopropyl-9,10-dihydroanthr-9-yl)propan-1-one (11)**: mp 116–117 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.91 (d, J = 6.9 Hz, 2 Me), 2.22–2.35 (m, CH of i-Pr), 3.20 (dd, ^3J = 4.5 Hz, ^2J = 17.6 Hz, 1 H, COCH), 3.45 (dd, ^3J = 8.6 Hz, ^2J = 17.6 Hz, 1 H, COCH), 3.61 (d, J = 5.0 Hz, 10-H), 4.34–4.41 (m, COCCH), 4.59 (d, J = 4.7 Hz, 9-H), 6.92–6.98 (m, 2 ortho H of Ph at saturated C), 7.03–7.54 (m, 14 H, aryl H except 4 ortho H), 7.79 (d, J = 7.4 Hz, 2 ortho H of benzoyl); IR (KBr) 1686 cm^{-1} (C=O). Anal. Calcd for $C_{32}H_{30}O$: C, 89.26; H, 7.02. Found: C, 89.21; H, 6.95.

***cis*-1,3-Diphenyl-3-(10-isopropyl-9,10-dihydroanthr-9-yl)propan-1-one (12)**: not pure, identified by ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.06 (d, J = 6.7 Hz, 1 Me), 1.08 (d, J = 6.5 Hz, 1 Me), 2.00 (mc, CH of i-Pr), 3.35–3.41 (m, 1 H, COCH), 3.43 (d, J = 10.0 Hz, 10-H), 3.55–3.68 (m, 2 H, 9-H, COCH), 4.01-4.08 (m, COCCH), 6.16 (d br, J = 7.8 Hz, 1 H, ortho H of pH at saturated C), 6.72 [td, (t) ^3J = 7.7 Hz, (d) ^4J = 1.3 Hz, 1 H neighboring meta H of Ph], 6.93–7.47 (m, 14 H, aryl H except 3 ortho H and 1 meta H), 7.66 (d, J = 7.3 Hz, ortho H of benzoyl); IR (KBr) 1687 cm^{-1} (C=O).

Table I, Entry 12. Chromatography (3 × 60) with toluene provided 100 mg (15%) of **8**. Elution with CH_2Cl_2 gave 420 mg, and elution with ethyl acetate gave 270 mg of mixtures of many unidentified products.

Table I, Entry 13. A 420-mg (47%) portion of A was removed by filtration. Chromatography (3 × 60) with CH_2Cl_2 of the filtrate gave a mixture of A and AH_2, then 65 mg (4%) of **15a**, and finally 600 mg (81%) of **16a**.

3-(9,10-Dihydroanthr-9-yl)-3-phenylbutan-2-one (15a): mp (MeOH) 119–120 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.96 (s, Me), 2.78–3.00 (m, $COCH_2$), 3.15 (d br, J = 18.5 Hz, 10-H pseudo ax), 3.48–3.57 (m, COCCH), 3.53 (d, J = 18.5 Hz, 10-H pseudo eq), 4.11 (d, J = 6.7 Hz, 9-H pseudo eq), 6.60 (d, J = 7.3 Hz, ortho H of pH at saturated C), 6.82 (d, J = 7.5 Hz, 1 H, 1-H of AH), 6.99–7.36 (m, 10 H, aryl H except 2 ortho H and one 1-H of AH); IR (KBr) 1710 cm^{-1} (C=O). Anal. Calcd for $C_{24}H_{22}O$: C, 88.30; H, 6.79. Found: C, 88.01; H, 6.61.

Table I, Entry 14. Chromatography (3 × 25) with toluene provided AH_2; elution with CH_2Cl_2 gave 740 mg (83%) of **15a**.

Table I, Entry 15. A 530-mg (72%) portion of A was removed by filtration. Chromatography (3 × 60) of the filtrate with toluene provided a mixture of A and AH_2 and then 470 mg (78%) of **16b** that soon began to change into **16c**: ^{1}H NMR of **16b** ($CDCl_3$, 60 MHz) δ 1.10 (d, J = 6.4 Hz, Me), 2.47–3.28 (m, $CHCH_2$), 7.18 (s br, Ph), 9.70 (s, CHO).

2-Methyl-3-phenylpropionic acid (16c): oil; lit.[21] mp 36.5 °C; ^{1}H NMR identical with that of an authentic sample prepared from ethyl benzylmethylacetoacetate according to ref 21; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 1.15 (d, J = 6.6 Hz, Me), 2.38–3.21 (m, $CHCH_2$), 6.99–7.31 (m, Ph), 11.03 (s br, OH); IR (film) 1705 cm^{-1}.

Table I, Entry 16. Chromatography (3 × 60) with CH_2Cl_2 provided AH_2 and 1.23 g (87%) of **15c**.

4-(9,10-Dihydroanthr-9-yl)-4-methylpentan-2-one (15c): mp 71–72 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.90 (s, 2 Me), 2.08 (s, COMe), 2.36 (s, $COCH_2$), 3.74 (d, J = 19.2 Hz, 10-H pseudo eq), 4.15 (d br, J = 19.2 Hz, 10-H pseudo ax), 4.23 (s br, 9-H pseudo eq ?), 7.20 (mc, aryl H); IR (KBr) 1709 cm^{-1} (C=O). Anal. Calcd for $C_{20}H_{22}O$: C, 86.28; H, 7.96. Found: C, 86.10; H, 8.15.

Acknowledgment. This research was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie. This support is gratefully acknowledged.

(20) Haller, A.; Bauer, E.; Ramart, P. *Ann. Chim.* **1924**, *2*(10), 269.

(21) Jones, L. W.; Wallis, E. S. *J. Am. Chem. Soc.* **1926**, *48*, 169.

Birch Reduction and Reductive Alkylation of Benzonitriles and Benzamides

Arthur G. Schultz* and Mark Macielag

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180-3590

Received May 27, 1986

In contrast to literature suggestions, benzonitriles and *N,N*-dialkylbenzamides are excellent substrates for Birch reduction and reductive alkylations. Thus, *o*-methoxybenzonitrile (**1a**) and benzonitrile (**1b**) give 1,4-cyclohexadienes **2a–2d** from alkali-metal reduction in NH_3–THF with *tert*-butyl alcohol (1 equiv), followed by sequential addition of an alkyl halide and excess NH_4Cl. The product of HCN elimination [e.g., diphenylmethane (**3**)] is obtained if NH_4Cl is not added prior to an aqueous workup. Birch reduction of **1a** followed by NH_4Cl quench gives 2-cyano-1-methoxy-1,3-cyclohexadiene (**4**), while benzonitrile (**1b**) gives the dimeric dinitrile **8**, isolated as a 7:5 mixture of diastereoisomers. Hydrogenation of the mixture, **8**, gives chromatographically separable **9a** and **9b**; a single-crystal X-ray diffraction study provided the molecular structure of **9b**. Birch reduction of *N,N*-dimethylbenzamide (**12a**) gives 1,4-cyclohexadiene **13a**, while reductive benzylation gives **13b**. The effect of alkali metal (type and quantity), the availability of a proton source, and variation in reaction temperature on the course of Birch reduction of *N,N*-dimethylbenzamide (**12a**) is reported.

For the past few years, we have been involved with the development of new strategies for chiral 2,4- and 2,5-cyclohexadien-1-one construction.[1] In the course of this work, we have examined the alkali metal in ammonia re-

0022-3263/86/1951-4983$01.50/0