1,10-, 1,4-, and 1,2-Eliminations and 1,5- and 1,7-Rearrangements in the Reactions of Substituted 9-Anisylidene-9,10-dihydroanthracenes and Anthrones in Acetic Acid

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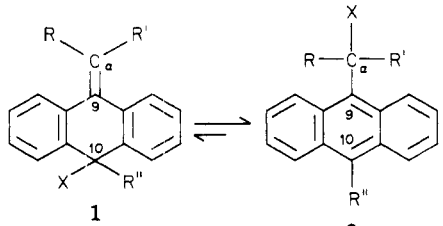
Solvolysis of 9-(α-bromoanisylidene)-9,10-dihydro-10-anthracenol (**12**) in dry AcOH gives first the 10-acetoxy derivative **13** and 9-anisoylanthracene (**16**) after a long reaction time. In wet AcOH/NaOAc 1,10-elimination of MeOH from **12** or of MeOAc from **13** takes place, giving 7-(9′-anthryl)-7-bromoquinone methide (**17**) probably by demethylation of the methoxy group of the intermediate α-(9-anthryl)-α-bromo-*p*-methoxybenzyl cation. The α-H analogue **9** gives a 1,5 solvolytic rearrangement to α-anisyl-9-anthrylmethyl acetate (**19**) in AcOH and to the ethyl ether **21** in EtOH, but anthracene is also formed by 1,4-elimination. The 10-methyl derivative **14** gives a 1,2-elimination and solvolysis of the vinyl bromide. Acetolysis of 9-(α-bromoanisylidene)anthrone (**11**) gives first the vinyl acetate **31** which by a 1,7-acetoxy rearrangement gives 9-acetoxy-10-anisoylanthracene (**29**). The mechanisms of these reactions are discussed in terms of a balance between the driving force for aromatization of the dihydroanthracene moiety and steric effects, especially at C_α, in the reaction intermediates.

Substituted 9-arylidene-9,10-dihydro-10-anthracenols are known to give several elimination and rearrangement reactions under acidic conditions via the initial formation of a carbonium ion.[1-4] Nucleophilic additions to 9-arylideneanthrones are also frequently accompanied by rearrangements.[5,6] A driving force for these reactions is the aromatization of the anthracene skeleton. An example is the 1,5-rearrangement **1** ⇌ **2** (eq 1) which was inves-



(1)

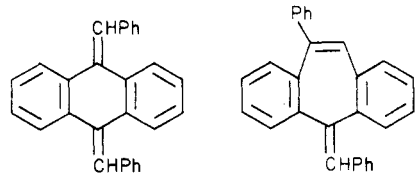
1 **2**

a, R = H; R′ = R″ = Ph; X = OH
b, R = H; R′ = Ph; R″ = $PhCH_2$; X = OH
c, R = H; R′ = Ph; R″ = Me; X = OH
d, R = R″ = H; R′ = Ph; X = *i*-PrO
e, R = R″ = H; R′ = 9-anthryl; X = OH
f, R = R″ = H; R′ = Ph

tigated in detail by Julian, Cole, and co-workers for the isomerization of 9-benzylidene-9,10-dihydro-10-phenylanthracenol (**1a**) to 9-(α-hydroxybenzyl)-10-phenylanthracene (**2a**).[1b] An alternative path to aromatization is shown by the reaction of either **1a** or **2a** with bromine which gives 9-bromo-10-phenylanthracene[1a] by an apparent brominative 1,4-elimination. Other 1,4-eliminations in substituted 9,10-dihydroanthracenes are known.[7] 9-*tert*-Butyl-9,10-dihydro-9-anthracenol with P_2O_5 gives *tert*-butylanthracene,[4] and solvolysis of the corresponding trifluoroacetate gives anthracene and *tert*-butyl trifluoroacetate.[4]

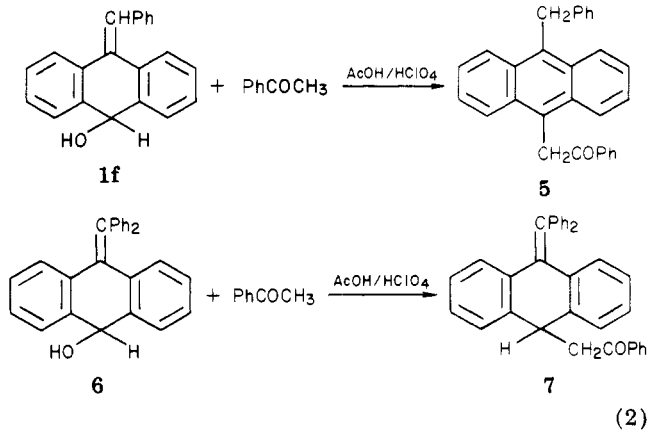
A change in the reaction conditions and the leaving group frequently changes the nature of the product. The reaction of **1b** with acetic anhydride gives the dibenzylidene derivative **3** by a 1,2-elimination, but the rearranged dibenzocycloheptatriene **4** is formed with *p*-toluenesulfonic acid/formic acid.[3] In contrast, **1c** gives the ether **2c** rather than 1,2-elimination, and **1d** gives **2**, R = R″ = H, R′ = Ph, and X = OEt, in ethanolic HCl.[2b]

The course of the reaction seems to depend on the steric environment around C_α. Whereas acetophenone reacts



3 **4**

with **1f** in AcOH in the presence of $HClO_4$ with the formation of the anthracene derivative **5**, its benzhydrylidene analogue **6** gives the dihydroanthracene derivative **7** under the same conditions[8] (eq 2). This suggests that structure



1f **5**

6 **7**

(2)

1 may be stable relatively to **2** if C_α is heavily substituted. An extreme steric effect can even reverse the direction of reaction 1. Applequist and Swart found recently that bis(9-anthryl)methanol **2e** reacts with $AlCl_3/LiAlH_4$ with the formation of **1e**, and reactions with $ZnCl_2$ in ethanol or with $SOCl_2$ in benzene give the 10-ethoxy- and the 10-chloro-**1** derivatives, respectively.[9]

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(1) (a) P. L. Julian and W. Cole, *J. Am. Chem. Soc.*, **57**, 1607 (1935); (b) P. L. Julian, W. Cole, G. Diemer, and J. G. Schafer, *ibid.*, 71, 2058 (1949).
(2) (a) K. G. Flynn and G. Bergson, *Acta Chem. Scand.*, **19**, 756 (1965); (b) *Ark. Kemi*, **27**, 393 (1967).
(3) E. D. Bergmann, M. Rabinovitz, and S. Glily, *Tetrahedron, Suppl.* **No. 8** (1), 141 (1966).
(4) R. C. Parish and L. M. Stock, *J. Org. Chem.*, **31**, 265 (1966).
(5) For a general reference see H.-U. Wagner and R. Gompper in "The Chemistry of the Quinonoid Compounds", S. Patai, Ed., Wiley, London, 1974, Part 2, Chapter 18, p 1145.
(6) (a) P. L. Julian and A. Magnani, *J. Am. Chem. Soc.*, **56**, 2174 (1934); (b) P. L. Julian and W. J. Gist, *ibid.*, **57**, 2030 (1935).
(7) S. J. Cristol, N. L. Hause, and J. S. Meek, *J. Am. Chem. Soc.*, **73** 674 (1951); S. J. Cristol and D. D. Fix, *ibid.*, **75**, 2647 (1953).
(8) B. Bodo, J. Andrieux, and D. Molho, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **273**, 170 (1971).

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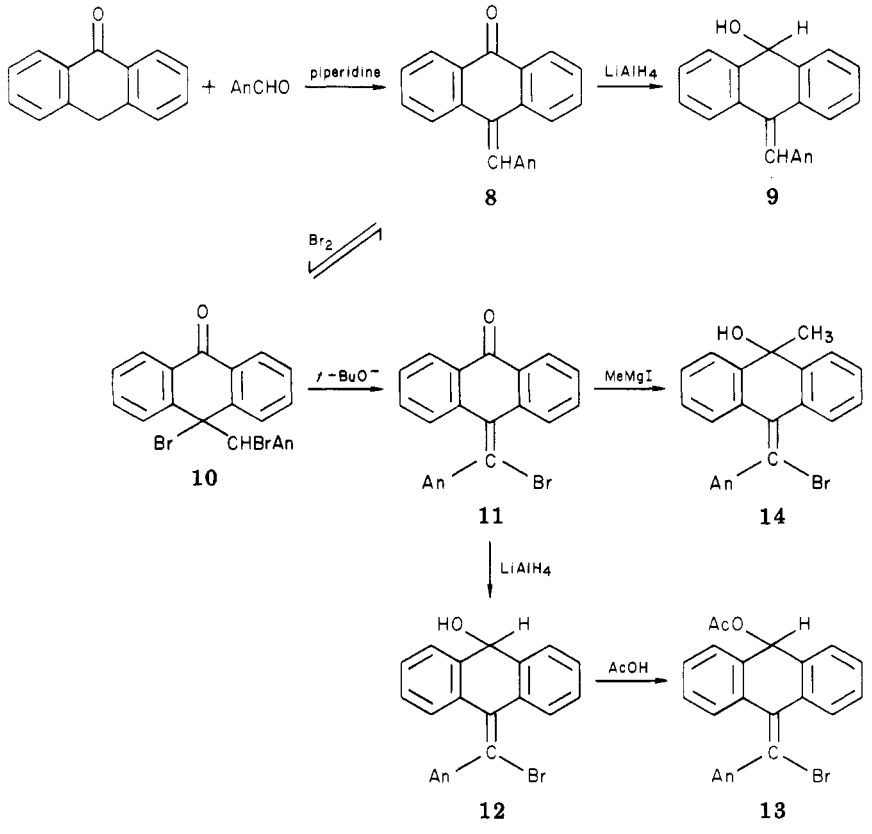
Scheme I[a]



[a] An = p-$MeOC_6H_4$.

These results are not surprising since the aromatization of the middle ring of the dihydroanthracene is not always accompanied by a gain in energy. For example, anthrone predominates in the anthrone ⇌ 10-anthracenol equilibrium both in the gas phase and in solution.[10]

During our studies of vinylic solvolysis we investigated the reactions of 9-(α-bromoanisylidene)anthrones[11] and 9-(α-bromoanisylidene)-9,10-dihydro-10-anthracenols[12] and of their nonbromo analogues in AcOH. We observed that small structural variations gave different elimination and rearrangement reactions. Some of these, such as the 1,10-eliminations of methanol and methyl acetate or the 1,7-acetoxy rearrangement, are either rare or unprecedented. Both aromatization and steric effects, especially around C_α, which are accentuated by the presence of the 1,8-peri hydrogens, play an important role in determining the reaction course. These reactions are discussed below.

Results and Discussion

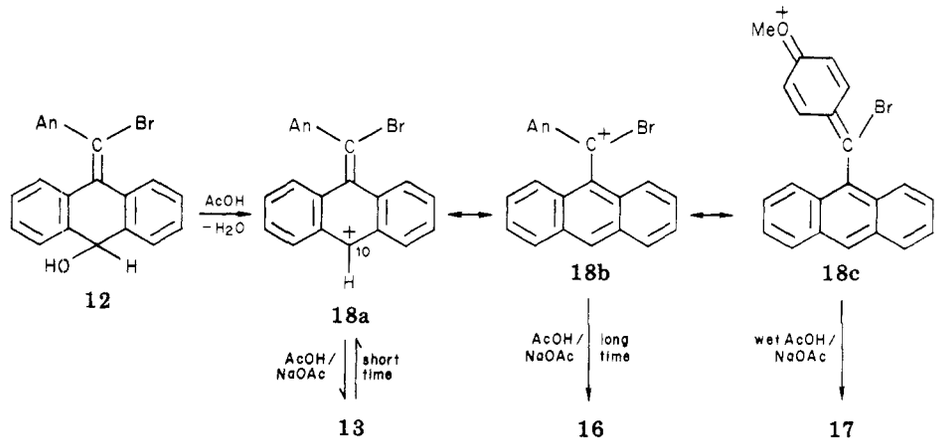
The five closely related precursors for the present work, **9** and **11–14**, were prepared according to Scheme I. There are four notable features of this synthesis. First, the bromination of **8** is rather slow and requires 24 h for completion. This is attributed to reduction of the nucleophilicity of the double bond due to electron withdrawal by the carbonyl group. The crowding at the double bond should have only a minor effect since addition of bromine to 9-anisylidene-10-ethyl-10-phenyl-9,10-dihydroanthracene is rapid even at −20 °C in CH_2Cl_2.[12b]

Second, the base-promoted dehydrobromination of the dibromide **10** is accompanied by an extensive debromination to **8** which becomes the main reaction when the temperature is raised. Similar debrominations accompany the dehydrobrominations of the p-tolyl, the o-anisyl, and the phenyl analogues of **10**[12b] and of substituted 9-bromo-9-(α-bromobenzyl)fluorenes.[13] We attribute the debromination to a mixture of steric and electronic effects. The pentasubstituted ethane **10** is crowded, and strain is relieved by attack of the base on the rather nonacidic α hydrogen, giving the tetrasubstituted ethylene **11**, or by attack on the relatively positive bromine at C-9 to give the trisubstituted ethylene **8**. Apparently, the steric effect and the acidity are sufficient to make the attack by the hard base on the soft 9-Br competitive with the attack on the harder α hydrogen.

Third, the reactions of **8** with $LiAlH_4$ and of **11** with $LiAlH_4$ or with MeMgI are 1,2-additions to the carbonyl group rather than the alternative routes of conjugate 1,6-addition to give the corresponding anthracenols or substitution of the vinylic bromide by the nucleophile. Conjugate 1,6-additions are common in additions to quinone methides,[5] e.g., in the addition of PhMgBr to 9-methylene- and 9-benzylideneanthrones.[6a] The vinylic bromide of the structurally related 9-(bromomethylene)-10-ethyl-1,8,10-trimethyl-9,10-dihydroanthracene was substituted by lithium diphenylphosphide,[14] and the bromide of triarylvinyl bromides was likewise replaced by

(9) D. E. Applequist and D. J. Swart, *J. Org. Chem.*, **40**, 1800 (1975).
(10) H. Baba and T. Takemura, *Bull. Chem. Soc. Jpn.*, **37**, 1241 (1964); *Tetrahedron*, **24**, 4779 (1968); G. Löber, *Acta Chim. Acad. Sci. Hung.*, **40**, 9 (1964); *Z. Phys. Chem., (Frankfurt Am Main)*, **54**, 73 (1967); Z. Majerski and N. Trinajstic, *Bull. Chem. Soc. Jpn.*, **43**, 2648 (1970); P. Beak, F. S. Fry, Jr., J. Lee, and F. Steele, *J. Am. Chem. Soc.*, **98**, 171 (1976).
(11) (a) Z. Rappoport, J. Kaspi, and Y. Apeloig, *J. Am. Chem. Soc.*, **96**, 2612 (1974); (b) Z. Rappoport, *Acc. Chem. Res.*, **9**, 265 (1976); (c) Z. Rappoport, I. Schnabel, and P. Greenzaid, *J. Am. Chem. Soc.*, **98**, 7726 (1976); (d) Y. Apeloig, Ph.D. Thesis, The Hebrew University, Jerusalem, 1974.
(12) (a) Z. Rappoport and J. Greenblatt, *J. Am. Chem. Soc.*, **101**, 1343 (1979); (b) *ibid.*, **101**, 3967 (1979).
(13) Z. Rappoport, A. Gal, and N. Pross, unpublished results.
(14) P.-T. Leung and D. Y. Curtin, *J. Am. Chem. Soc.*, **97**, 6799 (1975).

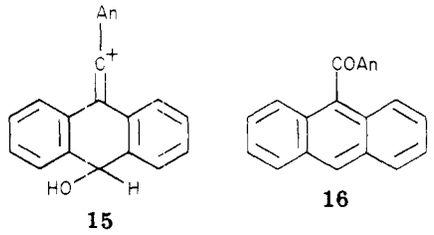
Scheme II



hydrogen in the reaction with $LiAlH_4$.[15] In contrast, in analogy with our reactions, MeMgI adds 1,2 to the carbonyl group of 9-benzhydrylideneanthrone,[6b] and $LiAlH_4$ reduced the carbonyl group of benzylideneanthrone.[16] We believe that steric effects are important in determining the course of these additions which occur at the carbonyl group when the double bond is sterically crowded. The formation of **12** and **14** by nucleophilic reactions of sterically hindered **11** is understood on this basis whereas the 1,2-addition to **8** or to its unsubstituted analogue indicates that the attack of a bulky reagent such as $LiAlH_4$ on the double bond of a trisubstituted ethylene still gives a crowded transition state.

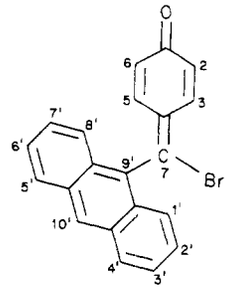
Finally, the reaction of **12** in AcOH/NaOAc gave the 10-acetoxy derivative **13**[12b] before any rearranged 9-substituted anthracene is formed. This reaction which proceeds via initial ionization of the 10-hydroxy group[12b] demonstrates again that C-10 rather than C_α can be the reactive center, as discussed elsewhere[12b] and below.

1,10-Elimination of Methanol or of Methyl Acetate. The solvolysis of **12** in 80% EtOH or in trifluoroethanol gives a substitution product of the vinylic bromide or a secondary product derived from it via an initial heterolysis of the C–Br bond to form the vinyl cation **15**.[12] In dry



AcOH the initial ionization site is C-10, as shown by the loss of optical activity of optically active **12** and the simultaneous formation of **13** before an appreciable replacement of the bromine takes place. 9-Anisoylanthracene (**16**) is formed after longer reaction times via heterolysis of the C_{10}–OAc bond of **13**.[12b]

However, the reaction of either **12** or **13** in wet AcOH follows a different course. For example, the reaction of **12** in wet AcOH (containing <10% water) buffered by NaOAc for 48 h at 49.6 °C gave both **13** and **16** as minor products and a main product which showed a strong C=O absorption at 1640 cm^{-1} and the absence of a methoxy signal in the NMR. The mass spectrum indicated the presence of a bromine and showed a molecular peak corresponding to a product which was formed by a loss of methanol from **12**. The same product was formed from **13** in wet AcOH. These data together with the NMR and the UV spectra suggest that the product is 7-(9′-anthryl)-7-bromoquinone methide (**17**) which is formed by



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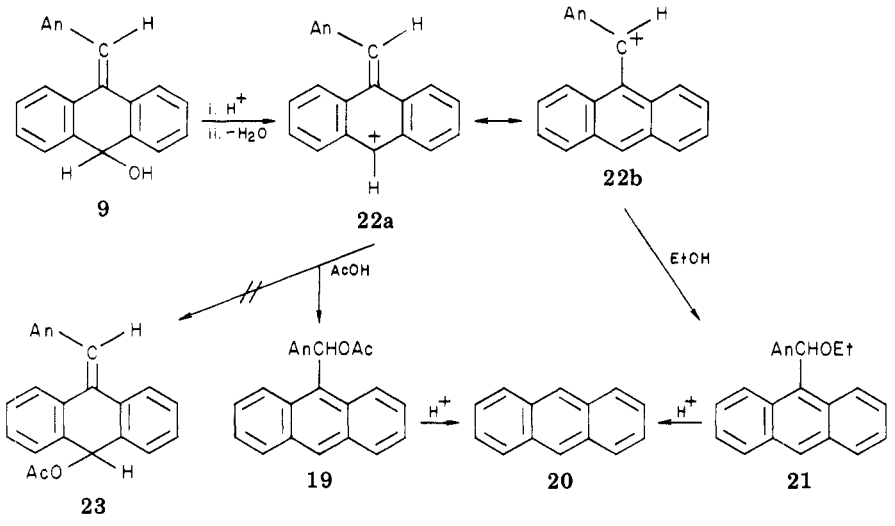
an unusual 1,10-elimination of MeOH from **12** or of methyl acetate from **13**. The 270-MHz NMR spectrum in $CDCl_3$ shows the H-10′ anthracenic proton as a low-field (δ 8.60) singlet; four of the other aromatic protons appear as two halves of AA′BB′ quartets centered at 7.88 and 8.09 ppm (probably H-1′, H-8′ and H-4′, H-5′, respectively), and the other four appear as a multiplet at 7.51–7.61 ppm. Each of the four protons of the quinone methide ring is well separated from the others and appears as half of a quartet with a further 1,3 splitting. The hydrogens at δ 6.05 and 6.65 are coupled with a 1,2 coupling constant of 8 Hz, and the hydrogen at 6.54 ppm is coupled to the low-field hydrogen at δ 8.16 with a coupling constant of 7.3 Hz. The 1,3 coupling constants of all the protons are 2.4 ± 0.6 Hz. Since the environments of H-2 and H-6 are closer than those for the other protons, the low-field proton is either H-3 or H-5. It is likely that it is H-5 which is cis to the anthryl group, being in its deshielding region, although this group is probably twisted from the plane of the other ring. The UV spectrum shows the characteristic fingerprints of the anthracene moiety at 327–393 nm, a high-intensity absorption at 253 nm, and a low-intensity absorption at 450 nm which is responsible for the red color of **17**. A gas chromatographic analysis of the crude reaction mixture from **12** shows a peak at the position of methyl acetate.

The suggested mechanism (Scheme II) involves an initial protonation of the 10-OH group of **12** or the 10-OAc group of **13** followed by formation of the hybrid carbonium ion, **18a–c**. Three possible reaction sites for nucleophilic attack on **18** are available, and products from reaction at each of them were observed. Reaction at C-10 gave the acetate **13** in dry AcOH, whereas the reaction at C_α after longer time gave the ketone **16**. The unique feature of the reaction in wet AcOH/NaOAc is that the base attacks the methyl of the methoxy group of **18**, giving the quinone

(15) C. C. Lee and U. Weber, *J. Org. Chem.*, **43**, 2721 (1978).
(16) M. Rabinovitz and G. Salemnik, *J. Org. Chem.*, **33**, 3935 (1968).

Scheme III



methide **17** by dealkylation and methyl acetate.

Precedents for dealkylation of an ether group during solvolysis usually involve the oxonium ion of the bridged species formed by neighboring alkoxy group participation. The dealkylation gives a stable oxygen heterocycle, e.g., a furan derivative in the case of 5-OMe participation.[17] We know of no precedent when a nonparticipating methoxy group is dealkylated during a solvolysis, and a search for this route in the solvolysis of *p*-anisylethyl tosylate gave a negative result.[18] The formation of fuchsone (7,7-diphenylquinone methide) by elimination of methyl chloride from *p*-methoxytrityl chloride at 180–200 °C[19a] or its bis(*p*-dimethylamino) derivative from the carbinol in $AcOH/H_2SO_4$[19b] probably involves dealkylation of the initially formed carbonium ion.

We believe that steric effects are mainly responsible for the attack on the methoxy group of **18**. Steric interactions between the peri 1 and 8 hydrogens of the anthryl group and the substituents on C_α reduce the planarity of the hybrid ion and the extent of charge delocalization. The most hindered position for nucleophilic attack is C_α since the steric crowding forces rotation of the anisyl and the 9-anthryl groups from the plane of the carbonium ion to the plane of the vacant p orbital and the entering nucleophile. The gain in aromatization is apparently not sufficient to counterbalance the steric interaction in the heavily tetrasubstituted methane formed by capture of C_α. The alternative reaction at C-10 where aromaticity is not gained becomes the kinetically favored process, as judged by the rapid formation of **13**. However, the least-hindered position for attack by AcO^- or AcOH is the methyl group of the oxonium ion, and this S_N2 process is still faster than attack on C_α. The loss of the aromaticity of the anisyl group is counterbalanced by the gain in the aromaticity of the anthryl group and the conjugation energy of the cross-conjugated α,β-unsaturated ketone. Indeed, aromatization of the quinonoid ring of **17** by protonation on the oxygen and consequent solvolysis of the vinylic bromide occurs only at a relatively high temperature and after long reaction times.[12b]

This situation is reminiscent of the dimerization of the triphenylmethyl radical where attack of one radical on the para position of another with a consequent loss of aromaticity is preferred over formation of the heavily substituted hexaphenylethane.[20]

At present we have no rationalization for the difference in the site of attack in dry and in wet AcOH/NaOAc. We found that the rate of formation of **17** decreases on decreasing the water content of the medium from ca. 1.2×10^{-5} s^{-1} in commercial AcOH to ca. 7×10^{-6} s^{-1} when 5% acetic anhydride is added to it. Solvation and different basicity of the base may be important, but explanation should wait until further work is completed.

1,5-Rearrangements and 1,4-Elimination. 9-Anisylidene-9,10-dihydro-10-anthracenol (**9**), the α-H analogue of **12**, reacts rapidly in AcOH/NaOAc. The UV spectrum indicates that an anthracene derivative is formed in a reaction with a half-life of 10 min at 20 °C.[12b] The main compound isolated under these conditions is α-anisyl-9-anthrylmethyl acetate (**19**), and when the reaction was interrupted after 1 half-life, only **9** and **19** were observed by TLC. However, when the mixture in AcOH was refluxed for 5 min, some anthracene **20** (<10%) was also formed.

When **9** was refluxed for 5 min in ethanol containing H_2SO_4, the main fraction isolated was α-anisyl-9-anthrylmethyl ethyl ether (**21**), whereas when the mixture was kept for 24 h at 100 °C, anthracene became the major product.

Two different reactions are therefore observed. A 1,5 solvolytic rearrangement gives **19** in AcOH and **21** in EtOH, and a 1,4-elimination gives **20** in both solvents. It is likely that the first steps of the 1,5-rearrangement again involve protonation on and ionization of the 10-OH group with the formation of the hybrid ion **22a–22b**. In contrast with its α-bromo analogue ion **18**, C_α of **22** is only disubstituted. Consequently, the steric hindrance to nucelophilic capture is smaller, and capture takes place exclusively at C_α with no evidence for reaction at C-10 with formation of **23** or for attack on the methoxy group (Scheme III). These rearrangements resemble those investigated by Julian and co-workers[1] and by Flynn and Bergson.[2] The latter authors observed that **1d** gave the rearranged ethyl ether **2**, R = R″ = H, R′ = Ph, X = OEt, in $EtOH/HCl$[2b] and the rearranged acetate **2**, R = R″ = H, R′ = Ph, X = OAc, in AcOH.[2a] The structure of the latter was proven by methanolysis in methanolic HCl to the methyl ether,[2a] whereas the NMR shows that the

(17) E.g.: R. Heck, J. Corse, E. Grunwald, and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3278 (1957); S. Winstein, E. Allerd, R. Heck, and R. Glick, *Tetrahedron*, **3**, 1 (1958); T. Sonoda, S. Kobayashi, and H. Taniguchi, *Bull. Chem. Soc. Jpn.* **49**, 2560 (1976).

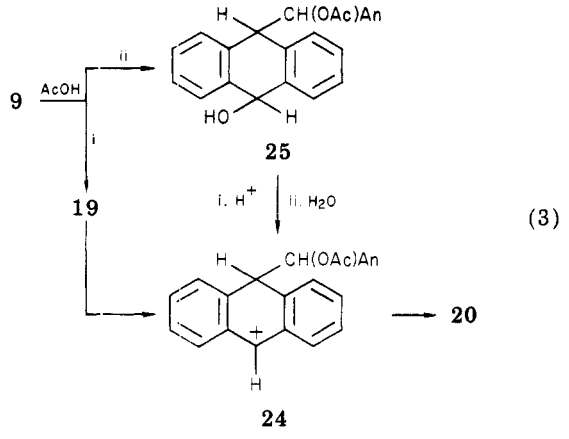
(18) R. Baird and S. Winstein, *J. Am. Chem. Soc.*, **85**, 567 (1963).

(19) (a) A. Bistrzycki and C. Herbst, *Ber. Dtsch. Chem. Ges.*, **36**, 2333 (1903); (b) W. Schenck, *Justus Liebigs Ann. Chem.*, **368**, 291 (1909).

(20) H. Lankamp, W. T. Nauta, and C. MacLean, *Tetrahedron Lett.*, 249 (1968); W. B. Smith, *J. Chem. Educ.*, **47**, 535 (1970).

acetate **19** was converted to the methyl ether on attempted crystallization from MeOH.

For formation of the anthracene by a 1,4-elimination the double bond of **9** has to be first converted to a single bond, and two routes are conceivable. (i) Initial rearrangement to **19** or **21** is followed by ipso attack of a proton on C-9 and a reverse Friedel–Crafts dealkylation of the electrofugal, stable α-acetoxyanisyl cation from cation **24** to give **20**. (ii) Addition of the acid (e.g., AcOH) across the double bond of **9** gives **25**, which by acid-catalyzed ionization of the 10-OH group forms **24** which gives anthracene (eq 3).



The very facile rearrangement and the appearance of anthracene under more severe conditions suggest that route i is followed. The 1,4-elimination is a consequence of a consecutive 1,5-rearrangement and an ipso substitution at C-9 This is supported by the observation that both the unrearranged **1a** and the rearranged **2a** undergo a formal 1,4-brominative elimination with bromine to 9-bromoanthracene.[1a]

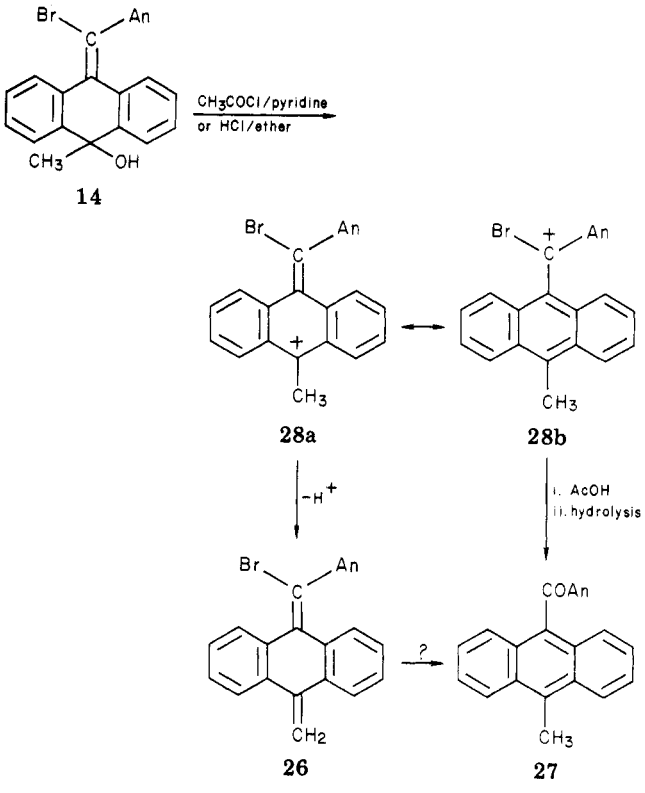
1,2-Elimination of Water. A different type of elimination was observed in the reactions of 9-(α-bromoanisylidene)-9,10-dihydro-10-methyl-10-anthracenol (**14**). A 1,2-elimination of water to form the quinodimethane derivative **26** takes place either with acetyl chloride in pyridine or with HCl in ether (Scheme IV).

On the other hand, solvolysis of **14** for 48 h in AcOH at 120 °C gives 70% of a product (by NMR) which shows a conjugate C=O at 1680 cm^{-1} and a methyl signal at δ 3.1. A one-point solvolysis of 0.043 M **14** in AcOH containing 0.087 M NaOAc at 120 °C gave 37.4% reaction. The corresponding k value of 2.2×10^{-5} s^{-1} is within the expected range for solvolysis of the vinylic bromide,[11d,12b] and the product is presumably 9-anisoyl-10-methylanthracene (**27**), although the reaction was not investigated further. A plausible mechanism involves the intermediacy of the hybrid ion **28a–28b** which eliminates a proton to form **26** or captures the acetate at C_α and reacts further to give **27**. Protonation of **26** can also be the first step in the formation of **27**. Steric effects may be again important since expulsion of a proton relieves the strain at C-10, whereas capture at C_α generates a strain at this carbon. However, we note that a similar 1,2-elimination by acetic anhydride took place even with **1b** which is less crowded at C_α.[3]

1,7-Rearrangement of an Acetoxy Group. The acetolysis of 9-(α-bromoanisylidene)anthrone (**11**) in AcOH/NaOAc at 120 °C gives 9-acetoxy-10-anisoylanthracene (**29**). This is the only product observed between 45% reaction and 10 half-lives.

The expected initial solvolysis product of **11** is the unrearranged 9-(α-acetoxyanisylidene)anthrone (**31**), formed by capture of the vinyl cation **30** at C_α. Since **31** may rearrange to **29** under the reaction conditions, the solvolysis was conducted under milder conditions in the presence of AgOAc in acetonitrile. The acetate **31** was indeed obtained, and its structure was determined by its acetoxy signal at δ 2.10, a position close to that of the acetoxy group in other vinyl acetates,[21] and by the positions and the intensities of the two UV maxima which are similar to those of **11**. In contrast, the acetoxy group of **29** which is in the plane of the anthracene ring is at a lower field (δ 2.70), and the UV spectrum is characterized by several "fingerprint" maxima similar to those of other anthracene derivatives. The shapes of the UV spectra resemble those of the analogous 9-benzoyloxymethyleneanthrone and 10-benzoyloxy-9-anthraldehyde, respectively.[22]

Scheme IV



In AcOH 0.087 M in NaOAc, **31** disappears completely after 1 h at 120.3 °C with the formation (according to the NMR spectrum) of 25% of **29** and two other compounds. From the NMR spectrum, these are the ketone **32** (45%) whose identity was deduced from the appearance of the characteristic H-9 signal at δ 5.98 and its tautomeric phenol **33** (30%) which gives a broad OH signal at δ 9.1 and an IR absorption at 3300 cm^{-1}.

A suggested mechanism for this unusual 1,7-acetoxy rearrangement is given in Scheme V. It involves a sequence of hydrolytic deacylation of the acetoxy group, followed by a consequent 1,3-keto–enol and 1,5-anthrone–anthracenol rearrangements and acylation of the formed C-10 phenolic group by the acetic anhydride formed in the first step. Precedents for each step are known. Ketones are formed during the solvolysis of α-cyclopropyl[23] and α-arylvinyl halides[24] in dry AcOH/NaOAc. A mechanism involving attack of the acetate ion

(21) (a) Z. Rappoport and A. Gal, *J. Am. Chem. Soc.*, **91**, 5246 (1969); *J. Org. Chem.*, **37**, 1174 (1972); (b) Z. Rappoport and Y. Apeloig, *J. Am. Chem. Soc.*, **91**, 6734 (1969).

(22) L. Nédélec and J. Rigaudy, *Bull. Soc. Chim. Fr.* 1204 (1960).

(23) S. A. Sherrod and R. G. Bergman, *J. Am. Chem. Soc.*, **93** 1925 (1971).

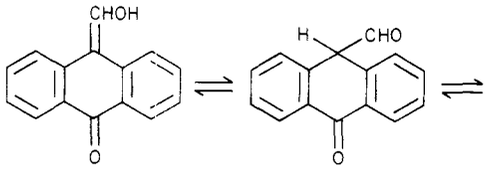
(24) E. g.: Z. Rappoport and A. Gal, *J. Chem. Soc., Perkin Trans. 2*, 301 (1973); Z. Rappoport, P. Shulman, and M. Thuval (Shoolman), *J. Am. Chem. Soc.*, **100**, 7041 (1978).

on the carbonyl group of the vinyl acetate which gives a ketone and acetic anhydride was suggested.[23] From the above data the rate constant for the disappearance of **31** is $>10^{-2}$ s^{-1} at 120 °C, and from the products distribution the first-order rate constant for the **32** + **33** → **29** reaction is ca. 8×10^{-5} s^{-1}. Since the initial solvolysis rate of **11** is 1.2×10^{-4} s^{-1} at 120.3 °C,[11a] the hydrolysis of **31** is ≥80 times faster than the solvolysis of **11**.[25] Due to the extensive common-ion rate depression during the solvolysis of **11**, the products were analyzed only after 17 h, conditions under which >99% of **32** and **33** are converted to **29**, thus accounting for its exclusive formation.

The electrophilic catalysis by AgOAc enhances the solvolysis rate of **11** by several orders of magnitude. On the other hand, the hydrolysis of **31** becomes slower at the lower temperature. Consequently, **31** is accumulated under these conditions, and careful workup enables its isolation.

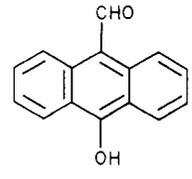
The solvolyses of the analogous α-bromo-*o*-methoxy- and α-bromo-*p*-methylbenzylideneanthrones and the α-bromo-unsubstituted compound in AcOH/NaOAc which require similar or more severe conditions than that of **11** give, accordingly, only the rearranged 9-aroyl-10-acetoxyanthracenes.[12b] In contrast, the pivalolysis of **11** in pivalic acid/sodium pivalate gave only the unrearranged vinyl pivalate even at 185.4 °C.[11c] Since the hydrolysis of other vinyl pivalates to the corresponding ketones in pivalic acid/sodium pivalate is much slower than the hydrolysis of the corresponding acetates in AcOH/NaOAc[11c] for steric reasons, the isolation of the nonrearranged pivalate corroborates the first step of the mechanism of Scheme V.

A somewhat related phenomenon is the tautomeric nature of 9-(hydroxymethylene)anthrone (**34**), where the **34a** ⇌ **34b** ⇌ **34c** process involves a similar 1,7-hydrogen rearrangement.[22,26] The benzoate esters of **34a** and **34c** are known, but under basic conditions both hydrolyze to **34**, and they do not interconvert.[22]



34a

34b



34c

The 1,7-acetoxy rearrangement involves aromatization of the dihydroanthracene moiety, but this driving force cannot be high in view of the predominance of anthrone in the anthrone ⇌ anthracenol equilibrium,[10] of the tautomerism of **34** and of other examples of the present paper. The practically irreversible acylation of the phenolic group probably drives the reaction in the **32** → **33** → **29** direction.

Conclusions

A delicate balance between the mild driving force for the aromatization of the 9,10-dihydroanthracene moiety and the steric effect around C_α of the hybrid cations **18**, **22**, and **28** is an important factor in determining the course of the reactions of the 9-anisylidene-9,10-dihydroanthracenes and anthrones described above. The presence of various reaction sites results in completely different and some unusual reaction courses with relatively small structural variations.

Experimental Section

Melting points are uncorrected. Nuclear magnetic resonance spectra were recorded with Varian T/60, AH 100, and EM-360 instruments and with a Brucker WH-270 instrument (at the Weizmann Institute) and are given in δ units downfield from internal tetramethylsilane. UV spectra were recorded with Varian Techtron 635 instrument, IR spectra with a Perkin-Elmer 337 instrument, and mass spectra with a Varian MAT 311 instrument.

Acetic acid was dried as described previously.[21b]

9-Anisylideneanthrone (8). Anthrone (50 g, 0.26 mol), anisaldehyde (49 g, 0.32 mol), and piperidine (5 mL) were refluxed in pyridine (150 mL) for 6 h. The solvent was evaporated, and the oil obtained was crystallized from butanol, giving 58 g (72%) of yellow crystals: mp 142–143 °C (lit.[27] mp 140.5–141.5 °C); λ_{max} (EtOH) 236 nm (ε 40 400), 294 sh (14 800), 388 (16 100); ν_{max} ($CHCl_3$) 2820 (MeO, m), 1658 (C=O, vs), 1595 (C=C, s) cm^{-1}; δ ($CDCl_3$) 3.87 (3 H, s, MeO), 6.75–8.41 (13 H, m, Ar and :CH); *m/e* (rel intensity) 312 (M, B), 311 (M − H, 32), 297 (M − Me, 10), 282 (M − CH_2O, 30), 270 (M − CH_2CO, 22), 269 (M − CH_3CO, 20), 239 (42), 121 (50), 79 (40). Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.73; H, 5.17.

α,9-Dibromo-9-(*p*-methoxybenzyl)anthrone (10). To a solution of 9-anisylideneanthrone (15.6 g, 0.05 mol) in carbon tetrachloride (30 mL) was added a solution of bromine (8 g, 0.05 mol) in carbon tetrachloride (30 mL). The mixture was left for 24 h at room temperature and then washed with an aqueous sodium bisulfite solution, and the organic phase was separated and dried. The solvent was evaporated at low temperature since on warming the solution bromine was liberated. The oil obtained was crystallized from a mixture of toluene and petroleum ether, giving 21 g (90%) of yellow crystals of **10**: mp 135–137 °C; ν_{max} ($CHCl_3$) 2830 (MeO, m), 1665 (C=O, vs), 1600 (C=C, s) cm^{-1}; δ ($CDCl_3$) 3.73 (3 H, s, MeO), 5.73 (1 H, s, CH), 7.23–8.60 (12 H, m, Ar). Anal. Calcd for $C_{22}H_{16}Br_2O_2$: C, 55.96; H, 3.38; Br, 33.85. Found: C, 56.27; H, 3.57; Br, 33.50.

9-(α-Bromoanisylidene)anthrone (11). (a) A heterogeneous mixture of the dibromide **10** (9.5 g, 0.021 mol) and potassium *tert*-butoxide (2.28 g, 0.021 mol) in *tert*-butyl alcohol (100 mL) was shaken for 48 h at room temperature until a homogeneous solution formed. The solvent was evaporated, the mixture was poured into water and extracted with chloroform, the organic phase was washed several times with water and dried ($CaCl_2$), and the solvent was evaporated. The oil obtained was crystallized from methanol, giving 7 g (85%) of yellow crystals of **11**: mp 145–146 °C; λ_{max} (EtOH) 233 nm (ε 42 600), 275 sh (16 600), 359 (9000); ν_{max} 2830 (MeO, m), 1658 (C=O, vs), 1590 (C=C, s) cm^{-1}; δ ($CDCl_3$) 3.87 (3 H, s, MeO), 6.76–8.63 (12 H, m, Ar); *m/e* (rel intensity) 392, 390 (M for ^{81}Br and ^{79}Br, 15 and 15), 311 (M − Br, B), 268 (M − Br − CO − CH_3, 15), 239 (18), 135 ($AnCO^+$, 16), 107 (An, 3). Anal. Calcd for $C_{22}H_{15}BrO_2$: C, 67.61; H, 3.86; Br, 20.42. Found: C, 67.67; H, 3.91; Br, 20.33.

(b) A mixture of **10** (3.5 g, 0.021 mol) and potassium *tert*-butoxide (2.28 g, 0.021 mol) in dry THF (100 mL) was stirred for 24 h at room temperature under a nitrogen atmosphere. The solvent was evaporated, water (100 mL) was added, the mixture was extracted in ether (200 mL), and the organic phase was washed with water, dried, and evaporated. Workup was continued as in method a. The yield of **11** was 6.5 g (79%).

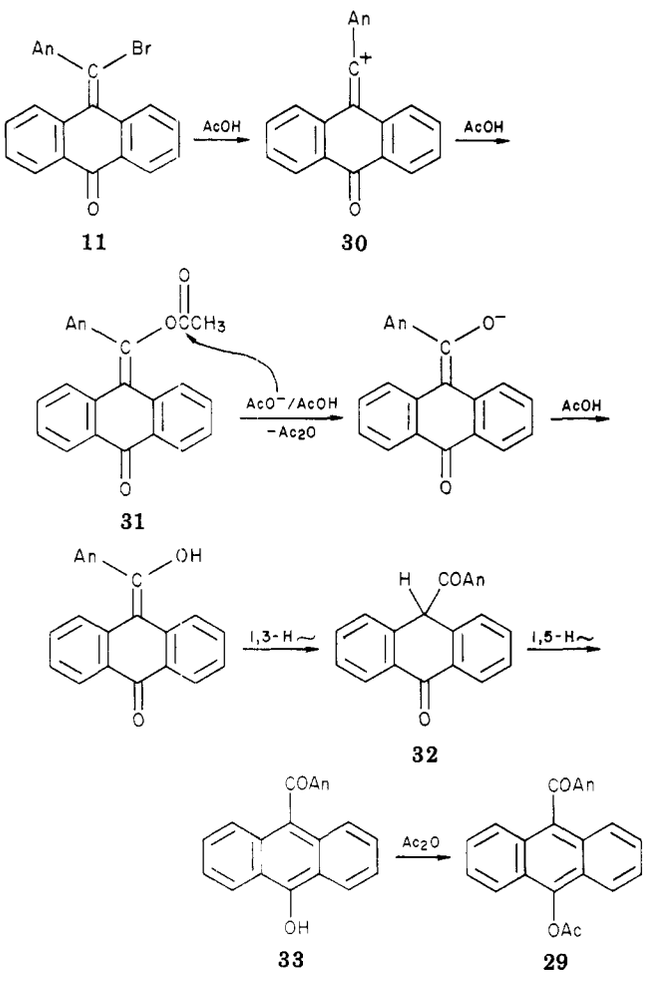
(c) To a solution of **10** (9.5 g, 0.021 mol) in (i) dry THF or in (ii) 1:5 THF–ether (100 mL) was added slowly under nitrogen a solution of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (2.6 g, 0.021 mol) in (i) THF or (ii) ether (25 mL), and the mixture was stirred for 24 h. The precipitate of DBN·HCl was filtered, the solvent was evaporated, and the workup was continued as in method a. The yield of **11** was 7 g (85%).

(25) This is a minimum value since common-ion rate depression reduced the solvolysis rate of **11** very appreciably.[11d]

(26) J. Rigaudy and L. Nédélec, *Bull. Soc. Chim. Fr.*, 400 (1960).

(27) A. Haller and R. Padova, *C. R. Hebd. Seances Acad. Sci.*, **141**, 857 (1905).

Scheme V



9-Anisylidene-9,10-dihydro-10-anthracenol (9). To a solution of 9-anisylideneanthrone (3.12 g, 0.01 mol) in dry ether (100 mL) at 0 °C was added $LiAlH_4$ (0.4 g, 0.01 mol) in small portions with stirring. The mixture was refluxed for an additional hour and cooled, methanol and then ice–water were added dropwise, and the mixture was filtered and separated. The organic phase was washed several times with water, dried ($MgSO_4$), and evaporated. The crude product was crystallized from ether–petroleum ether or from carbon tetrachloride, giving pale yellow crystals of **9**: mp 121–122 °C; λ_{max} (EtOH) 248 nm (ϵ 23 000), 255 sh (20 000), 320 (13 400); ν_{max} (Nujol) 3280 (O–H, s) 1605 (C=C, s) cm^{-1}; δ (CCl_4) 2.73 (1 H, br d, OH), 3.73 (3 H, s, MeO), 5.43 (1 H, br d, :CH), 6.60–7.68 (13 H, m, Ar and H-10); *m/e* (rel intensity) 314 (M, B), 298 (M – Me – H, 56), 297 (M – OH, 66), 281 (M – H_2O – Me, 19), 265 (M – H_2O – MeO, 37), 253 (20), 252 (23), 239 (15), 194 (19), 178 (M – An – CHO, 32), 135 (AnCO, 28). Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.24; H, 6.06.

9-(α-Bromoanisylidene)-9,10-dihydro-10-anthracenol (12). To a solution of 9-(α-bromoanisylidene)anthrone (2 g, 0.005 mol) in dry ether (50 mol) was added $LiAlH_4$ (0.19 g, 0.005 mol) in small portions with stirring. The solution was stirred at room temperature for an additional 30 min, and methanol and then water were added carefully to destroy the excess reagent. The solution was filtered and washed several times with ether, and the organic phase was separated, washed several times with water, dried ($MgSO_4$), and evaporated. The crude product (1.8 g, 90%) was crystallized from petroleum ether (bp, 60–80 °C) to give **12**: mp 141–143 °C; λ_{max} (EtOH) 230 nm (ϵ 16 700), 301 (9 200); ν_{max} (KBr) 3400 (O–H, s), 1600 (C=C, s) cm^{-1}; δ ($CDCl_3$) 3.45 (1 H, d J = 7 Hz, OH), 3.75 (3 H, s, MeO), 5.60 (1 H, d, J = 7 Hz, H-10), 6.65–8.20 (12 H, m, Ar) (on addition of D_2O the signal at δ 3.45 disappears, and the doublet at δ 5.60 becomes a singlet; on decoupling of the doublet at δ 3.45, the doublet at δ 5.60 becomes a singlet); *m/e* (rel intensity) 394, 392 (M, 29, 29), 377, 375 (M – OH, 14, 14), 313 (M – Br, B), 312 (M – HBr, 17), 311 (M – HBr – H, 19), 298 (22), 295 (M – Br – H_2O, 25), 281 (M – Br – H_2O – CH_2, 21), 253 (39). Anal. Calcd for $C_{22}H_{17}BrO_2$: C, 67.19; H, 4.36; Br, 20.32. Found: C, 67.15; H, 4.65; Br, 20.72.

9-(α-Bromoanisylidene)-9,10-dihydro-10-methyl-10-anthracenol (14). To 9-(α-bromoanisylidene)anthrone (7 g, 0.018 mol) in a mixture of benzene (80 mL) and ether (40 mL) was added dropwise over 30 min a Grignard reagent prepared from Mg (0.75 g) and methyl iodide (4.5 g, 0.032 mol) in ether (40 mL). The mixture, which turned orange and became warm, was refluxed for an additional 90 min and then poured into a cold, aqueous mixture of NH_4Cl and NH_3. The organic layer was separated, the aqueous mixture was extracted twice with benzene, the combined organic phase was dried ($MgSO_4$), and the solvent was evaporated. NMR showed a quantitative formation of **14**. The compound was crystallized from benzene, giving 4.16 g (60%) of a white-yellow solid: mp 162 °C; ν_{max} (CS_2 or $CHCl_3$) 3570 cm^{-1} (sharp, non-hydrogen-bonded OH); δ ($CDCl_3$) 1.76 (3 H, s, Me), 2.10 (1 H, br s, OH, disappears in D_2O), 3.75 (3 H, s, MeO), 6.73–8.26 (12 H, m, Ar); *m/e* (rel intensity) 408, 406 (M, 10, 10), 393, 391 (M – Me, 13, 19), 390, 388 (M – H_2O, 29, 29), 327 (M – Br, 31), 310 (M – Br – OH, 34), 309 (M – Br – H_2O, 100), 277 (M – HBr – H_2O – MeO, 12), 264 (33). Anal. Calcd for $C_{23}H_{19}BrO_2$: C, 67.99; H, 4.46; Br, 19.66. Found: C, 67.64; H, 4.56; Br, 19.20.

When the product was allowed to stand in an NMR tube for 2 weeks, a complete loss of water molecules took place. The NMR spectrum of the resultant compound is identical with that of the 10-methylene compound **26**.

7-(9′-Anthryl)-7-bromoquinone Methide (17). (a) 9-(α-Bromoanisylidene)-9,10-dihydro-10-anthracenol (**12**) (100 mg, 0.25 mmol) was dissolved in commercial AcOH (5 mL) containing NaOAc (310 mg, 3.8 mmol), and the mixture was kept for 48 h at 49.6 °C. On addition of ether the NaOAc precipitated and was filtered. Titration showed the absence of bromide ion. The solvent was evaporated, and the remainder was dissolved in toluene (1 mL) and separated on a TLC silica plate with toluene as the eluent. Three spots were observed and separated. The first two were formed in very small quantities and identified as 9-anisoylanthracene (**16**) (ν_{max} 1655 cm^{-1}) and 10-acetoxy-9-(α-bromoanisylidene)-9,10-dihydroanthracene (**13**) (δ (CCl_4) 2.06 (Me)).[12b] The main fraction (85 mg, 95%; R_f 0.2) was recrystallized from 2-propanol to give orange crystals, mp 185 °C. The compound was identified as 7-(9′-anthryl)-7-bromoquinone methide by the following spectra: λ_{max} (AcOH) 253 nm (ϵ 61 200), 327 (23 000), 354 sh (14 400), 374 (13 200), 393 (10 000), 450 (1400); the UV spectra in EtOH show the same maxima except that the maximum at 327 nm is shifted to 321 nm; ν_{max} (KBr) 1640 (vs, C=O), 1600 (s, C=C) cm^{-1}; δ ($CDCl_3$) 6.05 (1 H, dd, half of AA′BB′ q, J_{12} = 7.3 Hz, J_{13} = 1.8 Hz), 6.54 (1 H, dd, half of AA′BB′ q, J_{12} = 8 Hz, J_{13} = 2.5 Hz), 6.65 (1 H, dd, half of AA′BB′ q, J_{12} = 8 Hz, J_{13} = 2 Hz), 7.51–7.61 (4 H, m, Ar), 7.86–7.90 (2 H, m, Ar), 8.07–8.11 (2 H, m, Ar), 8.16 (1 H, dd, half of AA′BB′ q, J_{12} = 7.3 Hz, J_{13} = 2.5 Hz), 8.60 (1 H, s, H-10); *m/e* (rel intensity) 362, 360 (M, 14, 14), 281 (M – Br, 46), 253 (M – Br – CO, 11), 252 (M – HBr – CO, 21), 136 (100). Anal. Calcd for $C_{21}H_{13}BrO$: C, 69.82; H, 3.63; Br, 22.12. Found: C, 69.70; H, 3.79; Br, 22.26.

A 1-mL sample of the reaction mixture was diluted 10-fold by AcOH, water (1 mL) was added, and the solvent was distilled. The first milliliter of the distillate was analyzed by gas chromatography on a 15% ethylene glycol succinate column on 80/100 Chromosorb P at 50 °C. An important peak was shown to be methyl acetate by peak-enhancement experiment. When the crude reaction mixture was analyzed by NMR (no Me_4Si added), a signal at ca. 3.5 ppm was observed. Its intensity was enhanced by addition of authentic methyl acetate to the sample.

(b) Solutions of 9.5×10^{-4} M acetate **13** or of 1.6×10^{-3} M anthracenol **12** in a mixture of 95:5 AcOH–Ac_2O buffered with 4×10^{-3} M NaOAc were kept at 49.6 °C for 72 h. At the end of this time the spectra of the solutions were similar to that of authentic **17**.

9-Anisoylanthracene (16). An ampule containing 9-(α-bromoanisylidene)-9,10-dihydro-10-anthracenol (**12**) (200 mg, 0.5 mmol) in 2,2,2-trifluoroethanol (10 mL) containing 2,6-lutidine (100 mg, 1 mmol) was kept at 140 °C for 24 h. The solvent was evaporated, and the mixture was purified on a silica plate with 90:10 cyclohexane–acetone as the eluent to give 140 mg (90%)

of yellow crystals which on crystallization from ethanol gave **16**: mp 187 °C (lit.[28] mp 189–190.5 °C), mixture melting point with an authentic sample[28] 187 °C; λ_{max} (EtOH) 253 nm (ϵ 121 000), 290 (16 700), 330 (3 600), 346 (6 400), 364 (9 100), 385 (8 600); ν_{max} (KBr) 1655 (vs, C=O), 1595 (C=C) cm^{-1}; δ ($CDCl_3$) 3.66 (3 H, s, MeO), 6.72 (2 H, half of AA'BB' q, An), 7.16–7.98 (10 H, m, Ar), 8.38 (1 H, s, H-10); *m/e* (rel intensity) 312 (M, 100), 295 (18), 284 (M – C_2H_4, 26), 205 (M – An, 22), 177 ($C_{14}H_9^+$, 33), 176 ($C_{14}H_8^+$, 37), 135 ($AnCO^+$, 24), 107 (An, 5).

9-(α-Bromoanisylidene)-10-methylene-9,10-dihydroanthracene (26). To a solution of 9-(α-bromoanisylidene)-10-methyl-9,10-dihydro-10-anthracenol (**14**) (2 g, 0.005 mol) in pyridine (50 mL) was added freshly distilled acetyl chloride (0.8 g, 0.01 mol), and the mixture was refluxed for 2.5 h. The solvent was evaporated, the remainder was extracted with benzene (50 mL), the organic phase was washed with water and dried ($MgSO_4$), and the solvent was evaporated. The crude oil did not show an OH absorption in the IR. Separation by TLC on a silica plate, with 95:5 cyclohexane–ether as the eluent, gave as the main fraction **26**: mp 137 °C (0.95 g, 50%); ν_{max} (KBr) 1604 (C=C) cm^{-1}; δ (CCl_4) 3.60 (3 H, s, MeO), 5.68 (2 H, s, $:CH_2$), 6.53–7.58 (11 H, m, Ar), 8.13–8.28 (1 H, m, Ar); *m/e* (rel intensity) 390, 388 (M, 16, 16), 309 (M – Br, 100), 294 (M – Br – Me, 12), 278 (M – Br – MeO, 20), 265 (32). Anal. Calcd for $C_{23}H_{17}BrO$: C, 70.96; H, 4.40; Br, 20.52. Found: C, 70.65; H, 4.35; Br, 20.39.

(b) Dry gaseous HCl was bubbled slowly during 1 h through a solution of **14** (0.5 g, 0.0013 mol) in ether (20 mL) at 0 °C. Workup as above and separation on a silica plate with 90:10 petroleum ether–ether as the eluent gave **26** (0.24 g, 50%) as the product.

Crystalline **26** is stable for at least 2 years, but its solution in CCl_4 deposited after a few days a solid which is probably a dimer according to the mass spectrum: *m/e* (rel intensity) 780, 778, 776 (2M, 8, 16, 8), 699, 697 (2M – Br, 95, 85), 684, 682, 680 (6, 11, 6), 618 (2M – 2Br, 60), 617 (2M – HBr – Br, 58), 616 (2M – 2HBr, 47), 390, 388 (M, 20, 20), 309 (M – Br, 100). This reaction was not investigated further.

9-(α-Acetoxyanisylidene)anthrone (31). A mixture of 9-(α-bromoanisylidene)anthrone (**11**) (785 mg, 0.002 mmol), silver acetate (334 mg, 0.002 mol), and sodium acetate (328 mg, 0.004 mol) in acetonitrile was refluxed for 8 h in the dark. The mixture was filtered, the precipitate was washed with warm chloroform (10 mL), and the solvent was evaporated. The oil obtained was crystallized from ethanol to give 0.6 g (85%) of yellow crystals of **31**: mp 139–140 °C; λ_{max} (EtOH) 233 nm (ϵ 29 700), 363 (6600); ν_{max} (CS_2) 3060–2920 (m, C–H), 1758 (vs, AcO), 1656 (vs, C=O) cm^{-1}; δ ($CDCl_3$) 2.07 (3 H, s, AcO), 3.74 (3 H, s, MeO), 6.72–8.30 (12 H, m, Ar); *m/e* (rel intensity) 370 (M, 4), 329 (43), 328 (M – CH_2CO, 71), 327 (M – CH_3CO, 13), 311 (M – AcO, 23), 300 (M – CO – CH_2CO, 43), 299 (M – 2CO – CH_3, 11), 165 (fluorenyl$^+$, 16), 135 ($AnCO^+$, 100), 107 (An, 16), 77 (Ph, 23). Anal. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 77.54; H, 4.75.

9-Acetoxy-10-anisoylanthracene (29). A mixture of 9-(α-bromoanisylidene)anthrone (**11**) (785 mg, 0.002 mol) and sodium acetate (328 mg, 0.004 mol) in AcOH (30 mL) was refluxed for 1 week. Water was added to turbidity, and the mixture was cooled, giving 0.7 g (90%) of brown crystals of **29**: mp 195–196 °C; λ_{max} (EtOH) 254 nm (ϵ 147 500), 286 (20 000), 332 (4400), 349.5 (8200), 365 (12 400), 384.5 (11 300); ν_{max} ($CHCl_3$) 1770 (vs, AcO), 1660 (vs, C=O), 1600 (s, C=C) cm^{-1}; δ ($CDCl_3$) 2.70 (3 H, s, AcO), 3.87 (3 H, s, MeO), 6.85–8.16 (12 H, m, Ar); *m/e* (rel intensity) 370 (M, 16), 328 (M – CH_2CO, 100), 311 (43), 193 (M – AnCOMe, 18), 165 (fluorenyl$^+$, 24), 135 ($AnCO^+$, 90), 107 (An, 16), 77 (Ph, 26). Anal. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 78.01; H, 4.67.

Reactions of 9-Anisylidene-9,10-dihydro-10-anthracenol (9). (a) An ampule containing a solution of **9** (0.2 g, 0.0006 mol) in ethanol (10 mL) containing H_2SO_4 (0.5 mL) was kept at 100 °C for 24 h. The mixture was poured into water and extracted with benzene (50 mL). The organic layer was washed with water, dried ($MgSO_4$), and evaporated. TLC on a silica plate with cyclohexane as the eluent gave two fractions. The main fraction was identified as anthracene by melting point (216 °C, sinters at 140 °C) and by the mass spectrum [*m/e* (rel intensity) 178 (M, 100), 176 (M – 2H, 16), 152 (M – C_2H_2, 7), 89 (15), 77 (Ph, 12%)], which resembled the mass spectrum of an authentic sample.

(b) A solution of **9** (0.1 g, 0.0003 mol) in EtOH (55 mL) containing 0.05 mL of H_2SO_4 was refluxed for 5 min, cooled, and poured into water, and the solvent was evaporated. The residue was extracted with benzene (20 mL), washed with water, separated, and dried ($MgSO_4$), and the solvent was evaporated. The product was separated by TLC on a silica plate with benzene as the eluent. The minor fraction was identified as anthracene by its R_f value. The main product (87 mg, 80%) was α-anisyl-9-anthrylmethyl ethyl ether (**21**): mp 102.5 °C; λ_{max} (EtOH) 256 nm (ϵ 106 500), 315 sh (2650), 333 (4800), 348 (6500), 366 (9300), 386 (8700); ν_{max} (KBr) 1600 cm^{-1} (vs, C=C); δ (CCl_4) 1.0 (3 H, t, J = 8 Hz, Me), 3.15 (2 H, q, J = 8 Hz, CH_2), 3.35 (3 H, s, MeO), 6.46 (2 H, half of AA'BB' q, An), 6.68 (1 H, s, α-H), 6.95–8.35 (11 H, m, Ar); *m/e* (rel intensity) 342 (M, 80), 313 (M – Et, 10), 297 (M – EtO, 58), 265 (M – EtOH – MeO, 22), 252 (21), 205 ($AnthCO^+$, 11), 135 ($AnCO^+$, 100). Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 82.58; H, 6.32.

(c) A solution of **9** (0.2 g, 0.0006 mol) in AcOH (10 mL) 0.04 M in NaOAc was refluxed for 5 min and cooled, and the solvent was evaporated. The crude product was separated twice by TLC on a silica plate first with a mixture of 95:5 petroleum ether (40–60 °C) and acetone and then with a gradient of acetone in petroleum ether. A minor fraction (<10%) was anthracene which was identified by its melting point and mass spectrum which was identical with those of authentic anthracene. The major fraction (200 mg, 88%) was an oil which solidified to a solid, mp 105 °C. The compound was identified as α-anisyl-9-anthrylmethyl acetate (**19**) by the following data: λ_{max} (EtOH) 254 nm (ϵ 86 800), 315 sh (2000), 333 (3500), 349 (6300), 366 (9000), 386 (8500); ν_{max} (KBr) 1730 (vs, AcO), 1605 (s, C=C) cm^{-1}; δ ($CDCl_3$) 2.05 (3 H, s, AcO), 3.66 (3 H, s, MeO), 6.71 (2 H, half of AA'BB' q, An), 7.00 (1 H, s, CH), 7.15–8.43 (10 H, m, Ar), 8.43 (1 H, s, H-10); *m/e* (rel intensity) 356 (M, 49), 298 (M – Ac – Me, 100), 297 (M – AcO, 83), 265 (M – AcOH – MeO, 86), 252 (40), 135 ($AnCO^+$, 85). Anal. Calcd for $C_{24}H_{20}O_3$: C, 80.88; H, 5.66. Found: C, 80.90; H, 5.62.

In an attempted crystallization of **19** from MeOH α-anisyl-9-anthrylmethyl methyl ether was mainly obtained on cooling the methanolic solution. It was identified by NMR: δ (CCl_4) 3.13 (3 H, s, MeO), 3.46 (3 H, s, MeO), 6.49 (2 H, half of AA'BB' q, An), 6.95–8.33 (11 H, m, Ar), 8.18 (1 H, s, H-10).

(d) Reaction of **9** (6.2 mg) in AcOH (10 mL) 0.04 M in NaOAc at 20 °C was complete after 90 min and gave only **19**.

Rearrangement of 31 in AcOH. A solution of the vinyl acetate **31** (157 mg, 0.0004 mol) in acetic acid (10 mL) containing sodium acetate (0.087 M) was refluxed for 1 h and then poured into a mixture of water (30 mL) and chloroform (30 mL). The organic layer was separated, washed with aqueous sodium bicarbonate and with water, and dried ($CaCl_2$), and the solvent was evaporated. The NMR spectrum of the remaining oil showed the formation of 25% of 9-acetoxy-10-anisoylanthracene (**29**) (by integration of the OAc signal at δ 2.70), 45% of 9-anisoylanthrone (**32**) (by integration of the methine signal at δ 5.98), and 30% of 9-anisoyl-10-anthracenol (**33**). The presence of **33** was deduced from the presence of a weak broad signal which is ascribed to the OH group at δ 9.1 and from an OH absorption at 3300 cm^{-1} in the IR spectrum. Its percentage was calculated from the disparity between the integration of the total methoxy signals and the signals at 2.70 and 5.98 ppm, and the value involves a relatively large error.

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