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TRIPTYCENE-LIKE BEHAVIOUR OF TERTIARY 9,10-DIHYDRO-9-ANTHROLS

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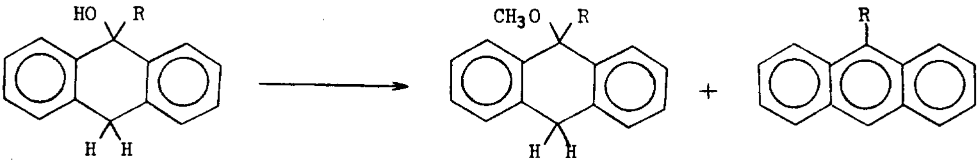
Summary: Secondary alcohols in the 9,10-dihydro-9-anthrol series frequently undergo acid-catalyzed elimination and substitution reactions more rapidly than do corresponding tertiary alcohols - a phenomenon attributed to predominant existence of the tertiary alcohols in triptycene-like conformations with the hydroxy groups in pseudoequatorial positions.

Secondary alcohols undergo substitution and elimination reactions in acidic solutions more slowly than do tertiary alcohols with similar structures. To the best of our knowledge, no exceptions to this rule have previously been reported.

We have now observed that acid-catalyzed elimination and substitution reactions of secondary alcohols in the 9,10-dihydro-9-anthrol series are frequently more rapid than those of the corresponding tertiary alcohols.

Dihydroanthrols 1a-1c are quantitatively converted to their methyl ethers in acidic methanol solutions. Dihydroanthrol 2c yields 9-benzylanthracene as the only detectable product, even at very short reaction times, while alcohols 2a and 2b yield mixtures of their dehydration products, anthracene and 9-methylanthracene, and substitution products 3a and 3b.

1a, R = H
1b, $R = CH_3$
1c, $R = CH_2\phi$



2a, R = H
2b, $R = CH_3$
2c, $R = CH_2\phi$

3a, R = H
3b, $R = CH_3$

Ethers **3a** and **3b** slowly lose methanol in acidic solutions, so that at long reaction times only anthracene is formed from **2a** and only 9-methylanthracene from **3b**. Extrapolation of the relative yields of addition and substitution products from reactions of **2a** and **2b** to t=0 shows that **2a** initially yields a mixture containing 69% of **3a** and 31% of anthracene, and **2b** initially yields a mixture containing 44% of **3b** and 56% of 9-methylanthracene.

The rates of disappearance of **1a**-**1c** and **2a**-**2c** in methanol solutions containing oxalic acid-oxalate buffers[1] were followed by NMR spectroscopy. Clean first order kinetics were observed for all reactions. The relative rates of elimination and substitution reactions of **2a** and **2b** were calculated from the initial yields of products of those reactions.

TABLE

RATES OF REACTIONS OF 9,10-DIHYDRO-9-ANTHROLS IN METHANOL AT 30.0°

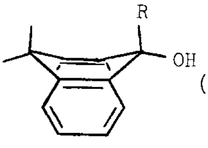
Dihydroanthrol	R	pH[1]	$k_1 \times 10^3$ (sec^{-1})^a	r	k_{rel}	$k_E \times 10^3$ (sec^{-1})^b	$k_S \times 10^3$ (sec^{-1})^c
1a	H	6.0	1.03	.993	29	----	(1.03)
1b	CH_3	6.0	1.19	.995	33	----	(1.19)
1c	$CH_2\phi$	6.0	0.0361	.990	1	----	(0.0361)
1c	$CH_2\phi$	5.2	0.207	.972			
2a	H	6.0	1.49	.988	41	0.46	1.03
2b	CH_3	6.0	0.79	.991	22	0.44	0.35
2c	$CH_2\phi$	6.0	0.0356	.978	.99	(0.356)	----
2c	$CH_2\phi$	5.2	0.210	.989			

a) Rate of disappearance of dihydroanthrols
b) Rate of formation of anthracenes at t = 0
c) Rate of formation of ethers at t = 0

As can be seen from the Table, the rate of disappearance of the secondary alcohol **1a** was much greater than that of the corresponding tertiary alcohol **1c**, and the disappearance of **2a** faster than those of **2b** and **2c**. Only tertiary alcohol **1b** reacts more rapidly than its secondary analog **1a**, and even in that case the difference in reaction rates is surprisingly small. Even if rates for elimination processes rather than overall rates of disappearance of starting alcohols are compared, it can be seen that secondary alcohol **2a** is at least as reactive as tertiary alcohol **2b**, and far more reactive than **2c**.

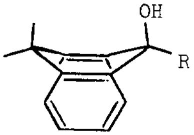
Although derivatives of secondary alcohols normally undergo solvolysis reactions with participation of the solvent, rather than by purely "limiting" (carbonium ion) processes,[2] we do not believe that participation by solvent can account for the high reactivities of secondary alcohols (compared to tertiary alcohols) in the 9,10-dihydro-9-anthrol series. It would be difficult to account for the fact that elimination in the secondary alcohol **2a** is faster than in the tertiary alcohols **2b** and **2c** on the basis of solvent participation, since the environment from which solvent would abstract a proton in a "concerted" reaction is identical for all three alcohols. Furthermore, the fact that the reactions of compounds **1a**-**1c** proceed at almost identical rates with those of their analogs lacking substituents at C-10, even though **1a**-**1c** are capable only of undergoing substitution while reactions of **2a**-**2c** proceed partially or entirely by elimination, strongly suggests that both groups of alcohols react by similar rate-limiting steps. The only reasonable rate-limiting steps which would be common to substitution and elimination reactions of **1** and **2** would be dissociation to form carbonium ions.

9,10-Dihydroanthracenes exist in boat conformations with the larger substituents at C-9 and C-10 preferentially in pseudoaxial positions.[3] Since hydroxy groups (like methoxy groups)[4] are smaller than methyl or benzyl groups, compounds **1b**, **1c**, **2b**, and **2c** should exist predominantly in conformations (A) in which the hydroxy groups are in equatorial positions. In these conformations, the bond between the hydroxy group and C-9 would be essentially orthogonal to the π-systems of the adjacent aromatic rings, so that the molecules would resemble somewhat flattened triptycene derivatives[5] lacking a bridge between C-9 and C-10. Formation of carbonium ions would be inhibited by the inductive effects of the aromatic rings, but not significantly accelerated by resonance stabilization of the transition state.



(unreactive conformation)

A



(reactive conformation)

B

In contrast, the secondary alcohols **1a** and **2a** would exist predominantly in conformation B, with the hydroxy group in the reactive pseudoaxial position. Since the overall rates of reaction would include terms for the conformation equilibrium constants, the normally large differences between the rates of reaction of secondary alcohols and those of tertiary alcohols should be appreciably reduced, despite the greater intrinsic stabilities of the tertiary carbonium ions.

We are presently attempting to determine whether other factors, aside from the conformational effects discussed above, are responsible for the remarkably high reactivities of secondary dihydroanthrols compared to their tertiary analogs.

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6) Formation of carbonium ions from **1c** and **2c** would doubtless be inhibited by the inductive effects of the phenyl groups. However, these effects should be relatively small [see, e.g. E. J. Kim and H. C. Brown, J. Amer. Chem. Soc., 91, 4286 (1969)] so that we believe the differences in reactivity between methyl and benzyl substituted dihydroanthrols are largely steric in origin.

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