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Buffer Catalysis of the Trifluoroethanolysis of Phenoxydimethylphenylsilane

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The acetic acid–acetate catalyzed trifluoroethanolysis of phenoxydimethylphenylsilane at constant ionic strength was studied. Plots of k_{obs} against total buffer concentration at a constant ratio of acid to base show upward curvature. The upward curvature is consistent with the trifluoroethanolysis occurring by three mechanisms involving (1) general acid catalysis, (2) general base catalysis, and (3) bifunctional acid–base catalysis. The observation of bifunctional catalysis is consistent with the trifluoroethanolysis of phenoxydimethylphenylsilane occurring by a concerted mechanism, involving a single transition state.

We have been interested in the mechanism of solvolysis of silyl ethers. The solvolysis of silicon compounds is interesting from a mechanistic viewpoint since, although silicon is located immediately below carbon on the periodic table, it shows quite different behavior from carbon. For example, it is possible that substitution at silicon, which is unlike carbon in that it posseses d orbitals, may involve the formation of pentavalent intermediates.[1-6] Indeed pentavalent silicon species have been isolated and characterized.[7] Another difference between silicon and carbon is that tetravalent silicon undergoes general base catalyzed solvolysis in protic solvents,[1,8-13] rather than direct nucleophilic attack. In contrast, for carbon the preferred reaction is nucleophilic substitution; general base catalyzed addition of solvent is uncommon.[14] It is important to understand the mechanism of formation and/or cleavage of the silicon oxygen bond as evidenced by the importance of silicon as a hydroxyl-protecting group in organic chemistry.[15,16]

The solvolysis of silyl ethers in protic solvents has been studied previously and the reaction is known to be catalyzed by acids and bases.[1,8-12,17] It is well documented that the solvolysis of silyl ethers shows general base catalysis. We have also shown that the solvolysis reactions can show general acid catalysis.[18] We now wish to report that the solvolysis of phenoxydimethylphenylsilane in trifluoroethanol buffered with acetic acid–tetramethylammonium acetate at 30 °C and ionic strength 0.05 M shows general acid (GA) catalysis, general base (GB) catalysis, and bifunctional catalysis, involving both a molecule of acid and molecule of base in the transition state. This type of catalysis, involving both acid and base catalyst in the transition state, is uncommon and rarely observed in solution. The existence of bifunctional catalysis supports a concerted mechanism involving a single transition state (S_N2-Si[1,8] or A_ND_N[20]) mechanism for the trifluoroethanolysis of phenoxydimethylphenylsilane, as we have previously suggested.[21]

Values of the observed rate constant, k_{obs}, for trifluoroethanolysis of phenoxydimethylphenylsilane in acetic acid–tetramethylammonium acetate buffers are plotted against total buffer concentration, $[\text{buffer}]_{\text{Total}}$ (Figure 1). The value for k_{obs} increases with increasing buffer concentration while the ratio of acidic to basic form of the buffer is kept constant and ionic strength is maintained with tetramethylammonium trifluoroacetate. However, the increase in rate with increasing buffer concentration is not linear and shows upward curvature, indicating a greater than first-order dependence of the rate on buffer

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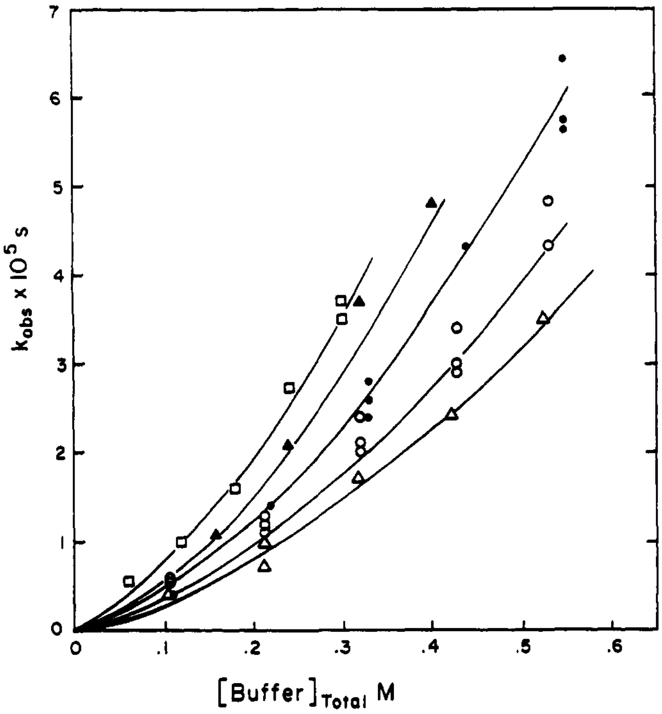

Figure 1. Plot of k_{obs} against total buffer concentration for solvolysis of phenoxydimethylphenylsilane at 30 °C in trifluoroethanol buffered with acetic acid–tetramethylammonium acetate at various buffer ratios A/B and constant ionic strength (tetramethylammonium trifluoroacetate): □, A/B = 5; ▲, A/B = 7; ●, A/B = 10; ○, A/B = 15; △, A/B = 20.

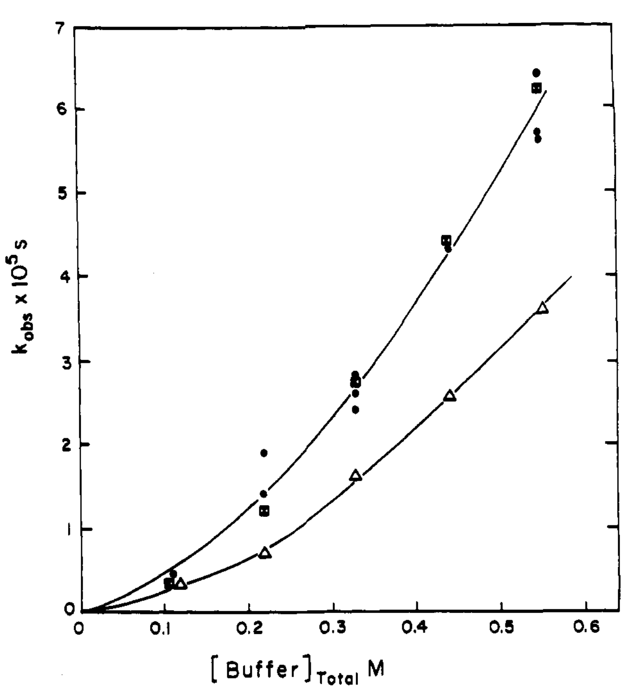

Figure 2. Plot of k_{obs} against total buffer concentration for solvolysis of phenoxydimethylphenylsilane at 30 °C in trifluoroethanol buffered with acetic acid–tetramethylammonium acetate ([acid]/[base] = 10) and constant ionic strength maintained with tetramethylammonium trifluoroacetate (●), tetramethylammonium nitrate (□), tetramethylammonium perchlorate (△), and ionic strength not maintained (×).

concentration. Plots of k_{obs} vs total buffer concentration for acid–base ratios of the buffer, [A]/[B], of 20, 15, 10, 7, and 5; all show upward curvature with intercepts of zero.

It is unlikely that the observed upward curvature is caused by a specific salt effect[22-25] since tetramethylammonium trifluoroacetate was employed to maintain ionic strength; trifluoroacetate closely resembles acetate and would not be expected to have any specific salt effect on the reaction. It is also weakly basic and therefore unlikely to be an effective catalyst. In addition, similar curvature was also observed in plots of k_{obs} vs $[\text{buffer}]_{total}$ for [A]/[B] = 10 when ionic strength was maintained with tetramethylammonium nitrate and when the ionic strength was not maintained (Figure 2). Curvature, although less marked, was also observed when tetramethylammonium perchlorate was used to maintain ionic strength. The less marked curvature observed when tetramethylammonium perchlorate is used to adjust ionic strength may represent a solvent-induced medium effect.[22-24]

It is also unlikely that the upward curvature is due to a nonspecific solvent effect[22] caused by the acetic acid component of the buffer. The value of k_{obs} for solvolysis in a buffer with constant [A]/[B] = 0.25/0.05 shows no dependence on added organic solutes. The values of k_{obs} for [A]/[B] = 0.25/0.05 in the presence of 0.25 M CH_3CN, 0.50 M CH_3CN, and 0.25 M CH_3CONH_2 are 4.1×10^{-5}, 4.3×10^{-5}, and 4.0×10^{-5} s^{-1}, respectively. These values are essentially the same as the value of 3.6×10^{-5} M^{-1} s^{-1} (average of two experiments) observed in the absence of any added cosolute.

The upward curvature is consistent with a rate law containing a term in both the acidic and basic forms of the buffer. Indeed, Schowen has observed that the methanolysis of phenoxytriphenylsilane in formic acid–formate buffers shows bifunctional catalysis.[33] A complete rate law including catalysis by all acidic and basic species present in solution is given by eq 1, where k_o is the rate

$$k_{obs} = k_o + k_H[H^+] + k_{TO}[TO^-] + k_A[A] + k_B[B] + k_{AB}[A][B] \quad (1)$$

constant for the uncatalyzed reaction, k_H and k_{TO} are the rate constants for reaction catalyzed by hydronium ion and trifluoroethoxide ion, respectively, and k_A and k_B are the rate constants for catalysis by the acidic form of the buffer, A, (i.e. GA catalysis) and by the basic form of the buffer, B, (i.e. GB catalysis). The final term of the rate equation k_{AB} represents the rate constant for bifunctional catalysis and presumably involves proton donation to the leaving group by the acidic component of the buffer and proton abstraction from an attacking trifluoroethanol molecule.

The trifluoroethanolysis of phenoxydimethylphenylsilane is best described as a one-step concerted displacement reaction.[21] The observation of bifunctional catalysis also supports a concerted mechanism. It is difficult to

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[25] In our earlier study on the buffer-catalyzed trifluoroethanolysis of ethoxydimethylphenylsilane[18] we suggested that upward curvature in plots of k_{obs} vs acid concentration was due to a salt effect. However, it is reasonable that the curvature in these experiments is also due to bifunctional catalysis.

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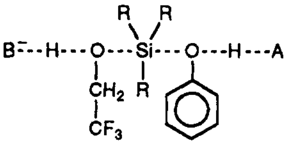
rationalize how proton abstraction and proton donation could stabilize the rate-determining transition state for a mechanism involving an intermediate, as was pointed out by Schowen for the formic acid–formate catalyzed methanolysis of methoxyphenoxymethylphenylsilane.[33] A possible transition state for bifunctional catalysis is depicted below:



The observation of bifunctional catalysis for the alcoholysis of alkoxysilanes is unusual and differs from what is observed for the alcoholysis of other esters. It has been pointed out that the alcoholysis of alkoxysilanes resembles the alcoholysis of carboxylate and phosphate esters;[12] however, for these esters bifunctional catalysis has not been reported. The alcoholysis of carboxylate[34,35] and phosphate[36] esters involves the formation of an intermediate and, as was indicated above, the observation of bifunctional catalysis would not be anticipated for a mechanism involving the formation of an intermediate. Indeed the inability to detect bifunctional catalysis may be used as evidence against a concerted mechanism for the ethanolysis of ethyl trifluoroacetate.[35] The solvolysis of carboxylate and phosphate esters often involve the formation of a metastable anionic intermediate where the negative charge can be placed on an electronegative oxygen atom, since carboxylate and phosphate esters both posseses a double bond to oxygen. If the solvolysis of alkoxysilanes were to involve an intermediate, the resulting negative charge on the intermediate could not be localized on an individual electronegative atom, as it can for the carboxylate and phosphate esters. This may be the reason that the trifluoroethanolysis of phenoxydimethylphenylsilane occurs through a concerted mechanism and therefore shows bifunctional catalysis. It should, however, be pointed out that pentavalent silicon salts have been isolated and characterized by both NMR and X-ray crystallography.[7,37] Pentavalent silicon species have also been proposed as intermediates in substitution reactions at silicon.[38]

There are also no examples of bifunctional catalysis for concerted substitution at saturated carbon.[14] In fact, there are very few examples of general base catalyzed solvolysis at saturated carbon,[14] a reaction that is common for solvolysis of silicon compounds.[1–8,14] General base catalyzed solvolysis at sp^3-hybridized carbon is only observed when the transition state has a large degree of bond formation to the nucleophilic alcohol, resulting in a relatively large development of positive charge on the attacking hydroxyl group and therefore a greater advantage for proton transfer to the catalyzing base.[14] The observation of general base catalysis for solvolysis of silicon compounds suggests that there is more bond formation between the attacking hydroxyl group and silicon than in the analogous reaction for carbon as the atom undergoing substitution. Since the solvolysis of carbon compounds rarely shows general base catalysis it is not expected to show bifunctional catalysis. In addition, the observation of bifunctional catalysis at carbon would require that the leaving group be sufficiently basic so that proton donation from the catalyzing acid would be thermodynamically favorable in the transition state.[39] However, compounds with basic leaving groups react very slowly making such a reaction impractical to study.

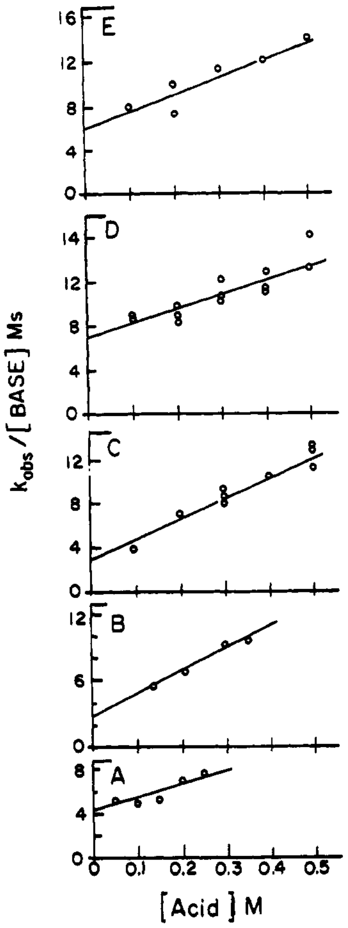


Figure 3. Plots of k_{obs}/[B] against [A] for solvolysis of phenoxydimethylphenylsilane at 30 °C in trifluoroethanol buffered with acetic acid–tetramethylammonium acetate and constant ionic strength (tetramethylammonium trifluoroacetate) at buffer ratios A/B of (A) 5, (B) 7, (C) 10, (D) 15, and (E) 20.

The general base catalyzed reaction presumably involves a similar transition state with a molecule of base abstracting a proton from an attacking trifluoroethanol molecule and a trifluoroethanol molecule assisting the departure of the leaving group; however, trifluoroethanol can only stabilize the negative charge developing on the phenolic oxygen by hydrogen bonding since there is no thermodynamic advantage to proton transfer. The transition state for the general acid catalyzed reaction involves nucleophilic attack on silicon by a trifluoroethanol molecule with a molecule of buffer acid donating a proton to the leaving phenoxide. In the transition state for the

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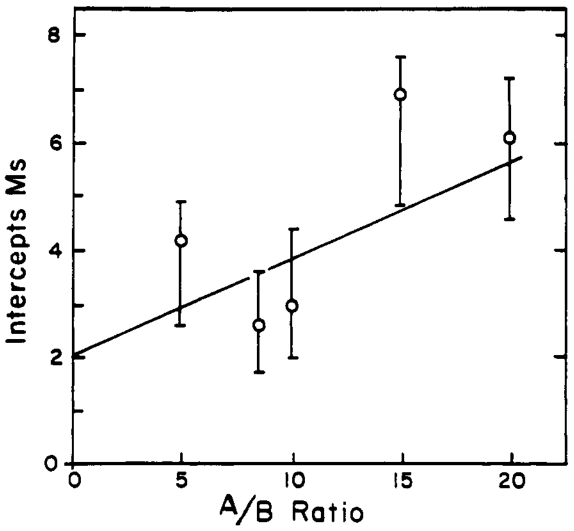

Figure 4. Plots of the intercepts obtained from Figure 3 against the buffer ratio A/B.

general acid catalyzed reaction a second molecule of trifluoroethanol presumably hydrogen bonds to the nucleophilic trifluoroethanol molecule.

The zero intercepts in Figure 1 indicate that the terms involving k_o, k_H, and k_{TO} are all small, and their contribution to k_{obs} is negligable so that eq 1 can be simplified to

$$k_{obs} = k_A[A] + k_B[B] + k_{AB}[A][B] \qquad (2)$$

Division of both sides of eq 2 by [B] gives

$$k_{obs}/[B] = k_A R + k_B + k_{AB}[A] \qquad (3)$$

where R is the ratio of the acid form of the buffer to the basic form of the buffer. According to eq 3 for a reaction conducted at a fixed buffer ratio plots of $k_{obs}/[B]$ vs [A] will be linear with slopes of k_{AB} and intercepts of ($k_A R + k_B$). Plots of $k_{obs}/[B]$ vs [A] are shown in Figure 3. The lines drawn in Figure 3 for [A]/[B] ratios of 20, 15, 10, 7, and 5 have slopes of $(1.5 \pm 0.3) \times 10^{-3}$, $(1.3 \pm 0.2) \times 10^{-3}$, $(1.8 \pm 0.2) \times 10^{-3}$ $(2.1 \pm 0.4) \times 10^{-3}$, and $(1.2 \pm 0.3) \times 10^{-3}$ $M^{-2}\ s^{-1}$, respectively, providing an average value for k_{AB} of $(1.6 \pm 0.3) \times 10^{-3}$ $M^{-2}\ s^{-1}$. The slopes of these lines were determined by a least-squares analysis of the data and errors are reported as standard deviations. A plot of the intercepts from Figure 3 against the buffer ratios, R, is shown in Figure 4. The error bars in Figure 4 were estimated by visual inspection of the plots in Figure 3. The slope of the line drawn in Figure 4 gives a value for k_A = $(2.3 \pm 1.0) \times 10^{-5}$ $M^{-1}\ s^{-1}$ and the intercept gives k_B = $(2.0 \pm 1.4) \times 10^{-4}$ $M^{-1}\ s^{-1}$. Errors are reported as standard deviations from a least-squares analysis. The value for k_B can also be determined by dividing both sides of eq 2 by [A] and plotting $k_{obs}/[A]$ at a fixed buffer ratio against [B], the intercepts of these plots (not shown) when plotted against the buffer ratio R will have a slope of k_B and intercept of k_A. The values of k_B and k_A obtained in this way are $(3.1 \pm 1.1) \times 10^{-4}$ and $(1.3 \pm 1.4) \times 10^{-5}$ $M^{-1}\ s^{-1}$, respectively.

The values for the catalytic rate constants obtained graphically agree well with the values obtained from a computer-generated least-squares fit of the data according to eq 2 from more than 50 rate experiments conducted at different ratios of [A]/[B] (supplemental material). The values of k_{AB}, k_A, and k_B obtained from the least-squares fit are $(1.6 \pm 0.1) \times 10^{-3}$ $M^{-2}\ s^{-1}$, $(1.7 \pm 0.3) \times 10^{-5}$, and $(2.2 \pm 0.3) \times 10^{-4}$ $M^{-1}\ s^{-1}$ respectively; errors are reported as standard deviations. The solid lines drawn in Figure 1 were calculated using eq 2 and values for $k_A = 1.7 \times 10^{-5}$ $M^{-1}\ s^{-1}$, $k_B = 2.2 \times 10^{-4}$ $M^{-1}\ s^{-1}$, and $k_{AB} = 1.6 \times 10^{-3}$ $M^{-2}\ s^{-1}$. It can be seen that the data are accurately described by eq 2.

There are several examples of bifunctional catalysis where the catalyst is a single molecule containing both acidic and basic groups.[26-28] Recently it has been shown that the hydrolysis of 4-*tert*-butylcatechol cyclic phosphate catalyzed by β-cyclodextrin 6,6′-bis(imidazoles) involves general acid–base catalysis with both imidizoles in the transition state, one in the protonated form and one in the free form.[29,30] There are, however, far fewer examples of bifunctional catalysis that involve both a molecule of acid and a molecule of base in the transition state. The enolization of acetone[22,31] and cyclohexanone[22,32] and the formic acid–formate catalyzed methanolysis of phenoxytriphenylsilane[33] are other examples of bifunctional catalysis, involving both a molecule of acid and a molecule of base. The occurrence of bifunctional catalysis in solution involving both a molecule of acid and a molecule of base is uncommon, presumably because of entropic difficulties. Bifunctional catalysis is a possible method for enzymes to catalyze reactions.[40]

Two possible mechanisms have been proposed for the solvolysis of silyl ethers.[1-6] The solvolysis reaction could occur by a mechanism involving the formation of a pentavalent intermediate (S_Ni-Si[1,8] or $A_N + D_N$[20] mechanism) or by a one-step concerted reaction (S_N2-Si[1,8] or A_ND_N[20] mechanism). We have suggested that the trifluorethanolysis of phenoxydimethylphenylsilane occurs by a concerted mechanism involving a single transition state.[20] The observation of bifunctional catalysis is consistent with this mechanism and difficult to explain by a mechanism involving a pentavalent intermediate.

In summary the results described here suggest that the trifluoroethanolysis of alkoxysilanes can show, in addition to general base and general acid catalysis, bifunctional catalysis involving both a molecule of the acid catalyst and a molecule of the base catalyst in the transition state. The observation of bifunctional catalysis suggests that the trifluoroethanolysis of phenoxydimethylphenylsilane occurs by a concerted S_N2-Si or A_ND_N mechanism.

Experimental Section

Materials. Trifluoroethanol, acetic acid tetramethylammonium acetate, tetramethylammonium nitrate, and tetramethylammonium perchlorate were commercially available. The tetramethylammonium acetate, tetramethylammonium nitrate, and tetramethylammonium perchlorate were recrystallized from ethanol and chloroform, respectively, before use.

Tetramethylammonium trifluoroacetate was prepared by adjusting the pH of an aqueous solution of tetramethylammonium hydroxide to a pH of 1.5 with trifluoroacetic acid. The water was removed under vacuum and the resulting wet solid recrystallized from acetone and dried in a vacuum desiccator overnight. The pH of an aqueous solution of the salt was 7.

The phenoxydimethylphenylsilane was prepared from dimethylphenylsilyl chloride according to a published procedure and was distilled under vacuum. The phenoxydimethylphenylsilane gave NMR and mass spectral data consistent with the desired product and was demonstrated to be better than 80% pure, the only impurity being the tetramethyldiphenylsiloxane as indicated by both NMR and GC/MS analysis. Mass spectral analysis was performed on a Hewlett-Packard Model 5988A GC/MS/DS and NMR spectra were recorded on a GE QE-300 NMR spectrometer.

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Kinetics. Pseudo-first-order rate constants, k_{obs}, for solvolysis of phenoxydimethylphenylsilane were determined by adding 0.6 μL of phenoxydimethylphenylsilane to 2.4 mL of a 2,2,2-trifluoroethanol (TFE) solution at 30.0 ± 0.5 °C buffered with an acetic acid-tetramethylammonium acetate buffer and at constant ionic strength of 0.05 M maintained with tetramethylammonium trifluoroacetate. The rate of solvolysis, k_{obs}, was determined by monitoring the increase in absorbance due to the formation of phenol at 280 nm as a function of time with a Shimadzu UV-160 spectrophotometer equipped with a thermostated cell holder. The spectrophotometer was interfaced to a personal computer and k_{obs} values were obtained by a nonlinear regression analysis of absorbance vs time data. Reactions were generally followed for more than three half-lives. The nonlinear regression analysis calculated the best end points. For reactions that were followed by completion the observed end points always agreed well with the calculated end points. Good pseudo-first-order kinetics were followed and semilog plots of $(A_\infty - A_t)$ were linear. Rate constants were generally reproducible within 10%.

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Registry No. TFE, 75-89-8; phenoxydimethylphenylsilane, 17915-17-2; acetic acid, 64-19-7; tetramethylammonium acetate, 10581-12-1.

Supplementary Material Available: Pseudo-first-order rate constants for the trifluoroethanolysis of phenoxydimethylphenylsilane (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

[*abc*]-Annealated [18]Annulenes

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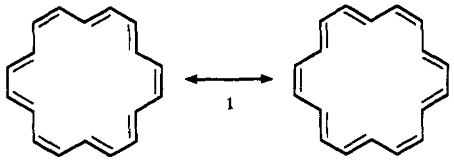
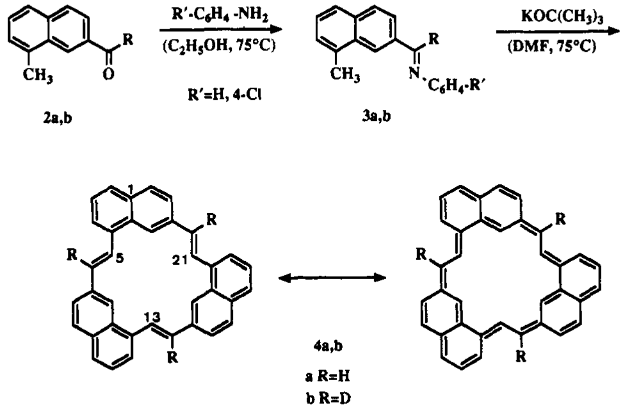
A 3-fold stereoselective cyclocondensation of the azomethines 3 and 11 yields the [18]annulenes 4 and 12, respectively. The [*abc*]-annelation of naphthalene or phenanthrene systems, realized here for the first time, leads to nonplanar molecules consisting of "aromatic islands", which are connected by (*E*)-configured olefinic bridges. The absence of a diamagnetic ring current rules out a macrocyclic aromaticity. The NMR investigation, based on selective deuterations, is sustained by force field calculations (MMX). The disc-like compounds represent discotic mesogens of an enormous diameter. The formation of thermotropic liquid crystals can be achieved by the introduction of long flexible alkoxy chains.

[18]Annulene[1] with the preferred conformation shown in formula 1 has two identical resonance structures. According to the VB theory, the anellation of benzene rings—from benzo[*a*]cyclooctadecene[2] up to kekulēne[3]—can change the "weight" of these resonance structures. The *diatropic* or *atropic* behavior of these macrocycles is directly connected to this effect.


1

Scheme I



If radical species are disregarded, the number of common carbon atoms of [18]annulene and condensed arenes must be even. The following systems fulfill this criterion:

type of annelation	no. of annealated arenes	known compounds
[*a*]	1, 2, 3, ...	benzo[*a*]cyclooctadecene[2]
[*ab*]	2, 4, 6	dibenzo[*ab*,*de*]cyclooctadecene,[4b] hexa-*m*-phenylene[4a]
[*abc*]	1, 2, 3, 4	
[*abcd*]	2	
[*abcde*]	1, 2, 3	phenanthro[3,4,5,6-*abcde*]cyclooctadecene[4b] 3,6':3,6'':3'',6-triphenanthrylene[5]

Analogous considerations are valid for other annulenes.

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