tigated structures of the cobalt/oxygen cluster ions by geometry optimization[11,13] based on an ionic model.[14] The low-energy structures (Figure 1a) of the unreactive oxygen-equivalent $[Co_xO_x]^+$ clusters consist of closed structures: rings, ladders, and cages.[1] The low-energy structures (Figure 1b) of the reactive oxygen-deficient $[Co_xO_{x-1}]^+$ clusters consist of chains and structures with terminal cobalt atoms.[11] The terminal cobalt atom in these reactive clusters is sterically accessible or on an edge of the cluster ion, which reacts by insertion into hydrocarbon bonds. The oxygen-equivalent cluster ions do not react because there are no cobalt atoms accessible for reaction. These arguments are analogous to the perception that catalysis occurs on steps or defects of metal surfaces.[15]

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Proton-Catalyzed Cis–Trans Stereomutation of *cis*-1,2-Diarylcyclobutanes

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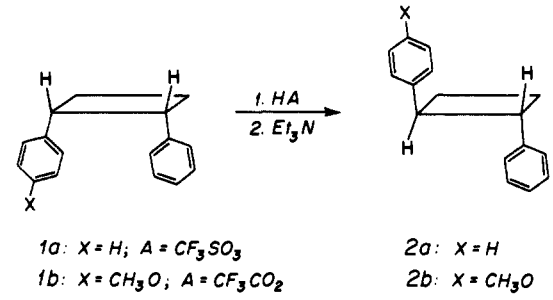
When cyclopropanes that possess vicinal aryl substituents are treated with trifluoroacetic acid they often undergo cis–trans stereomutation much more rapidly than they ring open.[2,3] Several studies of this unusual reaction have shown that (1) aryl substituents with electron-donating groups in the ortho or para position enhance the rate of stereomutation[2,3] and (2) when the reaction is catalyzed with deuterated acid the isolated products show no evidence of significant deuterium incorporation after short reaction times.[3] The mechanism of this reaction is not yet settled; however, we have suggested that it may proceed via a cyclization-induced rearrangement that requires acid catalysis.[3] An intriguing corollary of this hypothesis is that 1,2-diarylcycloalkanes other than cyclopropanes should also be susceptible to catalytic cis–trans stereomutation by Brønsted acids. In this paper we report that two new examples of facile, acid-catalyzed cis–trans stereomutation of *cis*-1,2-diarylcycloalkanes have been found.

Our initial work in this area focused on the reactions of *cis*-1,2-diphenylcyclobutane (**1a**) in Brønsted acids. Cyclobutane **1a** and an authentic sample of the corresponding trans diastereomer, **2a**, were prepared by the methods of Dodson and Zielske.[4] Cyclobutane **1a** was recovered unchanged after standing in trifluoroacetic acid at 25 °C for 20 h; however, when **1a** was allowed to react in 19:1 methylene chloride–trifluoromethanesulfonic acid at 0 °C for 5 min, followed by a triethylamine quench, we isolated analytically pure *trans*-1,2-diphenylcyclobutane (**2a**) in 95% yield (Figure 1).



1a: X = H; A = CF_3SO_3 2a: X = H
1b: X = CH_3O; A = CF_3CO_2 2b: X = CH_3O

Figure 1.

The stereomutation of **1a** was also carried out with 9:1 methylene chloride–trifluoromethanesulfonic acid-*d* at 0 °C and the reaction was quenched after 2 min. The crude product from this reaction consisted of a clean, 1:1 mixture of *cis*- and *trans*-1,2-diphenylcyclobutanes. Mass spectrometric analysis of the individual diastereomers isolated from the mixture confirmed extensive deuteration in both.[5] In fact, both diastereomers incorporated up to 10 deuterium atoms, approximately equal amounts of d_4 and d_5 species predominating in each. There was less than 2 mol % of d_0 material in either of the isolated products. ^2H NMR spectra of these products demonstated that deuterium exchange occurred exclusively in the phenyl rings.[6]

Unfortunately, even 19:1 methylene chloride–trifluoromethanesulfonic acid is partially heterogeneous at 0 °C. We desired to study the stereomutation reaction under homogeneous conditions; however, **1a** proved to be unreactive in trifluoroacetic acid and in chlorosulfonic acid over 0–25 °C. Reactions of **1a** in solvent systems containing fluorosulfonic acid or sulfuric acid produced varying amounts of intractable side products.

cis-1-(4-Methoxyphenyl)-2-phenylcyclobutane (**1b**)[7] proved to be conveniently soluble in a variety of Brønsted acids and much more reactive toward acid-catalyzed stereomutation than **1a** (Figure 1). Thus, when **1b** was allowed to react in trifluoroacetic acid at 25 °C for 3 h a 2:1 mixture of **1b** and *trans*-1-(4-methoxyphenyl)-2-phenylcyclobutane (**2b**), respectively, was obtained in 83% yield. When cyclobutane **1b** was allowed to react in trifluoroacetic acid-*d* at 25 °C for 5.25 h a 1:1 mixture of cis and trans diastereomers was isolated in 97% yield. Mass spectrometric analysis of the separate diastereomers from this reaction showed that both contained newly incorporated deuterium; however, the maximum amount of deuterium uptake in this case was only two atoms in each.[8] ^2H NMR analysis of the cis and trans products unambiguously demonstrated that deuterium incorporation occurred exclusively in the activated ring, ortho to the methoxy group in both.[9]

Our results can be rationalized by a cyclization-induced rearrangement mechanism (Scheme I).[10] Thus, protonation of an aromatic ring[11] of cyclobutane **1** may be followed by rearrange-

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(5) We are indebted to Phil Briggs (Harvard University) for obtaining the 70-eV EI mass spectra of these compounds and to Timothy Baker and John V. Amari (Northeastern University) for CI mass spectra.
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(9) Proton-decoupled ^2H NMR spectra of these compounds were obtained at 46 MHz on CCl_4 solutions containing acetone-d_6 as reference. Cis: δ 6.58. Trans: δ 6.72.
(10) A conceptually similar cyclization-induced rearrangement mechanism has been advanced to rationalize the facile transition-metal-catalyzed [3,3]-sigmatropic rearrangement of certain 1,5-dienes: (a) Overman, L. E.; Knoll, F. M. *J. Am. Chem. Soc.* **1980**, *102*, 865. (b) Overman, L. E.; Jacobsen, E. J. *J. Am. Chem. Soc.* **1982**, *104*, 7225.

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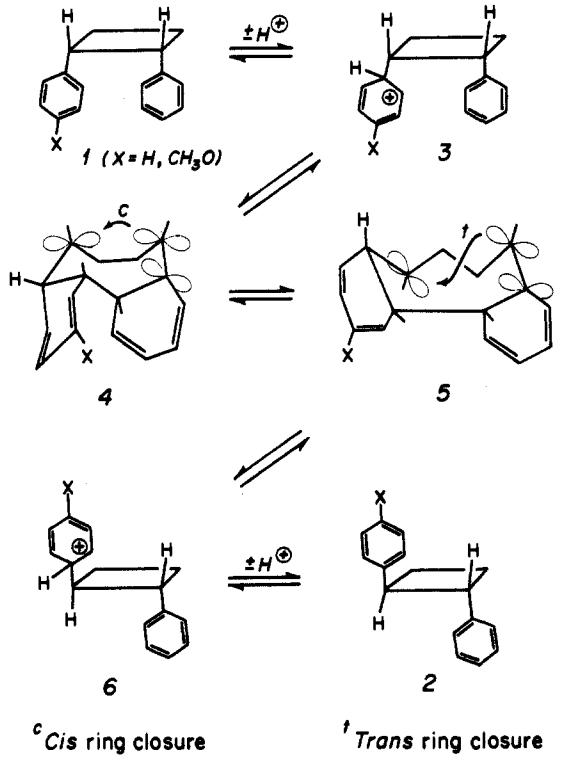
Scheme I



ment to a cyclooctenyl carbenium ion, **4**. Reclosure of the cyclobutyl ring directly from **4** would regenerate the protonated cis diastereomer **3**; however, **4** may alternatively suffer a conformational change to give **5**. Unlike **4**, which is certainly constrained to reclose with cis geometry, conformer **5** may undergo trans ring closure to afford **6** and, ultimately, **2**. The fact that no cis diastereomer could be detected in reaction mixtures which were allowed to approach equilibrium apparently reflects a large (≥3 kcal/mol)[12] free energy difference between the cis and trans diastereomers of the 1,2-diarylcyclobutanes in this study.

In contrast to the analogous reaction of *cis*-1,2-diarylcyclopropanes, the rates of stereomutation of *cis*-1,2-diarylcyclobutanes **1a** and **1b** are slower than the rates of deuterium exchange on their aryl rings. This fact may be the consequence of a relatively high barrier to (1) the rearrangement of **3** to **4**, (2) the interconversion of ion conformers **4** and **5**, or (3) both of these steps. Ongoing studies in our laboratory are aimed at resolving these questions and further defining the nature and scope of this unusual reaction type.

In conclusion, the present observations constitute the first evidence of a *general*, proton-catalyzed cis–trans stereomutation reaction in 1,2-diarylcycloalkanes.

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(11) Note that we depict ipso protonation in this scheme even though the isotope incorporation results do not require it. Our examination of appropriate molecular models suggested to us that the interconversion of the homoallylic carbenium ions **4** and **5**, as well as **5** and **6**, would be facilitated by tetrahedral geometry at C-1′; conversely, these interconversions appear to be relatively difficult in molecular models if C-1′ is sp^2 hybridized. Therefore, we currently disfavor a plausible, alternative scheme initiated by protonation at C-3′. The fact that no deuterium was incorporated into the unsubstituted ring when *cis*-1-(4-methoxyphenyl)-2-phenylcyclobutane was allowed to react in TFA-*d* precludes another alternative mechanism in which protonation of the unactivated ring is followed by ring-opening to a benzylic carbenium ion that could reclose to give *trans* cyclobutane.

(12) Our HPLC detection limits for the **1a,b** system were ~200:1 (Zorbax C-8 reverse-phase column, 4:1 methanol–water, refractive index detection).

Radical Anions. Electron Affinities of Benzene, Naphthalene, and Anthracene Having the Substituents CHO, CN, and NO_2

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We have recently reported determinations[1-7] of electron affinities based on measurement of gas-phase electron-transfer equilibria (1). These lead to $\Delta G_1°$ values. Determination of the

$$A^- + B = A + B^- \quad (1)$$

equilibrium constants K_1 at different temperatures lead to $\Delta H_1°$ and $\Delta S_1°$. Generally $\Delta S_1°$ is small such that $\Delta G_1° \approx \Delta H_1°$ within less than 1 kcal/mol. By anchoring a $\Delta H_1°$ scale from connected equilibria to a few compounds (SO_2, NO_2 with known absolute EA values, one obtains the absolute EA for all compounds in the scale. Determinations of EA's for close to 100 compounds were obtained in this manner.[1-8]

Here we consider the electron affinities of a selected group of benzenes,[1,5,6,9] naphthalenes,[6,9] and anthracenes,[7] namely, those carrying the strong-electron-withdrawing substituents X = CHO, CN, and NO_2. The changes of substituent effects with increasing size of the aromatic system observed for these compounds are quite interesting. The electron affinities are shown in Figure 1 plotted vs. the Hammett σ_p^-(g) parameter (see Table IV of ref 10) on the basis of the substituent effect on the gas-phase acidities of phenols.[10,11] Also shown in Figure 1 are the electron affinities of the 1,4 doubly substituted benzenes[1,5] X–$C_6H_4NO_2$ and X–C_6H_4CN and the relative gas-phase acidities[10] of the 1,4-phenols X–C_6H_4OH. The following trends are observed. The increase of the electron affinity due to the electron-withdrawing substituent X; i.e., the slope ρ in Figure 1 decreases in the series benzene, naphthalene, anthracene. Similarly, the ρ values decrease from X–C_6H_5 to X–C_6H_4CN to X–$C_6H_4NO_2$. Thus the approximate overall trend observed is that the ρ value decreases as the electron effinity of the first member (X = H) in a given series increases. This effect is not surprising, the increasing electron affinities of the first members X = H corresponds to progressively lower electron density in the π^*-type singly occupied molecular orbital (SOMO) extending over the aromatic ring of the negative ion. Thus, in the higher electron affinity compounds the electron-withdrawing X, attached to a ring carbon, has less SOMO electron density to operate on.

In addition to the above effect, there is an interesting reversal of the substituent effect between the CHO and CN group. For the low EA, i.e., high SOMO, ring density compounds CHO leads to a significantly higher EA than CN, while for the high electron affinity compounds and nitrobenzene–X the "normal" order,[10] CN

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