Rearrangement of Annelated Housanes to Triquinane-Like Hydrocarbons by Electron Transfer (1,3-Cyclopentanediyl Radical Cations) and Acid Catalysis (Cyclopentyl Carbenium Ions)

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Received October 22, 2001

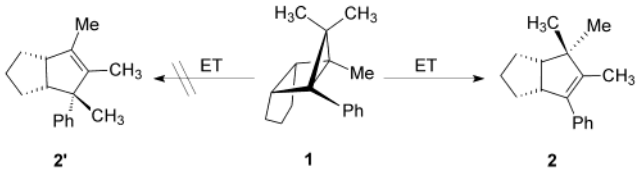
The electron-transfer-catalyzed rearrangement of the annelated housane **4a** on treatment with tris(*p*-bromophenyl)aminium hexachloroantimonate ($TBA^{\bullet+}SbCl_6^-$) affords regioselectively the two isomeric olefins *endo*-**5a** and **6a** by 1,2 migration of the two groups at the methano bridge. Acid-catalyzed rearrangement gives in addition to *endo* **5a** and **6a** also the regioisomer *endo*-**7a** as major product. The formation of both rearrangement products *endo*-**5a** and **6a** suggests a planar conformation for the radical-cation and carbocation intermediates. The regioselectivity is rationalized in terms of electronic stabilization of the radical versus cationic sites by the substituent at the rearrangement termini in the radical-cation and carbocation intermediates. Of interest for preparative purposes, the annelated housane **4a** leads under electron-transfer conditions to unusual triquinane-related olefins by means of an unprecedented synthetic pathway.

Introduction

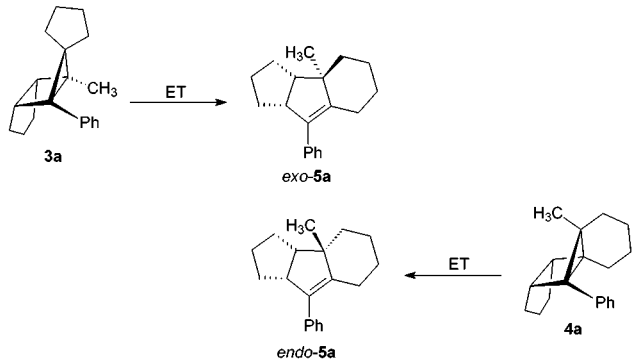
The remarkable chemical behavior of the 1,3-cyclopentanediyl radical cations derived from bicyclo[2.1.0]-pentanes (housanes) by electron-transfer oxidation is their regioselective and diastereoselective rearrangement to cyclopentenes, if properly substituted.[1] For example, the housane **1** (Scheme 1) afforded on treatment with triarylaminium hexachloroantimonate ($Ar_3N^{\bullet+}SbCl_6^-$) exclusively the cyclopentene **2**; the regioisomeric **2′** was not observed.[2] Responsible for this high regioselectivity is the preferential stabilization of the radical center by the bridgehead phenyl substituent, as rationalized in terms of a detailed molecular-orbital-interaction diagram for this Wagner−Meerwein-type rearrangement.[1] Since in the case of housane **1**, the regioisomer **2′** (migration of the methyl group to the phenyl-substituted rearrangement terminal) is not observed, the diastereoselectivity of whether the *endo*- or the *exo*-methyl group migrates preferably is inaccessible. Nevertheless, in view what is known experimentally[3] and computationally[4] about this 1,2 shift for the 1,3 radical cations generated from the parent housane and simple derivatives, the *endo*-methyl group should migrate to generate the *endo*-**2** rearrangement product.[1] For clarification, to differentiate between the methyl groups, the migrating ones at the methano bridge have been coded as "CH_3" and the ones at the rearrangement terminus as "Me".

A more informative case is the spirocyclic housane **3a** (Scheme 2), for which expectedly only the regioisomer **5a**

Scheme 1. Regioselective Rearrangement of the Housane 1



Scheme 2. Regioselective and Diastereoselective Rearrangement of Housanes 3a and 4a to the Triquinane-Type Structures *exo*-5a and *endo*-5a



(exclusive 1,2 shift to the methyl-bearing terminus) is obtained, on account of the electronic control by the phenyl substituent.[5] Moreover, of the two possible diastereomers *exo*-**5a** (migration of the *endo*-methylene group in the spiropentane ring) and *endo*-**5a** (migration of the *exo*-methylene group), exclusively the *exo*-**5a** rearrangement product is formed. This more complex housane example confirms that the 1,2 shift proceeds from a puckered conformation of the intermediary 1,3 radical cation (stereochemical memory effect), as established by

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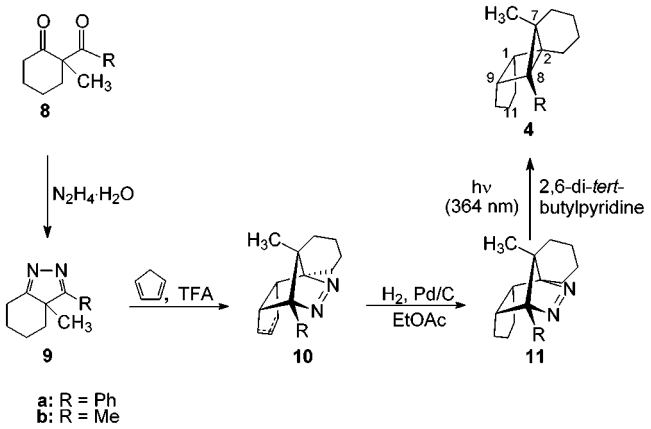
(1) Adam, W.; Heidenfelder, T. *Chem. Soc. Rev.* **1999**, *28*, 359−366.
(2) Adam, W.; Heidenfelder, T. *J. Am. Chem. Soc.* **1998**, *120*, 11858−11863.
(3) (a) Adam, W.; Walter, H.; Chen, G.-F.; Williams, F. *J. Am. Chem. Soc.* **1992**, *114*, 3007−3014. (b) Adam, W.; Sahin, C.; Sendelbach, J.; Walter, H.; Chen, G.-F.; Williams, F. *J. Am. Chem. Soc.* **1994**, *116*, 2576−2584.
(4) Blancafort, L.; Adam, W.; González, D.; Olivucci, M.; Vreven, T.; Robb, M. A. *J. Am. Chem. Soc.* **1999**, *121*, 10583−10590.
(5) Adam, W.; Heidenfelder, T.; Sahin, C. *Synthesis* **1995**, 1163−1170.

10.1021/jo016224x CCC: $22.00
Published on Web 12/22/2001

Scheme 3. Synthesis of the Azoalkanes 11 and the Housanes 4



EPR spectroscopy[3] and computations[4] for the simple derivatives of the parent housane.[1]

An alternative entry into the triquinane-type structure **5a**, but formation of the *endo*-**5a** diastereomer, would be to employ the cyclohexane-annelated housane **4a** (Scheme 2) in the electron-transfer rearrangement catalyzed by $Ar_3N^{\bullet+}SbCl_6^-$. In view of what has been said above, it is anticipated that the *endo*-methyl group in the intermediary 1,3 radical cation should be transposed to the methylene-substituted rearrangement terminus to afford regioselectively and diastereoselectively the *endo*-**5a** product. In this way, the stereoselective synthesis of complex triquinane-type structures would become feasible.

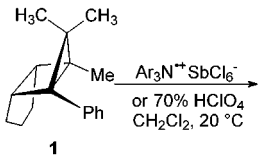
Herein we report the preparation of the unknown housanes **4a**,**b** by way of the Hünig isopyrazole route.[6] The methyl derivative **4b** was chosen to assess the regioselectivity and diastereoselectivity of the rearrangement without the electronic bias of the phenyl group. The electron-transfer rearrangement of the housane **4a**,**b** was effected by $Ar_3N^{\bullet+}SbCl_6^-$ as catalyst. For comparison purposes, also the acid-catalyzed rearrangement of the housane **1** and **4a**,**b** by $HClO_4$ was examined. The present results provide valuable mechanistic insight on the complexities of the rearrangement behavior of 1,3-cyclopentanediyl radical cations and the corresponding cylcopentyl cations.

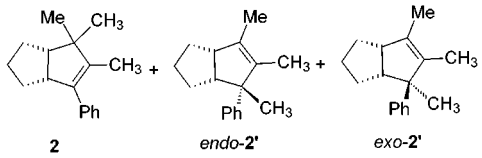
Results

Synthesis of the Azoalkanes 11 and Their Photolysis to the Tetracyclic Housanes 4. The synthetic route (Scheme 3) for the synthesis of the hitherto unknown tetracyclic azoalkanes **11** started from the 2-acetylcyclohexanones **8**, according to Hünig's isopyrazole-cycloaddition method.[1] The corresponding housanes **4** were obtained by photodenitrogenation from the azoalkane **11** (Scheme 3). The azoalkanes **11** exhibit absorption maxima at around 360 nm; thus, the direct photolyses were carried out by irradiation at the absorption maximum of the azo chromophore with the 364-nm line of the argon-ion laser in *n*-pentane at 20 °C. The azoalkanes **11** cleanly denitrogenated to the corresponding housanes **4**.

An attempt failed to detect the triplet diradical of the phenyl-substituted azoalkane **11a** by EPR spectroscopy in a 2-methyltetrahydrofuran(MTHF) matrix. Neither the half-field signal ($\Delta m_s = \pm 2$) nor the characteristic zero-field splitting pattern for the triplet species were detected even at such a low temperature as 4 K. Normally, however, direct photolysis of such aryl-substituted azoalkanes affords EPR-detectable triplet diradicals under matrix isolation at 77 K, which persist for months at this temperature.[7]

Table 1. Product Distribution of the Electron-Transfer Reaction and Acid-Induced Rearrangement of the Housane 1





	product distribution[a]		
mode[b]	2	endo-**2′**	exo-**2′**
$TBA^{\bullet+}\ SbCl_6^-$	>95	–	–
$HClO_4$	26 ± 3	51 ± 3	23 ± 3

[a] Determined by ^1H NMR spectroscopy on the crude product mixture; conversion >95%, mass balance >90%. [b] $TBA^{\bullet+}\ SbCl_6^-$ is tris(4-bromophenyl)aminium hexachloroantimonate, 70% aqueous $HClO_4$ was used.

Electron-Transfer and Acid-Catalyzed Rearrangement of the Housanes 1 and 4. The desired 1,3 radical cations were generated by electron transfer with $TBA^{\bullet+}SbCl_6^-$ {[tris(4-bromophenyl)aminium] hexachloroantimonate} as one-electron oxidant in methylene chloride. To rule out the involvement of acid-catalyzed rearrangement, the electron-transfer reactions were carried out in the presence of a slight excess (1.25 equiv) of the sterically hindered 2,6-di-*tert*-butylpyridine as buffer.

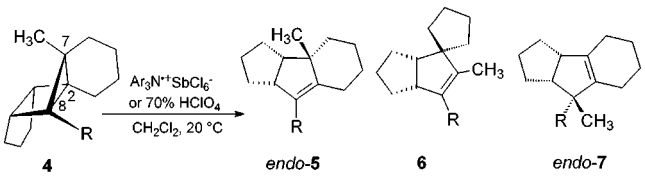
Treatment of the known housane **1**, prepared according to the literature procedure,[2] with catalytic amounts of $TBA^{\bullet+}SbCl_6^-$ afforded regio- and diastereoselectively only the diquinane-like olefin **2** in high yield (Table 1). In contrast, acid catalysis by $HClO_4$ led to a mixture of the three isomeric cyclopentenes **2** (26%), *endo*-**2′** (51%), and *exo*-**2′** (23%). The *exo*-**2′** diastereomer was previously overlooked, which requires reassessment of our earlier mechanistic analysis on the diastereoselectivity for the acid-catalyzed rearrangement.[2]

The phenyl-substituted housane **4a** (Table 2; entry 1) afforded with catalytic amounts of magic blue ($TBA^{\bullet+}SbCl_6^-$) the triquinane-like hydrocarbon *endo*-**5a** (55%) and the spirocyclopentyl-substituted diquinane **6a** (45%) in nearly equal amounts; the regioisomer *endo*-**7** was not observed. In contrast, the electron-transfer oxidation of the methyl-substituted housane **4b** (Table 1, entry 2) led to a mixture of the three isomeric olefins *endo*-**5b** (37%), **6b** (25%), and *endo*-**7b** (43%). For the acid-catalyzed reactions, 70% aqueous $HClO_4$ was used as proton source. Contrary to the electron-transfer reaction, acid catalysis led to a significantly different product distribution (Table 2).

(6) Beck, K.; Hünig, S. *Chem. Ber.* **1987**, *120*, 477−483.

(7) Adam, W.; Harrer, H. M.; Kita, F.; Nau, W. M. *Adv. Photochem.* **1998**, *24*, 205−254.

Table 2. Product Distribution of the Electron-Transfer and Acid-Induced Rearrangements of the Housanes 4



4 *endo*-**5** **6** *endo*-**7**

				product distribution[a]		
entry	substrate	R	mode[b]	*endo*-**5**	**6**	*endo*-**7**
1	**4a**	Ph	TBA•+$SbCl_6^-$	55 ± 4	45 ± 4	-
2	**4b**	Me	TBA•+$SbCl_6^-$	37 ± 6	25 ± 6	43 ± 6
3	**4a**	Ph	$HClO_4$	24 ± 2	9 ± 2	67 ± 2
4	**4b**	Me	$HClO_4$	> 95	-	-

[a] Determined on the crude product mixture by ^{1}H NMR spectroscopy, except entry 2 (quantitative ^{13}C NMR spectroscopy), conversion >95%, except entry 2 (77%), and mass balances >90%. [b] TBA•+$SbCl_6^-$ is tris(4-bromophenyl)aminium hexachloroantimonate, 70% aqueous $HClO_4$ was used.

The acid-catalyzed rearrangement of the phenyl-substituted housane **4a** (entry 3) gave the *endo*-**7a** as major product (67%), along with appreciable (24%) amounts of *endo*-**5a** and a small (9%) quantity of **6a**. The methyl-substituted housane **4b** (entry 4) yielded exclusively (>95%) the rearrangement product *endo*-**5b**.

The configurations of the rearrangement products **5**−**7** were assigned by means of NOE effects, combined with HH and CH correlations, and by spectral comparison with already known diquinane derivatives.[5] Additionally, the connectivity in the diquinanes *endo*-**5a**, **5b**, and **6a** was determined by 2D-INADEQUATE NMR experiments.

Discussion

The product distributions for the phenyl-substituted annelated housane **4a** (Table 2) and the reference housane **1** (Table 1) display similar regiochemical and stereochemical features for the electron-transfer and acid-catalyzed rearrangements. Thus, in regard to the regioselectivity, the housane **1** affords on electron transfer (Table 1, first entry) exclusively the diquinane regioisomer **2** by methyl migration to the methyl-bearing site; methyl migration to the phenyl-substituted terminal to generate the regioisomer **2′** is not observed. Analogously, electron transfer with the housane **4a** leads only to the rearrangement products *endo*-**5a** and **6a** (these correspond to the regioisomer **2** derived from housane **1**), and *endo*-**7a** (this one corresponds to the regioisomer *endo*-**2′**) is not formed (Table 2, entry 1). Again, absolute regiochemical control applies in that exclusive migration to the alkyl-substituted terminal (C-2 position) occurs. The triquinane-like product *endo*-**5a** results from migration of the *endo*-methyl substituent, whereas the spirocyclic diquinane **6a** is generated by the shift of the *exo*-methylene group in the annelated six-membered ring, both at the C-7 position. The advantage of the annelated housane **4a** is the fact that the two migrating substituents (methyl and methylene) are structurally distinct and, thus, provide stereochemical information on the rearrangement process. Mechanistically significant, both rearrangement products *endo*-**5a** (*endo*-methyl migration) and **6a** (*exo*-methylene migration) are formed in about equal amounts (Table 2, entry 1). It should be evident that for the reference housane **1** such stereochemical differentiation is not possible because migration of the *endo*-methyl and *exo*-methyl groups to the methyl-bearing terminal affords the same rearrangement product, namely the regioisomer **2**.

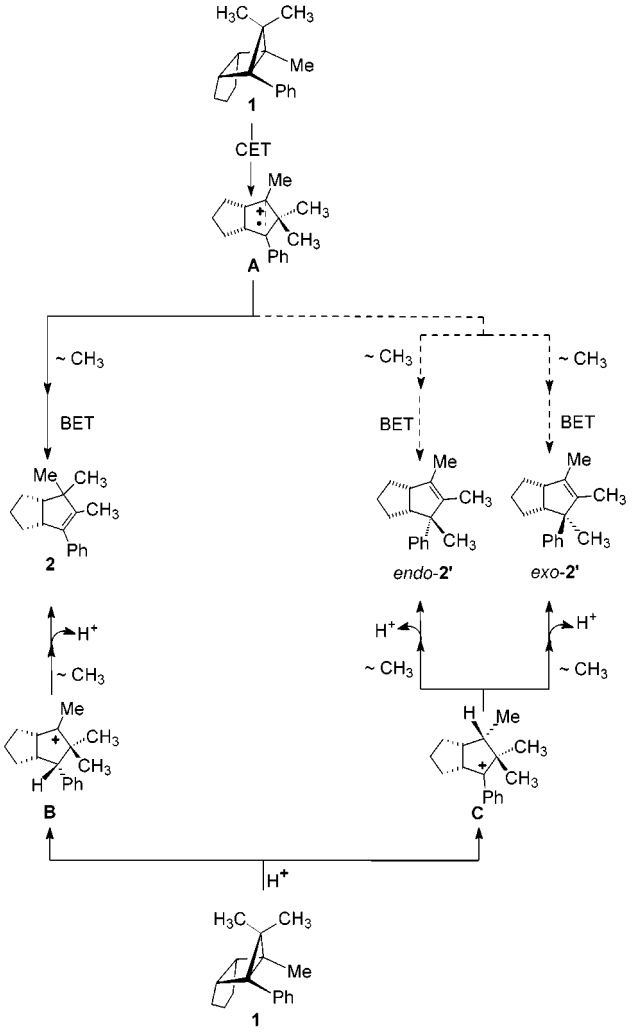
A similar scenario is observed for the acid-catalyzed rearrangement of the annelated housane **4a** (Table 2, entry 3) and the reference housane **1** (Table 1, second entry). Although the product distributions are nearly the same for the acid catalysis of these two housanes, they are quite different from the electron-transfer case. Specifically, housane **1** gives both regioisomers **2** and **2′**, the latter as a mixture of *endo*-**2′** (major) and *exo*-**2′** (minor) diastereomers. Thus, both the *exo*-methyl and *endo*-methyl groups migrate to the phenyl-substituted as well as the methyl-substituted terminal, but in the **2** regioisomer the *exo* and *endo* migrations are not distinguishable. Nearly the same regioisomeric ratio (*endo*-**5a**+**6a**/*endo*-**7a**) is obtained for the housane **4a**, with preferred migration to the phenyl-substituted site to afford the regioisomer *endo*-**7** (Table 2, entry 3). Since migration of the methylene group in the annelated six-membered ring would result in a highly strained olefin as rearrangement product, only the *endo*-**7** diastereomer is formed along the rearrangement path to the phenyl-bearing C-8 terminal.

The methyl-substituted housane **4b** displays quite different rearrangement behavior compared to the phenyl-substituted derivative **4a**, both for the electron-transfer and the acid-catalyzed reactions (Table 2, entries 2 and 4). In contrast to the phenyl case **4a**, the methyl derivative **4b** is neither regioselective nor stereoselective. Thus, for the electron-transfer rearrangement (entry 2), the ratio of the regioisomers (*endo*-**5b** + **6b**/*endo*-**7b**) is about equal within the experimental error, so that the methyl shift to the respective positions C-2 and C-8 takes place with nearly equal facility. For the migration to the C-2 position, both the *endo*-methyl substituent (product *endo*-**5b**) and the *exo*-methylene group in the annelated six-membered ring (product **6b**) transpose also in about the same amounts within the experimental error. Clearly, replacement of the phenyl (**4a**) by the methyl (**4b**) group erases the regioselective control displayed by the former, whereas the stereoselectivity is for both similarly low (Table 2, entries 1 and 2). Remarkable is the acid-catalyzed rearrangement of the methyl derivative **4b** (Table 2, entry 4), which affords exclusively the *endo*-**5b** product, that is, only *endo*-methyl migration to the position C-2 is found.

The observed regio- and stereoselectivities for the housane **1** (Table 1) and **4a** (Table 2) are mechanistically rationalized in Schemes 4 and 5. Analogous to the carbocations, the rearrangement of the 1,3 radical cations, generated by electron transfer, is of the Wagner−Meerwein type;[1,8] consequently, the preferred site of positive charge localization in the corresponding 1,3 radical cations determines the regioselectivity. As elaborated for the reference housane **1** (Scheme 4), the regioselectivity may be accounted for by comparison of the SOMO energies of the corresponding radical fragments.[1] For the radical cation **A**, the $Me(CH_3)_2C•$ radical fragment lies in energy above $Ph(CH_3)_2C•$, and thus the positive charge will be localized at the Me terminus and the 1,2 shift will occur preferentially to the methyl-

(8) Shaik, S. S.; Dinnocenzo, J. P. *J. Org. Chem.* **1990**, *55*, 3434−3436.

Scheme 4. Electron-Transfer and Acid-Catalyzed Rearrangements of the Housane 1



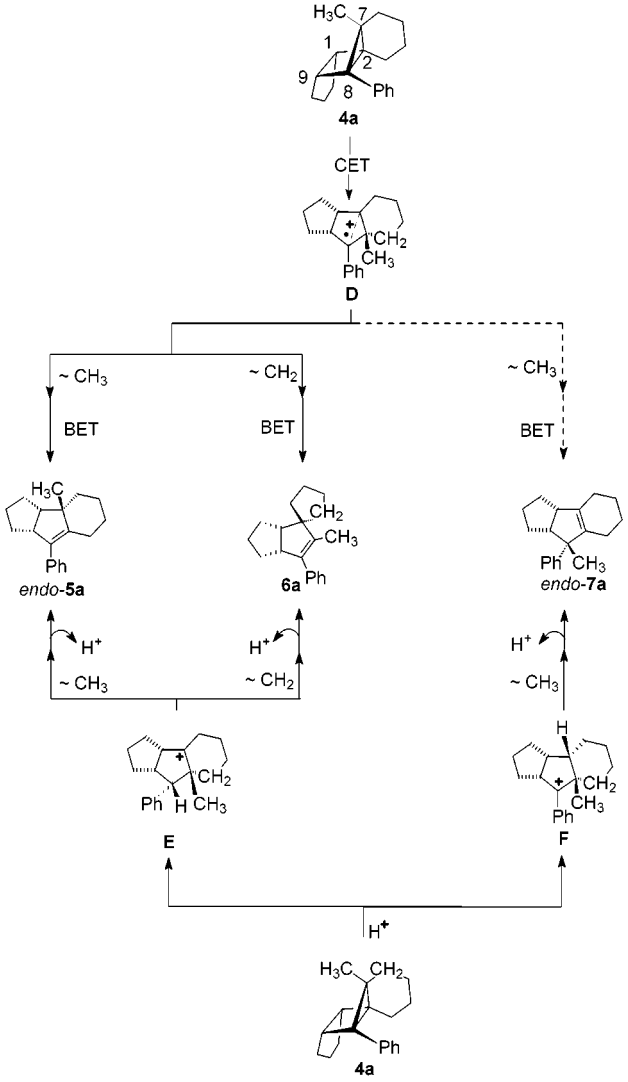
substituted bridgehead site to afford regioselectively the diquinane **2**.

The same rationale also applies to the radical cation **D** derived from the annelated housane **4a** (Scheme 5). Again, the positive charge is localized at the alkyl-substituted C-2 site due to the better radical-stabilizing ability of the phenyl group. Consequently, the migration takes place to the C-2 rearrangement terminus to afford the two cyclopentenes *endo*-**5a** and **6a** in nearly equal amounts (Table 2, entry 1).

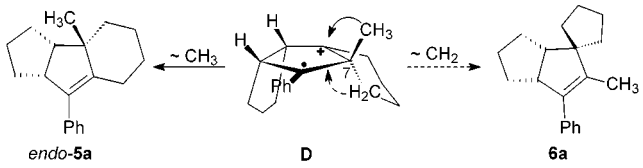
Besides the valuable mechanistic information on regioselectivity, the annelated housane **4a** additionally offers the opportunity to deduce the favored conformation of radical cation **D** for the two migrating groups at the C-7 position. The experimental fact that both rearrangement products *endo*-**5a** and **6a** are formed strongly suggests the intermediacy of a planar radical cation **D** in the rearrangement step (Scheme 6). Were a puckered conformation involved, dominant shift of the *endo*-methyl group would be expected.[3]

Replacement of the phenyl substituent in housane **4a** by a methyl group results in the total loss of the regioselectivity for the electron-transfer rearrangement (Table 2, entry 2). Since the methyl group at the C-2 and the methylene group at the C-8 rearrangement termini possess comparable ability to stabilize the radical and

Scheme 5. Electron-Transfer and Acid-Catalyzed Rearrangements of the Housane 4a



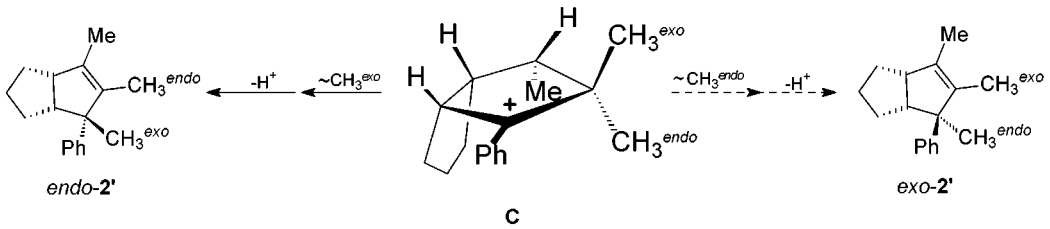
Scheme 6. Rearrangement of the Cyclopentane-1,3-diyl Radical Cation D Derived from the Housane 4a



cation centers, a low regioselectivity is expected, as observed. Consequently, migration to the bridgehead positions C-8 (product *endo*-**7b)** and C-2 (products *endo*-**5b** and **6b**) takes place with nearly equal facility (Table 2, entry 2).

The mechanistic details of the acid-catalyzed rearrangements are given in the lower pathways of Scheme 4 for the housane **1** and Scheme 5 for the housane **4a**. The product data for the housane **1** (Table 1) and **4a** (Table 2, entry 3) display that a reversal of the regioselectivity in the 1,2 shift has occurred compared to the electron-transfer rearrangement. This unequivocally reflects the different electronic nature of the carbocation and the radical-cation intermediates.[1] The addition of a proton to the housane should generate the most stable

Scheme 7. Diastereoselectivity for the 1,2 Migration of the *Exo*- and *Endo*-Methyl Groups in the Cation C Derived from the Housane 1



carbocation, and hence the charge-stabilizing ability of the phenyl group at the cationic site determines the regioselectivity in the 1,2 migration of this bona fide Wagner−Meerwein rearrangement.[9] Thus, in the case of the housane **1,** the carbocation **C** (Scheme 4) is preferentially formed over the carbocation **B** and subsequent 1,2 shift of both methyl groups would lead to the two diastereomeric diquinanes *endo*-**2′** and *exo*-**2′** after proton loss. The fact that both *endo*-**2′** and *exo*-**2′** diastereomers are formed implies an open planar conformation for the carbocation **C** as precursor to these rearrangement products (Scheme 7). The preference for the *endo*-**2′** diastereomer is presumably due to the lower steric repulsion of the *exo*-methyl migrant (originally the *endo*-methyl group in the housane **1**) during its transposition (Scheme 4).

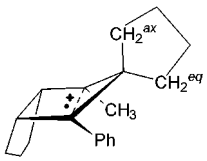
Evidently, the steric interactions between the annelated cyclopentane ring and the *exo*-methyl group are absent. Product stability is apparently not responsible for this diastereoselective discrimination, because DFT computations reveal that both the *endo*-**2′** and *exo*-**2′** diastereomeric diquinanes are about of equal energy and ca. 4 kcal/mol higher in energy than the minor regioisomer **2**. The latter regioisomer results from protonation at the phenyl-substituted bridgehead and subsequent methyl migration. The lack of stereochemical information in the rearrangement product **2** does not disclose whether only the *endo*-methyl or also the *exo*-methyl group migrates.

For the acid-catalyzed rearrangement of the annelated housane **4a**, the same electronic bias (positive charge stabilization) of the phenyl substituent at the position C-8 applies. Consequently, the carbocation **F** is preferentially formed over the carbocation **E** by protonation at the C-2 position of the housane **4a** (Scheme 5). Rearrangement of the carbocation **F** and subsequent proton loss leads to the triquinane-like *endo*-**7a** as major regioisomer. In the case of the carbocation **E,** migration of the methyl group to the C-2 position affords the *endo*-**5a** (major) and of the annelated cyclohexane ring the **6a** (minor) rearrangement products. The formation of both *endo*-**5a** and **6a** suggests again that migration occurs from a planar conformation of the carbocation **E** as precursor, analogous to the carbocation **C** (Scheme 7), except that the positive charge in **E** is localized at the alkyl-substituted bridgehead position C-2.

Acid-catalyzed rearrangement of the methyl-substituted housane **4b** yields exclusively the quinane *endo*-**5b** (Table 2, entry 4). Hence, in the absence of the electronic bias of phenyl stabilization, protonation solely occurs at the sterically less hindered C-8 methyl site. Presumably, the regioselectivity is thereby governed by steric and not by electronic factors. To account for the exclusive formation of the rearrangement product *endo*-**5b**, we suggest that the 1,2 shift of the *exo*-methyl group to the bridgehead position C-2 occurs before an open planar carbocation is attained.[10] A planar carbocation should additionally lead to the spirocyclic isomer **6b** by migration of the methylene group in the annelated six-membered ring.

Of mechanistic significance and synthetic importance is to analyze the observed selectivities of the two housanes **3a** and **4a** in terms of their structural differences, namely the spirocyclic skeleton of the former versus the annelated one of the latter. The fact to emphasize is that such distinct skeletal connectivities lead to the same triquinane-type regioisomer **5a**, but of opposite configuration at the migration terminus, i.e., *exo*-**5a** from the spirocyclic precursor **3a** and *endo*-**5a** from the annelated **4a** (Scheme 2).

In regard to the regioselectivity, the formation of the same regioisomer, namely exclusive migration to the alkylated terminus for both housanes **3a** and **4a**, cannot have a structural origin. It is imposed by the more effective electronic stabilization of the radical center by the phenyl group. This regiocontrol has been rationalized in terms of an molecular-orbital-interaction diagram of the respective radical fragments.[1]



G

The diastereoselectivity, however, is conformationally controlled, which definitely relates to the structural features of the housanes **3a** and **4a**. For a puckered radical cation **G** with the initial housane **3a** geometry (stereochemical memory effect),[1] the pseudoaxial *endo* substituent migrates in preference, because the stereoelectronic requirement of a coplanar alignment of the migrant relative to the migration terminus is best fulfilled.[4] Thus, the *endo*-methylene group in the spirocyclopentane ring transposes to afford the *exo*-**5a** rearrangement product; correspondingly, for the **4a** housane the *endo*-methyl substituent migrates to form the *endo*-**5a** diastereomer (Scheme 2). However, while for the spirocyclic housane **3a** the *exo*-**5a** diastereomer is the exclusive product,[5] for the annelated housane **4a** the *endo*-**5a** diastereomer is formed in about the same amount as the migration of the *exo*-methylene group in the cyclohexene ring to the **6a** isomer (Table 2, entry 1).

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(10) Wiberg, K. B.; Kass, S. R.; Bishop, K. C., III. *J. Am. Chem. Soc.* **1985**, *107*, 996−1002.

This lack of diastereoselectivity in the case of housane **4a** is attributed to a planar conformation of the intermediary radical cation (Scheme 6). The question is why the puckered radical cation **G** intervenes in the electron-transfer rearrangement of the spirocyclic housane **3a**, but the planar **D** in the annelated housane **4a**. In the absence of rigorous computations, we may only speculate: Presumably, the ring strain in the spirocyclic housane **3a** generates on electron transfer the puckered radical cation **G**, in which the pseudoaxial *endo* substituent shifts prior to planarization. In contrast, for the housane **4a**, the annelated cyclohexane ring promotes planarization to relieve strain in the radical cation **D**, and loss of diastereoselectivity is observed.

In conclusion, the regioselectivity in the electron-transfer as well as in the acid-catalyzed rearrangement of the housanes **1** and **4** is determined by electronic effects of the substituents at the rearrangement termini. The diastereoselectivity of the 1,2 migration, however, is controlled by conformational and steric factors in the intermediates. Moreover, the structurally more elaborate spirocyclic (**3a**) and annelated (**4**) housanes, conveniently prepared through the Hünig isopyrazole-cycloaddition method,[6] provide a practical and facile synthetic access to novel diquinane- and triquinane-related structures, whose regiochemical and stereochemical features may be manipulated by operating under electron-transfer or acid-catalyzed conditions.

Acknowledgment. Generous financial support by the Volkswagen-Stiftung, Deutsche Forschunggemeinschaft (DFG), and the Fonds der Chemischen Industrie is gratefully appreciated.

Supporting Information Available: Experimental section. This material is available free of charge via the Internet at http://pubs.acs.org.

JO016224X