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STEREOMUTATION OF ENDO-2-PHENYL-ENDO-6-TROPYLIOBICYCLO[2.2.2]OCTANE TO THE EXO-6-TROPYLIO ISOMER. STERIC REPULSION BETWEEN THE PHENYL AND TROPYLIUM RINGS SHOWING INTRAMOLECULAR CHARGE-TRANSFER

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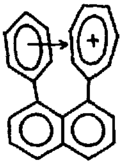
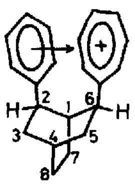
Abstract: endo-2-Phenyl-endo-6-tropyliobicyclo[2.2.2]octane **2** exhibits intramolecular charge-transfer (CT) interaction, but rearranges to exo-6-tropylio isomer **3** in acetonitrile with the **2**/**3** ratio of ca.0.07 at equilibrium.This ratio indicates that the steric repulsion between the face-to-face phenyl and tropylium rings at ca.2.5Å is estimated to be at least ca.1.6kcal/mol.

Tropylium ions containing a facing phenyl ring are stabilized by intramolecular charge-transfer (CT) interaction. This is evidenced by the appearance of charge-transfer bands[1] and greater cationic stability than their corresponding model compounds as determined by pK_R+ values or reduction potentials.[2] On the other hand, these *electronically stabilized* tropylium ions are supposed to be *sterically destabilized* by conflicting repulsive interaction between the two facing rings. We now wish to report on semiquantitative evaluation of the repulsion between a tropylium and a phenyl ring which are facing at a distance of ca. 2.5 Å.

Previously we reported the face-to-face charge-transfer interaction in 1-phenyl-8-tropylionaphthalene **1**.[2a] In order to eliminate the electronic effect of the naphthalene ring on the cationic stability of **1**, we decided to evaluate the cationic stabilities of endo-2-phenyl-endo-6-tropyliobicyclo[2.2.2]octane **2** and related model ions **3** and **4**. Molecular models show that **2** holds the phenyl and tropylium rings in a face-to-face arrangement with the C-2 - C-6 distance of ca. 2.5 Å just like in **1**. Unexpectedly, when **2**·SbF_6^-,[3] mp 146°C (dec.), was dissolved in acetonitrile-d_3 at 23°C, it rearranged to exo-6-tropylio isomer **3** ($t_{1/2}$ = ca. 8 days). The stereomutation of **2** to **3** was followed in acetonitrile-d_3 at 23°C by observing the change in the ^1H NMR spectra (Fig.1). After 40 days the equiliblium (**2** ⇄ **3**) was attained with the **2**/**3** ratio of 0.068±0.04. The ratio indicates that **2** is 1.5-1.6 kcal/mol less stable than **3** though **2** must be stabilized by the through-space π-electron donation from the facing phenyl ring. This stereomutation was not observed in less basic dichloromethane at 23°C over a period of 14 days (**2**/**3** ratio >24). Thus, the stereomutation seems to proceed



1



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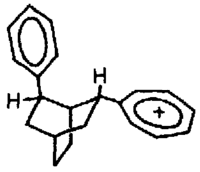

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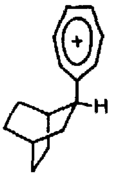

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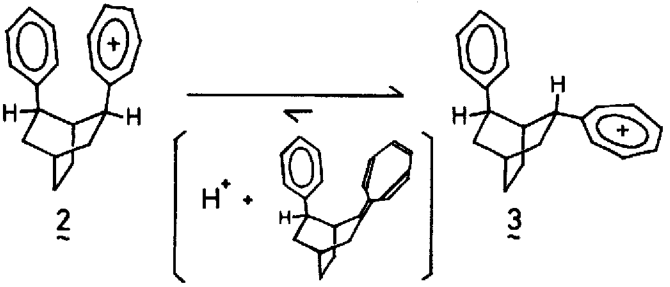


Scheme 1

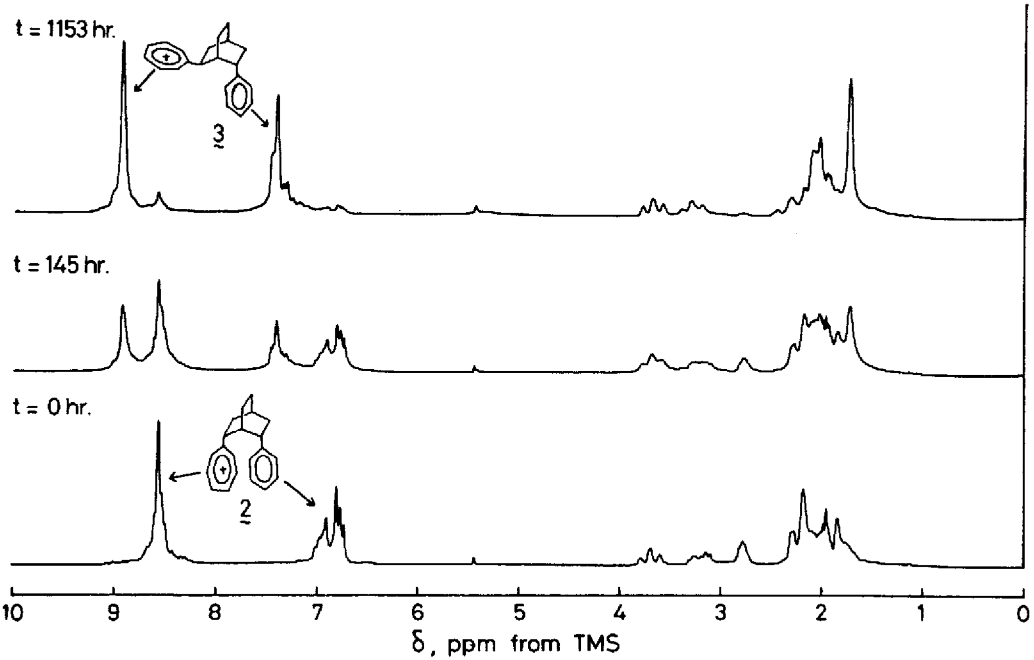


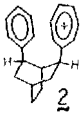
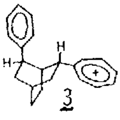
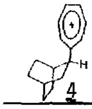
Fig. 1. Monitoring of the Stereomutation of **2** to **3** by 90MHz ^{1}H NMR in CD_3CN at 23°C.

through abstraction of the α-hydrogen by acetonitrile as a base followed by protonation of the heptafulvene from the opposite side (Scheme 1).[4]

In the electronic spectra taken in acetonitrile, **2** exhibits an absorption band at 362nm (ε 2470), which is absent in the spectrum of **3**, **4**, or endo-2-phenyl-endo-6-phenylbicyclo[2.2.2]octane **5**.[3] Based on a marked bathochromic shift observed upon changing the solvent to less polar dichloromethane (381nm) and the constancy of the absorption coefficient despite the change in concentration, this absorption is assigned to the intramolecular CT band. The value of the CT energy in **2** (3.35ev) is in good agreement with that observed in **1**(3.32ev).

The spectral data of **2**, **3**,[5] and **4**[6] are listed in Table 1. Due to mutual shielding of the facing aromatic rings, the ^{1}H NMR signals for the phenyl and tropylium ring protons of **2** are shifted upfield by 0.54 and 0.44ppm, respectively, as compared with those for the aromatic protones of **3** and **4**. The amounts of upfield shifts are quite close to those observed in **1**,[2a] suggesting the similarity in their molecular arrangement.

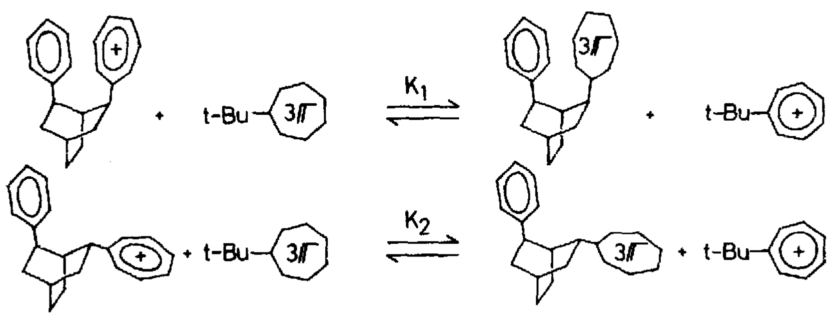
Table 1. Spectral Data for **2**·SbF_6^-, **3**·SbF_6^-, and **4**·ClO_4^-.[a]

Compd	^{13}C NMR (CD_2Cl_2)[b] δ/ppm	^{1}H NMR (CD_2Cl_2/TMS)[c] δ/ppm	UV (CH_3CN) λ/nm (log ε)
 **2**	24.7(t), 25.5(d), 28.7(t), 29.6(t), 31.6(t), 40.4(d), 42.2(d), 47.7(d), 127.0(d), 128.2(d), 128.7(d), 143.9(s), 150.0(d), 151.2(d), 152.1(d), 181.3(s)	1.7–2.4(m, 9H), 2.7–2.9(m, 1H), 3.1–3.4(m, 1H), 3.68(br t, 1H, J=9Hz), 6.7–7.1(m, 5H), 8.3–8.7(m, 6H)	362(3.39), 289(2.46), 214(4.35)
 **3**	21.1(t), 24.7(t), 25.6(d), 30.2(t), 32.8(t), 40.1(d), 42.2(d), 43.7(d), 126.7(d), 127.8(d), 128.9(d), 143.8(s), 152.5(d), 152.7(d), 154.2(d), 181.1(s)	1.6–2.5(m, 10H), 3.34(br t, 1H, J=9Hz), 3.72(br t, 1H, J=9Hz), 7.2–7.5(m, 5H), 8.7–9.1(m, 6H)	304(3.67), 283sh(3.59), 218(4.36)
 **4**	19.6(t), 24.3(d), 24.5(t), 25.0(t), 27.4(t), 32.4(t), 32.5(d), 48.9(d), 152.7(d), 154.3(d), 180.5(s)	1.3–2.4(m, 12H), 3.73(br t, 1H, J=9Hz), 9.14(s, 6H)	309(3.94), 253sh(4.04), 219(4.60)

a) All the new compounds gave satisfactory elemental analyses. b) 22.5 MHz. δ values calculated based on δ = 53.60 ppm for CD_2Cl_2. c) 90 MHz.

In order to examine the effect of this intramolecular CT interaction upon the electronic stability of the tropylium ion, the reduction potentials (E_{red}) were determined by cyclic voltammetry. The E_{red} values (peak potentials) of **2**, **3**, and **4** in dichloromethane are -0.715, -0.618, and -0.636 V vs Ag/Ag$^+$,[7] respectively, indicating that **2** is *electronically* more stabilized than **3** by ca. 2.2 kcal/mol.

Attempts to measure the pK_R+ value as another criterion of cation stability in aqueous organic solvents were unsuccessful due to the stereomutation occurring during the measurement. Therefore, as a substitute for the pK_R+ value, the relative stability of **2** and **3** with reference to t-Bu$C_7H_6^+$ was estimated by determining equilibrium constants K_1 and K_2[8] for the equation (1) and (2), respectively, by means of ^{1}H NMR in dichloromethane-d_2 at 25°C.[9] This method also indicated that **2** is *electronically* more stable than **3** by 0.4–1.1 kcal/mol.



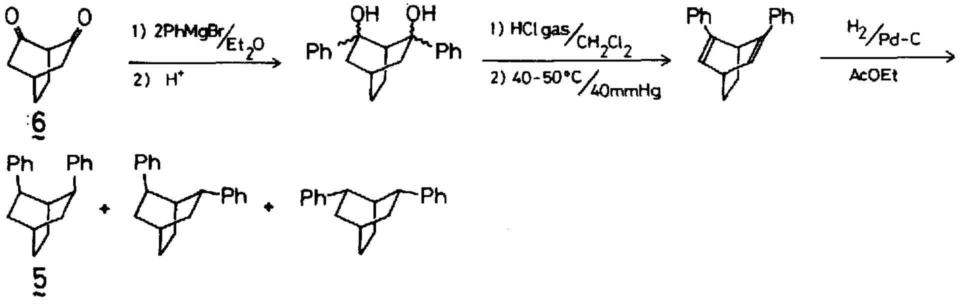
(1)

(2)

According to these observations, the tropylium ion **2** is certainly stabilized as compared with the tropylium ion **3**, by the through-space π-electron donation from the facing phenyl ring. But the ratio at equilibium for the stereomutation (**2**/**3**=ca.0.07) suggests that the tropylium ion **2** is *thermodynamically* less stable than **3**. Most probably, the major factor for the destabilization of **2** is the steric repulsion between the face-to-face phenyl and tropylium rings .

References and Notes

1. a) J. G. O'Connor and P. M. Keehn, J. Am. Chem. Soc., **98**, 8446 (1976); b) H. Horita, T. Otsubo, Y. Sakata, and S. Misumi, Tetrahedron Lett., **1976**, 3899; c) H. Horita, T. Otsubo, and S. Misumi, Chem. Lett., **1978**, 807; d) R. Gray and V. Boekelheide, J. Am. Chem. Soc., **101**, 2128 (1979); e) Y. Sekine and V. Boekelheide, ibid., **103**, 1777 (1981).
2. a) K. Komatsu, N. Abe, K. Takahashi, and K. Okamoto, J. Org. Chem., **44**, 2712 (1979); b) K. Komatsu, K. Takahashi, and K. Okamoto, Tetrahedron Lett., **1979**, 4747.
3. For the synthesis of 2, a new hydrocarbon 5 was synthesized from the diketone 6 [H. Gerlach and W. Müller, Angew. Chem., **84**, 1110 (1972).] as shown below. 5 was separated from other isomers by MPLC over SiO_2 (white plates, mp 95-96°C, 14% yield from 6). The CuBr-catalyzed reaction of 5 with CH_2N_2 in CH_2Cl_2 gave 20% of the cycloheptatriene derivatives. The hydride abstraction with $Ph_3C^+SbF_6^-$ in CH_2Cl_2 gave $2\cdot SbF_6^-$ in 76% yield as a greenish-yellow powder.



4. The intermediacy of the heptafulvene derivative in the stereomutation of 4 was proved by trapping with TCNE to give the [8+2] cycloaddition product. Detailes will be reported elsewhere.
5. exo-6-Tropylio isomer 3 was isolated as the SbF_6^- salt, pale-brown powder, mp 163°C (dec.) from the equiliblium mixture by repeated reprecipitation (CH_2Cl_2/Ether).
6. 4 (mp 123-126°C, dec.) was synthesized as the ClO_4^- salt from 2-phenylbicyclo[2.2.2]octane [A. N. Akopyan, V. S. Aslamazyan, and S. G. Kon'kova, Arm. Khim. Zh., **28**, 101 (1975).], which in turn was synthesized from 2-phenylbicyclo[2.2.2]oct-2-ene [D. C. Kleinfelter and P. v. R. Schleyer, J. Am. Chem. Soc., **83**, 2329 (1961).].
7. Scan rate, 0.1 V/sec; [cation] = 1mM in CH_2Cl_2; supporting electrolyte, Bu_4NClO_4 (0.1M); reference electrode, Ag/Ag^+ (0.01M) in CH_3CN.
8. The observed values of K_1 and K_2 were 0.1-0.2 and 0.4-0.6, respectively.
9. S. V. McKinley, J. W. Rakshys, Jr., A. E. Young, and H. H. Freedman, J. Am. Chem. Soc., **93**, 4715 (1971).

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