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A Facile Synthesis of Cyclohepta[*a*]thieno[*c*]naphthalenylium Ions. Intramolecular Cyclization of *o*-Thienylcycloheptatrienylbenzenes

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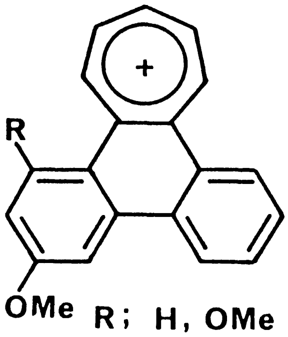
The intramolecular Friedel-Crafts type reaction of *o*-thienylcycloheptatrienylbenzenes in one pot reaction has allowed the construction of title compounds having new 18 π-electron systems with the isoelectronic structure of triphenylene.

Recently, we reported the synthesis of cyclohepta[*ℓ*]phenanthrenylium ions (1) by the intramolecular Friedel-Crafts type reaction of 2-tropyliobiphenyls which were prepared in situ from 2-biphenylylcycloheptatrienes.1) Although the intermolecular electrophilic substitution of the tropylium ion with electron-rich aromatic compounds such as polyphenols2) and azulenes3) to afford the corresponding tropylidene derivatives are well known, the above intramolecular reaction is the only example reported to date. Hence



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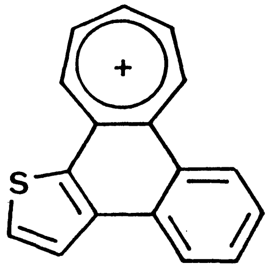

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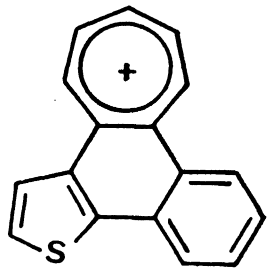

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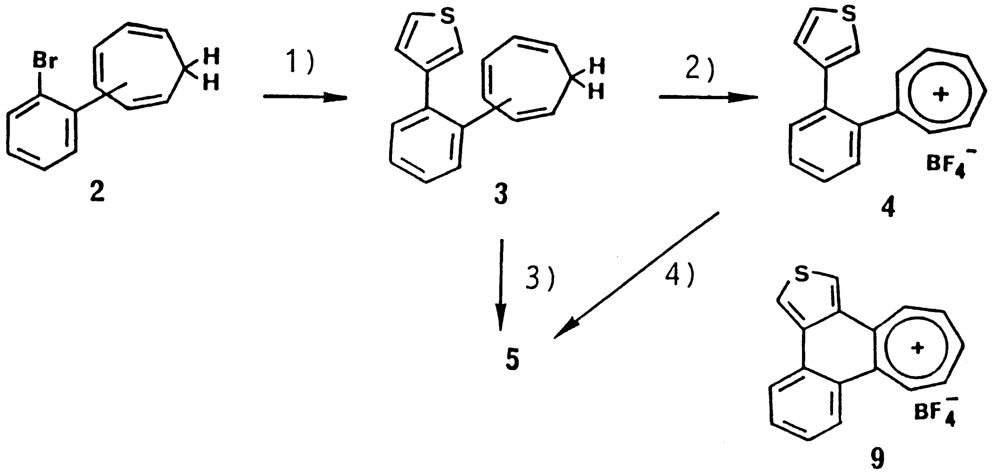
we wanted to apply such type of reaction to see the scope and limitation of the reaction and to construct new π-electron systems. In this communication we report the synthesis of two cyclohepta[*a*]thieno[*c*]naphthalenylium ions (**5** and **7**) which are the analogues of triphenylene4) having both electron-rich and electron-deficient aromatic rings, thiophene and tropylium ion, respectively, in place of phenyl rings.

The isomeric mixture of *o*-bromophenyltropylidene (**2**) prepared by palladium(II) catalyzed Heck reaction of cycloheptatriene and *o*-bromoiodobenzene was treated with 3-thienylmagnesium bromide in the presence of nickel(II) acetylacetonate in THF to give a mixture of isomers of *o*-[3-thienyl]phenyltropylidene (**3**) as colorless oil in 68.7% yield.6) When **3** was treated with an equimolar amount of triphenylmethyl (trityl) tetrafluoroborate in dichloromethane for 3 min at ambient temperature followed by addition of dry ether, *o*-[3-thienyl]tropyliobenzene (**4**) was obtained as orange powder (mp > 200°C), which changed spontaneously into cyclohepta[*a*]thieno[3,2-*c*]naphthalenylium tetrafluoroborate (**5**) on standing the dichloromethane solution of **4**. When **3** was treated with an equimolar amount of the trityl salt for 3 h, **5** was isolated (32%) as a sole crystalline product.7) When 2.5 equivalent of the trityl salt was employed the yield of **5** reached up to 74.0%. The structure of **5**8) was confirmed on the basis of its spectroscopic properties and elemental analysis.

The synthesis of another cyclohepta[*a*]thieno[*c*]naphthalenylium ion **7** was performed in a similar manner. Thus the isomeric mixture of **6** obtained from 2-thienylmagnesium bromide and **2** was treated with 2.5 equivalent of the trityl salt in dichloromethane for 70 h to give **7** as orange powder(mp >



Scheme 1. Reagents and Conditions: 1) 3-thienylmagnesium bromide, $Ni(acac)_2$, in THF. 2) Ph_3CBF_4(1 equiv.) in CH_2Cl_2, 3 min. 3) Ph_3CBF_4 (2.5 equiv.) in CH_2Cl_2, 3h. 4) on standing in CH_2Cl_2, 2 h.

200 °C) in 70.0% yield.[7)] When **6** was treated with an equimolar amount of the trityl salt in dichloromethane for 10 min at ambient temperature uncyclized tropylium ion (**8**) was obtained as yellow prisms (mp > 200°C) in 85.0% yield, which could be stored unchanged for long period at ambient temperature (Scheme 2).

As illustrated in Fig. 1, the electronic spectra of both **5** and **7** exhibit broad long wavelength absorption around 480 nm, suggesting positive charge delocalization in these molecules to some extent.

The chemical shifts of seven-membered ring protons in **5** and **7** (δ =8.88-9.06 for **5**, 8.52-9.02 for **7**, except H-8 and H-12) are at upper field than those of the tropylium ion itself (δ=9.20). On the contrary, the thiophene ring

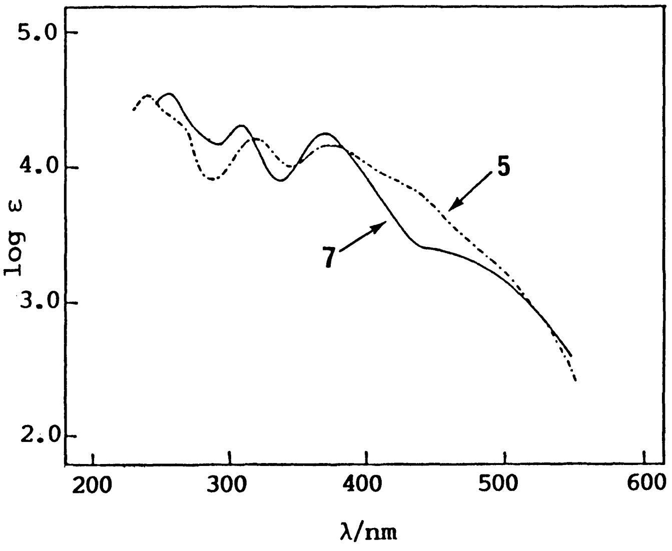
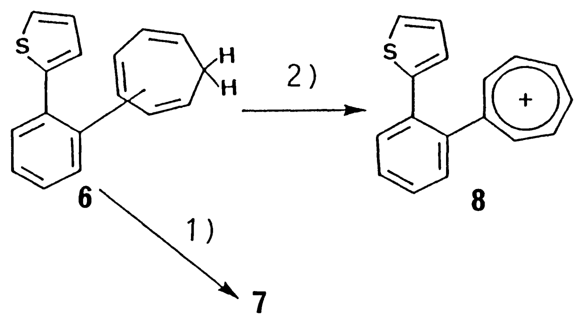


Fig. 1. UV-Vis spectra of 5 and 7 in CH_2Cl_2.



Scheme 2. Reagents and Conditions: 1) Ph_3CBF_4(2.5 equiv.) in CH_2Cl_2, 70h. 2) Ph_3CBF_4(1 equiv.) in CH_2Cl_2, 10 min.

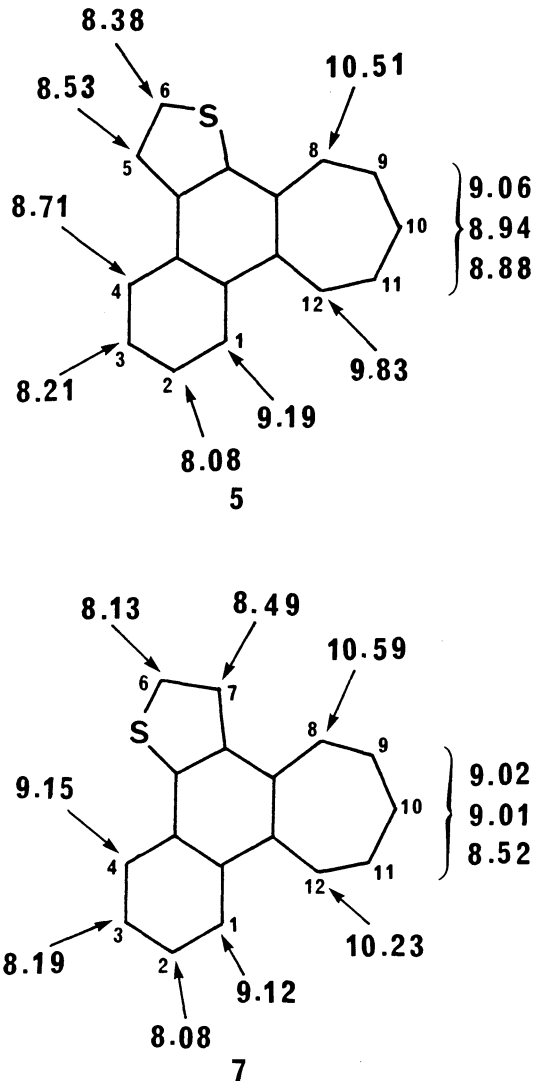


Fig. 2. ^1H-NMR data of 5 and 7. (δ value; in CD_3CN, 400 MHz).

protons and benzene ring protons resonated at the considerably lower magnetic fields than those of thiophene itself(δ=7.10 and 7.30) and of benzene itself, respectively. These facts also indicate the charge delocarization in the peripheral manner (Fig. 2).

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4)Recently, much attention is focused on substituted triphenylenes as potential organic ferromagnet. *cf.* R. Breslow, B. Jaun, R. Klutz, and C. -Z. Xia, *Tetrahedron,* **38**, 863 (1982); T.J. LePage and R. Breslow, *J. Am. Chem. Soc.*, **109**, 6412 (1987), and references therein.

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6)All the new compounds described in this paper afforded satisfactory spectroscopic data as well as elemental analyses.

7)The reduction potentials of **5** and **7** estimated by cyclic voltammetry (-0.015 V and -0.070 V, respectively) suggest the reduced stability of these cations compared with tropylium ion itself (-0.185 V) which is consistent with calculated results (HMO).

8)Though one more isomer of cyclohepta[*a*]thieno[*c*]naphthalenylium ions, *i.e.* **9**, is possible to be formed, it would be ruled out by general reactivity of the thiophene ring with higher nucleophilicity of 2-position than 3-position, which is also confirmed by the estimation of HMO calculations on **4** and by the observation of the ^{1}H-NMR coupling constant for the thiophene ring (J=5.3 Hz).

9)The satisfactory assignment of each proton and the coupling pattern was made by ^{1}H-^{1}H COSY-experiments.

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