

NOVEL PENTACYCLIC π -CONJUGATED CATIONS CONTAINING BOTH HETEROAROMATIC UNITS AND A TROPYLIUM ION. 2. SYNTHESIS OF CYCLOHEPTA[*a*]BENZOFURO[*c*]NAPHTHALENYLIUM AND CYCLOHEPTA [a]BENZOTHIENO[*c*]NAPHTHALENYLIUM IONS.

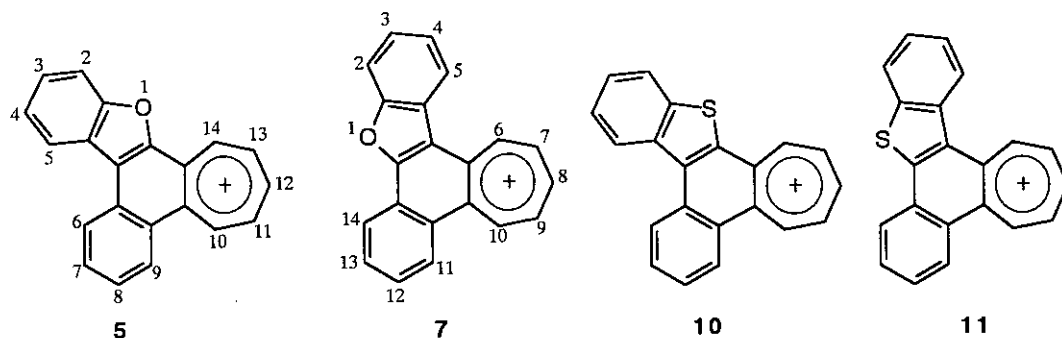
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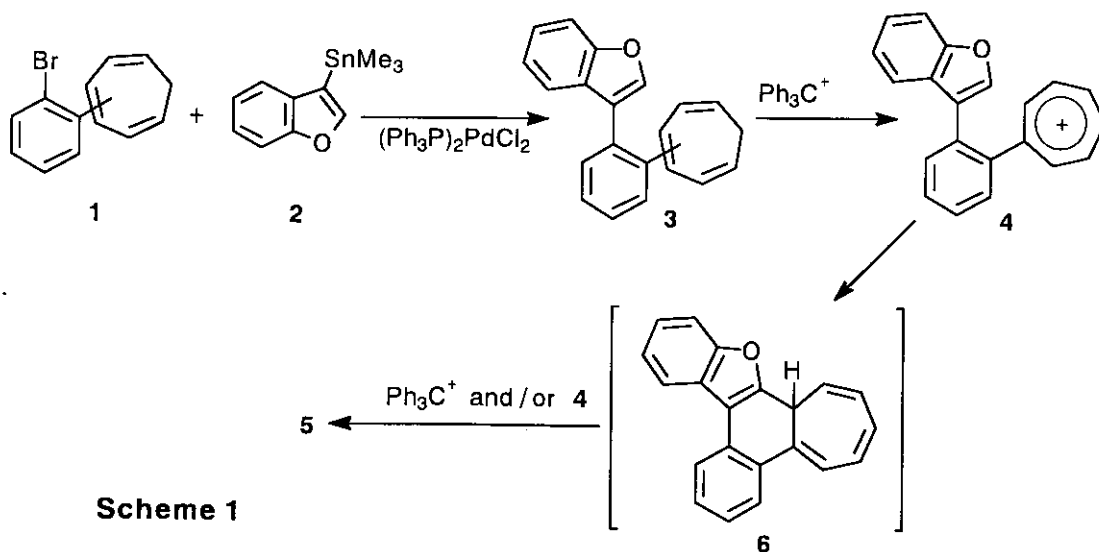
Abstract- Two isomeric pairs of cyclohepta[*a*]benzofuro[*c*]naphthalenylium ions (**5** and **7**) and cyclohepta[*a*]benzothieno[*c*]naphthalenylium ions (**10** and **11**) have been synthesized by an intramolecular Friedel-Crafts type reaction of *o*-benzofurylcycloheptatrienylbenzenes (**3** and **8**) and *o*-benzothienylcycloheptatrienylbenzenes (**14** and **15**), respectively, in a one-pot reaction.

Fused π -conjugated ring systems containing a tropylium unit are molecules of both theoretical and experimental interest, and various kinds of such compounds have been prepared.¹ However the reported synthetic methods generally suffered from tedious multistep procedures and low yields at the stage of construction of the unsaturated seven-membered ring.¹ Recently, we reported the one-pot synthesis of two isomers of tetracyclic cyclohepta[*a*]thionaphthalenylium ions on the treatment of the corresponding *o*-thienylcycloheptatrienylbenzenes with triphenylmethyl (trityl) tetrafluoroborate in reasonable yields.² Our synthetic strategy was to use commercially available 1,3,5-cycloheptatriene as the seven-membered unit. In order to study the general applicability of this reaction, we extended our study to benzoannulated heteroaromatic systems.³ Here we report a facile one-pot synthesis of the title compounds (**5**, **7**, **10** and **11**), which are the isoelectronic carbocations of the potent carcinogenic benzo[*g*]chrysene, by an intramolecular Friedel-Crafts type reaction of *o*-heteroaryltropyliobenzenes *in situ* from the corresponding



o-heteroarylcycloheptatrienylbenzenes. These carbocations are expected to show unique properties, because they are novel pentacyclic conjugated carbocations containing both an electron-deficient tropylium moiety and an electron-rich five-membered heteroaromatic moiety.

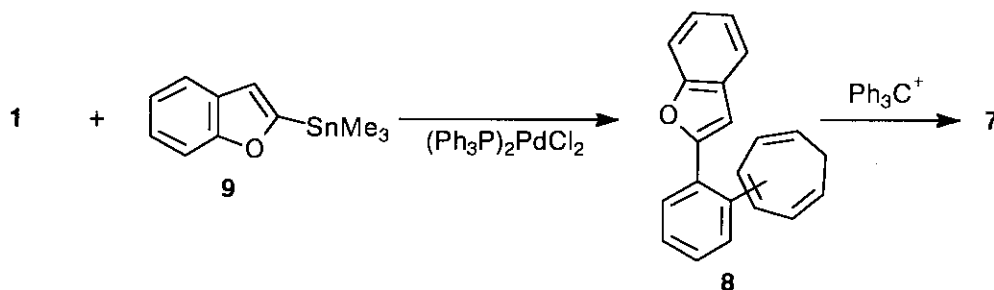
The palladium(II)-catalyzed cross-coupling reaction⁴ of the isomeric mixture of *o*-bromocycloheptatrienylbenzene (**1**),⁵ prepared from *o*-bromiodobenzene and 1,3,5-cycloheptatriene, with 3-trimethylstannylbenzofuran (**2**) afforded an isomeric mixture of *o*-[3-benzofuryl]cycloheptatrienylbenzene (**3**) as a pale yellow oil in 64.7 % yield. When **3** was treated with an equimolar amount of trityl tetrafluoroborate in dichloromethane at 0 °C for 3 min followed by addition of dry ether, *o*-[3-benzofuryl]tropolio benzene (**4**)⁶ was obtained as an orange powder in 76.8 % yield. On standing the dichloromethane solution of **4** or standing this orange powder in a desiccator, **4** changed spontaneously into a mixture including the cyclized tropylium ion, cyclohepta[*a*]benzofuro[2,3-*c*]naphthalenylium tetrafluoroborate (**5**). When **3** was treated with 2.5 equivalents of trityl tetrafluoroborate in dichloromethane at ambient temperature for 15 h followed by addition of dry ether, **5** was obtained as a reddish-brown powder in 68.9 % yield. The formation of



Scheme 1

5 from **3** is rationalized by the reaction sequence in Scheme 1. The initially formed tropylium ion derivative (**4**), which has both an electron-deficient site (tropylium ion) and an electron-rich site (furan ring), reacted intramolecularly to give the six-membered neutral intermediate (**6**). Although **6** could not be definitively identified in the reaction mixture, its production is feasible and therefore assumed in this procedure. Subsequent hydride abstraction from **6** with the trityl salt and/or the tropylium derivative (**4**),⁷ gave the final product (**5**). Although the intermolecular electrophilic addition of the tropylium ion to electron-rich aromatic compounds such as phenols⁸ and azulenes⁹ is well-known, such intramolecular Friedel-Crafts type reaction is very rare.¹⁰

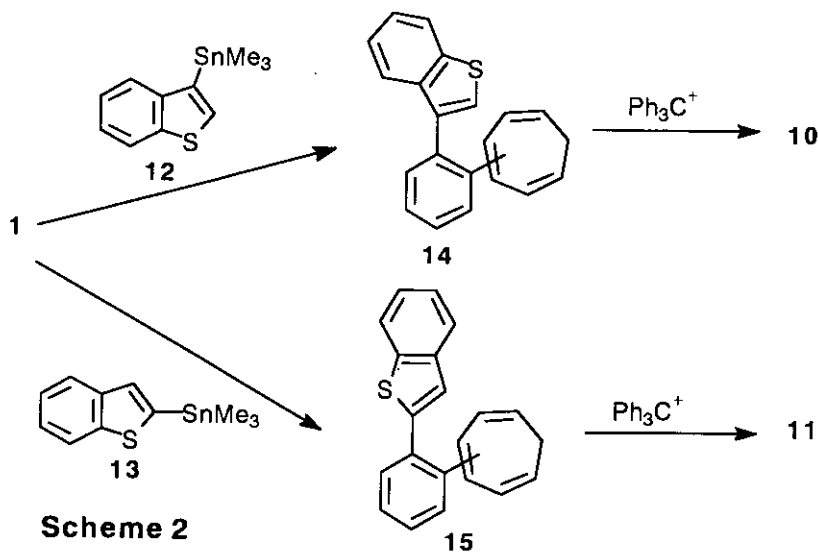
The synthesis of another isomer, cyclohepta[*a*]benzofuro[3,2-*c*]naphthalenylium tetrafluoroborate (**7**) was performed in a similar manner. Thus, *o*-[2-benzofuryl]cycloheptatrienylbenzene (**8**) obtained from 2-trimethylstannylbenzofuran (**9**) and **1** was treated with 2.5 equivalents of the trityl tetrafluoroborate in dichloromethane for 10 h at ambient temperature to give **7** as a crimson powder in 73.9 % yield.



The synthesis of benzothiophene systems, cyclohepta[*a*]benzothieno[2,3-*c*]naphthalenylium tetrafluoroborate (**10**) and cyclohepta[*a*]benzothieno[3,2-*c*]naphthalenylium tetrafluoroborate (**11**) was achieved in a similar manner as depicted in Scheme 2. **10** and **11** were obtained as thermally stable red needles in 60.0 and 61.5 % yields, respectively.

The structures of the obtained pentacyclic cations (**5**, **7**, **10** and **11**) were supported by their elemental analyses and their $^1\text{H-NMR}$, IR, and electronic spectral data, together with chemical reaction. Thus, on reduction with sodium borohydride in acetonitrile these cations were reduced to the corresponding tropyliidene compounds whose structures were determined from their mass and $^1\text{H-NMR}$ spectra. From these tropyliidene compounds the corresponding original cations (**5**, **7**, **10** and **11**) could be regenerated by the treatment with trityl tetrafluoroborate.

In conclusion, two isomeric pairs of cyclohepta[*a*]benzofuro[*c*]naphthalenylium ions and cyclohepta[*a*]benzothieno[*c*]naphthalenylium ions which are novel pentacyclic systems having both electron-rich and



electron-deficient aromatic rings, the heteroaromatic and tropylium ion, respectively, could readily be obtained. The key step is an intramolecular Friedel-Crafts type reaction of initially formed tropylium ion derivatives.

ACKNOWLEDGEMENTS

The authors wish to thank Miss Masuko Nishinaka for the elemental analyses and are grateful to Miss Reiko Yamamura and Miss Yasuko Mizuta for their helpful collaboration. The present work was supported in part by Grant-in-Aids for Scientific Research (C) (No. 08640685) from Ministry of Education, Science, Sports and Culture, Japan Government.

EXPERIMENTAL

All melting points were uncorrected. IR spectra were recorded on a Hitachi-Horiba FT-710 spectrophotometer. ¹H NMR spectra were obtained on a Hitachi R-24A spectrometer (60 MHz) and/or Bruker AC250 spectrometer (250 MHz). UV-vis spectra were taken on a Shimadzu UV-2200A spectrophotometer. Mass spectra were recorded on a Shimadzu GCMS QP2000A instrument.

Preparation of 3-trimethylstannylbenzofuran(2)

A solution of 3-bromobenzofuran (5.51 g, 28.0 mmol) in 20 mL of dry ether was treated with 48.6 mmol of *n*-butyllithium (30 mL of 1.62 M hexane solution) at -78 °C for 2 h under an argon atmosphere, and then a solution of trimethylstannyl chloride (11.0 g, 55.2 mmol) in 20 mL of dry ether was added dropwise

at -78°C during 30 min *via* a syringe. After stirring for 1 h at this temperature, the mixture was stirred for 2 h at room temperature, and then poured into ice-water. The mixture was extracted with ether, and the extracts were dried over Na_2SO_4 . After evaporating the solvent, the residue was distilled under reduced pressure to give 3-trimethylstannylbenzofuran as a pale yellow oil in 77.1% yield, 5.60 g; bp $103^{\circ}\text{C} / 3$ Torr; δ_{H} (60 MHz, CDCl_3 , Me_4Si) 0.52(s, 9H), 7.43~7.79(m, 5H).

Preparation of 3-trimethylstannylbenzothiophene(12)

In a similar manner as described above, **12** was prepared from 3-bromobenzothiophene as a pale yellow oil in 82.7% yield; bp $120^{\circ}\text{C} / 4$ Torr; δ_{H} (250 MHz, CDCl_3 , Me_4Si) 0.40(s, 9H), 7.28~7.39(m, 2H), 7.40(s, 1H), 7.80 (dd, 1H, $J=8.0$ Hz, $J=1.0$ Hz), 7.95(dd, 1H, $J=8.0$ Hz, $J=1.0$ Hz).

Preparation of 2-trimethylstannylbenzofuran(9)

A solution of benzofuran (5.52 g, 46.7 mmol) in 100 mL of dry ether was treated with 73.0 mmol of *n*-butyllithium (45 mL of 1.62 M hexane solution) at -20°C for 2 h under an argon atmosphere, and then a solution of trimethylstannyl chloride (16.7 g, 83.8 mmol) in 50 mL of dry ether was added dropwise at 0°C during 30 min *via* a syringe. The reaction mixture was stirred for 1 h at room temperature, and then poured into ice-water. The mixture was extracted with ether and the extracts were dried over Na_2SO_4 . After evaporating the solvent, the residue was distilled under reduced pressure to give 2-trimethylstannylbenzofuran as a pale yellow oil in 70.1% yield, 9.26 g; bp $105^{\circ}\text{C} / 6$ Torr, δ_{H} (60 MHz, CDCl_3 , Me_4Si) 0.30(s, 9H), 6.70(s, 1H), 6.90~7.43(m, 4H).

Preparation of 2-trimethylstannylbenzothiophene(13)

In a similar manner as described above, **13** was prepared from benzothiophene as a pale yellow oil in 93.7% yield; bp $131^{\circ}\text{C} / 4$ Torr; δ_{H} (250 MHz, CDCl_3 , Me_4Si) 0.40 (s, 9H), 7.20~7.32(m, 2H), 7.39(s, 1H), 7.77 (d, 1H, $J= 8.0$ Hz), 7.84(d, 1H, $J= 8.0$ Hz).

Preparation of o-[3-benzofuryl]cycloheptatrienylbenzene(3)

To a solution of **1** (1.64 g, 6.63 mmol) and **2** (1.85 g, 6.59 mmol) in 50 mL of dry THF was added bis(triphenylphosphine)palladium(II) chloride (450 mg, 0.64 mmol) under a nitrogen atmosphere, and the mixture was refluxed for 20 h. After cooling, the reaction mixture was poured into water, extracted with ether and the extracts were dried over Na_2SO_4 . The solvent was removed under reduced pressure, and the resulting residue was purified by column chromatography on silica gel to give **3** in 64.7% yield (1.22 g) as a pale yellow oil; MS: m/z 284(M^+); δ_{H} (60 MHz, CDCl_3 , Me_4Si) 1.83~2.31(m, 2H), 4.78~5.45(m, 2H), 5.68~7.94(m, 12H); Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{O}$; C,88.73; H,5.63. Found: C,88.68; H,5.70.

Preparation of *o*-[2-benzofuryl]cycloheptatrienylbenzene(8)

In a similar manner as described above, **8** was prepared in 64.7% yield as a pale yellow oil; MS: m/z 284(M^+); δ_H (60 MHz, $CDCl_3$, Me_4Si) 2.24~2.50(m, 2H), 5.07~5.53(m, 2H), 5.83~6.31(m, 2H), 6.57~6.75(m, 2H), 6.89~7.86(m, 8H); Anal. Calcd for $C_{21}H_{16}O$; C,88.73; H,5.63. Found: C,88.58; H,5.78.

Preparation of *o*-[3-benzothieryl]cycloheptatrienylbenzene(14)

In a similar manner as described above, **14** was prepared in 94.5% yield as a pale yellow oil; MS: m/z 300(M^+); δ_H (250 MHz, $CDCl_3$, Me_4Si) 1.70~2.80(m, 2H), 4.80~6.68 (m, 5H), 6.78~7.89(m, 9H); Anal. Calcd for $C_{21}H_{16}S$; C,83.96; H,5.37. Found: C,83.80; H,5.44.

Preparation of *o*-[2-benzothieryl]cycloheptatrienylbenzene(15)

In a similar manner as described above, **15** was prepared in 59.7% yield as a pale yellow oil; MS: m/z 300(M^+); δ_H (60 MHz, $CDCl_3$, Me_4Si) 2.26~3.27(m, 2H), 5.14~6.72 (m, 4H), 7.10~7.82(m, 10H); Anal. Calcd for $C_{21}H_{16}S$; C,83.96; H,5.37. Found: C,84.11; H,5.23.

Preparation of Cyclohepta[a]benzofuro[2,3-c]naphthalenylium Ions(5).

A solution of **3** (430 mg, 1.51 mmol) in 5 mL of dry dichloromethane was added to a solution of triphenylmethyl tetrafluoroborate (1,250 mg, 3.79 mmol) in 7 mL of dry dichloromethane, and the reaction mixture was stirred at ambient temperature for 15 h. After addition of dry ether (200 mL), the resultant precipitates of **5** were filtered and washed thoroughly with dry ether to give a reddish brown-powder, 254 mg (68.9%); mp > 200 °C(decomp); δ_H (250 MHz, CD_2Cl_2 , Me_4Si) 7.78(ddd, H_3 , $J=8.2$ Hz, $J=8.0$ Hz, $J=1.1$ Hz), 7.94(ddd, H_4 , $J=8.2$ Hz, $J=8.5$ Hz, $J=1.1$ Hz), 8.04(d, H_5 , $J=8.5$ Hz), 8.25(ddd, H_8 , $J=8.5$ Hz, $J=7.9$ Hz, $J=1.1$ Hz), 8.40(dd, H_7 , $J=9.4$ Hz, $J=7.9$ Hz), 8.71(d, H_2 , $J=8.0$ Hz), 9.11(d, H_6 , $J=9.4$ Hz), 9.00~9.09(m, H_{13}), 9.15~9.20(m, H_{11} , H_{12}), 9.49(d, H_9 , $J=8.5$ Hz), 10.32(d, H_{14} , $J=10.1$ Hz), 10.80(m, H_{10}); UV-Vis $\lambda_{max}^{CH_2Cl_2}$ nm (log ϵ) 261(4.59), 330(4.31), 362(4.20), 410(3.79)(sh), 473(3.51)(sh), 530(2.43)(sh); IR (KBr, cm^{-1}) 2300, 1590, 1425, 1335, 1050, 860, 795, 740; Anal. Calcd for $C_{21}H_{13}OBF_4$: C, 68.52; H, 3.56. Found: C, 68.40; H, 3.63.

Preparation of Cyclohepta[a]benzofuro[3,2-c]naphthalenylium Ions(7).

By a similar procedure to that described above, **7** was prepared in 73.9% yield as a crimson powder; mp >200°C(decomp); δ_H (250 MHz, CD_2Cl_2 , Me_4Si) 7.77~7.86(m, H_3 , H_4), 8.02~8.06(m, H_2), 8.32(ddd, H_{13} , $J=8.0$ Hz, $J=7.3$ Hz, $J=1.7$ Hz), 8.34(ddd, H_{12} , $J=9.1$ Hz, $J=7.3$ Hz, $J=1.2$ Hz), 8.68~8.72(m, H_5), 8.94~8.97(m, H_{14}), 9.13~9.20(m, H_7 , H_8 , H_9), 9.41(d, H_{11} , $J=9.1$ Hz), 10.32~10.37 (m, H_6), 10.73(dd, H_{10} , $J=7.0$ Hz, $J=2.9$ Hz); UV-Vis $\lambda_{max}^{CH_2Cl_2}$ nm (log ϵ)

270(4.65), 278(4.65), 365(4.00), 410(3.82)(sh), 455(3.70), 525(3.43)(sh); IR (KBr, cm^{-1}) 1595, 1420, 1340, 1235, 1150, 860, 740; Anal. Calcd for $\text{C}_{21}\text{H}_{13}\text{OBF}_4$: C, 68.52; H, 3.56. Found: C, 68.44; H, 3.61.

Preparation of Cyclohepta[a]benzothieno[2,3-c]naphthalenylium Ions (10).

By a similar procedure to that described above, **10** was prepared in 60.0% yield as red needles, mp $>180^\circ\text{C}$ (decomp); δ_{H} (250 MHz, CD_2Cl_2 , Me_4Si) 7.81~7.90(m, H_3 , H_4), 8.19(dd, H_7 or H_8 , $J=9.5$ Hz, $J=7.1$ Hz), 8.25~8.28 (m, H_5), 8.35(ddd, H_7 or H_8 , $J=9.5$ Hz, $J=7.1$ Hz, $J=1.1$ Hz), 8.92~9.01(m, H_{13}), 9.02~9.06(m, H_2), 9.10~9.15 (m, H_{11} , H_{12}), 9.33(d, H_6 , H_9 , $J=9.5$ Hz), 9.85(d, H_{14} , $J=11.0$ Hz), 10.58~10.62(m, H_{10}); UV-Vis $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ nm (log ϵ) 260(4.48), 280(4.37)(sh), 285(4.34)(sh), 335(4.28), 435(4.06), 530(3.39)(sh); IR (KBr, cm^{-1}) 1595, 1457, 1420, 1070, 720; Anal. Calcd for $\text{C}_{21}\text{H}_{13}\text{BF}_4\text{S}$: C, 65.65; H, 3.41. Found: C, 65.70; H, 3.52.

Preparation of Cyclohepta[a]benzothieno[3,2-c]naphthalenylium Ions (11).

By a similar procedure to that described above, **11** was prepared in 61.5% yield as red needles; mp $>200^\circ\text{C}$ (decomp); δ_{H} (250 MHz, CD_2Cl_2 , Me_4Si) 7.80(ddd, H_3 , $J=7.9$ Hz, $J=7.3$ Hz, $J=1.3$ Hz), 7.87(ddd, H_4 , $J=8.3$ Hz, $J=7.3$ Hz, $J=1.1$ Hz), 8.16~8.27(m, H_2 , H_{12} , H_{13}), 8.57(m, H_{14}), 8.78(d, H_5 , $J=8.3$ Hz), 9.04~9.11 (m, H_7 , H_8 , H_9), 9.23 (dd, H_{11} , $J=7.6$ Hz, $J=1.9$ Hz), 10.28(d, H_6 , $J=10.5$ Hz), 10.55(dd, H_{10} , $J=9.3$ Hz, $J=2.4$ Hz); UV-Vis $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ nm (log ϵ) 265(4.49), 290(4.51), 305(4.35)(sh), 365(4.10), 430(3.95)(sh), 515(3.58)(sh); IR (KBr, cm^{-1}) 1595, 1470, 1435, 1400, 1320, 1225, 1025, 745; Anal. Calcd for $\text{C}_{21}\text{H}_{13}\text{BF}_4\text{S}$: C, 65.65; H, 3.41. Found: C, 65.77; H, 3.45.

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Received, 11th November, 1996