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Neighboring Group Participation by Heteroaromatic Rings: The Wagner–Meerwein Type Skeletal Rearrangement in the Electrophilic Addition Reactions of Norbornadiene-Fused Furans, Pyrroles, and Thiophenes

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The electrophilic addition reactions of norbornadiene-fused furans, pyrroles, and thiophenes with bromine, arenesulfenyl chlorides, or a triazoledione generally afforded skeletally rearranged adducts except for a dibenzoyl-substituted thiophene. The formations of the adducts are attributable to the neighboring group participation by five-membered heteroaromatic rings, accompanied by the formations of bridged heteroarenium ions and the subsequent Wagner–Meewein type skeletal rearrangement.

Neighboring group participation has found to play an important role to control the reactivity and selectivity of organic reactions.[1,2] Participation of a benzene ring toward a remote cationic center has been investigated in detail;[3] 1,4-dihydro-1,4-methanonaphthalene (**1a**, benzonorbornadiene) is one of the suitable models to study the reactions by way of neighboring group participation by a benzene ring and the formations of bridged benzenium ion intermediates. Electrophilic addition reactions of benzonorbornadiene **1a** have presented an interesting mechanistic problem. Bromine addition of **1a** has been described as giving the 6,9-dibromo adduct **2** exclusively (Chart 1).[4—7] Treatment of **1a** with 4-phenyl-1,2,4-triazole-3,5(4*H*)-dione (**24**) has been reported similarly to provide the rearranged adduct **3**.[8] On the other hand, the reaction of **1a** or **1b** with arenesulfenyl chlorides has been found to give *trans*-adducts **4** as major products, accompanied by the formations of rearranged adducts **5** and *cis*-adducts **6**.[9—11] In the reactions described above, skeletally rearranged products would be derived from the intervention of a bridge benzenium ion[12—16] **7**, and the subsequent Wagner–Meerwein type rearrangement. As for the reaction with arenesulfenyl chlorides, the formation of a tight ion pair for the episulfonium ion **8** is considered to suppress the skeletal rearrangement.[9,10]

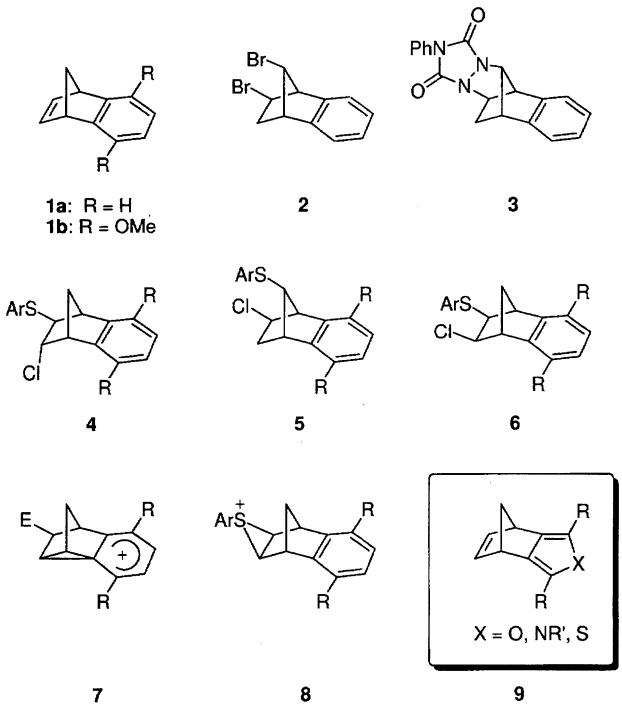


Chart 1.

In contrast to the detailed studies on the benzene ring systems, only a few examples of the neighboring group participation by heteroaromatic rings have been reported.[17—20] In the course of our studies concerning the bicycloalkene-fused heterocycles,[21—27] we have demonstrated that even an electron-deficient pyrazine ring is, to some extent, capable of participating in the stabilization of a remote cationic center to allow the Wagner–Meerwein type rearrangement.[27] Previously we reported on the syntheses of some norbornadiene-fused five-membered heteroaromatics **9**, and their unusual spectral properties[21] and peculiar cycloaddition reactions,[23] which are probably due to the angular strain effect of the fused norbornadiene. On the other hand, we surmised that there should be a lot of examples for the neighboring group participation, the formations of bridged heteroarenium ions, and the Wagner–Meerwein type rearrangement of electron-rich five-membered heteroaromatics. However, we could find no reference to them despite an extensive literature search. The results prompted us to investigate the electrophilic addition

reactions of norbornadiene-fused five-membered heteroaromatics.

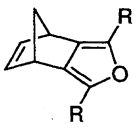
In this paper, we report on the synthesis of novel norbornadiene-fused thiophenes, and the electrophilic addition reactions of norbornadiene-fused furans, pyrroles, and thiophenes with bromine, arenesulfenyl chlorides **20**—**23**, and 4-phenyl-1,2,4-triazole-3,5(4*H*)-dione (**24**).

Results and Discussion

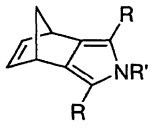
We have already accomplished the syntheses of the norbornadiene-fused furans **10** and **11**, the pyrroles **12** and **13**, and the diphenylthiophene **14** (Scheme 1).[21,23] However, the attempted synthesis of the 1,3-unsubstituted thiophene **16** by Wynberg's[28,29] or our group[23] was unsuccessful. Our new approach is the double-Wittig reaction of bicyclo[2.2.1]hept-5-ene-2,3-dione (**15**) with a bis-ylide derived from the phosphonium salt **18**. The reaction successfully provided **16** albeit in 34% yield. The Hinsberg condensation of **15** with bis(phenacyl) sulfide (**19**) similarly afforded the dibenzoylthiophene **17** in 47% yield.

The reactions of norbornadiene-fused furans **10** and **11** pyrroles **12** and **13**, and thiophenes **14**, **16**, and **17** with bromine, arenesulfenyl chlorides **20**—**23**, or the triazoledione **24** were examined; the yields of the products are summarized in Table 1. The reaction of the diphenylfuran **10** with an equimolar amount of bromine in carbon tetrachloride at room temperature gave exclusively the 5,8-dibromo derivative **25**. On the other hand, attempted bromination reactions of the 1,3-unsubstituted furan **11** and the pyrroles **12** and **13** failed to produce any characterizable products. The thiophenes **14** and **16** reacted with bromine to provide the rearranged adduct **26** and **27**, respectively (Chart 2). In contrast, bromination of the dibenzoylthiophene **17** gave the rearranged adduct **28** along with the 5,6-*exo*,*cis*-dibromo adduct **29** and the 5,6-*trans*-dibromo adduct **30**.

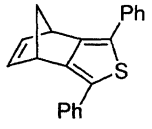
The structures of the skeletally rearranged adducts **25**—**28** were supported by the presence of AA′B splitting pattern at 5-H and 6-H protons in the ^{1}H NMR spectra. The stereochemistry of two bromine atoms was determined on the basis



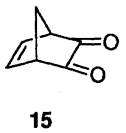
10: R = Ph
11: R = H



12: R = Ph, R' = H
13: R = H, R' = *p*-tolyl



14



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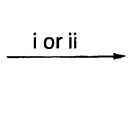
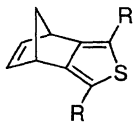
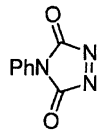




16: R = H
17: R = COPh

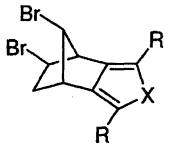
Scheme 1. Reagents and conditions: i) $(Ph_3P^+CH_2)_2S\,2Cl^-$ (**18**), BuLi, Et_2O, −78 °C, 34%; ii) $(PhCOCH_2)_2S$ (**19**), NaOMe, MeOH, reflux, 47%.

PhSCl **20** 4-$NO_2C_6H_4SCl$ **21**

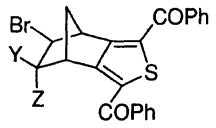


24

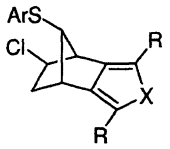
2-$NO_2C_6H_4SCl$ **22** 2,4-$(NO_2)_2C_6H_3SCl$ **23**



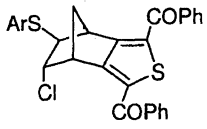
25: X = O, R = Ph
26: X = S, R = Ph
27: X = S, R = H
28: X = S, R = COPh



29: Y = Br, Z = H
30: Y = H, Z = Br



31: X = O, R = Ph, Ar = Ph
32: X = O, R = Ph, Ar = 4-$NO_2C_6H_4$
33: X = O, R = Ph, Ar = 2-$NO_2C_6H_4$
34: X = O, R = Ph, Ar = 2,4-$(NO_2)_2C_6H_3$
35: X = O, R = H, Ar = 4-$NO_2C_6H_4$
36: X = NH, R = Ph, Ar = 4-$NO_2C_6H_4$
37: X = NH, R = Ph, Ar = 2,4-$(NO_2)_2C_6H_3$
38: X = N-tolyl, R = H, Ar = 4-$NO_2C_6H_4$
39: X = S, R = Ph, Ar = 4-$NO_2C_6H_4$
40: X = S, R = H, Ar = 4-$NO_2C_6H_4$



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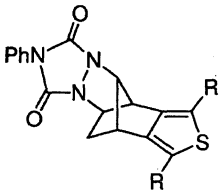


42: R = Ph
43: R = H
44: R = COPh

Chart 2.

of the observation of a long-range spin coupling (1—1.5 Hz) between 5-H and 8-H protons due to the W-arrangement. The homo decoupling experiments as well as H–H COSY measurements established the assignments of these spin couplings. The *exo* orientation of the *cis*-adduct **29** was clarified by the absence of a vicinal spin coupling between 4-H and 5-H.

The reaction of the diphenylfuran **10** with benzenesulfenyl chloride (**20**) only afforded the skeletally rearranged adduct **31**, and neither regio- nor stereoisomer was obtained, in contrast to the results as reported for benzonorbornadiene. Introduction of a nitro group on the benzene ring of

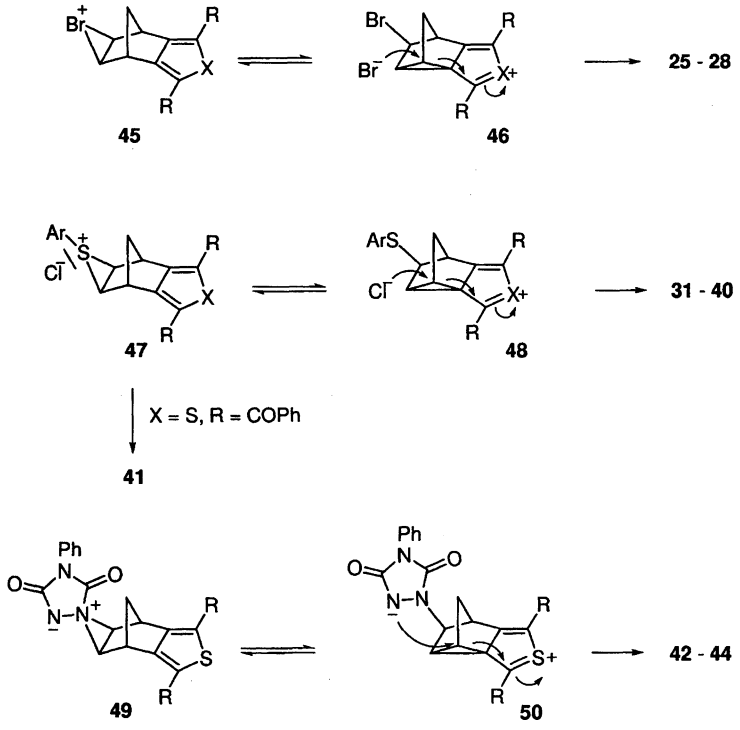
Table 1. Electrophilic Addition Reactions of Norbornadiene-Fused Furans, Pyrroles, and Thiophenes

Compd	Reagents: Br_2	20	21	22	23	24
		Products (Yield, %)				
10	**25** (85)	**31** (73)	**32** (84)	**33** (68)	**34** (56)	Complex
11	Complex	—	**35** (52)	—	—	Complex
12	Complex	—	**36** (73)	—	**37** (99)	Complex
13	Complex	—	**38** (59)	—	—	Complex
14	**26** (81)	—	**39** (98)	—	—	**42** (53)
16	**27** (87)	—	**40** (68)	—	—	**43** (63)
17	**28** (57) + **29** (11) + **30** (18)	—	**41** (99)	—	—	**44** (83)

the sulfenyl chloride, which might form a more tight ion pair of episulfonium ion, did not affect the products-distribution, and only the rearranged adducts **32**—**34** were obtained. Treatments of the furan **11**, the pyrroles **12** and **13**, and the thiophenes **14** and **16** with sulfenyl chlorides similarly provided the rearranged adducts **35**—**40**. The yields of some products are moderate. This is probably due to the loss at the stage of separation of the adducts from some decomposition products derived from sulfenyl chlorides. We could not observe the formations of any other isomers by ^{1}H NMR spectra of crude products. Stereochemistry of skeletally rearranged adducts was considered to be same as that of bromine adducts **25**—**28**, although the long-range spin couplings between 5-H and 8-H due to W-arrangement were clearly observed only for **35**, **38**, **39**, and **40** in the ^{1}H NMR spectra. On the contrary, the reaction of the dibenzoylthiophene **17** with 4-nitrobenzenesulfenyl chloride (**21**) resulted in the exclusive formation of the *trans*-adduct **41**. The electron-withdrawing benzoyl group was found to retard the skeletal rearrangement both for the reactions with bromine and those with an arenesulfenyl chloride.

The reactions of the norbornadiene-fused thiophenes **14** and **16** with the triazoledione **24** at room temperature exclusively afforded the rearranged adduct **42** and **43**, respectively. On the other hand, the reaction of the dibenzoylthiophene **17** and **24** did not proceed at room temperature, and the mixture was heated in refluxing benzene to give **44**. Unfortunately, the furans **10** and **11** and the pyrroles **12** and **13** gave mixtures of complex products upon treatments with **24**. Remarkable in the ^{1}H NMR spectra of these rearranged adducts **42**—**44** was the result that no vicinal spin coupling between 5-H and 6-H_{exo} protons was observed. The PM3-optimized structure of **43** indicates that the dihedral angle between 5-H and 6-H_{exo} is close to orthogonal (88°), which is consistent with the absence of any vicinal spin coupling.

A plausible mechanism for the electrophilic addition reactions of the norbornadiene-fused five-membered heteroaromatics is illustrated in Scheme 2. Addition of electrophiles should be favored on the *exo* face to give the bromonium ion **45**, the episulfonium ion **47**, and the aziridinium imide[30] **49**. The ring cleavage of these ions **45**, **47**, and **49** by the neighboring group participation of the heteroaromatic rings would



Scheme 2.

lead to the bridged heteroarenium ions **46**, **48**, and **50**, respectively. The bridged ions can be trapped stereoselectively to allow the Wagner–Meerwein type rearrangement. Formation of a tight ion pair for the episulfonium ion has been considered to suppress the formation of a bridged benzenium ion for the reactions of benzonorbornadiene with arenesulfenyl chlorides.[9,10] However, we found that the electron-rich five-membered heteroaromatic rings, except for a dibenzoylthiophene ring, have enough ability to participate in the C–S bond-cleavage of the episulfonium ions **47**, which would undergo the Wagner–Meerwein type rearrangement via the bridged heteroarenium ion **48**. The difference of the reaction pathways toward arenesulfenyl chlorides between benzonorbornadienes and its five-membered heteroaromatic congeners clearly suggests the existence of neighboring group effect at the stage of the ring opening of the episulfonium ion **47**. Substitution of benzoyl groups on the thiophene ring would retard the neighboring group participation and the formation of a bridged 3*H*-thiophenium ion due to its electron-withdrawing property, to result in the formations of adducts without rearrangement.

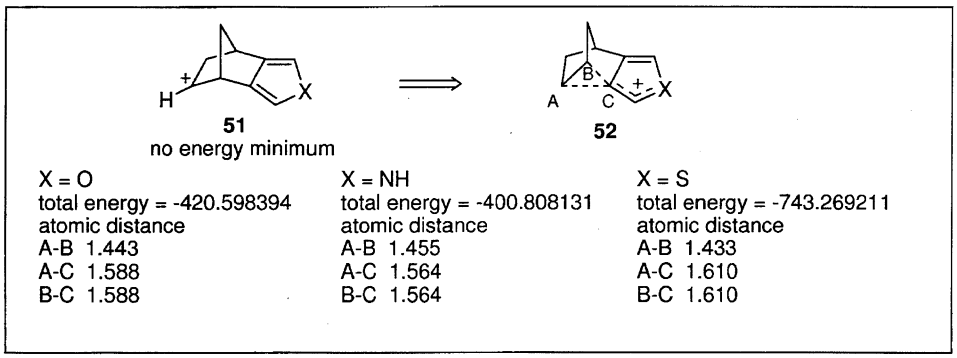
In order to obtain knowledge about the intermediacy of bridged heteroarenium ions, the ab initio calculations with 6-31G* level were performed on the cationic species **51** (X = O, NH, and S).[31] Every structure corresponding to **51** was found to have no energy minimum and the bridged heteroarenium ions **52** were obtained as the optimized structures (Fig. 1). The atomic distances of A–C and B–C in **52** suggest the existence of bonding interactions between these atoms. Calculations on the cationic species bearing two formyl groups **53** (X = O, NH, and S) similarly resulted in the formations of the heteroarenium ions **54** as the optimized structures. Although the atomic distances of A–C and B–C in **54** are somewhat longer than those of **52**, this outcome seems not to explain the significant difference of the reaction pathway for the dibenzoylthiophene **17**.

In conclusion, we present here novel examples of Wagner–Meerwein type rearrangement reactions of furan, pyrrole, and thiophene rings by electrophilic addition reactions of norbornadiene-fused derivatives. The selectivity of additions either with or without rearrangement seems to be sensitive to substituents on the heteroaromatic ring. Although we have no concrete evidence for the presence of heteroarenium ions, the stereoselective formations of the rearranged adducts as well as a notable substituent effect would suggest the intermediacy of the bridged heteroarenium ions by the neighboring group participation of five-membered heteroaromatic rings.

Experimental

General. All the melting points were determined with a Yanagimoto hot-stage apparatus and are uncorrected. IR spectra were obtained with a JEOL Diamond 20 spectrometer. NMR spectra were recorded either with JEOL JNM-LA300 (^{1}H: 300 MHz; ^{13}C: 75 MHz) or JEOL JNM-LA400 (^{1}H: 400 MHz; ^{13}C: 100 MHz) spectrometer. Assignments of the ^{1}H and ^{13}C signals are based on DEPT, H–H COSY, and C–H COSY measurements. Mass spectra were measured with a Shimadzu GCMS-QP1000EX spectrometer operating in the electron impact mode (70 eV). Elemental analyses were performed with a Perkin–Elmer Model 240 apparatus. MPLC separations were carried out by a Yamazen YFLC-600-10V system with a Yamazen Ultra Pack™ Column (Si-40B, silica gel). Solvents were dried and purified by standard methods. All the reactions with sulfenyl chlorides were carried out under nitrogen atmosphere.

4,7-Dihydro-4,7-methano-2-benzothiophene (16). A solution



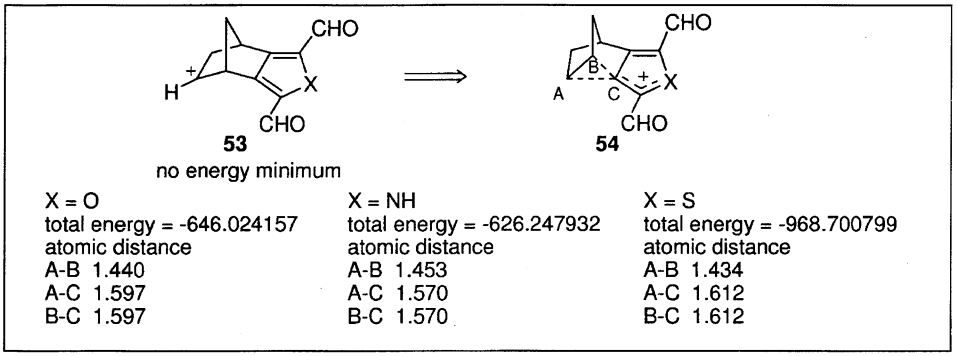


Fig. 1. Total energy (hartrees) and selected atomic distances (Å) of cationic intermediates by ab initio (6-31G*) calculations.

of BuLi in hexane (1.63 M, 6.2 cm^3, 10 mmol, 1 M = 1 mol dm^{-3}) was added to a mixture of the bisphosphonium salt[32] **18** (3.28 g, 5 mmol) in diethyl ether (700 cm^3) at room temperature over 10 min, and the mixture was stirred at room temperature for 3 h. To this mixture, a solution of bicyclo[2.2.1]hept-5-ene-2,3-dione[33] (**15**) (0.61 g, 5 mmol) in diethyl ether (20 cm^3) was added at −78 °C, and the mixture was stirred at room temperature for 60 h. The organic phase was washed with water, dried over Na_2SO_4, and concentrated. The residue was separated by MPLC (hexane) and the resulting oil was distilled at 150 °C (bath temp, 3 Torr, 1 Torr = 133.322 Pa) by a Kuhgelrohr apparatus to give **16** (0.25 g, 34%) which crystallized upon cooling: Colorless rods; mp 35.5–36.0 °C; IR (KBr) 3091, 2995, 2962, 2927, 1346, 1304, 1221, 1180, 785, 706 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 2.34 (1H, dm, J = 8 Hz, 8-H_s), 2.44 (1H, dt, J = 8 and 2 Hz, 8-H_a), 3.72 (2H, quintet, J = 2 Hz, 4-H and 7-H), 6.64 (2H, s, 1-H and 3-H), 6.67 (2H, t, J = 2 Hz, 5-H and 6-H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 46.1 (d, $^1J_{C-H}$ = 151 Hz, C-4 and C-7), 66.6 (t, $^1J_{C-H}$ = 134 Hz, C-8), 111.4 (d, $^1J_{C-H}$ = 186 Hz, C-1 and C-3), 141.3 (d, $^1J_{C-H}$ = 178 Hz, C-5 and C-6), 153.8 (C-3a and C-7a); MS m/z (rel intensity) 148 (M^+; 59), 147 (M − H; 100). Found: C, 72.85; H, 5.29%. Calcd for C_9H_8S: C, 72.93; H, 5.44%.

1,3-Dibenzoyl-4,7-dihydro-4,7-methano-2-benzothiophene (17). To a mixture of the norbornenedione **15** (0.24 g, 2 mmol) and bis(phenacyl) sulfide[34] (**19**) (0.60 g, 2.2 mmol) in methanol (25 cm^3) was added sodium hydride (60%, 0.10 g, 2.5 mmol). The mixure was refluxed for 2 h. Dichloromethane (50 cm^3) was added and the organic phase was washed with hydrochloric acid (1 M, 40 cm^3) and brine, and dried over Na_2SO_4. After removal of the solvent, the residue was separated by MPLC (hexane-ethyl acetate 5/1) to give **17** (0.33 g, 47%): Colorless needles (from ethanol); mp 134–136 °C; IR (KBr) 3022, 2975, 1674 (CO), 1279, 982, 721 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.37 (2H, br s, 8-H), 3.67 (2H, t, J = 2 Hz, 4-H and 7-H), 6.84 (2H, br s, 5-H and 6-H), 7.52 (4H, m), 7.63 (2H, m), 7.82 (4H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 48.0 (C-4 and C-7), 66.9 (C-8), 128.4, 129.1, 132.9, 134.3, 138.3, 142.7 (C-5 and C-6), 161.7 (C-3a and C-7a), 188.5 (CO); MS m/z (rel intensity) 356 (M^+; 100), 279 (M − Ph; 12), 251 (M − COPh; 17), 105 (COPh; 79). Found: C, 77.37; H, 4.50%. Calcd for $C_{23}H_{16}O_2S$: C, 77.50; H, 4.52%.

Reaction of the Norbornadiene-Fused Diphenylfuran 10 with Bromine. A solution of bromine (176 mg, 1.1 mmol) in carbon tetrachloride (2 cm^3) was added dropwise to a solution of the diphenylfuran **10** (284 mg, 1.0 mmol) in carbon tetrachloride (8 cm^3). The mixture was stirred at room temperature for 10 min, and dichloromethane (30 cm^3) and aqueous sodium thiosulfate were added. The organic phase was separated and dried over Na_2SO_4. After removal of the solvent, the residue was crystallized from hexane to give 5-*exo*,8-*anti*-dibromo-4,5,6,7-tetrahydro-4,7-methano-1,3-diphenylisobenzofuran (**25**) (375 mg, 85%): Colorless prisms (from benzene–hexane 1/1); mp 158—159 °C; IR (KBr) 3045, 3020, 2945, 2864, 1594, 1149 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.43 (1H, dd, J = 13 and 8 Hz, 6-H_{endo}), 3.00 (1H, dt, J = 13 and 4 Hz, 6-H_{exo}), 3.81 (1H, d, J = 4 Hz, 7-H), 4.00 (1H, ddd, J = 8, 4, and 1 Hz, 5-H), 4.03 (1H, br s, 4-H), 4.32 (1H, br s, 8-H), 7.25—7.69 (10H, m, Ph); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 38.2 (C-6), 44.6 (C-5), 46.5 (C-7), 51.8 (C-4), 55.7 (C-8), 124.1, 124.3, 126.1, 126.4, 127.5, 127.8, 128.9, 130.0, 130.2, 142.3, (C-3a or C-7a), 142.8 (C-7a or C-3a), 1C missing; MS m/z (rel intensity) 446 (M+4; 43), 444 (M+2; 82), 442 (M^+; 41), 284 (M − 2Br; 100). Found: C, 56.95; H, 3.68%. Calcd for $C_{21}H_{16}Br_2O$: C, 56.79; H, 3.63%.

Reaction of the Norbornadiene-Fused Diphenylthiophene 14 with Bromine. A Solution of bromine (120 mg, 0.75 mmol) in carbon tetrachloride (2 cm^3) was added dropwise to a solution of the diphenylthiophene **14** (150 mg, 0.5 mmol) in carbon tetrachloride (8 cm^3). The mixture was stirred at room temperature for 1 h, and dichoromethane (30 cm^3) and aqueous sodium thiosulfate solution were added. The organic phase was separated and the residue was crystallized from hexane to give 5-*exo*,8-*anti*-dibromo-4,5,6,7-tetrahydro-4,7-methano-1,3-diphenyl-2-benzothiophene (**26**) (187 mg, 81%): Colorless rods (from hexane–ethyl acetate 10/1); mp 167—168 °C; IR (KBr) 3074, 3055, 3020, 2995, 2945, 1601, 1489, 1444, 1284, 1254 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.50 (1H, dd, J = 13 and 8 Hz, 6-H_{endo}), 3.02 (1H, dt, J = 13 and 4 Hz, 6-H_{exo}), 3.80 (1H, d, J = 4 Hz, 7-H), 4.02 (1H, br s, 4-H), 4.08 (1H, ddd, J = 8, 4, and 1 Hz, 5-H), 4.28 (1H, br s, 8-H), 7.25—7.69 (10H, m, Ph); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 37.8 (C-6), 44.4 (C-5), 49.0 (C-7), 54.2 (C-4), 54.8 (C-8), 126.8, 126.9, 127.8, 128.0, 129.1, 129.2, 133.0, 133.1, 133.2, 139.5 (C-3a or C-7a), 140.5 (C-7a or C-3a), 1C missing; MS m/z (rel intensity) 462 (M^++4; 41), 460 (M^++2; 76), 458 (M^+; 36), 300 (M − 2Br; 100). Found: C, 54.65; H, 3.69%. Calcd for $C_{21}H_{16}Br_2S$: C, 54.81; H, 3.50%.

Reaction of the Norbornadiene-Fused Thiophene 16 with Bromine. A solution of bromine (82 mg, 0.51 mmol) in carbon tetrachloride (5 cm^3) was added dropwise to a solution of the thiophene **16** (76 mg, 0.51 mmol) in carbon tetrachloride (5 cm^3). The mixture was stirred at room temperature for 1 h and concentrated. The residue was purified by MPLC (hexane–ethyl acetate 3/1) to give **27** (ca. 150 mg) as a crude oil, which was distilled by a Kugelrohr apparatus to give 5-*exo*,8-*anti*-dibromo-4,5,6,7-tetrahydro-4,7-methano-2-benzothiophene (**27**) (138 mg, 87%): Colorless oil; bp 150 °C (bath temp, 1 Torr); IR (KBr) 3099, 2991, 2947, 1487, 1441, 1362, 1261 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.27 (1H, ddd, J = 13.5, 8, and 1.5 Hz, 6-H_{endo}), 2.89 (1H, dt, J = 13.5, and 4.5 Hz, 6-H_{exo}), 3.55 (1H, br d, J = 4.5 Hz, 7-H), 3.79 (1H, br s, 4-H), 3.82 (1H, ddd, J = 8, 4.5 and 1.5 Hz, 5-H), 4.13 (1H, br t, J = 1.5 Hz, 8-H), 6.89 (1H, d, J = 2 Hz, 1-H or 3-H), 6.97 (1H, d, J = 2 Hz, 3-H or 1-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 38.3 (C-6), 45.0 (C-5), 48.7 (C-7), 54.0 (C-4), 54.8 (C-8), 114.7 (C-1 or C-3), 114.8 (C-3 or C-1), 143.0 (C-3a or C-7a), 143.7 (C-7a or C-3a); MS m/z (rel intensity) 310 (M+4; 6), 308 (M+2; 11), 306 (M^+, 6), 229 (M − Br; 41), 227 (M − Br; 40), 147 (M − 2Br − H; 100). Found: C, 35.03; H, 2.47%. Calcd for $C_9H_8Br_2S$: C, 35.09; H, 2.62%.

Reaction of the Norbornadiene-Fused Dibenzoylthiophene 17 with Bromine. A solution of bromine (56 mg, 0.35 mmol) in carbon tetrachloride (5 cm^3) was added dropwise to a solution of the dibenzoylthiophene **17** (89 mg, 0.25 mmol) in carbon tetrachloride (5 cm^3). The mixture was stirred at room temperature for 30 min and concentrated. The residue was separated by TLC (alumina, carbon tetrachloride) to give 1,3-dibenzoyl-5-*exo*,8-*anti*-dibromo-4,5,6,7-tetrahydro-4,7-methano-2-benzothiophene (**28**) (73 mg, 57%), 1,3-dibenzoyl-5,6-*exo*,*cis*-dibromo-4,5,6,7-tetrahydro-4,7-methano-2-benzothiophene (**29**) (14 mg, 11%), and 1,3-dibenzoyl-5,6-*trans*-dibromo-4,5,6,7-tetrahydro-4,7-methano-2-benzothiophene (**30**) (23 mg, 18%).

For **28**: Colorless needles (from ethanol); mp 145—146 °C; IR (KBr) 1639 (CO), 1597, 1566, 1286, 1274 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.44 (1H, ddd, J = 13.5, 8, and 0.5 Hz, 6-H_{endo}), 2.93 (1H, dt, J = 13.5 and 4.5 Hz, 6-H_{exo}), 3.66 (1H, br d, J = 4.5 Hz, 7-H), 3.80 (1H, br s, 4-H), 4.00 (1H, ddd, J = 8, 4.5, and 1 Hz, 5-H), 4.36 (1H, br s, 8-H), 7.52—7.70 (6H, m), 7.81—7.86 (4H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 36.8 (C-6), 42.7 (C-5), 50.0

(C-7), 54.0 (C-4), 54.9 (C-8), 128.7, 128.8, 128.9, 129.0, 133.4, 133.5, 136.1, 136.5, 137.6, 137.8, 149.3, 150.6, 187.4 (CO), 187.5 (CO); MS *m/z* (rel intensity) 518 (M+4; 3), 516 (M+2; 5), 514 (M^+; 3), 437 (M − Br; 67), 435 (M − Br; 65), 355 (M − 2Br − H; 47), 105 (COPh; 100). Found: C, 53.23; H, 3.01%. Calcd for $C_{23}H_{16}Br_2O_2S$: C, 53.51; H, 3.12%.

For **29**: Colorless needles (from ethanol); mp 174—175 °C; IR (KBr) 1650 (CO), 1282, 1261, 1005 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 2.09 (1H, dt, J = 10.5 and 1 Hz, 8-H_s), 2.57 (1H, dt, J = 10.5 and 2 Hz, 8-H_a), 3.93 (2H, br s, 4- and 7-H), 4.67 (2H, br s, 5- and 6-H), 7.45—7.64 (6H, m), 7.90—7.93 (4H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 47.5 (C-8), 49.3 (C-4 and C-7), 52.2 (C-5 and C-6), 128.6, 129.2, 132.9, 137.5, 138.6, 151.8, 183.3, (CO); MS *m/z* (rel intensity) 437 (M − Br; 50), 435 (M − Br; 51), 356 (M − 2Br; 19), 105 (COPh; 100). Found: C, 53.80; H, 3.09%. Calcd for $C_{23}H_{16}Br_2O_2S$: C, 53.51; H, 3.12%.

For **30**: White solid (from ethanol); mp 68—71 °C; IR (KBr) 1641 (CO), 1597, 1564, 1446, 1265 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 2.46 (1H, dm, J = 10.5, 8-H_s), 2.57 (1H, br d, J = 10.5 Hz, 8-H_a). 3.64 (1H, br s, 4-H), 3.84 (1H, dm, J = 4 Hz, 5-H), 3.91 (1H, t, J = 2.5 Hz, 7-H), 4.59 (1H, dd, J = 4 and 2.5 Hz, 6-H), 7.49—7.67 (6H, m), 7.87—7.90 (4H, m), ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 47.2 (C-8), 50.1 (C-5), 51.3 (C-4), 54.9 (C-7), 56.0 (C-6), 128.6, 128.7, 128.9, 129.1, 133.0, 133.2, 135.6, 138.0, 138.3, 151.9, 152.3, 187.8 (CO), 188.0 (CO), 1C missing; MS *m/z* (rel intensity) 518 (M+4; 3), 516 (M+2; 5), 514 (M^+; 3), 437 (M − Br; 100). HR-MS Found: *m/z* 513.9255. Calcd for $C_{23}H_{16}Br_2O_2S$: M, 513.9237.

Reaction of the Norbornadiene-Fused Diphenylfuran 10 with Benzenesulfenyl Chloride. A solution of the Diphenylfuran **10** (142 mg, 0.5 mmol) and benzenesulfenyl chloride[35] (**20**) (87 mg, 0.6 mmol) in carbon tetrachloride (5 cm^3) was stirred at room temperature for 24 h. After removal of the solvent, the residue was separated by MPLC (benzene) to give the 5-*exo*-chloro-4,5,6,7-tetrahydro-4,7-methano-1,3-diphenyl-8-*anti*-phenylthioisobenzofuran (**31**) (156 mg, 73%): Colorless needles (from hexane); mp 166—167 °C; IR (KBr) 3080, 3047, 3018, 1597, 1693, 1437 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 2.40 (1H, dd, J = 13 and 7 Hz, 6-H_{endo}), 2.90 (1H, dt, J = 13 and 4 Hz, 6-H_{exo}), 3.75 (1H, d, J = 4 Hz, 7-H), 3.88 (1H, s, 4-H), 3.94 (1H, s, 8-H), 4.08 (1H, dd, J = 7 and 4 Hz, 5-H), 7.09—7.16 (15H, Ph); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 38.4 (C-6), 44.8 (C-7), 51.8 (C-4), 57.9 (C-5), 65.7 (C-8), 124.0, 124.3, 127.0, 127.2, 127.5, 127.8, 128.8, 128.9, 129.2, 129.5, 130.4, 130.5, 130.9, 136.5, 142.2, 142.3; MS *m/z* (rel intensity) 430 (M+2; 10), 428 (M^+; 25), 271 (1,3-diphenyisobenzofuran+H; 100). Found: C, 75.82; H, 4.81%. Calcd for $C_{27}H_{21}ClOS$: C, 75.60; H, 4.93%.

Reaction of the Norbornadiene-Fused Diphenylfuran 10 with 4-Nitrobenzenesulfenyl Chloride. By a procedure similar to that described for **31**, the diphenylfuran **10** (142 mg, 0.5 mmol) was treated with 4-nitrobenzensulfenyl chloride (**21**) (114 mg, 0.6 mmol) in carbon tetrachloride (10 cm^3) to give 5-*exo*-chloro-4,5,6,7-tetrahydro-4,7-methano-8-*anti*-(4-nitrophenylthio)-1,3-diphenylisobenzofuran (**32**) (199 mg, 84%): Light orange needles (from hexane–ethyl acetate 1/1); mp 242–243 °C; IR (KBr) 3091, 3080, 3059, 2034, 2991, 1576, 1508, 1444, 1336 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 2.47 (1H, dd, J = 13 and 8 Hz, 6-H_{endo}), 2.82 (1H, dt, J = 13 and 4 Hz, 6-H_{exo}), 3.84 (1H, d, J = 4 Hz, 7-H), 3.99 (1H, s, 4-H), 4.03 (1H, s, 8-H), 4.12 (1H, dd, J = 8 and 4 Hz, 5-H), 7.25—7.72 (12H, m, Ph), 8.14 (2H, d, J = 9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 38.7 (C-6), 44.5 (C-7), 51.7 (C-4), 57.6 (C-5), 62.6 (C-8), 124.1, 124.2, 124.3, 126.9, 127.4, 127.5, 127.7, 128.7, 128.9, 129.0, 130.1, 130.3, 142.5, 142.6, 145.6, 146.6; MS *m/z* (rel intensity) 475 (M+2; 15), 473 (M^+; 37), 271 (1,3-diphenyisobenzofuran+H; 100). Found: C, 68.59; H, 3.98; N, 3.21%. Calcd for $C_{27}H_{20}ClNO_3S$: C, 68.42; H, 4.25; N, 2.96%.

Reaction of the Norbornadiene-Fused Diphenylfuran 10 with 2-Nitrobenzenesulfenyl Chloride. By a procedure similar to that described for **31**, the diphenylfuran **10** (142 mg, 0.5 mmol) was treated with 2-nitrobenzenesulfenyl chloride (**22**) (114 mg, 0.6 mmol) in carbon tetrachloride (10 cm^3) to give 5-*exo*-chloro-4,5,6,7-tetrahydro-4,7-methano-8-*anti*-(2-nitrophenylthio)-1,3-diphenylisobenzofuran (**33**) (162 mg, 68%): Light yellow needles (from hexane–ethyl acetate 3/2); mp 237—239 °C; IR (KBr) 3080, 3055, 1591, 1510 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 2.45 (1H, dd, J = 13 and 8 Hz, 6-H_{endo}), 2.86 (1H, dt, J = 13 and 4 Hz, 6-H_{exo}), 3.87 (1H, d, J = 4 Hz, 7-H), 3.98 (1H, s, 4-H), 4.01 (1H, s, 8-H), 4.10 (1H, dd, J = 8 and 4 Hz, 5-H), 7.25—8.08 (13H, m), 8.10 (1H, d, J = 8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 38.7 (C-6), 44.4 (C-7), 51.6 (C-4), 57.4 (C-5), 63.4 (C-8), 124.1, 124.3, 125.7, 125.8, 127.3, 127.4, 127.7, 128.4, 128.8, 128.9, 129.0, 130.2, 130.4, 133.4, 135.6, 142.4, 147.8, 1C missing; MS *m/z* (rel intensity) 475 (M+2; 17), 473 (M^+; 43), 271 (1,3-diphenyisobenzofuran+H; 100). Found: C, 68.58; H, 4.02; N, 3.12%. Calcd for $C_{27}H_{20}ClNO_3S$: C, 68.42; H, 4.25; N, 2.96%.

Reaction of the Norbornadiene-Fused Diphenylfuran 10 with 2,4-Dinitrobenzenesulfenyl Chloride. By a procedure similar to that described for **31**, the diphenylfuran **10** (142 mg, 0.5 mmol) was treated with 2,4-dinitrobenzenesulfenyl chloride (**23**) (141 mg, 0.6 mmol) in carbon tetrachloride (10 cm^3) to give 5-*exo*-chloro-8-*anti*-(2,4-dinitrophenylthio)-4,5,6,7-tetrahydro-4,7-methano-1,3-diphenylisobenzofuran (**34**) (144 mg, 56%): Orange prisms (from ethyl acetate–ethanol 1/1); mp 206—207 °C; IR (KBr) 3086, 3034, 1595, 1518, 1446 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 2.51 (1H, dd, J = 14 and 8 Hz, 6-H_{endo}), 2.81 (1H, dt, J = 14 and 4 Hz, 6-H_{exo}), 3.91 (1H, d, J = 4 Hz, 7-H), 4.05 (2H, s, 4-H and 8-H), 4.14 (1H, dd, J = 8 and 4 Hz, 5-H), 7.25—7.75 (11H, m), 8.36 (1H, dd, J = 9 and 2 Hz), 8.97 (1H, d, J = 2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 38.9 (C-6), 44.0 (C-7), 51.5 (C-4), 57.2 (C-5), 62.0 (C-8), 121.7, 124.0, 124.2, 126.6, 127.2, 127.3, 127.7, 127.9, 128.3, 129.0, 129.1, 129.9, 130.1, 142.5, 142.6, 144.1, 145.4, 145.6, MS *m/z* (rel intensity) 520 (M+2; 17), 518 (M^+; 41), 271 (1,3-diphenyisobenzofuran+H; 100). Found: C, 62.65; H, 3.40; N, 5.29%. Calcd for $C_{27}H_{19}ClN_2O_5S$: C, 62.49, H, 3.69; N, 5.40%.

Reaction of the Norbornadiene-Fused Furan 11 with 4-Nitrobenzenesulfenyl Chloride. By a procedure similar to that described for **31**, the furan **11** (66 mg, 0.5 mmol) was treated with 4-nitrobenzenesulfenyl chloride (**21**) (133 mg, 0.7 mmol) in carbon tetrachloride (10 cm^3) to give 5-*exo*-chloro-4,5,6,7-tetrahydro-4,7-methano-8-*anti*-(4-nitrophenylthio)isobenzofuran (**35**) (84 mg, 52%): Yellow needles (from ethanol); mp 179—180 °C; IR (KBr) 3128, 2991, 1574, 1500, 1331, 1092, 1009 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 2.32 (1H, ddd, J = 13.5, 7.5, and 1.5 Hz, 6-H_{endo}), 2.70 (1H, dt, J = 13.5 and 4 Hz, 6-H_{exo}), 3.58 (1H, d, J = 4 Hz, 7-H), 3.72 (1H, s, 4-H), 3.83 (1H, br s, 8-H), 3.98 (1H, ddd, J = 7.5, 4, and 1 Hz, 5-H), 7.14 (1H, s, 1-H or 3-H), 7.18 (1H, s, 3-H or 1H), 7.41 (2H, d, J = 9 Hz), 8.14 (2H, d J = 9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 39.4 (C-6), 43.2 (C-7), 50.4 (C-4), 58.2 (C-5), 62.3 (C-8), 124.1 (C-3′), 127.1 (C-2′), 129.2, 130.6, 131.9 (C-1 or C-3), 132.0 (C-3 or C-1), 145.5, 147.0; MS *m/z* (rel intensity) 323 (M+2; 2), 321 (M^+; 6), 286 (M − Cl; 4), 119 (isobenzofuran+H; 100). Found: C, 55.69; H, 4.03; N, 4.35%. Calcd for $C_{15}H_{12}ClNO_3S$: 55.99; H, 3.76; N, 4.35%.

Reaction of the Norbornadiene-Fused Diphenylpyrrole 12

with 4-Nitrobenzenesulfenyl Chloride. A solution of the norbornadiene-fused diphenylpyrrole **12** (142 mg, 0.5 mmol) and 4-nitrobenzenesulfenyl chloride (**21**) (114 mg, 0.6 mmol) in carbon tetrachloride (10 cm^3) was stirred at room temperature for 2 h. The resulting precipitates were collected by suction to give 5-*exo*-chloro-4,5,6,7-tetrahydro-4,7-methano-8-*anti*-(4-nitrophenylthio)-1,3-diphenyl-2*H*-isoindole (**36**) (172 mg, 73%): Orange powder (from benzene–hexane 1/10); mp 197—198 °C; IR (KBr) 3433, 3080, 3058, 2993, 1595, 1576, 1508, 1502, 1334 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.38 (1H, dd, J = 13 and 8 Hz, 6-H_{endo}), 2.76 (1H, dt, J = 13 and 4 Hz, 6-H_{exo}), 3.81 (1H, d, J = 4 Hz, 7-H), 3.94 (1H, s, 4-H), 4.01 (1H, s, 8-H), 4.06 (1H, dd, J = 8 and 4 Hz, 5-H), 7.23—7.51 (12H, m), 8.12 (3H, m, Ar and NH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 39.0 (C-6), 45.1 (C-7), 52.4 (C-4), 58.7 (C-5), 62.9 (C-8), 123.9, 124.0, 124.1, 124.2, 124.4, 126.6, 126.9, 127.0, 129.0, 129.2, 131.6, 131.9, 145.3, 147.6, 2C missing; MS *m/z* (rel intensity) 474 (M+2; 10), 472 (M^+; 21), 282 (M − $NO_2C_6H_4SCl$; 100). Found: C, 68.45; H, 4.20; N, 5.89%. Calcd for $C_{27}H_{21}ClN_2O_2S$: C, 68.56; H, 4.47; N, 5.92%.

Reaction of the Norbornadiene-Fused Diphenylpyrrole 12 with 2,4-Dinitrobenzensulfenyl Chloride. A solution of the norbornadiene-fused diphenylpyrrole **12** (142 mg, 0.5 mmol) and 2,4-dinitrobenzenesulfenyl chloride (**23**) (141 mg, 0.6 mmol) in carbon tetrachloride (10 cm^3) was stirred at room temperature for 24 h. The resulting precipitates were collected by suction to give 5-*exo*-chloro-8-*anti*-(2,4-dinitrophenylthio)-4,5,6,7-tetrahydro-4,7-methano-1,3-diphenyl-2*H*-isoindole (**37**) (256 mg, 99%): Orange prisms (from benzene–hexane 2/1); mp 147—148 °C; IR (KBr) 3430, 3080, 3057, 2970, 1595, 1516, 1508, 1338 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.43 (1H, dd, J = 13 and 8 Hz, 6-H_{endo}), 2.75 (1H, dt, J = 13 and 4 Hz, 6-H_{exo}), 3.87 (1H, d, J = 4 Hz, 7-H), 4.01 (1H, s, 4-H), 4.02 (1H, s, 8-H), 4.08 (1H, dd, J = 8 and 4 Hz, 5-H), 7.25—7.50 (10H, m), 7.73 (1H, d, J = 9 Hz), 8.16 (1H, br s, NH), 8.33 (1H, dd, J = 9 and 2 Hz), 8.98 (1H, d, J = 2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 39.2 (C-6), 44.6 (C-7), 52.3 (C-4), 58.2 (C-5), 62.5 (C-8), 121.7, 123.9, 124.1, 124.2, 124.4, 126.6, 126.8, 127.0, 127.1, 127.2, 128.7, 129.3, 129.4, 131.5, 131.7, 143.9, 145.5, 146.2; MS *m/z* (rel intensity) 519 (M+2; 11), 517 (M^+; 26), 282 (M − $(NO_2)_2C_6H_3SCl$; 100). Found: C, 62.92; H, 3.92; N, 8.14%. Calcd for $C_{27}H_{20}ClN_3O_4S$: C, 62.61; H, 3.89; N, 8.11%.

Reaction of the Norbornadiene-Fused *N*-*p*-Tolylpyrrole 13 with 4-Nitrobenzenesulfenyl Chloride. A solution of the tolylpyrrole **13** (111 mg, 0.5 mmol) and 4-nitrobenzenesulfenyl chloride (**21**) (104 mg, 0.55 mmol) in carbon tetrachloride (10 cm^3) was stirred at room temperature for 10 h. The mixture was concentrated and the residue was purified by TLC (silica gel, hexane–dichloromethane 2/1) to give 5-*exo*-chloro-4,5,6,7-tetrahydro-4,7-methano-8-*anti*-(4-nitrophenylthio)-2-(*p*-tolyl)-2*H*-isoindole (**38**) (122 mg, 59%): Light yellow powder (from ethanol); mp 140—141 °C; IR (KBr) 2943, 1510, 1336, 1090, 1036 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.30 (1H, ddd, J = 13.5, 7.5 and 1.0 Hz, 6-H_{endo}), 2.37 (3H, s, CH_3), 2.68 (1H, dt, J = 13.5 and 3.5 Hz, 6-H_{exo}), 3.57 (1H, br d, J = 3.5 Hz, 7-H), 3.70 (1H, br s, 4-H), 3.89 (1H, br s, 8-H), 3.99 (1H, dd, J = 7.5 and 3.5 Hz, 5-H), 6.74, (1H, d, J = 0.5 Hz, 1-H or 3-H), 6.79 (1H, d, J = 0.5 Hz, 3-H or 1-H), 7.21 (4H, s), 7.43 (2H, d, J = 9 Hz), 8.14 (2H, d, J = 9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 20.9 (CH_3), 39.8 (C-6), 44.5 (C-7), 51.9 (C-4), 59.3 (C-8), 62.5 (C-5), 110.5 (C-1 or C-3), 110.6 (C-3 or C-1), 120.6, 124.1, 126.8, 129.7, 130.2, 131.5, 135.4, 138.5, 145.2, 147.9; MS *m/z* (rel intensity) 412 (M^++2; 3), 410 (M^+; 8), 375 (M − Cl; 21), 208 (M − $NO_2C_6H_4SCl$ − CH; 100). Found: C, 64.11; H, 4.65; N, 7.01%. Calcd for $C_{22}H_{19}ClN_2O_2S$: C, 64.30; H, 4.66; N, 6.82%.

Reaction of the Norbornadiene-Fused Diphenylthiophene 14 with 4-Nitrobenzenesulfenyl Chloride. A solution of the diphenylthiophene **14** (150 mg, 0.5 mmol) and 4-nitrobenzenesulfenyl chloride (**21**) (114 mg, 0.6 mmol) in carbon tetrachloride (10 cm^3) was stirred at room temperature for 24 h. The resulting solid was collected by suction to give 5-*exo*-chloro-4,5,6,7-tetrahydro-4,7-methano-8-*anti*-(4-nitrophenylthio)-1,3-diphenyl-2-benzothiophene (**39**) (242 mg, 98%): Light yellow prisms (from benzene–hexane 1/10); mp 239—240 °C; IR (KBr) 3105, 3015, 2993, 1576, 1502, 1334 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.53 (1H, ddd, J = 13, 8, and 1 Hz, 6-H_{endo}), 2.85 (1H, dt, J = 13 and 4 Hz, 6-H_{exo}), 3.81 (1H, d, J = 4 Hz, 7-H), 3.97 (2H, m, 4-H and 8-H), 4.19 (1H, ddd, J = 8, 4, and 0.5 Hz, 5-H), 7.25—7.55 (12H, m), 8.11 (2H, d, J = 9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 38.3 (C-6), 47.0 (C-7), 54.0 (C-4), 57.4 (C-5), 61.5 (C-8), 124.2, 126.7, 126.8, 127.4, 127.8, 128.3, 129.2, 129.3, 132.8, 133.0, 133.2, 133.3, 140.6, 142.7, 145.5, 146.7; MS *m/z* (rel intensity) 491 (M+2; 8), 489 (M^+; 18), 300 (M − $NO_2C_6H_4SCl$; 100). Found: C, 66.45; H, 4.34; N, 2.96%. Calcd for $C_{27}H_{20}ClNO_2S_2$: C, 66.18; H, 4.11; N, 2.86%.

Reaction of the Norbornadiene-Fused Thiophene 16 with 4-Nitrobenzenesulfenyl Chloride. A solution of the thiophene **16** (37 mg, 0.25 mmol) and 4-nitrobenzenesulfenyl chloride (**21**) (95 mg, 0.5 mmol) in carbon tetrachloride (5 cm^3) was stirred at room temperature for 3 h. The mixture was concentrated and the residue was separated by MPLC (hexane–ethyl acetate 3/1) to give 5-*exo*-chloro-4,5,6,7-tetrahydro-4,7-methano-8-*anti*-(4-nitrophenylthio)-2-benzothiophene (**40**) (57 mg, 68%): Light yellow plates (from ethanol); mp 134—135 °C; IR (KBr) 1593, 1579, 1510, 1504, 838 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.28 (1H, ddd, J = 13.5, 8, and 1 Hz, 6-H_{endo}), 2.71 (1H, dt, J = 13.5 and 4 Hz, 6-H_{exo}), 3.59 (1H, d, J = 4 Hz, 7-H), 3.73 (1H, br s, 4-H), 3.84 (1H, br s, 8-H), 3.93 (1H, ddd, J = 8, 4, and 0.5 Hz, 5-H), 6.91 (1H, d, J = 2 Hz, 1-H or 3-H), 6.99 (1H, d, J = 2 Hz, 3-H or 1-H), 7.41 (2H, d, J = 9 Hz), 8.14 (2H, d, J = 9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 38.9 (C-6), 46.6 (C-7), 53.8 (C-4), 57.9 (C-5), 61.5 (C-8), 114.5 (C-1 or C-3), 115.0 (C-3 or C-1), 124.1, 127.1, 144.1, 146.1, 147.1, 1C missing; MS *m/z* (rel intensity) 339 (M+2; 1), 337 (M^+; 3), 302 (M − Cl; 2), 147 (M − **21** − H; 70), 135 (M − **21** − CH; 100). Found: C, 53.05; H, 3.66; N, 3.95%. Calcd for $C_{15}H_{12}ClNO_2S_2$: C, 53.33; H, 3.58; N, 4.15%.

Reaction of the Norbornadiene-Fused Dibenzoylthiophene 17 with 4-Nitrobenzenesulfenyl Chloride. A solution of the norbornadiene-fused dibenzoylthiophene **17** (89 mg, 0.25 mmol) and 4-nitrobenzenesulfenyl chloride (53 mg, 0.28 mmol) in carbon tetrachloride (5 cm^3) was stirred at room temperature for 5 h. The solution was concentrated and the resulting solid was recrystallized from ethanol to give 1,3-dibenzoyl-5-*endo*-chloro-4,5,6,7-tetrahydro-4,7-methano-6-*exo*-(4-nitrophenylthio)-2-benzothiophene (**41**) (135 mg, 99%): Pale yellow powder; mp 182—183 °C; IR (KBr) 3006, 1645 (CO), 1628, 1508, 1335, 1271, 1093, 866 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.41 (1H, dm, J = 10.5 Hz, 8-H_s), 2.47 (1H, dm, J = 10.5 Hz, 8-H_a), 3.33 (1H, t, J = 3.5 Hz, 4-H), 3.79 (1H, br s, 7-H), 3.90 (1H, dm, J = 3.5 Hz, 6-H), 4.27 (1H, t, J = 3.5 Hz, 5-H), 7.36—7.91 (14H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 47.1 (C-8), 47.9 (C-7), 49.1 (C-6), 55.4 (C-4), 62.5 (C-5), 124.2, 127.1, 128.6, 128.8, 129.1, 129.2, 133.0, 133.4, 134.1, 137.8, 138.3, 138.7, 145.3, 145.6, 151.7, 153.8, 187.8 (CO), 188.0 (CO); MS *m/z* (rel intensity) 547 (M+2; 7), 545 (M^+; 15), 510 (M − Cl; 15), 355 (M − $NO_2C_6H_4SCl$ − H; 31), 105 (COPh; 100). Found: C, 63.88; H, 3.78; N, 2.38%. Calcd for $C_{29}H_{20}NO_4S_2$: C, 63.79; H, 3.69; N, 2.57%.

Reaction of the Norbornadiene-Fused Diphenylthiophene 14

with 4-Phenyl-1,2,4-triazole-3,5(4*H*)-dione (24). A solution of the diphenylthiophene **14** (74 mg, 0.25 mmol) and the triazoledione[36] **24** (90 mg, 0.51 mmol) in benzene (5 cm^3) was stirred at room temperature for 10 d. Insoluble material was removed by filtration and the filtrate was concentrated. The residue was recrystallized from ethanol to give **42** (62 mg, 53%) as colorless needles: Mp 246—247 °C; IR (KBr) 1712 (CO), 1502, 1491, 1396 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.81 (1H, ddd, J = 13, 4.5, and 1 Hz, 6-H_{endo}), 2.32 (1H, dd, J = 13 and 5.5 Hz, 6-H_{exo}), 3.83 (1H, br s, 4-H), 4.03 (1H, dd, J = 5.5 and 1.5 Hz, 7-H), 4.81 (1H, dd, J = 4.5 and 2 Hz, 5-H), 4.83 (1H, br d, J = 1.5 Hz, 8-H), 7.31—7.55 (15H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 35.1 (C-6), 43.4 (C-7), 50.6 (C-4), 59.5 (C-5), 76.1 (C-8), 125.4, 126.9, 128.1, 128.5, 129.1, 129.3, 131.4, 131.5, 133.0, 133.2, 133.7, 136.5, 143.0, 156.1 (CO), 156.3 (CO), 2C missing; MS m/z (rel intensity) 475 (M^+; 6), 299 (M − **24** − H; 71), 273 (M − **24** − C_2H_3; 100). Found: C, 73.57; H, 4.69; N, 9.05%. Calcd for $C_{29}H_{21}N_3O_2S$: C, 73.24; H, 4.45; N, 8.84%.

Reaction of the Norbornadiene-Fused Thiophene 16 with 4-Phenyl-1,2,4-triazole3,5(4*H*)-dione (24). A solution of the thiophene **16** (37 mg, 0.25 mmol) and the triazoledione **24** (176 mg, 1 mmol) in benzene (5 cm^3) was stirred at room temperature for 1 d. Insoluble material was removed by filtration and the filtrate was concentrated. The residue was separated by TLC (silica gel, hexane–ethyl acetate 4/1) to give **43** (51 mg, 63%): Colorless needles (from ethanol); mp 199—200 °C; IR (KBr) 3113, 3053, 3008, 2976, 2850, 1709 (CO), 1500, 1412, 1130 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.51 (1H, ddd, J = 13, 4.5, and 1 Hz, 6-H_{endo}), 2.18 (1H, dd, J = 13 and 5.5 Hz, 6-H_{exo}), 3.66, (1H, br s, 4-H), 3.74 (1H, dd, J = 5.5 and 1 Hz, 7-H), 4.61 (1H, dd, J = 4.5 and 2 Hz, 5-H), 4.73 (1H, m, 8-H), 6.90 (1H, d, J = 2 Hz, 1-H or 3-H), 7.06 (1H, d, J = 2 Hz, 3-H or 1-H), 7.37—7.52 (5H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 35.3 (C-6), 43.2 (C-7), 50.1 (C-4), 59.6 (C-5), 76.6 (C-8), 113.2 (C-1 or C-3), 118.2 (C-3 or C-1), 125.4, 128.5, 129.3, 131.5, 137.1, 146.4, 156.2, (CO), 156.4 (CO), MS m/z (rel intensity) 323 (M^+; 15), 147 (M − **24** − H; 100). Found: C, 62.95; H, 3.85; N, 12.93%. Calcd for $C_{17}H_{13}N_3O_2S$: C, 63.14; H, 4.05; N, 12.99%.

Reaction of the Norbornadiene-Fused Dibenzoylthiophene 17 with 4-Phenyl-1,2,4-triazole-3,5(4*H*)-dione (24). A solution of the dibenzoylthiophene **17** (89 mg, 0.25 mmol) and the triazoledione **24** (88 mg, 0.5 mmol) in benzene (5 cm^3) was refluxed for for 4 d. The mixture was concentrated and the residue was separated by column chromatography (silica gel, dichloromethane) to give **44** (110 mg, 83%): White powder (from ethanol); mp 213—214 °C; IR (KBr) 1720 (CO), 1645 (CO), 1404, 1284 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.70 (1H, ddd, J = 13, 5, and 1 Hz, 6-H_{endo}), 2.31 (1H, dd, J = 13 and 6 Hz, 6-H_{exo}), 3.81 (2H, m 4-H and 7-H), 4.77 (1H, dd, J = 5 and 2 Hz, 5-H), 4.83 (1H, dm, J = 1.5 Hz, 8-H), 7.36—7.91 (15H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 34.8 (C-6), 44.4 (C-4), 51.1 (C-7), 59.0 (C-5), 77.6 (C-8), 125.4, 128.6, 128.8, 129.0, 129.3, 131.2, 133.4, 133.5, 135.0, 137.7, 137.8, 138.5, 144.6, 152.6, 155.9 (CO), 156.5 (CO), 187.3 (CO), 187.7 (CO), 2C missing; MS m/z (rel intensity) 531 (M^+; 29), 426 (M − COPh; 18), 355 (M − **24** − H; 37), 105 (COPh; 100). Found: C, 70.11; H, 4.05; N, 7.86%. Calcd for $C_{31}H_{21}N_3O_4S$: C, 70.04; H, 3.98; N, 7.90%.

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