The Synthesis of Naphthosultine and Benzodisultines and their Pyrolysis with Dienophiles: Studies on *o*-Naphthoquinodimethane and Bis-*o*-quinodimethane

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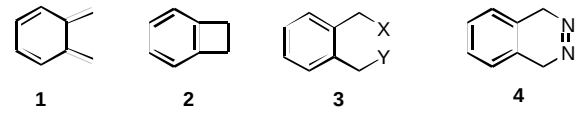
Sealed tube reactions of the naphthosultine **8** with a series of electron-deficient dienophiles (fumaronitrile, *N*-phenylmaleimide, dimethyl fumarate, and dimethyl acetylenedicarboxylate) in toluene at 180 °C gave corresponding 1:1 cycloadducts **11**-**14** in various amounts along with rearranged naphthosulfolene **7** in 67-95% yields. The reaction of 1,2,4,5-tetra(bromomethyl)benzene with Rongalite (sodium formaldehyde sulfoxylate) and tetrabutylammonium bromide in DMF gave benzodisultines **17** and **18** in a combined yield of 56%. Sealed tube reactions of benzodisultines **17** and **18** with a series of dienophiles in xylene at 200 °C gave corresponding 1:1 and 1:2 cycloadducts **20**-**27**. The results suggested that thermal extrusion of sulfur dioxide from these sultines led to either *o*-naphthoquinodimethane **6** (from **8**) or bis-*o*-quinodimethane **19** (from **17** and **18**); subsequent trapping of these reactive intermediates by dienophiles and SO_2 gave various 1:1 and 1:2 Diels-Alder adducts in modest to excellent yields.

INTRODUCTION

Much attention has been focused on the synthesis of polycyclic compounds using *o*-quinodimethane (*o*-QDM) **1** and its analogues, and numerous methods for the generation of the *o*-QDM intermediates have been developed.[1] Among them are ring-openings of benzocyclobutenes[2] **2**, 1,4-elimination of α,α′-disubstituted *o*-xylenes **3**,[3] and various "extrusion" reactions involving loss of a small molecule.[1] For example, losses of N_2 from diazene[4] **4** or SO_2 from sulfolene[1,5] **5** have been shown to lead to the *o*-QDM intermediates.



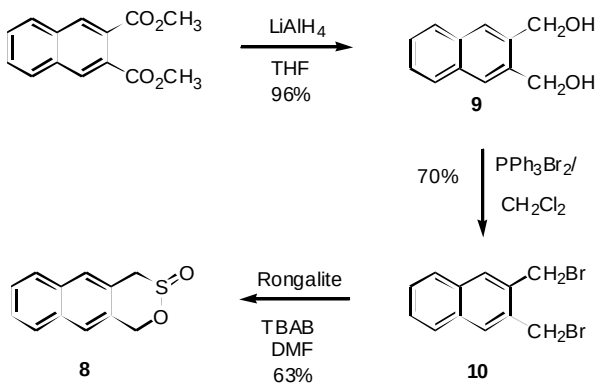
1 2 3 4 5 6 7

In a pioneering work by Cava and coworkers,[6a] the naphthoanalogue of *o*-QDM **6** was generated using SO_2 extrusion from sulfolene **7**; however, a reaction temperature of 300 °C was required! The naphthoquinodimethane **6** was later reported by Wirz et. al. using a diazene-precursor,[6b] but the diazene compound was unstable and had to be kept under -40 °C. Furthermore, an intractable mixture of products was obtained in deaerated solution of the diazene compound. Thus, finding an easy, high-yield method for generating naphthoquinodimethane **6** and a further extension to bis-*o*-QDM are of particular interests. Recently we described[7] the generation of a series of heteroaromatic *o*-QDMs, by thermal extrusion of SO_2 from corresponding sultines, and explored their application in Diels-Alder reactions with dienophiles including [60]fullerene. The advantages of using sultines are (1) their thermolysis occurs at a much lower temperature than that of corresponding sulfolenes,[7-8] and (2) they are usually stable above room temperature. We report here our work on the synthesis of naphthosultine **8** and benzodisultines **17** and **18** and their applications in Diels-Alder reactions with alkenes and alkynes.

RESULTS AND DISCUSSION

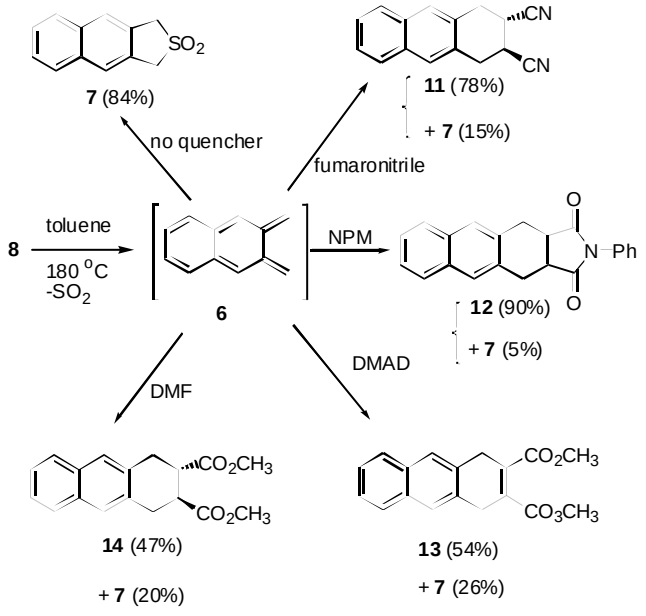
Naphthosultine **8** is readily synthesized in three steps from 2,3-naphthalene-dicarboxylate with an overall yield of 42%, as shown in Scheme I. The 2,3-di(bromomethyl)naphthalene **10** was obtained in 70% yield by bromination of the naphthodiol **9**, and the diol was obtained in 96% yield from a lithium aluminum hydride reduction of the dicarboxylate. Subsequent treatment of the dibromide **10** with Rongalite[8] (sodium formaldehyde sulfoxylate) and tetrabutylammonium bromide (TBAB) in DMF gave the desired sultine **8** in 63%. Sealed tube reactions of the naphthosultine **8** without and with 1.2 equiv. of various electron-deficient dienophiles (fumaronitrile, *N*-phenylmaleimide, dimethyl fumarate, and

Scheme I



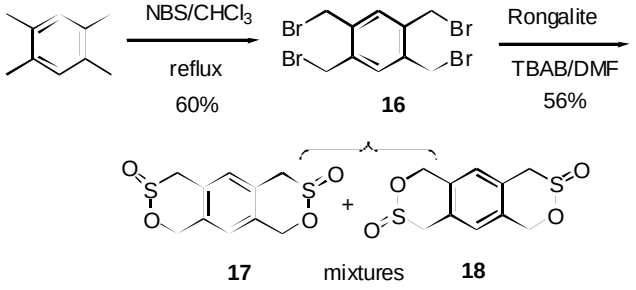
dimethyl acetylenedicarboxylate) in to lu ene at 180 °C gave the re ar ranged naphthosulfolene **7** and cor re spond ing 1:1 cycloadducts **11**-**14** in 67-95% yields (see Scheme II). In the ab sence of quencher, naphthosultine **8** un der went a ther mal re ar range ment to give the naphthosulfolene **7** in 84% yield. In con trast, **7** was re ported[6a] to un dergo ther mal ex tru sion of SO_2 in a boiling diethyl phthalate solution (300 °C) and formed the naphtho[*b*]cyclobutene **15** in 60% yield. The con com i tant for ma tion of Diels-Alder ad ducts **11**-**14** and sulfolene **7** in all re ac tions im plies that re ac tive in ter me di ate naphthoquinodimethane **6** was prob a bly formed but was then trapped ei ther by SO_2 or by dienophiles. Con se quently, higher yields of the Diels-Alder ad ducts **11**-**14** were ob tained if excess amounts of dienophiles or stron ger dienophiles (such as *N*-phenylmaleimide vs. dimethyl fumarate or dimethyl acetyl enedicarboxylate) were used.

Scheme II Where NPM is *N*-phenylmaleimide, DMAD is dimethyl acet y lene-dicarboxylate, and DMF is dimethyl fumarate



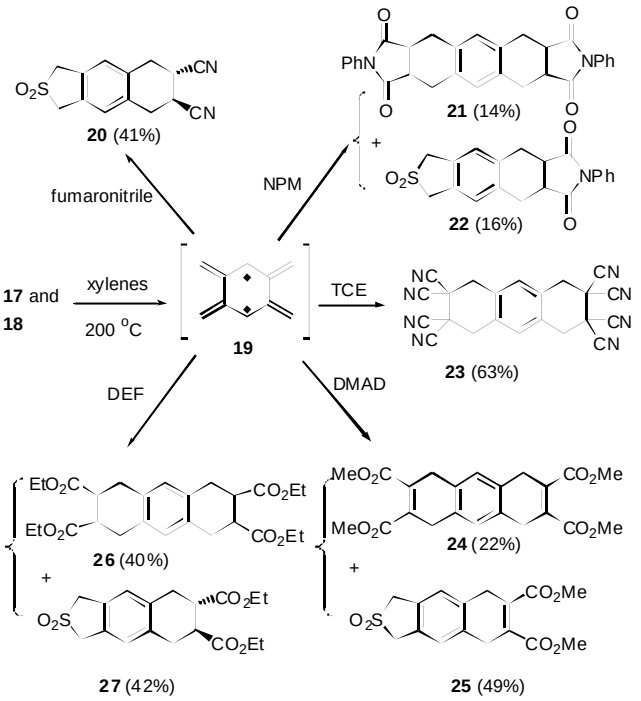
Benzodisultines were syn the sized in two steps from 1,2,4,5-tetramethylbenzene (see Scheme III). Standard bromination of 1,2,4,5-tetramethylbenzene by NBS in chloro form gave 1,2,4,5-tetra(bromomethyl)ben zene **16** in 60% yield. Subsequent treatment of tetrabromide **16** with 5.5 equiv. of Rongalite gave the de sired benzodisultines as a mixture of diastereomers **17** and **18** in 56% yield. Due to the co-ex is tence of two chiral cen ters and two regio po si tions of disultines, at least four diastereomeric prod ucts are ex pected. ^{1}H NMR Spec tra of the mix tures of disultines were quite com plex but their struc tures could be rec og nized by the char-ac ter is tic AB quar tet pat terns of the diastereotopic meth y lene pro tons of each sultine ring.[7] We used the mix ture of benzo-disultines for all the sealed tube trap ping ex per i ments shown in Scheme IV. Al though benzosultine was re ac tive at ca. 100 °C,[8] the re ac tion of benzodisultines at this tem per a ture was slug gish; there fore, all the thermolysis and trap ping ex per i-ments were car ried out at 200 °C for 10 min.

Scheme III



Since there are two sultine rings in a benzodisultine (**17** or **18**), in prin ci ple, these rings can be cleaved by a si mul ta-neous or a step wise se quen tial mech a nism.[9] It is thus not sur-pris ing for us to see two types of prod ucts formed in the sealed tube re ac tion of benzodisultine with a se ries of elec-tron-deficient dienophiles (Scheme IV). When tetracyano-ethylene (TCE) was used as dienophile, only dou ble Diels-Alder adduct **23** was formed in 63% yield; the yield is sim i lar to that re ported by Vogel et al.[9a] for the se quen tial trap ping of 7-oxa[2.2.1]hericene **28**. The ra tio for the two rate con stants k_1 and k_2 of the two suc ces sive Diels-Alder re ac tions of **28** with TCE was found to be around 21. Fur ther more, the ra tios of k_1/k_2 for the reaction of 2,3,5,6-tetramethylidenebicy-

Scheme IV Where the abbreviations are the same as those used in Scheme II, DEF is diethyl fumarate, and TCE is tetracyanoethylene



clo[2.2.1]heptane with a series of dienophiles are ca. 250-376,[9a] which were rationalized by Vogel to be due to the great differences in exothermicity between two successive Diels-Alder reactions. The pyrolysis of benzodisultine with other dienophiles (including *N*-phenylmaleimide, diethyl fumarate and dimethyl acetylenedicarboxylate) gave both 1:1 and 1:2 Diels-Alder adducts in about 1~2 ratio. Although there are competitive trappings of SO_2 and dienophile in both ends of the benzodisultine, the above results indicated that they either react independently, or they do not interfere with each other much; therefore, two successive Diels-Alder reaction products are similar in yields. It is important to note that due to the existence of a sulfolene group in adducts (**20**, **22**, **25**, and **27**), one can still add in another functionality through a second stage Diels-Alder reaction.[10] Thus, benzodisultine is useful for the synthesis of multifunctional polycyclic compounds.

CONCLUSION

Naphthosultine **8** and benzodisultines (**17** and **18**) were readily synthesized and their application in Diels-Alder reactions with a series of electron-deficient dienophiles are reported. The results suggested that thermal extrusion of sulfur dioxide from these sultines led to reactive *o*-naphthoquinodimethane **6** and bis-*o*-QDM **19**, subsequent trapping of these reactive intermediates by dienophiles or SO_2 gave various 1:1 and 1:2 Diels-Alder adducts in moderate to excellent yields. The bis-*o*-QDM is synthetically useful for polycyclic compounds with different functionalities.

EXPERIMENTAL SECTION

General

Melting points were determined on a Yanaca MP-500D melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz NMR, ^{13}C and DEPT were recorded at 75.4 MHz, and the chemical shifts are reported in parts per million (δ) in values relative to $CDCl_3$ (δ = 7.25 for proton and 77.00 ppm for carbon) or tetramethylsilane as internal standard. Coupling constants are reported in hertz (Hz). Mass spectra were recorded on a VG-Trio 2000 spectrometer. High-resolution mass was recorded on a Jouel JMS-HX110 or a JMS-SX/SX 102A spectrometer of the instrument center of National Tsing-Hua and National Chung-Hsin University. C, H, N combustion analyses were determined on a Heraeus analyzer and all analyzed compounds are within ±0.4% of the theoretical value unless otherwise indicated. Column chromatography was performed on silica gel of 70-230 or 230-400 mesh from E. Merck. The preparation of 1,2,4,5-tetra(bromomethyl)benzene **16** followed a literature procedure.[11]

[3-(Hydroxymethyl)-2-naphthyl]methanol 9

To a stirred solution of $LiAlH_4$ (0.89 g, 22.5 mmol) in THF under N_2 at 0 °C was added dimethyl 2,3-naphthalenedicarboxylate (1.00 g, 4.10 mmol). The solution was stirred for 30 min, and then acidified with 30% H_2SO_4. The precipitate was filtered off and the filtrate was extracted with CH_2Cl_2 (2 × 25 mL). The solution was concentrated under reduced pressure and the residue was purified by column chromatography (SiO_2, EtOAc/hexane, 1:3) to give a white solid **9** (0.74 g, 96%): mp 160-161 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82-7.85 (m, 4H), 7.48-7.52 (m, 2H), 4.91 (s, 4H), 2.96 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.94 (C_q), 133.16 (C_q), 128.81 (CH), 127.68 (CH), 126.51 (CH), 64.62 (CH_2); MS (EI) 188 (M^+, 54), 170 (100), 141 (83); HRMS (EI) calcd for $C_{12}H_{12}O_2$: 188.0838, found 188.0846.

2,3-Di(bromomethyl)naphthalene 10[6a]

To a stirred solution of **9** (1.00 g, 5.32 mmol) in CH_2Cl_2

(15 mL) was added PPh_3Br_2 (0.82 g, 2.54 mmol). The mixture was stirred at room temperature. After 10 h, a saturated $NaHCO_3$ solution (20 mL) was added to the mixture and the aqueous phase was extracted with CH_2Cl_2 (2 × 25 mL). The combined organic extracts were dried ($MgSO_4$) and then concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, EtOAc/hexane, 1:3) to give a white solid **10** (0.46 g, 70%): mp 116-118 °C; δ_H 7.85 (s, 2H), 7.82-7.77 (m, 2H), 7.52-7.48 (m, 2H), 4.88 (s, 4H); δ_C 133.76 (C_q), 133.29 (C_q), 130.79 (CH), 127.75 (CH), 127.24 (CH), 31.07 (CH_2); MS (EI) 316 (M^+, 9), 314 (25), 312 (13), 235 (100), 233 (91), 152 (39), 154 (94), 155 (13); HRMS (EI) calcd for $C_{12}H_{10}{}^{79}Br_2$ 311.9149, found 311.9153. Anal. Calcd for $C_{12}H_{10}Br_2$: C, 45.90; H, 3.21. Found: C, 45.79; H, 3.46.

3,4-Dihydro-1*H*-3λ^4-naphtho[2,3-*d*][1,2]oxathiin-3-one (naphthosultine) 8

A solution of **10** (0.5 g, 1.6 mmol), sodium formaldehyde sulfoxylate (Rongalite) (0.78 g, 5.08 mmol) and tetrabutylammonium bromide (TBAB) (0.82 g, 2.54 mmol) in DMF (10 mL) was stirred at rt for 3 h. The mixture was diluted with H_2O (10 mL) and extracted three times with CH_2Cl_2. The organic layer was dried over $MgSO_4$, and then concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, EtOAc/hexane, 1:3) to give a white solid **8** (0.22 g, 63%): mp 167-169 °C; δ_H 7.86-7.80 (m, 4H), 7.57-7.53 (m, 2H), 5.52, 5.15 (ABq, J = 13.3 Hz, 2H), 4.69, 3.77 (A'B'q, J = 15.2 Hz, 2H); δ_C 133.13 (C_q), 132.38 (C_q), 131.67 (C_q), 128.61 (CH), 127.73 (CH), 127.54 (CH), 126.77 (CH), 126.69 (CH), 125.04 (CH), 124.51 (C_q), 64.05 (CH_2), 58.41 (CH_2); MS (EI) 218 (M^+, 6), 154 (100), 149 (11), 139 (10); HRMS (EI) calcd for $C_{12}H_{10}O_2S$ 218.0402, found 218.0397. Anal. Calcd for $C_{12}H_{10}O_2S$: C, 66.03; H, 4.62. Found: C, 65.94; H, 4.98.

General Procedure for the Trapping Experiments of Naphthosultine 8 with Dienophiles such as Fumaronitrile, *N*-Phenylmaleimide, Dimethyl Acetylene-Dicarboxylate, and Dimethyl Fumarate

A solution of naphthosultine **8** (50 mg, 0.23 mmol), with or without respective dienophiles (0.28 mmol), in toluene (3 mL) was heated at 180 °C in a sealed tube under N_2 for 4 h. The solvent was evaporated under vacuum, and the residue was subjected to silica gel chromatography using hexane/ethyl acetate (3:1) as the eluent. Naphthosulfolene **7** was obtained in 84% yield (no quencher). For the trapping of naphthoquinodimethane **6**, the respective yields are: fumaronitrile, 78% of **11** (41.6 mg) and 15% of **7** (7.5 mg); *N*-phenylmaleimide, 90% of **12** (68 mg) and 5% of **7** (2.5 mg); dimethyl acetylenedicarboxylate, 54% of **13** (37 mg) and 26% of **7** (13 mg); and dimethyl fumarate, 47% of **14** (32 mg) and 20% of **7** (10 mg).

2,3-Dihydro-1*H*-2λ^6-naphtho[2,3-*c*]thiophene-2,2-dione (naphthosulfolene) 7

A white solid; mp 254-255 °C (lit.[6a] 254-256 °C); δ_H 7.80-7.84 (m, 4H), 7.26-7.55 (m, 2H), 4.52 (s, 4H); δ_C 133.06 (C_q), 128.90 (C_q), 127.73 (CH), 126.97 (CH), 125.36 (CH), 56.51 (CH_2); MS (EI) 218 (M^+, 22), 154 (100); HRMS (EI) calcd for $C_{12}H_{10}O_2S$: 218.0402, found 218.0403. Anal. Calcd for $C_{12}H_{10}O_2S$: C, 66.03; H, 4.62. Found: C, 65.72; H, 4.85.

1,2,3,4-Tetrahydro-2,3-anthracenedicarbonitrile 11

A white solid; mp 198-200 °C; δ_H 7.30-7.80 (m, 6H), 3.20-3.60 (m, 6H); δ_C 132.60 (C_q), 128.20 (C_q), 127.68 (CH), 127.29 (CH), 126.41 (CH), 118.57 (C_q), 30.87 (CH_2), 29.08 (CH); MS (EI) *m/z* 232 (M^+, 100), 154 (47); HRMS calcd for $C_{16}H_{12}N_2$ 232.1560, found 232.1594.

2-Phenyl-2,3,3a,4,11,11a-hexahydro-1*H*-naphtho[2,3-*f*]-isoindole-1,3-dione 12

A white solid; mp 231-232 °C (lit.[6a] 230-233 °C); δ_H 6.60-7.70 (m, 11H), 3.31-3.52 (m, 4H), 3.00-3.12 (m, 2H); δ_C 178.43 (C_q), 132.85 (C_q), 132.78 (C_q), 131.54 (C_q), 128.94 (CH), 128.5 (CH), 127.43 (CH), 126.38 (CH), 126.25 (CH), 125.76 (CH), 40.25 (CH_3), 30.1 (CH_2); MS (EI) *m/z* 327 (M^+, 93), 179 (100); HRMS (EI) calcd for $C_{22}H_{17}O_2N$ 327.1260 found 327.1255.

Dimethyl 1,4-dihydro-2,3-anthracenedicarboxylate 13

A white solid; mp 132-134 °C; δ_H 7.43-7.90 (m, 6H), 3.90 (s, 4H), 3.85 (s, 6H); δ_C 168.10 (C_q), 133.82 (C_q), 132.40 (C_q), 130.42 (C_q), 127.21 (CH), 126.17 (CH), 125.70 (CH), 52.43 (CH_3), 31.73 (CH_2); HRMS (EI) calcd for $C_{18}H_{16}O_4$ 296.1049, found 296.1048. Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.78; H, 5.50.

Dimethyl 1,2,3,4-tetrahydro-2,3-anthracenedicarboxylate 14

A white solid; mp 114-115 °C; δ_H 7.36-7.60 (m, 6H), 3.69 (s, 6H), 3.60-3.20 (m, 6H); δ_C 173.34 (C_q), 132.41 (C_q), 132.22 (C_q), 127.10 (CH), 127.06 (CH), 125.35 (CH), 52.03 (CH_3), 40.80 (CH), 29.85 (CH_2); MS (EI) *m/z* 298 (M^+, 25), 238 (59), 459 (80), 180 (18), 179 (100); HRMS (EI) calcd for $C_{18}H_{18}O_4$ 298.1205, found 298.1207.

1,2,4,5-Tetra(bromomethyl)benzene 16

A white solid;[11] mp 150-152 °C; δ_H 7.38 (s, 2H), 4.60 (s, 8H); δ_C 137.58 (C_q), 133.58 (CH), 28.66 (CH_2).

4,6,7,9-Tetrahydro-1*H*,3*H*-3λ^4,7λ^4-[1,2]oxathiino[5′,4′:4,5]-benzo[*d*][1,2]oxathiine-3,7-diones 17 and 18

A solution of **16** (1.0 g, 2.22 mmol), Rongalite (1.71 g, 11.10 mmol) and TBAB (0.36 g, 1.12 mmol) in DMF (10 mL) was stirred at rt for 6 h. The mixture was diluted with H_2O (10 mL) and extracted three times with CH_2Cl_2. The organic layer was dried over $MgSO_4$. Evaporation of the solvent and the residue was purified by column chromatography (EtOAc/hexane, 1:3) to give a mixture of **17** and **18** (0.32 g, 56%). **17** and **18**: δ_H 7.11-7.17 (m, 4H), 4.97, 5.30 (A′B′q, *J* = 13.8 Hz, 8H), 4.40, 4.30 (ABq, *J* = 15.0 Hz, 4H), 3.62, 3.56 (A′B′q, *J* = 15.0 Hz, 4H); δ_C 133.32 (C_q), 132.83 (C_q), 131.54 (CH), 131.02 (CH), 127.14 (CH), 126.74 (C_q), 126.12 (C_q), 125.54 (C_q), 123.06 (CH), 122.80 (CH), 62.40 (CH_2), 62.32 (CH_2), 56.31 (CH_2), 55.64 (CH_2); HRMS (EI) calcd for $C_{10}H_{10}O_4S_2$ 258.0021, found 258.0019.

General Procedure for the Trapping Experiments of Benzodisultines 17 and 18 with Dienophiles such as Fumaronitrile, *N*-Phenylmaleimide, Tetracyanoethylene, Dimethyl Acetylenedicarboxylate, and Diethyl Fumarate

A solution mixture of benzodisultines **17** and **18** (40 mg, 0.16 mmol), with respective dienophiles (0.93 mmol), in xylenes (3 mL) was heated at 200°C in a sealed tube under N_2 for 10 min. The solvent was evaporated under vacuum, and the residue was subjected to silica gel chromatography using hexane/ethyl acetate (from 2:1 to 8:1) as the eluent. Respective yields for the trapping experiments with various dienophiles are summarized in Scheme IV.

2,2-Dioxo-2,3,5,6,7,8-hexahydro-1*H*-2λ^6-naphtho[2,3-*c*]-thiophene-6,7-dicarbonitrile 20

41% yield; a white solid, mp 228-229 °C; δ_H 7.14 (s, 2H), 4.34 (s, 4H), 3.46-3.33 (m, 4H), 3.21-3.15 (m, 2H); δc 131.11 (C_q), 130.82 (C_q), 126.71 (CH), 118.00 (C_q), 56.46 (CH_2), 29.92 (CH_2), 28.02 (CH); MS (EI) *m/z* 272 (M^+, 2), 208 (100), 130 (15), 117 (22). HRMS calcd for $C_{14}H_{12}N_2O_2S$: 272.0620, found 272.0622.

2,8-Diphenyl-1,2,3,3a,4,6,6a,7,8,9,9a,10,12,12a-Tetradecahydropyrrolo[3′,4′:6,7]naphtho[2,3-*f*]isoindole-1,3,7,9-tetraone 21

16% yield, a white solid; mp > 270 °C; δ_H 7.16-7.09 (m, 8H), 6.83-6.80 (m, 4H), 3.41-3.39 (m, 4H), 3.20-3.14 (m, 4H), 3.02-2.96 (m, 4H); δc 178.27 (C_q), 134.22 (C_q), 131.40 (C_q), 128.89 (CH), 128.47 (CH), 127.40 (CH), 126.22 (CH), 40.17 (CH), 29.42 (CH_2); MS (EI) *m/z* 476 (M^+, 71), 328 (100), 179 (51), 165 (51).

7-Phenyl-1,2,3,5,5a,6,7,8,8a,9-decahydro-2λ^6-thieno-[3′,4′:4,5]benzo[*f*]isoindole-2,2,6,8-tetraone 22

14% yield, a white solid; mp 240-241 °C; δ_H 6.79-7.33 (m, 7H), 4.25 (s, 4H), 2.89-3.44 (m, 6H); δc 178.03 (C_q), 136.12 (C_q), 131.42 (C_q), 130.39 (C_q), 129.15 (CH), 128.78 (CH), 126.20 (CH), 125.56 (CH), 56.66 (CH_2), 39.86 (CH), 29.80 (CH_2); MS (EI) *m/z* 367 (M^+, 10), 335 (100), 179 (21).

1,2,3,4,5,6,7,8-octahydroanthracene-2,2,3,3,6,6,7,7-otacarbonitrile 23

63% yield, a brown solid; mp > 270 °C (lit.[9a] > 200 °C); ^{1}H NMR (300 MHz, acetone-d_6) δ_H 7.48 (s, 2H), 4.25 (s, 8H); ^{13}C NMR (75 MHz, acetone-d_6) δ_C 130.76 (CH), 127.58 (C_q), 111.78 (C_q), 39.71 (C_q), 34.66 (CH_2); MS (EI) *m/z* 386 (M^+, 8), 258 (100). HRMS calcd for $C_{22}H_{10}N_8$ 386.1031, found 386.1004.

Tetramethyl 1,4,5,8-tetrahydro-2,3,6,7-anthracenetetracarboxylate 24

22% yield, a white solid; mp 206-208 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 6.97 (s, 2H), 3.83 (s, 12H), 3.68 (s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δc 168.06 (C_q), 133.29 (C_q), 130.13 (C_q), 127.20 (CH), 52.38 (CH_3), 31.04 (CH_2); MS (EI) *m/z* 414 (M^+, 7), 382 (100), 323 (23), 263 (17), 178 (41).

Dimethyl 2,2-dioxo-2,3,5,8-tetrahydro-1*H*-2λ^6-naphtho-[2,3-*c*]thiophene-6,7-dicarboxylate 25

49% yield, a white solid, mp 210-211 °C; δ_H 7.13 (s, 2H), 4.33 (s, 4H), 3.84 (s, 6H), 3.72 (s, 4H); δc 167.65 (C_q), 132.85 (C_q), 132.63 (C_q), 129.79 (C_q), 125.44 (CH), 56.55 (CH_2), 52.45 (CH_3), 31.24 (CH_2); MS (EI) *m/z* 336 (M^+, 8), 304 (100), 277 (42), 239 (82), 212 (52), 181 (45), 154 (65). HRMS calcd for $C_{16}H_{16}O_6S$ 336.0668, found 336.0613.

Tetraethyl 1,2,3,4,5,6,7,8-octahydro-2,3,6,7-anthracenetetracarboxylate 26[9b]

40% yield, a white solid; mp 142-144 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 6.83 (s, 2H), 4.18 (q, *J* = 7.2 Hz, 8H), 3.11-2.89 (m, 12H), 1.28 (t, *J* = 7.1 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δc 174.35 (C_q), 131.95 (C_q), 128.34 (CH), 60.73 (CH_2), 42.16 (CH_3), 31.33 (CH_2), 14.11 (CH_3); MS (EI) *m/z* 474 (M^+, 12), 400 (30), 355 (15), 326 (37), 281 (25), 253 (29), 179 (100). HRMS calcd for $C_{26}H_{34}O_8$ 474.2254, found

474.2239.

Diethyl 2,2-dioxo-2,3,5,6,7,8-hexahydro-1*H*-2λ^6-naphtho-[2,3-*c*]thiophene-6,7-dicarboxylate 27

42% yield, a white solid; mp 127-128 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.06 (s, 2H), 4.30 (s, 4H), 4.17 (q, 7.2, 4H), 3.18-2.95 (m, 6H), 1.28 (t, J = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δc 173.84 (C_q), 135.02 (C_q), 129.20 (C_q), 125.95 (CH), 60.95 (CH_2), 59.56 (CH_2), 41.62 (CH), 31.17 (CH_2), 14.10 (CH_3); MS (EI) *m/z* 366 (M^+, 13), 321 (19), 292 (60), 228 (80), 155 (100). HRMS calcd for $C_{18}H_{22}O_6S$ 366.1137, found 366.1137.

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Key Words

Naphthosultine; Benzodisultine; Pyrolysis; Diels-Alder reaction; *o*-Quinodimethanes; Tetramethylenebenzene.

REFERENCES

1. (a) Charlton, J. L.; Alauddin, M. M. *Tetrahedron* **1987**, *43*, 2873. (b) Oppolzer, W. *Synthesis* **1978**, 793. (c) Martin, N.; Seoane, C.; Hanak, M. *Org. Prep. Proced. Int.* **1991**, *23*, 237. (d) Segura, J. L.; Martin, N. *Chem. Rev.* **1999**, *99*, 3199.
2. Kametani, T. *Pure Appl. Chem.* **1979**, *51*, 747.
3. For 1,4-elimination methods, see (a) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1982**, *104*, 7609. (b) Inaba, S.-i.; Wehmeyer, R. M.; Forkner, M. W.; Rieke, R. D. *J. Org. Chem.* **1988**, *53*, 339.
4. Flynn, C. R.; Michl, J. *J. Am. Chem. Soc.* **1974**, *96*, 3280.
5. Oppolzer, W. *Heterocycles* **1980**, *14*, 1615.
6. (a) Cava, M. P.; Shirley, R. L. *J. Am. Chem. Soc.* **1960**, *82*, 654. (b) Gisin, M.; Wirz, J. *Helv. Chim. Acta* **1976**, *59*, 2273.
7. (a) Chung, W.-S.; Lin, W.-J.; Liu, W.-D.; Chen, L.-G. *J. Chem. Soc. Chem. Commun.* **1995**, 2537. (b) Chung, W.-S.; Liu, J.-H. *Chem. Commun.* **1997**, 205. (c) Liu, J.-H.; Wu, A.-T.; Huang, M.-H.; Wu, C.-W.; Chung, W.-S. *J. Org. Chem.* **2000**, *65*, 3395.
8. For a review of sultines see: Dittmer, D. C.; Hoey, M. D. *The Chemistry of Sulphinic Acids, Esters and Their Derivatives*; Wiley: Chichester, 1990; pp 239-273.
9. For related tandem Diels-Alder reactions see (a) Rubello, A.; Vogel, P. *Helv. Chim. Acta* **1988**, *71*, 1268. (b) Reynolds, J. H.; Berson, J. A.; Kumashiro, K. K.; Duchamp, J. C.; Zilm, K. W.; Scaiano, J. C.; Berinstain, A. B.; Rubello, A. A.; Vogel, P. *J. Am. Chem. Soc.* **1993**, *115*, 8073. (c) Lu, H. S. M.; Berson, J. A. *J. Am. Chem. Soc.* **1996**, *118*, 265.
10. For an interesting application of this bis-*o*-QDM strategy, see: Gügel, A.; Belik, P.; Walter, M.; Kraus, A.; Harth, E.; Wagner, M.; Spickermann, J.; Müllen, K. *Tetrahedron* **1996**, *52*, 5007.
11. Hebbelynck, M. F.; Martin, R. H. *Bull. Soc. Chim. Belges.* **1950**, *59*, 206.