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Sealed tube re ac tions of the naphthosultine **8** with a se ries of elec tron-deficient dienophiles (fumaronitrile, *N*-phenylmaleimide, dimethyl fumarate, and dimethyl acetylenedicarboxylate) in to lu ene at 180 °C gave cor re spond ing 1:1 cycloadducts **11-14** in var i ous amounts along with re ar ranged naphthosulfolene **7** in 67-95% yields. The re ac tion of 1,2,4,5-tetra(bromomethyl)ben zene with Rongalite (so dium form aldehyde sulfoxylate) and tetrabutylammonium bro mide in DMF gave benzodisultines **17** and **18** in a com bined yield of 56%. Sealed tube re ac tions of benzodisultines **17** and **18** with a se ries of dienophiles in xylene at 200 °C gave cor re spond ing 1:1 and 1:2 cycloadducts **20-27**. The re sults sug gested that ther mal ex tru sion of sul fur di ox ide from these sultines led to ei ther *o*-naphthoquinodimethane **6** (from **8**) or bis-*o*-quinodimethane **19** (from **17** and **18**); sub se quent trap ping of these re ac tive in ter me di ates by dienophiles and SO₂ gave var i ous 1:1 and 1:2 Diels-Alder ad ducts in mod est to ex cel lent yields.

INTRODUCTION

Much at ten tion has been fo cused on the syn the sis of polycyclic com pounds us ing *o*-quinodimethane (*o*-QDM) **1** and its an a logues, and nu mer ous meth ods for the gen er a tion of the *o*-QDM in terme di ates have been de vel oped.¹ Among them are ring-openings of benzocyclobutenes² **2**, 1,4-eli mina tion of α , α' -disubstituted *o*-xylenes **3**,³ and various "extrusion" reactions in volving loss of a small mole cule.¹ For example, losses of N₂ from diazene⁴ **4** or SO₂ from sulfolene^{1,5} **5** have been shown to lead to the *o*-QDM intermediates.



In a pi o neer ing work by Cava and co work ers, 6a the naphtho an a logue of *o*-QDM **6** was gen er ated us ing SO₂ extru sion from sulfolene **7**; how ever, a re action tem per a ture of 300 °C was re quired! The naphthoquinodimethane **6** was later re ported by Wirz et. al. us ing a diazene-precursor, 6b but the diazene com pound was un sta ble and had to be kept un der -40 °C. Fur ther more, an in trac ta ble mix ture of prod ucts was ob tained in deaerated so lu tion of the diazene com pound.

Thus, finding an easy, high-yield method for generating naphthoquinodimethane **6** and a fur ther exten sion to bis-o-QDM are of partic u lar in terests. Recently we described⁷ the generation of a series of heteroaromatic o-QDMs, by ther mal extrusion of SO₂ from corresponding sultines, and ex plored their ap pli cation in Diels-Alder reactions with dienophiles in cluding [60]fullerene. The ad van tages of us ing sultines are (1) their thermolysis oc curs at a much lower tem per a ture than that of corre sponding sulfolenes,⁷⁻⁸ and (2) they are usu ally sta ble above room tem per a ture. We report here our work on the syn the sis of naphthosultine **8** and benzodisultines **17** and **18** and their applications in Diels-Alder reactions with alkenes and al kynes.

RESULTS AND DISCUSSION

Naphthosultine **8** is readily syn the sized in three steps from 2,3-naphthalene-dicarboxylate with an over all yield of 42%, as shown in Scheme I. The 2,3-di(bromomethyl)naphthalene **10** was ob tained in 70% yield by bromination of the naphthodiol **9**, and the diol was ob tained in 96% yield from a lith ium alu mi num hy dride re duc tion of the dicarboxylate. Sub se quent treat ment of the dibromide **10** with Rongalite⁸ (sodium formaldehyde sulfoxylate) and tetrabutyl ammonium bro mide (TBAB) in DMF gave the de sired sultine **8** in 63%. Sealed tube re ac tions of the naphthosultine **8** with out and with 1.2 equiv. of var i ous elec tron-deficient dienophiles (fumaronitrile, *N*-phenylmaleimide, dimethyl fumarate, and



dimethyl acetylenedicarboxylate) in to lu ene at 180 °C gave the re ar ranged naphthosulfolene 7 and cor re sponding 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 SO₂ in a boiling diethyl phthalate solution (300 °C) and formed the naphtho[*b*]cyclobutene **15** in 60% yield. The concom 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

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



Wu et al.

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 ace-tyl enedicarboxylate) were used.

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 coex is tence of two chiral cen ters and two regio po si tions of disultines, at least four diastereomeric products are expected. ¹H NMR Spec tra of the mix tures of disultines were quite com plex but their struc tures could be rec og nized by the characteristic AB quartet patterns of the diastereotopic methy lene pro tons of each sultine ring.⁷ We used the mix ture of benzodisultines 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 reaction of benzodisultines at this temper a ture was slug gish; there fore, all the thermolysis and trap ping ex per iments 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 taneous or a step wise se quential mech anism.⁹ It is thus not surprising for us to see two types of products formed in the sealed tube reaction of benzodisultine with a series of electron-deficient dienophiles (Scheme IV). When tetracyanoethylene (TCE) was used as dienophile, only double Diels-Alder adduct **23** was formed in 63% yield; the yield is sim i lar to that reported by Vogel et al.^{9a} for the se quential trap ping of 7-oxa[2.2.1]hericene **28**. The ratio for the two rate con stants k_1 and k_2 of the two succes sive Diels-Alder reactions of **28** with TCE was found to be around 21. Fur ther more, the ratios of k_1/k_2 for the reaction of 2,3,5,6-tetramethylidenebicy

Scheme IV Where the ab bre vi a tions are the same as those used in Scheme II, DEF is di ethyl fumarate, and TCE is tetracyanoethylene



clo[2.2.1]heptane with a se ries of dienophiles are ca. 250-376,^{9a} which were ratio nalized by Vogel to be due to the great differences in exothermicity be tween two succes sive Diels-Alder re actions. The py rol y sis of benzodisultine with other dienophiles (in clud ing N-phenylmaleimide, di ethyl fumarate and dimethyl acetylenedicarboxylate) gave both 1:1 and 1:2 Diels-Alder ad ducts in about 1~2 ra tio. Al though there are competitive trappings of SO_2 and dienophile in both ends of the benzodisultine, the above re sults in di cated that they either react in dependently, or they do not in ter fere with each other much; there fore, two suc ces sive Diels-Alder re ac tion products are sim i lar in yields. It is important to note that due to the ex is tence of a sulfolene group in ad ducts (20, 22, 25, and 27), one can still add in an other func tion al ity through a sec ond stage Diels-Alder re ac tion.¹⁰ Thus, benzodisultine is use ful for the syn the sis of multifunctional polycyclic compounds.

CONCLUSION

Naphthosultine 8 and benzodisultines (17 and 18) were readily syn the sized and their ap plication in Diels-Alder reactions with a series of elec tron-deficient dienophiles are reported. The re sults sug gested that ther mal ex tru sion of sul fur di ox ide from these sultines led to re ac tive o-naphtho quinodimethane **6** and bis-o-QDM **19**, sub se quent trap ping of these re active in terme di ates by dienophiles or SO₂ gave var i ous 1:1 and 1:2 Diels-Alder ad ducts in mod est to ex cel lent yields. The bis-o-QDM is syn thet i cally use ful for polycyclic compounds with different functionalities.

EXPERIMENTAL SECTION

General

Melting points were de ter mined on a Yanaca MP-500D meltingpoint apparatus and are un corrected.¹H NMR spec tra were re corded at 300 MHz NMR, 13C and DEPT were recorded at 75.4 MHz, and the chem i cal shifts are re ported in parts per mil lion (δ) in values relative to CDCl₃ ($\delta = 7.25$ for pro ton and 77.00 ppm for car bon) or tetramethylsilane as internal standard. Cou pling con stants are re ported in hertz (Hz). Mass spec tra were re corded on a VG-Trio 2000 spectrometer. High-resolution mass was recorded on a Jouel JMS-HX110 or a JMS-SX/SX 102A spec trom e ter of the instru ment cen ter of Na tional Tsing-Hua and Na tional Chung-Hsin University. C, H, N com bus tion analyses were deter mined on a Heraeus an a lyzer and all an a lyzed com pounds are within $\pm 0.4\%$ of the the o ret i cal value un less oth er wise in dicated. Col umn chro ma tog ra phy was per formed on sil ica gel of 70-230 or 230-400 mesh from E. Merck. The prep a ration of 1,2,4,5-tetra(bromomethyl)ben zene 16 fol lowed a lit er atureprocedure.¹¹

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

To a stirred so lu tion of LiAlH₄ (0.89 g, 22.5 mmol) in THF un der N₂ at 0 °C was added dimethyl 2,3-naphthalenedicarboxylate (1.00 g, 4.10 mmol). The so lu tion was stirred for 30 min, and then acid i fied with 30% H₂SO₄. The pre cip itate was fil tered off and the fil trate was ex tracted with CH₂Cl₂ (2 ×25 mL). The so lu tion was con cen trated un der re duced pres sure and the res i due was pu ri fied by col umn chro ma togra phy (SiO₂, EtOAc/hex ane, 1:3) to give a white solid**9** (0.74 g, 96%): mp 160-161 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.82-7.85 (m, 4H), 7.48-7.52 (m, 2H), 4.91 (s, 4H), 2.96 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 136.94 (Cq), 133.16 (Cq), 128.81 (CH), 127.68 (CH), 126.51 (CH), 64.62 (CH₂); MS (EI) 188 (M⁺, 54), 170 (100), 141 (83); HRMS (EI) calcd for C₁₂H₁₂O₂: 188.0838, found 188.0846.

2,3-Di(bromomethyl)naph tha lene 10^{6a}

To a stirred so lution of 9 (1.00 g, 5.32 mmol) in CH₂Cl₂

(15 mL) was added PPh₃Br₂ (0.82 g, 2.54 mmol). The mix ture was stirred at room temperature. After 10 h, a saturated NaHCO₃ so lu tion (20 mL) was added to the mix ture and the aque ous phase was ex tracted with CH₂Cl₂ (2 × 25 mL). The com bined or ganic ex tracts were dried (MgSO₄) and then concen trated un der re duced pres sure. The res i due was pu ri fied by col umn chro ma tog ra phy (SiO₂, EtOAc/hex ane, 1:3) to give a white solid **10** (0.46 g, 70%): mp 116-118 °C; $\delta_{\rm H}$ 7.85 (s, 2H), 7.82-7.77 (m, 2H), 7.52-7.48 (m, 2H), 4.88 (s, 4H); $\delta_{\rm C}$ 133.76 (C_q), 133.29 (C_q), 130.79 (CH), 127.75 (CH), 127.24 (CH), 31.07 (CH₂); MS (EI) 316 (M⁺, 9), 314 (25), 312 (13), 235 (100), 233 (91), 152 (39), 154 (94), 155 (13); HRMS (EI) calcd for C₁₂H₁₀⁷⁹Br₂ 311.9149, found 311.9153. Anal. Calcd for C₁₂H₁₀Br₂: C, 45.90; H, 3.21. Found: C, 45.79; H, 3.46.

3,4-Dihydro-1*H*-31⁴-naphtho[2,3-*d*][1,2]oxathiin-3-one (naphthosultine) 8

A solution of 10 (0.5 g, 1.6 mmol), so dium form al dehyde sulfoxylate (Rongalite) (0.78 g, 5.08 mmol) and tetrabutylammonium bro mide (TBAB) (0.82 g, 2.54 mmol) in DMF (10 mL) was stirred at rt for 3 h. The mix ture was diluted with H₂O (10 mL) and extracted three times with CH₂Cl₂. The or ganic layer was dried over MgSO₄, and then con cen trated un der re duced pres sure. The res i due was pu rified by column chro matog raphy (SiO₂, EtOAc/hex ane, 1:3) to give a white solid **8** (0.22 g, 63%): mp 167-169 °C; $\delta_{\rm H}$ 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); $\delta_{\rm C}$ 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 (CH₂), 58.41 (CH₂); MS (EI) 218 (M⁺, 6), 154 (100), 149 (11), 139 (10); HRMS (EI) calcd for C₁₂H₁₀O₂S 218.0402, found 218.0397. Anal. Calcd for C₁₂H₁₀O₂S: 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 so lu tion of naphthosultine **8** (50 mg, 0.23 mmol), with or with out re spec tive dienophiles (0.28 mmol), in to luene (3 mL) was heated at 180°C in a sealed tube un der N_2 for 4 h. The sol vent was evap o rated un der vac uum, and the res idue was sub jected to sil ica gel chro ma tog ra phy us ing hexane/ethyl ac e tate (3:1) as the eluent. Naphthosulfolene **7** was ob tained in 84% yield (no quencher). For the trap ping of naphthoquinodimethane **6**, the re spec tive 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*-2 λ^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 (CH₂); MS (EI) 218 (M⁺, 22), 154 (100); HRMS (EI) calcd for C₁₂H₁₀O₂S: 218.0402, found 218.0403. Anal. Calcd for C₁₂H₁₀O₂S: 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 (CH₂), 29.08 (CH); MS (EI) *m/z* 232 (M⁺, 100), 154 (47); HRMS calcd for C₁₆H₁₂N₂ 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); $\delta_{\rm H}$ 6.60-7.70 (m, 11H), 3.31-3.52 (m, 4H), 3.00-3.12 (m, 2H); $\delta_{\rm C}$ 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 (CH₃), 30.1 (CH₂); MS (EI) *m/z* 327 (M⁺, 93), 179 (100); HRMS (EI) calcd for C₂₂H₁₇O₂N 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 (CH₃), 31.73 (CH₂); HRMS (EI) calcd for C₁₈H₁₆O₄ 296.1049, found 296.1048. Anal. Calcd for C₁₈H₁₆O₄: 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; $\delta_{\rm H}$ 7.36-7.60 (m, 6H), 3.69 (s, 6H), 3.60-3.20 (m, 6H); $\delta_{\rm C}$ 173.34 (C_q), 132.41 (C_q), 132.22 (C_q), 127.10 (CH), 127.06 (CH), 125.35 (CH), 52.03 (CH₃), 40.80 (CH), 29.85 (CH₂); MS (EI) *m*/*z* 298 (M⁺, 25), 238 (59), 459 (80), 180 (18), 179 (100); HRMS (EI) calcd for C₁₈H₁₈O₄ 298.1205, found 298.1207.

1,2,4,5-Tetra(bromomethyl)ben zene 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 (CH₂).

4,6,7,9-Tetrahydro-1*H*,3*H*-3λ⁴,7λ⁴-[1,2]oxathiino[5',4':4,5]benzo[*d*][1,2]oxathiine-3,7-diones 17 and 18

A so lu tion 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 mix ture was di luted with H₂O (10 mL) and ex tracted three times with CH₂Cl₂. The or ganic layer was dried over MgSO₄. Evap o ra tion of the sol vent and the res i due was puri fied by col umn chro ma tog ra phy (EtOAc/ hex ane, 1:3) to give a mix ture of **17** and **18** (0.32 g, 56%). **17** and **18**: $\delta_{\rm H}$ 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); $\delta_{\rm C}$ 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 (CH₂), 62.32 (CH₂), 56.31 (CH₂), 55.64 (CH₂); HRMS (EI) calcd for C₁₀H₁₀O₄S₂ 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 so lu tion mix ture of benzodisultines **17** and **18** (40 mg, 0.16 mmol), with re spec tive dienophiles (0.93 mmol), in xylenes (3 mL) was heated at 200°C in a sealed tube un der N_2 for 10 min. The sol vent was evap o rated un der vac uum, and the res i due was subjected to sil ica gel chro ma tog ra phy us ing hex ane/ethyl ac e tate (from 2:1 to 8:1) as the eluent. Re spective yields for the trap ping ex per i ments with var i ous dienophiles are sum ma rized in Scheme IV.

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

41% yield; a white solid, mp 228-229 °C; $\delta_{\rm H}$ 7.14 (s, 2H), 4.34 (s, 4H), 3.46-3.33 (m, 4H), 3.21-3.15 (m, 2H); $\delta_{\rm C}$ 131.11 (C_q), 130.82 (C_q), 126.71 (CH), 118.00 (C_q), 56.46 (CH₂), 29.92 (CH₂), 28.02 (CH); MS (EI) *m*/*z* 272 (M⁺, 2), 208 (100), 130 (15), 117 (22). HRMS calcd for C ₁₄H₁₂N₂O₂S: 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-1,3,7,9tetraone 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); & 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 (CH₂); 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-2^{\lambda}-thieno-[3',4':4,5]benzo[*f*]isoindole-2,2,6,8-tetraone 22

14% yield, a white solid; mp 240-241 °C; $\delta_{\rm H}$ 6.79-7.33 (m, 7H), 4.25 (s, 4H), 2.89-3.44 (m, 6H); $\delta_{\rm C}$ 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 (CH₂), 39.86 (CH), 29.80 (CH₂); 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); ¹HNMR (300 MHz, ac e tone-*d*₆) δ_H 7.48 (s, 2H), 4.25 (s, 8H); ¹³C NMR (75 MHz, ac e tone-*d*₆) δ_C 130.76 (CH), 127.58 (C_q), 111.78 (C_q), 39.71 (C_q), 34.66 (CH₂); MS (EI) *m*/*z* 386 (M⁺, 8), 258 (100). HRMS calcd for C₂₂H₁₀N₈ 386.1031, found 386.1004.

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

22% yield, a white solid; mp 206-208 °C; ¹H NMR (300 MHz, CDCl₃) $\delta_{\rm H}$ 6.97 (s, 2H), 3.83 (s, 12H), 3.68 (s, 8H); ¹³C NMR (75 MHz, CDCl₃) & 168.06 (C_q), 133.29 (C_q), 130.13 (C_q), 127.20 (CH), 52.38 (CH₃), 31.04 (CH₂); MS (EI) *m*/*z* 414 (M⁺, 7), 382 (100), 323 (23), 263 (17), 178 (41).

Dimethyl 2,2-dioxo-2,3,5,8-tetrahydro-1H-2 λ^6 -naphtho-[2,3-*c*]t hiophene-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 (CH₂), 52.45 (CH₃), 31.24 (CH₂); MS (EI) *m*/*z* 336 (M⁺, 8), 304 (100), 277 (42), 239 (82), 212 (52), 181 (45), 154 (65). HRMS calcd for C₁₆H₁₆O₆S 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; ¹H NMR (300 MHz, CDCl₃) $\delta_{\rm H}$ 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); ¹³C NMR (75 MHz, CDCl₃) $\delta_{\rm C}$ 174.35 (C_q), 131.95 (C_q), 128.34 (CH), 60.73 (CH₂), 42.16 (CH₃), 31.33 (CH₂), 14.11 (CH₃); MS (EI) *m*/*z* 474 (M⁺, 12), 400 (30), 355 (15), 326 (37), 281 (25), 253 (29), 179 (100). HRMS calcd for C₂₆H₃₄O₈ 474.2254, found

474.2239.

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

42% yield, a white solid; mp 127-128 °C; ¹H NMR (300 MHz, CDCl₃) $\delta_{\rm H}$ 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); ¹³C NMR (75 MHz, CDCl₃) $\delta_{\rm C}$ 173.84 (C_q), 135.02 (C_q), 129.20 (C_q), 125.95 (CH), 60.95 (CH₂), 59.56 (CH₂), 41.62 (CH), 31.17 (CH₂), 14.10 (CH₃); MS (EI) *m*/*z* 366 (M⁺, 13), 321 (19), 292 (60), 228 (80), 155 (100). HRMS calcd for C₁₈H₂₂O₆S 366.1137, found 366.1137.

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Key Words

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

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