coupled 6-proton discernible *ca.* δ 8.04; J = 2.5 Hz), 3.92 (s, 3, OCH_3); mass spectrum M^+ 261 with 231 ($-OCH_3$), 203 ($-CO$), and M^+ 277 (low intensity).

Anal. Calcd for $C_{17}H_{11}NO_2$: C, 78.15; H, 4.24; N, 5.36. Found: C, 77.91; H, 4.36; N, 5.47.

5-Methoxy-7-hydroxy-1,2,3,11b-tetrahydro-7*H*-dibenzo[*de*,*h*]-quinoline (6).—Treatment of a suspension of **4a** in methanol with an excess (4–5 parts by weight) of $NaBH_4$ resulted in effervescence and solution of the material. After heating on a steam cone 20 min while evaporating most of the methanol, the cooled residue was treated with water. The collected, washed (water), and dried product, on recrystallization from methanol, gave colorless crystals: mp 191–193°; ir 6.18 μ (weak) together with bonded OH and NH bands; uv 276 nm (ϵ 1960) and 284 (2010).

Anal. Calcd for $C_{17}N_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.65; H, 6.58; N, 5.28.

The compound gave temporary, intense blue (or red) colors with strong acids.

***N*-Acetyl derivative 7** was obtained by warming a sample of the basic carbinol **6** with excess acetic anhydride at 100° for 1.5 hr. The solution was evaporated and the residue recrystallized from ethyl acetate, giving colorless crystals: mp 225–227°; ir 2.92 and 6.14 μ; uv 276 nm (ϵ 1810) and 283 (1870); nmr (DMSO) δ 7.83–6.6 (m, 6, aromatic protons), 6.36 (d, 1, D_2O exchange, OH), 5.9–5.4 (m, 2, benzhydryl protons), 3.74 (s, 3, OCH_3), 3.1–2.6 (m, 4, methylene protons), and 2.33–2.07 (complex s, 3, $NHCOCH_3$).

Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.76; H, 6.19; N, 4.53. Found: C, 73.84; H, 6.25; N, 4.38.

***O*,*N*-Diacetyl derivative 8** was obtained by refluxing **6** or **7** (1 g) with acetic anhydride (45 ml) for 4 hr. Evaporation, trituration of the brown-yellow residue with ether–ethyl acetate, and recrystallization from methanol gave slightly yellowish crystals: mp 188–190°; ir 5.71 and 6.07 μ; uv 278–279 nm (ϵ 1900); nmr ($CDCl_3$) δ 7.4–6.55 (m, 6, aromatic protons), 6.08 (broad s, 1, 7-proton), 5.43 (s, 1, 11b-proton), 3.8 (s, 3, OCH_3), 3.1–2.7 (m, 4, methylene protons), and 2.5–2.17 (m, 6, $COCH_3$; complexity of the latter signals indicating more than one isomer and/or slight contamination with a phenol acetate).

Anal. Calcd for $C_{21}H_{21}NO_4$: C, 71.78; H, 6.02; N, 3.99. Found: C, 71.76; H, 6.12; N, 3.93.

Hydrogenation of **7** or **8** in glacial HOAc in the presence of 10% Pd/C at 60–70° (3 hr) apparently led to hydrogenolysis of both benzhydryl (9,10-dihydroanthracene) groups and also to reduction of one of the aromatic rings, *i.e.*, to a crystalline **2-methoxy-4-(β-acetylaminoethyl)octahydroanthracene**, crystals from ether: mp 147–148°; ir 3.04, 6.12, and 6.45 μ; uv 274 nm (ϵ 1510) and 283 (1690).

Anal. Calcd for $C_{19}H_{27}NO_2$: C, 75.71; H, 9.03; N, 4.65. Found: C, 75.76; H, 9.06; N, 4.58.

Registry No.—**2b**, 28399-68-0; **2c**, 28455-52-9; **3**, 17416-64-7; **3** HCl, 28399-70-4; **4a**, 28399-71-5; **4b**, 28399-72-6; **4c**, 28399-73-7; **5**, 28399-74-8; **6**, 28399-75-9; **7**, 28399-76-0; **8**, 28399-77-1; 12b-hydroxy-5,6,8,-12b-tetrahydro-8-isoindolo[1,2-*a*]isoquinolone, 28455-53-0; 2-methoxy-4-(β-acetylaminoethyl)ctahydroanthracene, 28390-69-4.

Polycyclic Orthoquinonoidal Heterocycles. Thieno[3,4-*b*]quinoline and Naphtho[2,3-*c*]thiophene

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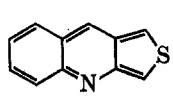
Received September 17, 1970

The formation of transient thieno[3,4-*b*]quinoline (**1**) and naphtho[2,3-*c*]thiophene (**2**) has been demonstrated in the synthesis of the exo NPMI adduct of **1** and a mixture of the exo and endo NPMI adducts of **2**. These adducts were isolated and characterized. Attempts to prepare **1** by the dehydration of 1,3-dihydrothieno[3,4-*b*]-quinoline 2-oxide (**8**) and dehydrogenation of 1,3-dihydrothieno[3,4-*b*]quinoline (**7**) were unsuccessful as were attempts to prepare **2** *via* the analogous dehydration of 1,3-dihydronaphtho[2,3-*c*]thiophene 2-oxide (**10**). The stabilities of **1** and **2** are discussed relative to one another and with regard to systems incorporating similar structural features.

This paper describes the attempted synthesis of thieno[3,4-*b*]quinoline (**1**) and naphtho[2,3-*c*]thiophene (**2**) from their precursor sulfoxides, 1,3-dihydrothieno-



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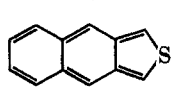
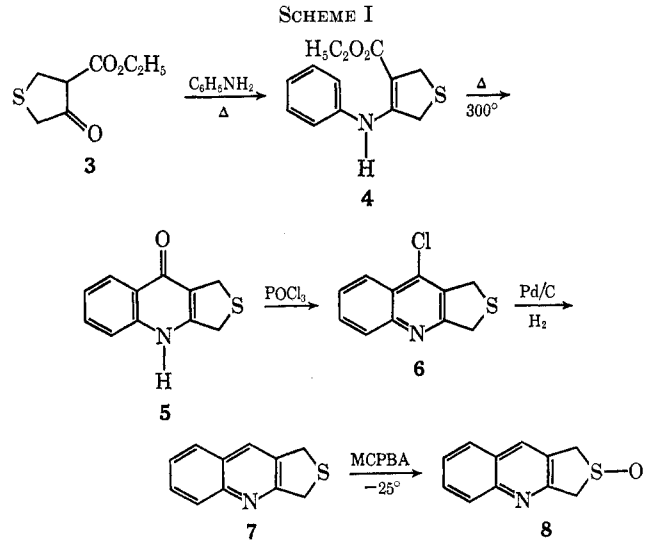


2

[3,4-*b*]quinoline 2-oxide (**8**) and 1,3-dihydronaphtho-[2,3-*c*]thiophene 2-oxide (**10**), or their precursor sulfides, 1,3-dihydrothieno[3,4-*b*]quinoline (**7**) and 1,3-dihydronaphtho[2,3-*c*]thiophene (**9**), in order to ascertain their relative stabilities compared to naphtho[1,2-*c*]thiophene.[2]

Synthesis of 1,3-Dihydrothieno[3,4-*b*]quinoline 2-Oxide (8).—The synthesis of **8** was accomplished as outlined in Scheme I. Reaction of aniline and ethyl 3-ketotetrahydrothiophene-4-carboxylate (**3**) following the procedure of Brown, *et al.*,[3] gave ethyl 3-anilino-2,5-dihydrothiophene-4-carboxylate (**4**) in 78% yield.

Scheme I



The occurrence of the imino tautomer of **4** was excluded by the presence of a sharp N–H stretching band at 3200 cm^{-1} in its infrared spectrum. Thermal ring closure to 4*H*-1,3,4,9-tetrahydrothieno[3,4-*b*]-quino-

(1) NDEA Fellow, 1967–1970.

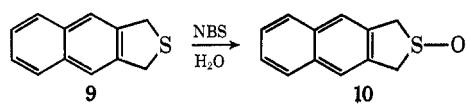
(2) M. P. Cava and N. M. Pollack, *J. Amer. Chem. Soc.*, **88**, 4112 (1966).

(3) R. J. Brown, F. W. S. Carver, and B. L. Hollingsworth, *J. Chem. Soc.*, 2624 (1962).

lin-9-one (**5**) was accomplished in 69–84% yield.[3] The ketone **5** was oxidized to 9-chloro-1,3-dihydrothieno[3,4-*b*]quinoline (**6**) by brief treatment with refluxing phosphoryl chloride in 80% yield. Reduction to **7** was accomplished in 63% yield using 5% Pd on charcoal in 2% ethanolic potassium hydroxide solution.[4] Selective oxidation of **7** to **8** was carried out in 63–66% yield using 1 equiv of *m*-chloroperbenzoic acid in methylene chloride at −25° to −30°.[5] The use of sodium metaperiodate to attain this product gave unsatisfactory results.

Synthesis of 1,3-Dihydronaphtho[2,3-*c*]thiophene 2-Oxide (10).—The synthesis of **10** is shown in Scheme II. Oxidation of 1,3-dihydronaphtho[2,3-*c*]thiophene[6]

SCHEME II



9 10

(**9**) was carried out in 69–73% yield using aqueous NBS as described by Oae and coworkers.[7]

Pyrolysis Experiments.—Attempts to isolate **1** and **2** by pyrolytic dehydration of mixtures of **8** and **10** with neutral alumina yielded only unreacted starting material and some colored amorphous material. Attempts to prepare **1** by the catalytic pyrolytic dehydrogenation technique of Meyer, *et al.*,[8] were also unsucessful.

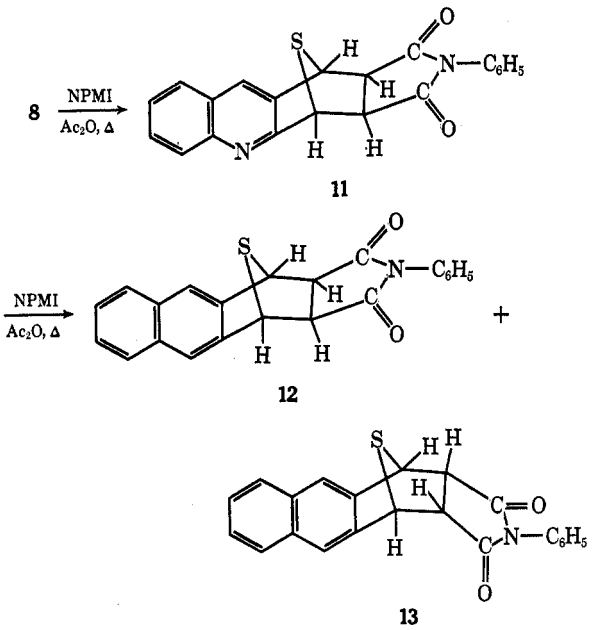
Trapping Experiments.—The transient existence of **1** was demonstrated when its exo NPMI adduct was isolated in low yield from a mixture of **8** and NPMI in refluxing acetic anhydride. Monitoring the reaction by tlc indicated that all of **8** was consumed after 20 min. The basis for the structure of **11** lies in its elemental analysis and ir, nmr, and mass spectra.

In an identical manner **10** was dehydrated in the presence of NPMI in refluxing acetic anhydride. The isolation of a mixture of the exo and endo NPMI adducts **12** and **13** in 68% yield confirms the existence of **2**. Tlc separation of the mixture afforded the individual components **12** and **13** which were present in an approximately 1:1 ratio (Scheme III).

Discussion

Although **11** and **12** are similar systems, their nmr spectra show significant differences. The spectrum of **12** (DMSO-d_6) exhibits singlets at τ 4.90 and 6.50 for the bridgehead hydrogens and hydrogens α to the imido carbonyls, respectively. Compound **11** ($CDCl_3$), on the other hand, also shows a singlet at τ 4.90 for the bridgehead hydrogens when, in theory, one would expect two singlets due to their chemical nonequivalence. Attempts to record the spectrum of **11** in DMSO-d_6 and chlorobenzene were unsuccessful due to solubility problems. The hydrogens α to the imido carbonyls in **11** show an AB pattern at τ 6.50. It is interesting that the bridgehead hydrogens of **11**

SCHEME III



are a singlet even though they are closer to the point of nonequivalence than the hydrogens α to the imido carbonyls which show an AB pattern. In **13** the splitting patterns and chemical shifts of the aliphatic hydrogens and the 1 and 4 hydrogens on the naphthalene ring are different due to the stereochemistry of the endo adduct. A broad two-proton multiplet between τ 3.80 and 4.15 arises from the 1 and 4 hydrogens on the naphthalene ring. These hydrogens are shifted out of the normal aromatic region of the α-imido carbonyl groups. A similar phenomenon has been observed by Cava[2] in the endo NPMI adduct of benzo[*c*]thiophene. The chemical shifts of the bridgehead hydrogens and the hydrogens α to the imido carbonyls of **13** are centered at τ 4.85 and 5.85 and are multiplets.

Both **11** and **12** exhibit identical infrared spectra from 800 to 600 cm^{-1} which are easily distinguishable from that of **13**. These distinctive patterns provide a useful means of distinguishing between the two NPMI stereoisomers.

The failure to isolate **1** and **2** under the conditions of the pyrolytic dehydration reaction is due to the polycyclic orthoquinonoidal structures of **1** and **2** arising from *c* fusion of the thiophene nucleus at the 2,3 bond of the quinoline and naphthalene nuclei, respectively. Naphtho[1,2-*c*]thiophene[2] which precludes structures of the type drawn for **1** and **2** has been isolated in 50% yield by the pyrolytic dehydration method. In addition, it is well known that the reactivity in the acene series increases with increasing linear annelation within the series. This enhanced reactivity is caused by the increased amount of orthoquinonoidal character present in these molecules.[9] A similar explanation can be evoked for the failure of the dehydrogenation of **7** to give **1**.

It is interesting to note the increased stability incorporated into several otherwise very unstable orthoquinoid type systems by the symmetrical addition of

(4) R. J. S. Beer, T. Broadhurst, and A. Robertson, *J. Chem. Soc.*, 2440 (1953).

(5) K. Kondo, A. Negishi, and M. Fukuyama, *Tetrahedron Lett.*, 2461 (1969).

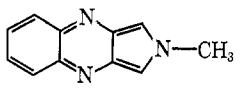
(6) M. P. Cava and R. L. Shirley, *J. Amer. Chem. Soc.*, **82**, 654 (1960).

(7) W. Tagaki, K. Kikukawa, K. Ando, and S. Oae, *Chem. Ind. (London)*, 1624 (1964).

(8) R. Meyer, H. Kleinert, S. Richter, and K. Gewald, *J. Prakt. Chem.*, **20**, 244 (1963).

(9) (a) E. Clar, "Polycyclic Hydrocarbons," Vol. 1, Academic Press, New York, N. Y., 1964, Chapters 6 and 7; (b) G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, New York, N. Y., 1969, pp 18–24.

two nitrogen atoms. Thus, 2-methyl-2*H*-pyrrolo[3,4-*b*]quinoxaline[10] (**14**) is a stable solid, whereas 2*H*-naphtho[2,3-*c*]pyrrole (**15**) could only be trapped as its exo NPMI adduct.[11] Cava[12] has reported that 1,3-diphenylnaphtho[2,3-*c*]furan (**16**) decomposes in the solid state but 1,3-diphenylfuro[3,4-*b*]quinoxaline (**17**) is a stable crystalline solid.[13] Likewise, naphtho[2,3-*c*]-2,1,3-thiadiazole (**18**)[13] is a stable solid, but up until now only **2** has been trapped.



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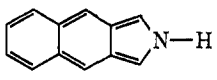

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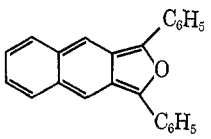

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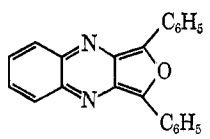

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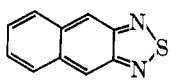

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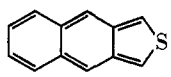

2

Experimental Section[14]

Ethyl 3-Anilino-2,5-dihydrothiophene-4-carboxylate (4).—Aniline (43.6 g, 0.470 mol) was mixed with ethyl 3-ketotetrahydrothiophene-4-carboxylate[15] (**3**, 79.6 g, 0.457 mol) and refluxed for 7 min. After cooling, removal of 8.5 ml of water by azeotropic distillation with benzene, followed by work-up, gave 114 g of crystalline solid which was recrystallized from 2:1 acetone–hexane to give 63.3 g (55%) of solid: mp 73–76°; the analytical sample (acetone–hexane) melted at 72–73°; ir (KBr) 3200 (NH), 1655 cm^{-1} (ester C=O); nmr (CCl_4) τ 0.10 (s, 1, NH), 2.8–3.2 (m, 5, aromatic), 5.8 (q, 2, J = 7 Hz), 8.68 (t, 3, J = 7 Hz).

Anal. Calcd for $C_{13}H_{15}NO_2S$: C, 62.65; H, 6.02; N, 5.62; S, 12.85. Found: C, 62.76; H, 6.02; N, 5.72; S, 13.10.

4*H*-1,3,4,9-Tetrahydrothieno[3,4-*b*]quinoline (5).—Ethyl 3-anilino-2,5-dihydrothiophene-4-carboxylate (**4**, 12 g, 0.0518 mol) was heated under reflux in a nitrogen atmosphere at 300°. After the initial temperature drop, the mixture was maintained at 290–300° until a vigorous evolution of ethanol accompanied by a cloud of smoke occurred. The solid residue was triturated with benzene to yield 69–84% of solid material which was used in the next step without further purification. An analytical sample (EtOH) had mp 345–347°; ir (KBr) 3000 (NH), 1600 cm^{-1} (ketone C=O); nmr (CF_3CO_2H) τ 1.4–1.6 (mound, 1, NH), 2.0–2.6 (m, 4, aromatic), 5.3 (s, 2, NCH_2), 5.6 (s, 2, CCH_2).

Anal. Calcd for $C_{11}H_9NOS$: C, 65.02; H, 4.43; N, 6.89; S, 15.77. Found: C, 64.89; H, 4.49; N, 7.60; S, 15.48.

9-Chloro-1,3-dihydrothieno[3,4-*b*]quinoline (6).—4*H*-1,3,4,9-Tetrahydrothieno[3,4-*b*]quinolin-9-one (**5**, 10.0 g, 0.049 mol) and distilled phosphoryl chloride (85 ml) were refluxed together for 4 min. The mixture was cooled and poured onto ice and then neutralized with 2 l. of cold 2 *M* ammonium hydroxide. The resulting gray solid was filtered and air-dried to leave 8.73 g (81%) of solid, mp 140–141°. The solid was best purified by chromatography of a benzene solution over aluminum. An analytical sample was obtained by recrystallization from ethanol: mp 151–155°; nmr ($CDCl_3$) τ 1.7–2.5 (m, 4, aromatic), 5.4 (s, 2, NCH_2), 5.5 (s, 2, CCH_2).

Anal. Calcd for $C_{11}H_8ClNS$: C, 59.59; H, 3.61; N, 6.33; S, 14.47. Found: C, 59.79; H, 3.55; N, 6.17; S, 14.65.

1,3-Dihydrothieno[3,4-*b*]quinoline (7).—9-Chloro-1,3-dihydrothieno[3,4-*b*]quinoline (**6**, 1.0 g, 4.5 mmol) was dissolved in 300 ml of warm ethanol containing 2.8 g of potassium hydroxide. To this solution was added 0.50 g of 5% palladium on carbon, and the mixture was hydrogenated under a pressure of 40 lb/in.^{2} for 1.5 hr, hydrogen uptake *ca.* 0.5 lb/in.^{2} The filtrates from five such 1-g experiments were evaporated nearly to dryness and then dissolved in ethyl acetate. The solution was washed with water and brine and dried ($MgSO_4$). Evaporation left 3.11 g (73%) of yellow solid, mp 105.5–107.5°. In this manner 35 g of **6** was converted to **7** in yields ranging from 73 to 87% after recrystallization (63%, mp 106–108°). An analytical sample was prepared by recrystallization from hexane followed by sublimation: mp 110–111°; nmr ($CDCl_3$) τ 1.9–2.7 (m, 4, aromatic), 5.65 (s, 2, NCH_2S), 5.75 (s, 2, CCH_2S).

Anal. Calcd for $C_{11}H_9NS$: C, 70.55; H, 4.85; N, 7.48; S, 17.12. Found: C, 70.59; H, 4.88; N, 7.49; S, 17.11.

1,3-Dihydrothieno[3,4-*b*]quinoline 2-Oxide (8).—To a 1-l., three-necked flask fitted with an addition funnel, a low temperature thermometer, and a calcium chloride drying tube was added 1,3-dihydrothieno[3,4-*b*]quinoline (**7**, 4.0 g, 0.002 mol) in 250 ml of methylene chloride. This solution was cooled in a Dry Ice–acetone bath and was maintained between −25 and −30° during the addition of *m*-chloroperbenzoic acid (4.40 g, 83.4% purity, 0.002 mol) dissolved in 400 ml of methylene chloride. The addition required about 10 min. The temperature was maintained for an additional 5 min before *ca.* 20 ml of liquid ammonia was added to the solution. The cooling bath was removed and the turbid solution was allowed to warm to room temperature, filtered through Super-Cel, and dried ($MgSO_4$).

Removal of the solvent left 2.90 g (66%) of solid, mp 127–129°. Recrystallization from benzene afforded an analytical sample: mp 133–134°; ir (KBr) 1045 cm^{-1} (SO); nmr ($CDCl_3$) τ 1.8–2.7 (m, 5, C_9H_5N), 5.61 (s, 2, NCH_2S), 5.68 (s, 2, CCH_2S).

Anal. Calcd for $C_{11}H_9NOS$: C, 65.00; H, 4.46; N, 6.89; S, 15.77. Found: C, 64.83; H, 4.55; N, 6.84; S, 15.64.

1,3-Dihydronaphtho[2,3-*c*]thiophene 2-Oxide (10).—1,3-Dihydronaphtho[2,3-*c*]thiophene[6] (**9**, 10.0 g, 5.38 × 10^{-3} mol) was dissolved in 900 ml of acetone. This solution was slowly diluted with 150 ml of water. To this yellow solution was added recrystallized *N*-bromosuccinimide (9.70 g, 5.45 × 10^{-2} mol) contained in 400 ml of 1:1 acetone and water over a 12-min period. The solution became colorless during addition but became yellow momentarily near the end of the addition period. The solution was allowed to stir 0.5 hr at room temperature and then the acetone was removed under reduced pressure. The white suspension was filtered and dried overnight under vacuum to leave 9.5 g (89%) of a gray solid. Recrystallization from methanol (Norite) left 7.6 g (69%) of a white solid, mp 199–201°. An analytical sample was obtained by recrystallization from methanol: mp 200.5–201°; nmr ($CDCl_3$) τ 2.0–2.65 (m, 6 H, aromatic), 5.75 (s, 4 H, CH_2).

Anal. Calcd for $C_{12}H_{10}OS$: C, 71.25; H, 4.98; S, 15.85. Found: C, 71.09; H, 5.11; S, 16.08.

***exo*-*N*-Phenylmaleimide Adduct of Thieno[3,4-*b*]quinoline.**—A mixture of 1.00 g (4.93 × 10^{-3} mol) of sulfoxide **8** and 0.855 g (4.94 × 10^{-3} mol) of *N*-phenylmaleimide were dissolved in 35 ml of freshly distilled acetic anhydride. The solution was protected under an atmosphere of dry nitrogen and refluxed for 20 min. The dark reaction mixture was poured into an ice–water mixture and extracted with chloroform. The chloroform solution was washed three times with water and twice with brine and dried (Na_2SO_4). Evaporation left 1.92 g of solid.

A portion of this solid (1.52 g) was partially dissolved in boiling benzene and placed on a column containing 140 g of neutral alumina. Elution with 1800 ml of benzene followed by elution with 5% ether:95% benzene caused the separation of a red band from the column. Evaporation of the appropriate benzene–ether fraction left 1.10 g of a brick red solid. Recrystallization from acetonitrile gave 0.30 g of a pink solid (17%), mp 268–269°. Further recrystallization produced an analytical sample: mp 278.5–279°; ir (KBr) 1775, 1700, 785 (m), 750 (s), 745 (sh), 685 cm^{-1} (m); nmr ($CDCl_3$) τ 1.9–2.8 (m, 10), 4.90 (s, 2, bridgehead), 6.30–6.45 (q, 2, *endo* H, J = 7 Hz); mass spectrum (70 eV; source 125°, probe, 225°) m/e (rel intensity) 360 (4), 359 (13),

(10) R. C. Anderson and R. H. Fleming, *Tetrahedron Lett.*, 1581 (1969).
(11) J. E. Shields and J. Bornstein, *Chem. Ind. (London)*, 1404 (1967).
(12) M. P. Cava and J. P. van Meter, *J. Org. Chem.*, **34**, 538 (1969).
(13) M. J. Haddadin, A. Yavrouian, and C. Issidorides, *Tetrahedron Lett.*, 1409 (1970).
(14) All temperature readings are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Nuclear magnetic resonance spectra were recorded on a Varian HA-60 spectrometer using tetramethylsilane as an internal standard (τ 10) and solvents as specified. Infrared spectra were recorded on a Perkin-Elmer Model 127 and Beckman IR-8 spectrophotometer.
(15) G. B. Brown, B. R. Baker, S. Bernstein, and S. R. Safir, *J. Org. Chem.*, **12**, 155 (1947).

358 (82), 211 (3), 187 (7), 186 (16), 185 (100), 179 (11), 118 (4), 167 (4), 140 (3).

Anal. Calcd for $C_{21}H_{14}O_2N_2S$: C, 70.37; H, 3.94; N, 7.82; S, 8.95. Found: C, 70.62; H, 3.82; N, 7.89; S, 8.72.

***N*-Phenylmaleimide Adducts of Naphtho[2,3-*c*]thiophene.**—Into a 250-ml flask was added 1,3-dihydronaphtho[2,3-*c*]thiophene 2-oxide (**10**, 1.0 g, 4.95 mmol), *N*-phenylmaleimide (0.86 g, 4.96 mmol), and 20 ml of acetic anhydride under dry nitrogen. The mixture was refluxed for 20 min. The yellow solution was cooled slightly and the excess acetic anhydride removed under reduced pressure to leave 1.80 g (101%) of a yellow crystalline solid. The separation of the isomeric adducts is detailed as follows.

Exo Adduct.—The yellow solid was recrystallized from acetonitrile to give 0.60 g (34%) of white solid. An analytical sample was obtained by recrystallization from chloroform–hexane: mp 281.5–282.5°; ir (KBr) 1765, 1700 (broad, imido C=O), 790 (m), 745 (s), 740 (sh), 690 cm^{-1} (m); nmr (DMSO-d_6) τ 2.2–3.05 (m, 11, aromatic), 4.89 (s, 2, bridgehead), 6.50 (s, 2, endo H); mass spectrum (70 eV; source 250°, probe 150°) *m/e* (rel intensity) 357 (9.7), 325 (3.1), 186 (5.9), 185 (13.8), 184 (100), 178 (10).

Anal. Calcd for $C_{22}H_{15}NO_2S$: C, 73.92; H, 4.23; N, 3.92; S, 8.97. Found: C, 73.89; H, 4.06; N, 3.73; S, 9.10.

Endo Adduct.—This isomer was separated by preparative thin layer chromatography on a 20 × 20 cm 1000-μ silica gel PF_{254} plates which had been activated 3 hr at 120°. Samples of 100 mg each, obtained in ether, were spread on the plates. Each plate was developed twice in 95% benzene–5% ethyl acetate in a presaturated chamber. Each plate was allowed to dry thoroughly between developments. The slower moving band from seven plates was scraped off and extracted with chloroform to yield 0.318 g of white solid. An analytical sample was obtained by recrystallization from ethanol: mp 214.5–215.5°; ir (KBr) 1775, 1700 (broad, imido C=O), 745 (s), 715 (s), 680 cm^{-1} (m); nmr ($CDCl_3$) τ 2.2–2.85, 2.9–3.3 (m, 9, aromatic), 3.8–4.15 (m, 2, H-1 and -4 on the naphthalene ring), 4.9 (m, 2, bridgehead), 5.8–6.0 (m, 2, exo hydrogens); mass spectrum (70 eV; source 275°, probe 110°) *m/e* 357 (9.3), 325 (2), 186 (6.4), 185 (13.7), 184 (100), 178 (6.4).

Anal. Found: C, 73.96; H, 4.23; N, 3.99; S, 9.05.

Registry No.—**4**, 28237-98-1; **5**, 28237-99-2; **6**, 28238-00-8; **7**, 28238-01-9; **8**, 28312-62-1; **10**, 28238-02-0; **11**, 28238-03-1; **12**, 28238-04-2; **13**, 28238-04-2.

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The Aromatization of Some Cyclopropene Adducts. An Approach to the Naphtho[*b*]cyclopropene System

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1,3-Diphenylisobenzofuran (**4**) reacts with cyclopropene, 1-methylcyclopropene, and 1,2,3-triphenylcyclopropene to give the Diels–Alder adducts **5**, **16**, and **17**, all of which are the exo isomers. Attempted dehydration of **5** to 2,7-diphenylnaphtho[*b*]cyclopropene (**3**) could not be effected, although a variety of transformation products of **5** was isolated and identified. Several acid-catalyzed transformations of **16** and **17** were also studied. All evidence points to the nonintermediacy of **3** in the acid-catalyzed reactions of **5**.

Benzocyclopropene (**1**) is the most highly strained member of the benzocycloalkene series. Since 1964 the synthesis of the very reactive but isolable **1**[2a] and of a number of its substitution products[2b] has been reported. No example of any other condensed cyclopropane aromatic system exists in the literature.[3]

The work described in this paper had as its main goal the synthesis of a derivative of naphtho[*b*]cyclopropene (**2**), a system in which the central ring might be expected to show a high degree of bond fixation. 2,7-Diphenylnaphtho[*b*]cyclopropene (**3**) was chosen as a convenient synthetic objective, since it appeared to be readily accessible by the Diels–Alder addition of cyclopropene to 1,3-diphenylisobenzofuran (**4**), followed by acid-catalyzed dehydration of the resulting adduct **5**. The corresponding naphtho[*b*]cyclobutene derivative **6** has indeed been synthesized from cyclobutene by an exactly analogous route.[4]

Results and Discussion

Cyclopropene was found to add to 1,3-diphenylisobenzofuran (**4**) to give a single crystalline adduct, mp 95–96°. This adduct was assigned the structure of the exo isomer **5** on the basis of its nmr spectrum, which indicated considerable deshielding of one of the two cyclopropane methylene protons (δ ~1.75 and ~1.15) by the oxido bridge.[5,6]

Reaction of adduct **5** with hydrogen chloride in benzene at room temperature led to a good yield of 1,4-diphenyl-2-chloromethylnaphthalene (**7**), no other product being detectable by tlc. The formation of chloride **7** could be explained as involving the formation of the desired cyclopropene **3** as a transient intermediate, followed by ring opening of **3** by hydrogen chloride. On the other hand, **3** might never be formed and formation of **7** could proceed by way of direct nucleophilic attack of chloride ion on the methylene of the cyclopropyl carbinyl cation **8**.

In an attempt to dehydrate **5** under milder conditions, it was heated in chloroform solution in the presence of a cation exchange resin (Dowex 50W X-2), which was later found to contain some chloride ion. The minor reaction product (16%) was again chloride **7**, but the

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(2) (a) E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Lett.*, 3625 (1965). (b) R. Anet and F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 525 (1964); G. L. Closs, *Advan. Alicycl. Chem.*, **1**, 64 (1966); G. L. Closs, L. R. Kaplan, and V. I. Bendall, *J. Amer. Chem. Soc.*, **89**, 3376 (1967); E. Vogel, S. Korte, W. Grimme, and H. Günther, *Angew. Chem., Int. Ed. Engl.*, **7**, 289 (1968).

(3) A compound originally believed to be a keto tautomer of a naphtho[*b*]cyclopropenediol was subsequently shown not to contain a three-membered ring: L. F. Fieser and M. A. Peters, *J. Amer. Chem. Soc.*, **53**, 4080 (1931); A. R. Bader and M. G. Ettlinger, *ibid.*, **75**, 730 (1953).

(4) C. D. Nenitzescu, M. Avram, I. G. Dinulescu, and G. Mateescu, *Justus Liebigs Ann. Chem.*, **653**, 79 (1962).

(5) M. P. Cava and F. M. Scheel, *J. Org. Chem.*, **32**, 1304 (1967).

(6) Other investigators have mentioned in the footnote of a recent paper that they have synthesized adduct **5**: M. A. Battiste and C. T. Sprouse, Jr., *Tetrahedron Lett.*, 3165 (1969).