

## Synthesis of an Asymmetric Heterotriptycene

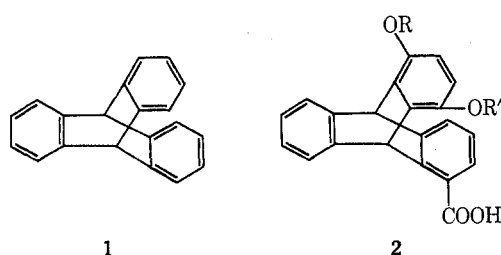
HANS WYNBERG, J. DE WIT, AND H. J. M. SINNIGE

Department of Organic Chemistry, The University, Bloemensingel 10, Groningen, The Netherlands

Received September 2, 1969

This paper describes the synthesis of an unsubstituted heterocyclic asymmetric triptycene, 5,12-dihydro-5,12-[2',3'-b]thienonaphthacene (8). The choice of the starting materials in this synthesis, naphtho[2,3-b]thiophene (5) and 1,4-epoxy-1,4-dihydronaphthalene (6), is based in part on Hückel molecular orbital computations and in part on experimental data.

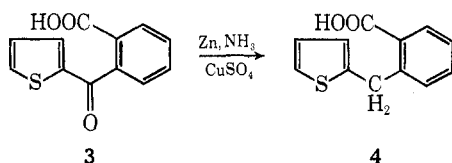
Triptycene (1)<sup>1,2</sup> has a rigid "propeller" structure and  $C_{3h}$  symmetry. Triptycenes are asymmetric when every one of the three aromatic rings is unlike the other two. This asymmetry can be achieved by attaching substituents at appropriate positions, as done by Ogura (2),<sup>3,4</sup> or by having every ring inherently different from the other two. An example of



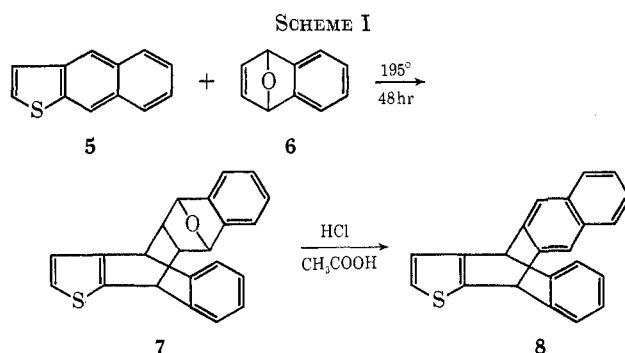
an unsubstituted asymmetric triptycene has not yet been reported. This would be of considerable interest, since calculations on transannular interactions<sup>5,6</sup> would be simplified. Professor L. J. Oosterhoff of the University of Leiden, The Netherlands, drew our attention to theoretical problems related to asymmetric triptycenes. When initial attempts by Drs. Huyser of Leiden University to prepare a benzenoid asymmetric triptycene failed, we turned our attention to the hetero analogs.

### Results

**Synthesis of 5,12-Dihydro-5,12-[2',3'-b]thienonaphthacene (8).**—The synthesis of the triptycene (8) is analogous to that of benzotriptycene (10).<sup>7</sup> The starting material, naphtho[2,3-b]thiophene (5), was made essentially according to the work of Carruthers<sup>8</sup> in an overall yield of 30%, based on 2-iodothiophene. Addition of copper(II) sulfate<sup>9</sup> to the intermediate keto acid 3 during the reduction to acid 4 raised the

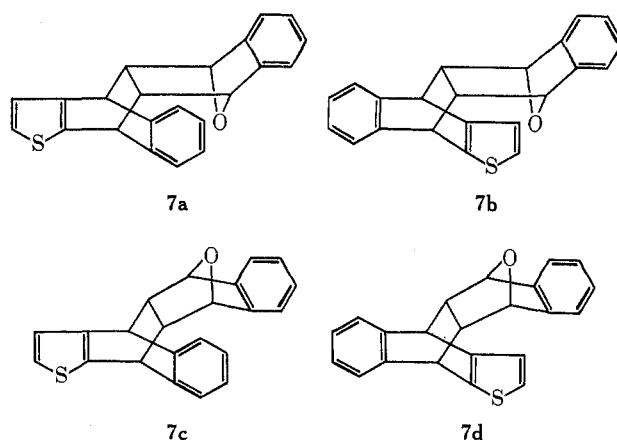


yield from 30 to 90% in this step. When 1,4-dihydro-1,4-epoxynaphthalene (6)<sup>10</sup> was heated during 48 hr at 195° with naphtho[2,3-b]thiophene (5), the adduct 7 was obtained in 70% yield (Scheme I). The



nmr spectrum of (7) in deuterochloroform consisted of a multiplet at  $\tau$  2.94 (10 H, aromatic) and broad singlets at 5.08 (1 H, bridgehead), 5.17 (1 H, bridgehead), 5.43 (2 H, aliphatic, deshielded by the oxygen atom), and 7.78 (2 H, aliphatic tertiary). The mass spectrum showed a parent peak at  $m/e$  328 and a base peak at 184, the latter being due to a retro Diels-Alder reaction. The ultraviolet spectrum in cyclohexane showed only benzene absorptions. These spectral data are consistent only with structure 7 and effectively rule out a possible 1,4 terminal addition.

The adduct 7 is probably a mixture of stereoisomers 7a and 7b, since dehydration to the triptycene 8 proceeded sluggishly and in moderate (40%) yield.<sup>11</sup> Examination of scale models reveals that, in stereoisomers having oxygen on the "outside" (isomers 7c and 7d;



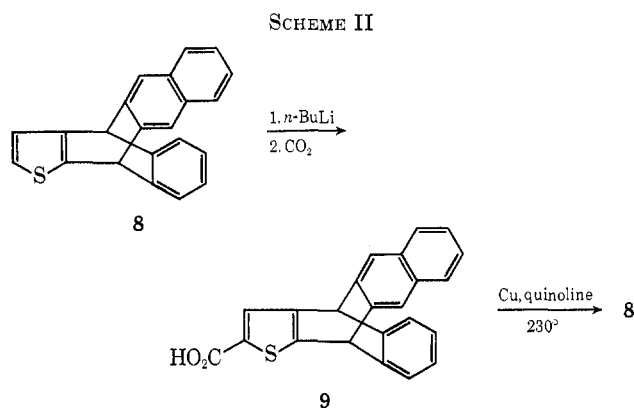
(10) The yield was improved over that reported by C. F. Fieser and M. J. Haddadin, *Can. J. Chem.*, **43**, 5991 (1965); see Experimental Section.

(11) A second product, i.e., naphtho[2,3-b]thiophene, was obtained concurrently in 45% yield. This heterocycle (5) is the result of a retro Diels-Alder reaction.

- (1) P. D. Bartlett and S. Cohen, *J. Amer. Chem. Soc.*, **64**, 2649 (1942).
- (2) B. H. Klanderma, *Org. Chem. Bull.*, **37**, 1 (1965).
- (3) F. Ogura, *Bull. Chem. Soc. Jap.*, **35**, 853 (1962).
- (4) F. Ogura, *ibid.*, **38**, 155 (1965).
- (5) M. S. de Groot and J. H. van der Waals, *Mol. Phys.*, **6**, 545 (1963).
- (6) L. J. Oosterhoff, personal communication.
- (7) G. Wittig, *Chem. Ber.*, **93**, 951 (1960).
- (8) W. Carruthers, *J. Chem. Soc.*, 704 (1962).
- (9) H. E. Schroeder and V. Weinmayr, *J. Amer. Chem. Soc.*, **74**, 4354 (1952).

*endo* and *exo* nomenclature is confusing in these systems), two aromatic rings undergo considerable steric interference. Thus the isomers having the oxygen on the "inside" (7a and 7b) are probably formed preferentially; this appears substantiated by the difficulty observed in the dehydration. The nmr spectrum of 8 showed one singlet for the bridgehead protons ( $\tau$  4.43, aromatic protons at 2.28–3.35) in deuteriochloroform, but two singlets for the bridgehead protons ( $\tau$  4.63 and 4.67, aromatic protons at 2.38–3.57) in benzene, which is an anisotropic solvent in nmr spectroscopy. The mass spectrum had a parent peak at  $m/e$  310 and two base peaks at 265 (loss of HCS fragment) and 155 (indicating the stability of the parent ion). The ultraviolet spectrum in cyclohexane showed a naphthalenelike pattern, but different from 2,3-dimethylnaphthalene.

**Purification of 5,12-Dihydro-5,12-[2',3'-b]thienonaphthacene (8).**—Initially neither the adduct 7 nor the triptycene 8 could be obtained analytically pure, although all spectra (nmr, ir, uv, mass) were in accord with the structures assigned. This difficulty was resolved by lithiation and carboxylation of the triptycene 8 to the acid 9 (Scheme II). Extraction of the acid 9

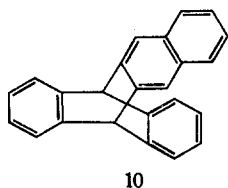


followed by decarboxylation furnished analytically pure triptycene 8.<sup>12</sup>

### Discussion

**Reactivities of Thiophene Analogs of Anthracene.**—Our choice of the starting materials for the synthesis of the desired unsubstituted asymmetric heterocyclic triptycene was based on the following considerations. We computed the Diels–Alder reactivities of possible substrates, potentially leading to asymmetric tripty-

(12) The neutral residue amounting to 6% was purified and examined. Physical and spectral data [the absorption at  $\tau$  4.52 in the nmr spectrum, taken in deuteriochloroform, of this material is the same as that given by T. H. Regan, *J. Org. Chem.*, **32**, 2789 (1967), for benzotriptycene] suggested that benzotriptycene (10) had been present in the final reaction product. Since



the starting material 5 was not contaminated with anthracene, a possible explanation is that benzyne (formed by a retro Diels–Alder reaction of 1,4-epoxy-1,4-dihydronaphthalene) attacks the triptycene 8 and displaces a  $C_4H_2S$  fragment.

enes. These reactivities were computed with the help of a general computer program for Hückel molecular orbital calculations, written by van Reyendam,<sup>13,14</sup> and the results are listed in Tables I and II. From

TABLE I  
DEWAR *para* LOCALIZATION ENERGIES (DPE)

| Compound       | DPE, $\beta$ units                                             | Diels–Alder position |
|----------------|----------------------------------------------------------------|----------------------|
| <br>12         | $W_{2-12} = 4.743$<br>$W_{5-11} = 4.456$<br>$W_{6-8} = 4.743$  | 5–11                 |
| <br>11         | $W_{2-12} = 4.693$<br>$W_{5-11} = 4.461$<br>$W_{8-10} = 4.693$ | 5–11                 |
| <br>5          | $W_{2-13} = 4.700$<br>$W_{5-12} = 4.253$<br>$W_{7-10} = 4.522$ | 5–12                 |
| <br>Anthracene | $W_{1-4} = 4.462$<br>$W_{6-13} = 4.026$                        | 6–13                 |

TABLE II  
*para* LOCALIZATION ENERGIES (PE) ACCORDING TO DEWAR AND BROWN

| Compound <sup>a</sup> | PE (Brown), $\beta$ units | PE (Dewar), $\beta$ units |
|-----------------------|---------------------------|---------------------------|
| 11                    | $W = 3.615$               | $W = 4.461$               |
| 12                    | $W = 3.618$               | $W = 4.456$               |
| 5                     | $W = 3.479$               | $W = 4.253$               |
| Anthracene            | $W = 3.314$               | $W = 4.026$               |

<sup>a</sup> See Table I for structures.

the computer data we calculated the *para* localization energies, which may be taken as a measure for Diels–Alder reactivities, according to Dewar<sup>15</sup> and Brown.<sup>16</sup> The values of the *para* localization energies for the possible sites of adduct formation indicate clearly (Table I) that a Diels–Alder reaction (if it occurred) would take place in the center ring preferentially. The reactivities for these positions are compared (Table II); a high value for the *para* localization energy means a low Diels–Alder reactivity. According to these calculations the Diels–Alder reactivity of naphtho[2,3-*b*]thiophene (5) should lie between that of anthracene and that of the two benzodithiophenes 11 and 12. This proved to be the case, since 11 (prepared by a different route from that used by Tilak,<sup>17</sup> Experimental Section) did not react with a variety of dienophiles even under drastic conditions, while 5 reacted, albeit sluggishly.

**Nmr Spectra of Some Thiophene Analogs of Anthracene.**—The nmr spectra of benzo[1,2-*b*:5,4-*b'*]dithiophene (11), of naphtho[2,3-*b*]thiophene (5), and of 4-acetoxynaphtho[2,3-*b*]thiophene (19) are given in Table III. There are four kinds of protons in these molecules: *meso*-anthracenelike protons (1 and 2), naphthalenelike protons (3), and benzene-thio-

(13) J. van Reyendam, HMO computer program, University of Groningen, The Netherlands.

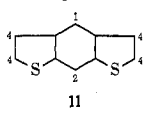
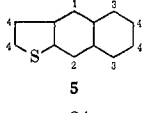
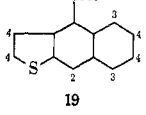
(14) In the calculations the following parameters were used:  $\alpha_S = \alpha + \beta$ ;  $\beta_{CS} = 0.7\beta$ .

(15) M. J. S. Dewar, *J. Amer. Chem. Soc.*, **74**, 3357 (1951).

(16) R. D. Brown, *J. Chem. Soc.*, 691 (1950).

(17) D. S. Rao and B. D. Tilak, *J. Sci. Ind. Res.*, **13**, 829 (1954).

TABLE III  
NMR SPECTRA OF SOME HETEROANTHRACENES

| Compound                                                                                | Solvent          | Absorption, $\tau$ | Position |
|-----------------------------------------------------------------------------------------|------------------|--------------------|----------|
| <br>11 | CCl <sub>4</sub> | 1.67 (s, 1 H)      | 1        |
|                                                                                         |                  | 1.95 (s, 1 H)      | 2        |
|                                                                                         |                  | 2.62 (s, 4 H)      | 4        |
| <br>5  | CCl <sub>4</sub> | 1.75 (s, 1 H)      | 1        |
|                                                                                         |                  | 1.82 (s, 1 H)      | 2        |
|                                                                                         |                  | 2.08-2.35 (m, 2 H) | 3        |
|                                                                                         |                  | 2.55-2.97 (m, 4 H) | 4        |
| <br>19 | CCl <sub>4</sub> | 1.90 (s, 1 H)      | 2        |
|                                                                                         |                  | 2.08-2.38 (m, 2 H) | 3        |
|                                                                                         |                  | 2.55-2.97 (m, 4 H) | 4        |

phenelike protons (4). *meso*-Anthracenelike protons are deshielded most and benzene-thiophene like protons least,<sup>18</sup> so that the signal at  $\tau \approx 2.7$  is attributed to protons of type 3, while the signal at  $\tau \approx 2.2$  is due to protons of type 4. Since in 4-acetoxynaphtho-[2,3-*b*]thiophene (19) the proton in the middle ring absorbs at  $\tau$  1.90, we have attributed the signals at  $\tau$  1.95 (for compound 11), 1.82 (for compound 5), and 1.90 (for compound 19) to protons of type 2, and the remaining signals to protons of type 1. From the spectra is seen that the protons in the middle rings are not coupled with other protons, but that protons of type 3 and 4 are coupled with each other, even through a long-range (W-like) coupling.

**Ultraviolet Spectra of Some Triptycenes.**—In view of the interest in transannular interactions in triptycene systems,<sup>5,19,20</sup> we have compared the uv spectra of triptycene (20)<sup>20</sup> with that of some appropriate model compounds, *i.e.*, *o*-xylene (21),<sup>21</sup> 9,10-dihydro-9,10-dimethylantracene (22),<sup>22</sup> and 9,10-dihydro-9,10-ethanoanthracene (23).<sup>23</sup> Considering Figure 1, it is clear that the difference in  $\lambda_{\max}$  of the longest wavelength absorption is negligible in going from 21 to 22 to 23. A shift is observed (8  $m\mu$ ) in going from the bridged compound (23) to the triptycene (20). The great difference in extinction coefficient of *o*-xylene (21) and the compounds 22, 23, and 20, the latter three compounds having the same spacial configuration, suggests some kind of interaction, which need not be merely or exclusive  $\pi$ - $\pi$  orbital interaction. Although Klanderman<sup>24</sup> correctly notes that no resonance can "circulate around and around the rings" because of a node in the lowest energy Hückel molecular orbital of triptycene, interaction between all three rings is still possible.<sup>25</sup> With the aid of appropriate model compounds as in Figure 1 and a calculational analysis, which is currently underway in this laboratory, the spectra can also be discussed in more detail. The results will be published in a subsequent paper.

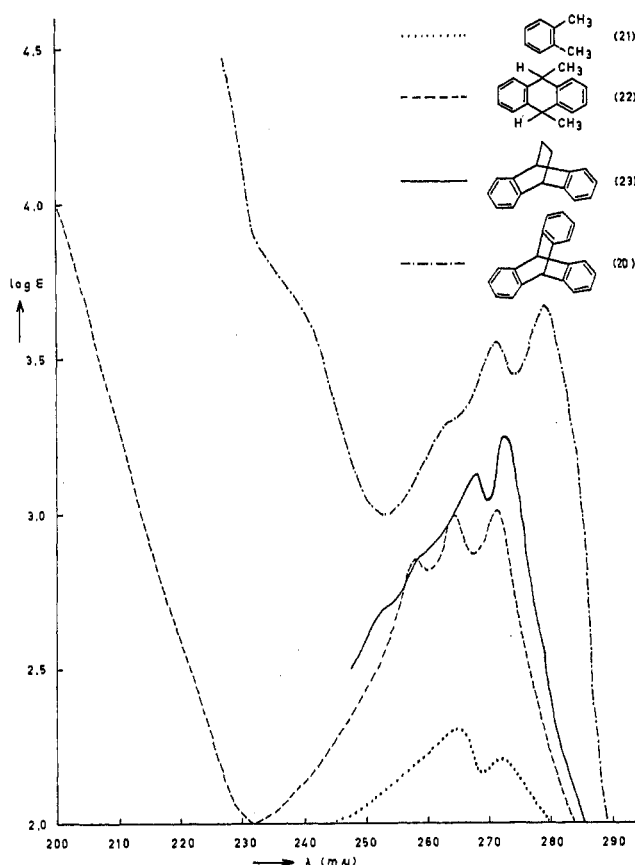
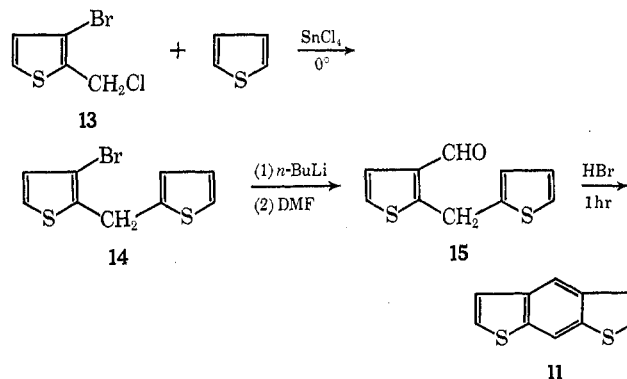


Figure 1.—Uv spectra in cyclohexane.

### Experimental Section

Melting points are uncorrected. Infrared spectra were taken on a Unicam SP200; only significant absorptions are given. Ultraviolet spectra were determined with a Zeiss PMQ II. Nmr spectra were obtained with a Varian A-60 using tetramethylsilane (TMS) as an internal standard. Mass spectra were taken on an AEI MS 9; only peaks with relative abundances above 10% are reported. Gas-liquid partition chromatography (glpc) was performed on an F & M 810. Microanalyses were carried out in the analytical section of our department under the supervision of Mr. M. W. Hazenberg.

**Benzo[1,2-*b*:5,4-*b'*]dithiophene (11).**—Since 3-bromo-2-thenyl chloride (13)<sup>26,27</sup> was available in our laboratory, we prepared 11 by the following scheme, the last step being analogous to the work of Bradsher<sup>28</sup> and Krakauer.<sup>29</sup>



(18) C. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, London, 1959.

(19) C. F. Wilcox, *J. Chem. Phys.*, **33**, 1874 (1960).

(20) W. Theilacker, *et al.*, *Chem. Ber.*, **98**, 428 (1965).

(21) R. Huisgen, *Ann. Chem.*, **586**, 1 (1954).

(22) D. D. Phillips and J. Cason, *J. Amer. Chem. Soc.*, **74**, 2934 (1952).

(23) R. C. Cookson and N. Levin, *Chem. Ind. (London)*, 984 (1956).

(24) B. H. Klanderman, *J. Org. Chem.*, **34**, 630 (1969).

(25) It is noteworthy in this connection that Klanderman evidently does not obtain any trinitrotriptycene in his nitration mixture, although his hypothesis would lead one to believe that this product is formed easily.

(26) A. Kraak and H. Wynberg, *J. Org. Chem.*, **29**, 2455 (1964).

(27) A. Kraak, A. K. Wiersema, P. Jordens, and H. Wynberg, *Tetrahedron*, **24**, 3381 (1968).

(28) C. K. Bradsher and L. E. Beavens, *J. Amer. Chem. Soc.*, **77**, 4812 (1955).

(29) M. Neeman, E. Krakauer, and Y. Shaw, *ibid.*, **79**, 4380 (1957).

**A. 2,2'-Dithienylmethane-3-carboxaldehyde (15).**—A solution of 0.028 mol of *n*-butyllithium<sup>30</sup> in 35 ml of ether was cooled to  $-10^{\circ}$  in a nitrogen atmosphere. To the vigorously stirred solution was added in 5 min a solution of 2.6 g (0.01 mol) of 3-bromo-2,2'-dithienylmethane (14) in 10 ml of ether. After another 5 min of stirring, the yellow solution was transferred rapidly into a dropping funnel and added in 2 min to a well stirred mixture of 3.5 g of dimethylformamide (DMF) in 20 ml of ether. After 1 night of stirring at room temperature, the yellow suspension was poured into 50 ml of ice water. The ether layer was extracted twice with 2 *N* hydrochloric acid, water, and a saturated solution of sodium bicarbonate. The solution was dried over  $MgSO_4$ , filtered, and evaporated, leaving a yellow oil, which was distilled *in vacuo*; 0.9 g of a yellow oil was obtained, bp 124–130° (0.5–0.7 mm),  $n_D^{20}$  1.6247. Gpc showed a 10% impurity of 3-bromo-2,2'-dithienylmethane. The aldehyde was characterized as a 2,4-dinitrophenylhydrazone, mp 156.5–158°.

*Anal.* Calcd for  $C_{16}H_{12}N_4O_4S_2$ : C, 49.47; H, 3.11; N, 14.42; S, 16.51. Found: C, 49.25; H, 3.32; N, 14.08; S, 16.62.

Ir spectra follow: 1600 (C=N stretch), 1580, 1500  $cm^{-1}$  (thiophene).

**B.**—The crude aldehyde, obtained from 5.2 g (0.02 mol) of 3-bromo-2,2'-dithienylmethane (14), was refluxed for 2.5 hr with 25 ml of 48% hydrobromic acid. The resulting black, tarlike material was removed by filtration and sublimed *in vacuo*, yielding 1.45 g (40% calcd on 3-bromo-2,2'-dithienylmethane) of pure benzo[1,2-*b*:5,4-*b'*]dithiophene as white crystals, mp 187–188° (lit.<sup>17</sup> 184°).

*Anal.* Calcd for  $C_{10}H_6S_2$ : C, 63.14; H, 3.18; S, 33.73. Found: C, 62.98; H, 3.23; S, 33.41.

Nmr, uv, and mass spectra follow. Nmr<sup>31</sup> ( $CCl_4$ ):  $\tau$  1.67 (s, 1 H), 1.95 (s, 1 H), 2.62 (s, 4 H). Uv (96% ethanol):  $\lambda_{max}$  247  $m\mu$  ( $\epsilon$  62,000), 254 (72,400), 302 (5900). Mass spectrum:  $m/e$  190 (parent peak), 191 (P + 1 = 15%, calcd 11.1%), 192 (P + 2 = 11%, calcd 9%), 164 (M -  $C_2H_2$ ), 158 (M - S), 145 (M - HCS), 132 (M -  $C_2H_2S$ ), 114 (M -  $CS_2$ ), 102 ( $C_8H_5^+$ ), 95 ( $M^{2+}$ ), 82, 69, 58 ( $C_8H_5S^+$ ), 45 (HCS<sup>+</sup>), 44 (CS<sup>+</sup>), 39 ( $C_8H_5^+$ ).

A picrate was prepared in 96% ethanol. The monopicate crystallized as fine red needles, mp 138.6–138.9° (lit.<sup>17</sup> 136°).

*Anal.* Calcd for  $C_{16}H_8N_3O_7S_2$ : C, 45.82; H, 2.16; N, 10.02; S, 15.28. Found: C, 46.15; H, 2.25; N, 10.03; S, 15.15.

**Reduction of Benzo[1,2-*b*:5,4-*b'*]dithiophene (11).**—A solution of 0.5 g of benzodithiophene (11) (mp 187–188°) in 100 ml of ethanol was refluxed for 3 hr with 20 g of freshly prepared Raney nickel (quality W I).<sup>32</sup> After filtration of the catalyst the ethanol was evaporated, leaving almost pure *m*-diethylbenzene (according to nmr and ir spectra).

**Preparation of Naphtho[2,3-*b*]thiophene (5).**—Naphtho[2,3-*b*]thiophene (5) was prepared from 2-iodothiophene<sup>33</sup> by the method of Carruthers,<sup>8</sup> using the modification of Schroeder<sup>9</sup> for the reduction of 2-(2'-thenoyl)benzoic acid to 2-(2'-thenyl)benzoic acid.

**1,4-Epoxy-1,4-dihydronaphthalene (6).**—A three-necked flask, equipped with a thermometer, a condenser, and two dropping funnels was filled with 200 ml of dimethoxyethane and heated to 75°. Solutions of 48 g (0.35 mol) of anthranilic acid in 440 ml of dimethoxyethane and 44 ml (0.32 mol) of isoamyl nitrite in 30 g (0.44 mol) of furan were added simultaneously over a period of 2 hr. The dark red solution was then heated for 30 min under reflux and poured into 1 l. of 6% sodium hydroxide solution. The dimethoxyethane was removed by distillation and the residue was extracted with six 250-ml portions of chloroform. The chloroform layer was dried over  $Na_2SO_4$ . After removal of the drying agent, the solution was evaporated and the residue (31.7 g, 69%) crystallized twice from petroleum ether (bp 40–60°). The snow white product had mp 54–55° (lit.<sup>10</sup> 51% crude yield, pure product mp 53–54.5°).

**5,5',6,11,11',12-Hexahydro-6,11-epoxy-5,12-[2',3'-*b*]thienonaphthacene (7).**—Twelve grams (0.065 mol) of naphtho[2,3-*b*]thiophene (5) and 19.5 g (0.136 mol) of 1,4-epoxy-1,4-dihydronaphthalene (6) were mixed with a few crystals of hydroquinone and heated to 195° over a period of 48 hr in a sealed tube. The contents of the tube were boiled with 96% alcohol for 30 min and

(30) H. Gilman and R. G. Jones, *Org. Reactions*, **8**, 285 (1954).

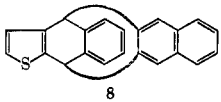
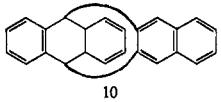
(31) The following abbreviations will be used in the nmr data: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet.

(32) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, Longmans, London, 1962, p 871.

(33) A. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 357.

TABLE IV

## UV SPECTRA OF SOME TRIPTYCENES IN CYCLOHEXANE

| Compound                                                                           | Absorption (log $\epsilon$ ), $m\mu$                                                                                     |
|------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------|
|  | 231 (4.9), 254 (4.3), 258 (4.3), 269 (4.3), 277 (4.3), 286 (3.5), 298 (3.1), 304 (3.0), 311 (3.3), 317 (3.0), 325 (3.5). |
|  | 227 (4.8), 234 (4.8), 242 (4.9), 267 (4.2), 276 (4.2), 287 (3.7), 301.5 (2.9), 308 (3.2), 314.5 (2.9), 322 (3.3).        |

the precipitate was collected. This brown precipitate was chromatographed over alumina with benzene. The eluate was concentrated and 15 g (71%) of almost pure oxotriptycene (7) was obtained. A sample of the product was crystallized from alcohol, mp 278–280°.

*Anal.* Calcd for  $C_{22}H_{16}OS$ : C, 80.49; H, 4.88; O, 4.88; S, 9.76. Found: C, 80.49; H, 5.04; O, 5.18; S, 9.08.

The following special data were obtained. Nmr ( $CDCl_3$ ):  $\tau$  2.67–3.20 (m, 10 H), 5.08 (s, 1 H), 5.17 (broad s, 1 H), 5.43 (broad s, 2 H), 7.78 (broad s, 2 H). Uv (cyclohexane):  $\lambda_{max}$  245  $m\mu$  (log  $\epsilon$  3.50), 259 (3.45), 266 (3.46), 273 (3.33). Mass spectrum ( $CHCl_3$ ):  $m/e$  328 (parent peak), 329 (P + 1 = 26%, calcd 24.2%), 330 (P + 2 = 8%, calcd 4.4%), 310 (M -  $H_2O$ ), 211, 210, 209, 208, 197, 184 (M - 144 = M -  $C_{10}H_8O$ ), 185, 144, 139, 128, 115, 86, 51 ( $C_8H_5^+$ ).

**5,12-Dihydro-5,12-[2',3'-*b*]thienonaphthacene (8).**—Optimal conditions, after much experimentation, proved to be the following. A suspension of 5.1 g (15.5 mmol) of oxotriptycene (7) in 80 ml of acetic acid and 1 ml of hydrochloric acid was heated to boiling. At the boiling point, enough acetic acid was added to ensure complete solution, and 9 ml of hydrochloric acid was then added. After 10 min of boiling the mixture was cooled to 40° and water was added until precipitation was complete. The precipitate was chromatographed over alumina with benzene, the eluate evaporated and the white residue sublimed *in vacuo*. The sublimate was naphtho[2,3-*b*]thiophene (5) (1.3 g, 45%), mp 190–192°. The residue (1.8 g, 38%) was crystallized from 96% alcohol, yielding 1.45 g of 5,12-dihydro-5,12-[2',3'-*b*]thienonaphthacene (8): mp 252–257°; nmr ( $CDCl_3$ ) 2.28–3.35 (m, 12 H), 4.43 (s, 2 H), 4.52 (s, 0.3 H).

**5,12-Dihydro-5,12-[2',3'-*b*]thienonaphthacene-5'-carboxylic Acid (9).**—To a suspension of 1.44 g (4.7 mmol) of 5,12-dihydro-5,12-[2',3'-*b*]thienonaphthacene (8) in 20 ml of ether was added 5 ml (5.0 mmol) of *n*-butyllithium under nitrogen atmosphere. The dark colored solution was refluxed for 0.5 hr and added quickly to a vigorously stirred suspension of 30 g of powdered Dry Ice in ether. The yellowish precipitate was decomposed with 50 ml of 6 *N* hydrochloric acid; the water layer was extracted with 50 ml of ether and the combined ether layer extracted three times with 50 ml of 5% ammonia. The resulting yellow ether layer was dried over  $Na_2SO_4$  and, after removal of the drying agent, concentrated and chromatographed over alumina with benzene. The basic layer was acidified with 6 *N* hydrochloric acid. The precipitate was collected on a Büchner funnel, washed with water and dried, yielding 1.05 g (63%) of triptycencarboxylic acid (9), mp 292° dec. No attempts were made to obtain an analytically pure sample of this intermediate.

Ir: 3000  $cm^{-1}$  (OH, acid), 1650 (C=O, acid), 1620 (ar-H), 1260 (C—O, acid), 1130, 1040, 880, 740. Nmr ( $CDCl_3$ ):  $\tau$  2.33–3.10 (m, 6 H), 4.20 (s, 1 H), 4.28 (s, 1 H). Mass spectrum ( $CH_3OH$ ):  $m/e$  354 (parent peak), 355 (P + 1 = 34%, calcd 25.3%), 356 (P + 2 = 10%, calcd 4.4%), 310 (M -  $CO_2$ ), 309 (M -  $CO_2H$ ), 308 (M -  $CO_2H_2$ ), 307 (M -  $CO_2H_2$ ), 306 (M -  $CO_2H_4$ ), 276 (M -  $CO_2H_2S$ ), 265 (M -  $C_2O_2HS$ ), 155, 154.

**Decarboxylation of 5,12-Dihydro-5,12-[2',3'-*b*]thienonaphthacene-5'-carboxylic Acid.**—To a boiling solution of 400 mg of triptycene (9) in 5 g of quinoline was added 100 mg of copper powder. Heating was continued until no more carbon dioxide was evolved (5 min). The dark brown mixture was cooled rapidly and poured into a mixture of 5 ml of concentrated hydrochloric acid, 5 ml of water, and 20 ml of chloroform. The copper powder was removed by filtration and washed with chloroform.

The combined red chloroform layer was washed with 4 *N* hydrochloric acid, 2 *N* sodium hydroxide solution, and water, and dried over CaCl<sub>2</sub>. Acidification of the basic layer gave no precipitate. The chloroform layer was filtered and concentrated. The residue was chromatographed over alumina with benzene. The benzene was evaporated and the residue (200 mg, 57%) crystallized several times from alcohol, mp 267–270°.

Anal. Calcd for C<sub>22</sub>H<sub>14</sub>S: C, 85.16; H, 4.52; S, 10.32. Found: C, 84.86; H, 4.59; S, 10.23.

Uv: see Table IV. Mass spectrum: *m/e* 310 (parent peak), 311 (P + 1 = 28%, calcd 24.2%), 312 (P + 2 = 5%, calcd 4.4%), 309 (M - H), 308 (M - 2H), 265 (M - HCS), 155

(M<sup>+</sup>), 154.5 (M - 1)<sup>2+</sup>, 154 ((M - 2)<sup>2+</sup>), 78, 45 (HCS<sup>+</sup>), 44 (CS<sup>+</sup>). Nmr (C<sub>6</sub>D<sub>6</sub>):  $\tau$  2.38–3.57 (m, 12 H), 4.63 (s, 1 H), 4.67 (s, 1 H).

Registry No.—Anthracene, 120-12-7; **5**, 268-77-9; **7a**, 22565-98-6; **7b**, 22565-99-7; **8**, 22566-00-3; **9**, 22566-01-4; **10**, 13395-89-6; **11**, 267-61-8; **12**, 267-65-2; **15**, 22566-39-8; **15** (2,4-dinitrophenylhydrazone), 22566-40-1; **19**, 22566-41-2; **20**, 477-75-8; **21**, 95-47-6; **22**, 22566-43-4; **23**, 5675-64-9.

## Generation of *o*-Quinone Methides in Solution. Trimerization

DONALD A. BOLON

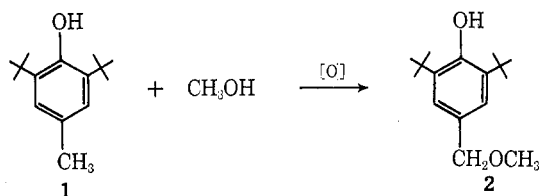
General Electric Research and Development Center, Schenectady, New York 12301

Received May 28, 1969

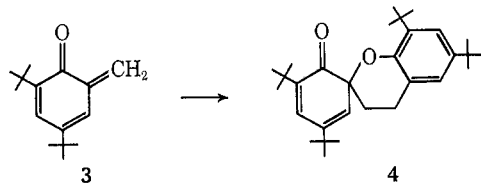
Three different 4-substituted 2,6-dimethylphenols were oxidized with various oxidizing agents such as silver oxide. The major product in each case is a trimer, which was characterized as arising from a trimerization of an *o*-quinone methide. The carbonyl group in the trimer was particularly unreactive, and the only easily run reaction was a reduction with acidic iodide, which not only cleaved a carbon-oxygen bond but caused an olefinic bond to shift out of conjugation.

Quinone methides have been postulated as reactive intermediates in organic reactions for many years. A review has been written<sup>1</sup> which covers the literature to 1964. The isolation of a quinone methide with an unsubstituted methylene group has not been accomplished except at low temperatures<sup>2,3</sup> or in the case of highly hindered molecules.<sup>4</sup> Filar and Winstein<sup>5</sup> have demonstrated the existence of a *p*-quinone methide in dilute solution.

Identification of a quinone methide intermediate usually results from product studies. Filar and Winstein<sup>5</sup> oxidized **1** in methanol and formed **2** by trapping the *p*-quinone methide with the nucleophilic methanol.



The second path involves the function of the *exo* methylene group as a dieneophile, which is illustrated by Waters's<sup>6</sup> work. Here the *o*-quinone methide **3** is acting as both the diene and dieneophile.



The only reports of isolated *o*-quinone methides is by Merijan, Shoulders, and Gardner,<sup>3</sup> who collected

(1) A. B. Turner, *Quart. Rev. (London)*, **28**, 347 (1964).

(2) S. B. Cavitt, H. Sarrafzadeh R., and P. D. Gardner, *J. Org. Chem.*, **27**, 1211 (1962).

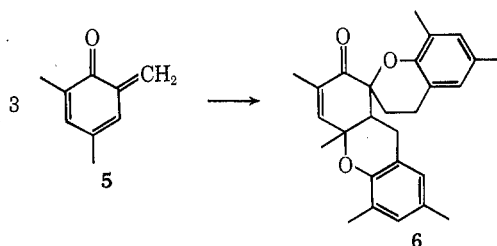
(3) A. Merijan, B. A. Shoulders, and P. D. Gardner, *ibid.*, **28**, 2148 (1963).

(4) A. Bistrzycki and C. Herbst, *Chem. Ber.*, **36**, 2335 (1903).

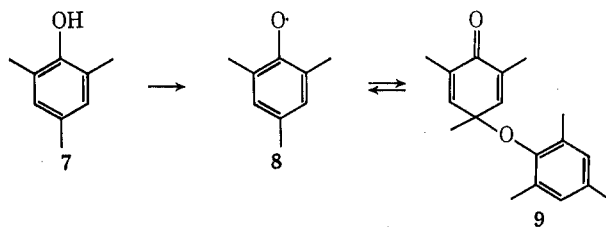
(5) L. J. Filar and S. Winstein, *Tetrahedron Lett.*, **25**, 9 (1960).

(6) R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 243 (1954).

the quinone methide **5** at liquid nitrogen temperature. It then spontaneously trimerized upon warming, in a most unusual reaction.



The exact mechanism of the formation of the quinone methides is not known. The first step is the oxidation of the phenol **7** to the phenoxy radical **8**. This radical in turn reversibly dimerizes to the quinol ether **9**.



Becker has demonstrated that dimers of this type disproportionate to 1 mol of the phenol and 1 mol of the *p*-quinone methide.<sup>7</sup> A similar sequence probably occurs for *o*-quinone methides, but has not yet been demonstrated prior to this work.

This work was undertaken to examine some of the methods of generating *p*-quinone methides and to see whether they could be used to generate *o*-quinone methides in solution. The generality and scope of the reaction was to be examined.

### Results and Discussion

In view of the results of Filar and Winstein,<sup>5</sup> who found that *p*-quinone methide formation was greatly

(7) H. D. Becker, *J. Org. Chem.*, **30**, 982 (1965).