

solvent was then evaporated under reduced pressure and the residue was chromatographed on a column of silica gel (B.D.H., 40 × 2 cm). The column was developed with 1.75 l. of pentane-ether (9:1) and then with pentane-ether (1:1), 100-ml fractions being collected. Fractions 18-26 on evaporation afforded dimethyl 2,3-benzotricyclo[5.1.0.0<sup>4,9</sup>]octa-2,5-diene-10,11-dicarboxylate (**19**, 60 mg, 91%) as a colorless liquid. The analytical sample was obtained by thin layer chromatography on silica gel plates (Merck kieselgel HF<sub>254+366</sub>, 20 × 20 × 0.09 cm), developed with pentane-ether (9:1): infrared spectrum (CCl<sub>4</sub>), bands at 2995 (w), 2950 (s), 1732 (vs), 1435 (s), 1355 (m), 1280 (s), 1200 (s), 1140 (m), 1115 (s), 1095 (m), 1030 (m), and 825 cm<sup>-1</sup> (m); electronic spectrum (ethanol), λ<sub>max</sub> 218 nm (ε 26,800) and λ<sub>inf</sub> ca. 270 nm (ε 7000); nmr spectrum, see Discussion; mass spectrum, molecular ion peak at *m/e* 270.

*Anal.* Calcd for C<sub>18</sub>H<sub>14</sub>O<sub>4</sub>: C, 71.10; H, 5.22. Found: C, 70.64; H, 5.22.

**Reaction of 4- (or 5-) Methylene-5- (or 4-) chloromethylene-*cis*-bicyclo[4.2.0]octa-2,7-diene (**12**) with Dimethyl Acetylenedicarboxylate.** A solution of **12** (14 mg) and dimethyl acetylenedicarboxylate (20 mg) in cyclohexane (5 ml) was boiled under reflux for 48 hr. The solvent was then evaporated under reduced pressure, and the residue was adsorbed onto a thin layer plate (Merck kieselgel HF<sub>254+366</sub>, 20 × 20 × 0.09 cm), which was developed with pentane-ether (9:1). Three bands could be detected under ultraviolet light, the first in order of elution being due to unchanged **12** and the second to dimethyl acetylenedicarboxylate. The third band on extraction with chloroform, filtration, and evaporation

gave a pale yellow liquid (12 mg, 52%) consisting of about equal parts of dimethyl 2,3-benzobicyclo[4.2.0]octa-2,4,7-triene-10,11-dicarboxylate (**22**) and dimethyl benzocyclooctatetraene-10,11-dicarboxylate (**23**),<sup>1</sup> as evidenced by careful examination of the nmr spectrum (see Discussion): electronic spectrum (ether), λ<sub>max</sub> 238 and 290 nm (relative optical density, *ca.* 6:1); mass spectrum, prominent molecular ion peak at *m/e* 270. The mixture of **22** and **23** could not be separated by thin layer chromatography on silica gel or alumina plates in a variety of solvent systems.

**Valence Tautomerism of Dimethyl 2,3-Benzobicyclo[4.2.0]octa-2,4,7-triene-10,11-dicarboxylate (**22**) to Dimethyl Benzocyclooctatetraene-10,11-dicarboxylate (**23**).** A solution of the 1:1 mixture of **22** and **23** (8 mg) in tetrachloroethylene (10 ml) was boiled under reflux for 72 hr. Removal of the solvent under reduced pressure gave **23** (8 mg), the infrared, electronic, nmr, and mass spectra of which were identical with those of an authentic sample.<sup>1</sup> Thin layer chromatography indicated that no decomposition had occurred during the reaction.

**Acknowledgments.** J. A. E. is indebted for the award of a C.S.I.R.O. (Australia) Overseas Postgraduate Studentship (1966-1967), and M. V. S. for the award of a Science Research Council Postdoctoral Fellowship (1964-1966) and an Imperial Chemical Industries Fellowship (1966-1967). We also thank the Royal Society for generous financial support.

## The Synthesis of [3,4-*c*]Furooctalene, [1,2:5,6]Di[*c*]furocyclooctatetraene, and 1,2-Benzo[5,6-*c*]furocyclooctatetraene<sup>1</sup>

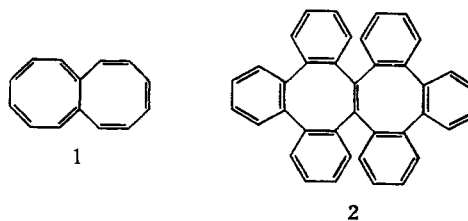
J. A. Elix, M. V. Sargent, and F. Sondheimer<sup>2</sup>

*Contribution from the University Chemical Laboratory, Cambridge, England. Received August 11, 1969*

**Abstract:** Oxidation of 1,2-bis(hydroxymethyl)cyclooctatetraene (**3**) with manganese dioxide gave cyclooctatetraene-1,2-dicarboxaldehyde (**4**), besides other products. Wittig reaction of **4** with furan-3,4-bis(methylenetriphenylphosphonium chloride) (**9**) and lithium ethoxide led to [3,4-*c*]furooctalene (**10**). The spectral properties of **10** show that the eight-membered rings are nonplanar and do not possess delocalized π electrons. Diels-Alder reaction of **10** with dimethyl fumarate yielded a monoadduct (**12**), derived by addition to the terminal eight-membered ring. Wittig reaction of furan-3,4-dicarboxaldehyde (**13**) with the furan salt **9** gave [1,2:5,6]di[*c*]furocyclooctatetraene (**14**). The related dimethyl [1,2:5,6]di[*c*]furocyclooctatetraene-3,8-dicarboxylate (**16**) was obtained by the reaction between **13** and furan-3,4-diacetic acid (**15**). Wittig reaction between *o*-phthalaldehyde (**19**) and the furan salt **9** led to 1,2-benzo[5,6-*c*]furocyclooctatetraene (**20**), a substance which was also obtained by the reaction between furan-3,4-dicarboxaldehyde (**13**) and *o*-xylylenebis(triphenylphosphonium bromide) (**7**). Diels-Alder reaction of **14** and **20** with dimethyl fumarate gave adducts (**18** and **21**, respectively) derived by addition to the furan rings.

Octalene (bicyclo[6.6.0]tetradecaheptaene, **1**) is a compound of considerable interest. It is a 14-π-electron system, formally derived from [14]annulene<sup>3</sup> by formation of a cross-linkage, and calculations made some time ago indicated it to be an aromatic system.<sup>4</sup> However, more recent theoretical work has led to the

conclusion that octalene in fact should not be aromatic.<sup>5</sup> The only derivative of octalene known when we commenced our work was hexabenzooctalene (**2**),<sup>6</sup> the properties of which threw no light on the possible aromaticity



(1) Unsaturated Eight-Membered Ring Compounds. IX. For Part VIII, see J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Am. Chem. Soc.*, **92**, 969 (1970).

(2) Author to whom inquiries should be addressed at the Chemistry Department, University College, London W.C.1, England.

(3) See F. Sondheimer, *Proc. Roy. Soc. (London)*, **A297**, 173 (1967), and references cited therein.

(4) D. P. Craig, *J. Chem. Soc.*, 3175 (1951); A. Rosowsky, H. Fleischer, S. T. Young, R. Partsch, W. H. Saunders, and V. Boekelheide, *Tetrahedron*, **11**, 121 (1960); A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, Chapter 10.

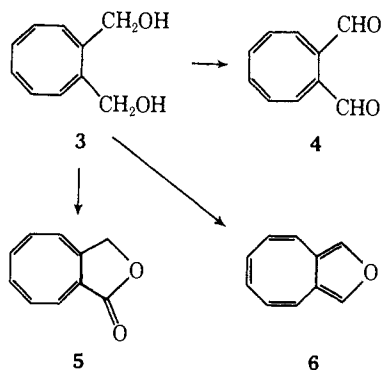
(5) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685 (1965); N. L. Allinger and C. Gilardeau, *Tetrahedron*, **23**, 1569 (1967).

(6) W. Tochtermann, *Angew. Chem.*, **75**, 418 (1963).

of the parent compound. It was of interest to synthesize octalene, or a simple derivative of this substance, in order to provide an experimental test for the theoretical calculations.

We now describe the synthesis of [3,4-*c*]furooctalene (10), a derivative of octalene containing a fused furan ring, as well as of the related furocyclooctatetraene derivatives 14 and 20.<sup>7</sup> It was found that 10 is nonplanar and nonaromatic, in agreement with the most recent calculations for octalene.<sup>5</sup> This work was carried out independently from that of Breslow, *et al.*,<sup>8</sup> who recently reported the synthesis of benzo[*c*]octalene (8) and showed that this substance is also nonaromatic.

Our projected route to octalene (1) and its derivatives involved the bis-Wittig reaction of a suitable bisphosphonium salt with cyclooctatetraene-1,2-dicarboxaldehyde (4), a substance which was unknown when this work was commenced. It was expected that 4 could be obtained by oxidation of 1,2-bis(hydroxymethyl)cyclooctatetraene (3), which we prepared by the method of



Le Goff and LaCount.<sup>9</sup> Several different oxidizing agents were investigated, but in no case could the dialdehyde 4 be obtained in satisfactory yield. The best yield (15%) of 4 was realized when the oxidation was carried out with manganese dioxide in chloroform, a reaction which also gave rise to 39% of the  $\gamma$ -lactone 5 and 14% of the known<sup>9</sup> [1,2-*c*]furocyclooctatetraene (6).<sup>10</sup> The structure of the yellow crystalline dialdehyde 4 (mp 124–125°) follows from the spectral properties, given in the Experimental Section.

Initial experiments were designed to lead to benzo[*c*]octalene (8), by the reaction of 4 with *o*-xylylenebis(triphenylphosphonium bromide) (7)<sup>11</sup> and lithium ethoxide in dimethylformamide. No 8 could be isolated from this experiment,<sup>12,13</sup> but it was observed that a

(7) Our syntheses of 10 and 14 have been reported in a preliminary communication (J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 5080 (1967)).

(8) R. Breslow, W. Horspool, H. Sugiyama, and W. Vitale, *ibid.*, **88**, 3677 (1966).

(9) E. Le Goff and R. B. LaCount, *Tetrahedron Lett.*, 2787 (1965).

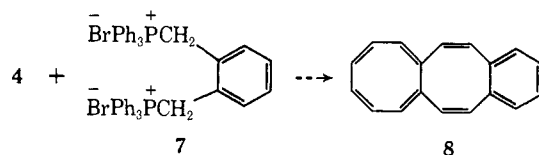
(10) The oxidation of 3 to 4, 5, and 6 was reported by us at a Lecture at the International Symposium on Aromaticity, Sheffield, July 6–8, 1966; see F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. Di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, Special Publication No. 21, The Chemical Society, London, 1967, p 103. The oxidation of 3 was carried out independently by Breslow, *et al.* (ref 8), who obtained 4 in 10–40% yield (as well as 5 and 6) by use of manganese dioxide or nickel peroxide.

(11) C. E. Griffin, K. R. Martin, and B. E. Douglas, *J. Org. Chem.*, **27**, 1627 (1962); C. E. Griffin and J. A. Peters, *ibid.*, **28**, 1715 (1963).

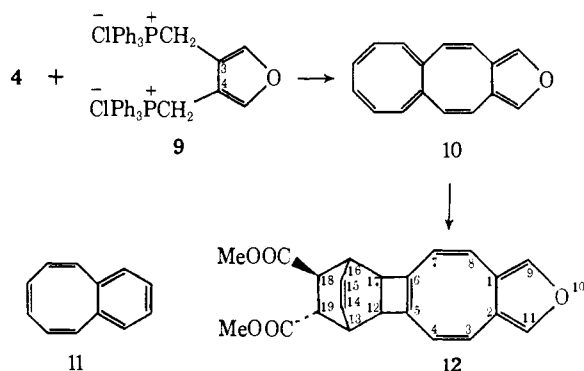
(12) Since this work was carried out, Breslow, *et al.* (ref 8), have reported the isolation of 8 in 1–2% yield from this type of Wittig reaction.

(13) An alternative synthesis of 8, by the Wittig reaction between cyclooctatetraene-1,2-bis(methylenetriphenylphosphonium bromide) and *o*-phthalaldehyde, was also unsuccessful.

considerable amount of triphenylphosphine was formed.<sup>14</sup> From other work (see below) it became ap-



parent that the Wittig reaction between a dialdehyde and furan-3,4-bis(methylenetriphenylphosphonium chloride) (9) usually results in a higher yield of cyclic product than when the corresponding benzenoid salt 7 is employed. This improved yield is presumably related to our observation that 9, in contrast to 7, gives no triphenylphosphine on treatment with lithium ethoxide in dimethylformamide. This lack of elimination may be accounted for by the low-bond order of the 3,4-furan bond in 9. In view of these results, the Wittig reaction between the dialdehyde 4 and the furan salt 9 was investigated, in order to obtain [3,4-*c*]furooctalene (10).



The furan salt 9 was prepared in over 90% yield from 3,4-bis(chloromethyl)furan<sup>15</sup> by treatment with triphenylphosphine in boiling dimethylformamide. Reaction between 4 and 9 in dimethylformamide in the presence of lithium ethoxide at 90° then gave [3,4-*c*]furooctalene (10) in 15% yield as an unstable pale yellow liquid.

The structure of 10 is based on its spectral properties. High-resolution mass spectrometry showed the expected molecular ion peak. The nmr spectrum (CCl<sub>4</sub>, 60 MHz) exhibited a singlet (2 H) at  $\tau$  2.70 due to the furan ring protons, a singlet (4 H) at 3.74 due to the central eight-membered ring protons, and a multiplet (6 H) at 4.13–4.36 due to the terminal eight-membered ring protons. The chemical shifts of the eight-membered ring protons in the nmr spectrum of 10 are similar to those of the eight-membered ring protons in benzo[*c*]octalene (8),<sup>8</sup> as well as in [1,2-*c*]furocyclooctatetraene (6),<sup>9</sup> and benzocyclooctatetraene (11).<sup>16</sup> The electronic spectrum of 10 [ $\lambda_{\text{max}}^{\text{EtOH}}$  237 nm ( $\epsilon$  22,300)] is also similar to that of 8,<sup>8</sup> 6,<sup>9</sup> and 11,<sup>16</sup> showing little extended conjugation. The nmr and ultraviolet spectra of 10 are in keeping with a molecule in which the eight-membered

(14) For a discussion of the elimination of triphenylphosphine from 7, see J. A. Elix and M. V. Sargent, *J. Am. Chem. Soc.*, **90**, 1631 (1968).

(15) K. Y. Novitskii, Y. K. Yur'ev, V. N. Zhingareva, and E. F. Egorova, *Dokl. Akad. Nauk SSSR*, **148**, 856 (1963); *Chem. Abstr.*, **59**, 3859c (1963).

(16) See J. A. Elix and M. V. Sargent, *J. Am. Chem. Soc.*, **91**, 4734 (1969).

rings exist in a tub-like conformation and do not possess delocalized  $\pi$  electrons.

[3,4-*c*]Furooctalene (**10**) underwent rapid oxidation on standing in the neat state in air, with the appearance of carbonyl absorption bands at 1708 and 1695  $\text{cm}^{-1}$  in the infrared spectrum. Exposure of a dilute ethanolic solution of **10** to diffuse daylight resulted in the appearance of new maxima at 255, 264, and 275 nm in the electronic spectrum. These maxima are characteristic of a 5,6-annelated [1,2-*c*]furocyclooctatetraene (*cf.* the spectra of the Diels–Alder adducts **12** and **18**, possessing this chromophore, described below), indicating that this system had been formed.

[3,4-*c*]Furooctalene (**10**) underwent Diels–Alder addition on the terminal cyclooctatetraene ring, and not on the furan ring. Thus, treatment of **10** with an excess of dimethyl fumarate in boiling cyclohexane led to the monoadduct **12** in 82% yield (based on unrecovered **10**). The reaction presumably involves valence tautomerism of the terminal eight-membered ring prior to cycloaddition, like cyclooctatetraene itself.<sup>17</sup> Structure **12** follows unambiguously from the nmr spectrum ( $\text{CCl}_4$ , 60 MHz), which exhibited a singlet (2 H) at  $\tau$  3.14 (protons 9 and 11), a multiplet (2 H) at 3.80–4.13 (protons 14 and 15), an AB quartet (4 H) centered at 4.55 and 5.08 (protons 3, 8, and 4, 7, respectively;  $J_{3,4} = J_{8,7} = 12$  Hz), two singlets (3 H each) at 6.29 and 6.35 (methyl protons), a broad band (4 H) at 7.00 (protons 12, 17, 18, and 19), and a multiplet (2 H) at 7.50–7.71 (protons 13 and 16).

The adduct **12** is a 5,6-annelated [1,2-*c*]furocyclooctatetraene. It is of interest that its electronic spectrum [ $\lambda_{\text{max}}^{\text{EtOH}}$  256 nm ( $\epsilon$  19,400), 266 (22,800), and 276 (16,600);  $\lambda_{\text{in.HI}}^{\text{EtOH}}$  247 nm ( $\epsilon$  13,300) and *ca.* 315 (2200)] was considerably more complex than that of [1,2-*c*]furocyclooctatetraene (**6**) itself [ $\lambda_{\text{max}}^{\text{cyclohexane}}$  244 nm ( $\epsilon$  9100)].<sup>9</sup> This difference is presumably due to the additional annelation in **12**, since the spectrum of the 5,6-annelated [1,2-*c*]furocyclooctatetraene derivative **18**, described below, was very similar to that of **12**.

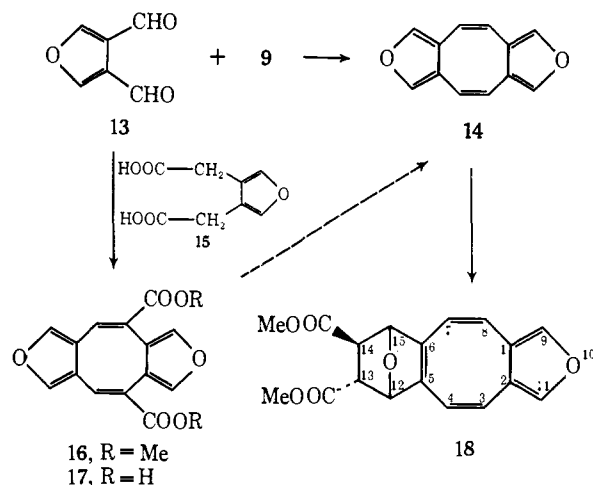
Other Wittig reactions of the furan salt **9** were studied. Thus, we investigated its reaction with furan-3,4-dicarboxaldehyde (**13**),<sup>13</sup> which we synthesized by manganese dioxide oxidation of 3,4-bis(hydroxymethyl)furan,<sup>15</sup> as well as by Kröhnke oxidation<sup>19</sup> of 3,4-bis(chloromethyl)furan.<sup>15</sup> Treatment of **9** with **13** and lithium ethoxide in dimethylformamide at 90° led to [1,2:5,6]di[*c*]furocyclooctatetraene (**14**) in a yield (44%) which is remarkably high for this type of reaction.

Substance **14** proved to be a colorless crystalline compound (mp 131–133° dec), which was unstable in the neat state in air; the crystals rapidly became yellow and then orange, with the appearance of carbonyl absorption bands at 1700 and 1670  $\text{cm}^{-1}$  in the infrared spectrum. The nmr spectrum ( $\text{CCl}_4$ , 60 MHz) of **14** confirmed the assigned structure, showing a singlet (4 H) at  $\tau$  2.73 due to the furan ring protons and a singlet (4 H) at 4.00 due to the eight-membered ring protons.

(17) See W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560**, 1 (1948).

(18) Substance **13** had been prepared by reduction of furan-3,4-dicarbonitrile with diisobutylaluminum hydride (S. Trofimenko, *J. Org. Chem.*, **29**, 3046 (1964)). Very recently, an improved synthesis of **13** has been described, by oxidation of 3,4-bis(hydroxymethyl)furan with lead tetraacetate, or with manganese dioxide and then lead tetraacetate (M. J. Cook and E. J. Forbes, *Tetrahedron*, **24**, 4501 (1968)).

(19) See F. Kröhnke, *Angew. Chem.*, **75**, 317 (1963).



[1,2:5,6]di[*c*]furocyclooctatetraene (**14**) contains 16  $\pi$  electrons and is not expected to behave as an aromatic system. It is formally derived from the 12  $\pi$ -electron system [1,2-*c*]furocyclooctatetraene (**6**), which has already been shown to be nonplanar and nonaromatic,<sup>9</sup> by fusion of a furan ring. The proton chemical shifts in the nmr spectrum of **14** are similar to those of **6** and indicate that **14** is also nonaromatic.

A further route to the [1,2:5,6]di[*c*]furocyclooctatetraene system (**14**) was explored, making use of a Perkin-type reaction, which has already been employed by Badger, *et al.*,<sup>20</sup> for the synthesis of macrocyclic conjugated compounds. Condensation of furan-3,4-dicarboxaldehyde (**13**) with furan-3,4-diacetic acid (**15**)<sup>21</sup> in acetic anhydride and trimethylamine at room temperature, followed by esterification with methanol and sulfuric acid, gave dimethyl[1,2:5,6]di[*c*]furocyclooctatetraene-3,8-dicarboxylate (**16**, mp 134–135°) in 3.3% yield. Unfortunately, attempted decarboxylation of the derived dicarboxylic acid **17** gave no **14**.

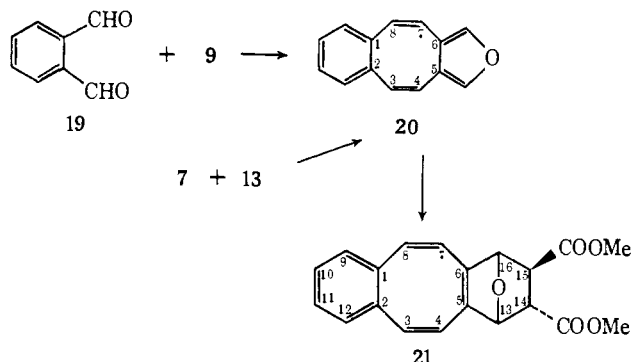
Diels–Alder reaction of **14**, unlike **10**, resulted in cycloaddition to one of the furan rings. Thus, treatment of **14** with an excess of dimethyl fumarate in boiling benzene gave the monoadduct **18** as orange crystals (mp 110–111°) in 76% yield (based on unrecovered **14**). The nmr spectrum ( $\text{CCl}_4$ , 60 MHz) of **18** confirmed the structural assignment, showing a singlet (2 H) at  $\tau$  3.03 (protons 9 and 11), two quartets (2 H each) centered at 4.09, 4.44 and 4.22, 4.65 (protons 3, 4, 7, and 8;  $J_{3,4} = J_{8,7} = 12$  Hz), a broad singlet (2 H) at 5.24 (protons 12 and 15), two singlets (3 H each) at 6.27 and 6.36 (methyl protons), and a quartet (2 H) with one doublet centered at 7.02 and the other obscured by the methyl resonances (protons 13 and 14;  $J_{13,14} = 4$  Hz). The electronic spectrum [ $\lambda_{\text{max}}^{\text{EtOH}}$  256 nm ( $\epsilon$  19,000), 265 (19,100), 276 (11,200), and 315 (3200);  $\lambda_{\text{in.HI}}^{\text{EtOH}}$  247 nm ( $\epsilon$  15,500)] was very similar to that of the adduct **12**, in accord with the fact that both substances are 5,6-annelated [1,2-*c*]furocyclooctatetraene derivatives.

Wittig reaction of the furan salt **9** with *o*-phthalaldehyde (**19**) under the previously described conditions gave rise to 1,2-benzo[5,6-*c*]furocyclooctatetraene (**20**) as colorless crystals (mp 86–88°) in 9.3% yield. The

(20) *Inter al.*, see G. M. Badger, J. A. Elix, and G. E. Lewis, *Aust. J. Chem.*, **19**, 1221 (1966).

(21) K. Y. Novitskii, Y. K. Yur'ev, V. N. Zhingareva, and K. Gresl, *Zh. Obshch. Khim.*, **34**, 2568 (1964); *J. Gen. Chem. USSR (Eng. Transl.)*, **34**, 2590 (1964).

same substance **20** was obtained, though only in 3.6% yield, by the Wittig reaction between *o*-xylylenebis(triphenylphosphonium bromide) (**7**) and furan-3,4-dicarboxaldehyde (**13**) under the same conditions. By comparison, the Wittig reaction between the furan salt **9** and the dialdehyde **13** had given **14** in 44% yield, showing the superiority of **9** over **7** in this type of synthesis.



The nmr spectrum ( $\text{CCl}_4$ , 60 MHz) of **20** showed a multiplet (6 H) at  $\tau$  2.63–3.08 due to the furan and benzene ring protons, and a quartet (4 H) centered at 3.24 and 3.54 due to protons 3,8 and 4,7, respectively ( $J_{3,4} = J_{8,7} = 12$  Hz). Substance **20** is a benz-annelated derivative of [1,2-*c*]furocyclooctatetraene (**6**);<sup>9</sup> as expected, **20** was more stable than **6**.

Diels-Alder reaction of **20** with an excess of dimethyl fumarate in boiling benzene resulted in cycloaddition to the furan ring, as did **14**. The product, obtained in 57% yield (based on unrecovered **20**) as pale yellow crystals (mp 110–112°), proved to have structure **21**. The nmr spectrum ( $\text{CCl}_4$ , 100 MHz) exhibited two multiplets (2 H each) centered at  $\tau$  2.90 and 3.30 (benzenoid protons), two quartets (2 H each) centered at 3.56, 4.12 and 3.67, 4.37 (protons 3, 4, 7, and 8;  $J_{3,4} = J_{8,7} = 12$  Hz), a broad singlet (2 H) at 5.17 (protons 13 and 16), two singlets (3 H each) at 6.38 and 6.49 (methyl protons), and a quartet (2 H) with one doublet centered at 7.24 and the other obscured by the methyl resonances (protons 14 and 15;  $J_{14,15} = 4$  Hz). The electronic spectrum of **21** showed  $\lambda_{\text{max}}^{\text{EtOH}}$  243 nm ( $\epsilon$  18,600). The nmr and electronic spectra of **21** resembles those of benzocyclooctatetraene (**11**),<sup>16</sup> in keeping with the fact that **21** is a 5,6-annelated derivative of **11**.

## Experimental Section<sup>22</sup>

Oxidation of 1,2-Bis(hydroxymethyl)cyclooctatetraene (**3**) with Manganese Dioxide. Freshly chromatographed 1,2-bis(hydroxymethyl)cyclooctatetraene (**3**, 1.44 g)<sup>9</sup> in nitrogen-purged chloroform (250 ml) was stirred with manganese dioxide (20 g)<sup>23</sup> at room temperature for 15 hr in an atmosphere of nitrogen. The oxide was removed by filtration and washed well with chloroform. The solvent was evaporated under reduced pressure, and the partially crystalline residue, dissolved in the minimum amount of benzene, was chromatographed on a column of silicic acid (40 g; Mallinckrodt, 100 mesh), mixed with celite (20 g), and made up with pentane. The column was developed with pentane-ether (500 ml of 19:1, 500 ml of 9:1, 500 ml of 17:3, and then 1 l. of 4:1; the solvents were freshly distilled and purged with nitrogen directly before use); fractions of 100 ml were collected.

Fractions 2–5 contained [1,2-*c*]furocyclooctatetraene (**6**, 180 mg, 14%), which showed infrared, nmr, and mass spectra identical with those described previously.<sup>9</sup>

(22) For general procedures, see J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Am. Chem. Soc.*, **92**, 962 (1970).

(23) Prepared by the method of O. Mancera, G. Rosenkranz, and F. Sondheimer, *J. Chem. Soc.*, 2189 (1953).

Fractions 16–20 yielded the  $\gamma$ -lactone **5** (545 mg, 39%), which crystallized from ether-pentane as yellow needles, mp 120.5–121.5°; infrared spectrum ( $\text{CHCl}_3$ ), band at 1775  $\text{cm}^{-1}$  ( $\gamma$ -lactone); nmr spectrum ( $\text{CDCl}_3$ , 100 MHz), multiplet at  $\tau$  3.80–4.38 (6 H, olefinic protons) and singlet at 5.38 (2 H, methylene protons); mass spectrum, molecular ion peak at  $m/e$  160.

Anal. Calcd for  $\text{C}_{10}\text{H}_8\text{O}_2$ : C, 74.99; H, 5.03. Found: C, 75.23; H, 5.19.

Fractions 21–24 yielded cyclooctatetraene-1,2-dicarboxaldehyde (**4**, 215 mg, 15%), which crystallized from ether-pentane as pale yellow prisms, mp 124–125°; infrared spectrum (KBr), band at 1685  $\text{cm}^{-1}$  (aldehyde); nmr spectrum ( $\text{CDCl}_3$ , 100 MHz), singlet at  $\tau$  0.42 (2 H, aldehyde protons), doublet at 2.95 (2 H,  $J = 3.5$  Hz), and multiplet at 3.70–4.05 (4 H) (olefinic protons);<sup>24</sup> mass spectrum, molecular ion peak at  $m/e$  160.

Anal. Calcd for  $\text{C}_{10}\text{H}_8\text{O}_2$ : C, 74.99; H, 5.03. Found: C, 74.86; H, 5.11.

Furan-3,4-bis(methylenetriphenylphosphonium chloride) (**9**). A solution of 3,4-bis(chloromethyl)furan (26.4 g)<sup>15</sup> and triphenylphosphine (86.0 g) in absolute dimethylformamide (300 ml) was maintained under gentle reflux for 3 hr. The solution was concentrated under reduced pressure, cooled, and diluted with ether. The product was collected by filtration, washed thoroughly with ether, and crystallized from ether-methanol. The resulting furan-3,4-bis(methylenetriphenylphosphonium chloride) (**9**, 102.9 g, 93%) formed colorless plates, which decomposed  $>250^\circ$  without melting.

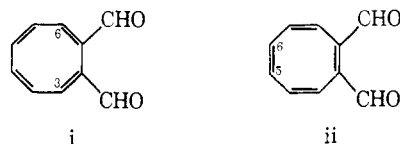
Anal. Calcd for  $\text{C}_{22}\text{H}_{16}\text{Cl}_2\text{OP}_2$ : Cl, 10.28. Found: Cl, 10.09.

[3,4-*c*]Furooctalene (**10**). A solution of the dialdehyde **4** (370 mg) and the salt **9** (1.70 g) in absolute dimethylformamide (60 ml) was heated to 90°, and a solution of lithium ethoxide (prepared from 42 mg of lithium) in absolute ethanol (10 ml) was then added dropwise during 4.5 hr at 90° with stirring in an atmosphere of dry nitrogen. The solution was stirred at 90° for a further 30 min and was then cooled and diluted with water (500 ml). The mixture was extracted with ether, and the organic extract was washed several times with water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated. The residue was preadsorbed onto neutral alumina (10 g), which was then poured on top of a column of silicic acid (Mallinckrodt, 100 mesh; 30  $\times$  2.75 cm) made up with pentane-ether (49:1). The column was developed with this solvent mixture, 50-ml fractions being collected. Fraction 6 on evaporation gave [3,4-*c*]furooctalene (**10**, 78 mg, 15%) as a pale yellow liquid; infrared spectrum ( $\text{CCl}_4$ ), bands at 3010 (s), 1630 (m), 1520 (m), 1375 (w), 1225 (w), 1219 (w), 1140 (m), 1075 (s), 1060 (s), 1038 (w), 960 (w), 930 (w), 905 (w), 878 (s), 848 (m), 700 (m), 668 (m), 653 (w), and 640 (m)  $\text{cm}^{-1}$ ; electronic and nmr spectra, see Discussion; mass spectrum, molecular ion peak at  $m/e$  220.089 (calcd for  $^{12}\text{C}_{16}\text{H}_{12}^{16}\text{O}$ : 220.089). The substance was too unstable (see Discussion) for significant microanalytical results to be obtained.

Adduct **12** from [3,4-*c*]Furooctalene (**10**) and Dimethyl Fumarate. A solution of **10** (25 mg) and dimethyl fumarate (100 mg) in cyclohexane (15 ml) was boiled under reflux for 12 hr. The residue obtained on evaporation was preadsorbed onto neutral alumina (10 g), which was poured on top of a column of silicic acid (Mallinckrodt, 100 mesh; 30  $\times$  2.75 cm) made up with pentane-ether (9:1). The column was developed with this solvent mixture (1 l.), followed by pentane-ether (4:1, 2 l.) and then ether (1 l.), 100-ml fractions being collected. Fractions 2 and 3 gave unchanged **10** (5 mg). Fractions 10–20 on evaporation yielded the adduct **12** (27 mg, 82% based on unrecovered **10**) as an orange glass; infrared spectrum ( $\text{CCl}_4$ ), bands at 1740 (ester) and 1630  $\text{cm}^{-1}$  (double bond); electronic and nmr spectra, see Discussion; mass spectrum, molecular ion peak at  $m/e$  364.

Anal. Calcd for  $\text{C}_{22}\text{H}_{20}\text{O}_5$ : C, 72.51; H, 5.53. Found: C, 72.41; H, 5.65.

(24) The nmr spectrum of **4** (as in the case of dimethyl cyclooctatetraene-1,2-dicarboxylate)<sup>25</sup> indicates a considerable degree of bond fixation. The doublet at  $\tau$  2.95 is presumably due to protons 3 and 8 in structure i, rather than protons 5 and 6 in structure ii.



(25) See E. Grovenstein, T. C. Campbell, and T. Shibata, *J. Org. Chem.*, **34**, 2418 (1969).

**Furan-3,4-dicarboxaldehyde (13).** **A. Manganese Dioxide Method.** Manganese dioxide (30 g)<sup>23</sup> was added to a solution of 3,4-bis(hydroxymethyl)furan (2.0 g)<sup>15</sup> in chloroform (250 ml), and the stirred mixture was boiled under reflux for 72 hr. The oxide was removed by filtration and washed well with ether. The filtrate was evaporated, and the residue was chromatographed on a column of silica gel (B.D.H., 150 g). Elution with pentane-ether (17:3 to 7:3), evaporation, and crystallization from cyclohexane gave furan-3,4-dicarboxaldehyde (**13**, 220 mg, 11%) as colorless feathery needles, mp 76–77°; infrared spectrum (CCl<sub>4</sub>), band at 1695 cm<sup>-1</sup> (aldehyde); electronic spectrum,  $\lambda_{\text{max}}^{\text{EtOH}}$  263 nm ( $\epsilon$  4250); nmr spectrum (CCl<sub>4</sub>, 60 MHz), singlet at  $\tau$  -0.21 (2 H, aldehyde protons) and singlet at 1.92 (2 H, ring protons).

*Anal.* Calcd for C<sub>6</sub>H<sub>4</sub>O<sub>3</sub>: C, 58.07; H, 3.25. Found: C, 58.05; H, 3.39.

**B. Kröhnke Method.**<sup>19</sup> 3,4-Bis(chloromethyl)furan (26.8 g),<sup>15</sup> absolute pyridine (39.5 ml), and absolute ethanol (33 ml) were heated on a steam bath under reflux for 1 hr. The cooled solution was then added to a solution of *p*-nitrosodimethylaniline (49 g) in ethanol (140 ml), and the temperature of the stirred mixture was maintained at -4° while a solution of potassium hydroxide (13 g) in water (325 ml) was added rapidly. The mixture was then allowed to stand at 0° for 16 hr, water (810 ml) was added, and the mixture was allowed to stand at 0° for a further 24 hr. The solid was collected by filtration and dried in a vacuum desiccator. Crystallization from ethanol (charcoal) gave furan-3,4-bis(*N*-*p*-dimethylamino-phenyl)nitron (22.5 g, 35%) as pale yellow plates, mp 210–211° dec.

*Anal.* Calcd for C<sub>22</sub>H<sub>24</sub>N<sub>4</sub>O<sub>3</sub>: C, 67.33; H, 6.16; N, 14.28. Found: C, 67.21; H, 6.12; N, 14.01.

The bisnitron (22.5 g) was dissolved in 2 *N* hydrochloric acid (200 ml) at 0°; the dark solution was allowed to stand at 25° for 30 min and was then extracted with ether (4 × 200 ml). The aqueous phase was warmed to 40–50° for 30 min, cooled, and extracted with ether (200 ml). The combined ether extracts were washed successively with water, sodium carbonate solution, and water, and were then dried and evaporated. Crystallization of the residue from cyclohexane (charcoal) gave furan-3,4-dicarboxaldehyde (**13**, 1.02 g, 14%), mp 76–77°, undepressed on admixture with a sample prepared by method A.

**[1,2:5,6]Di[c]furocyclooctatetraene (14).** A solution of the dialdehyde **13** (460 mg) and the salt **9** (2.70 g) in absolute dimethylformamide (75 ml) was heated to 90°, and a solution of lithium ethoxide (prepared from 70 mg of lithium) in absolute ethanol (16.5 ml) was then added dropwise during 5 hr at 90° with stirring in an atmosphere of dry nitrogen. The solution was stirred at 90° for a further 30 min, and was then cooled and diluted with water (500 ml). The mixture was extracted with ether, and the organic extract was washed several times with water, dried (MgSO<sub>4</sub>), and evaporated. The residue was adsorbed onto a column of silicic acid (Mallinckrodt, 100 mesh; 25 × 2.75 cm), which was developed with pentane-ether (49:1). Fractions of 50 ml were collected. Fraction 6 on evaporation and crystallization from pentane yielded [1,2:5,6]di[c]furocyclooctatetraene (**14**; 298 mg, 44%) as colorless needles, mp 131–133° dec; infrared spectrum (CCl<sub>4</sub>), bands at 3120 (m), 3010 (m), 1600 (w), 1540 (s), 1220 (s), 1145 (s), 1075 (s), 1060 (m), 980 (m), 880 (s), and 675 (s) cm<sup>-1</sup>; electronic spectrum,  $\lambda_{\text{max}}^{\text{EtOH}}$  239 nm ( $\epsilon$  43,500), 246 (46,300), and 308 (6200),  $\lambda_{\text{inf}}^{\text{EtOH}}$  296 nm ( $\epsilon$  5600) and 320 (4800); nmr spectrum, see Discussion; mass spectrum, molecular ion (base) peak at *m/e* 184.055 (calcd for <sup>12</sup>C<sub>12</sub><sup>1</sup>H<sub>8</sub><sup>16</sup>O<sub>2</sub>: 184.052). The substance was too unstable (see Discussion) for significant microanalytical results to be obtained.

**Dimethyl [1,2:5,6]Di[c]furocyclooctatetraene-3,8-dicarboxylate (16).** Furan-3,4-dicarboxaldehyde (**13**, 620 mg), furan-3,4-diacetic acid (**15**, 920 mg),<sup>21</sup> acetic anhydride (5 ml), and triethylamine (5 ml) were mixed and set aside at room temperature for 1 hr. The solution was cooled to 0°, and concentrated hydrochloric acid (10 ml) was added dropwise. Water (10 ml) was then added, and the precipitate was collected by filtration, washed with water, and air dried. The crude product was esterified by boiling under reflux for 2 hr with absolute methanol (50 ml) and concentrated sulfuric acid (0.5 ml). The solution was cooled, diluted with water (200 ml), and extracted with chloroform. The organic extract was washed successively with water, saturated sodium bicarbonate solution, and water, and was then dried (MgSO<sub>4</sub>) and evaporated. The residue was adsorbed onto a silica gel tlc plate (Merck; 20 × 20 × 0.1 cm), which was developed with pentane-ether (7:3). A strip was sprayed with ethanolic dodecamolybdophosphoric acid, and the most intense

band was removed and extracted with ether. Filtration, evaporation, and crystallization from pentane gave dimethyl [1,2:5,6]di[c]furocyclooctatetraene-3,8-dicarboxylate (**16**, 50 mg, 3.3%) as colorless prisms, mp 134–135°; infrared spectrum (CHCl<sub>3</sub>), bands at 1718 (ester) and 1655, 1645 cm<sup>-1</sup> (double bond); electronic spectrum,  $\lambda_{\text{max}}^{\text{EtOH}}$  250 nm ( $\epsilon$  17,100) and 315 (6000),  $\lambda_{\text{inf}}^{\text{EtOH}}$  242 nm ( $\epsilon$  15,200); nmr spectrum (CCl<sub>4</sub>, 60 MHz), 3 singlets at  $\tau$  2.23, 2.46, and 2.53 (2 H each, olefinic protons) and a singlet at 6.18 (6 H, methyl protons); mass spectrum, molecular ion peak at *m/e* 300.

*Anal.* Calcd for C<sub>16</sub>H<sub>12</sub>O<sub>6</sub>: C, 64.00; H, 4.03. Found: C, 64.09; H, 4.21.

**Adduct 18 from [1,2:5,6]Di[c]furocyclooctatetraene (14) and Dimethyl Fumarate.** A solution of **14** (50 mg) and dimethyl fumarate (300 mg) in benzene (15 ml) was boiled under reflux for 96 hr. The residue obtained on evaporation was preadsorbed onto neutral alumina (20 g), which was poured on top of a column of silica gel (B.D.H., 45 × 2.75 cm) made up with pentane-ether (17:3). The column was developed with this solvent mixture (1 l.), followed by pentane-ether (7:3, 8 l.), 250-ml fractions being collected. Fractions 2 and 3 gave unchanged **14** (28 mg). Fractions 14–32 on evaporation and crystallization from cyclohexane yielded the adduct **18** (30 mg, 76% based on unrecovered **14**) as orange prisms, mp 110–111°; infrared spectrum (CCl<sub>4</sub>), bands at 1745 (ester) and 1635 cm<sup>-1</sup> (double bond); electronic and nmr spectra, see Discussion; mass spectrum, molecular ion peak at *m/e* 328.

*Anal.* Calcd for C<sub>18</sub>H<sub>14</sub>O<sub>6</sub>: C, 65.85; H, 4.91. Found: C, 65.61; H, 5.02.

**1,2-Benzo[5,6-c]furocyclooctatetraene (20).** **A. From Furan-3,4-bis(methylenetriphenylphosphonium chloride) (9) and *o*-Phthalaldehyde (19).** A solution of the dialdehyde **19** (500 mg) and the salt **9** (2.70 g) in absolute dimethylformamide (75 ml) was treated with lithium ethoxide (prepared from 70 mg of lithium) in absolute ethanol (16.5 ml) at 90°, and the product was isolated and chromatographed, as described above for the preparation of **14**. The crystalline solid obtained from fractions 4 and 5 on sublimation at 50° (0.05 mm) yielded 1,2-benzo[5,6-c]furocyclooctatetraene (**20**, 67 mg, 9.3%) as colorless prisms, mp 86–88°; infrared spectrum (CCl<sub>4</sub>), bands at 3055 (w), 3020 (s), 1650 (w), 1530 (m), 1493 (s), 1435 (w), 1220 (w), 1140 (s), 1055 (vs), 950 (w), 880 (s), 725 (m), 695 (w), and 635 (s) cm<sup>-1</sup>; electronic spectrum,  $\lambda_{\text{max}}^{\text{EtOH}}$  236 nm ( $\epsilon$  25,500),  $\lambda_{\text{inf}}^{\text{EtOH}}$  ca. 275 nm ( $\epsilon$  4600); nmr spectrum, see Discussion; mass spectrum, molecular ion peak at *m/e* 194.

*Anal.* Calcd for C<sub>14</sub>H<sub>10</sub>O: C, 86.57; H, 5.19. Found: C, 86.32; H, 5.48.

**B. From *o*-Xylylenebis(triphenylphosphonium Bromide) (7) and Furan-3,4-dicarboxaldehyde (13).** The salt **7** (3.0 g)<sup>11</sup> and the dialdehyde **13** (450 mg) were treated with lithium ethoxide (prepared from 70 mg of lithium) exactly as described for the preparation of **14**. Chromatography as before gave substance **20** (25 mg, 3.6%), mp 86–88°, identified with the sample obtained by method A by mixture melting point determination and comparison of the infrared spectra. In addition, triphenylphosphine (160 mg, 8%), mp 78–80°, was isolated.

**Adduct 21 from 1,2-Benzo[5,6-c]furocyclooctatetraene (20) and Dimethyl Fumarate.** A solution of **20** (38 mg) and dimethyl fumarate (100 mg) in benzene (15 ml) was boiled under reflux for 144 hr. The residue obtained on evaporation was preadsorbed onto neutral alumina (10 g), which was poured on top of a column of silicic acid (Mallinckrodt, 100 mesh; 30 × 2.75 cm) made up with pentane-ether (9:1). The column was developed with this solvent mixture (1 l.), followed by pentane-ether (4:1, 2 l.) and then ether (1 l.), 100-ml fractions being collected. Fractions 2–4 gave unchanged **20** (24 mg). Fractions 15–17 on evaporation and crystallization from cyclohexane led to the adduct **21** (14 mg, 57% based on unrecovered **20**) as pale yellow needles, mp 110–112°; infrared spectrum (CCl<sub>4</sub>), band at 1745 cm<sup>-1</sup> (ester); electronic and nmr spectra, see Discussion; mass spectrum, molecular ion peak at *m/e* 338.115 (calcd for <sup>12</sup>C<sub>20</sub><sup>1</sup>H<sub>18</sub><sup>16</sup>O<sub>3</sub>: 338.115).

**Acknowledgments.** J. A. E. is indebted for the award of a C.S.I.R.O. (Australia) Overseas Postgraduate Studentship (1966–1967), and M. V. S. for the award of a Science Research Council Postdoctoral Fellowship (1964–1966) and an Imperial Chemical Industries Fellowship (1966–1967). We also thank the Royal Society for generous financial support.