Cycloaddition Reactions of 7-Benzylidenecycloocta-1,3,5-triene with Ethenetetracarbonitrile and 4-Phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione

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Dedicated to Professor *Rolf Huisgen* on the occasion of his 85th birthday

An (*E*)/(*Z*) mixture (3:2) of 7-benzylidenecycloocta-1,3,5-triene (**5**) is obtained when 1-benzylcycloocta-1,3,5,7-tetraene (**7**), prepared by an improved procedure, is treated with *t*-BuOK in THF. Alternatively, a *ca.* 9:1 mixture (*E*)/(*Z*)-**5** can be prepared in a *Wittig* reaction involving benzaldehyde and cycloocta-2,4,6-trien-1-ylidenetriphenylphoshorane (**9**). Treatment of (*E*)/(*Z*)-**5** 88:12 with ethenetetracarbonitrile (TCNE) gave a complex mixture of products, from which seven mono-adducts and two bis-adducts were isolated (*Sect. 2.2.1*). Of the mono-adducts, four are $\pi4+\pi2$ adducts: two ((*E*)- and (*Z*)-isomers) are derived from valence tautomers of the two isomers of (*E*)/(*Z*)-**5**, while it is tentatively suggested that the other two (again (*E*)- and (*Z*)-isomers) are formed from the intermediacy of a pentadienyl zwitterion (*Sect. 2.3*). The remaining three mono-adducts, two of which are epimers, are $\pi8+\pi2$ adducts. It is suggested that they are derived from the intermediacy of homotropylium zwitterions (*Sect. 2.3*). For the two bis-adducts, it is postulated that they are derived from an initial $\pi2+\pi2$ cycloaddition involving the homotropylium zwitterions followed by $\pi4+\pi2$ cycloaddition to the valence tautomer of each of the $\pi2+\pi2$ cycloadducts. With 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (**6**), (*E*)/(*Z*)-**5** 91:9 yielded two $\pi4+\pi2$ cycloadducts ((*E*)- and (*Z*)-isomers) as well as two epimeric $\pi8+\pi2$ cycloadducts (*Sect. 2.2.2*). The intermediacy of pentadienyl (tentative suggestion) and homotropylium zwitterions accounts for the formation of the products (*Sect. 2.3*).

1. Introduction. – In 1990, it was reported [1] that a number of 7-alkylidenecycloocta-1,3,5-trienes undergo interesting $\pi8+\pi2$ cycloaddition reactions with a variety of $\pi2$-addends. As a representative example, 7-methylenecycloocta-1,3,5-triene (**1**) reacts with ethenetetracarbonitrile (= tetracyanoethylene = TCNE) to give the adducts **2** and **3**. It was postulated [1] that the intermediate homotropylium zwitterion **4** was involved with charge annihilation occurring by bond formation at C(2) and C(7) to give **2** and **3**, respectively.

As an extension of the above studies, the synthesis of 7-benzylidenecyclocta-1,3,5-triene (**5**) (as an (*E*)/(*Z*) mixture) and its addition reactions with TCNE and 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (= PTAD; **6**) are the subject of this paper.

2. Results and Discussion. – 2.1. *Synthesis of 7-Benzylidenecycloocta-1,3,5-triene* (**5**). The fact that alkylcyclooctatetraenes can be converted into equilibrium mixtures with 7-alkylidenecycloocta-1,3,5-trienes by treatment with *t*-BuOK [1] led to the first of two successful routes to 7-benzylidenecycloocta-1,3,5-triene (**5**). Treatment of 1-benzylcycloocta-1,3,5,7-tetraene (**7**) with *t*-BuOK in tetrahydrofuran (THF) gave an equilibrium mixture (95:5) of **5** and starting material **7** which was freed of the latter by

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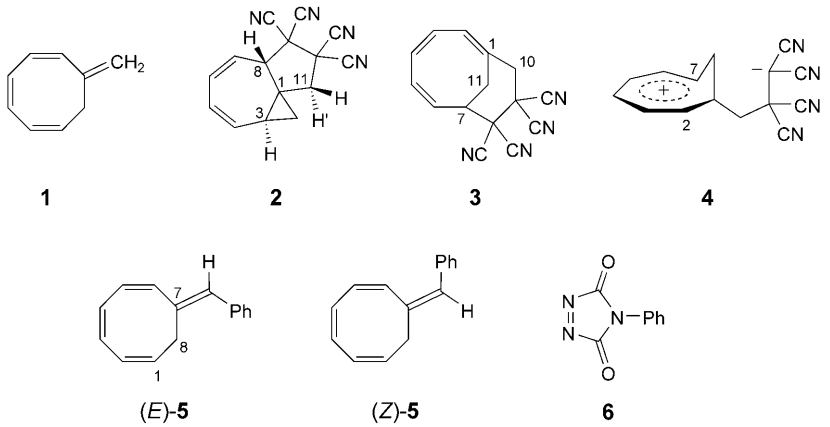
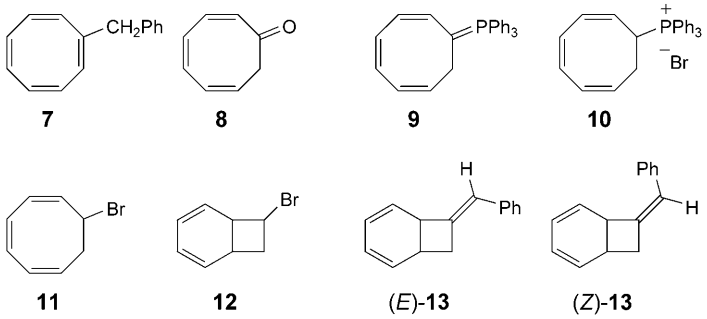


extraction with a 20% aqueous $AgNO_3$ solution [2] to give **5** (84%) as a 3:2 (*E*)/(*Z*) mixture. Benzylcyclooctatetraene **7**, which had been prepared previously in low yields by two procedures [2], was now obtained in high yield (88%), but mixed with bibenzyl (4%), from the reaction of 1-bromocycloocta-1,3,5,7-tetraene with an excess of benzylmagnesium chloride catalyzed by $FeCl_3$ [3]. Purification, though relatively inefficient, was effected by extraction with 20% aqueous $AgNO_3$ solution.



Since 7-methylenecycloocta-1,3,5-triene (**1**) can be prepared by a *Wittig* reaction between cycloocta-2,4,6-trienone (**8**) [4] and methylenetriphenylphosphorane [1], it was envisaged that the benzylidenecyclooctatriene **5** might be synthesized from the same ketone and benzylidenetriphenylphosphorane. The reaction between the phosphorane, generated from benzyltriphenylphosphonium chloride [5] under different conditions, and the ketone gave, however, only a trace, if any, of **5**. The compound was, however, prepared as a (*E*)/(*Z*) mixture in ratios varying from 84:16 to 91:9 by a *Wittig* reaction between benzaldehyde and cycloocta-2,4,6-trien-1-ylidenetriphenylphosphorane (**9**). The precursor of **9**, cycloocta-2,4,6-trien-1-yltriphenylphosphonium bromide (**10**), was prepared from a *ca.* 7:3 mixture of 7-bromocycloocta-1,3,5-triene (**11**) and its valence tautomer **12** [6]. It was a most unstable and difficult-to-handle compound and could not be recrystallized. The selective reaction of **11**, and not **12**, with triphenylphosphine is the result of the much greater reactivity of an allylic bromide

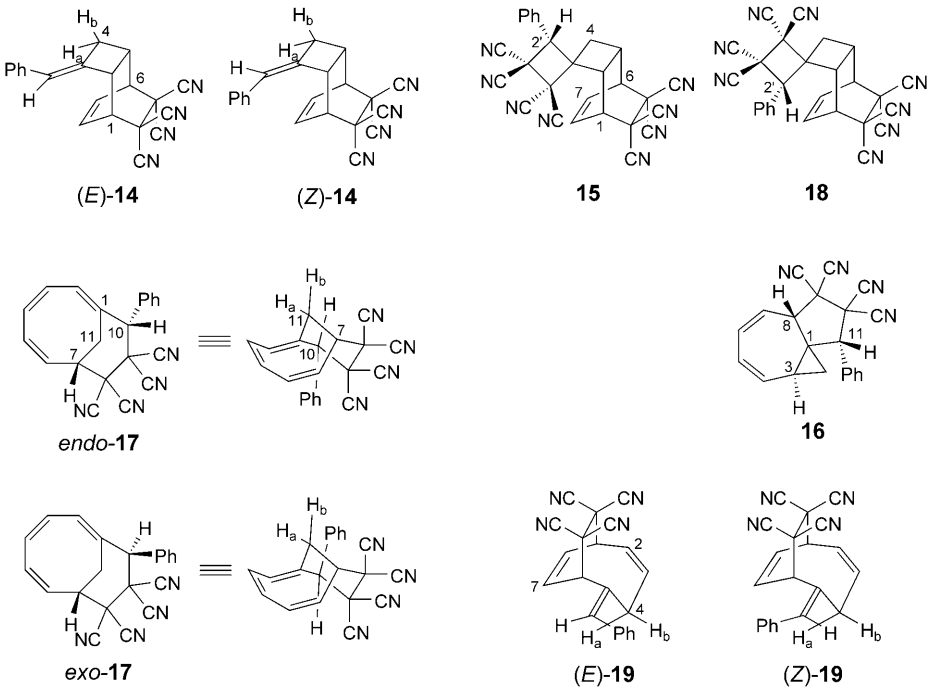
compared with a cyclobutyl bromide [7] for such a reaction. A similar selectivity was observed in the reaction of **11**/**12** with sodium azide to give 7-azidocycloocta-1,3,5-triene [6]. The two isomers (*E*)- and (*Z*)-**5** could not be separated by gas-liquid (GLC) or thin-layer chromatography (TLC). Recognition of their presence and assignment of their configurations was based on NMR spectroscopy.

In the ^{1}H-NMR spectrum of **5**, a pair of *d* at δ 3.30 and 3.40 was present for the two H-atoms at C(8) of each isomer. Although the relative areas of each of the *d* enabled the proportions of the two isomers to be determined, ^{13}C-NMR spectroscopy was used initially to assign the configurations. Resonances for C(8) of each isomer ((*E*)/(*Z*)-**5** 9 : 1) were observed as a *t* at δ 29.39 and a much less intense one at δ 37.76 in the off-resonance spectrum. Because the two H-atoms at C(8) are shielded by the Ph group in the (*E*)-isomer, the higher-field and more intense *t* was assigned to (*E*)-**5** [8]. For the ^{1}H-NMR spectrum, it was therefore concluded that the *d* of greater intensity and at slightly lower field (δ 3.40) corresponded to (*E*)-**5**. This assignment was confirmed by examination of the ROESY plot where interaction between the olefinic H–C=C(7) at δ 6.23 with H–C(8) at δ 3.30 clearly established the (*Z*) configuration at C(7) of the minor isomer. It should be noted that the ^{1}H-NMR spectrum of the mixture (*E*)/(*Z*)-**5** did not contain any resonances that could be attributed to the presence of the bicyclic valence tautomers (*E*)- and (*Z*)-**13**.

Essentially pure (*E*)-**5** can be obtained as recovered starting material (*ca.* 20%) when the initially obtained (*E*)/(*Z*) mixture (*ca.* 9 : 1) is treated with 0.8 equiv. of PTAD (**6**). Other 7-arylidenecycloocta-1,3,5-trienes have been prepared successfully from phosphorane **9** [9].

2.2. *Products of Cycloadditions.* 2.2.1. *With Ethenetetracarbonitrile* (TCNE). Treatment of a 88 : 12 mixture of (*E*)/(*Z*)-**5** with an excess of TCNE in boiling AcOEt gave a complex mixture from which nine products, (*E*)-**14** (8%), (*Z*)-**14** (0.6%), **15** (8%), **16** (11%), *endo*-**17** (8%), *exo*-**17** (20%), **18** (5%), (*E*)-**19** (15%), and (*Z*)-**19** (0.3%) were isolated. After fractional crystallization of the crude mixture had given some (*E*)-**14** and **15**, chromatography (silica gel) of the remaining mixture gave four fractions. From these, the nine products were isolated, in general after exhaustive fractional crystallization. Structures of the products were elucidated by the extensive use of NMR spectroscopy and, in three cases, confirmed by X-ray analysis of single crystals.

Compounds (*E*)- and (*Z*)-**14** were shown to be a pair of isomeric mono-adducts by elemental analysis, the observation of four signals attributable to the CN groups in their ^{13}C-NMR spectra, and mass spectrometry. The structural framework of (*E*)-**14**, the 3-benzylidenetricyclo[4.2.2.0^{2,5}]dec-7-ene skeleton, was readily elucidated on the basis of the ^{1}H-and ^{13}C-NMR and COSY data. Assignment of (3*E*)- configuration was derived from the ROESY plot. In particular, interactions between H–C(1) and H–C(2) with the olefinic H–C=C(3) clearly indicated the orientation of the benzylidene group (see *Fig. 1*). The structure of (*E*)-**14** was confirmed by X-ray crystallographic analysis [10]. Although only a small quantity of (*Z*)-**14** was isolated, its structure was readily deduced by NMR spectroscopy. As would be expected, its ^{1}H- and ^{13}C-NMR spectra had features similar to those of the geometric isomer (*E*)-**14**. The resonance for H–C(2) in (*Z*)-**14** was shifted downfield by *ca.* 0.3 ppm compared with that for H–C(2) in (*E*)-**14** due to deshielding by the Ph group. Confirmation of the (3*Z*)-configuration was derived from the ROESY plot. In particular, the interaction between the olefinic H–C=C(3) and H_a–C(4)/H_b–C(4) together with the interaction of the H_o of Ph with H–C(1)/H–C(2) clearly indicated the opposite geometry of the benzylidene residue



(see *Fig. 1*). The mass spectrum of (*Z*)-**14** showed a major peak at *m*/*z* 322 for M^+ and another one at *m*/*z* 194 as a result of the expected retro-*Diels–Alder* fragmentation.

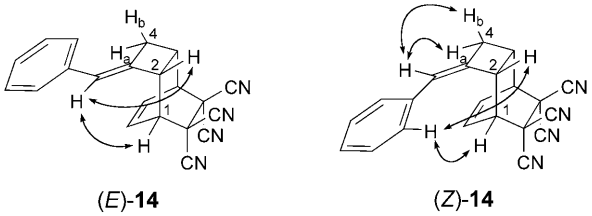


Fig. 1. *ROESY Interactions for* (E) *and* (Z)-**14**

Compounds **15** and **18** were shown to be a pair of bis-adducts by consideration of microanalyses, and ^{1}H- and ^{13}C-NMR data. For each of **15** and **18**, the key skeletal fragment, tricyclo[4.2.2.0^{2,5}]dec-7-ene, was again readily elucidated from their ^{1}H-NMR and COSY data. The attachment of the additional spiro-linked ring was then derived by interpretation of the HMQC and HMBC data. For both isomers, the orientation of the spiro-linked ring and the configuration at C(2′)[2]) was determined by consideration of their ROESY plots. The key ROESY interactions that support these structures are shown in *Fig. 2*. The proposed structures for **15** and **18** are also supported by a number of chemical shift differences observed for these structures. In particular, those for

[2]) Arbitrary numbering; systematic names are given in parentheses in the *Exper. Part*

H–C(7) and H–C(8) of **15** are shifted 0.80 and 1.01 ppm downfield in comparison to the same H-atoms of **18** (consistent with substantial shielding of these olefinic H-atoms by the proximal CN groups in **15**). A similar observation is made for the chemical shift of H_a–C(4); its proximity to the C(7)=C(8) π-bond results in an anisotropic shielding in **18** (an upfield shift of 0.46 ppm).

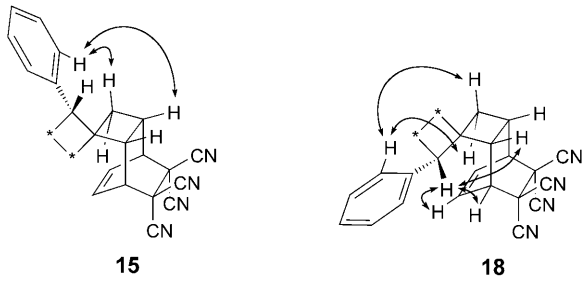


Fig. 2. *ROESY Interactions for* **15** *and* **18**. An asterisk is used to indicate the fragment $C(CN)_2$ which is omitted for clarity.

Importantly, **15** and **18** are not derived simply by the addition of TCNE to any of the mono-adducts (*E*)-**14**, **16**, *endo*-**17**, *exo*-**17**, or (*E*)-**19**. This was established by the finding that each of these compounds was recovered unchanged when treated with the π2-addend under the conditions of the initial reaction. Attempts to produce crystals of **15** and **18** suitable for X-ray analysis were unsuccessful.

The structure of **16** was deduced from ^{1}H- and ^{13}C-NMR data which, when account is taken of the Ph group at C(11), were similar to those of the adduct **2** formed from 7-methylenecycloocta-1,3,5-triene (**1**) [1]. Assignment of the configuration was deduced by reference to the ROESY plot where H–C(3) showed a cross-peak with one of the cyclopropyl H-atoms at C(2), and the H_o of Ph and H–C(11) also showed cross-peaks with one of the cyclopropyl H-atoms at C(2). The proposed configuration was confirmed by X-ray crystallography [11].

The spectral properties of *endo*-**17** bore similarities to those of the 1:1 adduct **3** formed in the reaction between **1** and TCNE [1]. The replacement of one of the H-atoms at C(10) in the adduct **3** by the Ph group caused the expected [12] downfield shift (from δ 3.26 to 4.25) in the chemical shift of H–C(10). Analysis of the ^{1}H-NMR and COSY data revealed the bicyclo[5.3.1]deca-1,3,5-triene framework. *Dreiding* models show that the six-membered ring in *endo*-**17** would exist in a chair conformation with the Ph group in an equatorial position and H–C(10) axial. Evidence to support this deduction was obtained from NOE difference experiments (irradiation at δ 2.46 (*d*, H_b–C(11)) → NOEs at δ 4.25 (13.7%, H–C(10)), 3.34 (35.0%, H_a–C(11)), 3.88 (8.0%, H–C(7)). These results demonstrate that H–C(7) and H–C(10) are *cis* to each other as shown.

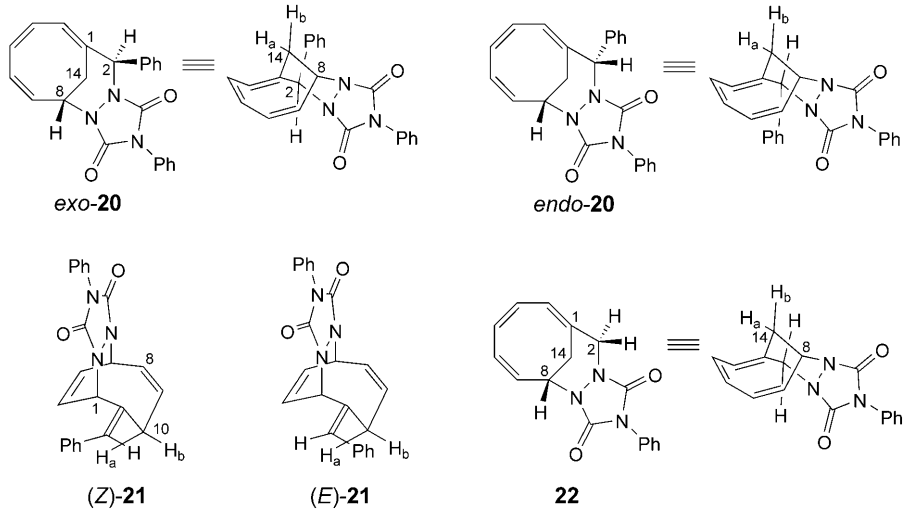
The ^{1}H-NMR spectral features of *exo*-**17**, the epimer of *endo*-**17**, allowed assignment of this structure to be made without difficulty. For *exo*-**17**, steric interactions between the Ph group and one of the CN groups at C(8) is likely to cause the ring to adopt a conformation other than the chair form. The Ph group causes considerable deshielding of H_b–C(11) and this, combined with an unexpected upfield shift in the resonance of

$H_a-C(11)$, results in the chemical-shift difference between the two H-atoms at C(11) in *exo*-**17** being only 0.14 ppm compared with 0.88 ppm for the corresponding H-atoms in *endo*-**17**. The inverted configuration at C(10) is supported by the lack of NOE between H−C(10) and either of the H-atoms at C(11).

Assignment of the structure to (*E*)-**19** rested initially on ^{1}H-NMR and microanalytical data. *Dreiding* models showed that the preferred conformation is as shown for (*E*)-**19** with C(4) pointing away from C(9) and C(10)[2]) which bear the CN groups. Shielding of $H_a-C(4)$ by the π-bond C(7)=C(8) and deshielding of $H_b-C(4)$ by the Ph group account for the chemical shifts of this pair of H-atoms. The magnitudes of the coupling constants are consistent with the dihedral angles in the proposed conformation (*E*)-**19**, particularly $J(3,4b) = 10.0$ Hz (consistent with dihedral angle of *ca.* 0°) and $J(3,4a) = 4.5$ Hz (higher than normal for a dihedral angle of *ca.* 110°). It should be noted that the small difference between the chemical shifts of H−C(1) and H−C(6) is consistent with the compound being the (*E*)-isomer (*E*)-**19** and not the (*Z*)-isomer (*Z*)-**19** (see below). The characteristics of the UV spectrum of (*E*)-**19** resembled closely those of *β*,*β*-dimethylstyrene (=(2-methylprop-1-enyl)benzene) [13] and benzylidenecyclohexane [14] as would be expected. Finally, the structure was confirmed by X-ray crystallography [15].

That (*Z*)-**19** was an isomer of (*E*)-**19** was clear from both the ^{13}C-NMR spectrum which showed the presence of four CN groups and the MS which showed an M^+ at *m*/*z* 322 and an intense peak for the fragment ion at *m*/*z* 194, which corresponds to a loss of TCNE. As would be expected, the ^{1}H-NMR spectrum of (*Z*)-**19** showed features allowing ready recognition that the compound was the (*Z*)-isomer of (*E*)-**19**. Assignment of the configuration was made by consideration of the ROESY data where interactions between the H_o of Ph and H−C(6) (*δ* 4.41) and H−C(7) (*δ* 6.22) confirmed this geometry.

2.2.2. *With 4-Phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione* (**6**). A (91:9) mixture (*E*)/(*Z*)-**5** in AcOEt reacted readily with **6** at room temperature to give a mixture of four mono-adducts: *exo*-**20** (46%), *endo*-**20** (28%), (*Z*)-**21** (4%), and (*E*)-**21** (16%). The first two and the last compounds were obtained in crystalline forms after chromatography (silica gel). That *exo*- and *endo*-**20** were related to **22** [1], and were epimeric at C(2), was clearly indicated by the ^{1}H- and ^{13}C-NMR data. Replacement of one of the H-atoms at C(2) in **22** by the Ph group caused the expected downfield shift [12] of the remaining H-atom at C(2) (*δ* 2.06 in *exo*-**20** and 1.26 in *endo*-**20**). As well, the introduction of the Ph group at C(2) caused the expected downfield shift of that C-atom in the ^{13}C-NMR spectrum: the downfield shifts were 11.3 and 15.4 ppm, respectively, compared to **22**. Assignment of the relative configurations at C(2) and C(8) in *exo*-**20** rested on *i*) the relatively small chemical-shift difference ($\Delta\delta \approx 0.3$ ppm) for H−C(13) between *exo*-**20** and **22** (models show that the pseudoaxially disposed Ph group in *exo*-**20** should not have a significant effect on H−C(13)), *ii*) absence of allylic coupling between H−C(13) and H−C(2) (this is consistent with the dihedral angle between the two H-atoms being close to 0° as shown by *Dreiding* models), and *iii*) the absence of an NOE at H−C(2) (*δ* 6.05) after irradiation at $H_b-C(14)$ (*δ* 2.23). Expected NOEs were observed for the signals of $H_a-C(14)$ (*δ* 2.86, 36.8%) and H−C(8) (*δ* 5.26, 5.2%). Confirmation of the structure of *exo*-**20** was provided by X-ray crystallography [16].

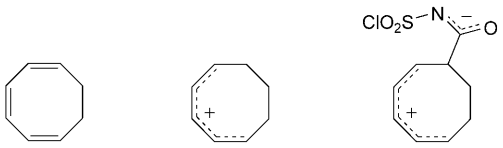


For *endo*-**20**, the relative configurations at C(2) and C(8) were determined from the ^{1}H-NMR spectrum by *i*) the marked chemical-shift difference (1.05 ppm) for H–C(13) in *exo*-**20** compared to *endo*-**20** (models show that the pseudoequatorially disposed Ph group in *endo*-**20** should shield H–C(13) compared with *exo*-**20**), *ii*) the allylic coupling, as revealed by the ^{1}H,^{1}H-COSY plot, between H–C(13) and H–C(2) (models show that the dihedral angle between the two H-atoms is close to 90° thus leading to a large allylic coupling ($J(2,13) = 3.0$ Hz)), and *iii*) an NOE for the *s* of H–C(2) (δ 5.79, 7.8%) on irradiation of the signal of H_b–C(14) (δ 2.64). The observation of the NOE between H–C(2) and H_b–C(14) is compatible with the 1,3-di-pseudoaxial orientation as is clearly shown in the *Dreiding* model. Unfortunately, satisfactory crystals of *endo*-**20** for an X-ray crystallographic analysis could not be obtained. The correctness of the deduced structure was supported, however, by an X-ray analysis [17] of the corresponding 4-methoxy-substituted derivative (formed from 7-(4-methoxybenzylidene)cycloocta-1,3,5-triene and **6** [9]) whose ^{1}H- and ^{13}C-NMR spectral characteristics for the appropriate resonances were very similar to those of *endo*-**20**.

Although it could be obtained only in a noncrystalline form and not entirely pure, (*Z*)-**21** possessed ^{1}H- and ^{13}C-NMR and COSY characteristics which bore marked similarities to those of (*E*)-**21**. In the ^{1}H-NMR spectrum of (*Z*)-**21**, the signal for H–C(1) was observed at δ 5.85 compared with δ 5.57 for H–C(1) in (*E*)-**21** (as would be expected for deshielding by the Ph group in (*Z*)-**21**). Confirmation of the deduced configuration was provided by the ROESY plot of (*Z*)-**21** where cross-peaks were observed between the signals for H–C=C(11) and both H_a–C(10) and H_b–C(10) together with a cross-peak between the signals for H–C(1) and the H_o of Ph. Initially, the structure of (*E*)-**21** was deduced from ^{1}H- and ^{13}C-NMR data which, not surprisingly, were similar to those of (*E*)-**19** when account is taken of the anticipated downfield shifts of the resonances of H–C(1) and H–C(7) caused by the two N-atoms in (*E*)-**21**. Models of (*E*)-**21** do not show that there should be a preference for one of

the two conformations with C(10) pointing towards, or away from, the π-bond C(12)=C(13) (*cf.* (*E*)-**19**). Indeed, it would seem that interconversion between the two conformations should occur readily. This is consistent with the coupling constants observed between H–C(9) and the two H-atoms at C(10) where the values appear to be averaged (5.4 and 6.6 Hz). That the compound in the crystalline state exists in the conformation with C(10) pointing towards the π-bond C(12)=C(13) was determined by X-ray crystallography [18].

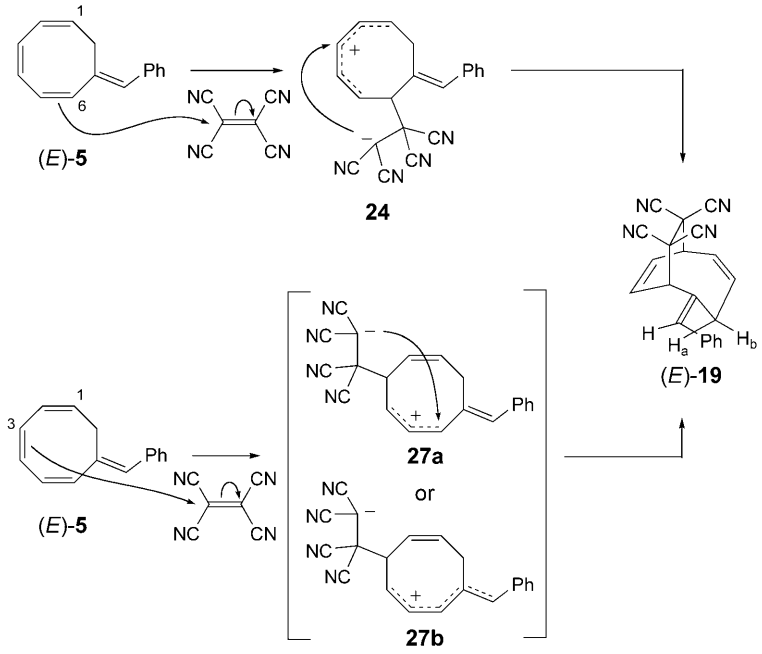
2.3. *Mechanisms of the Cycloadditions.* Let us now consider mechanisms which can be postulated to account for the cycloadditions involving **5** reported here. As was the case for 7-alkylidenecycloocta-1,3,5-trienes [1], cycloaddition reactions involving concerted processes, and thus being thermally allowed by the *Woodward–Hoffmann* rules [19], for the tetraene **5** might be considered to be unlikely because its eight-membered ring is tub-shaped and the extent of π-orbital overlap is limited. This is in harmony with its UV spectrum in which the absorption maxima are at considerably shorter wavelengths and are much less intense than would be expected for a completely conjugated system. Indeed, the UV spectrum of **5** was similar to that of β,β-dimethylstyrene [13] and benzylidenecyclohexane [14] establishing that conjugation with the endocyclic C=C bonds was absent. It cannot be assumed, however, that **5** is unable to undergo cycloaddition reactions *via* concerted processes. It has been postulated by *Isaken* and *Snyder* [20] that cyclooctatetraene, which is tub-shaped and, therefore, in general unable to undergo concerted cycloaddition reactions, does so with the very reactive PTAD (**6**) *via* the planar arrangement of the parent compound involved in its ring-inversion process. It was suggested that the free-energy difference (estimated to be 4.4 kcal/mol at 20°) between cyclooctatetraene and its planar form is sufficiently low to allow the concerted process to take place. At present, the free-energy difference between the tub and planar forms of 7-methylenecycloocta-1,3,5-triene (**1**), or any of its analogues, is not known. It should be noted that models indicate that ring inversion for this class of molecules can occur with planarity of the ring π-system only and with the alkylidene or arylidene portion almost perpendicular to the plane. As a result, the ring-inversion process might be similar to that of cycloocta-1,3,5-triene (**23**) where a free energy of 6.7 kcal/mol has been determined for the barrier to ring inversion involving 'near coplanarity' of the three C=C bonds in the transition state [21] (see also [22]). At this stage, the possibility that some of the $\pi4+\pi2$ cycloadditions that take place with **5** might involve its planar form during ring inversion cannot be discounted. On the other hand, the $\pi8+\pi2$ cycloadditions which occur with **5** cannot be concerted not only because of the difficulty of attaining planarity of all four π-bonds but more importantly because the distance between the two C-atoms that are involved is too great for a $\pi2$-addend to be able to react in this way.



23 **25** **26**

Compound (*E*)-**19** is a $\pi 4 + \pi 2$ cycloadduct, and three possibilities can be considered for its origin. In the first, (*E*)-**5** in its planar form during ring inversion undergoes an allowed concerted $\pi 4 + \pi 2$ cycloaddition with TCNE; this of course can occur only when the free energy for the formation of the planar form is sufficiently low. The second possibility is outlined in *Scheme 1*. It involves the intermediacy of the pentadienyl zwitterion **24** formed by initial attack of the reagent at C(6) followed by charge annihilation with bond-formation at C(3) to give (*E*)-**19**. Under super-acid conditions, cyloocta-1,3,5-triene (**23**) gives the pentadienyl cation **25** [23], while its $\pi 4 + \pi 2$ cycloaddition reactions with chlorosulfonyl isocyanate are believed to proceed via the zwitterion **26** [24]. The remaining possibility (also shown in *Scheme 1*) for the formation of (*E*)-**19** involves initial reaction at C(3) to give the allylic zwitterion **27a** or the pentadienyl zwitterion **27b** stabilized by the Ph group followed by bond-formation as a result of charge annihilation at C(6). There would, however, be very considerable strain associated with the planar portion of **27b**. As well, conjugation of the dienyl portion with the Ph group would be hindered because of a steric interaction with one of the H-atoms at the methylene C-atom if formed from (*E*)-**5** or at C(6) (as in (*Z*)-**5**) if formed from (*Z*)-**5**. At this stage, it is tentatively suggested that (*E*)-**19** is formed from the pentadienyl zwitterion **24**. It follows that the corresponding zwitterion is tentatively suggested for the origin of (*Z*)-**19**.

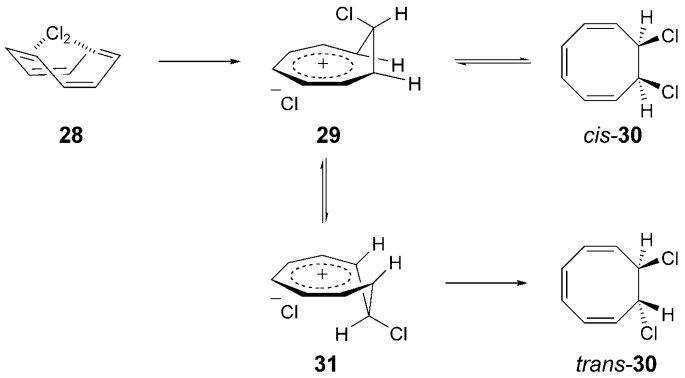
Scheme 1



In the case of the $\pi 8 + \pi 2$ adducts **2** and **3** formed from **1** [1] (see *Introduction*), it was postulated that they arose *via* the intermediacy of the homotropylium zwitterion **4**. Similarly, it is suggested that the three corresponding adducts **16**, *endo*-**17** and *exo*-**17**

from **5** and TCNE arise from the intermediacy of homotropylium zwitterions. Before their nature is discussed, it is most relevant to take account of the classical studies of *Huisgen* and co-workers [25] on the chlorination of cyclooctatetraene at low temperatures. The reaction involves initial *endo*-attack (within the 'tub' conformation of the molecule as a result of the formation of a π-complex **28**) by Cl_2 to give the homotropylium salt **29** followed by a second *endo*-attack by a Cl^- ion to give the *cis*-dichloro compound *cis*-**30** (*Scheme 2*). A rise in temperature gives the *trans*-dichloro derivative *trans*-**30** as a result of regeneration of the homotropylium salt **29** and ring inversion of the homotropylium ion to give **31** followed by *endo*-attack by a Cl^- ion (*Scheme 2*).

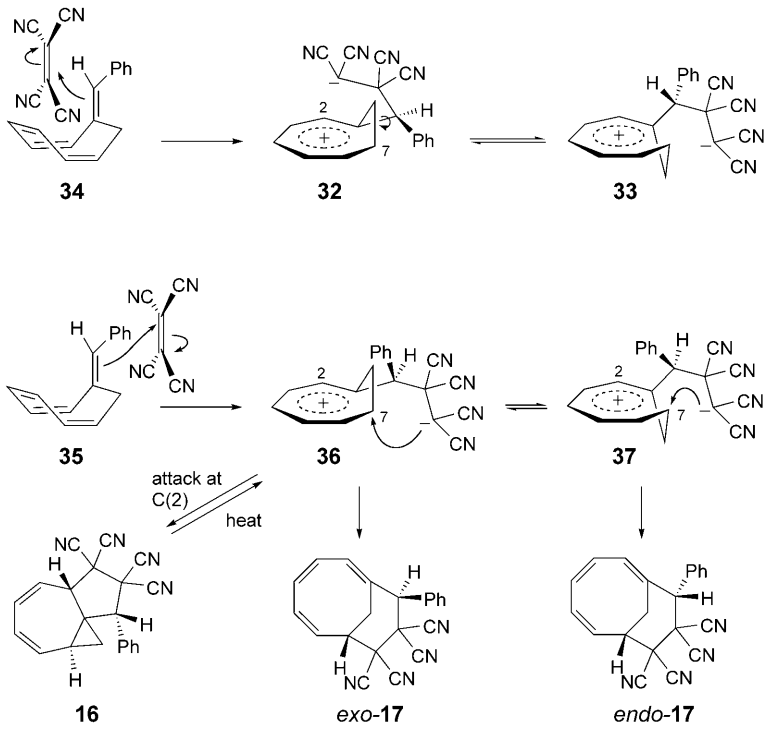
Scheme 2



Evidence that the parent homotropylium ion undergoes ring inversion is available [26] and that it might be occurring with the zwitterions formed from (*E*)-**5** and (*Z*)-**5** is presented below. Before considering whether the products **16**, *endo*-**17**, and *exo*-**17** might be formed in *endo,endo* processes or involve one or two *exo* processes (reactions occurring outside of the tub or ring) involving homotropylium zwitterions as intermediates, it is pertinent to mention the following: *1*) when (*E*)-**5** which was essentially free of its (*Z*)-isomer was treated with TCNE, **16** was formed in an estimated yield of 14% compared with 11% when the (*E*)/(*Z*) ratio was 3 : 2. It would seem that the formation of **16** is dependent on the (*E*)/(*Z*) composition of **5** used in the reactions. A method to prepare pure (*Z*)-**5**, or mixtures of (*E*)- and (*Z*)-**5** with the latter dominating, is needed, however, in order to confirm this preliminary finding; *2*) the ratio of the two diastereoisomers *endo*- and *exo*-**17** is definitely dependent on the ratio of (*E*)- and (*Z*)-**5** used in the reactions. When the (*E*)(*Z*) ratios were 60 : 40, 72 : 28, and 88 : 12, the ratios *endo/exo*-**17** were 1.00 : 0.72, 1.00 : 1.16 and 1.00 : 2.45, respectively. Most importantly, however, a sample of (*E*)-**5** in which (*Z*)-**5** was barely detectable (by ^{1}H-NMR) gave with TCNE a *ca.* 1 : 7 mixture of *endo*- and *exo*-**17**. In this case, the yield of *endo*-**17** was estimated to be at least 3% which clearly shows that the compound could have been derived only from (*E*)-**5**; *3*) when **16** was heated at 100° in MeCN for 24 h, it was converted into a 1.00 : 8.2 mixture of *endo*- and *exo*-**17**. The ratio is not too different from that mentioned in *2*) above.

It is now appropriate to discuss the origin of **16**, *endo*-**17**, and *exo*-**17**. That initial formation of π-(charge-transfer) complexes with **5** and TCNE occurred was shown by the strongly colored solutions formed when the TCNE was added to **5**. In one scenario, the zwitterions **32** and **33** can be formed as follows: if (*E*)-**5** were to react initially with the complexed TCNE within the tub (*endo*-mode) of the ring as in **34**, the zwitterion **32**, which is the same as that formed from (*Z*)-**5** by *exo*-attack, would be generated (*Scheme 3*). Ring inversion of **32** would yield **33** which is the same species as that formed from (*Z*)-**5** by *endo*-attack by TCNE (Note: the apparent change in configuration at the benzylic C-atom in the side-chain in **33** is the result of a conformational change caused by rotation of the bond between C(1) and C(1′) in **32**). On the other hand, if the initial reaction of (*E*)-**5** with TCNE were to occur as in **35** *via* the *exo*-mode, the zwitterion **36**, which is the same as that formed from (*Z*)-**5** by *endo*-attack, would be produced. Ring inversion of **36** would give **37** which is the same species as that formed by *exo*-attack with TCNE on (*Z*)-**5**.

Scheme 3

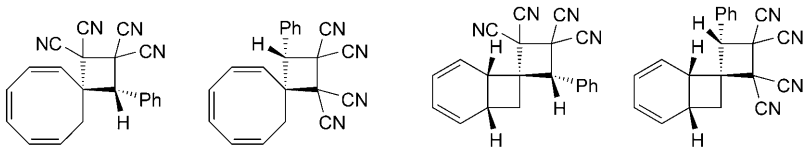


After consideration of the various *endo*- and *exo*-modes of attack by the internal nucleophile in each of the zwitterions **32**, **33**, **36**, and **37** (*Scheme 3*), it can be concluded that the latter two (as a result of initial *exo*-attack) with a slow equilibrium between them accommodate the three findings *1*)–*3*) mentioned above. Most important is the slow equilibrium between **36** and **37**; it accounts for the conversion of **16** into *endo*-**17** and *exo*-**17** on heating and for the formation of *endo*-**17** from (*E*)-**5** essentially free of

(*Z*)-**5**. The origin of **16**, *endo*-**17**, and *exo*-**17** can be accommodated as follows: *exo*-attack by the nucleophilic part of **36** at C(2) gives **16** and at C(7) gives *exo*-**17**, while the corresponding reaction at C(7) in **37** yields *endo*-**17**.

The formation of (*E*)- and (*Z*)-**14** can be readily accounted for: they are the result of $\pi4+\pi2$ cycloadditions involving the valence tautomers (*E*)- and (*Z*)-**13** of (*E*)- and (*Z*)-**5**, respectively. In the valence tautomers, the diene portions are planar and the cycloadditions are thermally allowed by the *Woodward–Hoffmann* rules [19]. That cycloocta-1,3,5-trienes can exist in equilibrium with bicyclic tautomers and that these are the reactants with dienophiles is well established [27]. As already mentioned, the bicyclic tautomers of (*E*)- and (*Z*)-**5** could not be detected in the ^{1}H-NMR spectrum of the mixture of the two compounds. Their presence in the mixture must, therefore, be very small but once formed they react readily with the $\pi2$-addend.

It is postulated that the two bis-adducts **15** and **18** are formed in three steps. Initially, the mono-adducts **38** and **39** are formed as a result of a $\pi2+\pi2$ cycloaddition resulting from charge annihilation by bond-formation at C(1) in one or more of the homotropylium zwitterions **32**, **33**, **36**, and **37** (see *Scheme 3*). These compounds **38** and **39**, which have not been detected in the mixture formed from (*E*)- and (*Z*)-**5** with TCNE, exist in a valence-tautomeric equilibrium with the bicyclic forms **40** and **41** which undergo allowed $\pi4+\pi2$ cycloadditions with the $\pi2$-addend to give **15** and **18**. It should be noted that $\pi2+\pi2$ cycloadditions in homotropylium zwitterions involving TCNE have been reported [28]. The formation of **38** can be ascribed to the attack by the internal nucleophile in **36** at C(1) by the *exo*-mode. Formation of **39** is, however, at variance with the *exo*-attack by the internal nucleophile postulated for the other products discussed above involving the homotropylium zwitterions **36** and **37**. It can be formed by *endo*-attack in **37**, the species formed by the *exo*-mode initially from (*Z*)-**5**. It must be borne in mind, however, that the ratio **15**/**18** of *ca.* 2:1 did not vary with changes in the (*E*)/(*Z*) ratio in **5**.

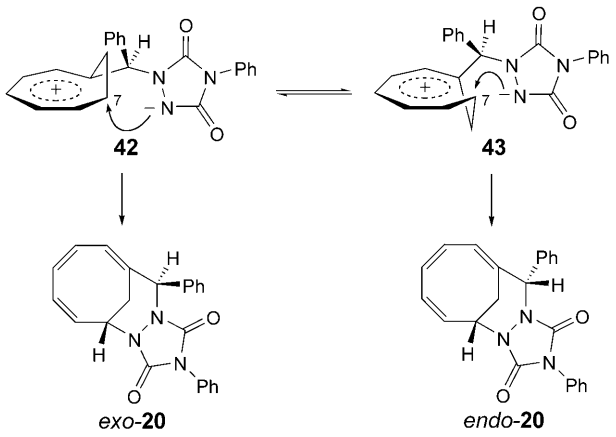


38 **39** **40** **41**

In the case of the reaction between (*E*)/(*Z*)-**5** 91:9 with **6**, the number of adducts isolated was four compared with nine when TCNE was the $\pi2$-addend. In discussing the origin of *exo*- and *endo*-**20** which are $\pi8+\pi2$ adducts, it is most important to note that both were formed in significantly greater amounts (46 and 28%, resp.) than the amount (9%) of (*Z*)-**5** in the starting material; the two compounds must be derived mostly from (*E*)-**5**. Their origin can be rationalized in the same way that was suggested for the corresponding two adducts *endo*- and *exo*-**17** from TCNE, namely *via* the equilibrating zwitterions **42** and **43** (for the case of initial *exo*-attack by the $\pi2$-addend on (*E*)- and (*Z*)-**5**; *Scheme 4*). Charge annihilation by bond-formation at C(7) in these species by the *exo*-mode gives *exo*-**20** and *endo*-**20**. In a preliminary study involving the reaction of a (*E*)/(*Z*)-**5** 65:35 with **6**, the yield of *exo*-**20** was found to be 45% (the same as for

(*E*)/(*Z*)-**5** 91:9) implying that its formation is independent of the nature of the composition of **5** and that it involves equilibrating homotropylium zwitterions. On the other hand, the yield of *endo*-**20** was reduced (from 28 to 17%) indicating that its formation is dependent on the composition of **5**. Clearly more work is required to define this aspect more precisely.

Scheme 4



As in the case of (*E*)- and (*Z*)-**19**, (*Z*)- and (*E*)-**21** are $\pi4+\pi2$ adducts, and their origin cannot be explained with confidence. Tentatively, it is suggested that they are derived from pentadienyl zwitterions corresponding to the species **24** suggested for the corresponding product from (*E*)-**5** and TCNE. The absence of adducts corresponding to (*E*)- and (*Z*)-**14** in the reaction with **6** can be attributed to the rapidity of the reaction compared with that of TCNE; reaction of (*E*)- and (*Z*)-**5** with **6** occurs before meaningful quantities of the bicyclic valence tautomers (*E*)- and (*Z*)-**13** to be trapped by the dienophile can be formed. The absence of a cyclopropyl derivative corresponding to **2** and **16** formed by bond-formation with charge annihilation at C(2) in **42** is interesting. Perhaps it is formed but is rapidly isomerized into compounds *exo*- and *endo*-**20** under the conditions of the reaction. Bis-adducts corresponding to **15** and **18**, or of their precursor mono-adducts corresponding to **38** and **39** (or their tricyclic forms **40** and **41**) were not detected in the mixture of products formed in the reaction of (*E*)/(*Z*)-**5** with **6**.

To conclude, it is clear that access to pure (*Z*)-**5**, or at least mixtures with (*E*)-**5** highly enriched in (*Z*)-**5**, is highly desirable in order that more-definitive conclusions can be drawn about its cycloaddition reactions with typical $\pi2$-addends.

The authors wish to thank Prof. *J. H. Bowie* for helpful comments about mass spectra, Mr. *T. Blumenthal* for recording mass spectra, and Dr. *E. R. T. Tiekink* for collaboration with X-ray crystallography. A *Commonwealth Postgraduate Award*, a *University of Adelaide Research Scholarship* (to *P. H. K.*), and support of the project by the former *Australian Research Grants Committee* are gratefully acknowledged.

Experimental Part

1. *General.* All solvents were distilled before use. Petroleum ether refers to the fraction of b.p. 64–68°. All org. extracts were dried over anh. $MgSO_4$. Anal. gas-liquid chromatography (GLC): *Perkin-Elmer Sigma-3B* instrument; flame-ionization detector. Flash chromatography (FC): *Merck* silica gel 60; CC = column chromatography. M.p.: *Kofler* hot-stage apparatus, uncorrected. B.p.: uncorrected. UV Spectra: EtOH solns., unless stated otherwise; *Unicam SP8-100* spectrophotometer; λ_{max} (ε) in nm. IR Spectra: *Jasco IRA-1* grating spectrometer for IR and *ATI-Mattson Genesis-Series-FTIR* spectrometer for FT-IR; films for liquids and nujol mulls for solids; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: $CDCl_3$ solns., unless stated otherwise, with Me_4Si as internal standard; *Bruker WP-80* (20.1 MHz, ^{13}C), *Varian Gemini* (200 MHz, ^1H; 50.32 MHz, ^{13}C), *Varian Gemini-2000* (300 MHz, ^1H; 75.47 MHz, ^{13}C), *Bruker ACP-300* (300 MHz, ^1H; 75.47 MHz, ^{13}C), and *Varian INOVA* (600 MHz, ^1H; 150.84 MHz, ^{13}C) instruments; routine ^1H-NMR at 200 and 300 MHz, spectra of adducts at 600 MHz, unless stated otherwise; multiplicities for ^{13}C-NMR were determined at 20.1 MHz, if quoted. Mass spectra: *VG-ZAB-2 HF* mass spectrometer; at 70 eV; in *m/z* (rel. %); in general, recording of *m/z* of abundance greater than 25%. Elemental analyses were carried out by the *Australian Microanalytical Service* (Melbourne) and the Chemistry Department, University of Otago (New Zealand). The accurate mass measurement was carried out in the Chemistry Department, Monash University.

2. *1-Benzylcycloocta-1,3,5,7-tetraene* (**7**). A soln. of benzyl chloride (4.92 g, 38.8 mmol) in dry THF (40 ml) was added dropwise over 80 min to a stirred suspension of Mg turnings (2.10 g, 86.4 mmol) in THF (40 ml) (to which a small crystal of I_2 had been added) at r.t. under N_2. After the mixture had been stirred at r.t. for a further 1.5 h, it was heated at 65–70° for another 1.5 h and kept overnight at r.t. The soln. was separated from unchanged Mg by syringe and transferred to a 250-ml flask and cooled to −15°. Bromocyclooctatetraene [29] (4.00 g, 21.9 mmol) in THF (35 ml) was added rapidly to the stirred soln. under N_2, followed immediately by a soln. of anh. $FeCl_3$ (23 mg) in THF (1.0 ml) → immediately deep-red soln. After the mixture had been stirred at −10° for 1.5 h, it was stirred at r.t. for a further 3.5 h, and then cooled (ice-water). Sat. NH_4Cl soln. (50 ml) was slowly added to the mixture, followed by petroleum ether (120 ml). The org. phase was washed with H_2O (3 × 100 ml), 20% aq. $AgNO_3$ soln. (5 × 30 ml), and H_2O (3 × 100 ml), dried, and evaporated. The residue was distilled to give a mixture (2.68 g; b.p. 83–87°/0.1 Torr), consisting of **7** (94%) and bibenzyl (6%) (^1H-NMR). The $AgNO_3$ extract was treated with excess of 25% NH_4OH soln., and the mixture was extracted with petroleum ether (3 × 75 ml). The combined org. extracts were washed with H_2O (4 × 75 ml), dried, and evaporated to give pure (^1H-NMR) **7** (1.22 g). Bulb-to-bulb distillation at 90–95° (block)/0.08 Torr gave **7** (1.16 g) whose ^1H-NMR and IR data were identical to reported data [2]. Overall, the yields (including the product extracted with $AgNO_3$) of **7** and bibenzyl were 88% and 4%, resp.

Note: The use of excess of the *Grignard* reagent in the reaction avoided the formation of bi(cyclooctatetraenyl) which caused problems during purification of the desired product when an equiv. of the reagent was used.

3. *Cycloocta-2,4,6-trien-1-yltriphenylphosphonium Bromide* (**10**). A *ca.* 7:3 mixture (by ^1H-NMR; see [30] where a ratio of 65:35 has been reported) of 7-bromocycloocta-1,3,5-triene (**11**) and its valence tautomer **12** (2.82 g, 15.2 mmol), prepared by the method of *Kröner* [6], in benzene (5 ml) was added dropwise to a stirred soln. of PPh_3 (3.72 g, 14.2 mmol) in benzene (15 ml) cooled to 3°. After the mixture had been stirred at 3–5° for 3.5 h, it was filtered under N_2, and the solid material was washed with benzene (2 × 10 ml) and dry Et_2O (6 × 20 ml) and 'dried' at r.t./0.01 Torr for 40 min: **10** (4.39 g, *ca.* 91%, based on estimated **11** in the starting material) as a highly electrostatic powder. On exposure to air, **10** was rapidly converted into a sticky gum. Even at −18° under N_2, the lifetime of **10** was only a few days. ^1H-NMR (200 MHz): 2.67 (*q*, *J* = 7.0, 2 H–C(8)); 5.45–5.57 (*m*, H–C(1)); 5.68–5.84 (*m*, 2 olef. H); 5.85–6.46 (*m*, 3 olef. H); 6.30–6.46 (*m*, 1 olef. H); 7.60–7.85 (*m*, 10 arom. H); 7.85–8.06 (*m*, 5 arom. H).

4. (7E)/(7Z)-*7-Benzylidenecycloocta-1,3,5-triene* ((*E*)/(*Z*)-**5**). 4.1. In preliminary experiments, it was shown by GLC (15% *SE-30* on *Varaport 30*) that an equilibrium (95:5) between **5** and starting material was established readily when **7** was treated with *t*-BuOK in THF. A stirred soln. of **7** (220 mg, 1.13 mmol) in dry THF (8.0 ml) at 0° under N_2 was treated with finely powdered *t*-BuOK (64 mg, 0.57 mmol). After 5 min, the cooling bath was removed and the mixture was stirred for a further 5.5 h. The deep-brown mixture was diluted with petroleum ether (25 ml), washed with brine (1 × 15 ml), H_2O (3 × 20 ml), 20% aq. $AgNO_3$ soln. (2 × 10 ml), and H_2O (3 × 20 ml), dried, and evaporated: (*E*)/(*Z*)-**5** (185 mg, 84%). Yellow liquid. B.p. 105° (block)/0.03 Torr. UV: 209 ($1.80 \cdot 10^4$), 252 ($1.57 \cdot 10^4$), 306 ($1.20 \cdot 10^4$). IR: 3099*s*, 1602*m*, 753*m*, 711*s*. ^1H-NMR (300 MHz): 3.30 (*d*, *J*(1,8) = 8.1, H–C(8) (*Z*)); 3.40 (*d*, *J* (1,8) = 8.1, H–C(8) (*E*)); 5.75–6.18 (*m*, 5 olef. H); 6.23 (*s*, H–C=C(7) (*Z*)); 6.48 (*d*, *J*(6,5) = 12.9, H–C(6) (*E*)); 6.57 (*s*, H–C=C(7) (*E*)); 6.85 (*d*, *J* (6,5) = 12.9,

H–C(6) (*Z*)); 7.20–7.40 (*m*, 5 arom. H); (*E*)/(*Z*) ratio was 3:2. ^{13}C-NMR (50.32 MHz): 29.39 (C(8) (*E*)); 37.76 (C(8) (*Z*)); 124.71; 126.03; 126.82; 126.84; 127.61; 127.86; 127.91; 128.10; 128.35; 128.52; 128.61; 128.42; 128.92; 129.65; 130.81; 130.87; 132.51; 136.56; 137.85; 137.94; 137.98; 138.82; 139.27; 139.62. MS: 195 (13, $[M+H]^{+\cdot}$), 194 (100, $M^{+\cdot}$), 179 (56), 178 (61), 165 (56), 152 (25), 128 (26), 117 (26), 116 (43), 115 (81), 105 (58), 91 (40), 77 (25), 57 (35), 51 (38), 41 (70), 39 (69). Anal. calc. for $C_{15}H_{14}$ (194.26): C 92.74, H 7.26; found: C 92.44, H 7.12.

The mixtures having (*E*)/(*Z*) ratios of 73:27 and 65:35 mentioned in the *General Part* were obtained during preliminary investigations when the amounts of *t*-BuOK used, and the reaction times, were smaller than those given above.

4.2. A stirred suspension of **10** (1.802 g, 4.03 mmol) in dry Et_2O (45 ml) under N_2 at 0° was treated dropwise with 2.24M BuLi in petroleum ether (1.8 ml, 4.03 mmol) (→deep maroon color). After the mixture had been stirred at 0° for 45 min and then at r.t. for 15 min, it was cooled to 0° and treated dropwise with a soln. of benzaldehyde (428 mg, 4.03 mmol) in Et_2O (5 ml). The mixture was stirred at r.t. for 3 h and then filtered. The filtrate was washed with H_2O (4 × 40 ml), dried and evaporated, and the yellow residue subjected to CC (*Sorbsil*, (16 g), petroleum ether): (*E*)/(*Z*)-**5** 88:12 (by ^{1}H-NMR; 314 mg, 40%). Yellow liquid.

In several preparations by this method, the (*E*)/(*Z*) ratio ranged from 91:9 to 84:16.

5. *Reaction of* **5** *with Ethenetetracarbonitrile* (TCNE). 5.1 *Isolation of the Products.* A stirred soln. of (*E*)/(*Z*)-**5** 88:12 (377 mg, 1.94 mmol) and TCNE (448 mg, 3.49 mmol) in dry AcOEt (8 ml) under N_2 was heated at 80–83° for 5 h (initially deep blue → finally golden-yellow). The cooled soln., after the addition of AcOEt (30 ml), was washed with H_2O containing some brine (20 ml), 20% aq. sodium metabisulfite (3 × 35 ml), and brine (2 x 20 ml) and dried. TLC (silica gel, AcOEt/petroleum ether 3:7, UV detection): three distinct and two overlapping product 'spots'. The soln. was evaporated to give a greenish-brown glass (695 mg). A soln. of the glass in hot AcOEt (3 ml), when diluted with hot petroleum ether (7 ml), gave on cooling *(3*E*)-3-benzylidenetricyclo[4.2.2.0^{2,5}]dec-7-ene-9,9,10,10-tetracarbonitrile (=((3*E*)-benzylidenetricyclo[4.2.2.0^{2,5}]dec-9-ene-7,7,8,8-tetracarbonitrile*; (*E*)-**14**; 47 mg). Small, hard, colorless crystals. M.p. 270–271° (AcOEt/petroleum ether) with browning. ^{1}H-NMR: 2.58–2.64 (*m*, H_a–C(4)); 3.25–3.28 (*m*, H–C(5)) overlapping 3.26 (*ddd*, *J*(4b,4a) = 16.8, *J*(4b,5) = 9.6, *J*(4b,H–C=C(3)) = 3.0, H_b–C(4)); 3.71 (*ddd*, *J*(6,7) = 6.6, *J*(6,5) = 3.0, *J*(6,8) = 1.2, H–C(6)); 3.78 (*ddd*, *J*(1,8) = 6.6, *J*(1,2) = 4.2, *J*(1,7) = 1.2, H–C(1); 3.80–3.84 (*m*, H–C(2)); 6.23 (q, *J*(4a,H–C=C(3)) = *J*(4b,H–C=C(3)) = *J*(2,H–C=C(3)) = 2.4, H–C=C(3)); 6.65 (*ddt*, *J*(7,8) = 8.4, *J*(7,6) = 6.6, *J*(7,5) = *J*(7,1) = 1.2, H–C(7)); 6.73 (*ddt*, *J*(8,7) = 8.4, *J*(8,1) = 7.2, *J*(8,2) = *J*(8,6) = 1.2, H–C(8)); 7.10–7.12 (*m*, 2 H_o); 7.23 (*tt*, *J* = 7.2,1.2, H_p); 7.30–7.33 (*m*, 2 H_m). ^{13}C-NMR (75.47 MHz): 27.57; 35.03; 40.86; 41.54; 42.19; 42.37; 42.50; 110.97, 111.05, 111.70 and 111.81 (4 CN); 126.57; 127.68; 127.75; 128.91; 130.31; 133.86; 135.99; 136.24. MS: 322 (5, $M^{+\cdot}$), 194 (100), 193 (36), 179 (43), 165 (26), 116 (52), 115 (48), 101 (34), 81 (50), 77 (34), 57 (48), 55 (56), 51 (34), 41 (85), 39 (35). Anal. calc. for $C_{21}H_{14}N_4$ (322.35): C 78.24, H 4.38, N 17.38; found: C 77.98, H 4.26, N 17.52.

The residue from the initial mother liquor in hot AcOEt (1.5 ml), on dilution with hot petroleum ether (3.5 ml), yielded on cooling two crops of *spiro[2′-*(RS)*-phenylcyclobutane-1′,3-(1*RS*,2*SR*,3*RS*,5*SR*,6*SR*)-tetracyclo[4.2.2.0^{2,5}]dec-7-ene-3′,3′,4′,4′,9,9,10,10-octacarbonitrile] (=(1′*RS*,2′*SR*,3′*RS*,4*RS*,5′*SR*,6′*SR*)-4-phenylspiro[cyclobutane-1,3′-tetracyclo[4.2.2.0^{2,5}]dec[9]ene]-2,2,3,3,7′,7′,8′,8′-octacarbonitrile*; **15**, 37 mg). Small, hard, colorless crystals. M.p. 250° (dec., AcOEt/petroleum ether). ^{1}H-NMR ((D$_6$)acetone): 2.52 (*ddd*, *J*(4a,4b) = 15.0, *J*(4a,5) = 5.8, *J*(4a,2) = 1.3, H_a–C(4)); 2.93 (*ddd*, *J*(4b,4a) = 15.0, *J*(4b,5) = 9.0, *J*(4b,2) = 1.3, H_b–C(4)); 3.24 (*ddddd*, *J*(5,4b) = 9.0, *J*(5,2) = 8.3, *J*(5,4a) = 5.8, *J*(5,6) = 3.6, *J*(5,7) = 1.2, H–C(5)); 3.91 (*dddt*, *J*(2,5) = 8.3, *J*(2,1) = 3.8, *J*(2,4a) = *J*(2,4b) = 1.3, *J*(2,8) = 0.9, H–C(2)); 4.31 (*ddd*, *J*(6,7) = 6.7, *J*(6,5) = 3.6, *J*(6,8) = 0.9, H–C(6)); 4.65 (*ddd*, *J*(1,8) = 6.5, *J*(1,2) = 3.8, *J*(1,7) = 1.2, H–C(1)); 5.45 (*s*, H–C(2′)); 7.21 (*ddt*, *J*(7,8) = 8.1, *J*(7,6) = 6.7, *J*(7,1) = *J*(7,5) = 1.2, H–C(7)); 7.32 (*ddt*, *J*(8,7) = 8.1, *J*(8,1) = 6.5, *J*(8,2) = *J*(8,6) = 0.8, H–C(8)); 7.59–7.61 (*m*, H_p); 7.64–7.66 (*m*, 2 H_m); 7.72–7.74 (*m*, 2 H_o). ^{13}C-NMR (150 MHz, (D$_6$)acetone): 28.48 (C(5)); 30.18 (C(4)); 40.04 (C(1)); 41.04 (C(2)); 42.02 (C(6)); 42.43 (C(9)); 42.96 (C(10)); 43.66 (C(3)); 44.19 (C(3′)); 54.16 (C(2′)); 55.45 C(4′)); 110.23, 111.10, 111.59, 111.62, 111.95, 112.16, 112.91, 113.01 (8 CN); 128.11 (arom); 130.63 (arom); 130.70 (arom); 131.46 (arom); 133.62 (C(8)); 139.50 (C(7)). MS: 322 (2, [*M*-TCNE]$^{+\cdot}$), 194 (100), 193 (28), 179 (30), 116 (34), 115 (33), 96 (25), 91 (23), 83 (28), 71 (33), 69 (31), 57 (61), 55 (43), 44 (62), 41 (46), 39 (26). Anal. calc. for $C_{27}H_{14}N_8$ (450.45): C 71.99, H 3.13. N 24.88; found: C 71.70, H 3.16, N 24.85.

The residue from the mother liquor from which **15** was obtained was purified by FC (silica gel (144 g), AcOEt/petroleum ether 3:7), 8 to10-ml fractions, TLC monitoring as above. Fractions showing two 'spots' were combined and rechromatographed as above on fresh silica gel (144 g). Fractions showing a single 'spot' from the two chromatographic separations were combined to give four fractions, *Fr. A* (4 mg), *B* (140 mg), *C* (261 mg), and *D* (115 mg). Elution of the first column with AcOEt gave *Fr. E* (27 mg), an amorphous, brown material. *Fr. A:* ^{1}H-NMR showed that in part it consisted of recovered (*E*)/(*Z*)-**5** 59:41.

Fraction B: Extraction of the solid of *Fr. B* with warm Et_2O (4 × 5 ml) gave an insoluble portion (43 mg) which, from acetone/petroleum ether, gave two crops of **15** (25 mg; total yield 62 mg, 8%). The residue from the mother liquor from which **15** was obtained yielded, from AcOEt/petroleum ether, additional (*E*)-**14** (4 mg; total yield 51 mg, 8%). The Et_2O-soluble portion (92 mg) was crystallized from Et_2O, followed by Et_2O/petroleum ether, to give four crops of *(1*RS*,3*RS*,8*SR*,11*SR*)-11-phenyltricyclo[6.3.0.0^{1,3}]undeca-4,6-diene-9,9,10,10-tetracarbonitrile* (**16**; 67 mg, 11%). M.p. 184–186°, raised to 185–187° (AcOEt/petroleum ether). UV: 257 ($4.97 \cdot 10^3$), 208 ($1.60 \cdot 10^4$). ^{1}H-NMR: 0.90–0.96 (*m*, 2 H–C(2)); 1.44–1.48 (*m*, H–C(3)); 3.65–3.67 (*m*, H–C(8)); 4.11 (*s*, H–C(11)); 5.92 (*dd*, *J* = 11.4, *J* = 6.0, H–C(5) or H–C(6)); 6.27–6.36 (*m*, 3 olef. H); 7.37–7.40 (*m*, 2 arom. H); 7.42–7.48 (*m*, 3 arom. H). ^{13}C-NMR (75.47 MHz): 20.73 (*d*, C(3)); 22.94 (*t*, C(2)); 37.03 (*s*, C(1)); 47.97, 52.04 (C(9), C(10)); 55.90 (*d*, C(8)); 60.82 (*d*, C(11)); 109.22, 109.55, 111.10, 111.61 (4 CN); 125.89 (*d*); 126.74 (*d*); 129.65 (*d*); 130.25; 130.59 (*d*); 131.40 (*d*); 131.73; 136.19 (*d*). MS: 322 (30, $M^{+\bullet}$), 194 (100), 193 (33), 179 (38), 178 (26), 165 (25), 116 (46), 115 (43), 103 (31), 91 (21), 78 (34), 77 (37), 76 (28), 51 (55), 50 (34), 39 (62). Anal. calc. for $C_{21}H_{14}N_4$ (322.35): C 78.24, H 4.38, N 17.38; found C 77.85, H 4.61, N 17.67.

Fraction C: Extraction of the solid of *Fr. C* with warm Et_2O (2 × 5 ml) gave an insoluble, white powder (*Fr. C1*, 31 mg; see below). The residue from the soluble portion was recrystallized from Et_2O/petroleum ether 1:1 (10 ml) to give *(7*RS*,10*SR*)-10-phenylbicyclo[5.3.1]deca-1,3,5-triene-8,8,9,9-tetracarbonitrile* (*endo*-**17**; 45 mg). M.p. 221.5–222.5° (after sublimation at 100°/0.1 Torr). UV: 260 ($2.31 \cdot 10^3$), 211 ($2.59 \cdot 10^4$). ^{1}H-NMR: 2.46 (*d* with fine splitting, *J*(11a,11b) = 13.8, H_a–C(11)); 3.34 (*dd*, *J*(11b,11a) = 13.8, *J*(11b,7) = 2.4, H_b–C(11)); 3.88 (br. *s*, H–C(7)); 4.25 (s, H–C(10)); 6.11 (*ddd*, *J* = 11.4, 7.8, 1.2, olef. H); overlapping 6.12–6.14 (*m*, 4 olef. H); 7.48–7.52 (*m*, 3 arom. H); 7.58 – 7.60 (*m*, 2 arom. H). ^{13}C-NMR (75.47 MHz): 30.64 (*t*, C(11)); 46.96; 47.86 (*d*, C(7)); 56.06 (*d*, C(10)); 110.24, 110.43, 111.18, 111.28 (4 CN); 126.25 (*d*); 128.33 (*d*); 128.68 (*d*); 129.47 (*d*); 129.69 (*d*); 130.11 (*d*); 130.44 (*d*); 131.14; 131.52 (*d*); 136.39 (*s*). MS: 322 (4, $M^{+\bullet}$), 194 (100), 179 (33), 116 (15), 115 (15), 77 (8), 51 (11), 39 (13). Anal. calc. for $C_{21}H_{14}N_4$ (322.35): C 78.24, H 4.38; found: C 78.30, H 4.21.

The residue from the mother liquor from which *endo*-**17** had been obtained was crystallized from Et_2O/petroleum ether 2:1 (15 ml) to give *(7*RS*,10*RS*)-10-phenylbicyclo[5.3.1]undeca-1,3,5-triene-8,8,9,9-tetracarbonitrile* (*exo*-**17**; 68 mg). M.p. 155–157° (AcOEt/petroleum ether). ^{1}H-NMR: 2.93 (*dd*, *J*(11b,11a) = 13.8, *J*(11b,7) = 7.2, H_b–C(11)); 3.07 (*d*, *J*(11a,11b) = 13.8, H_a–C(11)); 3.96 (br. *s*, H–C(7)); 4.70 (*s*, H–C(10)); 6.09 (*dd*, *J*(3,4) = 12.6, *J*(3,2) = 7.8, H–C(3)); 6.14–6.21 (*m*, H–C(4), and H–C(6)); 6.38 (br. *s*, H–C(2)); 6.42–6.49 (*m*, H–C(5)); 7.49 (*s*, 5 arom. H); assignments by COSY and ROESY. ^{13}C-NMR (50.4 MHz): 24.87 (*t*, C(11)); 45.69 (C(8), C(9)); 46.87 (*d*, C(7)); 55.07 (*d*, C(10)); 109.50, 110.20, 111.79, 112.34 (4 CN); 125.73; 126.70; 127.69; 128.56; 129.75; 129.93; 130.29; 134.12. MS: 322 (6, $M^{+\bullet}$), 194 (100), 193 (29), 179 (33), 116 (36), 115 (33), 103 (15), 76 (12), 51 (16), 39 (11). Anal. calc. for $C_{21}H_{14}N_4$ (322.35): C 78.24, H 4.38, N 17.38; found C 78.42, H 4.43, N 17.64.

The residue from the mother liquor from which *exo*-**17** had been obtained was crystallized from Et_2O/petroleum ether 3:1 (10 ml) to give additional *exo*-**17** (35 mg). Crystallization of the residue from the mother liquor from AcOEt/petroleum ether 2:5 (7 ml) gave additional *endo*-**17** (5 mg; total yield 50 mg, 8%). A soln. of the residue from the mother liquor in AcOEt (*ca.* 0.5 ml) on dilution with petroleum ether gave two crops of additional *exo*-**17** (21 mg; total yield 124 mg, 20%). The residue from the mother liquor in acetone/petroleum ether at – 18° yielded pale-brown crystals of *(3*Z*)-3-benzylidenetricyclo[4.2.2.0^{2,5}]dec-7-ene-9,9,10,10-tetracarbonitril*e (= *(3*Z*)-3-benzylidenetricyclo[4.2.2.0^{2,5}]dec-9-ene-7,7,8,8-tetracarbonitrile;* (*Z*)-**14**; 4 mg, 0.6%) which gave colorless crystals (2 mg). M.p. 167–169° (AcOEt/petroleum ether). ^{1}H-NMR: 2.38 (*dddd*, *J*(4a,4b) = 17.4, *J*(4a,5) = 3.0, *J*(4a,H–C=C(3)) = 2.4, *J*(4a,2) = 1.2, H_a–C(4)); 3.10 (*ddd*, *J*(4b,4a) = 17.4, *J*(4b,5) = 9.0, *J*(4b, H–C=C(3)) = 2.4, H_b–C(4)); 3.20 (*dddd*, *J*(5,4b) = 9.0, *J*(5,6) = 3.6, *J*(5,4a) = 3.0, *J*(5,7) = 1.2, H–C(5)); 3.68 (*ddd*, *J*(1,8) = 7.2, *J*(1,2) = 4.2, *J* (1,7) = 1.2, H–C(1)); 3.77 (*ddd*, *J*(6,7) = 6.6, *J*(6,5) = 3.6, *J*(6,8) = 1.2, H–C(6)); 4.12 (*ddt*, *J*(2,1) = 4.2, *J*(2, H–C=C(3)) = 2.4, *J*(2,4a) = *J*(2,8) = 1.2, H–C(2)); 6.15 (*q*, *J*(H–C=C(3),2) = *J*(H–C=C(3),4a) = *J*(H–C=C(3),4b) = 2.4, H–C=C(3)); 6.47 (*ddt*, *J*(7,8) = 8.4, *J*(7,6) = 6.6, *J*(7,5) = *J*(7,1) = 1.2, H–C(7)); 6.63 (*ddt*, *J*(8,7) = 8.4, *J*(8,1) = 7.2, *J*(8,6) = *J*(8,2) = 1.2, H–C(8)); 7.18–7.19 (*m*, 2 H_o); 7.28–7.30 (*m*, H_p); 7.38–7.41 (*m*, 2 H_m). ^{13}C-NMR (150.84 MHz): 26.97; 31.11; 34.31; 40.06; 40.64; 41.46; 42.19; 111.02, 111.10, 111.62, 111.79 (4 CN); 127.30; 127.55; 127.85; 129.31; 130.08; 133.52; 135.72; 135.92. MS: 322 (48, $M^{+\bullet}$), 194 (29), 179 (27), 142 (42), 141 (34), 116 (90), 115 (100), 91 (12), 78 (12), 69 (12), 51 (14), 41 (16), 39 (21). HR-ESI MS: 345.1108 ($[M + Na]^+$); $C_{21}H_{14}N_4Na^+$; calc. 345.1116)

^{1}H-NMR ((D$_6$)acetone) of the insoluble *Fr. C1* (see above) indicated that it was essentially pure *spiro[2′-*(SR)*-phenylcyclobutane-1′,3-(1*RS*,2*SR*,3*SR*,5*SR*,6*SR*)-tetracyclo[4.2.2.0^{2,5}]dec-7-ene-3′,3′,4′,4′,9,9,10,10-octacarbonitrile]* (= *(1′*RS*,2′*SR*,3′*SR*,4*SR*,5′*SR*,6′*SR*)-4-phenylspiro[cyclobutane-1,3′-tetracyclo[4.2.2.0^{2,5}]dec-[9]ene]-2,2,3,3,7′,7′,8′,8′-octacarbonitrile*; **18**; 4%). Recrystallization from AcOEt/petroleum ether gave clusters

of soft radiating needles (15 mg). M.p. 197–202° (unchanged on further crystallization). ^{1}H-NMR ((D$_6$)acetone): 2.67 (*ddd*, *J*(4a,4b) = 15.1, *J*(4a,5) = 6.1, *J*(4a,2) = 1.6, H$_a$–C(4)); 2.98 (*ddd*, *J*(4b,4a) = 15.1, *J*(4b,5) = 9.0, *J*(4b,2) = 2.1, H$_b$–C(4)); 3.54 (*ddddd*, *J*(5,4b) = 9.0, *J*(5,2) = 8.6, *J*(5,4a) = 6.1; *J*(5,6) = 3.9, *J*(5,7) = 1.3, H–C(5)); 3.87 (*ddddd*, *J*(2,5) = 8.6, *J*(2,1) = 3.4, *J*(2,4b) = 2.1, *J*(2,4a) = 1.6, *J*(2,8) = 0.8, H–C(2)); 4.04 (*ddd*, *J*(6,7) = 6.8, *J*(6,5) = 3.9, *J*(6,8) = 1.3, H–C(6)); 4.62 (*ddd*, *J*(1,8) = 6.5, *J*(1,2) = 3.4, *J*(1,7) = 1.3, H–C(1)); 4.99 (s, H–C(2′)); 6.31 (*dddd*, *J*(8,7) = 8.3, *J*(8,1) = 6.5, *J*(8,6) = 1.3, *J*(8,2) = 0.8, H–C(8)); 6.41 (*ddt*, *J*(7,8) = 8.3, *J*(7,6) = 6.8, *J*(7,5) = *J*(7,5) = 1.3, H–C(7)); 7.60–7.63 (*m*, H$_o$); 7.64–7.67 (*m*, 2 H$_m$, H$_p$). ^{13}C-NMR (600 MHz, (D$_6$)acetone): 27.59 (C(5)); 30.28 (C(4)); 40.53 (C(1)); 41.25 (C(2)); 42.45 (C(6)); 43.12 (C(9)); 43.40 (C(10)); 48.08 (C(3)); 52.80 (C(3′)); 52.83 (C(2′)); 53.60 C(4′)); 110.38, 110.90 (2C), 112.09, 112.13, 112.24, 113.06, 113.09 (8 CN); 130.20 (arom. C); 131.34 (arom. C); 131.36 (arom. C); 131.52 (arom. C); 133.89 (C(8)); 135.05 (C(7)). MS: 322 (24, [*M* – TCNE]$^+$), 194 (73), 193 (23), 189 (29), 154 (35), 128 (65), 116 (38), 115 (42), 103 (23), 78 (32), 77 (27), 76 (58), 71 (60), 69 (42), 68 (53), 57 (100), 41 (69), 39 (33). Anal. calc. for $C_{27}H_{14}N_8$ (450.45): C 71.99, H 3.13, N 24.88; found: C 72.22, H 3.46, N 24.28.

Fraction D: Recystallization of the crude product from AcOEt/ petroleum ether gave (5E)-*5-benzylidenebicyclo[4.2.2]deca-2,7-diene-9,9,10,10-tetracarbonitrile* (=(5E)-*5-benzylidenebicyclo[4.2.2]deca-2,9-diene-7,7,8,8-tetracarbonitrile;* (*E*)-**19**; 91 mg, 15%). M.p. 170–171°. ^{1}H-NMR (300 MHz): 2.97 (*dquint.*, *J*(4a,4b) = 15.3, '*J*' = 2.4, H$_a$–C(4)); 3.29 (*dd*, *J*(4b,4a) = 15.3, *J*(4b,3) = 9.9, H$_b$–C(4)); 3.96 (*t*, *J*(1,2) = 7.2, H–C(1)); 4.22 (*d*, *J*(6,7) = 6.4, H–C(6)); 5.83 (*ddd*, *J*(2,3) = 11.6, *J*(2,1) = 7.2, *J*(2,4a) = 2.9, H–C(2)); 6.27 (*ddd*, *J*(3,2) = 11.6, *J*(3,4b) = 9.9, *J*(3,4a) = 4.5, H–C(3)); 6.41–6.56 (overlapping *m*, H–C(7), H–C(8)); 6.92 (*d* (poorly resolved), *J*(H–C=C(5),4b) ≈ 1.6, H–C=C(5)); 7.24–7.30 (*m*, H$_o$); 7.32–7.43 (*m*, 2 H$_m$, H$_p$); the *quint.* within *δ* 2.97 was shown from double irradiation experiments to arise from *J*(4b,3) = 4.5, *J*(4b,2) = 2.9, *J*(4b,H–C=C(5)) = 1.6 Hz. ^{13}C-NMR (50.32 MHz): 26.01 (*t*, C(4)); 42.45 (*d*, C(1)); 45.02, 45.63 (C(9), C(10)); 51.98 (*d*, C(6)); 110.81, 110.88, 111.96, 113.41 (4 CN); 120.90 (*d*); 127.46 (*d*); 128.19 (*d*); 128.49; 128.61; 129.32; 135.64; 136.94 (*d*); 139.27 (*d*). MS: 322 (20, $M^{+\cdot}$), 194 (100), 193 (28), 179 (35), 116 (52), 115 (60), 91 (35), 78 (25), 77 (41), 69 (38), 65 (25), 63 (25), 57 (34), 55 (33), 51 (51), 41 (67), 39 (80). Anal. calc. for $C_{21}H_{14}N_4$ (322.35): C 78.24, H 4.38; found: C 78.13, H 4.40.

Fraction E: The complex mixture (^{1}H-NMR) was extracted with warm Et_2O (2 × 3 ml). The Et_2O soluble material (17 mg), a brown powder, was then extracted with $CHCl_3$ (2 × 3 ml), and the soluble portion (14 mg), on crystallization from acetone/petroleum ether, gave colorless crystals of (5Z)-*5-benzylidenebicyclo[4.2.2]-deca-2,7-diene-9,9,10,10-tetracarbonitrile* (= *(5Z)-5-benzylidene[4.2.2]deca-2,9-diene-7,7,8,8-tetracarbonitrile*; (*Z*)-**19**; 2 mg, 0.3%). M.p. 214–216° (with browning). ^{1}H-NMR: 2.96 (*dd,* *J*(4b,4) = 15.6, *J* (4b,3) = 10.2, H$_b$–C(4)); 3.50 (*dddd*, *J*(4a,4b) = 15.6, *J*(4a,3) = 4.2, *J*(4a,2) = 3.0, *J*(4a,H–C=C(5)) = 2.4, H$_a$–C(4)); 3.92 (*t*, *J*(1,2) = *J*(1.8) = 7.2, H–C(1)); 4.41 (*d*, *J*(6,7) = 6.6, H–C(6)); 5.80 (*ddd*, *J*(2,3) = 12.0, *J*(2,1) = 7.2, *J*(2,4a) = 3.0, H–C(2)); 6.22 (*dd*, *J*(7,8) = 9.6, *J*(7,6) = 6.6, H–C(7)); 6.36 (*dddd*, *J*(3,2) = 12.0, *J*(3,4b) = 10.2, *J*(3,4a) = 4.2, *J*(3,1) = 0.6, H–C(3)); 6.48 (*dd*, *J*(8,7) = 9.6, *J*(8,1) 7.2, H–C(8)); 7.04 (*d*, *J*(H–C=C(5),4a) = 2.4, H–C=C(5)); 7.26–7.28 (*m*, 2 H$_o$); 7.38–7.39 (*m*, H$_p$); 7.45–7.48 (*m*, 2 H$_m$)). ^{13}C-NMR (75.47): 33.33 (C(4)); 42.74 (C(1)); 43.91 (C(9) or C(10)); 44.82 (C(6)); 45.67 (C(9) or C(10)); 110.99, 111.53, 111.85, 112.5 (4 CN); 120.06; 127.54; 128.42; 128.57; 129.31; 129.68; 135.39; 136.33; 139.07; 139.77. MS: 322 (25, $M^{+\cdot}$), 194 (100), 193 (27), 116 (100), 115 (31), 91 (16), 77 (12), 51 (12), 39 (13).

5.2. *Composition of the Product Mixtures of Other Reactions of* **5** *with TCNE. (*7E)-7-Benzylidenecycloocta-1,3,5-triene ((*E*)-**5**), containing a trace (^{1}H-NMR) of the (*Z*)-isomer, was recovered (*ca.* 20%) after CC (silica gel) when (*E*)/(*Z*)-**5** *ca.* 9:1 was treated with 0.8 equiv. of **6** in AcOEt. Mixtures enriched in (*Z*)-**5** were obtained from treatment of **7** with t-BuOK in THF. The various mixtures were each treated with TCNE as described in *Exper. 5.1* above, and the crude products (after ^{1}H-NMR ((D$_6$)acetone/$CDCl_3$) determination of the ratios of some of the products) were separated by FC (silica gel) as above. The composition of each of the appropriate weighed fractions was determined by ^{1}H-NMR, and the yields were calculated.

5.3. *Conversion of* **16** *into* endo-**17** *and* exo-**17**. A soln. of **16** (3.2 mg) in MeCN (0.3 ml) was heated under N_2 in a sealed tube at 100° for 24 h. The solvent was evaporated, and ^{1}H-NMR showed that the product consisted of *endo*- and *exo*-**17** in the ratio of 1.00:8.2 (mean of two determinations). When *endo*- and *exo*-**17** were each subjected to the same conditions, they were recovered unchanged (^{1}H-NMR).

6. *Reaction of* **5** *with PTAD* **6**. A stirred soln. of (*E*)/(*Z*)-**5** 91:9 (247 mg, 1.27 mmol) in AcOEt (5 ml) under N_2 was treated dropwise at r.t. with a soln. of **6** (223 mg, 1.27 mmol) in AcOEt (4 ml). After the color of the reagent had been discharged (80 min), the resulting pale yellow soln. was evaporated and the residue subjected to CC (silica gel (148 g), AcOEt/petroleum ether 1:1, 5- to 10-ml fractions) with TLC (silica gel, AcOEt/petroleum ether 2:3, UV detection) monitoring. Fractions giving two 'spots' were rechromatographed to give fractions giving only one; these were combined with the relevant fractions obtained initially. In order of

elution, the following compounds were obtained: unchanged (*E*)-**5** (18 mg) free of (*Z*)-**5** (^{1}H-NMR), *exo*-**20** (199 mg, 46%), *endo*-**20** (121 mg, 28%), (*Z*)-**21** (16 mg, 4%; impure), and (*E*)-**21** (68 mg, 16%).

*Data of (2*RS,*8*RS*)-2,5-Diphenyl-3,5,7-triazatricyclo[6.5.1.0^{3,7}]tetradeca-9,11,13-triene-4,6-dione* (*exo*-**20**); Colorless crystals. M.p. 169–170° (AcOEt/petroleum ether). FT-IR: 1763*s*, 1707*vs*, 1597*w*, 1403*s*, 1284*m*, 1153*w*, 764*m*, 1128*w*, 764*m*. ^{1}H-NMR: 2.23 (*ddd*, *J*(14b,14a) = 13.0, *J*(14b,8) = 3.4, *J*(14b,13) = 1.6, H_b–C(14)); 2.86 (*ddd*, *J*(14a,14b) = 13.0, *J*(14a,8) = 4.2, *J*(14a,13) = 1.2, H_a–C(14)); 5.26 (br. *s*, H–C(8)); 6.05 (*s*, H–C(2)) overlapping 5.96–6.10 (*m*, H–C(9), H–C(10), H–C(11)); 6.25 (*dd*, *J*(12,11) = 10.5, *J*(12,13) = 3.1, H–C(12)); 6.54 (*d*, *J*(13,12) = 3.1, H–C(13)); 7.18–7.63 (*m*, 10 arom. H); double-irradiation experiments (at δ 5.26 and 6.50) and COSY confirmed the values and attributions of the *J*. ^{13}C-NMR (50.32 MHz): 25.81 (C(14)); 57.48 (C(8)); 62.77 (C(2)); 125.68; 126.03; 128.00; 128.19; 128.77; 128.95; 129.15; 129.30; 131.88; 136.43; 137.25; 149.39, 151.42 (2 C=O). MS: 369 (63, $M^{+\bullet}$), 256 (28), 225 (30), 206 (25), 197 (31), 157 (32), 115 (30), 101 (40), 91 (38), 81 (32), 69 (81), 42 (100), 40 (64). Anal. calc. for $C_{23}H_{19}N_3O_2$ (369.41): C 74.78, H 5.18; found: C 74.42, H 5.04.

*Data of (2*RS,*8*SR*)-2,5-Diphenyl-3,5,7-triazatricyclo[6.5.1.0^{3,7}]tetradeca-9,11,13-triene-4,6-dione* (*endo*-**20**). Colorless crystals. M.p. 205–207° (AcOEt/petroleum ether). FT-IR: 1759*m*, 1699*vs*, 1597*w*, 1491*m*, 1415*m*, 1396*w*, 1132*m*, 768*m*. ^{1}H-NMR: 2.65 (*dd*, *J*(14b,14a) = 12.6, *J*(14b,8) = 5.4, H_b–C(14)); 3.17 (*dd*, *J*(14a,14b) = 12.6, *J*(14a,8) = 1.2, H_a–C(14)); 5.25 (*ddt*, *J*(8,14b) = 5.4, *J*(8,9) = 4.1, *J*(8,14a) = *J*(8,10) = 1.2, H–C(8)); 5.50 (*t*, *J*(13,12) = *J*(13,2) = 3.0, H–C(13)); 5.79 (*t*, *J*(2,9) = *J*(2,13) = 3.0, H–C(2)); 5.95 (*dd*, *J*(11,12) = 11.4, *J*(11,10) = 6.0, H–C(11)); 6.01–6.08 (*m*, H–C(10), H–C(12)); 6.29 (*ddd*, *J*(9,10) = 13.2, *J*(9,8) = 4.1, *J*(9,11) = 1.2, H–C(9)); 7.26–7.56 (*m*, 10 arom. H); assignments by spin decoupling, NOE, and COSY. ^{13}C-NMR (75.47 MHz): 28.98 (C(14)); 60.78 (C(8)); 66.64 (C(2)); 125.40; 126.44; 127.15; 128.00; 128.74; 128.79; 128.89; 129.05; 129.12; 130.42; 131.63; 136.93; 137.64; 150.12, 152.90 (2 C=O); assignments of C(2) and C(8) by HMQC. MS: 369 (26, $M^{+\bullet}$), 193 (31), 115 (36), 101 (45), 42 (100), 40 (28). Anal. calc. for $C_{13}H_{19}N_3O_2$ (369.41): C 74.78, H 11.38; found: C 74.85, H 5.13.

*Data of (11*Z*)-11-benzylidene-4-phenyl-2,4,6-triazatricyclo[5.4.2.0^{2,6}]trideca-8,12-diene-3,5-dione* ((*Z*)-**21**): The obtained powder was pure by TLC but 1 H-NMR revealed minor impurities; no crystals could be obtained. ^{1}H-NMR: 3.15 (*ddd*, *J*(10b,10a) = 16.2, *J*(10b,9) = 8.4 , *J*(10b,1) = 1.2, H_b–C(10); 3.32 (*ddt*, *J*(10a,10b) = 16.2, *J*(10a,9) = 6.0, *J*(10a,8) = *J*(10a,H–C=C(11)) = 1.2, H_a–C(10)); 5.23 (*t*, *J*(7,8) = *J*(7,13) = 6.6, H–C(7)); 5.85 (*dd*, *J*(1,12) = 7.2, *J*(1,10b) = 1.2, H–C(1)); 5.91 (*ddd*, *J*(9,8) = 11.4, *J*(9,10b) = 8.4, *J*(9,10a) = 6.0, H–C(9)); 6.03 (*ddd*, *J*(8,9) = 11.4, *J*(8,7) = 6.6, *J*(8,10b) = 1.2, H–C(8)); 6.08 (*dd*, *J*(12,13) = 9.6, *J*(12,1) = 7.2, H–C(12)); 6.36 (*dd*, *J*(13,12) = 9.6, *J*(13,7) = 6.6, H–C(13)); 6.58 (br. *s*, H–C=C(11)); 7.27–7.58 (*m*, 10 arom. H); assignments by spin decoupling, COSY, and ROESY. ^{13}C-NMR (50.32 MHz): 34.82 (C(4)); 50.27, 51.61 (C(1), C(6)); 125.79; 126.74; 127.67; 127.72; 128.17; 128.63; 128.85; 128.99; 129.11; 129.89; 130.82; 131.84; 133.64; 136.30; 148.40, 149.01 (2 C=O).

*Data of (11*E*)-11-benzylidene-4-phenyl-2,4,6-triazatricyclo[5.4.2.0^{2,6}]trideca-8,12-diene-3,5-dione* ((*E*)-**21**). Colorless crystals. M.p. 170–172° (AcOEt/petroleum ether). FT-IR: 1747*m*, 1693*s*, 1599*w*, 1502*m*, 1408*m*, 1377*m*, 1227*w*, 762*m*, 748*m*. ^{1}H-NMR: 3.11 (*ddd*, *J*(10b,10a) = 15.6, *J*(10b,9) = 3.6, *J*(10b,1) = 1.2, H_b–C(10)); 3.24 (*dd*, *J*(10a,10b) = 15.6, *J*(10a,9) = 6.6, H_a–C(10)); 5.29 (*t*, *J*(7,8) = *J*(7,13) = 6.6, H–C(7)); 5.57 (*dd*, *J*(1,12) = 6.6, *J*(1,10b) = 1.2, H–C(1)); 5.97–6.01 (*m*, H–C(8), H–C(9)); 6.37 (*dd*, *J*(12,13) = 9.6, *J*(12,1) = 6.6, H–C(12)); 6.43 (*dd*, *J*(13,12) = 9.6, *J* (13,7) = 6.6, H–C(13)); 6.81 (br. *s*, H–C=C(11)); 7.20–7.55 (*m*, 10 arom. H). ^{13}C-NMR (50.32 MHz): 26.74 (C(4)); 49.60 (C(1)); 57.38 (C(6)); 125.70; 126.34; 127.05; 127.63; 127.66; 128.05; 128.53; 128.95; 129.20; 131.83; 132.10; 132.25; 136.61; 137.29; 148.48, 148.67 (2 C=O); assignments by spin decoupling, COSY, HMQC, and HMBC. MS: 369 (22, $M^{+\bullet}$), 157 (28), 115 (29), 101 (46), 69 (35), 42 (100), 40 (47). Anal. calc. for $C_{23}H_{19}N_3O_2$ (369.41): C 74.78, H 5.18; found: C 74.70, H 5.08.

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