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VALENCE ISOMERS OF AZULENE AND HEPTALENE†[1]

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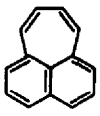
Abstract—Synthetic methods for the valene type valence isomers **6a,b**, and Dewar type isomers **7a,b** of azulene have been elaborated utilizing the same intermediate **12a**. Cyano-Dewar heptalene **9** has also been synthesized. Thermal and photochemical isomerizations of these prototype molecules are discussed briefly.

For more than 20 years the synthesis[2] and ground- and excited-state reactions[3] of the valence isomers of benzenoid hydrocarbons have attracted the attention of physical organic chemists from both static and dynamic points of view. During this same period, the study on non-benzenoid aromatic compounds has also developed dramatically.[4] These two large areas of current research are formally separate fields of study, which might be tied together by the synthesis of the valence isomers of non-benzenoid aromatic compounds.

The origin of our present work stems from the synthesis of naphtho[1,8]bicyclo[3.2.0]heptene (**2**) by Meinwald *et al.*[5] and naphtho[1,8]tricyclo-[4.1.0.$0^{2,7}$]heptene (**3**) by us[6] and Pagni and co-workers,[7] which constitute the first examples of Dewar and valene type valence isomers, respectively, of a non-alternant hydrocarbon, pleiadiene (**1**).[8] Subsequent studies on the thermal,[7] photochemical,[7] and transition-metal promoted reactions[6,9] of these hydrocarbons have had an important effect on the development of current interest in both the electronic structures[10] and the mechanism of ground- and excited-state isomerizations.[11]



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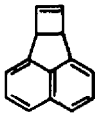

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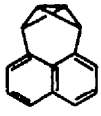

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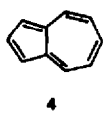
In order to advance the rich area of valence isomers of non-alternant hydrocarbons, a project has been launched to investigate the synthesis and chemistry of the valence isomers of azulene and heptalene. The choice of azulene (**4**) and heptalene (**5**) as the basic conjugate systems was dictated by three considerations: (a) the ground and excited properties of azulene, which enjoys aromatic stability to some extent, have been extensively examined;[12] (b) heptalene, a higher vinylog of azulene, is a representative antiaromatic molecule;[13] (c) comparative studies of a series of valence isomers are of great interest. Hence, we selected tetracyclo[5.3.0.$0^{2,4}$.$0^{3,5}$]deca - 6,8,10 - triene (azulvalene, **6**) and tricyclo[5.3.0.$0^{2,5}$]deca-3,6,8,10-tetraene (Dewar azulene, **7**) as azulene isomers, and tetracyclo[5.5.0.$0^{2,4}$.$0^{3,5}$]dodeca - 6,8,10,12 - tetraene (heptalvalene, **8**) and tricyclo[5.5.0.$0^{2,5}$]dodeca-3,6,8,10,12-pentaene (Dewar heptalene, **9**) as heptalene isomers for our target molecules.



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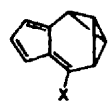

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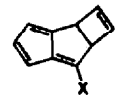
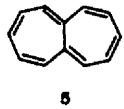
6b, X = H



7a, X = OCH_3
7b, X = H



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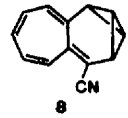

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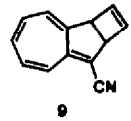

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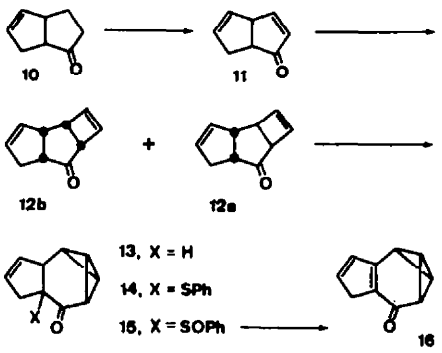
RESULTS AND DISCUSSION

Synthesis of 4-methoxyazulene isomers

In considering the synthesis of azulvalene **6**, we noted the possibility of stabilizing the pentafulvene moiety in **6** by introduction of an electron-donating methoxyl group at the 6 - position; 6 - methoxytetracyclo-[5.3.0.$0^{2,4}$.$0^{5,3}$]deca-6,8,10-triene (**6a**) ought then to be convertible to the hydrocarbon **6b** by means of hydride reduction. As far as the synthetic method for the valene-type isomers of cyclic conjugated systems is concerned, the utility of the Katz reaction,[14] which possesses an advantage over routine construction of bicyclobutane skeleton,[15] has been well documented by the successful synthesis of benzvalene,[14] naphthovalene,[14] anthracenovalene,[16] indenovalene,[2l] naphtho[1,8]tricyclo[4.1.0.$0^{2,7}$]heptene (**3**),[6,7] and some heterocyclic systems.[17] Unfortunately, however, the Katz method cannot be used for the synthesis of **6** because of the inaccessibility of a suitable precursor. On the other hand, tetracyclic dienone **16** is a logical precursor to **6a**, and its synthesis is shown in Scheme 1. Thus, we envisioned early stage construction of the required bicyclobutane skeleton utilizing oxa-di-π-methane rearrangement[18] of an appropriately designed tricyclic ketone **12a**, which in turn was anticipated to be readily accessible via [2+2]-photocycloaddition of acetylene to bicyclo[3.3.0]-octa-3,6-dien-2-one (**11**). It should be noted that a double bond in the cyclopentene ring of **12a** must be located between the 9- and 10-positions as shown in Scheme 1 in order to effect the desired photorearrangement; an 8,9-double bond allows an additional and unfavorable oxa-di-π-methane rearrangement.

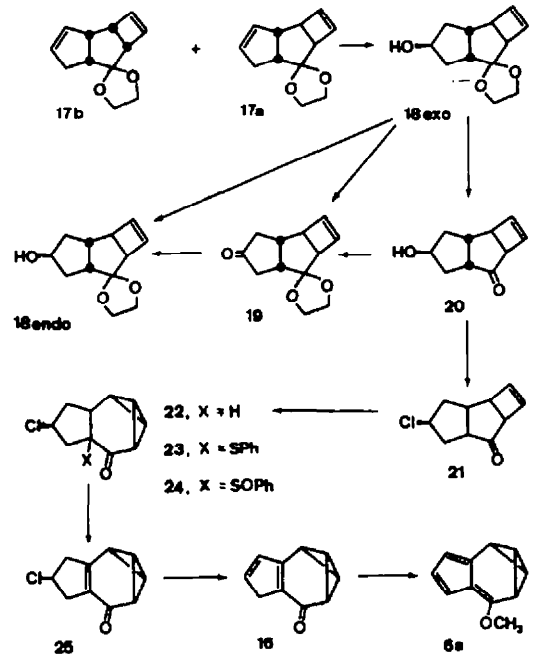
† This paper is dedicated to Professor Emeritus Tetsuo Nozoe on the occasion of his 84th birthday.



Scheme 1.

The synthesis of **16** was initiated from the bicyclic ketone **10**,[19] available on a large scale from bicyclo[3.2.0]hept-2-en-6-one in two steps [(a) CHN_2CO_2Et/BF_3-etherate, (b) K_2CO_3/dioxane–H_2O/reflux] followed by separation from the isomeric bicyclo[3.3.0]oct-6-en-3-one. Introduction of an α,β-double bond into **10** was effected with NaH and methyl *p*-toluenesulfinate in DME[20] followed by thermal elimination in 58% yield. Irradiation of **11** thus obtained in an *E*/*Z*-mixture of 1,2-dichloroethylene afforded tricyclic dichloride which was readily converted to the desired tricyclic ketone **12** through acetalization, reductive elimination, and deacetalization. Tricyclic ketone **12** proved by ^{1}H-NMR to be a 9 : 1 mixture of stereoisomers. These could be separated by column chromatography on silica gel. The major isomer **12a** (tentatively assigned as *cis*-anti-*cis*) could be converted to bicyclobutane **13** by way of an oxa-di-π-methane rearrangement[21] in 20–25% yield. Treatment of **13** with LDA at $-35°$, followed by quenching at 0° with diphenyl disulfide,[21c,d,22] gave **14** in 73% yield. Oxidation of **14** with *m*CPBA afforded a 6:4 diastereomeric mixture of sulfoxide **15**, readily separable by recrystallization, quantitatively. While the exact stereochemistry of each isomer was not determined, the major isomer suffers smooth elimination to give the key intermediate **16** as a labile colorless liquid. The presence of a tropovalene skeleton[21,23] in **16** is based on the characteristic ^{1}H-NMR pattern for the bicyclobutane protons which appeared at δ 2.65 (1H, dt, J = 5.4, 2.6 Hz, H-2), 3.33 (2H, t, J = 2.6 Hz, H-3,4), and 2.83 (1H, dt, J = 5.4, 2.6 Hz, H-5), together with the low frequency carbonyl band at 1669 cm^{-1} in the IR spectrum.

Despite completion of the synthesis of our key intermediate **16**, this synthetic route consists of multistep reactions via unstable intermediate compounds. Furthermore, the overall yield of **16** is quite low. In order to improve the approach we examined an alternative pathway leading to **16** (Scheme 2). Toward this end, tricyclic ketone **12** protected as ethylene acetal **17** was subjected to oxymercuration to give *exo*-alcohol **18exo**. The regioselective introduction of the hydroxyl group at the 9-position was confirmed by the fact that four deuterium atoms were incorporated when the ketone **19** derived from **18exo** by PCC oxidation was treated with $K_2CO_3/MeOD/D_2O$. Reduction of **19** with DIBAH afforded an epimeric *endo*-alcohol **18endo** which was identical with that obtained by direct epimerization of **18exo**. Deacetalization of **18exo** proceeded without event to afford hydroxy ketone **20**, which on treatment with triphenylphosphine and carbon tetrachloride gave a single *endo*-chloride **21** in 52% yield based on **17**. When a dilute solution ($\sim 10^{-3}$ M) of **21** in acetone was irradiated with a 450 W high-pressure Hg lamp for 1 h, the expected bicyclobutane **22** was obtained in 55.4% yield. Introduction of a double bond into **22** was then accomplished via the usual sulfenylation ($PhSO_2SPh$), oxidation (*m*CPBA), and elimination (CCl_4, reflux) procedure to afford **25** as colorless needles of m.p. 55.5–56.5° in 86% yield based on **23**. Dehydrochlorination of **25** with two equivalents of t-BuOK followed by quenching with aq NH_4Cl solution gave the desired dienone **16** in 50–70% yield. Compound **16** thus obtained was essentially pure and could be used without further purification. This procedure is superior to the original method since the overall yield of **16** is 6–7 times higher. Furthermore, because of its high stability **25** can be stored without change and converted to **16** according to need.

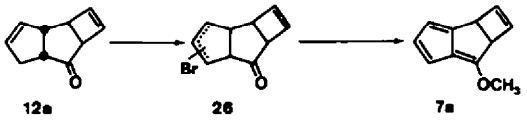


Scheme 2.

With the construction of dienone **16** complete, there remained only fixation of the enolate derived from **16**. Toward this end, we examined several usual methods; however, all attempts to effect O-alkylation, acylation, and silylation, proved unsuccessful.† The goal was finally achieved under very strictly controlled conditions. Thus, treatment of **16** with t-BuOK in benzene, followed by quenching with CH_3OSO_2F, led to the anticipated 6-methoxytetracyclo[5.3.0.0^{2,4}.0^{3,5}]deca-6,8,10-triene (methoxyazulvalene) (**6a**) as air- and acid-sensitive yellow plates of m.p. 71–73°.

Our attention next focused on the synthesis of methoxy-Dewar azulene **7a**, which is required for comparison to **6a**. To date, known compounds having

† We have examined LDA/THF/Me_2SO_4, LDA/THF/$MeOSO_2F$, LDA/THF/Me_3SiCl, LDA/THF/MeCOCl, and $Bu_4NF/Me_3SiCH_2CO_2CH_3$/THF.



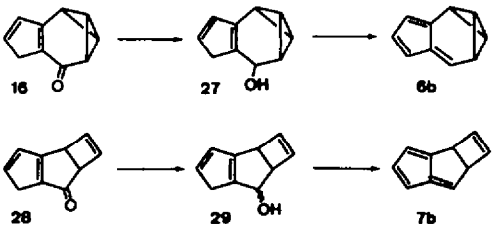
Scheme 3.

the Dewar azulene skeleton are confined only to heavily substituted derivatives obtained through cycloaddition reactions of pentalenes with acetylene.[24] Our synthesis (Scheme 3) begins with tricyclic ketone **12a** available in high yield in our previous synthesis of **6a**. Bromination of **12a** with N-bromosuccinimide afforded a mixture of allylic bromides **26** which, without separation, was treated with two equivalents of t-BuOK in HMPA and then quenched with CH_3OSO_2F to give **7a** as an extremely air-sensitive yellow oil in 30–60% yield. However, it could be stored at ambient temperature under an argon atmosphere. Although **7a** was too labile to allow its combustion analysis, the available spectral data are consistent with the proposed structure (Experimental).

Synthesis of parent azulene isomers

Although valence isomers of 4-methoxyazulene have been synthesized, the methoxy substitution in **6a** and **7a** causes some perturbation of the electronic structure intrinsic to the azulene isomers. To eliminate this complication the synthesis of the parent compounds **6b** and **7b** were attempted. The cornerstone of our initial synthetic strategy was envisioned to be reductive replacement of the methoxy groups of **6a** and **7a** to the parent compounds. Given the precedents found in fulvene chemistry,[25] such a transformation was anticipated to be accomplishable by reduction with hydride reagents.[26] However, all attempts to convert **6a** to **6b** and **7a** to **7b** by way of hydride reduction failed; **6b** and **7b** were finally prepared by a two-step sequence as shown in Scheme 4. Tetracyclic dienone **16** was reduced with a large excess of $NaBH_4$ to give alcohol **27** contaminated with a double bond isomer. The mixture was extracted with CH_2Cl_2 and used in the next step without separation. Reaction of **27** with CH_3COCl in the presence of a large excess of 4-(dimethylamino)pyridine in CH_2Cl_2 resulted in efficient acetylation and elimination of acetic acid to provide **6b** as an acid- and air-sensitive orange oil in 25% yield.

Similarly, tricyclic ketone **28**, obtained from **12a** through allylic bromination with N-bromosuccinimide followed by dehydrobromination with t-BuOK, was reduced with a large excess of $NaBH_4$ to give an epimeric mixture of alcohol **29**. Treatment of **29** with tri-n-butylphosphine produces **7b** as an air-sensitive yellow oil in 40% yield, which can be isolated virtually pure by column chromatography on silica gel. It should be pointed out that the above synthetic methods provide azulene-free valence isomers **6b** and **7b**. Especially noteworthy is that the bicyclobutane skeletons in **6a** and **b** survived without aromatization[27] to the more stable 4-methoxyazulene (4-OCH_3) and azulene (**4**), respectively, in the final synthetic steps. This makes the purification of these labile compounds easier. Although **6b** and **7b** were too labile to allow their combustion analyses, these structures were unequivocally confirmed by their spectroscopic properties (Experimental).

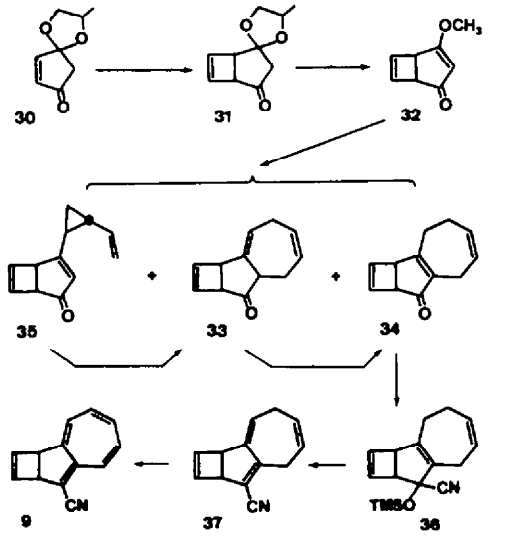


Scheme 4.

Synthesis of cyano-Dewar heptalene

One of the most recurrent features of non-alternant hydrocarbon chemistry is the elucidation of the relationship between these conjugated systems and their valence isomers. (Such studies have already been done in pleiadiene and azulene fields.) Thus, attempts to synthesize heptalene isomer(s) were made. We selected cyano-Dewar heptalene **9** and cyanoheptalvalene **8** as our target molecules since these molecules possess a labile heptafulvene[28] moiety which would be stabilized by a cyano substituent at the exocyclic carbon atom.[29]

The synthesis of **9** is summarized in Scheme 5 showing the use of sequential annulation of four- and seven-membered rings. In considering the formation of the seven-membered ring, we noted the possibility of forming the cycloheptadiene system by Cope rearrangement of the appropriately constructed *cis*-divinylcyclopropane unit. Accordingly, the first step in the synthesis of **9** was the photocycloaddition of cyclopent-2-ene-1,4-dione mono-acetal (**30**), available readily from cyclopent-2-ene-1,4-dione[30] and propylene oxide,[31] with acetylene followed by treatment with methanol saturated with hydrogen chloride to form the key precursor, 2-methoxybicyclo[3.2.0]hept-2,6-dien-4-one (**32**), in 30% yield. Reaction of **32** with a mixture of *cis*- and *trans*-1-lithio-2-vinylcyclopropane[32] and subsequent treatment with hydrochloric acid gave a mixture of products which can be



Scheme 5.

separated into seven-membered ring annulated ketones **33** and **34**, together with the uncyclized *trans*-cyclopropyl derivative **35** in 41, 22, and 32% yields, respectively. Ketone **33** smoothly isomerizes to the desired **34** on simple filtration through a short plug of alumina in 90% yield. In addition, irradiation of **35** with a 100 W high-pressure Hg lamp in acetone at room temperature causes formation of **33** (65%) and **34** (8%). Introduction of the unsaturated nitrile functionality was then accomplished, although in low yield, via treatment of **34** with $(CH_3)_3SiCN$ and ZnI_2[33] to afford cyanohydrin silyl ether **36**. Without purification the latter was treated with $POCl_3$ in pyridine[34] to provide the unsaturated nitrile **37** in 15% yield. Finally, introduction of a double bond by DDQ proceeded to afford 6-cyanotricyclo[5.3.0.0^{2,5}]dodeca-3,6,8,10,12-pentaene (cyano-Dewar heptalene **9**), as red needles, m.p. 99.5–100.5°, in 39% yield. As expected, and contrary to the azulene isomers, **9** is quite a stable compound. The structural assignment of **9** as a Dewar heptalene was made by comparison of the spectral data compared with those of 8-cyanoheptafulvene.[35]

With the synthesis of cyano-Dewar heptalene complete, there remained the preparation of only a valene type isomer **8** of heptalene as our target. Suffice it to say, quite recently we succeeded in synthesizing **8** in eleven steps from tricyclo[4.1.0.0^{2,7}]heptan-4-one; this will be published elsewhere.[36]

Spectroscopic properties

The full ^{1}H-NMR, ^{13}C-NMR, IR, UV–VIS, and MS spectral data for all new valence isomers are consistent with the assigned structures and are tabulated in the Experimental. Some aspects of these spectra deserve comment here.

Since the azulene isomers **6a,b** and **7a,b** possess a common pentafulvene chromophore, the UV–VIS spectra of these compounds resemble those of pentafulvene.[37] Therefore, the azulene isomers were expected to appear yellow in color, and indeed they do as a consequence of low intensity long wavelength absorption maxima near the edge of the visible region. Figure 1 shows a comparison of the observed spectra of these azulene isomers. In spite of the increased strain imposed on the pentafulvene chromophore, the long wavelength maxima of **7a** and **b** exhibit blue shifts by 10 and 16 nm compared to those of **6a** and **b**, respectively. This implies that there is a conjugation effect between the fulvene and bicyclobutane moieties in **6a** and **b** to some extent. Actually, conjugation effects between bicyclobutane and some π-systems have already been suggested in benzvalene[38] and in tropovalene.[21a]

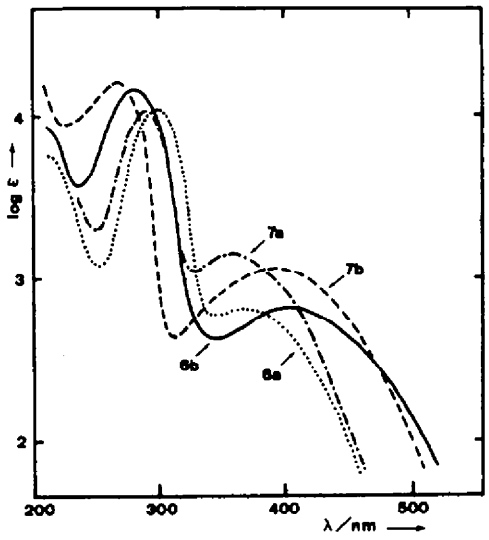


Fig. 1. Electronic spectra of **6a** (· · · · ·), **6b** (——), **7a** (–·–·–), and **7b** (– – –) in cyclohexane.

As expected, the absorption spectrum with vibrational fine structures observed for cyano-Dewar heptalene **9** (Fig. 2) is quite similar to that of 8-

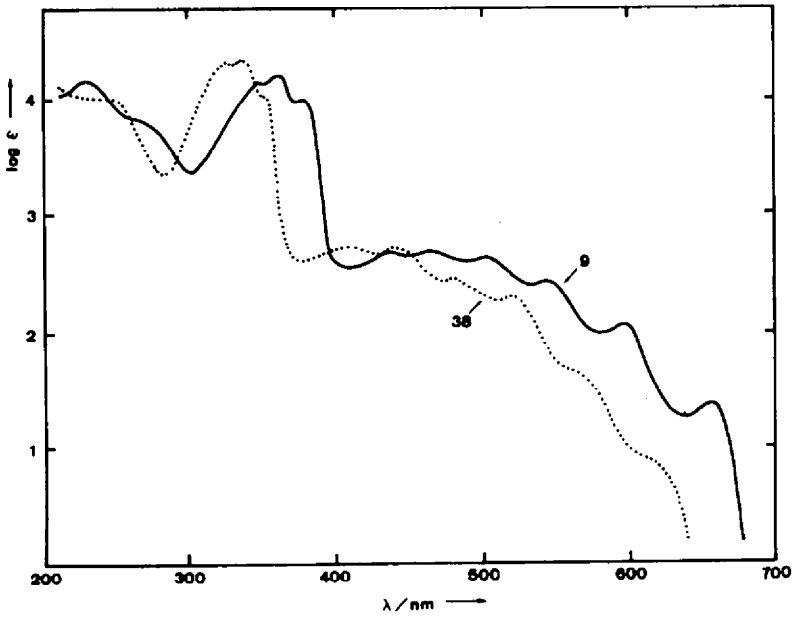


Fig. 2. Electronic spectra of **9** (——) and **38** (· · · · ·) in cyclohexane.

Table 1. Kinetics of the thermal isomerization of azulvalenes (**6a,b**), Dewar azulenes (**7a,b**) and cyano-Dewar heptalene (**9**)

Compound	Temp range (°)	k (s^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (eu)	E_a (kcal mol^{-1})	Log A
6a[a]	110–140				~31	
6b[b]	90–120	$k^{90} = 1.78 \times 10^{-5}$ $k^{100} = 4.85 \times 10^{-5}$ $k^{110} = 1.44 \times 10^{-4}$ $k^{120} = 3.44 \times 10^{-4}$	27.5 ± 0.5	−4.8 ± 1.1	28.6 ± 0.5	12.3 ± 0.3
7a[c]	155–182	$k^{155} = 1.24 \times 10^{-5}$ $k^{165} = 3.66 \times 10^{-5}$ $k^{174} = 8.00 \times 10^{-5}$ $k^{182} = 1.66 \times 10^{-4}$	35.8 ± 0.6	2.1 ± 1.9	36.7 ± 0.6	13.9 ± 0.2
7b[b]	120–140	$t_{1/2}(120) = 10$ h[e] $t_{1/2}(130) = 2$ h[e] $t_{1/2}(140) = 50$ min[e]			~32	
9[d]	118–140	$k^{118.8} = 1.94 \times 10^{-5}$ $k^{122.7} = 2.43 \times 10^{-5}$ $k^{130.3} = 5.83 \times 10^{-5}$ $k^{140.8} = 1.76 \times 10^{-4}$	32.3 ± 1.3	2.0 ± 3.2	33.1 ± 1.3	13.8 ± 0.7

[a] In dodecane.
[b] In toluene-d_8–TMEDA.
[c] In benzene-d_6.
[d] In toluene-d_8.
[e] Half-life.

cyanoheptafulvene (**38**).[35] However, the first and second absorption bands in **9** are red shifted by 26 nm presumably due to the increased strain involved in the heptafulvene skeleton and to the alkyl substitution at 1,8-positions of heptafulvene where the atomic orbital coefficients in the HOMO are large.

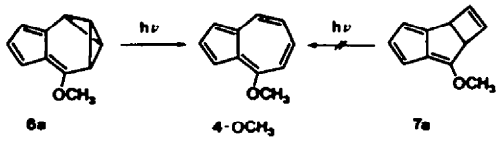
The most conspicuous feature in the ^{1}H-NMR spectra of azulvalene **6b** is the dtd signal at δ 3.03 which corresponds to one of the wing protons, H-2, of the bicyclobutane segment. The large doublet splitting (3.9 Hz) of this signal corresponds to the well-known long-range coupling between two wing protons, $J_{2,5}$, and the triplet splitting (2.4 Hz) corresponds to $J_{2,3} = J_{2,4}$. Further small doublet splitting (0.8 Hz) is attributed to the zigzag coupling with H-8. These spectral patterns strongly support the existence of a bicyclobutane skeleton. The somewhat downfield chemical shift of the bridgehead protons, H-3,4 at δ 3.47, which can be compared with those of benzvalene (δ 3.53) and tropovalene (δ 3.35), reflects the aforementioned conjugation effect. The same propensity can also be found in the ^{13}C-NMR chemical shift of C-3 and C-4.

Thermal isomerizations

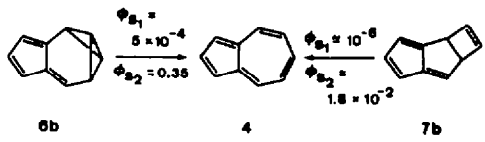
As expected **6a**, **7a** and **6b**, **7b** are thermally rearranged to 4-methoxyazulene (4-OCH_3)[39] and azulene (**4**), respectively. Furthermore, **9** undergoes quantitative isomerization to 1-cyanoheptalene (5-CN). These thermal reactions provide not only new routes to the difficulty accessible substituted azulenes and heptalenes but also a clear contrast between the roles of pentafulvene (6π) and heptafulvene (8π) systems in the isomerization reactions of **6**, **7**, and **9**.

The isomerization rates of **7a**, **6b**, **7b**, and **9** were determined by means of ^{1}H-NMR spectroscopy. From the first-order rate constants the activation parameters, shown in Table 1, were obtained. Inspection of these data compared with those reported for the related compounds indicate that the activation energies for the ring opening of both **6b** and **7b** are substantially higher than those of benzvalene (E_a = 25.9 kcal mol^{-1})[40] and Dewar benzene (23.0 kcal mol^{-1}),[41] respectively. However, the values found for **6b** and **7b** are smaller than those of tricyclo[4.1.0.0^{2,7}]heptane (38.8 kcal mol^{-1}),[42] tricyclo[4.1.0.0^{2,7}]hept-3-ene (32.4 kcal mol^{-1}),[42] and **3** (32.9 kcal mol^{-1})[11b] for bicyclobutane ring openings and of bicyclo[3.2.0]hept-6-ene (45.9 kcal mol^{-1}),[43] bicyclo[4.2.0]oct-7-ene (43.2 kcal mol^{-1}),[44] and **2** (39.3 kcal mol^{-1})[11b] for cyclobutene ring openings, respectively. Although most bicyclobutanes incorporated into a cyclic framework with *endo-endo'* bridging are known to be thermally converted to the corresponding cyclobutene isomer, it can be concluded that the thermolyses of **6a** and **b** give rise directly to 4-OCH_3 and **4**, respectively, without any intervention of **7a** and **b**, since the activation energies for the thermolyses of **6a** and **b** are substantially smaller than those of **7a** and **b**, respectively. The plausible explanation for these processes is that the pentafulvene 6π systems in **6a** and **b** do not play a passive role during these ring openings but assist in the fission of the bicyclobutane rings.† The observed rate retardation by methoxyl substitution in **7a** is mainly due to the increase in repulsive force with the progress of the disrotatory bond fission of **7a** with antiaromatic transition state.[45] In view of the fact that the pentafulvene acts as a 6π-component in pericyclic reactions[46] and that Dewar benzene isomerizes to benzene even at room temperature whereas Dewar azulenes **7a** and **b** isomerize only at elevated temperature, [3,7]sigmatropic shifts in **7a** and **b** would have been expected *a priori*. Contrary to this

† In the case of thermal isomerization of benzvalene to benzene it has been suggested that the extra double bond does not play a passive role in this process.[40]



Scheme 6.



Scheme 7.

expectation, Dewar azulenes did not give any products through a [3,7]sigmatropic shift during the thermolyses.[47,48] These observations for the azulene isomers **6** and **7** are, at least phenomenalogically, parallel to the thermal behaviors of benzvalene and Dewar benzene, in which a bicyclobutane and a cyclobutene, respectively, are perturbed by a 2π-electron ethylenic double bond.

On the other hand, the activation energy for the ring opening of **9** is substantially higher than that for Dewar benzene[41] and bicyclo[4.2.0]octa-2,4,7-triene (E_a = 18.8 kcal mol^{-1})[49] yet smaller than that of **7a** (36.7 kcal mol^{-1}) and **2** (39.3 kcal mol^{-1}).[11b] Because the strain imposed on the central σ-bond in the bicyclo[3.2.0]heptane skeleton of **9** seems to be smaller than that in **7a** and **2**, the lower value observed for the thermally allowed isomerization of **9** may be interpreted in terms of transition-state aromaticity (Evans' principle).[50] Namely, the transition state for the isomerization of **9** is isoconjugate with Hückel azulenocyclobutadiene and would be stabilized to some extent.

Photochemical isomerization

On irradiation with a 100 W Hg lamp in hexane through Pyrex at room temperature, **6a** undergoes clean isomerization (monitored by UV–VIS spectroscopy, six sharp isosbestic points) to 4-methoxyazulene (4-OCH_3). In sharp contrast, photolysis of **7a** resulted in slow decomposition instead of isomerization to 4-OCH_3 (Scheme 6). We also examined direct irradiation in hexane and acetone-sensitized irradiation and low-temperature irradiation in methylcyclohexane–isopentane (1 : 4) at 77 K with a high-pressure Hg lamp through Pyrex and/or a quartz filter; all resulted in slow decomposition.

Under strictly selected irradiations with monochromatic light,† parent azulvalene **6b** isomerizes almost quantitatively throughout the overall reaction whereas parent Dewar azulene **7b** isomerizes to azulene (**4**) in only about 60% yield, at least in the initial stage of the photolysis. The quantum yields for isomerizations of **6b** and **7b** in argon-purged cyclohexane with irradiation in their first or second absorption bands are Φ_{S_1} (excited at 460 nm) = 5×10^{-4} and Φ_{S_2} (excited at 300 nm) = 0.35 for **6b**; Φ_{S_1} (excited at 400 nm) $\simeq 10^{-6}$ and Φ_{S_2} (excited at 280 nm) = 1.8×10^{-2} for **7b** (Scheme 7). Since addition of isoprene (E_T = 60.1 kcal mol^{-1}) or 1,3-cyclohexadiene (E_T = 52.4 kcal mol^{-1}) does not affect the above data, **6b** and **7b** presumably isomerize from their two distinct singlet excited states. The higher quantum yields from excitation of the upper states of each compound should be ascribed to the longer lifetimes of S_2 states as compared with those of S_1 states.[51]

In the photochemical behavior of cyano-Dewar heptalene **9**, there are several aspects worthy of comment.[52] The fluorescence spectrum of **9** was found to be a close mirror image of the S_0–S_2 absorption band, and the fluorescence excitation spectrum was in satisfactory agreement with the absorption spectrum below 400 nm as shown in Fig. 3. The fluorescence quantum yield, $\Phi_f = 2.8 \times 10^{-3}$ (in cyclohexane at room temperature), determined by reference to 9,10-diphenylanthracene (Φ_f = 0.86),[53] was not affected by degassing or oxygen saturation. No fluorescence was observed to the red end of the first absorption bands, $\lambda > 658$ nm.

Interestingly, 8-cyanoheptafulvene (**38**)[35] and 8,8-dicyanoheptafulvene (**39**)[29] did not give rise to any detectable fluorescence emission ($\Phi_f \ll 10^{-4}$). Since the bond order of the exocyclic double bond is strongly reduced upon S_0–S_2 excitation of heptafulvenes ($\Delta_p \simeq 0.35$),[54] radiationless deactivation of the S_2 state due to rotational relaxation of this bond appears to be rapid even on a picosecond time scale in non-fused heptafulvenes. To confirm this hypothesis, we have synthesized and examined 6-cyano-10,10-dimethylbicyclo[5.3.0]deca - 1,3,5,7 - tetraene (**40**).[53] The absorption, emission, and excitation spectra of **40** were very similar ($\Phi_f = 2.1 \times 10^{-3}$) to those of **9** except for a blue shift of about 10 nm. We conclude that S_2-emission from heptafulvenes is readily observable only

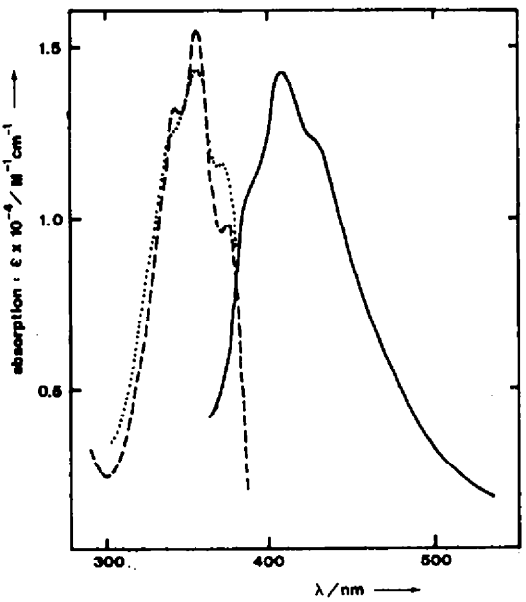
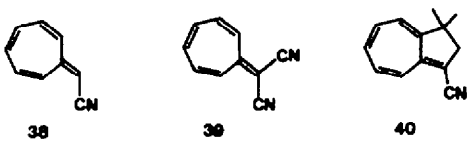


Fig. 3. Absorption (——), fluorescence excitation (·····), and fluorescence emission spectra (——) of **9** in cyclohexane at ambient temperature.

† For the photoisomerizations of **6b** in excitation at 460 nm and **7b** in excitation at 400 nm, Toshiba Y-43 (> 430 nm) and UV-35 (> 350 nm) were used, respectively, to shut off the leaking of shorter wavelength light.



38 39 40

if the free rotor effect[55] of the exocyclic double bond is suppressed by fusion to a small ring.

Although **9** is stable under irradiation using a 450 W high-pressure Hg lamp through Pyrex for 5.5 h in a degassed mixture of methylcyclohexane and isopentane (1:1 v/v) at 0°, isomerization of **9** to 1-cyanoheptalene (**5**-CN) takes place readily upon irradiation with either a 450 W high- or low-pressure Hg lamp through quartz within 2 h. Using monochromatic light we have confirmed this observation: the quantum yield $\Phi_{(9\rightarrow 5\text{-CN})}$ is less than 10^{-6} at 365 nm (S_2 excitation), but the reaction proceeds smoothly upon irradiation at 308 nm or at 254 nm. If this wavelength dependence is due to anti-Vavilov photoreactivity[56] from an upper excited singlet state S_x ($x > 2$), the primary photochemical process would have to be extremely fast to compete with internal conversion to the close-lying, non-reactive S_2 state. However, the rate of the reaction **9**→**5**-CN on 308 nm irradiation monitored spectrophotometrically using samples of different path lengths but identical absorbance ($A = 0.3$ at 308 nm) was found to be directly proportional to the initial concentration of **9** in the range of 10^{-4}–10^{-3} M and did not decrease with irradiation time as the absorbance of **9** decreased due to photolysis. These results are consistent with Suppan *et al*'s mechanism[57] involving chemical sensitization by trace impurities which absorb at shorter wavelength than the photochemical substrate. In fact, the reaction rate is strongly enhanced by the deliberate addition of various impurities such as naphthalene, duroquinone, or N-methylindole.

To conclude, we have completed the total synthesis, isolation, and characterization of the valence isomers of azulene and heptalene, representative non-alternant hydrocarbons. In addition, both thermal and photochemical isomerization reactions on these valence isomers have been carried out. We believe that our achievements permit access to a full understanding of the ground- and excited-state properties of these prototypical molecules.

EXPERIMENTAL

All m.ps are uncorrected. ^{1}H-NMR (100 MHz) and ^{13}C-NMR (22.5 MHz) were recorded on Varian XL-100 and JEOL FX-90Q spectrometers, respectively. Chemical shifts are given in ppm (δ) downfield from TMS as internal standard and coupling constants are given in Hz. IR, UV, emission, and mass spectra were obtained on JASCO A-100, Hitachi 340, Hitachi 650-60, and JEOL JMS-01SG-2 spectrometers, respectively.

All reactions were carried out under N_2 or Ar. Ether, tetrahydrofuran and dimethoxyethane were dried with sodium-benzophenone ketyl, and other aprotic solvents were dried over CaH_2 as necessary. For the use in photochemical syntheses, acetone was distilled from $KMnO_4$, dried over K_2CO_3, and distilled. All solvents were purified before use. Abbreviations: AIBN, azobisisobutyronitrile; DDQ, dichlorodicyano-*p*-benzoquinone; DIBAH, diisobutyl aluminum hydride; DME, dimethoxyethane; HMPT, hexamethylphosphortriamide; LDA, lithium diisopropylamide; *m*CPBA, *m*-chloroperbenzoic acid; NBS, N-bromosuccinimide; PCC, pyridinium chlorochromate; THF, tetrahydrofuran; TMEDA, tetramethylethylenediamine; TMSCN, trimethylsilylcyanide; aq, aqueous; sat, saturated; dil, diluted; rt, room temp; i.v., *in vacuo*.

Bicyclo[3.3.0]*oct-6-en-2-one* (**10**)

A soln of bicyclo[3.2.0]hept-1-en-6-one (11.1 g, 100 mmol) and N_2CHCO_2Et (12.9 g, 110 mmol) in dry ether (100 ml) was cooled with ice–H_2O and $BF_3 \cdot Et_2O$ (1 ml) was added over a period of 5 min. An additional 7.5 ml of $BF_3 \cdot Et_2O$ was added in small portions over 30 min. The mixture was stirred until the evolution of N_2 was complete (about 7 h) and then was washed with H_2O, and the solvent was removed i.v. The residual yellow oil and Na_2CO_3 (6 g, 566 mmol) were dissolved in a mixture of dioxane (200 ml) and H_2O (40 ml), and the soln was refluxed for 15 h. After cooling, H_2O was added and the mixture was extracted four times with ether. The combined ether layer was washed with H_2O and dried ($MgSO_4$). After removal of solvent, the isomeric ketones were distilled (70–86°/15 mm Hg) and separated by chromatography over SiO_2 (250 g) with a mixture of hexane and ether (4:1 v/v) to give **10** (7.8 g, 64%) and its isomer, bicyclo[3.3.0]oct-6-en-3-one (1.8 g, 15%).

Bicyclo[3.3.0]*octa-3,6-dien-2-one* (**11**)

In a 500 ml three-necked flask, NaH (2.38 g, 55–65% in oil) was placed and washed three times with dry hexane. A soln of methyl *p*-toluenesulfinate (10.11 g, 59.3 mmol) in dry DME (170 ml) was added. The mixture was heated to reflux, and a soln of **10** (7.255 g, 59.5 mmol) in dry DME (11 ml) was added over 90 min with vigorous stirring. After an additional 90 min at reflux, the mixture was cooled and poured into 5% NaOH aq (300 ml). The aq layer was washed twice with ether, acidified to pH 4 with 4 N HCl, and extracted with ether (100 ml × 2). The combined ether layer was washed successively with H_2O, sat $NaHCO_3$ aq (small amount), H_2O, and brine, and dried ($MgSO_4$). Removal of the solvent afforded crude sulfoxide as a black oil (14.1 g, 91.4%).

The crude sulfoxide in dry benzene (500 ml) was refluxed for 4.5 h. After cooling, the soln was washed successively with sat $NaHCO_3$ aq, H_2O and brine, and dried ($MgSO_4$). The solvent was removed i.v. and the residue was distilled (30–70°/0.3 mm Hg) to give **11** as a colorless oil (3.876 g, 58.2%); b.p. 80°/15 mm Hg; IR (neat, cm^{-1}) 1705; ^{1}H-NMR ($CDCl_3$) δ 7.78 (1H, dd, J = 5.8, 3.0 Hz, H-4), 6.03 (1H, dd, J = 5.8, 1.8 Hz, H-3), 5.83–5.50 (2H, m, H-6,7), 3.99 (1H, m, H-5), 3.20–2.60 (3H, m, H-1,8,8'). (Found: C, 79.57; H, 6.64. Calc for C_8H_8O: C, 79.97; H, 6.71%.)

anti - *Tricyclo*[5.3.0.0^{2,5}]*deca-3,9-dien-6-one* (**12a**)

A soln of **11** (1.565 g, 13.0 mmol) in *trans*-1,2-dichloroethylene (250 ml) was placed in Pyrex test tubes and dry N_2 was bubbled through for 10 min. The soln was irradiated with a 450 W high-pressure Hg lamp with ice cooling. After 3 h, dichloroethylene was removed, and the residue was passed through deactivated SiO_2 (10% H_2O, 35 g) with a mixture of benzene and hexane (6:4).

The crude adducts (2.7 g) were dissolved in benzene (200 ml) and acetalized with $HOCH_2CH_2OH$ (5 ml) and *p*-TsOH (catalytic amount) using a Dean–Stark apparatus. After 18 h, the mixture was cooled, washed successively with sat $NaHCO_3$ aq, H_2O and brine, and dried ($MgSO_4$). Removal of solvent afforded the crude acetal as a yellow oil (3.1 g).

In a 300 ml three-necked flask cooled with a dry ice–EtOH bath, liquid NH_3 (100 ml) was placed and a soln of the acetal (3.1 g) in dry ether (10 ml) was slowly added. To the soln, sodium was added in portions with stirring until the color of the soln became blue. After an additional 10 min of stirring, the liquid NH_3 was evaporated. The mixture was extracted into ether (100 ml), washed with H_2O and treated with 2 N HCl for 12 h. The ether layer was washed successively with H_2O, sat $NaHCO_3$ aq, H_2O and brine. After drying ($MgSO_4$), the ether was removed i.v. to give a pale yellow oil (1.374 g), which was chromatographed over deactivated SiO_2 (10% H_2O, 20 g) with

a mixture of benzene and hexane (2:3) to afford **12a** (1.198 g, 62.9%). *Syn*-isomer **12b** was contained in the latter fractions (< 5%).

The selectivity on the ring junction is dependent on the stereochemistry of dichloroethylene used in this process. The percent *syn*-isomer is 12 or 19% when the *trans*:*cis* ratio of dichloroethylene are 1:1 and 1:3, respectively; **12a**: b.p. 30°/0.3 mm Hg; IR (neat, cm^{-1}) 1720; ^{1}H-NMR ($CDCl_3$) δ 6.45 (1H, d, J = 2.2 Hz), 6.09 (1H, d, J = 2.2 Hz), 5.72 (1H, m), 5.60 (1H, m), 3.45–3.10 (4H, m), 2.80–2.30 (2H, m). (Found: C, 82.17; H, 6.98. Calc for $C_{10}H_{10}O$: C, 82.17; H, 6.90%.) **12b**: IR (neat, cm^{-1}) 1718; ^{1}H-NMR (CCl_4) δ 6.22 (1H, d, J = 2.2 Hz), 5.96 (1H, d, J = 2.2 Hz), 5.75–5.55 (2H, sharp m), 3.60–2.45 (6H, m).

Tetracyclo[5.3.0.0^{2,4}.0^{3,5}]*dec* - 9 - *en* - 6 - *one* (**13**)

A soln of **12a** (727 mg, 4.97 mmol) in dry acetone (500 ml) was placed in Pyrex test tubes and dry N_2 was bubbled for 40 min. The soln was irradiated by means of a 450 W high-pressure Hg lamp with ice cooling. After 2 h, acetone was evaporated i.v. and the residual oil was carefully chromatographed over deactivated Al_2O_3 (10% H_2O, 12 g) with a mixture of hexane and benzene (8.5:1.5) to afford **13** (455 mg, 62.5%). A small amount of **12b** was obtained in the latter fractions. The yield of **12b** varied from run to run (~10%). For use in the next sulfenylation step, the chromatography was repeated two or three times to yield sufficiently pure **13** (20–25%); b.p. 52°/0.3 mm Hg; IR (neat, cm^{-1}) 1700; ^{1}H-NMR ($CDCl_3$) δ 5.75 (1H, ddd, J = 6.0, 2.0, 2.0 Hz), 5.64 (1H, ddd, J = 6.0, 2.0, 2.0 Hz), 3.23 (1H, m, H-1), 2.80–2.50 (5H, m), 2.40 (1H, dt, J = 9.4, 2.6 Hz, H-3), 2.25 (1H, dtd, J = 9.4, 2.6, 1.0 Hz, H-4). (Found: C, 81.48; H, 7.00. Calc for $C_{10}H_{10}O$: C, 82.16; H, 6.90%.)

7 - *Phenylsulfinyltetracyclo*[5.3.0.0^{2,4}.0^{3,5}]*dec* - 9 - *en* - 6 - *one* (**14**).

A soln of LDA (1.96 mmol) in THF (2 ml) was prepared in the usual manner. To the soln, **13** (208 mg, 1.42 mmol) in dry HMPT (1.2 ml) was added over 15 min at −35°. After 30 min of stirring at −35°, the temperature was kept at −10° for 30 min and then at 0° for 40 min. Then, a soln of PhSSPh (429 mg, 1.96 mmol) in dry THF (2 ml) was added over 15 min at −10°. The mixture was stirred at 0° for 1 h and poured into wet ether (15 ml). The organic layer was washed three times with H_2O and once with brine, and dried ($MgSO_4$). After removal of solvent i.v., the residual oil was subjected to column chromatography over deactivated SiO_2 (20% H_2O). Excess PhSSPh was eluted with hexane, and **14** was eluted with a mixture of hexane–benzene (8:2). Removal of solvent afforded **14** as a pale yellow oil (264 mg, 72.9%), which crystallized after standing overnight at −15°. Recrystallization from CCl_4 gave colorless needles; m.p. 67–68°; IR (KBr, cm^{-1}) 1698; ^{1}H-NMR ($CDCl_3$) δ 7.35 (5H, m), 6.68 (2H, m), 3.36 (1H, m), 3.24–3.10 (4H, m), 2.36 (2H, t, J = 2.4 Hz). (Found: C, 75.09; H, 5.58. Calc for $C_{16}H_{14}OS$: C, 75.55; H, 5.55%.)

7 - *Phenylsulfoxyltetracyclo*[5.3.0.0^{2,4}.0^{3,5}]*dec* - 9 - *en* - 6 - *one* (**15a**)

To a soln of **14** (119 mg, 0.46 mmol) in dry CH_2Cl_2 (30 ml) was added a soln of *m*CPBA (80% content, 107 mg, 0.46 mmol) in dry CH_2Cl_2 (5 ml) over 30 min at −78°. After 1 h of stirring the mixture was poured into wet ether (70 ml) and washed successively with 5% Na_2SO_3 aq, sat $NaHCO_3$ aq, H_2O, and brine. After drying ($MgSO_4$, 0°, 1 h), solvent was removed i.v. The residual oil was dissolved in CCl_4 (0.5 ml); the soln was allowed to stand at −15° until the desired product **15a** crystallized. This was filtered, washed with CCl_4 and dried i.v. (76 mg, 61%). The mother liquor was concentrated and the residual oil was chromatographed over deactivated SiO_2 (20% H_2O) with a mixture of hexane and ether (1:1 v/v) to give the diastereomer (**15b**), which was recrystallized from CCl_4 (27 mg, 23%); **15a**: m.p. 101–102.5°; IR (KBr, cm^{-1}) 1680; ^{1}H-NMR ($CDCl_3$) δ 7.46 (5H, m), 5.38 (2H, m), 3.63 (1H, m, H-1), 2.91–2.57 (4H, m), 2.33 (2H, t, J = 2.8 Hz); MS: *m/e* 270 (M^+, 100%). **15b**: m.p. 95–96°; IR (KBr, cm^{-1}) 1675; ^{1}H-NMR ($CDCl_3$) δ 7.54 (5H, m), 5.70 (1H, ddd, J = 6.0, 1.8, 1.8 Hz), 5.60 (1H, ddd, J = 6.0, 1.8, 1.8 Hz), 3.62 (1H, m, H-1), 3.30 (1H, dm, J = 18.0 Hz, H-8), 3.06 (1H, dm, J = 18.0 Hz, H-8'), 2.52 (2H, m, H-2,5), 2.22 (1H, dtd, J = 8.8, 2.5, 1.8 Hz, H-3), 1.48 (1H, dt, J = 8.8, 2.5 Hz, H-4); MS: *m/e* 270 (M^+, 100%). (Found: C, 70.59; H, 5.18. Calc for $C_{16}H_{14}O_2S$: C, 71.08; H. 5.22%.)

Tetracyclo[5.3.0.0^{2,4}.0^{3,5}]*deca* - 1(7),9 - *dien* - 6 - *one* (**16**)

A soln of **15a** (70 mg, 0.26 mmol) in dry CCl_4 (30 ml) was heated at 60°. After 30 min, the mixture was cooled, washed, and dried ($MgSO_4$, 0°, 30 min). The soln was concentrated i.v. and the residual oil was chromatographed at 0° over deactivated SiO_2 (30% H_2O, 1.2 g) with a mixture of hexane and ether (7:3 v/v). The eluate was collected in 0.5 ml portions; fractions (6–10), which contained **16**, were concentrated to give a colorless oil (13 mg, 40%), which was used in the next step without further purification; b.p. ~50°/0.3 mm Hg; IR ($CHCl_3$, cm^{-1}) 1669; ^{1}H-NMR ($CDCl_3$) δ 6.60 (1H, dt, J = 5.4, 0.8 Hz), 6.43 (1H, dt, J = 5.4, 1.2 Hz), 3.33 (2H, t, J = 2.6 Hz, H-3,4), 3.10 (2H, m, H-8,8'), 2.83 (1H, dt, J = 5.4, 2.6 Hz, H-5), 2.65 (1H, dt, J = 5.4, 2.6 Hz, H-2); MS: *m/e* 116 ($M^+ - CO$, 45%), 115 ($M^+ - CHO$, 100%).

Compound **16** was also derived from **25** by the reaction sequence, dehydrochlorination with 2 equiv of t-BuOK in dry ether at −10 to 0° and quenching with sat NH_4Cl aq (50–70%).

9(β) - *Hydroxytricyclo*[5.3.0.0^{2,5}]*dec* - 3 - *en* - 6 - *one* (**20**)

Acetal **17** (*syn*:*anti* = 1:4–1:5, 1.545 g, 8.12 mmol) was dissolved in a mixture of H_2O and THF (1:1 v/v, 90 ml) and treated with $(CH_3COO)_2Hg$ (2.589 g, 8.124 mmol) at 0° for 1 h and then at rt for 3 h. After 3 N NaOH aq was added, the mixture was reduced with $NaBH_4$ (3.03 g, 80.1 mmol) in 3 N NaOH aq (40 ml) for 1 h. The mixture was extracted three times with CH_2Cl_2, washed with H_2O and dried ($MgSO_4$). The solvent was removed to give an oil (1.566 g), which was dissolved in ether (80 ml) and treated with 2 N HCl (50 ml) for 7 h. The aq layer was extracted twice with CH_2Cl_2. The combined organic layer was washed with H_2O and sat $NaHCO_3$ aq, and dried ($MgSO_4$). The mixture was concentrated and chromatographed over deactivated SiO_2 (10% H_2O, 10 g) with benzene and then with ether. The ether fraction was dried and concentrated to give a colorless oil (**20**) as a sole product (1.05 g, 78.6%). **20**: IR (neat, cm^{-1}) 1724; ^{1}H-NMR ($CDCl_3$) δ 6.40 (1H, d, 2.5 Hz), 6.08 (1H, dd, J = 2.5, 1.0 Hz), 4.25 (1H, m), 2.45–2.10 (3H, m), 2.30 (1H, s, OH), 2.88 (1H, ddd, J = 10.8, 7.6, 7.6 Hz), 1.70–2.25 (3H, m), 1.16 (1H, ddd, J = 12.8, 10.8, 4.5 Hz). The benzene fraction contained a mixture (9.1%) of **12a** and **b**, which was enriched in *syn*-isomer (**12b**). The structure of **20** was further confirmed as its benzoate; colorless needles; m.p. 50–51.5°; IR (KBr, cm^{-1}) 1720; ^{1}H-NMR ($CDCl_3$) δ 7.99 (2H, m), 7.62–7.28 (3H, m), 6.45 (1H, d, J = 2.5 Hz, H-3), 6.13 (1H, dd, J = 2.5, 1.0 Hz, H-4), 6.39 (1H, m, H-9), 3.50–3.20 (2H, m), 3.16 (1H, d, J = 2.2 Hz), 2.94 (1H, ddd, J = 12.0, 7.5, 7.5 Hz), 2.54–1.95 (3H, m), 1.29 (1H, ddd, J = 16.0, 12.5, 5.0 Hz). (Found: C, 75.81; H, 6.01. Calc for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01%.)

9(α) - *Chlorotricyclo*[5.3.0.0^{2,5}]*dec* - 3 - *en* - 6 - *one* (**21**)

A soln of **20** (2.10 g, 12.8 mmol) in dry CCl_4 (200 ml) was treated with Ph_3P (5.032 g, 19.2 mmol) for 45 h under reflux. After filtration through deactivated SiO_2 (10% H_2O, 10 g) with benzene, the mixture was chromatographed over deactivated SiO_2 (3% H_2O, 40 g) with benzene to give **12a** (140 mg) and **21** (1.548 g, 66%). **21**: IR (neat, cm^{-1}) 1728; ^{1}H-NMR ($CDCl_3$) δ 6.43 (1H, d, 2.5 Hz), 6.10 (1H, dd, J = 2.5, 1.0 Hz), 4.30 (1H, m), 3.51 (1H, dd, J = 2.1, 1.0 Hz), 3.30–3.10 (2H, m), 2.9–2.0 (4H, m), 1.76 (1H, ddd, J = 13.5, 5.0, 5.0 Hz).

9(α) - *Chlorotetracyclo*[5.3.0.0^{2,4}.0^{3,5}]*decan* - 6 - *one* (**22**)

To a soln of **21** (802 mg, 4.39 mmol) in dry acetone (1.2 l), dry N_2 was bubbled for 1.5 h. The soln was irradiated by means of a 450 W high-pressure Hg lamp through Pyrex with ice cooling. After 1 h, the mixture was concentrated i.v. and

chromatographed over deactivated SiO_2 (10% H_2O, 10 g) with benzene to give a colorless oil (**22**) (444.5 mg, 55.4%), which crystallized on cooling; m.p. 11–14°; IR (neat, cm^{-1}) 1698; ^{1}H-NMR ($CDCl_3$) δ 4.09 (1H, m), 2.83 (1H, td, J = 4.2, 2.4 Hz), 2.80–1.54 (9H, m). (Found: C, 65.81; H, 6.03. Calc for $C_{10}H_{11}OCl$: C, 65.76; H, 6.07%.)

9(α) - *Chloro* - 7 - *phenylsulfinyltetracyclo*[5.3.0.0^{2,4}.0^{3,5}]*decan* - 6 - *one* (**23**)

A soln of LDA (3.914 mmol) in dry THF (6 ml) was prepared in the usual manner. To the soln cooled at −78° was added dropwise **22** (596 mg, 3.262 mmol) in dry THF (3 ml). After 30 min, the mixture was taken up into a syringe and added dropwise to a soln of phenylthiobenzenesulfonate (897 mg, 3.588 mmol) in dry THF (3 ml) at 0°. After 30 min of stirring, the mixture was extracted, washed with H_2O and dried ($MgSO_4$). The mixture was concentrated i.v. and chromatographed over deactivated SiO_2 (20% H_2O, 3 g) with benzene to yield **23** (607 mg, 64%) as a pale yellow oil; IR (neat, cm^{-1}) 1698; ^{1}H-NMR ($CDCl_3$) δ 7.46–7.12 (5H, m), 4.27 (1H, m), 2.79 (1H, dt, J = 4.1, 2.4 Hz), 2.63–2.25 (8H, m), 1.80 (1H, m).

9 - *Chlorotetracyclo*[5.3.0.0^{2,4}.0^{3,5}]*dec* - 1(7) - *en* - 6 - *one* (**25**)

To a soln of **23** (405 mg, 1.39 mmol) in dry CH_2Cl_2 (80 ml), *m*CPBA (80% content, 315.6 mg, 1.52 mmol) in dry CH_2Cl_2 (10 ml) was added dropwise at −70°. After 7 h of stirring, the mixture was extracted into ether, washed with dil Na_2SO_3 aq and sat $NaHCO_3$ aq, and dried ($MgSO_4$). The mixture was concentrated i.v., dissolved in dry CCl_4 (40 ml) and heated at 60° for 2 h. The solvent was removed i.v. and the residue was chromatographed over deactivated SiO_2 (20% H_2O, 17 g) with a mixture of hexane and benzene to give **25** (143 mg, 67.5%), which was recrystallized from ether; colorless needles; m.p. 55.5–56.5°; IR (KBr, cm^{-1}) 1638; ^{1}H-NMR ($CDCl_3$) δ 4.93 (1H, tt, J = 6.5, 3.5 Hz), 3.38 (2H, t like, 2.3 Hz), 3.12 (1H, dm, J = 6.5 Hz), 2.98 (1H, ddd, J = 6.5, 2.4, 2.4 Hz), 2.88 (1H, dm, J = 6.5 Hz), 2.69 (1H, dt, J = 4.2, 2.3 Hz), 2.62 (1H, dt, J = 4.2, 2.3 Hz). (Found: C, 66.46; H, 5.02. Calc for $C_{10}H_9OCl$: C, 66.49; H, 5.02%.)

6 - *Methoxytetracyclo*[5.3.0.0^{2,4}.0^{3,5}]*deca* - 6,8,10 - *triene* (**6a**)

All the operations were carried out in an Ar atmosphere. In a 30 ml flask, t-BuOK (purified by sublimation, 53.5 mg, 0.478 mmol) was dissolved in dry HMPT (3 ml). To the ice cooled soln, **16** (20 mg, 0.13 mmol) in dry benzene (0.7 ml) was added with stirring over the period of 1 min. After 5 min of stirring, freshly distilled CH_3OSO_2F (3 drops) was slowly added. After 2 min of stirring, the mixture was quenched with H_2O (a few drops), extracted rapidly with deaerated hexane, washed with H_2O and dried ($MgSO_4$). The solvent was removed i.v. and the residue was separated by chromatography on a short column of deactivated Al_2O_3 (10% H_2O, 0.6 × 1 cm) with deaerated hexane into four 0.5 ml fractions. The second and third fractions afforded 10 mg of yellow crystals which on recrystallization from hexane gave pure **6a** as yellow plates (~40%); m.p. 71–73°; ^{1}H-NMR ($CDCl_3$) δ 6.27 (1H, dd, J = 5.2, 2.2 Hz, H-9), 6.20 (1H, ddd, J = 5.2, 1.5, 0.5 Hz, H-8), 6.10 (1H, dd, J = 2.2, 1.5 Hz, H-10), 4.08 (3H, s, OMe), 3.46 (2H, t, J = 2.5 Hz, H-3,4), 3.09 (1H, dtd, J = 4.0, 2.5, 0.5 Hz, H-2), 2.52 (1H, dt, J = 4.0, 2.5 Hz, H-5); UV (n-hexane) λ_{max} 300 nm (ε 12,000), 367 (689); MS: *m/e* 158 (M^+, 57%), 128 (100), 115 (93). (Found: C, 83.12; H, 6.37. Calc for $C_{11}H_{10}O$: C, 83.51; H, 6.37%.)

Tetracyclo[5.3.0.0^{2,4}.0^{3,5}]*deca* - 6,8,10 - *triene* (**6b**)

All the operations were carried out in an Ar atmosphere. To a soln of **16** (70 mg, 0.6 mmol) in dry benzene (2 ml) was added dry MeOH (4 ml) and the mixture was cooled with ice–H_2O. $NaBH_4$ (110 mg, 3 mmol) was added over the period of 1 h. The mixture was quenched with H_2O, extracted twice with CH_2Cl_2, washed twice with H_2O and dried ($MgSO_4$). The dried soln of the allylic alcohol (**27**) in CH_2Cl_2 was concentrated to 5 ml and 4-(dimethylamino)pyridine (500 mg, 4.09 mmol) was added. After cooling with ice–H_2O, the mixture was treated with freshly distilled AcCl (0.05 ml, 0.6 mmol) for 2 h. The mixture was extracted with pentane deaerated by Ar bubbling (25 ml), washed with dil $NaHCO_3$ aq and H_2O, and dried ($MgSO_4$). The dried organic layer was passed through deactivated SiO_2 (20% H_2O, 6.5 g) and the solvent was removed by blowing an Ar stream onto the soln to leave **6b** as a reddish yellow oil (18 mg, 25%); ^{1}H-NMR ($CDCl_3$) δ 6.67 (1H, dd, J = 4.8, 1.7 Hz, H-6), 6.31 (1H, dd, J = 5.3, 2.0 Hz, H-9), 5.90 (1H, m, H-10), 5.83 (1H, ddd, J = 5.3, 1.1, 0.9 Hz, H-8), 3.47 (2H, t, J = 2.4 Hz, H-3,4), 3.03 (1H, dtd, J = 3.9, 2.4, 0.8 Hz, H-2), 2.49 (1H, m, H-5); ^{13}C-NMR ($CDCl_3$) δ 137.4, 133.2, 121.3, 116.9, 40.1, 38.5, 36.0; UV (cyclohexane) λ_{max} 281 nm (ε 11,000), 400 (370).

Tricyclo[5.3.0.0^{2,5}]*deca* - 1(7),3,9 - *trien* - 6 - *one* (**28**)

A soln of **12a** (500 mg, 3.42 mmol), NBS (732 mg, 4.104 mmol) and AIBN (20 mg) in dry CCl_4 (20 ml) was refluxed. After 1 h, the mixture was cooled, filtered, and washed successively with H_2O, dil $Na_2S_2O_3$ aq, and dried ($MgSO_4$).

The dried CCl_4 soln was concentrated i.v. and the residual bromide (**26**) was dissolved in dry benzene (0.5 ml). The benzene soln was slowly added to t-BuOK (purified by sublimation, 1.25 g, 10.3 mmol) in dry ether (30 ml) at 0°. After 20 min of stirring, the mixture was quenched with sat NH_4Cl aq (10 ml) and washed with H_2O. The aq layer was extracted once with ether and the combined ether layer was dried ($MgSO_4$). Removal of solvent gave **28**, as a colorless oil (45% yield). Though freshly prepared **28** was practically pure in most cases, samples contaminated with decomposition products were purified by chromatography over deactivated SiO_2 (20% H_2O) with a mixture of benzene and ether (3 : 2 v/v); IR (CCl_4, cm^{-1}) 1680; ^{1}H-NMR ($CDCl_3$) δ 7.03 (1H, dt, J = 5.2, 1.3 Hz, H-9), 6.70 (1H, dt, J = 5.2, 1.5 Hz, H-10), 6.55 (1H, dm, J = 2.5 Hz, H-3), 6.44 (1H, dd, J = 2.5, 2.2 Hz, H-4), 4.03 (1H, m, H-2), 3.95 (1H, m, H-5), 3.11 (2H, m, H-8,8').

6 - *Methoxytricyclo*[5.3.0.0^{2,5}]*deca* - 3,6,8,10 - *tetraene* (**7a**)

All operations were carried out in an Ar atmosphere. A soln of a mixture of bromide **26** (500 mg, 3.42 mmol) in dry benzene (0.5 ml) was added dropwise to freshly sublimed t-BuOK (645 mg, 5.29 mmol) in dry HMPT (20 ml) with ice cooling. After 10 min of stirring, the mixture was carefully quenched with freshly distilled CH_3OSO_2F (0.4 ml) with ice cooling. The mixture was diluted with deaerated hexane, washed three times with H_2O, dried ($MgSO_4$) and concentrated. The residual oil was chromatographed over deactivated Al_2O_3 (10% H_2O, 8 g) with deaerated hexane to give **7a** as a yellow oil (178 mg, 33%); ^{1}H-NMR ($CDCl_3$) δ 6.73 (1H, dd, J = 4.8, 2.2 Hz, H-9), 6.55 (1H, dd, J = 2.6, 1.0 Hz, H-3 or 4), 6.49 (1H, dd, J = 2.6, 1.0 Hz, H-4 or 3), 6.25 (1H, dd, J = 4.8, 1.1 Hz, H-8), 6.02 (1H, m, H-10), 4.24 (1H, dd, J = 2.7, 1.0 Hz, H-5), 4.11 (1H, m, H-2), 4.11 (3H, s, OMe); ^{13}C-NMR ($CDCl_3$) δ 172.4, 146.3, 144.1, 138.6, 135.2, 124.9, 113.2, 110.2, 60.1, 59.9, 44.8; UV (hexane) λ_{max} 289 nm (ε 12,000), 357 (950); MS: *m/e* 158 (M^+, 64%), 128 (66), 115 (100).

Tricyclo[5.3.0.0^{2,5}]*deca* - 3,6,8,10 - *tetraene* (**7b**)

All operations were carried out in an Ar atmosphere. To a soln of **28** (144 mg, 1 mmol) in a mixture of MeOH (10 ml) and benzene (5 ml) was added a large excess of $NaBH_4$ (1.2 g, 31.7 mmol) in small portions over a period of 30 min with ice cooling. After **28** had disappeared by TLC, the mixture was diluted with H_2O, extracted four times with CH_2Cl_2, and washed with H_2O and dried ($MgSO_4$).

The dried soln of allylic alcohol **29** was concentrated and the residual oil was dissolved in a mixture of dry CH_2Cl_2 (10 ml) and CCl_4 (0.5 ml). The mixture was treated with (n-Bu)$_3$P (0.3 ml) under reflux. After 30 min, H_2O was added and the mixture was extracted with pentane and dried ($MgSO_4$). The dried soln was concentrated by blowing down in an Ar stream and chromatographed over deactivated SiO_2 (10% H_2O, 1 g) with deaerated pentane. The solvent was removed by a blowing Ar stream to leave a yellow oil **7b** (~50 mg, ~40%); ^{1}H-NMR ($CDCl_3$) δ 6.83 (1H, dd, J = 4.8, 2.0 Hz, H-6), 6.81 (1H, dd, J

= 5.2, 2.1 Hz, H-9), 6.48 (1H, dd, J = 2.4, 0.8 Hz, H-4), 6.41 (1H, dm, J = 2.4 Hz, H-3), 6.13 (1H, dd, J = 5.2, 0.8 Hz, H-8), 6.04 (1H, m, H-10), 4.48 (1H, m, H-5), 4.00 (1H, m, H-2); UV (cyclohexane) λ_{max} 270 nm (ε 17,000), 384 (1400).

2-*Methoxybicyclo*[3.2.0]*hepta*-2,6-*dien*-4-*one* (**32**)

A soln of **30** (4.04 g, 26 mmol) in dry acetone (500 ml) was cooled with a dry ice–EtOH bath. Dry N_2 was bubbled through for 30 min and then HC≡CH (passed successively through conc H_2SO_4, KOH, and $CaCl_2$) was introduced for 1 h. With HC≡CH being introduced, the soln was irradiated by means of a 100 W high-pressure Hg lamp. After 2 h of irradiation, the mixture was concentrated i.v. and treated with MeOH saturated with hydrogen chloride (30 ml) for 2.5 h. The mixture was concentrated i.v. and dissolved in ether and neutralized with sat $NaHCO_3$ aq and solid Na_2CO_3. The ether layer was separated and the aq layer was extracted with ether. The combined ether layer was washed with H_2O and brine, and dried ($MgSO_4$). The dried soln was concentrated and chromatographed over deactivated SiO_2 (10% H_2O, 40 g) with a mixture of benzene and ether (8 : 2 v/v) to give **32** (1.02 g, 30%); m.p. 46–48.5°; IR ($CHCl_3$, cm^{-1}) 1670, 1580; ^{1}H-NMR ($CDCl_3$) δ 6.39 (1H, dd, J = 2.5, 0.8 Hz), 6.34 (1H, dd, J = 2.5, 1.0 Hz), 5.48 (1H; s), 3.77 (3H, s), 3.61 (1H, d, J = 2.4 Hz), 3.40 (1H, m); MS: *m/e* 136 (M^+, 29%), 121 ($M^+ - CH_3$, 4), 108 (55), 65 (100).

Tricyclo[5.5.0.0^{2,5}]*dodeca*-1(7),3,9-*trien*-6-*one* (**34**)

To a soln of 1-bromo-2-vinylcyclopropane (372 mg, 2.53 mmol) in dry ether (4 ml), s-BuLi (0.62 N, 4.47 ml, 2.78 mmol) was added dropwise at −78° and stirred for 1.5 h at this temp. To the mixture, **32** (344 mg, 2.53 mmol) in a mixture of dry ether (0.2 ml) and dry THF (0.2 ml) was added over 5 min. After 2.5 h of additional stirring at −78°, the mixture was warmed to rt, treated with 1 N HCl (15 ml) for 30 min and extracted four times with ether. The combined ether layer was washed with sat $NaHCO_3$ aq, H_2O and brine, and dried ($MgSO_4$). After removal of solvent i.v. the residual oil (452 mg) was chromatographed over deactivated SiO_2 (10% H_2O, 9 g) with a mixture of benzene and ether (8 : 2 v/v) to give **33** (102 mg, 22%), **34** (181 mg, 41%) and **35** (140 mg, 22%). **33**: yellow oil; IR (neat, cm^{-1}) 1740; ^{1}H-NMR ($CDCl_3$) δ 6.27 (1H, d, J = 3.0 Hz), 6.08 (1H, d, J = 3.0 Hz), 5.90–5.26 (3H, m), 3.70–3.14 (3H, m), 3.03–2.70 (2H, bs), 2.63–1.90 (2H, m). **34**: yellow oil; b.p. 50–65°/0.3 mm Hg; IR (neat, cm^{-1}) 1688, 1626, 1554; ^{1}H-NMR ($CDCl_3$) δ 6.61 (1H, d, J = 2.5 Hz), 6.41 (1H, dd, J = 2.5, 1.3 Hz), 6.04–5.70 (2H, m), 3.60 (1H, bs), 3.46 (1H, dd, J = 2.5, 1.3 Hz), 3.15–2.90 (2H, m), 2.70–2.26 (4H, m); MS: *m/e* 172 (M^+, 29%), 144 ($M^+ - CO$, 36), 129 (100), 115 (65). (Found: C, 83.59; H, 6.95. Calc for $C_{12}H_{12}O$: C, 83.69; H, 7.09%.) **35**: yellow oil; b.p. 80°/0.3 mm Hg; IR (neat, cm^{-1}) 1687, 1637, 1596; ^{1}H-NMR ($CDCl_3$) δ 6.55 (1H, t like, J = 3.0 Hz), 6.41 (1H, m), 5.83 (1H, t, J = 1.0 Hz), 5.71–4.96 (3H, m), 3.70 (1H, dd, J = 5.0, 2.0 Hz), 3.51 (1H, bs), 2.00–1.76 (2H, m), 1.42–1.15 (2H, m); MS: *m/e* 172 (M^+, 28%), 143 (20), 131 (100), 129 (88). (Found: C, 82.87; H, 7.09. Calc for $C_{12}H_{12}O$: C, 83.69; H, 7.02%.) **33** was converted to **34** by filtration through deactivated Al_2O_3 (3% H_2O, 3.8 g) with benzene in a yield of 90.2% (92 mg). A soln of **35** (456 mg, 2.65 mmol) in dry acetone (500 ml) was irradiated for 1 h by means of a 100 W high-pressure Hg lamp through Pyrex. The mixture was concentrated i.v. and chromatographed over deactivated SiO_2 (10% H_2O, 5 g) with a mixture of benzene and hexane (1 : 1 v/v) to give **33** (297 mg, 65.1%) and **34** (37 mg, 8.1%).

6-*Cyanotricyclo*[5.5.0.0^{2,5}]*dodeca*-3,6,9,12-*tetraene* (**37**)

In a 30 ml flask, **34** (715.9 mg, 4.16 mmol) and ZnI_2 (catalytic amount) were placed. TMSCN (0.8 ml, 6.24 mmol) was added over 3 min. After 40 min of stirring at rt, the soln was poured into a mixture of $CHCl_3$ and cold H_2O. The aq layer was extracted three times with $CHCl_3$. The combined organic layer was washed with H_2O and brine, and dried ($MgSO_4$). The dried soln was concentrated i.v. to give an oil (1.20 g, 4.16 mmol), which was treated with $POCl_3$ (1.14 ml, 12.5 mmol) in dry pyridine (6.7 ml) for 3 h at 60–70°. After cooling, the soln was poured into a mixture of ether and cold H_2O. The aq layer was extracted four times with ether. The combined organic layer was washed with dil HCl, H_2O, sat $NaHCO_3$ aq, and brine, and dried ($MgSO_4$). The dried soln was concentrated to give a red oil, which was chromatographed over deactivated SiO_2 (10% H_2O, 33 g) with a mixture of benzene and hexane (1 : 1 v/v) to yield **37** (114.5 mg, 15.2%) and **9** (14 mg, 1.6%). **37** pale orange oil; b.p. 50°/0.3 mm Hg; IR (neat, cm^{-1}) 2210, 1582, ^{1}H-NMR ($CDCl_3$) δ 6.33 (1H, d, J = 2.5 Hz), 6.13 (1H, d, J = 2.5 Hz), 6.05–5.69 (3H, m), 3.78 (2H, bs), 3.28 (2H, d, J = 4.3 Hz), 2.95 (2H, t, J = 6.0 Hz); MS: *m/e* 181 (M^+, 76%), 180 (60), 166 (82), 153 (100). (Found: C, 85.67; H, 6.07; N, 7.69. Calc for $C_{13}H_{11}N$: C, 86.16; H, 6.12; N, 7.73%.)

6-*Cyanotricyclo*[5.5.0.0^{2,5}]*dodeca*-3,6,8,10,12-*pentaene* (**9**)

A mixture of **37** (114.5 mg, 0.63 mmol) and DDQ (215 mg, 0.95 mmol) in dry benzene (10 ml) was heated at 60–70° for 2 h. After cooling, the mixture was filtered through a glass filter and the filtrate was washed with 5% NaOH aq, H_2O and brine. The aq layer was extracted with benzene and the benzene layer was washed and dried in a similar manner. The combined organic layer was concentrated to give an oil, which was chromatographed over deactivated Al_2O_3 (5% H_2O, 2.2 g) with deaerated hexane to afford **9** (44.5 mg, 39%); red needles; m.p. 99.5–100.5° under argon; IR (KBr, cm^{-1}) 2200, 1596, 1548, 1520; ^{1}H-NMR ($CDCl_3$) δ 6.41 (1H, dm, J = 11.1 Hz), 6.15 (1H, dd, J = 2.7, 0.4 Hz), 6.06–5.86 (5H, m), 3.78 (1H, d, J = 2.9 Hz), 3.69 (1H, bs); ^{13}C-NMR ($CDCl_3$) δ 156.8, 152.2, 141.1, 135.0, 133.4, 133.1, 131.1, 130.1, 125.8, 118.2, 100.9, 52.9, 51.1; UV (cyclohexane) λ_{max} 230 nm (13,500), 270 (6300, sh), 347 (12,900), 361 (15,500), 380 (9500), 436 (440), 466 (470), 504 (410), 546 (270), 598 (120), 658 (20); MS: *m/e* 179 (M^+, 13%), 153 (100). (Found: C, 86.64; H, 5.04; N, 7.61. Calc for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82%.)

1-*Cyanoheptalene* (**5-CN**)

In a 10 ml flask **9** (30 mg, 0.17 mmol) was placed and the flask was fitted to a horizontal quartz tube equipped with a cold trap. The tube was heated to 400° with an external electric furnace and **9** was sublimed i.v. (< 1 mm Hg) with an air bath (~60°) into the hot tube. After cooling, the pyrolysate collected in a cold trap was dissolved in deaerated benzene. The benzene soln was concentrated and the residue was crystallized from hexane to give light brown crystals of **5-CN** in quantitative yield; m.p. 33.5–35° under Ar; IR (KBr, cm^{-1}) 2202; ^{1}H-NMR ($CDCl_3$) δ 6.38–5.86 (6H, m), 5.70 (1H, d, J = 10.3 Hz), 5.44–5.20 (2H, m); ^{13}C-NMR ($CDCl_3$) δ 145.5, 138.0, 136.7, 135.9, 135.4, 135.3, 131.7, 131.5, 131.3, 130.9, 127.8, 117.8, 109.6; UV (cyclohexane) λ_{max} 267 nm (ε 21,900), 362 (4900), long tailing up to 740 nm. MS: *m/e* 179 (M^+, 41%), 153 (100), 128 (36). (Found: C, 87.19; H, 5.00; N, 7.83. Calc for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82%.)

6-*Cyano*-10,10-*dimethylbicyclo*[5.3.0]*deca*-1,3,5,7-*tetraene* (**40**)

Compound **40** was synthesized from 3-methoxy-4,4-dimethylcyclopent-2-en-1-one by a method similar to that for the synthesis of **9**; red leaflets; m.p. 71–72° under Ar; IR (KBr, cm^{-1}) 2180; ^{1}H-NMR ($CDCl_3$) δ 6.41 (1H, dd, J = 11.5, 1.3 Hz), 6.10–5.70 (3H, m), 5.63 (1H, d, J = 7.3 Hz), 2.43 (2H, s), 1.13 (6H, s); ^{13}C-NMR ($CDCl_3$) δ 164.0, 156.0, 133.4, 132.4, 129.9, 129.3, 122.9, 118.3, 97.8, 46.3, 43.0, 29.2; UV (cyclohexane) λ_{max} 230 nm (ε 12,600), 265 (5000), 333 (14,800), 347 (18,200), 364 (11,500), 428 (460), 456 (490), 494 (420), 537 (270), 586 (120), 640 (20); MS: *m/e* 183 (M^+, 100%), 168 (54), 153 (55). (Found: C, 85.21; H, 7.18; N, 7.64. Calc for $C_{13}H_{13}N$: C, 85.20; H, 7.15; N, 7.64%.)

Determination of the regio- and stereochemistry of hydroxy group in **20**

A soln of **20** (2.397 g, 11.51 mmol) in dry CH_2Cl_2 (200 ml) was treated with $POCl_3$ (2.977 g, 13.81 mmol) for 3 h with ice cooling. After 5% NaOH aq was added, the organic layer was

separated, washed twice with H_2O and dried ($MgSO_4$). The dried soln was concentrated to give a dark yellow oil, which was chromatographed over deactivated SiO_2 (10% H_2O) with benzene to yield **19** (1.75 g, 83%). Crystallization from hexane gave colorless needles (m.p. 68–70.5°).

Ketone **19** was treated with K_2CO_3 (catalytic amount) in MeOD for 5 min at rt to give deuterated **19** (quantitative yield), the NMR and MS spectra of which show that four deuteriums are introduced into **19**.

Ketone **19** was reduced in dry benzene with DIBAH at 40° for 2 h and then treated with 2 N HCl to afford the epimeric alcohol of **20** (79%), which was also derived directly from **18exo** by inversion[5b] of the OH group followed by deacetalization.

Thermolyses

All the deuterated solvents were distilled from CaH_2 under an Ar atmosphere.

Compound **7a** or **9** was dissolved in benzene-d_6 and toluene-d_8, respectively, and each soln was degassed and sealed in an NMR tube at reduced pressure. The tubes were immersed in a thermostatted, stirred oil bath and removed at appropriate intervals and immediately cooled to rt. The disappearance of the starting material and the appearance of the product were monitored by NMR integration. A soln of **6b** or **7b** in toluene-d_8 in the presence of a small amount of TMEDA was sealed in an NMR tube in a similar way and the thermolysis was carried out in the NMR cavity.

Compound **6a** was dissolved in dodecane (purified for spectroscopy) and the soln was degassed and sealed in a UV cell. The thermolysis was performed in a thermostatted, stirred oil bath. The decay rate was monitored by UV spectroscopy.

Photolyses of **6b**, **7b** *and* **9**

Compound **6b** or **7b** was dissolved in Ar-purged cyclohexane and irradiated with isolated lines of a Xe lamp in a Hitachi 650-60 fluorescence spectrophotometer. For the photoisomerizations of **6b** in excitation at 460 nm and **7b** at 400 nm, Toshiba Y-43 (>430 nm) and UV-35 (>350 nm) filters were used, respectively, to cut out shorter wavelength light. A soln of **9** in a deaerated mixture of methylcyclohexane and isopentane (1 : 1 v/v) was irradiated by means of a Ushio 450 W high-pressure Hg lamp or Ushio 6 W low-pressure Hg lamp.

The quantum yields were determined by potassium ferrioxatate actinometry in the usual way.

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