Tetrahedron Vol. 49, No. 28, pp. 6331-6348, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

Periselectivity in the Reactions of Cyclopentadienones with 8-Aryl-8-azaheptafulvenes

Anna Gamba and Remo Gandolfi*

Dipartimento di Chimica Organica, Universita' di Pavia, V.le Taramelli 10, 27100 Pavia, Italy

Roberta Oberti and Nicola Sardone

CNR, Centro di Studio per la Cristallochimica e la Cristallografia, Via Bassi 4, 27100 Pavia, Italy

(*Received in UK* 20 *April* 1993)

Key Words: Periselectivity; Cycloadditions; Dienes; Trienes

Abstract. *8-Aryl-8-azaheptafulvenes* **2** *reacted smoothly with 2,5-dimethyl-3,4-diphenylcyclopentadienone* (**1a**) *to give exo [6+4] adducts, i.e.* **4**, *as the dominant adducts along with minor amounts of endo [4+2] adducts, i.e.* **7** *and* **8**, *and trace amounts of [8+2] adducts, i.e.* **6**. *Passing from 2,5-dimethyl to 2,5-dimethoxycarbonyl-3,4-diphenylcyclopentadienone* (**1c**) *brought about an increase in reaction rate without any relevant change in selectivity. Structures of the exo [6+4] adducts* **4** *rest firmly on spectroscopic data and chemical behavior. Upon heating the [6+4] adducts* **4** *underwent a [3,3] aza-Cope rearrangement followed by [1,5-H] sigmatropic shifts to afford the [8+2] adducts* **6**. *Mechanisms of formation of all the adducts are discussed. We conclude that only concerted cycloadditions are at work in the reactions of azaheptafulvenes with cyclopentadienones*

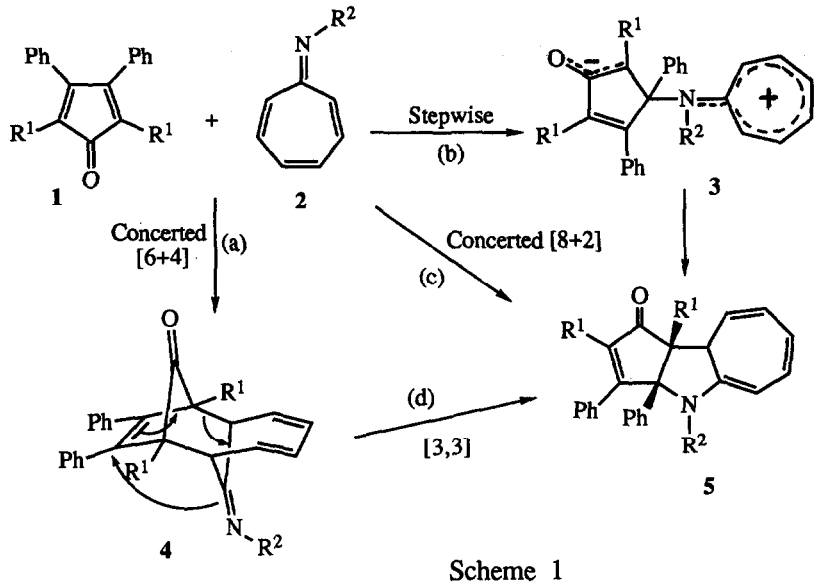
INTRODUCTION

Cyclic polyenes, in particular tropone, have played a pivotal role in the study of periselectivity in cycloadditions.[1-5] For example, tropone reacts with cyclopentadienone **1a** to give *exo* [6+4] (kinetically favored), [8+2] and *endo* [4+2] adducts in a complex reaction scheme of reversible competing concerted cycloadditions, all of them allowed by the Woodward-Hoffmann rules.[4a]

Surprisingly enough, nothing has been reported so far on the reactions of dienes with the easily attainable 8-azaheptafulvenes **2**.[6] These azapolyenes react readily with 1,3-dipoles,[7] electron-poor triple bonds[8] and heterocumulenes,[9-11] acting as formal $\pi 8$ or $\pi 2$ components. All of these cycloadditions involve an attack to the nitrogen atom of **2**. A stepwise process through a dipolar intermediate lends itself as the most reasonable mechanism for most of these reactions.

Only one example of cycloadditions involving the sole endocyclic carbon-carbon double bonds of 8-azaheptafulvenes has so far been reported. Benzyne reacts with the C_2-C_5 diene moiety of 8-trichloroacetyl-8-azaheptafulvene to give good yields of a Diels-Alder adduct.[12]

The aim of our study was to investigate whether this tendency of azaheptafulvenes to act as $\pi 8$ components in a stepwise reaction involving an attack at their nitrogen atom to give a zwitterion (i.e., **3**) [pathway (b), Scheme 1] would prevail over the well known tendency of a cycloheptatriene moiety to enter concerted cycloadditions [in particular a [6+4] cycloaddition, pathway (a) in Scheme 1] wit dienes.[3-5] It should be emphasized that pathway (b) can end up with formation of a formal [8+2] adduct (i.e., **5**)[13] which, however, can



Scheme 1

also originate from either a concerted [$\pi 8_S + \pi 2_S$] cycloaddition [pathway (c), Scheme 1] or a [3,3] sigmatropic rearrangement of the [6+4] adduct **4** [pathway (d), Scheme 1]. Thus, while the absence of [8+2] adducts in the reaction mixture proves beyond doubt that the reaction does not follow the stepwise process (b), the presence of this type of adducts, in itself, does not allow one to draw a definitive conclusion about the presence of a zwitterionic intermediate.

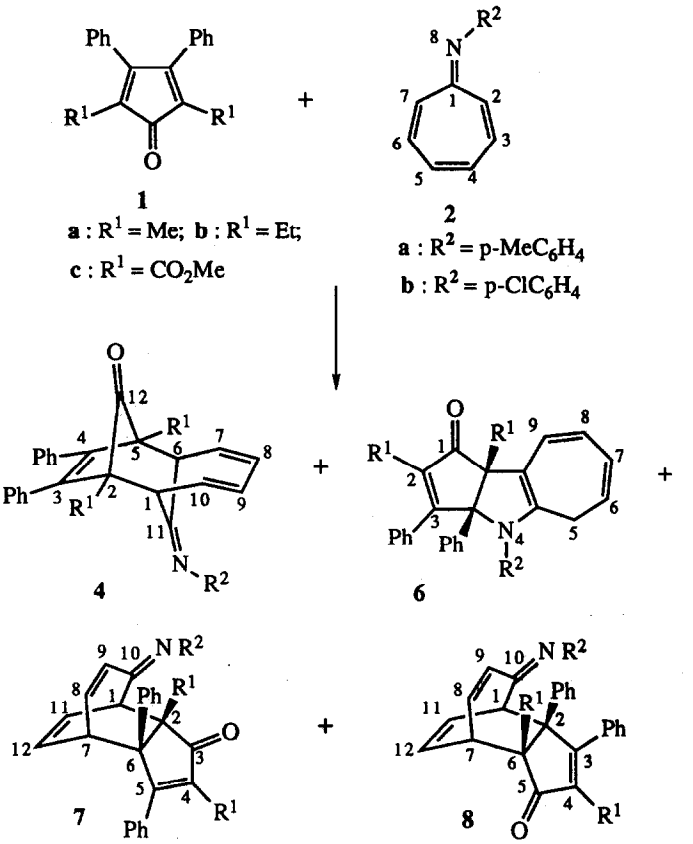
RESULTS AND DISCUSSION

Cyclopentadienone **1a** reacted smoothly with azaheptafulvene **2b** in refluxing benzene under nitrogen to give the [6+4] adduct **4d** (50%) along with minor amounts of the [4+2] adducts **7d** (≈3.5%) and **8d** (≈3.0%) and trace amounts of the yellow [8+2] adduct **6d** (≤ 2%) (Scheme 2). Likewise the reaction of **1a** and **1b**, respectively, with **2a** led to **4a** (45%) and **4b** (50%), respectively, as the highly dominant products once again accompanied by compounds **6-8** as minor products. Then we studied the reaction of the electron poor **1c** (R^1 = COOMe) with both **2a** and **2b**. We reasoned that the presence of two methoxycarbonyl groups should stabilize the anionic moiety of the dipolar intermediate **3** and make the reaction pathway involving this intermediate [i.e., (b) in Scheme 1] show it up clearly in the reaction of **1c** with compounds **2**. Consequently an increase in the yield of the [8+2] adduct **6** was anticipated. However, once again, the only products formed in relevant amounts were the [6+4] adducts, i.e. **4c** (61%) and **4e** (51%), respectively, and only trace amounts of **6c** and **6e** were detected.

Relative reaction rates suggest that in the reactions of compounds **1** with compounds **2** and tropone, respectively, cyclopentadienones act as electron acceptors and the triene derivatives as electron donors. In fact, **1c** reacted with **2a** ≈ 9 times as fast as the electron-richer **1b** as shown by a competition reaction of **2a** with an excess mixture of **1b** and **1c**. Likewise tropone reacted with **1c** 4.5 times as fast as with **1b**.

Competition reactions also showed that azaheptafulvenes enter a [6+4] reaction with cyclopentadienones more slowly than tropone (e.g., in the reaction with **1c** tropone was ≈ 8 times as reactive as **2a** and only the adduct to tropone could be isolated in a competition reaction of **1b** with a mixture of **2a** and of tropone).

Structures of the [6+4] adducts **4** rest firmly on spectroscopic [e.g., ^{1}H NMR of **4a**: δ($CDCl_3$) 1.06, 1.18 and 2.33 (three s, Me), 3.80 (m, H-1 and H-6), 5.70 and 5.91 (two m, H-7 and H-10), 6.12 (m, H-8 and H-9)]



a : R^1 = Me; **b** : R^1 = Et; **c** : R^1 = CO_2Me

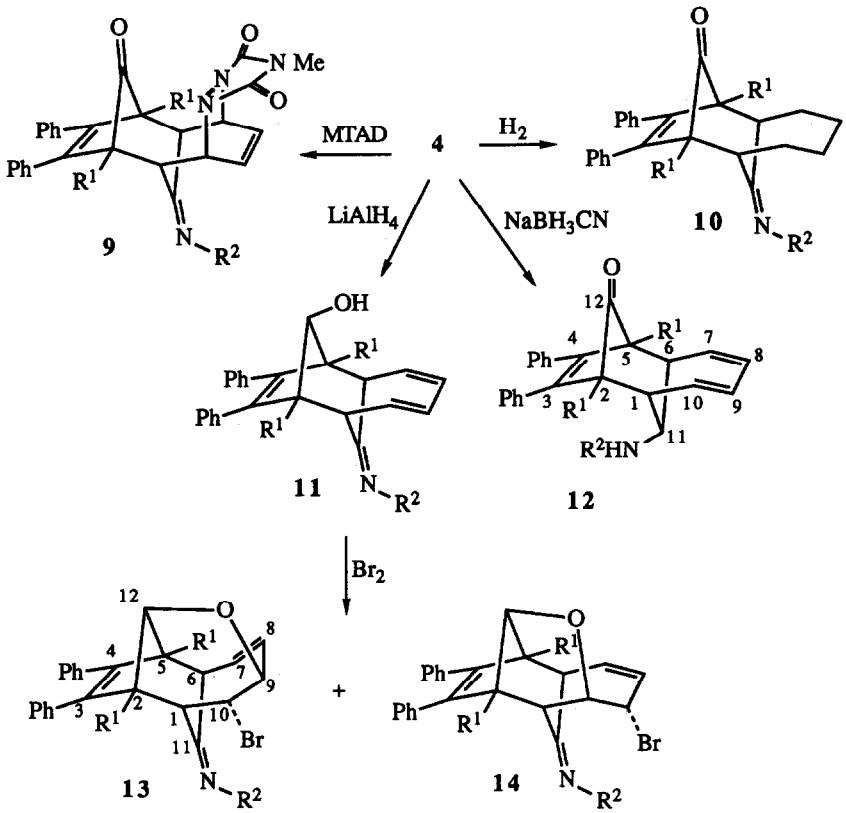
a : R^2 = p-MeC_6H_4; **b** : R^2 = p-ClC_6H_4

a : R^1 = Me, R^2 = p-MeC_6H_4; **b** : R^1 = Et, R^2 = p-MeC_6H_4; **c** : R^1 = CO_2Me, R^2 = p-MeC_6H_4; **d** : R^1 = Me, R^2 = p-ClC_6H_4; **e** : R^1 = CO_2Me, R^2 = p-ClC_6H_4

Scheme 2

and chemical data (Scheme 3).[14] Catalytic hydrogenation of **4a** in the presence of Pd/C led to the tetrahydro derivative **10a** while the reaction of **4a** with N-methyltriazolinedione (MTAD) produced the Diels-Alder adduct **9a**. Even if the reaction of **4a** with MTAD takes place at room temperature, compound **4a** does not react easily as a diene. For example, no adducts could be detected in the reaction of **4a** with tetracyanoethene in benzene at r.t. after a week. The carbon-oxygen double bond and the carbon-nitrogen double bond of **4a** (IR ν_{max}: 1758 and 1650 cm^{-1}, respectively) could be selectively reduced with $LiAlH_4$ and $NaBH_3CN$, respectively, to give **11a** [IR ν_{max}: 3558, 3350 (broad) and 1655 cm^{-1}) and **12a** (IR ν_{max}: 3415 and 1755 cm^{-1}) in almost quantitative yields. All the above reactions are 100% diastereoselective, most probably, as a result of steric control. However, face selectivity in the reactions with MTAD and $NaBH_3CN$ could not be established. Thus, the proposed structures, i.e. **9a** and **12a** , are tentative.

The structure of alcohols **11** and, consequently, the exo nature of the [6+4] adducts **4** could easily be demonstrated by treating alcohol **11d** with bromine to give a mixture of two bromoethers, i.e. **13d** and **14d** (Scheme 3). This very same reaction was successfully used by Houk to prove the exo nature of the [6+4] adducts

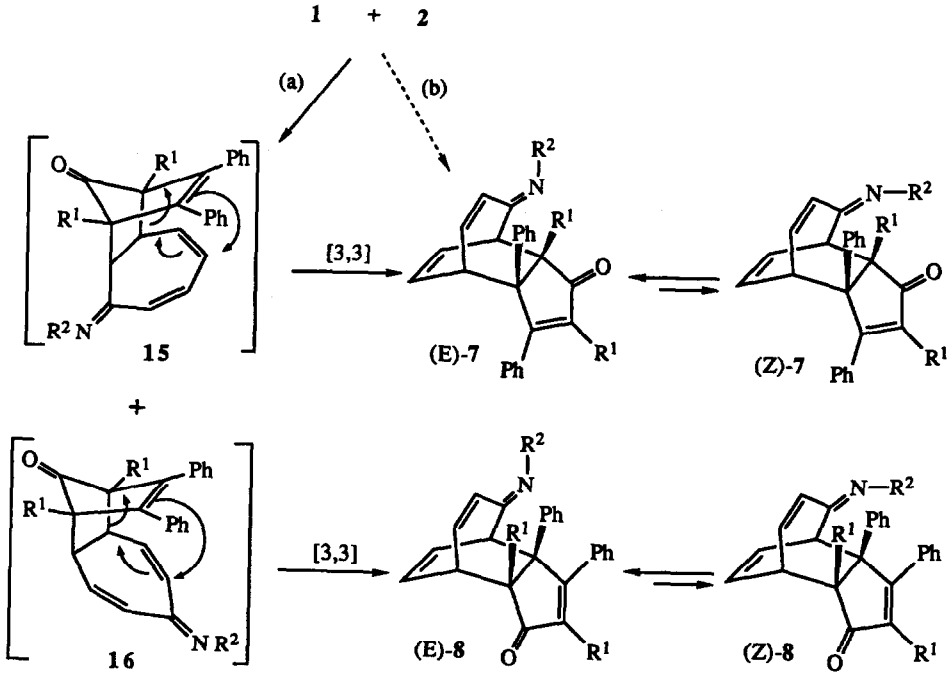


a - **e** as in Scheme 2

Scheme 3

of **1a** to tropone and cycloheptatriene, respectively.[4a] The structure of **13d** and **14d** was established by ^1H NMR and ^{13}C NMR spectra, ^1H-^{13}C heterocorrelated spectra and LIS experiments (see Experimental).

As far as the [4+2] adducts, i.e. **7** and **8**, are concerned they exhibited very similar ^1H NMR and IR spectra. The presence of an α,β-unsaturated carbonyl group as well as of a conjugated carbon-nitrogen bond in these compounds was clearly disclosed by IR spectra (**7d**, ν_{max}: 1690, 1623 and 1588 cm^{-1}; **8d**, ν_{max}: 1688, 1620 and 1592 cm^{-1}). This observation rules out the structures **15** and **16** (Scheme 4) and suggests the endo structures **7** and **8** or their exo counterparts for these adducts. The structure of **8d** was definitely established by a single crystal X-ray analysis (Figure 1). Only one of the two possible (E) and (Z) isomers (Scheme 4) is present in the solid state, namely the less congested one (E)-**8d**. However, the two isomers (E)-**8d** and (Z)-**8d** equilibrate readily at r.t. as demonstrated by the observation that they both were present [^1H NMR ($CDCl_3$), isomer ratio = 2.8] when the crystals used for X-ray analysis were dissolved in $CDCl_3$. Likewise, the ^1H NMR spectrum of a deuterochloroform solution of the other [4+2] adduct, i.e. **7d**, revealed the presence of two isomers (ratio = 1.1) whose ratio changed on passing to a deuterobenzene solution (ratio = 1.8). Unfortunately ^1H NMR data do not allow a complete unambiguous structure assignment to the [4+2] adducts, in particular they do not allow a choice between endo and exo structures. We tentatively advance the endo structure **7d** as the most reasonable one for this latter compound. In the reaction of tropone with **1a** the only [4+2] adduct isolated was an endo adduct with a structure of the type **7**.



Scheme 4

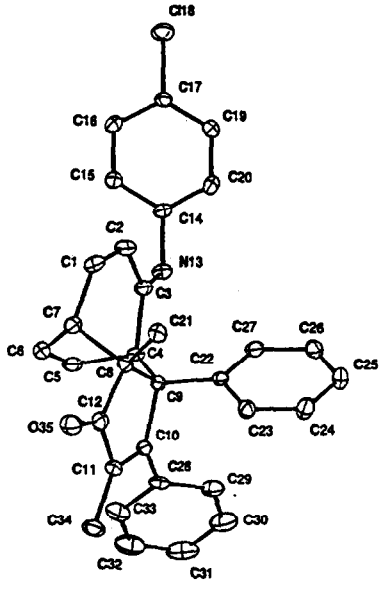


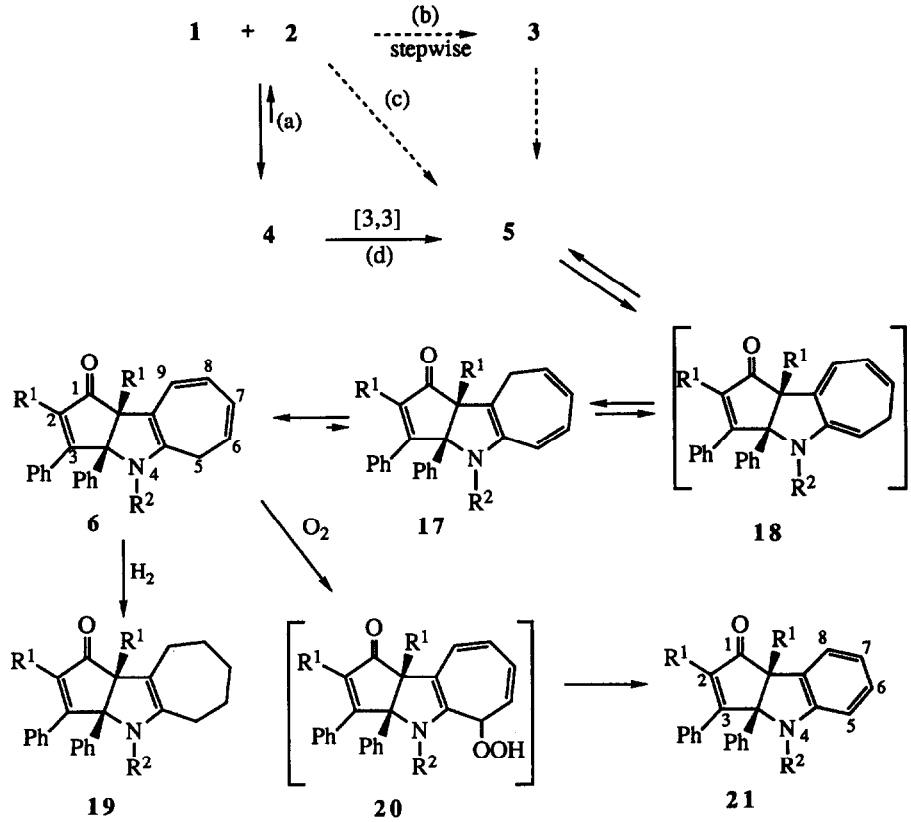
Figure 1. A perspective view of (E)-**8d** showing the numbering scheme used in Table 1-3.

Compounds **7** and **8** can originate either directly from two regioisomeric transition states in which **2** behaves as the $\pi 4$ component and cyclopentadienone as the $\pi 2$ component [pathway (b), Scheme 4] or from the other way round in which **2** acts as the $\pi 2$ component using either its 2,3 or 4,5 carbon-carbon double bond to give **15** and **16**, respectively, which then rearranges through a [3,3] Cope rearrangement to **7** and **8** [pathway (a), Scheme 4]. It is well known that adduct of the type **15**[15] and **16**[16] can undergo a Cope rearrangement under very mild conditions (for example in acetone at r.t.[15] or in refluxing chloroform[16]).

Structure **6** was assigned to the yellow products, detected in trace amounts in all the reactions, on the basis of analytical and spectroscopic data as well as chemical reactions. In fact, the IR spectra (e.g., **6a**: ν_{max} = 1704 and 1609 cm^{-1}) of these compounds are consistent with the presence in them of a cyclopentenone moiety. This observation was confirmed by ^{13}C NMR spectra in which i) the hydrogens of both the methyl groups of this moiety [resonating at δ ($CDCl_3$) 0.70 and 1.88, respectively, in **6a**] are coupled to the carbonyl carbon ii) the lower field of these two methyl groups is also coupled to two vinyl carbons [i.e., C-2 and C-3 at δ ($CDCl_3$) 140.1 and 161.0, respectively, in **6a**] while the other is also coupled to two saturated carbons [i.e., C-3a and C-9b at δ ($CDCl_3$) 87.4 and 65.2, respectively, in **6a**]. ^1H NMR spectra of the yellow products, in agreement with the presence in them of a 1,2 disubstituted cycloheptatriene system, displayed at low fields the complex multiplets of four olefinic protons [**6a**: $\delta(CDCl_3)$ 5.12 (m, H-6), 6.18 (m, H-7 and H-8), 6.52 (m, H-9)] and at high fields a typical AB pattern of an ABX system [**6a**: $\delta(CDCl_3)$ 2.62 (dd, H-5, $J_{5,5'}$ = 14.5 and $J_{5,6}$ = 6.4 Hz), 2.85 (dd, H-5', $J_{5',6}$ = 6.9 Hz)] that can be safely attributed to the protons of a methylene group coupled to only one vinyl proton. Compound **6d** was catalytically hydrogenated to the tetrahydro derivative **19d** in which the two tetrasubstituted double bonds were left unchanged. These observations are in accord not only with structure **6** but also with structure **17**. NOESY experiments with **6a** (R^2 = p-MeC_6H_4) showed an NOE between the methylene protons and the aromatic protons (in ortho position with respect to nitrogen atom) of the p-tolyl group thus supporting structure **6**. We do not have any explanation for the higher stability of **6** than **17** but NMR spectra show the presence of only one isomer. Compounds **6** derive from compounds **5** through a series of suprafacial [1,5-H] sigmatropic shifts (Scheme 5). These shifts take place readily in seven membered rings.[17] Formation of compounds **6** from compounds **4** (see below) provides a further proof of the structure of the formers, in particular as far as heavy atom connectivity is concerned.

A slow evaporation of a solution of compound **6a** in toluene gave rise to formation of a new compound, i.e. **21a**, in good yield, along with minor amounts of formyl derivatives of **21a** (see Experimental). ^1H NMR spectrum of **21a** displayed only signals attributable to aromatic protons (aside from the three methyl singlets) while its IR spectrum still exhibited the absorption of a conjugated carbonyl group (e.g., **21a**: ν_{max} = 1690 and 1605 cm^{-1}). These findings along with elemental analysis, mass spectral data and ^{13}C NMR spectrum clearly showed that transformation **6a**→**21a** was the result of the loss of the methylene group from **6a**. An oxidation of the cycloheptatriene moiety by triplet oxygen to afford a cycloheptatrienyl hydroperoxide derivative (i.e., compound **20a**, Scheme 5) which then decomposes through its norcaradiene isomer to benzene, carbon monoxide and water provides a convincing mechanism for formation of **21a**. In fact, in the absence of oxygen this reaction did not take place either at r.t. or upon heating at ≥110°. The decomposition of cycloheptatrienyl hydroperoxide to benzene, carbon monoxide and benzaldehyde is a known reaction.[18] Also compounds **6c,d** were transformed into **21c,d** under similar conditions.

At this point the question arises whether formation of compounds **5**, precursors of compounds **6**, involves an [8+2] cycloaddition [either stepwise or concerted, pathway (b) and (c), respectively, in Scheme 5] or an aza-Cope rearrangement of the [6+4] adducts **4** [pathway (d)]. Heating a solution of **4a** in toluene at 110° led to rearrangement of **4a** to **6a** accompanied by cycloreversion reaction with formation of very small amounts of **2a** and **1a**. In refluxing benzene, i.e. under the cycloaddition conditions, the rearrangement **4a**→**6a** took place very slowly. However, compounds **6** were obtained in good yields when the reaction of cyclopentadienones with azaheptafulvenes was carried out in refluxing toluene. The presence of cycloreversion products during the transformation of **4a** into **6a** can lead one to argue that there is not any direct rearrangement of **4a** to **5a** [(d), Scheme 5)] but that actually all the reaction goes through a cycloreversion followed by an [8+2] cycloaddition [(a)



a - e as in Scheme 2

Scheme 5

+ (b) or (a) + (c), Scheme 5]. In order to disprove this possibility we carried out the rearrangement **4a**→**6a** in the presence of N-phenylmaleimide. N-phenylmaleimide reacts very readily with cyclopentadienone **1a** to give the related Diels-Alder adducts which is stable and, in particular, does not cyclorevert at 110° in toluene. Consequently, should the cycloreversion-cycloaddition pathway be adhered to exclusively in the transformation **4a**→**6a**, formation of **6a** should be suppressed in the presence of N-phenylmaleimide. Actually, formation of **6a** from **4a** was not suppressed by the presence of N-phenylmaleimide but it was still the dominant reaction. All these findings force us to conclude that the [3,3] aza-Cope rearrangement is the reaction mechanism which most satisfactorily accounts for the isomerization of **4a** to **6a**. Moreover, it is also reasonable to assume that the small amounts of **6a** isolated from the cycloaddition reaction are formed through the same reaction pathway. The results obtained for **4a** were confirmed by similar experiments with **4c** and **4d**.

The behavior of azaheptafulvenes in their reaction with cyclopentadienones conforms to that of tropone thus providing further convincing evidence that the cycloheptatriene system has a very high propensity to act as a $\pi 6$ component in cycloaddition reactions. Moreover, our results strongly suggest that also in the reaction of tropone formal [8+2] adducts are the result of a [6+4] cycloaddition followed by a Claisen rearrangement[3e] and not of a [8+2], either stepwise or concerted, reaction.[4a]

The only relevant difference between azaheptafulvenes and tropone is the presence in the reactions of the former of two [4+2] adducts, i.e. **7** and **8**, in similar amounts. Adduct of the type **8** is missing in the reaction of

tropone. It is difficult to explain these observations if one chooses a direct Diels-Alder cycloaddition [path (b), Scheme 4] as the mechanism of formation of **7** and **8**. As far as orbital interactions are concerned there is not any reason to anticipate either formation of only one regioisomer in the reaction of tropone or a change in selectivity on passing from tropone to azaheptafulvenes. In fact, the coefficients of the frontier MOs of tropone are very similar to those of azaheptafulvenes [MNDO calculations. 8-Methyl-8-azaheptafulvene, HO: ε = -8.71 eV (c_1 = 0.14, c_2 = -0.39, c_3 = -0.25, c_4 = 0.41, c_5 = 0.38, c_6 = -0.31, c_7 = -0.40, c_8 = 0.42); LU: ε = -0.58 eV (c_1 = -0.05, c_2 = -0.48, c_3 = 0.35, c_4 = 0.43, c_5 = -0.49, c_6 = -0.20, c_7 = 0.42, c_8 = 0.05). NLU: ε = -0.15 eV (c_1 = 0.44, c_2 = 0.19, c_3 = -0.41, c_4 = -0.22, c_5 = 0.07, c_6 = -0.45, c_7 = 0.31, c_8 = -0.48). Tropone, HO: ε = -9.25 eV (c_1 = -0.01, c_2 = -0.43, c_3 = -0.25, c_4 = 0.44, c_5 = 0.44, c_6 = -0.25, c_7 = -0.43, c_8 = 0.33); LU: ε = -0.80 eV (c_1 = 0.00, c_2 = -0.45, c_3 = 0.27, c_4 = 0.47, c_5 = -0.47, c_6 = -0.27, c_7 = 0.45, c_8 = 0.00); NLU: ε = -0.31 eV (c_1 = 0.46, c_2 = 0.26, c_3 = -0.46, c_4 = 0.16, c_5 = 0.16, c_6 = -0.46, c_7 = 0.26, c_8 = -0.42)].[19,20] Moreover, the coefficients at position 2 and 5 in either HOMO or LUMO of azaheptafulvenes as well as of tropone are almost the same. This means that both FO interactions give rise to a very similar stabilization of the two TSs leading to **7** and **8**, respectively. Thus, in contrast with experimental data, a mixture of **7** and **8** is predicted for the reactions of both polyenes. Even more, a clear-cut dominance of **8** should be anticipated if one takes into account that in the TS which gives rise to **7** there is a much worse dipole-dipole alignment as compared to that in the TS which leads to **8**.

On the basis of mechanism (a) (Scheme 4) dominance of adducts of the type **7** in the reaction of tropone can easily be explained as a result of the higher loss of conjugation which characterizes formation of **16** as compared to that of **15** (which is obviously already present in the related TS). In the reaction of azaheptafulvenes, as compared to that of tropone, there is an increase in steric congestion of the attack that leads to **15** whereas the N-Ar group of azaheptafulvene is too far from the reacting double bond to significantly enhance the steric hindrance of the attack which gives rise to **16.** Thus, in the reaction of azaheptafulvenes steric effects counteract electronic ones leading to formation of mixtures. In our opinion the very same steric effects, which in the reaction of azaheptafulvenes slow down the rate of formation not only of **15** but also of **4**, may be held responsible for the lower reactivity of these polyenes as compared to tropone.

CONCLUSION

Azaheptafulvenes react with cyclopentadienones to give, as primary products, [6+4] (dominant) and [4+2] adducts. These products are formed in concerted reactions in which azaheptafulvenes act as π6 or π2 components and the cyclopentadienones always as π4 components. We suggest that the same interpretation should be given to the results obtained previously by other authors for the reaction of tropone. The [8+2] adducts, in particular, originate neither from a concerted nor from a stepwise [8+2] cycloaddition but are the result of a [3,3] sigmatropic rearrangement of the [6+4] adducts. The reactions described above provide a rare example of a reaction of azaheptafulvenes in which their nitrogen atom is not involved in the primary processes.

EXPERIMENTAL

Melting points are uncorrected. Elemental analyses were made on a Carlo Erba CHN analyser, model 1106. Infrared spectra were recorded as either Nujol suspensions or films on a Perkin-Elmer 157 spectrophotometer. NMR spectra were recorded on a Bruker AE 300 (at 300 MHz) spectrometers tetramethylsilane as internal standard for $CDCl_3$ solutions unless otherwise stated. Protons were correlated by decoupling experiments. In the case of the two bromoethers **13d** and **14d** the signals of the ^{1}H NMR spectrum were assigned on the basis of ^{1}H-^{13}C correlated spectra. ^{1}H NMR spectra were evaluated as first order spectra. The signals of aromatic protons of the phenyl rings are not, as a rule, reported. In compounds **4**, **9**, **10**, and **11** hydrogens and carbons at positions 4, 5, 6, 7 and 8 resonate at different fields from the related hydrogens and carbons at at positions 3, 2, 1, 10 and 9 owing to the absence of a symmetry plane. However, it is not possible to reliably know which set of

nuclei is syn to the R^2 group and which is anti. Thus, when an assignement for the resonances of these nuclei is found in the text [e.g., 52.6 (d, C-1), 59.4 (d, C-6) in **4a**] it should not be considered as a true assignment [e.g., it must be read 52.6 (d, C-1 or C-6), 59.4 (d, C-6 or C-1)]. Lanthanide-induced shifts (LIS) were measured in $CDCl_3$ solutions with $Eu(fod)_3$ as shift reagent. ΔM values (shifts for the 1:1 mole ratio) were evaluated by extrapolation from measurements carried out in the range of 1:0.03 to 1:0.2 mole ratios of substrate and shift reagent. Mass spectra were measured on a Finnigan MATT 8222 using electron impact mode. Thin-layer chromatograms were done on plates precoated with silicagel 60 GF_{254} (Merck). Spots were visualized either by spraying with 3% chromic oxide in sulphuric acid (50%) followed by heating at 120 °C or under UV light. Column chromatography was performed with Silicagel 60 (70-230 mesh) Merck eluting with cyclohexane-ethyl acetate or benzene-cyclohexane mixtures. Cyclopentadienones **1b**[21] and **1c**[22] and azaheptafulvenes[6] were prepared according to literature procedures. Cyclopentadienones **1b** and **1c** are stable as monomer whereas **1a** (commercially available) is stable as a dimer which heated in solution readily produces the monomer.

*Reactions of cyclopentadienones **1a, 1b and 1c**, respectively, with azaheptafulvene **2a**.*

A solution of **1a** (0.986 g, 3.79 mmol) and equimolar amounts of **2a** (0.740 g) in benzene (20 mL) was heated at 80 °C for 96 h under argon in the dark. Evaporation of the solvent and column chromatography (cyclohexane/AcOEt, 9:1, as eluant) afforded the following compound in order of elution: **6a** (≈ 2%, contaminated by unreacted cyclopentadienone), **4a** (0.770 g, 45%), **8a** (34 mg, 2.0%) and **7a** (43 mg, 2.5%).

The reaction of **1b** with **2a** was carried out under similar conditions and led to 50% yield of **4b** together with minor amounts of **6b** and an inseparable mixture of **7b** and **8b** (5%).

The reaction of **1c** (0.178 g, 0.51 mmol) with equimolar amounts of **2a** (0.100 g) was conducted in refluxing benzene (10 mL) under argon for 24 h. The dominant reaction product [i.e., **4c**, 0.170 g, (61%)] was isolated by column chromatography (cyclohexane/AcOEt, 4:1, as eluant).

4a: colorless prisms from ethanol, mp 185-187 °C; IR ν_{max} 1758 and 1650 cm^{-1}; ^1H NMR δ 1.06 (s, Me), 1.18 (s, Me), 2.33 (s, Me), 3.80 (m, H-1 and H-6), 5.70 and 5.91 (two m, H-7 and H-10), 6.12 (m, H-8 and H-9), 6.62 and 7.08 (two bd, aromatic protons of the tolyl group); ^{13}C NMR δ 13.2 (q, Me), 13.4 (q, Me), 20.8 (q, Me), 52.6 (d, C-1), 57.4 (s, C-2), 58.4 (s, C-5), 59.4 (d, C-6), 167.0 (s, C=N), 208.6 (s, C=O). Anal. Calcd for $C_{33}H_{29}NO$: C, 87.0; H, 6.4; N 3.1. Found: C, 86.7; H, 6.3; N, 3.2.

6a: orange-yellow prisms from petrol ether, mp 182-183 °C; IR ν_{max} 1704 and 1609 cm^{-1}; ^1H NMR δ 0.70 (s, Me at position 9b), 1.88 (s, Me at position 2), 2.09 (s, Me in the p-tolyl group), 2.62 (dd, H-5, $J_{5,6}$ = 6.5 Hz and $J_{5,5'}$ = 14.5 Hz), 2.84 (dd, H-5', $J_{5',6}$ = 7.0 Hz), 5.12 (m, H-6), 6.18 (m, H-7 and H-8), 6.37 (bd, 2H, protons ortho to the nitrogen atom in the tolyl ring), 6.52 (m, H-9), 6.60 (bd, 2H, protons meta to the nitrogen atom in the tolyl ring), 6.90-7.40 (aromatic protons); ^{13}C NMR δ 9.9 (q, Me at position 2), 18.5 (q, Me at position 9b), 20.5 (q, Me in the p-tolyl group), 26.6 (t, CH_2) 65.2 (s, C-9b), 87.4 (s, C-3a), 116.5 (d, C-6), 116.6 (s, C-9a), 122.9 (d, C-8), 125.4 (d, C-9), 125.6 and 127.5 (d, carbons ortho and meta to the nitrogen atom, respectively, in the p-tolyl group), from 127.6 to 129.3 (six signals, olefinic and aromatic CH), 133.4, 135.5, 136.8, 137.7, 138.2 (s, substituted olefinic and aromatic carbons), 140.1 (s, C-2), 161.0 (s, C-3), 207.5 (s, C=O); mass spectrum (EI, 75 eV) m/z 455 (100%, $M^{+\cdot}$), 441 (9%), 194 (31%). Anal. Found: C, 87.2; H, 6.6; N, 3.1.

7a: slightly yellow prisms from methanol, mp 232-235 °C; IR ν_{max} 1691, 1625 and 1596 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.06, 1.84 and 2.28 (three s, Me), 3.33 (ddd, H-7, $J_{7,8}$ = 8.4 Hz, $J_{7,11}$ = 1.1 Hz and $J_{7,12}$ = 7.0 Hz), 3.61 (m, H-1), 5.81 (dd, H-9, $J_{1,9}$ = 2.0 Hz and $J_{8,9}$ = 11.1 Hz), 6.15 (ddd, H-11, $J_{1,11}$ = 7.2 Hz and $J_{11,12}$ = 8.3 Hz), 6.26 (ddd, H-12, $J_{1,12}$ = 1.3 Hz), 6.71 (dd, H-8) for (E)-**7a** and 0.88, 1.73 and 2.32 (three s, Me), 3.49 (ddd, H-7, $J_{7,8}$ = 8.4 Hz, $J_{7,11}$ = 1.0 Hz and $J_{7,12}$ = 7.0 Hz), 3.61 (m, H-1), 5.87 (ddd, H-11, $J_{1,11}$ = 7.2 Hz and $J_{11,12}$ = 8.3 Hz), 6.01 (dd, H-9, $J_{1,9}$ = 2.2 Hz and $J_{8,9}$ = 11.1 Hz), 6.22 (ddd, H-12, $J_{1,12}$ = 1.1 Hz), 6.84 (dd, H-8) for (Z)-**7a**. Ratio (E)-**7a**/(Z)-**7a** = 55:45. In deuterobenzene the following chemical shifts were observed: δ 1.31, 1.83 and 2.12 (Me), 2.96 (H-7), 4.09 (H-1), 5.81 (H-9), 5.94 (H-11 and H-12), 6.08 (H-8) for (E)-**7a** and δ 1.22, 1.71 and 2.08 (Me), 3.06 (H-7), 4.01 (H-1), 5.71 (H-11), 5.94 (H-12), 6.17 (H-

9), 6.27 (H-8) for (Z)-**7a**. Ratio (E)-**7a**/(Z)-**7a** = 60:40. It was assumed that (E)-**7a** is more stable than (Z)-**7a** in solution too. Anal. Found : C, 87.3; H, 6.3; N, 3.0.

8a: glassy solid; ^{1}H NMR δ ($CDCl_3$) 1.17, 1.75 and 2.23 (three s, Me), 3.22 (dddd, H-7, $J_{7,9}$ = 0.5 Hz, $J_{7,8}$ = 8.4 Hz, $J_{7,11}$ = 1.2 Hz and $J_{7,12}$ = 7.0 Hz), 3.87 (ddd, H-1, $J_{1,9}$ = 1.5 Hz, $J_{1,11}$ = 7.2 Hz and $J_{1,12}$ = 1.1 Hz), 5.89 (ddd, H-9, $J_{8,9}$ = 11.0 Hz), 6.08 (ddd, H-11, $J_{11,12}$ = 8.4 Hz), 6.25 (ddd, H-12), 6.41 (dd, H-8) for (E)-**8a**. The presence of (Z)-**8a** could be inferred from signals at δ 3.73 (ddd, J = 7.2, 1.5 and 1.2 Hz) and 5.54 (ddd, J = 8.3, 7.2 and 1.2) attributable to H-7 and H-11 of this isomer [ratio (E)-**8a**/(Z)-**8a** = 4:1]. Anal. Found: C, 86.8; H, 6.1; N, 2.9.

4b: colorless needles from methanol, mp 163-164 °C; IR ν_{max} 1758 and 1645 cm^{-1}; ^{1}H NMR (80 MHz) δ 0.52 and 0.70 (two t, Me), 0.90 - 2.0 (m, 4 H, CH_2), 2.34 (s, Me), 3.90 (m, H-1 and H-6), 5.5 - 6.35 (m, 4 H, H-7 - H-10). Anal. Calcd for $C_{35}H_{33}NO$: C, 86.9; H, 6.9; N, 2.9. Found: C, 86.8; H, 7.0; N, 3.1.

6b: yellow glassy solid; ^{1}H NMR (80 MHz) δ 0.30 (bt, Me), 0.87 (m, Me and CH_2), 2.05 (s, Me), 2.10 (m, CH_2), 2.60 (dd, H-5, $J_{5,6}$ = 6.0 Hz and $J_{5,5'}$ = 14.0 Hz), 3.10 (dd, H-5', $J_{5',6}$ = 7.5 Hz), 5.15 (m, H-6), 6.0 - 6.7 (H-7, H-8, H-9 and protons of the tolyl ring). Anal. Found: C, 86.7; H, 6.8; N, 3.1.

7b + **8b** : colorless powder; IR ν_{max} 1695, 1645 and 1650 cm^{-1}; this mixture could be enriched in **7b** by crystallization from methanol [(E)-**7b**/(Z)-**7b** = 7:3). (E)-**7b**:^{1}H NMR δ 1.03 (t, Me), 2.29 (s, Me), 3.22 (ddd, H-7, $J_{7,8}$ = 8.5 Hz, $J_{7,11}$ = 1.1 Hz and $J_{7,12}$ = 6.9 Hz), 3.99 (ddd, H-1, $J_{1,9}$ = 1.9 Hz, $J_{1,11}$ = 7.2 Hz and $J_{1,12}$ = 1.5 Hz), 5.88 (dd, H-9, $J_{8,9}$ = 11.2 Hz), 6.19 (ddd, H-11, $J_{11,12}$ = 8.3 Hz), 6.27 (ddd, H-12), 6.68 (dd, H-8). (Z)-**7b**: ^{1}H NMR δ 0.68 (t, Me), 0.95 (t, Me), 3.29 (ddd, H-7, $J_{7,8}$ = 8.4 Hz, $J_{7,11}$ = 1.0 Hz and $J_{7,12}$ = 7.0 Hz), 3.79 (ddd, H-1, $J_{1,9}$ = 2.1 Hz, $J_{1,11}$ = 7.2 Hz and $J_{1,12}$ = 1.0 Hz), 6.01 (ddd, H-11, $J_{11,12}$ = 8.3 Hz), 6.10 (dd, H-9, $J_{8,9}$ = 11.1 Hz), 6.22 (ddd, H-12), 6.84 (dd, H-8). Anal. Found: C, 86.6; H, 7.0; N, 3.0

4c: colorless needles from methanol, mp 165 °C dec; IR ν_{max} 1775, 1740 and 1660 cm^{-1}; ^{1}H NMR δ 2.29 (s, Me), 3.52 and 3.71 (two s, OMe), 4.39 (dd, H-1, $J_{1,6}$ = 4.5 Hz and $J_{1,10}$ = 7.8 Hz), 4.47 (dd, H-6, $J_{6,7}$ = 6.9 Hz), 6.11 (m, 3 H, H-7 - H-9), 6.21 (m, H-10), 6.53 and 7.04 (two bd, aromatic protons of the tolyl group). Anal. Calcd for $C_{35}H_{29}NO_5$: C, 77.3; H, 5.4; N, 2.6. Found: C, 77.4; H, 5.5; N, 2.5.

Reactions of cyclopentadienones ***1a*** *and* ***1c****, respectively, with azaheptafulvene* ***2b****.*

A solution of **2b** (0.800 g, 3.71 mmol) and equimolar amounts of **1a** (0.962 g) in anhydrous benzene (20 mL) was heated at 80 °C for 96 h under nitrogen in the dark. The solvent was evaporated and the brown oily residue was treated with 10 mL of cyclohexane/AcOEt (9:1). Most part of **4d** (0.570 g) precipitated as colorless prisms and was filtered off. The mother liquors were column chromatographed to give in order of elution **6d** (30 mg, 2%), **4d** (0.31 g, total yield 50%), and a mixture of **7d**+**8d** (115 mg, 6.5%). This mixture was separated by fractional crystallization from cyclohexane/EtOH to give pure **7d** (60 mg) as slightly yellow needles and **8d** (50 mg) as slightly yellow prisms.

In the case of the reaction of **2b** (100 mg, 0.46 mmol) with equimolar amounts of **1c** (162 mg) in benzene (5 mL) at 80 °C under argon in the dark, heating was interrupted after 24 h. TLC analysis (cyclohexane/AcOEt, 4:1) showed the presence of only one major adduct, of trace amounts of an orange-red compound and minor amounts of other products. Only the dominant product (i.e., **4e**) was isolated in a pure state by column chromatography (133 mg, 51%).

4d: colorless prisms from cyclohexane, mp 188-190 °C; IR ν_{max} 1755 and 1650 cm^{-1}; ^{1}H NMR δ 1.08 and 1.19 (two s, Me), 3.76 (m, H-1 and H-6), 5.68 and 5.91 (two m, H-7 and H-10), 6.01 (m, H-8 and H-9); mass spectrum (EI, 75 eV) m/z 477 (26%, M^+), 475 (64%, $M^{+\cdot}$), 260 (50%), 217 (32%), 215 (78%), 78 (100%). Anal. Calcd for $C_{32}H_{26}ClNO$: C, 80.7; H, 5.5; N 2.9. Found: C, 80.7; H, 5.7; N, 2.9.

6d: orange-yellow prisms from petrol ether, mp 189-192 °C; IR ν_{max} 1708, 1610 and 1590 cm^{-1}; ^{1}H NMR (80 MHz) δ (C_6D_6) 0.93 (s, Me), 1.83 (s, Me), 2.54 (dd, H-5, $J_{5,5'}$ = 14.7 Hz and $J_{5,6}$ = 6.8 Hz), 2.75 (dd, H-5', $J_{5',6}$ = 7.5 Hz), 5.10 (m, H-6), 6.10-6.45 (m, H-7, H-8 and H-9), 6.27 and 6.63 (two bd, protons of the p-chlorophenyl group) 6.95-7.45 (aromatic protons) ; ^{13}C NMR (80 MHz) δ 10.1 (q, Me), 19.3 (q, Me), 27.2 (t, C-5), 66.1 (s, C-9b), 88.4 (s, C-3a), 117.2 (d, C-6), 119.1 (s, C-9a), 124.5-130.5 (olefinic and aromatic CH

and CCl), 136.0, 136.4, 138.3 and 141.4 (s, substituted olefinic and aromatic carbons), 140.4 (s, C-2), 160.7 (s, C-3), 205.9 (s, CO); mass spectrum (EI, 75 eV) m/z 477 (40%, $M^{+\cdot}$), 475 (100%, $M^{+\cdot}$), 463 (15%), 461 (6%), 216 (17%), 214 (44%). Found: C, 80.6; H, 5.7; N, 3.1.

7d: slightly yellow needles from cyclohexane, mp 239-240 °C; IR ν_{max} 1690, 1623 and 1588 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.98 and 1.80 (two s, Me), 3.28 (ddd, H-7, $J_{7,8}$ = 8.5 Hz, $J_{7,11}$ = 1.0 Hz and $J_{7,12}$ = 7.2 Hz), 3.53 (ddd, H-1, $J_{1,9}$ = 2.0 Hz, $J_{1,11}$ = 7.3 Hz and $J_{1,12}$ = 1.2 Hz), 5.68 (dd, H-9, $J_{8,9}$ = 11.2 Hz), 6.08 (ddd, H-11, $J_{11,12}$ = 8.3 Hz), 6.21 (ddd, H-12), 6.73 (dd, H-8) for (E)-**7d** and δ ($CDCl_3$) 0.79 and 1.70 (two s, Me), 3.34 (ddd, H-7, $J_{7,8}$ = 8.5 Hz, $J_{7,11}$ = 0.9 Hz and $J_{7,12}$ = 7.2 Hz), 3.48 (ddd, H-1, $J_{1,9}$ = 2.0 Hz, $J_{1,11}$ = 7.3 Hz and $J_{1,12}$ = 1.1 Hz), 5.78 (ddd, H-11, $J_{11,12}$ = 8.3 Hz), 5.94 (bdd, H-9, $J_{8,9}$ = 11.0 Hz), 6.18 (ddd, H-12), 6.83 (dd, H-8) for (Z)-**7d** [ratio (E)-**7d**/(Z)-**7d** = 53:47]; δ (C_6D_6) 1.22 and 1.82 (Me), 2.94 (H-7), 4.02 (H-1), 5.53 (H-9), 5.90 (H-11 and H-12), 6.07 (H-8) for (E)-**7d** and δ (C_6D_6) 1.12 and 1.72 (Me), 3.04 (H-7), 3.81 (H-1), 5.60 (H-11), 5.90 (H-12), 6.07 (H-9), 6.25 (H-8) for (Z)-**7d** [(E)-**7d**/(Z)-**7d** = 64:36); mass spectrum (EI, 75 eV) m/z 477 (25%, $M^{+\cdot}$), 475 (59%, $M^{+\cdot}$), 260 (54%), 217 (32%), 215 (100%), 78 (74%). Anal. Found: C, 80.7; H, 5.5; N, 3.2.

8d: slightly yellow prisms from methanol, mp 178-180 °C; IR ν_{max} 1688, 1620 and 1592 cm^{-1}; ^1H NMR δ (C_6D_6) 1.05 and 1.85 (two s, Me), 3.15 (dddd, H-7, $J_{7,8}$ = 8.4 Hz, $J_{7,9}$ = 0.5 Hz, $J_{7,11}$ = 1.1 Hz and $J_{7,12}$ = 7.5 Hz), 4.18 (ddd, H-1, $J_{1,9}$ = 1.8 Hz, $J_{1,11}$ = 7.5 Hz and $J_{1,12}$ = 1.1 Hz), 5.68 (dd, H-9, $J_{8,9}$ = 11.2 Hz), 5.85 (ddd, H-11, $J_{11,12}$ = 8.5 Hz), 5.93 (dd, H-8), 5.99 (ddd, H-12) for (E)-**8d** and δ (C_6D_6) 0.90 and 1.89 (two s, Me), 3.21 (ddd, H-7, $J_{7,8}$ = 8.4 Hz, $J_{7,11}$ = 1.1 Hz and $J_{7,12}$ = 7.4 Hz), 3.81 (ddd, H-1, $J_{1,9}$ = 1.8 Hz, $J_{1,11}$ = 7.5 Hz and $J_{1,12}$ = 1.0 Hz), 5.36 (ddd, H-11, $J_{11,12}$ = 8.5 Hz), ≈ 6.00 (H-12), 6.18 (dd, H-8, $J_{8,9}$ = 11.0 Hz), 5.94 (dd, H-9) for (Z)-**8d** [ratio (E)-**8d**/(Z)-**8d** = 71:29]; δ ($CDCl_3$) 1.01 and 1.84 (Me), 3.33 (H-7), 3.94 (H-1), 5.91 (H-9), 6.13 (H-11), 6.33 (H-12), 6.54 (H-8) for (E)-**8d**; as far as isomer (Z)-**8d** is concerned its presence in this solvent could be inferred by the signals at δ 3.71 (ddd, H-1) and at δ 5.65 (ddd, H-11) [ratio (E)-**8d**/(Z)-**8d** = 74:26]; mass spectrum (EI, 75 eV) m/z 477 (15%, $M^{+\cdot}$), 475 (38%, $M^{+\cdot}$), 260 (37%), 217 (49%), 215 (100%), 78 (38%). Anal. Found: C, 80.9; H, 5.5; N, 3.2.

4e: slightly yellow prisms from cyclohexane, mp 183-184 °C dec.: IR ν_{max} 1775, 1735 and 1648 cm^{-1}; ^1H NMR δ 3.52 and 3.71 (two s, OMe), 4.39 (m, H-1 and H-6),5.98, 6.12 and 6.28 (three m corresponding to 1 H, 2 H and 1 H, respectively, H-7 -H-10). Anal. Calcd for $C_{34}H_{26}ClNO_5$: C, 72.4; H, 4.6; N 2.5. Found: C, 72.7; H, 4.8; N, 2.7.

Competition reactions.

A solution of **2a** (130 mg, 0.666 mmol), tropone (72 mg, 0.679 mmol) and **1c** (116 mg, 0.333 mmol) in benzene (10 mL) was heated at 80 °C for 2 h under argon in the dark. Column chromatography (cyclohexane/AcOEt, 4:1, as eluant) allowed isolation of **4c** (22 mg) and of the [6+4] adduct of **1c** to tropone (130 mg). This competition reaction was also carried out in refluxing acetone for 4.5 h (by using the very same amounts of **2a**, tropone and **1c** as in the reaction in benzene) to afford 24 mg of **4c** and 119 mg of the [6+4] tropone adduct. Consequently, one can evaluate[23] that the [6+4] cycloaddition of tropone with **1c** is ≈ 8.7 times (in benzene) and 7.1 times (in acetone) as fast as the related [6+4] reaction of **2a** with **1c**.

In a competition reaction of **1b** with an excess of equimolar amounts of **2a** and tropone we managed to isolate only the adduct to tropone.

A solution of **1b** (0.138 g, 0.479 mmol), **1c** (0.167 g, 0.479 mmol) and **2a** (0.085 g, 0.436 mmol) in benzene (10 mL) was heated under reflux for 48 h. Column chromatography led to isolation of 117 mg of **4c** and 15 mg of **4b** (k_{1c+2a}/k_{1b+2a} = 8.9).

A solution of **1b** (0.179 g, 0.621 mmol), **1c** (0.217 g, 0.623 mmol) and tropone (60 mg, 0.566 mmol) in acetone (10 mL) was heated under reflux for 24 h. The adducts of tropone to **1b** (0.053 g) and **1c** (0.192 g) ($k_{1c+tropone}/k_{1b+tropone}$ = 4.6) were isolated by column chromatography (cyclohexane/AcOEt, 4:1, as eluant).

*Reaction of **4a** with N-methyltriazolinedione and tetracyanoethene.*

A solution of **4a** (60 mg) and N-methyltriazolinedione (20 mg) in dichloromethane (5 mL) was kept at r.t. for 24 h. Column chromatography (cyclohexane/AcOEt/CH_2Cl_2, 5:4:1, as eluant) allowed isolation of pure **9a** (63 mg, 84%) as colorless prisms which started decomposing at ≈ 160 °C [IR ν_{max} 1772, 1733 and 1703 cm^{-1}; ^1H NMR δ 1.04, 1.20, 2.35 and 3.08 (four s, Me), 3.61 (dd, H-1, $J_{1,6}$ = 3.3 Hz and $J_{1,10}$ = 8.4 Hz), 4.18 (dd, H-6, $J_{6,7}$ = 8.7 Hz), 5.33 (ddd, H-7, $J_{7,8}$ = 6.8 Hz and $J_{7,9}$ = 1.3 Hz), 5.39 (ddd, H-10, $J_{9,10}$ = 6.8 Hz and $J_{8,10}$ = 1.3 Hz), 6.39 (ddd, H-8, $J_{8,9}$ = 8.7 Hz), 6.47 (ddd, H-9). Anal. Calcd for $C_{36}H_{32}N_4O_3$: C, 76.0; H, 5.7; N, 9.9. Found: C, 76.2; H, 5.8; N, 10.0.

We tried to react **4a** (20 mg) with excess tetracyanoethene (10 mg) in dichloromethane at r.t.. However, after 7 days no new products could be detected by TLC and most part of **4a** was recovered unchanged.

*Catalytic hydrogenation of **4a**.*

A solution of **4a** (0.134 g) in ethyl acetate (15 mL) was hydrogenated at r.t. and under atmospheric pressure in the presence of Pd/C 10% (50 mg). After the uptake of hydrogen was complete, the solvent was evaporated and the crude residue (only one product as shown by TLC analysis) was purified by column chromatography and by crystallization from ethanol to afford 55 mg (40%) of **10a** as colourless prisms, mp 212-215 °C [IR ν_{max} 1749 and 1640 cm^{-1}; ^1H NMR δ 1.04, 1.19 and 2.39 (three s, Me), 1.40-2.00 (8H, $CH_2CH_2CH_2CH_2$), 3.18 and 3.45 (two m, H-1 and H-6)]. Anal. Calcd for $C_{33}H_{33}NO$: C, 86.2; H, 7.2; N 3.1. Found: C, 86.5; H, 7.1; N, 3.0.

*Reduction of **4a** with sodiumcyanoborohydride.*

Compound **4a** (100 mg, 0.22 mmol) was dissolved in acetonitrile and was reduced at r.t. with a high excess (0.500 g) of $NaBH_3CN$ in the presence of p-toluensulfonic acid (0.480 g). The latter two reagents were added portionwise and simultaneously during two hours under stirring. The reaction mixture was further stirred at r.t. for one hour, then diluted with water and extracted several times with ethyl ether. The ether extracts were dried with anhydrous sodium sulfate and evaporated to give **12a** (94 mg, 94%).

12a: colorless needles from cyclohexane, mp 226-230 °C. IR ν_{max} 3415 and 1755 cm^{-1}; ^1H NMR δ 1.10 and 2.26 (two s, Me), 3.22 (d, 2 H, H-1 and H-6, J = 6.0 Hz), 4.14 (d, H-11, $J_{11,NH}$ = 10.0 Hz), 4.46 (d, NH), 6.00 (m, 4 H, H-7 - H-10), 6.38 and 6.98 (two bd, aromatic protons of the tolyl group). Anal. Calcd for $C_{33}H_{31}NO$: C, 86.6; H, 6.8; N 3.1. Found: C, 86.7; H, 7.0; N, 3.1.

*Reduction of **4a** and **4d** with $LiAlH_4$.*

Reduction was carried out in anhydrous ether at r.t. with excess $LiAlH_4$. After 30 minutes the reaction was quenched with some drops of water, the precipitated inorganic salts filtered off and the solution dried with anhydrous sodium sulfate. Evaporation of the solvent afforded quantitatively alcohol **11**.

11a: colorless prisms from ethanol, mp 195-197 °C; IR ν_{max} 3558, 3350 (broad) and 1655 cm^{-1}; ^1H NMR δ 1.20, 1.30 and 2.32 (three s, Me), 3.16 (d, OH, $J_{12,OH}$ = 11.6 Hz), 3.29 (d, H-12), 3.48 (bdd, H-1, $J_{1,6}$ = 3.8 and $J_{1,10}$ = 7.0 Hz), 3.63 (bdd, H-6, $J_{6,7}$ = 7.8 Hz), 6.05 (m, 1 H, H-7), 6.30 (m, 3 H, H-8 - H-10), 6.58 and 7.04 (two bd, aromatic protons of the tolyl group). Anal. Calcd for $C_{33}H_{31}NO$: C, 86.6; H, 6.8; N 3.1. Found: C, 86.6; H, 6.6; N, 3.2.

11d: colorless prisms from ethanol, mp 191-193 °C; IR ν_{max} 3560, 3350 (broad) and 1650 cm^{-1}; ^1H NMR δ 1.23, 1.31 (two s, Me), 3.11 (d, OH, $J_{12,OH}$ = 11.6 Hz), 3.28 (d, H-12), 3.47 (bdd, H-1, $J_{1,6}$ = 3.8 and $J_{1,10}$ = 7.0 Hz), 3.58 (bdd, H-6, $J_{6,7}$ = 7.7 Hz), 6.02 (m, 1 H, H-7), 6.32 (m, 3 H, H-8 - H-10). Anal. Calcd for $C_{32}H_{28}ClNO$: C, 80.4; H, 5.9; N 2.9. Found: C, 80.1; H, 6.1; N, 2.9.

*Synthesis of **13d** and **14d**.*

To a solution of **11d** (0.260 g, 0.54 mmol) in chloroform (5 mL) cooled at 0 °C was added a solution of bromine (100 mg, 0.62 mmol) in chloroform (3 mL) dropwise under stirring. TLC analysis of the reaction

mixture showed the presence of two products which, after usual work-up, were isolated by column chromatography (cyclohexane/AcOEt, 9:1, as eluant) in 53% (160 mg, higher R_f compound, **13d**) and 37% (113 mg, lower R_f compound, **14d**).

13d: colorless prisms from ethanol, mp 230-233 °C; IR ν_{max} 1650 cm^{-1}; ^1H NMR δ 1.17 and 1.31 (two s, Me), 2.86 (dddd, H-6, $J_{6,7}$ = 8.7 Hz, $J_{1,6} \approx J_{6,8} \approx J_{6,12}$ = 1.3 Hz), 3.48 (m, H-1, $J_{1,10}$ = 4.0 Hz, $J_{1,9} \leq 0.5$ Hz and $J_{1,12}$ = 1.3 Hz), 3.82 (dd, H-12), 4.59 (ddd, H-9, $J_{8,9}$ = 7.2 Hz, $J_{9,10}$ = 6.3 Hz, $J_{7,9}$ = 0.7 Hz), 5.02 (dd, H-10), 5.80 (ddd, H-7, $J_{7,8}$ = 10.3 Hz), 6.20 (ddd, H-8); ΔM [Eu(fod)$_3$] (ppm): Me (0.40), Me (0.42), H-6 (0.57), H-1 (0.79), H-12 (2.1), H-9 (1.75), H-10 (0.81), H-7 (0.52), H-8 (0.44); ^{13}C NMR δ 18.6 (q, Me), 18.9 (q, Me), 46.3 (d, C-6), 48.4 (s, C-2 or C-5), 48.7 (d, C-10), 50.7 (s, C-5 or C-2), 57.2 (d, C-1), 70.5 (d, C-9), 86.1 (d, C-12), 129.7 (d, C-7), 134.5 (d, C-8), 167.6 (s, CN). Anal. Calcd for $C_{32}H_{26}BrClNO$: C, 69.1; H, 4.7; N, 2.5. Found: C, 68.9; H, 4.9; N, 2.6.

LIS shifts and ^1H-^{13}C heterocorrelated spectra allowed a safe choice between the signal of the proton attached to the carbon atom which bears the oxygen atom (i.e., H-9 in **13d** and H-10 in **14d**) and that of the proton attached to the carbon atom bearing the bromine atom (i.e., H-10 in **13d** and H-9 in **14d**). This assignment provided the starting point for the choice between **13d** and **14d**.

14d: colorless prisms from ethanol, mp 214-216 °C; IR ν_{max} 1660 cm^{-1}; ^1H NMR δ 1.11 and 1.32 (two s, Me), 2.88 (dddd, H-6, $J_{6,7}$ = 8.7 Hz, $J_{1,6}$ = 1.6 Hz and $J_{6,12}$ = 1.1 Hz), 3.55 (dd, H-1, $J_{1,10}$ = 4.9 Hz and $J_{1,12} \approx 0.5$ Hz), 4.22 (bs, H-12), 5.02 (dd, H-9, $J_{8,9} = J_{9,10}$ = 6.5 Hz), 5.19 (ddd, H-10, $J_{8,10}$ = 0.7 Hz), 5.72 (dd, H-7, $J_{7,8}$ = 10.8 Hz), 5.95 (ddd, H-8); ΔM [Eu(fod)$_3$] (ppm): Me (0.13), Me (0.13), H-6 (0.22), H-1 (0.33), H-12 (0.60), H-9 (0.23), H-10 (0.48), H-7 (0.29), H-8 (0.14); ^{13}C NMR δ 18.4 (q, Me), 19.3 (q, Me), 46.3 (d, C-9), 47.0 (d, C-6), 54.8 (s, C-2 or C-5), 58.2 (d, C-1), 59.1 (s, C-5 or C-2), 83.8 (d, C-10), 98.5 (d, C-12), 129.5 (d, C-8), 130.5 (d, C-7), 170.0 (s, CN). Found: C, 69.0; H, 4.8; N, 2.4.

Rearrangement of compounds 4 to compounds 6.

A solution of **4a** (200 mg, 0.44 mmol) in degassed toluene (10 mL) was refluxed for 48 h under argon in the dark. Careful TLC analysis of the reaction mixture with different eluant mixtures (cyclohexane/AcOEt, 9:1 and 97:3, and cyclohexane/benzene, 1:1) showed the presence, in addition to unreacted **4a**, of a yellow compound as dominant product along with minor amounts of azaheptafulvene **2a** and of a spot with the same R_f of the cyclopentadienone dimer. After evaporation of the solvent the oily brown residue was column chromatographed to give 150 mg (75%) of yellow **6a** and 6 mg of azaheptafulvene **2a** whereas we did not mange to isolate and characterize the cyclopentadienone dimer.

Compound **6a** was also obtained in good yield (310 mg) by conducting the cycloaddition of **1a** (300 mg, 1.15 mmol) with excess **2a** (310 mg, 1.59 mmol) in toluene at 110 °C under argon for 50 h.

The rearrangement of **4a** (85 mg, 0.19 mmol) was also carried out in the presence of N-phenylmaleimide (65 mg, 0.38 mmol) in refluxing toluene for 20 h. Column chromatography (cyclohexane/AcOEt, 9:1, as eluant) allowed us to isolate from the complex reaction mixture 28 mg (33%) of **6a**. We were not able to isolate the adduct of N-phenylmaleimide to cyclopentadienone **1a** even if TLC analysis had showed a spot (of very low intensity) with the same R_f as that of the adduct of **1a** to N-phenylmaleimide.

The reaction between **1a** and N-phenylmaleimide in benzene at reflux took less than 1 h to go to completion to give the endo[3e] adduct in quantitative yield [colorless needles from methanol, mp 215-218 °C dec.; IR ν_{max} 1790, 1773 and 1713 cm^{-1};.^1H NMR δ 1.75 (s, 6 H, Me), 3.38 (s, 2 H, bridgehead protons), 6.85-7.80 (m,15 H, aromatic protons). Anal. Calcd for $C_{29}H_{23}NO_3$: C, 80.4; H, 5.4; N 3.2. Found: C, 80.6; H, 5.3; N, 2.9].

Heating a solution of this adduct in the presence of azaheptafulvene **2a** for 24 h or in toluene for 48 h did not produce new products. Only some darkening was observed.

Under the very same conditions as those reported above for **4a** also **4d** could be transformed into **6d** (55%) and TLC analysis showed that **6d** kept on being the dominant product even in the presence of N-phenylmaleimide. Also **6d** was prepared in good yield (62%) directly from **1a** (1.0 mmol) and excess **2b** (1.3 mmol) in refluxing toluene (48 h) under argon.

After refluxing **4c** (66 mg) for 48 h in degassed toluene under argon compound **6c** was isolated by column chromatography and crystallization from petrol ether in 55% (36 mg) yield. A 50% yield of **6c** was obtained from the reaction in the presence of N-phenylmaleimide under otherwise similar conditions.

6c: reddish prisms from petrol ether, mp 188-192 °C; IR ν_{max} 1740, 1710 and 1650 cm^{-1}; ^1H NMR (80 MHz) δ 2.08 (s, Me), 2.73 (m, 2 H, H-5 and H-5'), 3.06 and 3.74 (two s, OMe), 5.15 (m, H-6), 6.10- 7.75 (several complex m, 17 H, aromatic and olefinic protons); mass spectrum (EI, 75 eV) m/z 543 (100%, $M^{+\cdot}$), 529 (5%), 484 (17%), 452 (32%), 354 (41%), 194 (35%), 91 (12%), 78 (21%). Anal. Found for $C_{35}H_{29}NO_5$: C, 77.1; H, 5.5; N, 2.7.

Catalytic hydrogenation of compound 6d.

Compound **6d** (200 mg, 0.42 mmol) was catalytically hydrogenated in ethyl acetate in the presence of Pd/C 10% (25 mg) at r. t. and under atmospheric pressure. The only product present in the reaction mixture at the end of hydrogenation was purified by crystallization from benzene/methanol (140 mg, 70%).

19d: yellow prisms, mp 190-192 °C; IR ν_{max} 1695, 1658, 1630 and 1588 cm^{-1}; ^1H NMR δ 0.57 and 1.85 (two s, Me), 1.30-1.80 (m, 6 H, CH_2 at position 6, 7 and 8), 2.20-2.45 (m, 4 H, CH_2 at position 5 and 9), 6.12 and 6.72 (two bd, protons of the p-chlorophenyl group). ^{13}C NMR δ 9.7 (q, Me at position 2), 17.0 (q, Me at position 9b), 24.3, 27.0, 27.8, 28.5, 31.7 (five t, $CH_2CH_2CH_2CH_2CH_2$), 67.6 (s, C-9b), 85.9 (s, C-3a), 121.2 (C-9a), 125.8-129.2 (nine signals, aromatic CH and CCl), 135.8 and 137.6 (s, substituted carbons of the two phenyl rings), 139.6 (s, C-2), 140.9 (s, C-N of the p-chlorophenyl group), 142.2 (s, C-4a), 161.3 (s, C-3), 207.2 (s, CO). Anal. Calcd for $C_{32}H_{30}ClNO$: C, 80.0; H, 6.3; N 2.9. Found: C, 79.7; H, 6.4; N, 3.1.

Oxidation of compound 6.

A solution of compounds **6a, c** and **d**, respectively, in toluene was left evaporating at r. t. under atmospheric pressure. This process was repeated several times until compound **6** was completely converted as shown by TLC analysis (cyclohexane/benzene, 1:1, as eluant). The dominant product, i. e. compounds **21a, c** and **d**, respectively, was isolated in ≈ 50% yield by column chromatography.

21a: orange-yellow prisms from petrol ether, mp 190-192 °C; IR ν_{max} 1690, 1605 and 1592 cm^{-1}; ^1H NMR δ 0.85, 1.90 and 2.10 (three s, Me), 6.58 and 6.64 (two bd, 4 H, aromatic protons of the tolyl group), 6.70-7.50 (several m, 14 H, aromatic protons); ^{13}C NMR δ 10.2 (q, Me at position 2), 20.4 (q, Me at position 9b), 20.5 (q, Me in the tolyl group), 64.0 (s, C-8b), 86.9 (s, C-3a), 110.4 (d, C-5), 119.1 (d, C-7), 125.4-129.3 (eight signals, aromatic CH), 131.1 (s, C-8a), 133.2, 135.2, 138.3 and 139.1 (s, substituted aromatic protons), 140.3 (s, C-2), 147.2 (s, C-4a), 163.0 (s, C-3), 206.5 (s, CO); mass spectrum (EI, 75 eV) m/z 441 (100%, $M^{+\cdot}$), 297 (45%), 235 (71%), 194 (32%), 132 (27%). Anal. Calcd for $C_{32}H_{27}NO$: C, 87.0; H, 6.2; N 3.2. Found: C, 86.9; H, 6.2; N, 3.3

21c: orange-yellow prisms from methanol, mp 212-213 °C; IR ν_{max} 1690, 1605 and 1592 cm^{-1}; ^1H NMR δ 2.10 (s, Me), 3.08 and 3.75 (two s, OMe), 6.58 and 6.70 (two bd, 4 H, aromatic protons of the tolyl group), 6.88-7.85 (several m, 14 H, aromatic protons); mass spectrum (EI, 75 eV) m/z 529 (100%, $M^{+\cdot}$), 470 (19%), 428 (11%), 341 (50%), 310 (38%), 194 (39%), 129 (21%). Anal. Calcd for $C_{34}H_{27}NO_5$: C, 77.1; H, 5.1; N 2.7. Found: C, 77.4; H, 5.0; N, 2.5.

21d: orange yellow prisms from ethanol, mp 199-202 °C; mass spectrum (EI, 75 eV) m/z 463 (43%, $M^{+\cdot}$), 461 (100%, $M^{+\cdot}$), 315 (12%), 317 (33%), 257 (15%), 255 (47%), 216 (8%), 214 (20%).

Minor amounts of lower R_f products were also revealed by TLC analysis of the reaction mixtures. In the case of the reaction of **6a** two further products were isolated aside from **21a**. The higher R_f (yellow glassy solid; IR ν_{max} 2720, 1700, 1688,1595 and 1580 cm^{-1}) of these products consisted of a mixture of two formyl derivatives as shown by the singlets at δ ($CDCl_3$) 9.55 and 9.85. The other consisted of only one compound [yellow needles from cyclohexane, mp 237-239 °C; IR ν_{max} 2720, 1692, 1680, 1595 and 1578 cm^{-1}; ^1H NMR δ 0.88, 2.00 and 2.10 (three s, Me), 6.60 and 6.70 (two bd, aromatic protons of the tolyl group), 6.68 (d, H-5, $J_{5,6}$ = 8.5 Hz), 6.95 (m, 4 H), 7.10 (m, 1 H), 7.39 (m, 3 H), 7.52 (bs, 2 H), 7.67 (dd, H-6, $J_{6,8}$ = 1.5 Hz), 7.81 (d, H-8), 9.78 (s, CHO)] and its spectroscopic data are consistent with a 7-CHO derivative of **21a**.

Crystal data and X-ray single crystal structure refinement for compound (E)-8d.

$C_{32}H_{26}ClNO$, yellow crystals from methanol, monoclinic, space group $P2_1/n$; a = 14.247(1), b = 15.420(1), c = 11.263(1) Å; β = 93.25(5)° ; V = 2470.4 Å^3; Z = 4; D_c = 1.28 g/cm^3; F(000) = 1000; μ = 1.77 cm^{-1}. X-ray single crystal analysis and data collection performed on a Philips PW1100 four-circle diffractometer (monochromatic MoKα radiation, λ = 0.7107 Å). Unit-cell dimensions calculated by least-squares refinement of 25 rows in the ϑ range 2-20°; 2303 independent reflections (-12<*h*<13, 0<*k*<13, 0<*l*<10) measured in the J range 2-20° , corrected for absorption (max. = 1.078). Correction for intensity variation applied (max. = 4.4%). Structure solved by direct methods (MULTAN80);[24] full-matrix least-squares refinement on F performed with a locally rewritten version of the program ORFLS[25] on the 1670 reflections with I≥3σ(I). Scattering factors for neutral atoms from International Tables for X-ray Crystallography.[26]

Refinement of the anisotropics atomic displacement parameters for only non-H atoms; the positions of the H atoms were calculated at convergence with program PARST[27], inserted with an overall isotropic atomic displacement parameter equal to 5 Å^2 but not refined. At convergence, R_{all} = 5.9%, R_{obs} = 3.7%, S = 0.912; secondary extinction = 1.56 10^{-4}; scale factor = 2.848; the final difference Fourier map did not show peaks higher than 0.35 el.Å^{-3}. Bond distances in Table 1, bond angles in Table 2, atomic coordinates and equivalent isotropic atomic displacement parameters for non-H atoms in Table 3; Figure 1, drawn with program ORTEP,[28] illustrates the molecular structure and the atomic numbering. A list of observed and calculated structure factors and of anisotropic atomic displacement parameters for non-H atoms may be obtained on request from the authors; hydrogen coordinates have been deposited within the Cambridge Crystallographic Data Center.

Table 1. Bond Distances for non-Hydrogen Atoms. Uncorrected and corrected for riding motion.

C1 - C2	1.323(4)	1.325	N13 - C14	1.423(4)	1.430
C1 - C7	1.510(4)	1.510	C14 - C15	1.382(4)	1.387
C2 - C3	1.464(4)	1.471	C14 - C20	1.390(4)	1.402
C3 - C4	1.533(4)	1.533	C15 - C16	1.383(4)	1.383
C3 - N13	1.281(4)	1.287	C16 - C17	1.367(4)	1.372
C4 - C5	1.510(4)	1.519	C17 - CL18	1.750(3)	1.771
C4 - C9	1.570(4)	1.575	C17 - C19	1.364(4)	1.373
C5 - C6	1.309(5)	1.318	C19 - C20	1.380(4)	1.382
C6 - C7	1.502(5)	1.508	C22 - C23	1.394(4)	1.404
C7 - C8	1.573(4)	1.581	C22 - C27	1.399(4)	1.404
C8 - C9	1.577(4)	1.580	C23 - C24	1.368(4)	1.379
C8 - C12	1.523(4)	1.527	C24 - C25	1.388(5)	1.390
C8 - C21	1.542(4)	1.551	C25 - C26	1.370(5)	1.378
C9 - C10	1.547(4)	1.547	C26 - C27	1.387(4)	1.398
C9 - C22	1.532(4)	1.533	C28 - C29	1.390(5)	1.401
C10 - C11	1.338(4)	1.345	C28 - C33	1.381(5)	1.401
C10 - C28	1.481(4)	1.488	C29 - C30	1.387(5)	1.401
C11 - C12	1.455(4)	1.457	C30 - C31	1.358(6)	1.365
C11 - C34	1.503(4)	1.523	C31 - C32	1.362(7)	1.364
C12 - O35	1.216(4)	1.237	C32 - C33	1.384(5)	1.399

Table 2. Bond Angles (°) for non-Hydrogen Atoms.

C2 - C1 - C7	124.5(.3)	C8 - C12 - C11	109.9(.2)
C1 - C2 - C3	124.9(.3)	C11 - C12 - O35	126.2(.3)
C2 - C3 - N13	124.8(.3)	C8 - C12 - O35	123.9(.3)
C2 - C3 - C4	119.5(.3)	C3 - N13 - C14	121.4(.3)
C4 - C3 - N13	115.6(.3)	N13 - C14 - C20	119.1(.3)
C3 - C4 - C9	118.7(.2)	N13 - C14 - C15	121.4(.3)
C3 - C4 - C5	105.2(.2)	C15 - C14 - C20	119.1(.3)
C5 - C4 - C9	107.9(.2)	C14 - C15 - C16	120.7(.3)
C4 - C5 - C6	117.9(.3)	C15 - C16 - C17	119.2(.3)
C5 - C6 - C7	118.4(.3)	C16 - C17 - C19	121.2(.3)
C1 - C7 - C6	111.7(.3)	C16 - C17 - CL18	119.3(.2)
C6 - C7 - C8	110.5(.2)	CL18 - C17 - C19	119.5(.2)
C1 - C7 - C8	109.1(.2)	C17 - C19 - C20	120.1(.3)
C7 - C8 - C21	107.9(.2)	C14 - C20 - C19	119.8(.3)
C7 - C8 - C12	106.4(.2)	C9 - C22 - C27	123.2(.2)
C7 - C8 - C9	110.6(.2)	C9 - C22 - C23	119.4(.2)
C12 - C8 - C21	110.0(.2)	C23 - C22 - C27	117.2(.3)
C9 - C8 - C21	117.2(.2)	C22 - C23 - C24	122.0(.3)
C9 - C8 - C12	104.3(.2)	C23 - C24 - C25	120.1(.3)
C4 - C9 - C8	112.4(.2)	C24 - C25 - C26	119.0(.3)
C8 - C9 - C22	114.4(.2)	C25 - C26 - C27	121.1(.3)
C8 - C9 - C10	102.3(.2)	C22 - C27 - C26	120.5(.3)
C4 - C9 - C22	113.9(.2)	C10 - C28 - C33	118.6(.3)
C4 - C9 - C10	105.9(.2)	C10 - C28 - C29	123.8(.3)
C10 - C9 - C22	106.7(.2)	C29 - C28 - C33	117.6(.3)
C9 - C10 - C28	121.9(.2)	C28 - C29 - C30	120.4(.3)
C9 - C10 - C11	113.3(.2)	C29 - C30 - C31	120.5(.4)
C11 - C10 - C28	124.7(.3)	C30 - C31 - C32	120.2(.4)
C10 - C11 - C34	128.9(.3)	C31 - C32 - C33	119.8(.4)
C10 - C11 - C12	109.9(.3)	C28 - C33 - C32	121.4(.4)
C12 - C11 - C34	121.2(.3)		

Table 3. Atomic Fractional Coordinates (x 10^4) and Equivalent Isotropic Atomic Displacement Factors ($Å^2$) for non-Hydrogen Atoms.

	X/a	*Y/b*	*Z/c*	*Beq*
C1	.9168(2)	.6344(2)	.7409(3)	3.66(.10)
C2	.8562(2)	.6106(2)	.6536(3)	3.59(.10)
C3	.8139(2)	.6690(2)	.5630(3)	3.04(.10)
C4	.8257(2)	.7673(2)	.5780(3)	2.85(.10)
C5	.9286(2)	.7844(2)	.5623(3)	3.67(.11)
C6	.9887(2)	.7640(2)	.6500(3)	4.09(.11)
C7	.9517(2)	.7260(2)	.7609(3)	3.46(.10)

Table 3. Continues.

C8	.8693(2)	.7832(2)	.8056(3)	2.66(.09)
C9	.7995(2)	.8100(2)	.6982(2)	2.43(.09)
C10	.8200(2)	.9080(2)	.6854(3)	2.53(.09)
C11	.8798(2)	.9389(2)	.7710(3)	3.00(.10)
C12	.9134(2)	.8684(2)	.8482(3)	3.21(.10)
N13	.7708(2)	.6444(2)	.4660(2)	3.40(.08)
C14	.7687(2)	.5556(2)	.4312(3)	2.94(.10)
C15	.8502(2)	.5112(2)	.4095(3)	3.32(.10)
C16	.8464(2)	.4296(2)	.3587(3)	3.40(.10)
C17	.7607(2)	.3924(2)	.3319(3)	2.99(.10)
CL18	.7554(1)	.2924(1)	.2583(1)	5.17(.03)
C19	.6794(2)	.4339(2)	.3556(3)	3.73(.11)
C20	.6824(2)	.5162(2)	.4039(3)	3.65(.11)
C21	.8272(2)	.7355(2)	.9104(3)	3.47(.10)
C22	.6953(2)	.8019(2)	.7233(2)	2.46(.09)
C23	.6607(2)	.8466(2)	.8191(3)	3.29(.10)
C24	.5676(2)	.8447(2)	.8428(3)	4.22(.11)
C25	.5038(2)	.7993(2)	.7686(3)	4.41(.12)
C26	.5358(2)	.7556(2)	.6731(3)	3.84(.11)
C27	.6302(2)	.7566(2)	.6492(3)	3.06(.10)
C28	.7806(2)	.9592(2)	.5830(3)	3.37(.10)
C29	.6851(3)	.9659(2)	.5523(3)	4.36(.11)
C30	.6534(3)	1.0167(2)	.4565(4)	5.80(.14)
C31	.7153(4)	1.0608(2)	.3918(3)	6.37(.16)
C32	.8094(3)	1.0540(2)	.4187(3)	6.25(.15)
C33	.8418(3)	1.0044(2)	.5149(3)	4.83(.12)
C34	.9130(2)	1.0305(2)	.7917(3)	4.60(.11)
O35	.9703(2)	.8746(1)	.9324(2)	4.50(.07)

Acknowledgement.

Financial support from MURST and CNR is gratefully acknowledged.

REFERENCES AND NOTES

1. Woodward, R. B.; Hoffmann, R. *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 781-853.
2. Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*, Wiley, New York, 1976.
3. (a) Cookson, R. C.; Drake, B. V.; Hudec, J.; Morrison, A. *Chem. Commun.* **1966**, 15. (b) Ito, S.; Fujise, Y.; Okuda, T.; Inoue, Y. *Bull. Chem. Soc. Jap.* **1966**, *39*, 135. (c) Ito, S.; Ohtani, H.; Narita, S.; Honma, H. *Tetrahedron Lett.* **1972**,2223-2226. (d) Sasaki, T.; Kanematsu, K.; Iizuka, K. *J. Org. Chem*, **1976**, *41*, 1105-1112. (e) Mori, M.; Hayamizu, A.; Kanematsu, K. *J. Chem. Soc. Perkin I* **1981**, 1259-1272.
4. (a) Houk, K. N.; Woodward, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 4143-4145 and 4145-4147.(b) Tegmo-Larsson, I.-M.; Houk, K. N. *Tetrahedron Lett.***1978**, 941-944.
5. (a) Harano, K.; Takashi, B.; Yasuda, M.; Kanematsu, K. *Tetrahedron Lett.* **1979**, 1599-1602. (b) Takashi, B.; Wakita, Y.; Kanematsu, K. *J. Org. Chem.* **1980**, *102*, 5415-5416.
6. Sanechika, K.; Kajigaeshi, S.; Kanemasa, S. *Synthesis*, **1977**, 202-204.

7. (a) Gandolfi, R.; Toma, L. *Tetrahedron* **1980**, *36*, 935-941. (b) *1,3-Dipolar Cycloaddition Chemistry*; Padwa, Ed.; Wiley-Interscience; New York 1984, Vol. 1, p. 353. (c) Gandolfi, R. to be published. (d) Ito, K.; Saito, K.; Takahashi, K. *Heterocycles* **1993**, *36*, 21.
8. Sanechika, K.; Kajigaeshi, S.; Kanemasa, S. *Chem. Lett.* **1977**, 861-864.
9. (a) Yamamoto, K.; Kajigaeshi, S.; Kanemasa, S. *Chem. Lett.* **1977**, 85-88. (b) Idem, *Ibidem* **1977**, 91-94. (c) Iwasaki, T.; Kajigaeshi, S.; Kanemasa, S. *Bull. Chem. Soc. Jap.* **1978**, *51*, 229.
10. (a) Truce, W. E.; Shepard, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 6453-6454. (b) Truce, W. E.; Dean, B. D. *J. Org. Chem.* **1980**, *45*, 5429-5430.
11. (a) Ito, K.; Saito, K.; Takahashi, K. *Heterocycles* **1991**, *32*, 1117-1122. (b) Idem, *Bull. Chem. Soc. Jap.* **1992**, *65*, 812-816. (c) Ito, K.; Saito, K.; Takeuchi, S.; Takahashi, K. *Heterocycles* **1992**, *34*, 1415-1422.
12. Kato, M.; Okamoto, Y.; Miwa, T. *Tetrahedron* **1971**, *27*, 4013-4020.
13. Obviously, the zwitterion **3** can also close to a spiro compound, that is to a formal $[\pi 2 + \pi 2]$ cycloadduct involving the sole C=N moiety of **2**.
14. Unfortunately, we did not manage to hydrolyse the C=NAr bond to the C=O bond. Only decomposition products were isolated from attempted hydrolyses.
15. (a) Frank-Neumann, M.; Martina, D. *Tetrahedron Lett.* **1975**, 1759-1762. (b) Bonadeo, M.; Gandolfi, R.; De Micheli, C. *Gazz. Chim. Ital.* **1977**, *107*, 577-578.
16. Harano, K.; Takashi, B.; Yasuda, M.; Kanematsu, K. *J. Org. Chem.* **1980**, *45*, 4455-4462.
17. Spangler, C. W. *Chem. Rew.* **1976**, *76*, 186-217.
18. (a) Vol'pin, M. E.; Kursanov, D. N.; Dulova, V. G. *Tetrahedron*, **1960**, *8*, 33-37. (b) Kobayashi, S.; Tetzuka, T.; Ando, W. *Tetrahedron Lett.* **1979**, 261-262.
19. The standard version of MNDO as implemented in the MOPAC package of computer programs was used.
20. In N-methylazaheptafulvene the orbital that can be assigned to the lone pair on the nitrogen atom has an energy of -10.37 eV. Dipole moments of tropone and N-methylazaheptafulvene (both molecules exhibited a planar geometry) were calculated to be 3.6 D and 2.3 D, respectively. The net atomic charge on the oxygen atom of tropone and on the nitrogen atom of N-methylazaheptafulvene were found to be 0.29 and 0.31, respectively. The experimental value of the dipole moment of tropone (4.3 D, Giacomo, A. D.; Smith, C. P. *J. Am. Chem. Soc.* **1952**, *74*, 4411-. 4.2 D, Kurita, Y.; Seto, S.; Nozoe, T.; Kubo M. *Bull. Chem. Soc. Jap.* **1953**, *26*, 267) suggests that MNDO calculations underestimate dipole moments of these cyclic polyenes. For previous MNDO calculations on N-arylazaheptafulvenes see Ref. 11a and 11c and on tropone see Meier, H.; Pauli, A.; Kolshorn, H. *Chem. Ber.* **1989**, *122*, 101-104.
21. Allen,M. C. M.; van Allen, J. *J. Am. Chem. Soc.* **1950**, *72*, 5165-5167.
22. White, D. M. *J. Org. Chem.* **1974**, *39*, 1951-1952.
23. Bast, K.; Christl, M.; Huisgen, R.; Mack, W. *Chem. Ber.* **1973**, *106*, 3312-3344.
24. Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M., Universities of York (England) and Louvain (Belgium) (1980).
25. Busing, W. R.; Martin, K. O.; Levy, H. A., ORLFS, Report ORNL-TM 305, Oak Rdge National Laboratory, Oak Rdge TN, USA (1962).
26. International Tables for X-ray Crystallography, Vol, IV, Kynoch Press, Birminghaam (1974) (Present distributor: D. Reidel, Dordrecht).
27. Nardelli, M. *Comput. Chem.* **1983**, *7*, 95-98.
28. Johnson, C. K., ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge TN, USA (1962).