

9. Synthesis and Properties of 1,5-Dimethyltricyclo[3.3.0.0^{2,8}]octane- and 1,5-Dimethyltetracyclo[3.3.0.0^{2,8}0^{4,6}]octane Derivatives

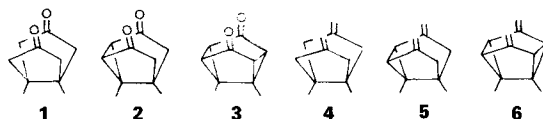
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The synthesis of 1,5-dimethyltricyclo[3.3.0.0^{2,8}]octane-3,7-dione (**2**), 1,5-dimethyltetracyclo[3.3.0.0^{2,8}0^{4,6}]octane-3,7-dione (**3**), the corresponding dienes **5** and **6** as well as the mixed enones **13–15** is reported. Using He(I) photoelectron spectroscopy (PE) as a tool, a considerable interaction between the n orbitals on the O-atoms and the σ frame in **2** and **3** as well as of the double bonds in **5** and **6** and the σ frame is found. These interactions are also traced back by the electronic absorption spectra of these compounds. The molecular structures of **2** and **3** have been investigated by X-ray analysis.

Introduction. – The interaction between two n or two π orbitals with the connecting σ frame depends on the chain length of the σ skeleton [1] [2] and on the basis energy of the σ bonds [3]. To contribute to this topic, we have investigated spectroscopic properties of 1,5-dimethylbicyclo[3.3.0]octane-3,7-dione (**1**), 1,5-dimethyltricyclo[3.3.0.0^{2,8}]octane-3,7-dione (**2**), 1,5-dimethyltetracyclo[3.3.0.0^{2,8}0^{4,6}]octane-3,7-dione (**3**) as well as of the corresponding dienes **4–6**.

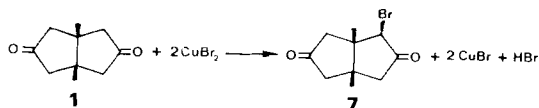


In **1** and **4**, the two carbonyl groups or the two ethylene groups are connected by two C₃ chains, in **2** and **5** by a C₃ and C₂ chain, while in **3** and **6** two C₂ chains link the functional groups. Molecule **3** can be regarded as a cyclohexane-1,4-dione whose C–C bonds are strained due to the three-membered ring moieties, and **6** as a strained 1,4-*exo*-dimethyldienecyclohexane.

Recently, we reported briefly on the synthesis of **2–6** as well as on their PE spectra [4] [5]. In this paper, a full account of the synthesis of **2–6**, their spectroscopic properties and of the molecular structures of **2** and **3** is given.

Preparation of 2, 4, and 5. – The preparation of **2**, **4**, and **5** is rather simple and good yields are obtained. The starting material for the synthesis of **2** is **1** which was prepared according to Weiss *et al.* [6]. Monobromination of **1** was achieved according to Scheme 1 by using CuBr₂ in boiling AcOEt/CHCl₃ [7]. Using somewhat less than equimolar amounts of CuBr₂, a 60% yield of 2-*exo*-bromo-1,5-dimethylbicyclo[3.3.0]octane-3,7-dione (**7**) can be isolated. As side-product, the 1,6-dibromide (**8**) was obtained. The

Scheme 1

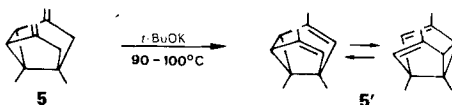


exo-configuration of the Br substituent is based on comparison of the ^1H - and ^{13}C -NMR spectra of **7** with those of **8** and **10** (see below).

Base-induced elimination of the HBr from **7** yields **2**. The highest yield was observed with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in MeCN [**8**] (70–74% yield) although other bases could also be used to generate **1**. The tricyclic structure (point group C_s) of **2** is supported by its ^1H - and ^{13}C -NMR spectra (see *Exper. Part*), and is confirmed by X-ray investigations (see below). The bi- and tricyclic *exo*-methylidene compounds **4** and **5** were obtained from **1** and **2**, respectively, by Wittig reaction using 4 equiv. of triphenylmethylphosphonium bromide in DMSO.

The diene **5** is an isomer of 1,3,5,7-tetramethyltricyclo[3.3.0.0^{2,8}]octa-2,7-diene (**5'**), a semibullvalene derivative. To elucidate a path from **5** to **5'**, we heated **5** with base in DMSO (Scheme 2) to 90–100°. After 3 h, about 50% of **5** had been converted to **5'**. The ^1H -NMR spectrum recorded for **5'** is identical to that reported in [**9**].

Scheme 2

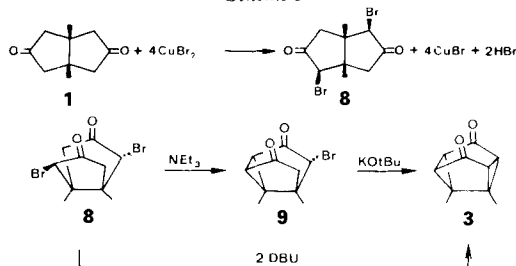


Preparation of 3 and 6. – The reaction of 1 equiv. of **1** with 4 equiv. of CuBr_2 in $\text{CHCl}_3/\text{AcOEt}$ yielded a mixture of isomeric dibromides in 80% overall yield (Scheme 3). Recrystallization from MeOH afforded 2-*exo*, 6-*exo*-dibromo-1,5-dimethylbicyclo[3.3.0]octane-3,7-dione (**8**) in 70% yield. The structure of **8** is based on its spectral properties, especially the ^{13}C -NMR spectrum, showing only five lines and on the assumption that the *exo,exo*-isomer is the most stable 2,6-dibromoderivative of **1**.

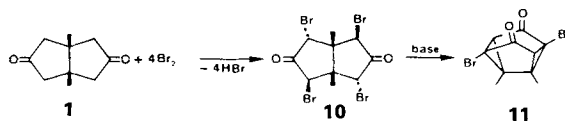
Further reaction of **8** to yield **3** can be achieved in one step using 2 mol of DBU or in two steps using Et_3N followed by *t*-BuOK (Scheme 3).

The structural assignment of **3** is based on its ^1H - and ^{13}C -NMR spectra. Due to its C_{2v} symmetry, both spectra are simple and easy to assign. The stable *exo,exo*-dimethylidene derivative of **3**, **6**, was obtained in good yield *via* a Wittig reaction from **3**.

Scheme 3



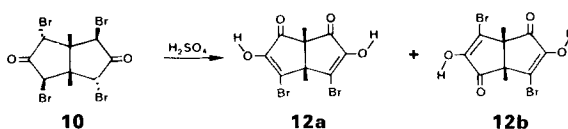
Scheme 4



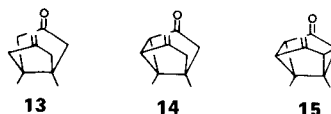
The reaction of **1** with an excess of Br_2 yielded the tetrabromide **10** (Scheme 4). The configuration of the substituents can be deduced from the ^1H - and ^{13}C -NMR spectra of **10**. Both results can be rationalized by assuming that two Br-atoms are *endo*- and the other two are *exo*-configured, i.e. 1,5-dimethyl-2-*endo*, 4-*exo*, 6-*endo*, 8-*exo*-tetrabromobicyclo[3.3.0]octane-3,7-dione (**10**).

Treatment of **10** with AcONa/AcOH yielded the tetracyclic dibromopropduct **11**. An oxidative debromination of **10** was achieved using concentrated H_2SO_4 (Scheme 5). This reaction afforded the two tetraketones **12a** and **12b** in the ratio 3.5:1. In MeCN and DMSO solution, both tetraketones are completely enolized.

Scheme 5



Preparation of the Monoolefins. – When the Wittig reaction of the diketones **1–3** was carried out with 1.3 equiv. of methylenetriphenylphosphane, we obtained the monoolefins **13–15** in 30–40% yields.



PE-Spectroscopic Investigations. – a) *PE Spectra of 1–3.* The PE spectra of **1–3** have been discussed in [4]. The first ionization energies are compared in Fig. 1. The first two

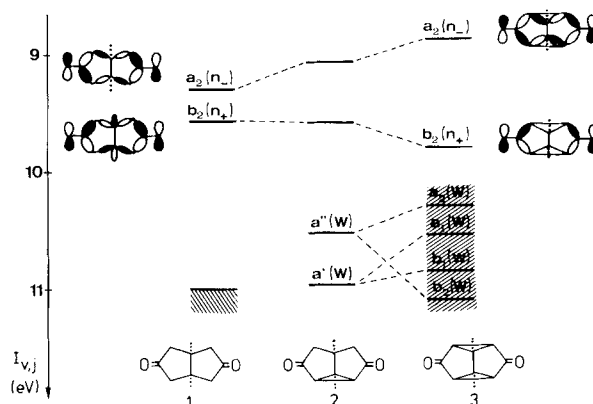


Fig. 1. Comparison between the first bands of the PE spectra of **1–3**. A schematic drawing of the n_- and n_+ MO's of **1** and **3** is given at left and right, respectively.

bands were assigned to ionizations from the n_+ and n_- linear combinations of the two oxygen lone-pair 2p orbitals. The next bands of **2** and **3** (Fig. 1) are due to ionizations from *Walsh*-type (W) orbitals localized mainly at the three-membered ring(s). Going from **1** to **3**, the increase in split between the first two bands is attributed to changes in the interaction between the two oxygen lone-pair orbitals and the σ frame, as indicated by the schematic drawings of the orbitals n_- and n_+ of **1** and **3** in Fig. 1. We observe an increase of the σ/π interaction for n_- and a decrease for n_+ . Based on the calculated distances between the O-atoms for **1** (6.2 Å), **2** (5.0 Å), and **3** (4.8 Å), we can rule out any significant through-space interaction between the oxygen 2p lone pairs.

b) *PE Spectra of 4–6*. The PE spectra of **4–6** are shown in Fig. 2. A comparison between the three spectra shows that the number of peaks in the low-energy region increases with the number of cyclopropane rings. To aid the assignment, we have carried out MINDO/3 [10] calculations on **4–6**. Since the geometries of the three compounds are unknown, we have varied these geometries to minimize their heat of formation. The calculated orbital energies ϵ_i and the resulting assignment assuming the validity of *Koopmans'* theorem [12] are given in Table 1. In addition, we list also the results of a HAM/3 [13] calculation, which are in close agreement with experiment. In Fig. 3, we correlate the

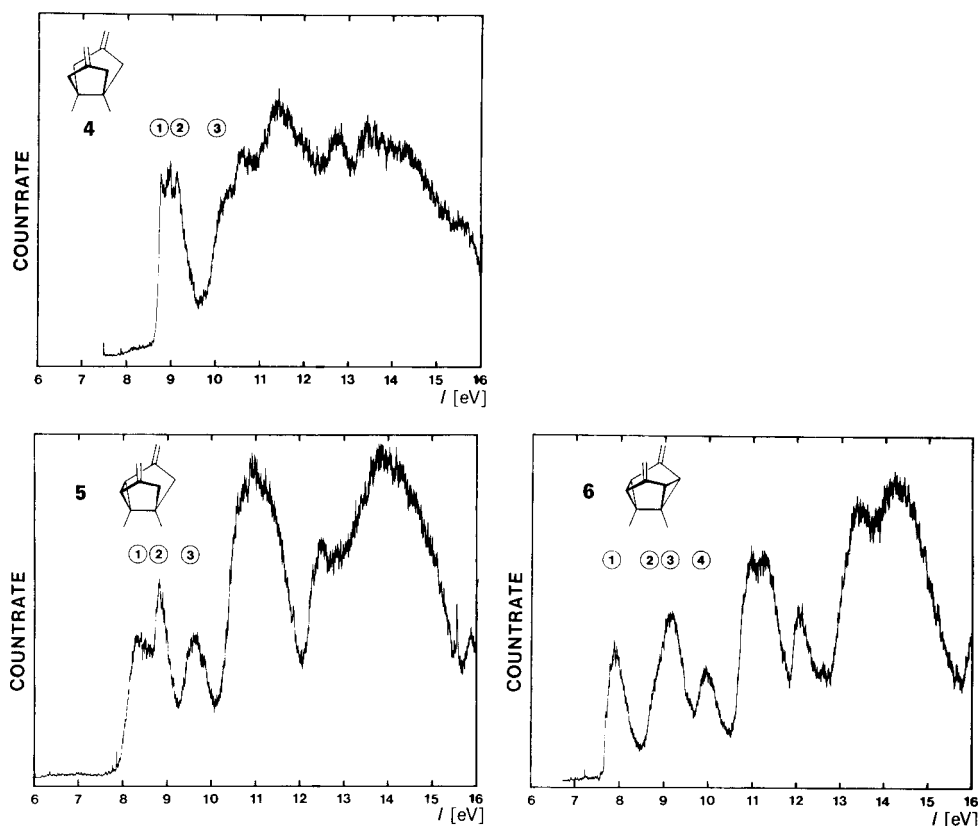


Fig. 2. He(I) PE spectra of **4**, **5**, and **6**

Table 1. Measured Vertical Ionization Energies, $I_{v,j}$, and the Calculated Orbital Energies, ϵ_j (in eV) of **4**, **5**, and **6**

Compound	Band	$I_{v,j}$	Assignment	$-\epsilon_j$ (MINDO/3)	$-\epsilon_j$ (HAM/3)
4	①	8.9	$b_1(\pi_-)$	9.50	8.53
	②	9.1	$a_1(\pi_+)$	9.61	8.74
	③	10.3	$a_1(\sigma)$	10.20	10.85
5	①	8.36	$a'(\pi_+)$	8.84	8.43
	②	8.77	$a''(\pi_-)$	8.95	8.80
	③	9.60	$a''(W)$	10.03	9.74
6	①	7.89	$a_1(\pi_+)$	8.45	8.19
	②	8.93	$a_2(W)$	8.76	8.94
	③	9.15	$b_1(\pi_-)$	9.34	9.26
	④	9.93	$b_2(W)$	9.77	10.06

first bands of **4–6**. In the PE spectrum of **4**, the first two peaks are due to ionizations from the two linear combinations π_- and π_+ of the orbitals π_1 and π_2 . For **5** and **6**, the bands at higher energy are due to the ejection of electrons from *Walsh* (W) type σ orbitals. Similar to the comparison **1–3**, we observe for the series **4–6** an increase in the split between the π_+ and π_- bands from 0.2 eV (**4**) to 1.3 eV (**6**).

Analysis of the wave functions for the two highest-occupied MO's of **4–6** shows a strong increase in the π/σ mixing for the $a_1(\pi_+)$ linear combination in going from **4** to **6**, whereas the interaction between $b_1(\pi_-)$ and the σ -frame remains essentially constant (see Fig. 3).

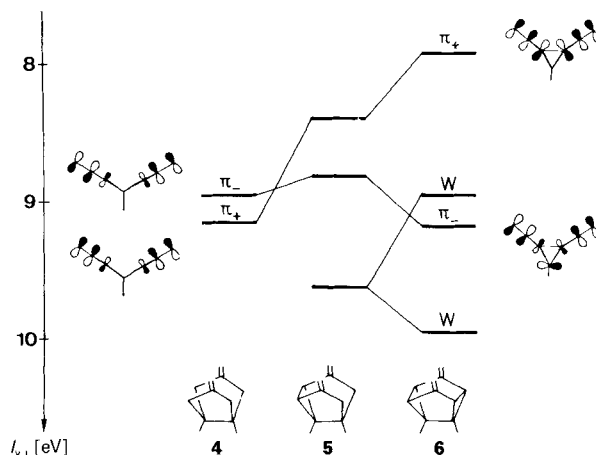


Fig. 3. Comparison between the first bands of the PE spectra of **4–6**. A schematic drawing of the π_- and π_+ MO's of **4** and **6** is given at left and right, respectively.

c) *PE Spectra of 13–15*. The PE spectra of the enones **13–15** are shown in Fig. 4. Below 10 eV, all three exhibit two close-lying bands, ① and ②, which can be assigned to ionizations from the 2p-type lone-pair orbital of the O-atom and the π orbital of the C=C bond. In Table 2, we list the measured ionization energies and the results of a MINDO/3 [10] and a HAM/3 [11] calculation. Both methods predict close-lying energies for the orbitals mainly localized at the 2p orbital of the O-atom and the π orbital of the C=C bond.

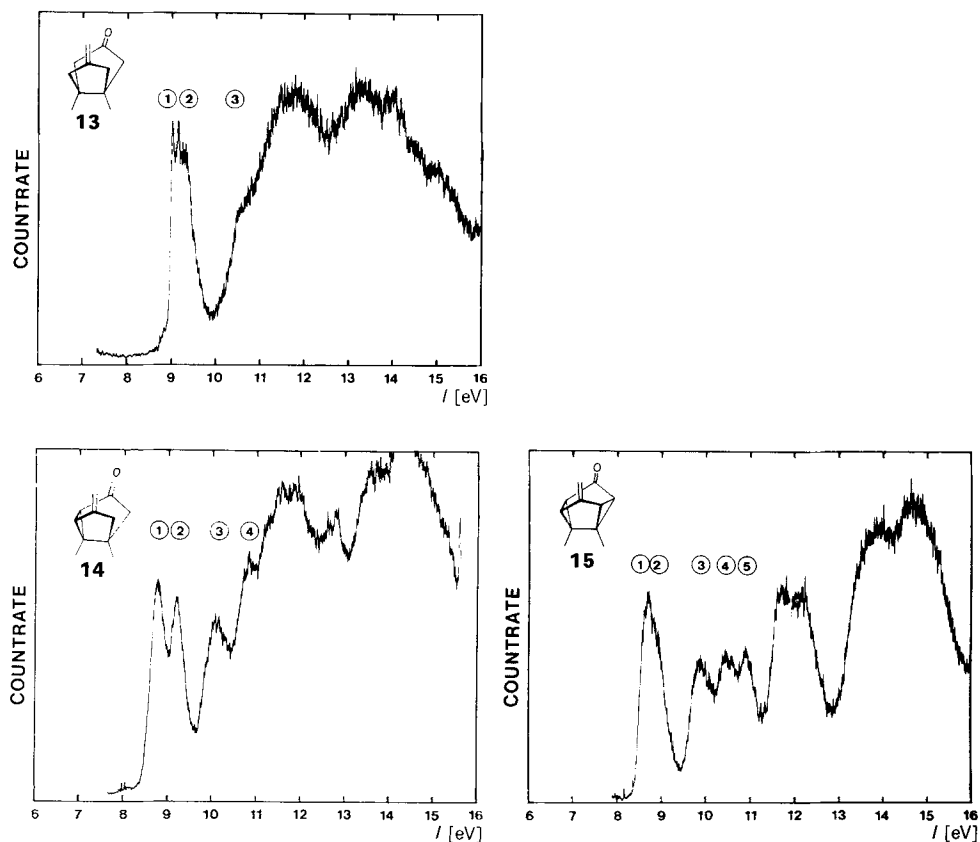


Fig. 4. He(I) PE spectra of 13, 14, and 15

Table 2. Measured Vertical Ionization Energies, I_{vj} , and the Calculated Orbital Energies, ϵ_j (in eV) of 13–15

Compound	Band	I_{vj}	$-\epsilon_j(\text{MINDO/3})$	$-\epsilon_j(\text{HAM/3})$
13	①	8.99	9.76 (π)	8.76 (π)
	②	9.17	9.51 (n)	8.89 (n)
14	①	8.78	9.68 (π)	8.72 (π)
	②	9.16	9.01 (n)	9.00 (n)
15	①	8.73	9.16 (π)	8.78 (π)
	②	8.99	8.86 (n)	9.10 (n)

Electronic Absorption Spectra of 1–6 and 13–15. – a) *Electronic Absorption Spectra of 1–3.* The electronic spectrum of 1 shows a single band at wavelengths longer than 200 nm, while 2 and 3 show a band around 300 nm with low intensity and a more intense one around 210 nm. Replacing cyclohexane by EtOH (Table 3) results in a hypsochromic shift of the first band and a bathochromic shift of the second one. Furthermore, the fine structure of the first band (Fig. 5) disappears in EtOH. These findings suggest the assignment of the first band to a $\pi^* \leftarrow n$ transition and of the second one to a transition involving the cyclopropane-ring Walsh orbitals and the π^* MO of the CO groups.

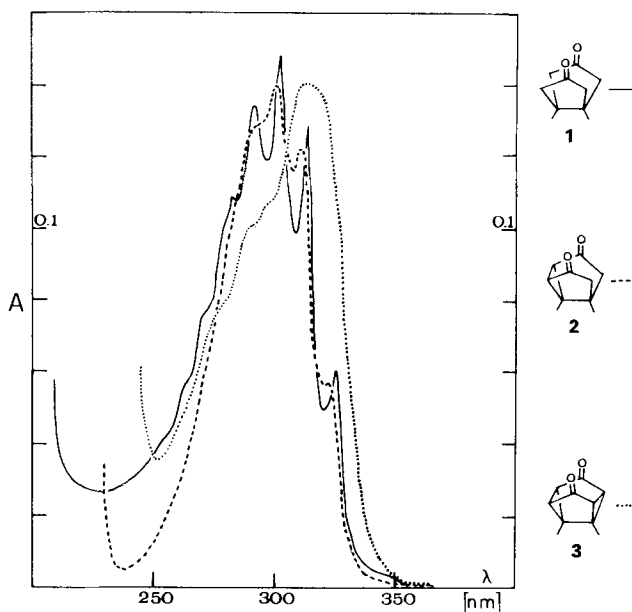


Fig. 5. Low-energy absorption band of **1–3** in cyclohexane. The measurements were carried out in a 1-cm cell using the following concentrations: **1**: $3.78 \cdot 10^{-3}$ mol/l, **2**: $3.95 \cdot 10^{-3}$ mol/l and **3**: $3.64 \cdot 10^{-3}$ mol/l.

As discussed in the previous chapter, the highest occupied valence orbitals of **1–3** are of n_- and n_+ lone-pair-type orbitals. Electron transmission (ET) spectroscopy reveals [14] two low-lying π^* orbitals (π^* below π_+). This suggests four transitions as likely candidates for the first band, namely a $\pi^* \leftarrow n_+$, $\pi^* \leftarrow n_-$ as well as $\pi^* \leftarrow n_+$ and $\pi^* \leftarrow n_-$. To find out the true nature of the first absorption band, we have carried out CNDO/S-CI calculations [15] on **1–3**. These calculations predict that the first band in all three spectra is due to two almost degenerate states composed of the four transitions mentioned above, as listed in Table 3.

The assignment of the second band in the case of **2** and **3** is less certain. The arguments in favour of a $\pi^* \leftarrow W$ transition are the bathochromic solvent shift and the observation that this band is absent in the spectrum of **1** above 200 nm. If we compare the position of the first two bands of **1–3** (cyclohexane), it is found that the introduction of the first cyclopropane ring (**1** $\rightarrow$ **2**) does not affect the position of the low intensity band. The comparison of **2–3**, however, yields a small bathochromic shift of both bands. This can be rationalized by considering the results of the PE and ET spectra of all three compounds. These show that the means of the two n -orbital and of the two π^* -orbital energies of **1** are essentially the same as for **2**. A comparison of **2–3** of the same data yields a slight narrowing of the gap between these two means.

b) *Electronic Spectra of 4–6*. The electronic spectra of **4–6** show one band between 190 and 230 nm with relatively large ϵ values (see Table 3). According to a CNDO/S-CI [15] calculation, this band is due to four almost degenerate transitions of the $\pi^* \leftarrow \pi$ type for **4** and **5** and two $\pi^* \leftarrow \pi$ and two transitions originating from the Walsh (W) orbitals of the $\pi^* \leftarrow W$ type for **6**. As anticipated, we notice a constant shift of the first band in going

Table 3. Observed and Calculated (CNDO/S-CI) Transitions for 1–6 and 13–15

Com- pound	Observed		Calculated		
	$\lambda_{\max}$ [nm]	$\log \varepsilon$	λ [nm]	$\log \varepsilon$	Leading configurations (%)
1	302 ^{a)}	1.59	{ 321.5	–	$\pi^* \leftarrow n_-$ (50); $\pi^* \leftarrow n_+$ (30)
	291 ^{b)}	1.61	{ 321.3	0.37	$\pi^* \leftarrow n_-$ (49); $\pi^* \leftarrow n_+$ (31)
2	300 ^{a)}	1.56	{ 316.5	1.32	$\pi^* \leftarrow n_+$ (43); $\pi^* \leftarrow n_-$ (32)
	290 ^{b)}	2.01	{ 315.8	0.87	$\pi^* \leftarrow n_+$ (43); $\pi^* \leftarrow n_-$ (32)
	209 ^{a)}	3.18	{ 173.4	3.88	$\pi^* \leftarrow W$ (53); $\pi^* \leftarrow \sigma$ (36)
	216 ^{b)}	3.26	{ 168.7	2.75	$\pi^* \leftarrow W$ (53); $\pi^* \leftarrow \sigma$ (38)
3	311 ^{a)}	1.59	{ 321.5	–	$\pi^* \leftarrow n_+$ (34); $\pi^* \leftarrow n_-$ (33)
	313 ^{b)}	1.84	{ 317.5	–	$\pi^* \leftarrow n_+$ (39); $\pi^* \leftarrow n_-$ (29)
	219 ^{a)}	2.89	{ 189.9	3.05	$\pi^* \leftarrow W$ (56); $\pi^* \leftarrow \sigma$ (35)
	230 ^{b)} (sh)	3.00	{ 172.2	2.84	$\pi^* \leftarrow W$ (62); $\pi^* \leftarrow \sigma$ (20)
4	197 ^{a)}	4.24	{ 175.2	4.34	$\pi^* \leftarrow \pi_-$ (65); $\pi^* \leftarrow \pi_+$ (34)
			{ 171.4	3.89	$\pi^* \leftarrow \pi_+$ (36); $\pi^* \leftarrow \pi_-$ (64)
5	210 ^{a)}	4.12	{ 188.6	4.15	$\pi^* \leftarrow \pi_+$ (90)
			{ 184.6	3.60	$\pi^* \leftarrow \pi_-$ (68)
			{ 182.2	2.82	$\pi^* \leftarrow \pi_-$ (79)
			{ 181.1	4.00	$\pi^* \leftarrow \pi_+$ (58)
6	228 ^{a)}	4.26	{ 204.6	4.24	$\pi^* \leftarrow \pi_+$ (99)
			{ 195.2	0.51	$\pi^* \leftarrow W$ (98)
			{ 195.2	3.07	$\pi^* \leftarrow \pi_+$ (86)
			{ 185.2	–	$\pi^* \leftarrow W$ (98)
13	295 ^{a)}	1.32	320.0	–	$\pi^*_{CO} \leftarrow n$ (96)
	290 ^{b)}	1.36			
14	285 ^{a)}	1.59	316.0	–	$\pi^*_{CO} \leftarrow W$ (17); $\pi^*_{CO} \leftarrow n$ (60)
	275 ^{b)}	1.89			
	207 ^{a)}	4.03	185.2	4.20	$\pi^*_{CC} \leftarrow \pi_{CC}$ (84)
	202 ^{b)}	4.07			
15	277 ^{a)}	1.88	321.0	–	{ $\pi^*_{CC} \leftarrow n$ (18); $\pi^*_{CO} \leftarrow W$ (18)
	279 ^{b)}	2.28			
	227 ^{a)}	3.90	188.0	4.19	{ $\pi^*_{CO} \leftarrow n$ (46)
	236 ^{b)}	3.47			

^{a)} In cyclohexane. ^{b)} In EtOH.

from **4** to **6**. This shift can be ascribed to a larger π/σ interaction in the series **4** to **6** as evidenced by the corresponding PE spectra and also a larger $\pi^*_+ - \pi^*_-$ split (**5–6**) as obtained by the ETS investigations [14].

c) *Electronic Absorption Spectra of 13–15*. For all three compounds, we observe a low intensity band between 270 and 300 nm. For **14** and **15**, a second band marginally above 200 nm with a large ε value is also observed. The long wave-length band in cyclohexane solution shows vibrational fine structure which disappears in EtOH solution. The change from cyclohexane to EtOH causes a hypsochromic shift of the band with low intensity for **13** and **14**, and a slight bathochromic shift for **15** (*cf.* Table 3). Adopting the geometrical parameters calculated for **13–15** by using the MINDO/3 method, we have carried out a CNDO/S-CI calculation to interpret the UV spectra. These calculations suggest the assignment of the long wave-length band to a $\pi^* \leftarrow n$ transition mainly localized on the CO group. The low intensity of this band is in agreement with this interpretation.

The band with high intensity is assigned to a $\pi^* \leftarrow \pi$ transition with a strong charge-transfer character, *i.e.* the electron originates from the olefinic π orbital and terminates in the π^* orbital of the CO group. The close proximity of both fragments is responsible for the high intensity of the band.

X-Ray Structure Analysis of 2 and 3. – The experimentally determined distances in **2** and **3** are shown in *Fig. 6*. It is found that in all three cyclopropane rings of **2** and **3** the C(2)–C(8), C(4)–C(6) bonds are lengthened relative to the mean values ($\bar{d}$) of the individual rings (**2**: [C(2)–C(8)]- $\bar{d} = +0.040$ Å; **3**: [C(2)–C(8)]- $\bar{d} = +0.027$ and [C(4)–C(6)]- $\bar{d} = 0.029$ Å). The remaining bonds of the three-membered rings are shortened (**2**: -0.020 Å; **3**: -0.014 Å). Within $\pm 30^\circ$, the favourable *trans*-bisected conformation is found for all the CO groups.

The observed bond-length changes are in line with other studies on cyclopropane derivatives with acceptor groups [17]. They can be rationalized by assuming a strong interaction between the π^* MO of the CO group(s) and the *Walsh*-type MO's of the cyclopropane-ring moiety [18].

In **3**, the bicyclopentyl moiety is fixed in an eclipsed conformation by the CO groups. For such a conformation, the non-bonding repulsions and the result of the higher *s* character at the cyclopropane C-atoms [19] oppose each other. The resulting bond distances in bicyclopentanes with a similar conformation are found to vary between 1.49–1.52 Å [20]. The additional repulsive forces due to the methyl groups (C(9) and C(10)) give rise to an additional lengthening of the C(1)–C(5) bond of **3** to a distance of 1.549 (2) Å (*Fig. 6*). The corresponding bond length of 1.574 (3) Å (*Fig. 6*) in **2** is significantly longer than in **3**. Here, only one C-atom has higher *s* character, and thus a longer bond is anticipated. The eclipsed conformation, however, is also preserved in **2** (C(9)–C(1)–C(5)–C(10) = 1.6° (3)).

In a comparable molecule, this bond is also lengthened (1.572 Å) [21]. Due to the additional bridging bond in **3**, the contact distance C(3)...C(7) 2.816 (3) Å between the CO groups is significantly shorter than the corresponding distance of 3.015 (3) Å in **2** and considerably shorter than the *van der Waals* distance of 3.4 Å. The intramolecular distances

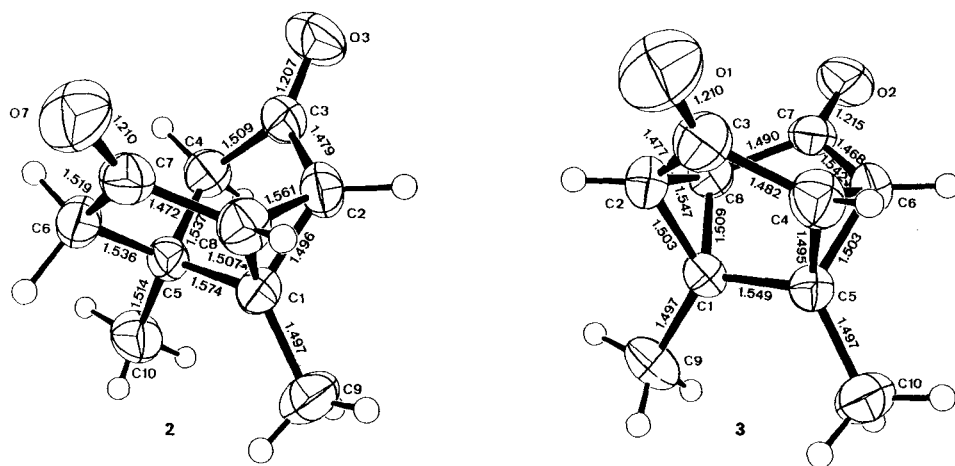


Fig. 6. Bond lengths of **2** and **3**. Standard deviations 0.002–0.004 Å.

between the O-atoms of the CO groups (**2**: 4.498 (3) Å; **3**: 4.701 (3) Å) are too long to allow significant through-space interactions between their lone pairs.

Conclusions. – The compounds synthesized have allowed us to study the interaction of two carbonyl, two ethylene, and an ethylene and carbonyl moiety at different distances.

For **1–3**, we find an increase in the splitting between the two lone-pair orbitals, due to a stronger n/σ interaction as evidenced by our PE studies. For the low-lying π^* MO's, recent investigations using ET spectroscopy show [14] also a strong π^*/σ interaction as evidenced by a destabilization of π^* . For **4–6**, we observe also a dominance of π/σ interaction which shows up in a destabilization of π_+ and π_+ .

Experimental Part

General. All solvents were distilled prior to use, and all reactions were performed under N_2 . M.p. are uncorrected and were determined using a Büchi melting-point apparatus. UV light absorption data were obtained using a Varian Cary 17 D spectrometer, the maxima of the bands are characterized in nm (log ϵ). IR spectra were recorded with a Beckmann 4200 instrument, the bands are characterized in cm^{-1} . NMR data were obtained with Varian EM 360 (1H), Varian 390 (1H), Bruker WH 300 (1H , ^{13}C), Varian FT-20 (^{13}C), and Bruker HFX 90 (^{13}C) spectrometers and refer to soln. in $CDCl_3$ with TMS as internal standard unless indicated otherwise. Mass spectra (MS) refer to data from a Finnigan 3200 GC/MS (CI) and from a ZAB instrument from Vacuum Generators (EI, 70 eV). Elemental analyses were performed at the Mikroanalytisches Labor des Chemischen Instituts der Universität Heidelberg. PE spectra refer to data from a Perkin Elmer PS18 instrument and are calibrated with Ar and Xe. A resolution of 0.03 eV has been achieved for the $Ar\ 2P_{3/2}$ line.

For the X-ray analysis of **2** and **3**, the colourless, needle-like crystals were grown from mixtures of Et_2O and $EtOH$. The crystallographic data and the parameters of structure refinement are listed in Table 4. The data were collected on an automatic diffractometer (CAD4 Enraf-Nonius; $MoK\alpha$ radiation, graphite monochromator, $2\theta-\omega$ scanning). The solutions of the structures with direct methods and the refinements in full-matrix technique of F^2 were carried out with the SDP program system (Enraf-Nonius [22]) on a PDP 11/44 computer. The atomic coordinates are listed in Table 5¹⁾.

Table 4. Crystallographic Data and Refinement Parameters of **2** and **3**

Compound	2	3
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	Cc
Z	4	4
a [Å]	7.193(1)	7.255(1)
b [Å]	8.604(1)	18.917(2)
c [Å]	13.968(2)	6.537(1)
β [°]		111.49(1)
Crystal size [mm ³]	$0.55 \times 0.35 \times 0.35$	$0.45 \times 0.25 \times 0.12$
Reflections collected	2857	2190
Unique reflections	1486	1012
Observed reflections [$I > 3\sigma(I)$]	1213	870
Refinement		
R/R_w	0.039/0.047	0.030/0.039
Max. heights of difference synthesis [$e\text{Å}^{-3}$]	0.14	0.13
$R_w = \sqrt{\frac{\sum w(F_o - F_c)^2}{\sum wF_o^2}}; \quad w = \frac{1}{\sigma^2(F_o)}$		

¹⁾ Further informations about the structural data may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen, Federal Republic of Germany, giving the deposition number CSD 51526, the name of the authors and the journal numbers.

Table 5. Atomic Coordinates of **2** and **3** ($U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$)

Compound 2					Compound 3				
Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{eq} \times 10^3$	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{eq} \times 10^3$
C(1)	0.5826(3)	0.4901(3)	0.0997(1)	40(1)	C(1)	0.3204	0.1020(1)	0.5046	37(1)
C(2)	0.6643(3)	0.3344(3)	0.0771(2)	44(1)	C(2)	0.1530(3)	0.1490(1)	0.5038(3)	48(1)
C(3)	0.8111(3)	0.2958(3)	0.1474(1)	44(1)	C(3)	0.1799(3)	0.2195(1)	0.4218(3)	52(1)
C(4)	0.8217(3)	0.4270(3)	0.2189(2)	44(1)	C(4)	0.3301(3)	0.2128(1)	0.3186(3)	48(1)
C(5)	0.7226(3)	0.5662(2)	0.1726(1)	38(1)	C(5)	0.4329(2)	0.1432(1)	0.3817(3)	37(1)
C(6)	0.8608(3)	0.6550(3)	0.1091(2)	47(1)	C(6)	0.2897(3)	0.1524(1)	0.1494(3)	44(1)
C(7)	0.8635(3)	0.5684(3)	0.0143(1)	45(1)	C(7)	0.1150(3)	0.1082(1)	0.1174(3)	43(1)
C(8)	0.6922(3)	0.4754(3)	0.0082(1)	46(1)	C(8)	0.1161(3)	0.0874(1)	0.3377(3)	43(1)
C(9)	0.3778(3)	0.5208(3)	0.1007(2)	58(1)	C(9)	0.4274(4)	0.0534(1)	0.6911(3)	56(1)
C(10)	0.6331(4)	0.6710(3)	0.2465(2)	59(1)	C(10)	0.6506(3)	0.1329(1)	0.4390(4)	55(1)
O(3)	0.8978(3)	0.1759(2)	0.1511(1)	70(1)	O(1)	0.1017(3)	0.2741(1)	0.4429(4)	38(1)
O(7)	0.9803(3)	0.5816(2)	-0.0475(1)	71(1)	O(2)	0.0002(3)	0.0864(1)	-0.0579(2)	66(1)

2-*exo*-Bromo-1,5-dimethylbicyclo[3.3.0]octane-3,7-dione (**7**). A soln. of **1** [6] (24.9 g, 150 mmol) in a mixture of $\text{CHCl}_3/\text{EtOAc}$ (200 ml/200 ml) was heated under reflux for 0.5 h, while dry N_2 was passed through. Powdered CuBr_2 (44.6 g, 200 mmol) was added in small portions during 3–4 h. The soln. turned green on the addition of CuBr_2 , and the next portion was only added after the initial green colour had faded to yellow. After all of the CuBr_2 had been added, the mixture was heated under reflux for another 4–5 h. The resulting yellow suspension was cooled, the precipitated CuBr was filtered off, washed with CHCl_3 (100 ml), and the solvent was removed *in vacuo*. The residue was dissolved in CHCl_3 (300 ml) and washed successively with H_2O (70 ml), 5% aq. NaHCO_3 soln. (2×70 ml), and brine (50 ml). The org. layer was dried (MgSO_4), concentrated to ca. 250 ml, heated under reflux with activated C, filtered, and concentrated *in vacuo*. The residue was suspended in 100 ml of cold MeOH and stirred at r.t. for 15 min. The suspension was filtered with suction, washed with 20 ml ice-cold MeOH, and dried (KOH). Yield: 60%. An anal. sample was recrystallized from MeOH, m.p. 174° (dec). UV (EtOH): 310 (sh; 1.64), 298 (1.73), 210 (sh; 2.81). IR (KBr): 1755, 1740. $^1\text{H-NMR}$ (90 MHz): 4.50 (s, 1 H); 2.55–2.25 (m, 6 H); 1.30 (s, 6 H). $^{13}\text{C-NMR}$ (20 MHz): 213.21 (s); 207.62 (s); 60.40 (d); 51.40 (t); 50.51 (s); 50.17 (t); 48.71 (t); 43.70 (s); 22.35 (q); 20.07 (q). MS: 246 (M^+), 165 ($M^+ - \text{Br}$), 137 ($M^+ - \text{Br} - \text{CO}$), 55 (100). Anal. calc. for $\text{C}_{10}\text{H}_{13}\text{BrO}_2$ (245.12): C 48.98, H 5.31, Br 32.65; found: C 48.85, H 5.48, Br 32.59.

1,5-Dimethyltricyclo[3.3.0.0^{2,8}]octane-3,7-dione (**2**). A soln. of DBU (16.7 g, 110 mmol) in dry MeCN (50 ml) was added dropwise (2 h) with stirring to a soln. of **7** (24.5 g, 100 mmol) in dry MeCN (250 ml). The mixture was stirred at r.t. for 16 h. The mixture was filtered and concentrated *in vacuo* (max 50° bath temp.). The residue was cooled (ice-salt mixture) and 1N H_2SO_4 (150 ml) was carefully added. The resulting mixture was stirred at r.t. (2 h); H_2O was added (100 ml) and the soln. was extracted with CHCl_3 (3×150 ml). The org. layer was washed with aq. sat. NaHCO_3 soln. (3×50 ml), aq. sat. Na_2SO_4 soln. (3×70 ml), filtered, dried (MgSO_4), heated under reflux with activated C, filtered, and concentrated *in vacuo*. The residue was recrystallized from EtOH/Et₂O 1/1. Yield: 70–75%. White crystals, m.p. $140\text{--}142^\circ$. UV (EtOH): 290 (2.01), 216 (3.43). UV (cyclohexane): 322 (1.16), 311 (1.49), 300 (1.55), 293 (sh; 1.51), 209 (3.18). IR (KBr): 1720, 1685. $^1\text{H-NMR}$ (300 MHz): 2.55 (d, $^2J = 17.3$, 2 H); 2.35 (s, 2 H); 2.16 (d, $^2J = 17.3$, 2 H); 1.51 (s, 3 H); 1.47 (s, 3 H). $^{13}\text{C-NMR}$ (75.46 MHz): 208.44 (s); 56.32 (t); 47.60 (d); 47.03 (s); 41.85 (s); 22.89 (q); 13.66 (q). MS: 164 (M^+), 122 ($M^+ - \text{C}_2\text{H}_2\text{O}$, 100). Anal. calc. for $\text{C}_{10}\text{H}_{12}\text{O}_2$ (164.20): C 73.23, H 7.32; found: C 72.98, H 7.30.

2-*exo*, 6-*exo*-Dibromo-1,5-dimethylbicyclo[3.3.0]octane-3,7-dione (**8**). A soln. of **1** (16.6 g, 100 mmol) in a mixture of $\text{CHCl}_3/\text{EtOAc}$ (200 ml/200 ml) was heated under reflux for 0.5 h, while dry N_2 was passed through. Powdered CuBr_2 (89.2 g, 400 mmol) was added in small portions during 4 h. On the addition of CuBr_2 , the soln. turned green, and the next portion was only added after the initial green colour had faded to yellow. After all the CuBr_2 had been added, the mixture was heated under reflux for another 4–5 h. The resulting yellow suspension was cooled, the precipitated CuBr was filtered off, washed with CHCl_3 (100 ml), and the solvent was removed *in vacuo*. The residue was dissolved in CHCl_3 (300 ml), washed with H_2O (70 ml), 5% aq. NaHCO_3 soln. (2×70 ml), and brine (50 ml). The org. layer was dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The crude residue which melts at $174\text{--}180^\circ$ is pure enough for most purposes: white powder. Yield: 65–70%. M.p. $207\text{--}209^\circ$ (MeOH). UV (EtOH): 298 (1.84), 218 (3.07). IR (KBr): 1755. $^1\text{H-NMR}$ (90 MHz): 4.52 (s, 2 H); 2.36 (s, 4 H); 1.36 (s, 6 H).

^{13}C -NMR (20 MHz): 205.25 (s); 60.82 (d); 48.68 (s); 46.67 (t); 20.44 (q). MS: 326 (M^+), 324 (M^+), 322 (M^+), 243 ($M^+ - \text{Br}$), 109 ($M^+ - \text{C}_4\text{H}_6\text{Br} - \text{HBr}$, 100). Anal. calc. for $\text{C}_{10}\text{H}_{12}\text{Br}_2\text{O}_2$ (324.02): C 37.04, H 3.70, Br 49.38; found: C 37.28, H 3.94, Br 49.66.

4-*exo*-Bromo-1,5-dimethyltricyclo[3.3.0.0^{2,8}]octane-3,7-dione (9). Dry Et_3N (10.3 g, 102 mmol) was added dropwise to a hot soln. of **8** (15 g, 46.3 mmol) in dry CHCl_3 (300 ml). The mixture was stirred and heated under reflux for 4 h. The cooled soln. was washed with 2N HCl (3×100 ml) and H_2O (3×50 ml). The org. layer was dried (Na_2SO_4), filtered, activated C was added, and the mixture was boiled for 10 min. The filtered soln. was concentrated *in vacuo*, and the residue was recrystallized from EtOH : white spangles. Yield: 70–75%. M.p. 198–200°. UV (EtOH): 292 (1.93). IR (KBr): 1755, 1725. ^1H -NMR (90 MHz): 4.54 (d, $^4J = 1.5$, 1 H); 2.75 (d, $^2J = 18$, 1 H); 2.44 (s, 2 H); 2.28 (dd, $^2J = 18$, $^4J = 1.5$, 1 H); 1.55 (s, 3 H); 1.51 (s, 3 H). ^{13}C -NMR (75.46 MHz): 207.03 (s); 199.60 (s); 64.26 (d); 50.36 (t); 47.03 (d); 46.04 (s); 43.08 (s); 40.77 (d); 21.57 (q); 13.60 (q). MS: 202 ($M^+ - \text{C}_2\text{H}_2\text{O}$), 200 ($M^+ - \text{C}_2\text{H}_2\text{O}$), 163 ($M^+ - \text{Br}$), 121 ($M^+ - \text{Br} - \text{C}_2\text{H}_2\text{O}$, 100). Anal. calc. for $\text{C}_{10}\text{H}_{11}\text{BrO}_2$ (243.11): C 49.38, H 4.53, Br 32.92; found: C 49.14, H 4.51, Br 32.72.

1,5-Dimethyltetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane-3,7-dione (3). 1. From **8**. A soln. of DBU (41.2 g, 270 mmol) in dry MeCN (100 ml) was added dropwise (ca. 2 h) to a soln. of **8** (40 g, 123 mmol) in dry MeCN (500 ml). After all the base had been added, the mixture was warmed to ca. 50° and was stirred overnight. The crude mixture was concentrated *in vacuo* (max. 50° bath temp.). The residue was cooled with ice and was carefully treated with 1N H_2SO_4 (250 ml) and stirred at r.t. for 2 h. The mixture was extracted with CHCl_3 (4×150 ml). The org. layer was washed with sat. aq. NaHCO_3 soln. (3×50 ml) and sat. aq. Na_2SO_4 soln. (3×50 ml). The org. phase was filtered, dried (MgSO_4), and concentrated *in vacuo*. The dark brown residue was filtered through a column (silica/ EtOAc) and the eluates were concentrated *in vacuo* yielding a crude reaction product which was recrystallized from CCl_4 : white crystals. Yield: 75–80%. M.p. 145–147°.

2. From **9**. A soln. of freshly sublimed *t*-BuOK (5.04 g, 45 mmol) in dry THF (50 ml) was added dropwise with stirring to a cooled soln. of **9** (5 g, 20.5 mmol) in dry THF (150 ml). The mixture was stirred for 1 h at 0° and then for 3 h at r.t. The crude mixture was slowly added to 3N HCl (300 ml), stirred (20 min), and extracted with CHCl_3 (3×150 ml). The org. layer was washed with H_2O (2×80 ml), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue solidified and was recrystallized from toluene or $\text{EtOH}/\text{Et}_2\text{O}$: white needles. Yield: 70–75%. M.p. 141–143°. UV (EtOH): 313 (1.84), 282 (1.62), 272 (sh; 1.61), 228 (sh; 3.00). UV (cyclohexane): 319 (sh; 1.57), 311 (1.59), 295 (sh; 1.46), 289 (sh; 1.44), 278 (sh; 1.32), 219 (2.88). IR (KBr): 3070, 3060, 1765, 1745, 1734, 1720, 1685, 1675, 1660. ^1H -NMR (60 MHz): 1.80 (s, 4 H); 1.58 (s, 6 H). ^{13}C -NMR (20 MHz): 202.64 (s); 39.68 (s); 38.03 (d); 13.52 (q). MS: 162 (M^+), 147 ($M^+ - \text{CH}_3$), 134 ($M^+ - \text{CO}$), 106 ($M^+ - 2 \text{CO}$), 105 ($M^+ - 2\text{CO} - \text{H}$), 91 ($M^+ - 2\text{CO} - \text{CH}_3$, 100). Anal. calc. for $\text{C}_{10}\text{H}_{10}\text{O}_2$ (162.19): C 74.08, H 6.17; found: C 73.80, H 6.13.

General Procedure for the Preparation of the *exo*-Methylidene Derivatives **4**, **5**, and **6**. NaH (5.8 g, 200 mmol, 80% oil dispersion) was placed in a three-necked round-bottomed flask and washed several times with dry pentane under Ar. With stirring, dry DMSO (100 ml) was added and the mixture was warmed to 80° (bath temp.), until the evolution of H_2 had ceased (ca. 45 min). The mixture was cooled in an ice bath, and a soln. of dry $\text{Ph}_3\text{PCH}_3^+\text{Br}^-$ (71.4 g, 200 mmol) in dry DMSO (200 ml) was added dropwise. After all the reagent had been added, the soln. was stirred at r.t. for another 10 min, and a soln. of **1**, **2**, or **3** (50 mmol) in dry DMSO was added. The mixture was stirred for 88 h at 60°. The crude mixture was poured into ice water (500 ml), and the precipitated Ph_3PO was filtered off. The filter cake washed thoroughly with pentane, the filtrate was extracted with ice-cold pentane (6×150 ml), and the combined org. layers were washed with brine (2×70 ml) and H_2O (2×70 ml), and dried (Na_2SO_4). The soln. was concentrated *in vacuo* and the yellow oily residue was fractionated *via* a small Vigreux column.

1,5-Dimethyl-3,7-dimethylidenetetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane (6). Colourless oil. Yield: 64.5%. B.p. 87°/25 Torr. UV (cyclohexane): 228 (4.26). IR (film): 2955, 1655. ^1H -NMR (90 MHz): 4.83 (s, 4 H); 1.83 (s, 4 H); 1.33 (s, 6 H). ^{13}C -NMR (75.46 MHz): 148.27 (s); 102.34 (t); 39.94 (d); 38.98 (s); 14.21 (q). MS: 158 (M^+), 143 ($M^+ - \text{CH}_3$, 100). Anal. calc. for $\text{C}_{12}\text{H}_{14}$ (158.24): C 91.13, H 8.86; found: C 90.77, H 9.06.

1,5-Dimethyl-3,7-dimethylidenetricyclo[3.3.0.0^{2,8}]octane (5). Colourless oil. Yield: 56%. B.p. 72–75°/40 Torr (Kugelrohr). UV (EtOH): 208 (4.11). UV (cyclohexane): 210 (4.12). IR (film): 2980, 2940, 1655. ^1H -NMR (300 MHz): 4.86 (br. s, 2 H); 4.82 (br. s, 2 H); 2.55 (dq, $^2J = 15$, $^4J = 2.5$, 2 H); 2.04 (d, $^2J = 15$, 2 H); 2.01 (s, 2 H); 1.28 (s, 3 H); 1.18 (s, 3 H). ^{13}C -NMR (75.46 MHz): 150.90 (s); 104.92 (t); 53.54 (t); 48.87 (s); 44.29 (s); 43.24 (d); 22.84 (q); 15.20 (q). MS: 160 (M^+), 145 ($M^+ - \text{CH}_3$, 100). Anal. calc. for $\text{C}_{12}\text{H}_{16}$ (160.26): C 89.94, H 10.06; found: C 89.73, H 10.17.

1,5-Dimethyl-3,7-dimethylidenetricyclo[3.3.0]octane (4). Colourless oil. Yield: 61%. B.p. 83°/25 Torr. UV (EtOH): 198 (4.26). UV (cyclohexane): 197 (4.24). IR (film): 3070, 2980, 2960, 2920, 2870, 2840, 1650. ^1H -NMR

(300 MHz): 4.83 ($J = 2.2, 4\text{ H}$); 2.35 ($dq, {}^2J = 16.4, {}^4J = 2.2, 4\text{ H}$); 2.21 ($dq, {}^2J = 16.4, {}^4J = 2.2, 4\text{ H}$); 0.94 ($s, 6\text{ H}$). $^{13}\text{C-NMR}$ (75.46 MHz): 150.69 (s); 106.54 (t); 50.52 (s); 45.76 (t); 21.64 (q). MS: 162 (M^+), 147 ($M^+ - \text{CH}_3$), 107 ($M^+ - \text{CH}_3 - \text{C}_3\text{H}_4$, 100). Anal. calc. for $\text{C}_{12}\text{H}_{18}$ (162.28): C 88.84, H 11.16; found: C 88.92, H 11.33.

Rearrangement 5→5'. Freshly sublimed *t*-BuOK (100 mg, 0.9 mmol) was added to a soln. of **5** (150 mg, 0.9 mmol) in dry DMSO (5 ml). The mixture was stirred and heated at 90° (bath temp.) for 3 h. The mixture was cooled and added to ice-water (30 ml) with stirring. The aq. layer was extracted with ice-cold pentane ($3 \times 30\text{ ml}$). The org. layer was washed with brine ($2 \times 30\text{ ml}$), dried (Na_2SO_4), and concentrated *in vacuo*. By means of $^1\text{H-NMR}$, it was shown that the resulting oil consisted of **5** and **5'** (ca. 1:1).

2-endo,4-exo,6-endo,8-exo-Tetrabromo-1,5-dimethylbicyclo[3.3.0]octane-3,7-dione (10). A soln. of Br_2 (256 g, 1.6 mmol) in dry CCl_4 (300 ml) was added (5–6 h) at r.t. to a soln. of **1** (66.4 g, 400 mmol) in 1500 ml dry CCl_4 . After all the Br_2 had been added, the mixture was stirred at r.t. for 72 h. N_2 was bubbled through the suspension for 2 h; the precipitate was filtered with suction, washed with CCl_4 ($5 \times 40\text{ ml}$), and air-dried. The crude product was suspended in H_2O (600 ml), filtered with suction, and washed with H_2O , until the washings showed pH 7. Finally, the crude product was washed with cold MeOH and dried (NaOH). Recrystallization from CHCl_3 afforded an anal. pure sample: white needles. Yield: 85%. M.p. 228–230° (dec.). IR (KBr): 1770. $^1\text{H-NMR}$ (90 MHz, (D_6) acetone): 5.22 ($s, 2\text{ H}$); 5.09 ($s, 2\text{ H}$); 1.61 ($s, 6\text{ H}$). $^{13}\text{C-NMR}$ (20 MHz, (D_6) acetone): 201.39 (s); 56.93 (d); 56.14 (d); 52.29 (s); 19.81 (q). MS: 486 (M^+), 401 ($M^+ - \text{Br}$, 100), 321 ($M^+ - \text{Br} - \text{HBr}$). Anal. calc. for $\text{C}_{10}\text{H}_{10}\text{Br}_4\text{O}_2$ (481.82): C 24.90, H 2.08, Br 66.39; found: C 25.17, H 2.24, Br 66.47.

2,6-Dibromo-1,5-dimethyltetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane-3,7-dione (11). Anhyd. NaOAc (3.92 g, 40 mmol) and **10** (48 g, 10 mmol) were suspended in a mixture of glacial AcOH (50 ml) and Ac_2O (10 ml), and the mixture was stirred and heated at 80° for 12 h. The pink soln. was cooled to r.t. and slowly added to H_2O (150 ml). The precipitate was stirred for 30 min, filtered with suction, and washed with H_2O ($3 \times 50\text{ ml}$). The filtrate was extracted with CHCl_3 ($2 \times 100\text{ ml}$) and the CHCl_3 extract was washed with H_2O ($2 \times 30\text{ ml}$). The org. layer was dried (Na_2SO_4) and concentrated *in vacuo*. The residue and the above filter cake were suspended in H_2O (50 ml), filtered with suction, and recrystallized from much EtOH: colourless spangles. Yield: 78–80%. M.p. 220–222°. UV (EtOH): 291 (1.79). IR (KBr): 1755, 1735, 1100, 1050, 1030, 900. $^1\text{H-NMR}$ (90 MHz): 2.30 ($s, 2\text{ H}$); 1.70 ($s, 6\text{ H}$). $^{13}\text{C-NMR}$ (75.46 MHz): 193.76 (s); 44.40 (s); 44.16 (s); 41.01 (d); 12.73 (q). MS (Cl , CH_4): 323, 321, 319 ($M\text{H}^+$). Anal. calc. for $\text{C}_{10}\text{H}_8\text{Br}_2\text{O}_2$ (319.99): C 37.50, H 2.50, Br 50.00; found: C 37.52, H 2.78, Br 49.87.

4,6-Dibromo-3,7-dihydroxy-1,5-dimethylbicyclo[3.3.0]octa-3,6-diene-2,8-dione (12a) and 2,6-Dibromo-3,7-dihydroxy-1,5-dimethylbicyclo[3.3.0]octa-2,6-diene-4,8-dione (12b). Compound **10** (48.2 g, 100 mmol) was added portionwise to conc. H_2SO_4 (500 ml). The resulting suspension was stirred at r.t. for 18 h. The crude, darkbrown (Br_2) soln. was added dropwise into ice-water (2 l). A precipitate was formed and the suspension was stirred for 30 min, filtered with suction, and washed with ice-cold H_2O , until the washings showed pH 7. The air-dried product was recrystallized from boiling MeOH/ H_2O 1:1. The precipitate consisted of pure **12a**. The mother liquor was concentrated *in vacuo*. Chromatography (silica/toluene-EtOH 2:1) yielded **12b** and additional **12a**. Both isomers gave a green-brown colour with methanolic FeCl_3 . Yield: 90% (**12a** + **12b**); **12a**/**12b** 3.5:1; white crystalline powder.

12a. M.p. 265° (dec.). UV (EtOH): 346 (3.05), 274 (4.19). IR (KBr): 3330, 2990, 2940, 1730, 1690, 1665, 1390, 1375, 1050. $^1\text{H-NMR}$ (90 MHz, (D_6) DMSO): 10.70 (s , D_2O exchangeable, 2 H); 1.43 ($s, 3\text{ H}$); 1.38 ($s, 3\text{ H}$); $^{13}\text{C-NMR}$ (20 MHz, (D_6) DMSO): 191.36 (s); 148.10 (s); 132.67 (s); 64.72 (s); 51.92 (s), 19.14 (q); 16.71 (q). MS (Cl , CH_4): 395, 393, 391 ($M\text{C}_3\text{H}_5^+$), 383, 381, 379 ($M\text{C}_2\text{H}_5^+$), 355, 353, 351 ($M\text{H}^+$). Anal. calc. for $\text{C}_{10}\text{H}_8\text{Br}_2\text{O}_4$ (351.99): C 34.09, H 2.27, Br 45.45; found: C 34.36, H 2.45, Br 45.25.

12b. M.p. 290–293° (dec.). UV (EtOH): 370 (sh; 2.81), 346 (3.08), 339 (3.09), 321 (3.00), 264 (3.24). IR (KBr): 3310, 2980, 2740, 1760, 1755, 1740, 1660, 1370, 1360, 1045. $^1\text{H-NMR}$ (90 MHz, (D_6) DMSO): 10.75 (s , D_2O exchangeable, 2 H); 1.40 ($s, 6\text{ H}$). $^{13}\text{C-NMR}$ (20 MHz, (D_6) DMSO): 194.79 (s); 147.60 (s); 128.51 (s); 56.47 (s); 16.74 (q). MS: 354, 352, 350 (M^+), 308, 306, 304 ($M^+ - \text{CO} - \text{H}_2\text{O}$, 100). Anal. calc. for $\text{C}_{10}\text{H}_8\text{Br}_2\text{O}_4$ (351.99): C 34.09, H 2.27, Br 45.45; found: C 34.08, H 2.43, Br 45.36.

1,5-Dimethyl-7-methylidenbicyclo[3.3.0]octane-3-one (13), 1,5-Dimethyl-7-methylidenetetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane-3-one (14) and 1,5-Dimethyl-7-methylidenetetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane-3-one (15). Compounds **13**, **14**, and **15** were prepared, as the dienes **4–6**, by Wittig reaction of the diketones **1**, **2**, and **3**, resp. Quantities: 50 mmol of diketone and 65 mmol of NaH and $\text{Ph}_3\text{PCH}_3^+\text{Br}^-$. Reaction time: 62 h at 60°. The enones were separated from the dienes by column chromatography (silica, Et_2O /pentane 1:4).

13. Colourless oil. Yield: 41% (+17% diene). UV (EtOH): 290 (1.36). UV (cyclohexane): 295 (1.32). IR (film): 2945, 2910, 1740. $^1\text{H-NMR}$ (300 MHz): 4.91 (*quint.*, ${}^4J = 2.3, 2\text{ H}$); 2.41 (t , ${}^4J = 2.3, 4\text{ H}$); 2.31 (d , ${}^2J = 19.2, 2\text{ H}$); 2.15 (d , ${}^2J = 19.2, 2\text{ H}$); 1.08 ($s, 6\text{ H}$). $^{13}\text{C-NMR}$ (75.46 MHz): 217.22 (s); 148.65 (s); 107.91 (t); 50.75 (t); 47.87 (s);

45.51 (*t*); 21.57 (*q*). MS: 164 (M^+), 149 ($M^+ - \text{CH}_3$), 136 ($M^+ - \text{CO}$), 122 ($M^+ - \text{C}_2\text{H}_2\text{O}$), 107 ($M^+ - \text{CH}_3 - \text{C}_2\text{H}_2\text{O}$, 100). Anal. calc. for $\text{C}_{11}\text{H}_{16}\text{O}$ (162.25): C 80.44, H 9.74; found: C 80.67, H 9.84.

14. Colourless oil. Yield: 31% (+11% **2a**). UV (EtOH): 275 (1.89), 202 (4.07). UV (cyclohexane): 285 (1.59), 207 (4.03). IR (film): 2950, 1720. ^1H -NMR (300 MHz): 5.03 (*m*, 1 H); 4.98 (*m*, 1 H); 2.74 (*dq*, 1 H), $^2J = 14.2$, $^4J = 2.5$, 1 H); 2.38 (*d*, $^2J = 9.9$, 1 H); 2.32 (*dq*, $^2J = 17.8$, $^4J = 1.2$, 1 H); 2.12 (*d*, $^2J = 14.2$, 1 H); 2.03 (*d*, $^2J = 9.9$, 1 H); 1.95 (*d*, $^2J = 17.8$, 1 H); 1.38 (*s*, 3 H); 1.32 (*s*, 3 H). ^{13}C -NMR (75.46 MHz): 212.31 (*s*); 147.63 (*s*); 108.98 (*t*); 55.33 (*t*); 55.06 (*t*); 48.86 (*d*); 46.25 (*s*); 45.50 (*s*); 42.78 (*d*); 22.86 (*q*); 14.71 (*q*). MS: found: 162.1044 (M^+); calc.: 162.1056.

15. Colourless crystals, m.p.: 40–41°. Yield: 29% (+15% **2b**). UV (EtOH): 279 (2.28), 236 (3.48). UV (cyclohexane): 277 (1.88), 227 (3.10). IR (KBr): 2950, 2930, 1685. ^1H -NMR (300 MHz): 5.08 (*s*, 2 H); 2.15 (*d*, $^3J = 9.3$, 2 H); 1.69 (*d*, $^3J = 9.3$, 2 H); 1.44 (*s*, 6 H). ^{13}C -NMR (22.26 MHz): 205.50 (*s*); 144.83 (*s*); 106.92 (*t*); 41.08 (*d*); 40.33 (*s*); 39.60 (*d*); 13.91 (*q*). MS: 160 (M^+), 145 ($M^+ - \text{CH}_3$), 132 ($M^+ - \text{CO}$, 100), 117 ($M^+ - \text{CO} - \text{CH}_3$). Anal. calc. for $\text{C}_{11}\text{H}_{12}\text{O}$ (160.22): C 82.46, H 7.55; found: C 82.47, H 7.52.

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