# 156. Dimers of 3,7-Dehydrotropones[1]) (Bicyclo[3.2.0]hepta-1(7),2,4-trien-6-ones)

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(23.V.84)

*Summary*

2-(*tert*-Butyl)-3,7-dehydrotropone (7-(*tert*-butyl)bicyclo[3.2.0]hepta-1(7),2,4-trien-6-one; **1**) was found to dimerize reversibly to **2A** by [2 + 4]-cycloaddition/cycloreversion reaction. The equilibrium lies on the side of the highly strained dimer **2A** in the solid state, and on the side of the monomer **1** in solution. The [2 + 4]-reaction is fully peri-, site-, regio- and stereoselective. Above room temperature, **1** irreversibly formed a decarbonylated dimer **6**, probably *via* the intermediate **9A** or **9B**, which resulted either from a dimerisation of **1** by [4 + 6]-cycloaddition or from a sigmatropic rearrangement of the originally formed dimer **2A** or **2B**. Similary, the 6-bromo derivative **14** afforded the corresponding decarbonylated dimer **15**. Should the formation of **6** and **15** be due to a primary cycloaddition then that reaction is fully peri-, site- and regioselective. Mild $LiAlH_4$-reduction of **6** and subsequent acetylation yielded the acetate **11**, the structure of which was established by an X-ray analysis. More vigorous $LiAlH_4$-treatment also reduced the terminal fulvenoid double bond of **6** and acetylation of the crude product led to the acetates **12** and **13**.

**1. Introduction.** – In a previous publication [1b] we described the preparation of several 3,7-dehydrotropones[1]) and alluded to the precarious balance between stabilizing and destabilizing factors in these compounds, formally containing two trans double bonds in a planar [2] seven-membered ring. We now show that 2-(*tert*-butyl)-3,7-dehydrotropone (**1**) is in equilibrium with a dimer, and that it is readily converted into a decarbonylated dimer *(Scheme 1)*. The results are of interest in the light of the various selectivities of cycloadditions of cyclic polyenes.

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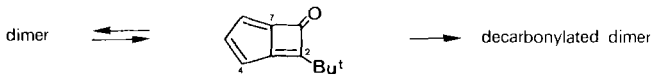
[3]) Deccased, 6.9.1979.

*Scheme 1*



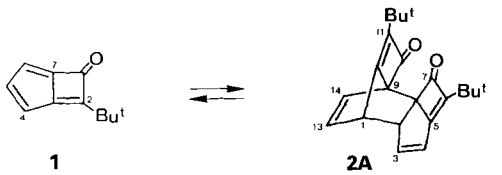

**1**

**2. Monomer-Dimer Equilibrium.** – In our previous work (see *Footnote 7* in [1b]), we had noted that solutions, prepared at −20°, of what then was taken to be crystalline **1** showed ancillary $^1$H- as well as $^{13}$C-NMR signals, in addition to those belonging to **1**. We have further examined this effect and found that solutions of the crystalline sample, prepared and kept at −50°, did not contain any **1**. The $^1$H- and the $^{13}$C-NMR spectra of this solution displayed signals for six different H- and fourteen different C-atoms, respectively, both in addition to signals for two different *t*-Bu-groups. This means that the molecules which were brought into solution at low temperature and thus also those in the crystals, m.p. 65°, are molecules of a non-symmetrical dimer of **1**. Its structure **2A** will be discussed in *Chapter 3*.

When this low-temperature solution of dimer **2A** was allowed to warm up to, and kept at 0°, a gradual transformation to **1** took place within 30 min, as observed by monitoring the $^1$H-NMR spectrum. Cooling this solution again did not cause any dimerization of **1** during a period of at least 2 h at −50°. However, when this solution of **1** was concentrated at −20° and the residue allowed to warm up to room temperature, dimer **2A** was again formed and crystallized.

These observations suggest that **1** and its dimer **2A** are readily interconvertible, and that the equilibrium between the two lies on the side of the monomer to the extent of > 95% in a 0.5M $CHCl_3$-solution *(Scheme 2)*. That the dimer **2A** could nevertheless be observed in solution is attributed to the slow rate of its dissociation to **1** as compared to the rate of its dissolution at −50°. Here, two equilibria should be considered: $\mathbf{1} \leftrightarrows \mathbf{2A}_{soln.} \leftrightarrows \mathbf{2A}_{cryst.}$; both should be concentration-dependant.

*Scheme 2*



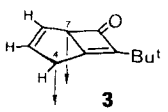

**1** **2A**

**3. Structural Evidence for the Dimer 2A.** – The ready reversion of **2A** to **1** suggests that the dimerization of **1** is not accompanied by a deep-seated rearrangement of **1** as well as of **2A**. On this basis, we present the following arguments for the structure of the dimer **2A**.

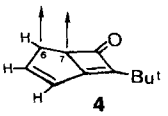
The two $^1$H-NMR *ABX*-signal systems, one at $\delta$ = 6.82, 6.48 and 3.59 ppm ($J_{AB}$ = 5.9, $J_{AX}$ = 1.0, $J_{BX}$ = 2.5 Hz) and the other at $\delta$ = 6.70, 6.35 and 4.15 ppm ($J_{AB}$ = 5.5, $J_{AX}$ < 0.5, $J_{BX}$ = 2.3 Hz) show that **2A** contains two different −CH=CH−CH− units. This means that one of the new bonds formed during the dimerization of **1** involved either C(4) or C(6) in each of the molecules of **1**, so that two saturated methine groups were created. These two groups also caused the two d seen in the quadriligant C-atom region ($\delta$ = 57.9 and 48.3 ppm) of the $^{13}$C-NMR spectrum of **2A**. The only other signals in this region (aside from those of the *t*-Bu-group) are two *s*

at 82.8 and 77.7 ppm. Thus the second new bond formed in the dimerization reaction of **1** must involve two C-atoms not carrying any H-atoms, *i.e.* either C(2), C(3) or C(7) of the two molecules of **1**. That the involvement of C(2) and C(3) must be excluded in each of the molecules of **1**, is derived from the following observation: Selective irradiation at the two (closely positioned) *t*-Bu H-atom frequencies (at $\delta = 1.13$ ppm) radically changed only two of the ten $^{13}$C-NMR signals of triligant C-atoms, inasmuch as the widths of the broad signals at 155.5 and 145.1 ppm were both reduced from 80 and 60 Hz, respectively, to $\approx 10$ Hz. The irradiation evidently eliminated the $^3J_{(C,H)}$-couplings (usually 4–9 Hz) between the protons of the *t*-Bu groups and the two C-atoms to which the *t*-Bu groups are attached. Since these two C-atoms are triligant, the original C(2), C(3) double bond of **1** has remained intact in both halves of the dimer. The second bond formation in the dimerization, therefore, cannot have involved C(2) or C(3), which leaves only C(7) in both molecules of **1**.

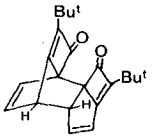
We can now represent the two halves of the dimer **2A** as either **3** or **4** or both (arrows show new bonds) and, since the dimer is not symmetrical, the combination must be **3** and **4** to give **2**. For the constitution **2**, two regioisomers and, for each of these, two stereoisomers are possible. These are shown as structures **2A** to **2D**. Other spectral features of the dimer are in agreement with all four of these potential structures. They include the $^{13}$C-NMR signals for two carbonyl C-atoms ($\delta = 184.5$ (*s*) and 181.3 (*s*) ppm), for four triligant methine C-atoms ($\delta = 145.8$ (*d*), 134.9 (*d*), 133.0 (*d*) and 128.5 (*d*) ppm) and for two triligant C-atoms without H-atoms ($\delta = 174.6$ (*s*) and 168.3 (*s*) ppm), as well as the solid-state ($BaSO_4$) UV absorptions at 230 and 283 nm (conjugated enone and dienone) and the solid-state (KBr) IR bands at 1760 and 1722 $cm^{-1}$. These properties, however, do not offer any immediately evident argument for the selection of one of the four potential structures **2A**–**2D**.



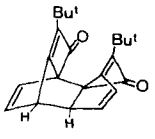

**3**



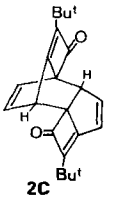

**4**



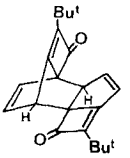

**2A**




**2B**




**2C**



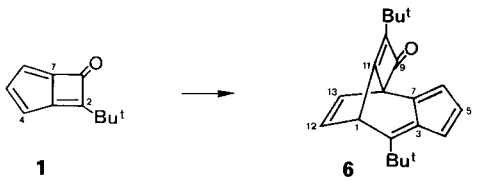

**2D**

An argument for a decision between **2A** to **2D** was obtained by noting the mutual coupling between the two H-atoms in allylic position ($^1$H-NMR signals at $\delta = 4.15$ and 3.59 ppm) to be 1.4 Hz (decoupling experiment). Therefore, these two H-atoms must be in vicinal position; otherwise 1,3 such a coupling should be absent, as has been shown in norbornene systems [3]. The dimer, therefore, must be **2A** or **2B** where H–C(1) and H–C(2) are vicinal. The magnitude of this mutual coupling (1.4 Hz) suggests a torsional angle of 50° and certainly excludes one of 80–90° [3]. Since the torsional angle between these two H-atoms (from models) is about 50° in **2A** and 80–90° in **2B**, we conclude that the dimer has structure **2A**.

In contrast to **1**, other 3,7-dehydrotropones, namely the 6-bromo-2-(*tert*-butyl)-, the 2-phenyl- and the 2-chloro-4,5-benzo-derivatives [1b] seem to exist as monomers in the solid state. In each case the fingerprint region of the IR spectrum in the solid state (KBr) and in solution ($CHCl_3$ or $CCl_4$) are almost superimposable (bands differing by $< 5$ cm$^{-1}$ and $< 20\%$ intensity, see *Sect. 7, Exper. Part*). In contrast, the IR-fingerprint regions of **2A** (solid phase) and of **1** (in solution) show notable differences. That the 2-dialkylamino-3,7-dehydrotropones [4] are also monomeric in the solid state has been shown by an X-ray analysis [2] of the dimethylamino derivative.

**4. The Decarbonylated Dimer 6.** – When a *ca.* 0.1M solution of **1** in $CH_2Cl_2$, prepared (see *Exper. Part*) at about 0°, was concentrated at ambient temperature and normal pressure, a gradual evolution of a gas was noted. From the residue, a 40% yield of a light-orange substance, m.p. 110°, was isolated, which we call the decarbonylated dimer. We present the following arguments for structure **6** of this product *(Scheme 3)*.

*Scheme 3*




**1** **6**

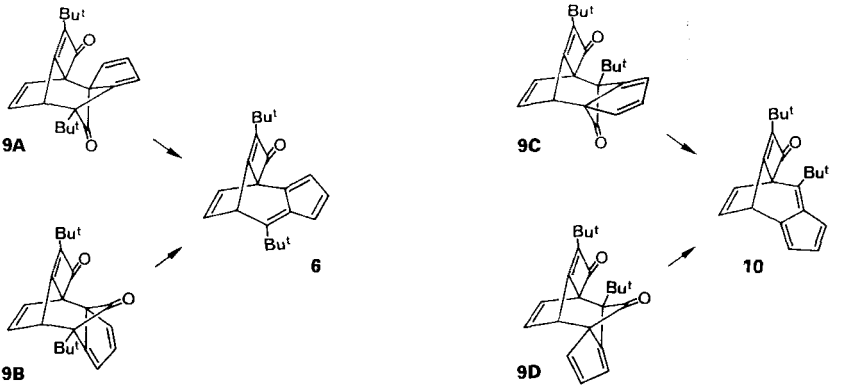
Elementary analysis and the MS ($M = 292$ $m/z$) indicate a molecular formula of $C_{21}H_{24}O$ ( = two molecules of **1** minus one of CO). The loss of CO must be due to a cheletropic reaction, which is only possible from an intermediate dimer if the bonds formed in the dimerization involved C(2) and C(7) of one of the dimerization partners. Since the product **6** contains a –HC=CH–CH– substructure ($^1$H-NMR *ABX*-system at $\delta = 6.73$, 6.43 and 4.35 ppm; $J_{AB} = 5.4$, $J_{AX} = 0.6$, $J_{BX} = 2.4$ Hz, very similar to one found in **2A**) the new bonds formed in the second molecule of **1** must involve C(4) and C(7).


**3** **7**

The two halves of the intermediate dimer (before decarbonylation) can now be represented as **3** and **7**, the combination of which gives **9**. For the constitution **9**, two regioisomers and, for each of these, two stereoisomers are possible. They are shown schematically as structures **9A** to **9D** *(Scheme 4)*.

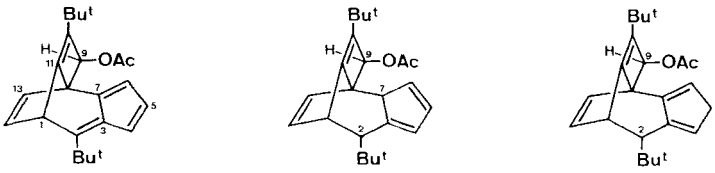
Any effect of the stereoselectivity of such a dimerization is not noticeable in the final decarbonylated dimer, since the stereoisomers **9A** and **9B** could both decarbonylate to **6** and the stereoisomers **9C** and **9D** could both decarbonylate to **10**. The spectral properties of the decarbonylated dimer agree with both structures **6** and **10** (IR bands at 1753 and 1656 cm$^{-1}$ of a cyclobutenone [5], low-intensity UV absorption at 406 nm of a fulvene [6]. $^1$H-NMR pattern at 6.27, 6.12 and 6.07 ppm of a 2,6,6-trisubstituted fulvene [7]) but do not offer an immediately evident argument for the preference of either of them. A decision in favor of the structure **6** is possible on the basis

*Scheme 4*




of an X-ray analysis (see *Chapter 6*) of a reduction and acetylation product (see *Chapter 5*) of **6**.

**5. Reduction of the Decarbonylated Dimer 6.** – When the decarbonylated dimer **6** was reduced with $LiAlH_4$ at 0°, and the product acetylated, an orange-colored acetate **11**, m.p. 121°, was obtained in 40% yield. Elementary analysis ($C_{23}H_{28}O_2$), the MS ($M$ = 336 $m/z$), an IR band at 1736 $cm^{-1}$, as well as the $s$ in the $^1$H-NMR spectrum at $\delta$ = 2.09 ppm for the acetoxy $CH_3$-group and the finely split signal ($\delta$ = 5.55 ppm) for H–C(9) confirm the structural changes expected for simple reduction of a carbonyl group and acetylation of the resulting secondary alcohol. The absence of a C-skeleton rearrangement is shown by the similarity of the spectral features of the ring system of **11** with those of **6**, namely the UV maximum at 407 nm ($\varepsilon$ = 500) and the 3-proton $^1$H-NMR signal pattern for the unchanged fulvene system, as well as the $^1$H-NMR signals for two further vicinal vinyl H-atoms and for two $t$-Bu groups. The structure of **11** was established by an X-ray crystal structure analysis (see *Chapter 6*), which also shows the acetoxy group to be located *syn* to the fulvene moiety. The structure of **11**, together with the above argument on the minimal changes during the reduction and acetylation of **6**, confirms the structure of **6** as given in *Chapter 4*.

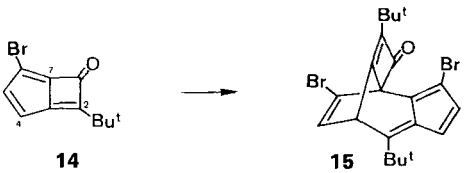



Under more vigorous conditions, $LiAlH_4$ reduced not only the carbonyl group but also the terminal double bond of the fulvene moiety in **6**, as was shown by the isolation of the acetates **12** and **13** when the reduction was performed in refluxing ether and the crude reduction product was acetylated.

The structures of **12** and **13** were established by the spectroscopic properties (see *Exper. Part*), particularly by the $^1$H-NMR-spectra, which also showed that **12** consisted of a 7:3 mixture of two diastereoisomers. The configuration of the acetoxy group (*syn* to the cyclopentadiene moiety) in **12** and **13** follows from that of the acetate **11**, because it is unlikely that the vigorous and the mild reduction of **6** proceded with different stereoselectivity. No conclusion could be drawn from the available data on the relative configurations at C(2) and C(7) in **12** and at C(2) in **13**.

**6. The Decarbonylated Dimer 15.** – When a benzene solution of 2-bromo-2-(*tert*-butyl)-3,7-dehydrotropone (**14**) [1b] was heated, a 70% yield of the light-orange decarbonylated dimer **15**, m.p. 151°, was isolated *(Scheme 5)*. Its properties, namely the composition $C_{21}H_{22}Br_2O$, the IR bands at 1758 and 1658 cm$^{-1}$, the *AB*- ($\delta$ = 6.52 and 6.17 ppm, $J$ = 5.8 Hz) and the *AX*-system ($\delta$ = 6.50 and 4.42 ppm, $J$ = 2.6 Hz) in the $^1$H-NMR spectrum as well as the UV maximum at 407 nm ($\varepsilon$ = 600), demonstrate its close relationship to the dimer **6**.

*Scheme 5*




**14** **15**

**7. X-Ray Crystal Structure of the Acetate 11.** – Compound **11** crystallizes as colorless monoclinic crystals, space group $P2_1/b$, $a$ = 11.85(1), $b$ = 28.45(2), $c$ = 6.10(1) Å, $\sigma$ = 75.6(1)°. There are four molecules per unit cell. A *Syntex* diffractometer was used for the measurement of 1865 reflections of which 817 with $I > 3\sigma(I)$ were considered as observed. The program system X-ray [8] was used for the structure analysis. The refinement (including H-atoms with fixed thermal parameters) converged to $R$ = 0.06 ($R_w$ = 0.038). The final coordinates are given in the *Table*.

In the ring system of the molecule **11**, three planes can be recognized: plane I with the nine atoms C(1) through C(8) and C(14), plane II with the four atoms C(1), C(8), C(12) and C(13), and plane III with the six

Table. *Final Atomic Coordinates of the Acetate* **11**

| Atom | $X$ | $Y$ | $Z$ | Atom | $X$ | $Y$ | $Z$ |
|---|---|---|---|---|---|---|---|
| C(1) | −0.3355(5) | 0.3864(2) | −0.010(1) | C(14) | −0.4929(5) | 0.3444(2) | 0.115(1) |
| C(2) | −0.3660(4) | 0.3446(2) | 0.1200(9) | C(15) | −0.5335(6) | 0.3452(2) | −0.127(1) |
| C(3) | −0.2748(5) | 0.3128(2) | 0.2183(9) | C(16) | −0.5212(5) | 0.3000(2) | 0.228(1) |
| C(4) | −0.2655(7) | 0.2691(3) | 0.351(1) | C(17) | −0.5612(5) | 0.3907(2) | 0.234(1) |
| C(5) | −0.1532(6) | 0.2514(2) | 0.415(1) | C(18) | −0.2274(7) | 0.4833(2) | 0.294(1) |
| C(6) | −0.0824(5) | 0.2827(2) | 0.327(1) | C(19) | −0.1693(8) | 0.5155(3) | 0.164(1) |
| C(7) | −0.1539(5) | 0.3188(2) | 0.2121(9) | C(20) | −0.1946(8) | 0.4856(3) | 0.529(1) |
| C(8) | −0.1350(6) | 0.3606(2) | 0.0862(9) | C(21) | −0.3579(7) | 0.5017(2) | 0.261(1) |
| C(9) | −0.0704(6) | 0.3986(3) | 0.176(1) | C(22) | 0.1097(5) | 0.3662(2) | 0.358(1) |
| C(10) | −0.1895(6) | 0.4329(2) | 0.213(1) | C(23) | 0.1715(6) | 0.3516(3) | 0.564(1) |
| C(11) | −0.2407(5) | 0.4016(3) | 0.117(1) | O(1) | −0.0025(3) | 0.3850(1) | 0.3701(6) |
| C(12) | −0.2578(7) | 0.3659(3) | −0.212(1) | O(2) | 0.1536(3) | 0.3609(2) | 0.1780(7) |
| C(13) | −0.1461(6) | 0.3521(2) | −0.160(1) | | | | |

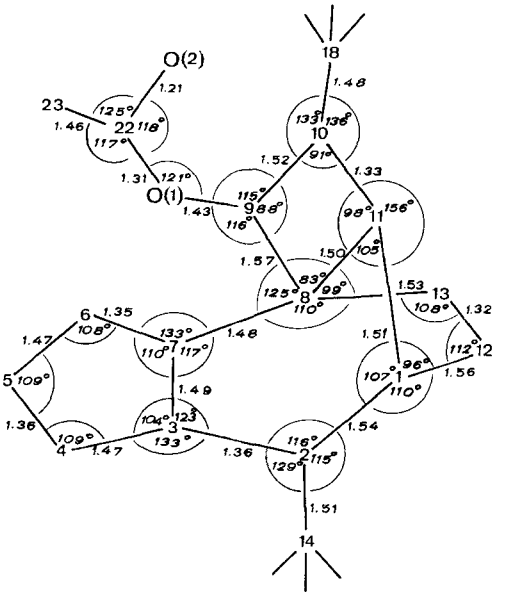



Fig. 1. *Bond lengths and bond angles of the acetate* **11**

Fig. 2. *Stereoscopic plot of the acetate* **11**

atoms C(8) through C(11), C(1) and C(18). The three planes intersect at the line passing through C(1) and C(8). The only marked deviation from a plane is that of C(1) (by 0.38 Å) from plane III; the deviations of the other atoms from their planes are an order of magnitude smaller. The acute angle between planes I and II is 70°. Inspection of the bond angles (see *Fig. 1*) reveals that the tetracyclic system **11** is not strained much more than is expected from its small and bridged rings. *Fig. 2* shows a stereoscopic plot of the acetate **11**.

**8. Discussion.** – We now consider some implications of the two major results of the present work: *a*) that **1** exists in a rapidly established equilibrium with the dimer **2A**, and *b*) that **1** also forms another dimer, **9A**, which decarbonylates to **6**.

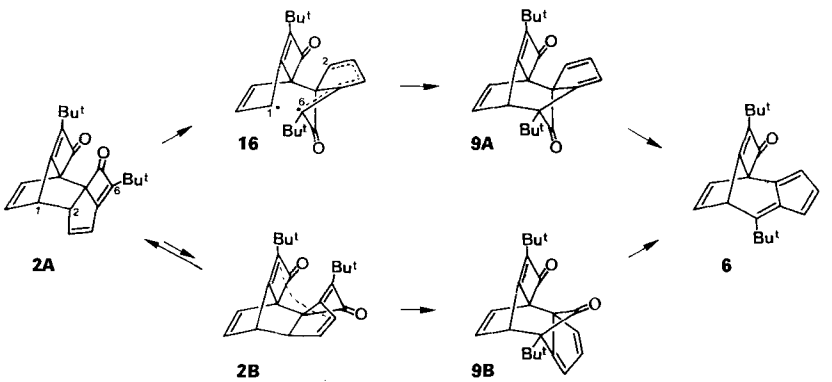
First we discuss result *a*: the formation of **2A** from two molecules of **1** corresponds to a cycloaddition with full [4 + 2]-periselectivity, [C(4) to C(6) and C(7) to C(7)]-siteselectivity, [head-to-head]-regioselectivity and [*endo*]-stereoselectivity. With respect to the peri- and stereoselectivity the 3,7-dehydrotropone system behaves more like a fulvene (see [9] [10]) than like tropone, which has been dimerized (to give various products)

only photochemically [11]. It is not clear, however, which factors control the (possibly interdependent) site- and regioselectivities.

Turning to result *b*, we consider two explanations: in the first one, the formation of **9A** or **9B** from two molecules of **1** is assumed to be also the result of a cycloaddition. In that case the reaction is fully [6 + 4]-periselective, [C(2) to C(4) and C(7) to C(7)]-siteselective and [head-to-head]-regioselective. No conclusion is possible at present as to the stereoselectivity, since **6** could have arisen from **9A** or **9B** (see *Chapter 4*). With respect to the peri- and siteselectivity, the 3,7-dehydrotropone system again behaves like a fulvene [12], while the regioselectivity is not comparable to a known case. On the basis of this explanation of result *b* our two results (*a* and *b*) represent competing [4 + 2]- and [6 + 4]-cycloadditions between two equal reaction partners. This corresponds to the experience made with 6,6-dimethylfulvene [9] [11]. While the [4 + 2]-dimerization of **1** is certainly a fast and reversible reaction, our results do not permit a conclusion on whether the [6 + 4]-dimerization of **1** is faster or slower than the decarbonylation of **9A** or **9B**. Note that in both our dimers, *i.e.* in **2A** and in **9A** or **9B**, bond formation has occurred between C(7) of both dimerization partners and that both dimers are formed under unusually mild conditions.

The competition of formal [4 + 2]- and [6 + 4]-cycloadditions between two different reaction partners have been described for the reaction of tropones with cyclopentadiene [13], with fulvenes [14], with cyclopentadienones [15], with butadiene [16] and with isobenzofurane [17] as well as for the addition of cycloheptatriene to a cyclopentadienone [18]. In the case of tropone, the [6 + 4]-are generally favored over the [4 + 2]-additions, an effect which has been rationalized by FMO treatment [19].

*Scheme 6*




The second explanation of our result *b* considers the dimer **9A** resp. **9B** to be formed from the primary [4 + 2]-cycloadduct **2A**, either by a direct [1,5]-migration of C(1) from C(2) onto C(6) (possibly *via* **16**) or by an *endo*/*exo*-equilibration of **2A** (*via* **1**) followed by a [3,3]-rearrangement of the *exo*-adduct **2B** *(Scheme 6)*. Similar rearrangements have been observed in related systems [18] [20].

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## Experimental Part

**1. General.** – The abbreviations and the spectral data notations used here have been described previously [21]. For $^1$H-NMR decoupling experiments, the chemical shift of the irradiated signal is given in square brackets [$\delta$], followed by the multiplicity of the ensuing signal.

**2. 6,11-Di(*tert*-butyl)pentacyclo[7.3.2.0$^{2,8}$.0$^{5,8}$.0$^{9,12}$]tetradeca-3,5,11,13-tetraen-7,10-dione (2A).** – The dimer **2A**, m.p. 65°[4]), was prepared as described in [1b]. UV ($BaSO_4$): max. 283, max. 230. IR (KBr): 1760*vs*, 1722*vs*, 1660*s*, 1599*s*. Samples of dimer **2A** were dissolved at −50° to −70° in $CDCl_3$. $^1$H-NMR (100 MHz, 40 mg/0.5 ml, $CDCl_3$ at −50°): 6.82 (*dd*, *J* = 5.9 and 1.0, 1H, H–C(3); [3.59] *d*, *J* = 5.9); 6.70 (*d*, *J* = 5.5, 1H, H–C(14)); 6.48 (*dd*, *J* = 5.9 and 2.5, 1H, H–C(4); [3.59] *d*, *J* = 5.9); 6.35 (*dd*, *J* = 5.5 and 2.3, 1H, H–C(13); [4.15] *d*, *J* = 5.5); 4.15 (*dd*, *J* = 2.3 and 1.4, 1H, H–C(1); [6.35] *d*, *J* = 1.4; [3.59] *d*, *J* = 2.3); 3.59 (*ddd*, *J* = 2.5, 1.4 and 1, 1H, H–C(2)); 1.19 (*s*, 9H, $(CH_3)_3C$); 1.07 (*s*, 9H, $(CH_3)_3C$). When this solution (of **2A**) was allowed to warm from −50° and then kept at 0° in the probe of the $^1$H-NMR spectrometer, the characteristic signals of **1** (*cf.* [1b]) gradually appeared within 30 min, after which time they were the only signals visible. This solution of **1** was recooled and kept at −50° for 2 h; its $^1$H-NMR spectra, which were recorded at 30 min intervals, showed only the unchanged signals of **1**. The solution of **1** was then concentrated at below −20°/0.01 Torr and the residual yellow oil was allowed to warm to r.t., whereby it gradually solidified. The solid, after drying at 20°/0.01 Torr, was dissolved at −70° to −50° in $CDCl_3$. The $^1$H-NMR spectrum of this solution, recorded at −50°, showed the presence of > 90% of the dimer **2A** and < 10% of the monomer **1**. $^{13}$C-NMR (25.2 MHz, 250 mg/1.2 ml, $CDCl_3$ at −30°): 184.5 (*s*, C(10)); 181.3 (*s*, C(7)); 174.6 (*s*, C(12)); 168.3 (*s*, C(5)); 155.5 (*s*, C(11)); 145.1 (*s*, C(6)); 145.8, 134,9, 133.0 and 128.5 (*d*, C(3), C(4), C(13), C(14)); 82.8 and 77.7 (*s*, C(8), C(9)); 57.9 and 48.3 (*d*, C(1), C(2)); 32.9 and 31.2 (*s*, $(CH_3)_3C$); 27.8 and 27.6 (*q*, $(CH_3)C$). The chemical shifts are taken from a proton-noise-decoupled spectrum, the multiplicities (only $^1$H couplings are considered) from an off-resonance experiment. Selective decoupling: Irradiation at 1.13 (H-atoms of *t*-Bu) converted the signal at 155.5 (width ≈ 80 Hz), the signal at 145.1 (width ≈ 60 Hz), the *q* at 27.6 and the *q* at 27.8 (both *J* = 125) to *s* (all widths < 10 Hz), whereas all the other C-atom signals remained essentially unchanged.

**3. 2,10-Di(*tert*-butyl)tetracyclo[6.3.2.0$^{3,7}$.0$^{8,11}$]trideca-2,4,6,10,12-pentaen-9-one (6).** – To a stirred solution of 3.22 g (10 mmol) of 4-*exo*-7-*exo*-dibromo-7-*endo*-(*tert*-butyl)bicyclo[3.2.0]hept-2-en-6-one [1b] in 50 ml of $CH_2Cl_2$ at 5° 2.2 g (10% excess) of $Et_3N$ in 10 ml of $CH_2Cl_2$ was added slowly. The mixture was then stirred for 15 min and washed with dil. HCl and $H_2O$. After drying ($MgSO_4$), the orange solution of **1** [1b] was evaporated slowly at 20–30° under a stream of $N_2$ and kept there until it was dry. From the black residue, 660 mg (40%) of **6** was separated by prep. TLC. Recrystallization from pentane gave light-orange needles, m.p. 110–111°. UV (EtOH): max. 406 (400), max. 290 (6100), max. 224 (8500), max. 213 (8700). IR (KBr): 2965*s*, 2908*w*, 2873*w*, 1753*s*, 1656*s*, 1580*m*, 1500*m*, 1481*m*, 1467*m*, 1370*m*, 1353*m*, 780*s*, 763*m*, 738*m*. $^1$H-NMR (100 MHz, $CCl_4$): 6.73 (*dd*, *J* = 5.4 and 0.6, 1H, H–C(13)); 6.43 (*dd*, *J* = 5.4 and 2.4, 1H, H–C(12)); 6.27 (*dd*, *J* = 5.6 and 1.1, 1H, H–C(4)); 6.12 (*dd*, *J* = 5.6 and 2.2, 1H, H–C(5)); 6.07 (*dd*, *J* = 2.2 and 1.1, 1H, H–C(6)); 4.35 (*dd*, *J* = 2.4 and 0.6, 1H, H–C(1)); 1.42 (*s*, 9H, $(CH_3)_3C$); 1.17 (*s*, 9H, $(CH_3)_3C$); these coupling constants and multiplicities were obtained from a 360-MHz $^1$H-NMR spectrum in $CDCl_3$. $^{13}$C-NMR ($CDCl_3$): 184.4 (*s*, C(9)); 180.0 (*s*, C(11)); 158.8 (*s*, C(10)); 140.0 (*d*, C(12)); 139.7 (*d*, C(13)); 137.1 (*s*, C(3) or C(7)); 136.0 (*s*, C(7) or C(3)); 131.2 (*d*, C(5)); 130.2 (*s*, C(2)); 121.0 (*d*, C(6)); 119.4 (*d*, C(4)); 74.2 (*s*, C(8)); 45.7 (*d*, C(1)); 39.9 and 31.3 (*s*, $(CH_3)_3C$); 29.8 and 27.9 (*q*, $(CH_3)C$). The multiplicities and assignments were based on proton-noise-decoupled, off-resonance, non-decoupled and selective coherent irradiated ($\delta$ = 4.3 at proton frequency) spectra. The signals at 180.0, 158.8 and 130.2 are broadened to a larger extent than the others by long-range couplings (with protons of t-Bu). The assignment of C(2)–C(7) was based on the similarity with the corresponding signals of 6-(*tert*-butyl)fulvene [7]; the signal at 139.7 was assigned to C(13) because it showed a visible coupling with H–C(1). MS (70 eV): 292 (54, $M^+$), 277 (27), 249 (72), 235 (100), 222 (27), 220 (16), 207 (20), 203 (15), 202 (15), 195 (10), 193 (29), 192 (24), 191 (26), 190 (15), 189 (25), 180 (10), 179 (25), 178 (28), 177 (11), 176 (15), 165 (39), 153 (13), 152 (25), 151 (12), 121 (20), 115 (12). Anal. calc. for $C_{21}H_{24}O$ (292.42): C 86.25, H 8.27; found: C 85.69, H 8.28.

**4. 9-Acetoxy-2,10-di(*tert*-butyl)tetracyclo[6.3.2.0$^{3,7}$0$^{8,11}$]trideca-2,4,6,10,12-pentaen (11).** – A solution of 292 mg (1 mmol) of **6** in 20 ml dry $Et_2O$ was added dropwise to a suspension of 20 mg (0.53 mmol) $LiAlH_4$ in 10 ml dry $Et_2O$ at 0°. After 20 min a small amount of $H_2O$, followed by dil. NaOH, was added and the precipitate was filtered off. Evaporation of the solvent left an oily residue, which was treated with 1 ml of pyridine/$Ac_2O$ 1:1 and left for 4 h at r.t. $Et_2O$ was added (50 ml) and the solution was washed with dil.

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[4]) This solid is identical with what was called 2-(*tert*-butyl)-3,7-dehydrotropone in [1b].

$NaHCO_3$, dil. HCl and finally with $H_2O$, dried and evaporated to dryness. The residual brown oil was purified by prep. TLC giving 135 mg (40%) of **11**. Recrystallization from pentane afforded orange needles, m.p. 120–121°. UV (EtOH): max. 407 (500), max. 305 (5100), max. 241 (7000), max. 215 (6600). IR (KBr): 2990*m*, 2965*m*, 2935*w*, 2903*w*, 2892*w*, 1736*s*, 1723*m* (sh), 1594*w*, 1582*m*, 1500*w*, 1477*w*, 1373*m*, 1367*m*, 1360*m*, 1245*vs*, 1225*m*, 1045*s*, 1022*m*, 780*m*, 732*m*. $^1$H-NMR (90 MHz, $CDCl_3$): 6.65 (*dd*, *J* = 5.3 and 0.6, 1H, H–C(13)); 6.50 (*ddd*, *J* = 5.3, 2.3 and 0.6, 1H, H–C(12)); 6.40 (*dd*, *J* = 5.6 and 1.1, 1H, H–C(4)); 6.22 (*dd*, *J* = 5.6 and 2.3, 1H, H–C(5)); 5.85 (*dd*, *J* = 2.3 and 1.1, 1H, H–C(6)); 5.55 (*dd*, *J* = 0.6 and 0.6, 1H, H–C(9)); 4.04 (*ddd*, *J* = 2.3, 0.6 and 0.6, 1H, H–C(1)); 2.09 (*s*, 3H, AcO); 1.33 (*s*, 9H, $(CH_3)_3C$); 1.02 (*s*, 9H, $(CH_3)_3C$). MS (70 eV): 336 (4, $M^+$), 279 (5), 165 (10), 157 (10), 119 (10), 105 (10), 91 (12), 77 (11), 57 (40), 43 (100). Anal. calc. for $C_{23}H_{28}O_2$ (336.48): C 82.10, H 8.39; found: C 81.82, H 8.38.

**5. Vigorous Reduction of 6 with $LiAlH_4$.** – A solution of 292 mg (1 mmol) of **6** in 20 ml dry $Et_2O$ was added dropwise to a heated suspension of 50 mg (1.3 mmol) $LiAlH_4$ in 10 ml dry $Et_2O$. After 10 min a small amount of $H_2O$, followed by dil. NaOH, was added and the precipitate filtered off. Evaporation of the solvent, subsequent acetylation as in the preceeding experiment and separation by prep. TLC (pentane/AcOEt) afforded two colorless solid fractions. *a*) Faster moving fraction: 36 mg (11%) of a 7:3 mixture of two diastereoisomers of **11**, m.p. 94–101°. IR (KBr): 2960*s*, 2908*w*, 2868*m*, 1740*vs*, 1375*m*, 1363*m*, 1260*vs*, 1125*w*, 1043*m*, 1023*m*, 817*m*, 768*m*, 753*w*. $^1$H-NMR (360 MHz, $CDCl_3$): Signals of major isomer in the mixture: 6.30 (*dt*, *J* = 5.3 and 1.8, 1H, H–C(5)); 6.02 (*dq*, *J* = 5.3 and 1.3, 1H, H–C(6)); 5.98 (br. *s*, 1H, H–C(4)); 5.87 (*dd*, *J* ≈ 6 and 2.4, 1H, H–C(12)); 5.72 (*d*, *J* ≈ 6, 1H, H–C(13)); 5.36 (*s*, 1H, H–C(9)); 3.38 (*t*, *J* ≈ 2, 1H, H–C(1)); 3.16 (br. *s*, 1H, H–C(7)); 2.59 (*d*, *J* ≈ 2, 1H, H–C(2)); 2.10 (*s*, 3H, $CH_3CO$); 1.08 (*s*, 9H, $(CH_3)_3C$); 0.99 (*s*, 9H, $(CH_3)_3C$); signals of minor isomer in the mixture: *ca.* 6.28 (*dt*, partly hidden, *J* ≈ 5, 1H, H–C(5)); 6.17 (br. *s*, 1H, H–C(4)); 5.95 (*dq*, *J* ≈ 5.3 and 2, 1H, H–C(6)); 5.80 (*dd*, *J* ≈ 6 and 2.4, 1H, H–C(12)); 5.65 (*d*, *J* ≈ 6, 1H, H–C(13)); 5.40 (*s*, 1H, H–C(9)); 3.42 (br. *s*, 1H, H–C(1)); 2.94 (*q*, *J* ≈ 2 1H, H–C(7)); 2.74 (*t*, *J* ≈ 2, 1H, H–C(2)); 2.09 (*s*, 3H, $CH_3CO$)); 1.08 (*s*, 9H, $(CH_3)_3C$); 1.05 (*s*, 9H, $(CH_3)_3C$). MS (70 eV): 338 (7, $M^+$), 221 (13), 183 (13), 162 (62), 147 (35), 119 (38), 91 (20), 77 (12), 57 (59), 43 (100).

*b*) Slower moving fraction: 98.7 mg (29%) of *9-acetoxy-2,10-di(*tert*-butyl)tetracyclo[6.3.2.0$^{3,7}$0$^{8,11}$]-trideca-3,6,10,12-tetraen* (**13**), m.p. 91–102°. IR (KBr): 2970*s*, 2960*s*, 2906*w*, 2875*w*, 2837*w*, 1736*vs*, 1477*w*, 1465*w*, 1395*w*, 1389*w*, 1375*m*, 1369*m*, 1269*m*, 1262*m*, 1245*s*, 1049*m*, 1024*m*, 769*m*, 728*m*. $^1$H-NMR (360 MHz, $CDCl_3$): 6.23 (*t* or *quint.*, *J* ≈ 2, 1H, H–C(6) or H–C(4)); 6.17 (*d*, *J* ≈ 5, 1H, H–C(13)); 6.04 (*dd*, *J* ≈ 5.2, 1H, H–C(12)); 5.64 (split *s*, 1H, H–C(4) or H–C(6)); 5.40 (*s*, 1H, H–C(9)); 3.48 (*t* or *quint.*, *J* ≈ 2, 1H, H–C(1)); 2.86 (*t* or *quint.*, *J* ≈ 2, 2H, 2H–C(5)); 2.74 (*q*, *J* ≈ 2, 1H, H–C(2)); 2.03 (*s*, 3H, $CH_3CO$); 1.01 (*s*, 9H, $(CH_3)_3C$); 0.99 (*s*, 9H, $(CH_3)_3C$). MS (70 eV): 338 (6, $M^+$), 239 (14), 221 (14), 183 (15), 165 (15), 91 (7), 77 (6), 57 (64), 43 (100).

**6. 6,13-Dibromo-2,10-di(*tert*-butyl)tetracyclo[6.3.2.0$^{3,7}$0$^{8,11}$]trideca-2,4,6,10,12-pentaen-9-one (15).** – A solution of 130 mg (0.54 mmol) *6-bromo-2-(*tert*-butyl)-3,7-dehydrotropone* (*4-bromo-7-(*tert*-butyl)-bicyclo[3.2.0]hepta-1(7),2,4-trien-6-one*, **14**), m.p. 82°, [1b] in 5 ml benzene was refluxed for 4 h, evaporated and the residue purified by prep. TLC to give 85 mg (70%) of **15** as yellow needles, m.p. 149–151° (dec.). UV (EtOH): max. 407 (600), max. 314 (5500), max. 273 (8100), infl. 226 (9000), max. 209 (14200). IR (KBr): 2970*m*, 2935*w*, 2910*w*, 2873*w*, 1758*s*, 1658*m*, 1600*w*, 1578*w*, 1550*w*, 1500*w*, 1367*m*, 1226*m*, 879*w*, 827*m*, 771*m*. $^1$H-NMR (100 MHz, $CDCl_3$): 6.52 (*d*, *J* = 5.8, 1H, H–C(4) or H–C(5)); 6.50 (*d*, *J* = 2.6, 1H, H–C(12)); 6.17 (*d*, *J* = 5.8, 1H, H–C(5) or H–C(4)); 4.42 (*d*, *J* = 2.6, 1H, H–C(1)); 1.39 (*s*, 9H, $(CH_3)_3C$); 1.19 (*s*, 9H, $(CH_3)_3C$). MS (70 eV): 452, 450, 448 (10, 20, 10, $M^+$); 395, 393, 391 (2.5, 5, 2.5); 371, 369 (8, 8); 275 (12); 247 (25); 232 (22); 217 (29); 216 (21); 215 (35); 205 (21); 203 (30); 202 (46); 190 (35); 189 (100); 178 (26); 176 (33); 175 (16); 174 (18); 165 (40); 163 (30); 153 (19); 152 (34); 151 (20); 150 (21); 139 (18). Anal. calc. for $C_{21}H_{22}Br_2O$ (450.23): C 56.02, H 4.93, Br 35.50; found: C 56.10, H 5.19, Br 35.27.

**7. IR Bands of 3,7-Dehydrotropones[1]).** – The following previously reported [1b] IR spectra have been reexamined for the sake of direct comparison. *2-(*tert*-butyl)-3,7-dehydrotropone* (*7-(*tert*-butyl)bicyclo[3.2.0]-hepta-1(7),2,4-trien-6-one;* **1**): IR ($CHCl_3$): 3010*w*, 2973*s*, 2937*w*, 2908*w*, 2885*w*, 1755*s*, 1735*s*, 1697*w*, 1615*s*, 1605*m*, 1545*w*, 1525*w*, 1480*m*, 1462*m*, 1408*w*, 1370*m*, 1352*m*, 1289*m*, 1179*s*, 1075*w*, 1047*m*, 962*w*, 928*w*, 878*w*, 852*m*, 846. *Dimer:* IR (KBr): 3067*w*, 3010*w*, 2965*s*, 2940*w*, 2910*w*, 1873*m*, 1760*s*, 1722*s*, 1660*s*, 1599*s*, 1560*w*, 1462*m*, 1459*m*, 1396*w*, 1370*s*, 1363*m*, 1350*w*, 1293*m*, 1282*w*, 1242*m*, 1205*m*, 1161*m*, 1138*m*, 1119*m*, 1099*m*, 1072*w*, 1056*w*, 1028*w*, 1017*w*, 990*w*, 972*m*, 940*w*, 916*w*, 895*m*, 829*m*, 804*m*. **14**: IR ($CHCl_3$): 2960*m*, 2925*w*, 2900*w*, 2862*w*, 1855*w*, 1845*w*, 1768*s*, 1738*s*, 1610*s*, 1600*m*, 1473*w*, 1457*m*, 1365*m*, 1338*m*, 1278*s*, 1186*m*, 1120*w*, 1090*s*, 1075*w*, 984*w*, 945*m*, 918*w*, 862*s*. IR (KBr): 3082*w*, 2960*m*, 2925*w*, 2895*w*, 2860*w*, 1858*w*, 1845*w*, 1764*s*,

1735*s*, 1608*s*, 1595*m*, 1473*w*, 1457*w*, 1407*w*, 1386*w*, 1362*m*, 1337*m*, 1278*m*, 1220*w*, 1204*w*, 1190*m*, 1121*w*, 1090*s*, 1072*m*, 984*w*, 947*m*, 927*w*, 862*s*. *2-Phenyl-3,7-dehydrotropone (7-phenylbicyclo[3.2.0]hepta-1(7),2,4-trien-6-one)* [1b]. IR ($CHCl_3$): 3070*w*, 3030*w*, 3015*m*, 1760 (sh), 1736*s*, 1603*s*, 1533*m*, 1491*w*, 1450*m*, 1382*s*, 1363*s*, 1302*w*, 1283*w*, 1178*s*, 1068*m*, 1049*m*, 998*w*, 926*m*, 849*w*, 832*m*. IR (KBr): 3060*w*, 1830*w*, 1815*w*, 1760 (sh), 1738*s*, 1605*s*, 1533*m*, 1491*w*, 1450*m*, 1378*s*, 1365*s*, 1302*w*, 1285*w*, 1183*s*, 1071*m*, 1049*m*, 998*w*, 924*w*, 853*w*, 835*m*. *2-Chloro-4,5-benzo-3,7-dehydrotropone* [1b]: IR ($CCl_4$): 3075*w*, 3042*w*, 2925*w*, 1845*w*, 1805*s*, 1780*s*, 1670*w*, 1624*s*, 1597*m*, 1538*m*, 1466*w*, 1434*w*, 1419*w*, 1320*w*, 1302*m*, 1245*w*, 1177*s*, 1150*m*, 1101*m*, 1080*s*, 1017*w*, 1048*w*, 922*m*, 873*m*, 833*m*. IR (KBr): 1845*w*, 1802*s*, 1780*s*, 1670*w*, 1623*s*, 1597*m*, 1538*m*, 1466*w*, 1434*w*, 1419*w*, 1321*w*, 1299*m*, 1245*w*, 1176*s*, 1150*m*, 1099*m*, 1083*s*, 1051*w*, 1017*w*, 923*m*, 873*m*, 838*m*.

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