3. Synthesis and Properties of 3,7-Dehydrotropones[1])

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(9. X. 75)

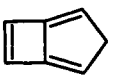
Synthese und Eigenschaften von 3,7-Dehydrotroponen. – *Zusammenfassung.* 7-*exo*-Brom-7-*endo*-*t*-butyl-(**9**) und 7-*exo*-Chlor-7-*endo*-phenyl-bicyclo[3.2.0]hept-2-en-6-on(**12**) sowie 7,7-Dichlor-2,3-benzo-bicyclo[3.2.0]hept-2-en-6-on (**16**), das letztere hergestellt aus Dichlorketen und Inden (**15**), wurden mit 1 Moläquiv. N-Bromsuccinimid behandelt. Die entsprechenden Hauptprodukte waren 4-*exo*-, 7-*exo*-Dibrom-7-*endo*-*t*-butyl-(**10**) und 4-*exo*-Brom-7-*exo*-chlor-7-*endo*-phenyl-bicyclo[3.2.0]hept-2-en-6-on (**13**) sowie 4-*exo*-Brom-7,7-dichlor-2,3-benzo-bicyclo[3.2.0]hept2-en-6-on (**17**). Neben dieser «normalen» Bromierung fand in zwei Fällen eine solche unter Allylisomerisierung statt: Als Nebenprodukt bei der Monobromierung von **12** wurde 4-*exo*-Brom-6-*exo*-chlor-6-*endo*-phenyl-bicyclo[3.2.0]hept-2-en-7-on (**14**) gebildet und bei der Dibromierung von **9** (wahrscheinlich via **10**) war das Hauptprodukt 2,4-*exo*,6-*exo*-Tribrom-6-*endo*-*t*-butyl-bicyclo[3.2.0]hept-2-en-7-on (**11**).

Aus der Behandlung der vier bromierten Bicycloheptenon-Derivate **10**, **11** und **13** sowie **17** mit 1,1 mol Triäthylamin bei tiefer Temperatur liessen sich 2-*t*-Butyl-(**5**), 6-Brom-2-*t*-butyl-(**6**) und 2-Phenyl-3,7-dehydrotropon(**7**) sowie 2-Chlor-4,5-benzo-3,7-dehydro-tropon (**8**) isolieren.

Das Reaktionsverhalten und die spektralen Eigenschaften (^{1}H-NMR., ^{13}C-NMR., IR. und UV.) der Dehydrotropone **5**, **6**, **7** und **8**, sowie ihr Zusammenhang mit deren Struktur werden detailliert beschrieben.

1. Introduction. – Dehydroannulenes, dehydroannulenium ions and dehydroannulenones are the products of the formal removal of two hydrogen atoms from annulenes, annulenium ions and annulenones [1]. Of particular interest are such compounds if they are *Hückel* systems and contain only *small rings*. The small size of the rings may have two opposite effects: 1. the ring system is forced to be coplanar which should be conducive to 'aromatic stabilization' and 2. the intraannular angles are compressed which introduces a destabilizing strain. The salient questions in this connection are, therefore, whether such compounds are stable and, if so, whether their physical properties reflect the factors which counteract the strain destabilization. Usually efforts are concentrated on the more easily observed *kinetic* stability since it determines the life-time and is used as a rough indication of thermodynamic stability.

In recent years several attempts have been made to prepare dehydrotropenium ion and dehydrotropone which possess a four-plus-five-membered fused-ring-system.



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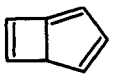

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[1]) The systematic name for 3,7-dehydrotropone is bicyclo[3.2.0]hepta-1(7),2,4-trien-6-one. We here use the dehydrotropone nomenclature in accord with the literature [1] to express the potential theoretical significance.

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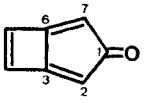
While for the synthesis of the former only the potential intermediates **1** [2] and **2** [3] have become available, two examples of the latter have been described, namely 3,6-dehydrotropone (**3**) [4] and 2-dialkylamino-3,7-dehydrotropones (**4**) [5]. Compounds **1**, **2** and **3** dimerize or polymerize readily at ambient temperature, but two compounds of type **4** ($R_2 = (CH_3)_2$ or $(i\text{-Pr})_2$) were isolated in pure form. The insta-



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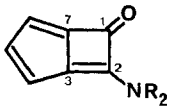

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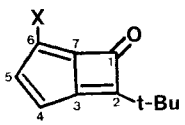
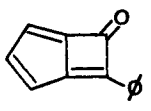
bility of **1** and **2** illustrates the effect of strain alone and that of **3** shows that the strain may overcome a stabilization by cyclic conjugation. It is still uncertain whether the relative stability of **4** should be attributed to the 3,7-dehydrotropone ring system or to the third order vinylogous amide conjugation[3]). We now report the preparation and isolation of three 3,7-dehydrotropones substituted in the 2-position by a *t*-butyl- (**5** and **6**) and a phenyl group (**7**), as well as of 2-chloro-4,5-benzo-3,7-dehydrotropone (**8**). The synthetic approach was analogous to the one described previously [5] for **4**. Of particular interest is compound **5**, since it lacks the capacity for any conjugation except for the one due to the 3,7-dehydrotropone system. The other compounds (**6**, **7** and **8**) might show effects of additional conjugation.



5: X = H
6: X = Br



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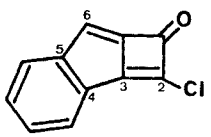

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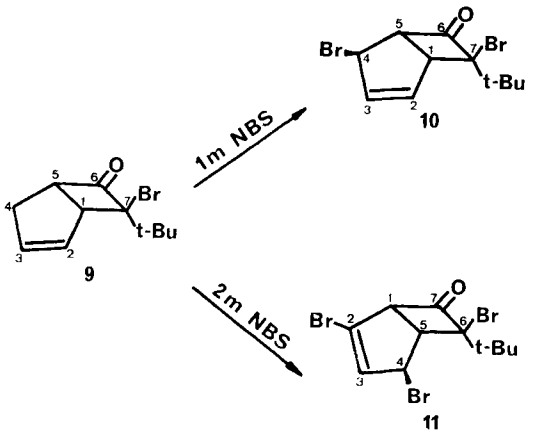
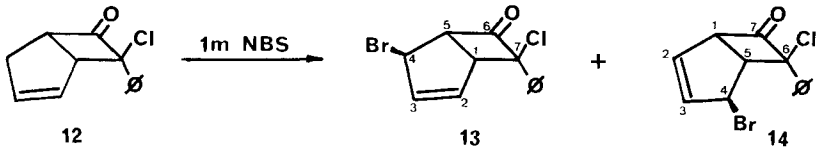
2. Preparation and structure of the precursors. – Treatment of 7-*exo*-bromo-7-*endo*-*t*-butyl-bicyclo[3.2.0.]hept-2-en-6-one (**9**) [6] with 1 mol of N-bromosuccinimide for 15 minutes afforded an excellent yield of 4-*exo*, 7-*exo*-dibromo-7-*endo*-*t*-butyl-bicyclo[3.2.0.]hept-2-en-6-one (**10**), accompanied by about 1% of 2,4-*exo*, 6-*exo*-tribromo-6-*endo*-*t*-butyl-bicyclo[[3.2.0]hept-2-en-7-one (**11**). The tribromoketone **11** was the major product (56%) when **9** was treated with 2 mol-equiv. of N-bromosuccinimide for 2 hours.

The bromination of 7-*exo*-chloro-7-*endo*-phenyl-bicyclo[3.2.0]hept-2-en-6-one (**12**) [7] with 1 mol-equiv. of N-bromosuccinimide required 10 hours and addition of ben-

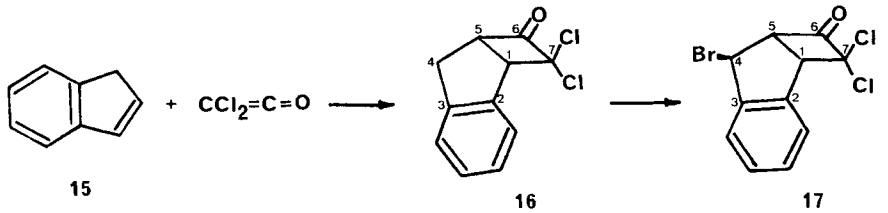
[3]) Recently Dr. *R. W. Gray* in this laboratory isolated 2-thiophenyl-3,7-dehydrotropone, which might also be stabilized by such a conjugation.



zoyl peroxide: a good yield of an 8:2 mixture of 4-*exo*-bromo-7-*exo*-chloro-7-*endo*-phenyl-bicyclo[3.2.0]hept-2-en-6-one (**13**), and 4-*exo*-bromo-6-*exo*-chloro-6-*endo*-phenyl-bicyclo[3.2.0]hept-2-en-7-one (**14**) was obtained.

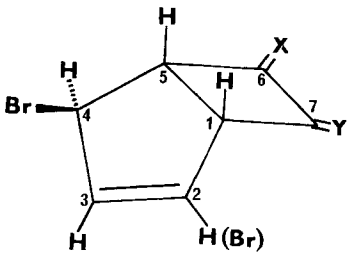


7,7-Dichloro-2,3-benzo-bicyclo[3.2.0]hept-2-en-6-one (**16**), prepared according to [8] by the addition of dichloroketone to indene (**15**), was also brominated with 1 mol-equiv. N-bromosuccinimide to give a quantitative yield of the oily 4-*exo*-bromo-7,7-dichloro-2,3-benzo-bicyclo[3.2.0]hept-2-en-6-one (**17**).



The *exo-configuration* of the newly entered bromine atom in **10**, **11**, **13**, **14** and **17**, is deduced from the consideration that bromine attack should occur from the less hindered *exo*-side and from the observation that the NMR.-signal of H–C(Br), recognizable by its chemical shift (δ between 5.1 and 5.7), shows only small coupling with its vicinal neighbour H–C(5) due to a torsional angle of near 90° (compare [5]). Less evident are the *constitutions* of **10**, **11**, **13** and **14** since the N-bromosuccinimide bromination can be accompanied by an allylic rearrangement[4]). Two types of isomers, summarized by formulae **18** and **19**, must be distinguished in the products. The following argument is proposed to decide between **18** and **19**: The ^{1}H-NMR.-spectra permit ready identification of the signals due to the two angular hydrogen atoms (H–C(1) and H–C(5)) since they appear at relatively high field (δ between 3.8 and 4.9)

and show a large mutual coupling (J = 6 to 7). One of these two signals is always a 'double multiplet' broadened by several small and medium sized additional couplings (J from 0.5 to 3.3), and the other is a fairly 'sharp doublet' with less and only very



18: X = O; Y = two substituents at quadriligant carbon atom.
19: X = two substituents at quadriligant carbon atom; Y = O.

small additional couplings (J from 0.5 to 0.8). In compounds **10** and **13** the sharp doublet is at lower (δ = 4.71 and 4.66) and the double multiplet at higher field (δ = 4.14 and 4.28), whereas in compounds **11** and **14** the chemical shift of these signal types are reversed (sharp doublet at δ = 4.08 and 3.88, double multiplet at δ = 4.80 and 4.87).

In both constitutions **18** and **19** H–C(1) is expected to show larger couplings than H–C(5) (in addition to the mutual coupling): H–C(1) can couple vicinally with H–C(2) (in all but **11**), allylically with H–C(3), and homoallylically with H–C(4), whereas H–C(5) can couple vicinally only with a torsional angle of near 90° with H–C(4), and by a near *W*-geometry with H–C(2) and possibly also with H–C(3). Since the signal of the angular hydrogen atom α to the carbonyl group is always at lower field than that of the other angular hydrogen atom, it is possible to deduce constitution **18** for those compounds which have the sharp doublet at lower field than the double multiplet, and constitution **19** for those that have the double multiplet at lower field than the sharp doublet. From the chemical shifts mentioned above it is concluded that compounds **10** and **13** are of type **18** and compounds **11** and **14** of type **19**.

This argument is of particular significance in connection with the tribromo-ketone **11** since its constitution will influence a structural argument on the bromo-dehydrotropone **6** (see section 3) and consequently the assignment of certain ^{1}H-NMR.-signals (see section 4).

Compound **11** is probably the product of further bromination of **10**. It may be noted that the N-bromosuccinimide brominations are accompanied by allylic rearrangements of varying extent: in the case of **10** complete, in the case of **12** partial, and in the case of **9** almost no rearrangement is observed. The preponderance of allylic isomerization on bromination of **10** may be due to a reluctance of the bromine atom to enter at a position which already carries a bromine atom.

3. Preparation of 3,7-dehydrotropones. – Four of the five brominated bicyclo[3.2.0]heptenone-derivatives, namely **10**, **11**, **13** and **17**, were converted to the

[4] This rearrangement, as well as the structural arguments for the products were first observed and developed by Mr. *M. Rey* and Dr. *S. Roberts* in this laboratory.

slightly buff-colored 2-*t*-butyl-3,7-dehydrotropone (**5**), m.p. 65° (51%), the yellow 6-bromo-2-*t*-butyl-3,7-dehydrotropone (**6**), m.p. 82° (31%), the rust-colored 2-phenyl-3,7-dehydrotropone (**7**), m.p. 53° (90%) and the yellow 2-chloro-4,5-benzo-3,7-dehydrotropone (**8**), m.p. 100° (10%), respectively, by the short action of a slight excess of triethylamine in methylene chloride or carbon tetrachloride at temperatures between −10° and 5°. The products were obtained essentially pure (see exper. part) and could all be stored as solids, at least at 0°. However, fairly rapid decomposition was observed with all but **8** in concentrated solution (attempted recrystallization) and on melting. In the cases of **5** and **6** the decomposition war accompanied by the evolution of a gas[5]).

It is of interest that triethylamine is a strong enough dehydrohalogenating base for the formation of 3,7-dehydrotropones. In the previously reported case [5] lithium dialkylamide was used leading to the replacement of the chlorine atom by a dialkylamino group in the intermediate 2-chloro-3,7-dehydrotropone, a third order vinylogous acid chloride. In the case of the benzo-derivative **17** the use of triethylamine allowed the isolation, albeit in low yield, of the 2-chloro-3,7-dehydrotropone-derivative **8**. Preliminary experiments[6]) indicate that this method may be generally applicable to the preparation of 2-chloro-3,7-dehydrotropones. The relative ease of the two dehydrohalogenations in 4,7-dihalo-bicyclo[3.2.0]hept-2-en-6-ones (compounds **10**, **13** and **17**) and in 4,6-dihalo-bicyclo[3.2.0]hept-2-en-7-ones (compound **11**) may be attributed to the fact that for both steps in both cases deprotonations at positions activated by the carbonyl group may be formulated, and perhaps also to some stabilization of a transition state on the way to a cyclic conjugated system in the second step (compare [5]).

The structures of all four dehydrohalogenation products as derivatives of 3,7-dehydrotropone appear to be certain based on their physical properties (see below). Since no rearrangements are probable under such mild conditions, the positions of the substituents in **5**, **7** and **8** are reasonable. The conclusion, however, that the bromine atom in **6** is at C(6) and not C(4) depends also on the argument that its educt **11**, which is the result of double bromination of the bicycloheptenone **9**, belongs to the constitution type **19** and not **18** (see section 2).

4. Physical properties of 3,7-dehydrotropones. – Some of the physical properties of the new 3,7-dehydrotropone-derivatives **5**, **6**, **7** and **8** are given in the table together with the ones of the earlier described [5] 3,7-dehydrotropone-derivative **4**.

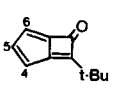
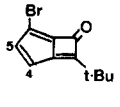
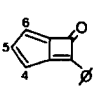
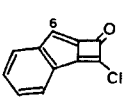
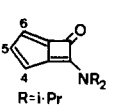
In the ^{1}H-NMR.-spectrum of **5**[7]) the signal due to H–C(5) can be identified as the lowest field signal ($\delta = 7.83$) by the fact that it couples with both other ring hydrogen atoms (H–C(4) and H–C(6)) and that the latter do not couple with each other. H–C(4)

[5]) The 'decomposition' of **5** and **6** is a decarbonylative dimerization which will be dealt with in another paper.

[6]) Dr. *R. W. Gray* was able to observe a 3,7-dehydrotropone species only in solution at low temperature when 4-*exo*-bromo-7,7-dichloro-bicyclo[3.2.0]hept-2-en-6-one was treated with triethylamine at − 40°.

[7]) When solutions of **5** were prepared at − 20° and the NMR.-spectra (^{1}H- and ^{13}C-) were measured at low temperature, some additional signals were present which disappeared on warming to 0°.

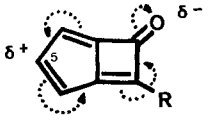
Table. *Physical properties of diagnostic value for 3,7-dehydrotropone-derivatives*

					
	5	**6**	**7**	**8**	**4**
^{1}H-NMR. ($CDCl_3$):					
H-C(4)	6.85	6.78	6.95	–	6.48
$J_{4,5}$	4.0	4.4	4.0	–	3.6
H-C(5)	7.83	7.50	7.88	–	7.51
$J_{5,6}$	2.0	–	2.0	–	3.2
H-C(6)	6.39	–	6.46	6.55	6.40
IR. ($CHCl_3$):					
C=O range	1755 *s* 1735 *s*	1768 *s* 1738 *s*	1760 (sh) 1738 *s*	1805 *vs* 1780 *s*	1730 *s*
C=C range	1613 *m* 1605 (sh)	1610 *s* 1600 (sh)	1605 *ms* 1595 (sh)	1624 *ms* 1597 *m*	1630 *s*
UV. (C_2H_5OH):					
			210 (9900)	–	
		225 (16500)	225 (11800)		252 (33100)
	233 (21600)	244 (20300)	267 (11500)		304 (14000)
	275 (4500)	280 (4300)	325 sh (14500)		350 (1200)
	282 (4700)	288 (4700)	335 (16800)		
	293 (3200)	299 (3300)	347 (sh) (12500)		
	375 (sh) (100)	387 (sh) (270)	415 (sh) (570)		

and H–C(6) give rise to signals at $\delta = 6.85$ ($J = 4.0$), and at $\delta = 6.39$ ($J = 2.0$), the couplings being due to interaction with H–C(5). The signal ($\delta = 6.85$) with the larger coupling constant is assigned to H–C(4) since the bromo-3,7-dehydrotropone **6**, which according to the argument given in section 3 has the bromine atom in the 6-position, shows the larger type coupling ($J = 4.4$) between the two ring hydrogen atoms. Consequently, the signal ($\delta = 6.39$) with the smaller coupling in **5** should be due to H–C(6).

While other effects such as a field induced ring current or neighbouring atoms may also influence the chemical shifts of H–C(4), H–C(5) and H–C(6), it appears likely that the π-electron density distribution is a major factor in determining the difference between them. The large $\Delta\delta$-values between H–C(5) and H–C(4) (= 0.98)

and between H–C(5) and H–C(6) (= 1.44) lead to the conclusion that there is considerable alternating π-electron density at positions 4, 5 and 6 in 3,7-dehydrotropone systems, the electron density being particularly low at position 5. Three delocalization schemes involving an electron pull towards the carbonyl oxygen atom should be considered to explain alternating π-electron density: delocalizations as shown in **20** and **21** express similarity to tropones and the one in **22** to fulvenes. Only **20** rational-



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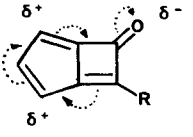

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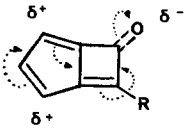

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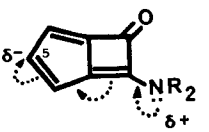
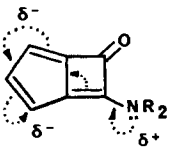
izes a low electron density at position 5; thus **21** and **22** must contribute much less to the structure of 3,7-dehydrotropones than **20**. It is of interest that canonical formulations derived from **21** or **22** with positive charges at C(4) and C(6) include a cyclobutadiene moiety. Neither tropone nor 6-*t*-butylfulvene show ring proton signals at such low fields as H–C(5) in **5** [9].

It is uncertain whether the difference in chemical shifts of H–C(4) and of H–C(6) in **5** is due to a different π-electron density at C(4) and C(5) or to the difference of chemical environment (carbonyl oxygen *vs.* *t*-butyl group). The larger coupling of H–C(5) with H–C(4) than with H–C(6) probably expresses a higher bond order between C(4) and C(5) than between C(6) and C(5), due to a larger contribution of the 'localized structure' normally written for **5** (and for the other 3,7-dehydrotropone-derivatives).

Replacing the *t*-butyl group in **5** with a phenyl group as in **7** affects the ^{1}H-NMR.-signals of H–C(4), H–C(5) and H–C(6) only very little. However, replacement with a dialkylamino group as in **4** largely reduces the difference between the signals of H–C(4) and H–C(6) with respect to both chemical shifts and coupling constants. Obviously the electron pair on the 2-dialkylamino group participates in the delocalization. This can be expressed by the delocalization schemes **23** and **24**. **23** stresses



23



24

a similarity to 2-amino-tropones and **24** to 6-amino-fulvenes. An alternating charge density at positions 4, 5 and 6 had been previously [5] noted in 2-dialkylamino-3,7-dehydrotropones (**4**)[8]), but it could not be decided whether this was due to the 3,7-dehydrotropone system or whether the dialkylamino group played an important role. Since the chemical shift difference between H–C(5) and H–C(6) is smaller in **4** ($\Delta\delta = 1.11$) than in **5** ($\Delta\delta = 1.44$), we can now conclude that the former is the case

(the chemical shift of H–C(4) is not used to support this conclusion since the different substituents at position 2 may have an additional effect) and that in fact the 2-dialkylamino group acts against the delocalization **20**. This is expressed by **23** which may also be responsible for the similarity of bond orders of C(4)–C(5) and C(5)–C(6) as suggested by the equalization of the H–C(4)/H–C(5) and H–C(5)/H–C(6) coupling constants in **4** compared to those in **5**. It is of interest that the electron donation of the dialkylamino group can be reinforced by the electron acceptance of the carbonyl group in delocalization **23**, but not in **24**.

The ^{13}C-NMR.-spectrum of **5**[7]) (see exper. part) also fits the 3,7-dehydrotropone structure. Next to the singlet ($\delta = 189.8$) due to the carbonyl carbon atom (C(1)) three more singlets are seen at $\delta = 174.2$, 169.0, and 163.3 which are attributed to C(2), C(3), and C(7) (not necessarily in this order). Therefore, the three doublets of the spectrum belong to C(4), C(5), and C(6). If position 5 is indeed the one of low π-electron density as expressed in the delocalization scheme **20**, then the doublet at $\delta = 157.2$ should be assigned to C(5) and the other two ($\delta = 114.4$ and 111.7) to C(4) and C(6). A comparison of the ^{13}C-NMR.-spectrum of **5** with that of 2-diisopropylamino-3,7-dehydrotropone (**4**, R = *i*-Pr) [5] shows that the chemical shifts of essentially all carbon atoms of **4** are at higher field than the corresponding ones of **5**, the effects being particularly large for C(5) ($\Delta\delta = 11.6$) and C(1) ($\Delta\delta = \sim 20$). This supports the proposition that the 2-alkylamino group participates in the delocalization by pumping electron density into the 3,7-dehydrotropone ring system.

The IR.-spectra of 3,7-dehydrotropones in solution are characterized by two types of absorption in the C=O/C=C stretching region: a strong one at 1730–1770 and a medium to strong one at 1595–1625 cm^{-1}. Both absorptions are split into two bands of similar intensities separated by 5 to 30 cm^{-1}, so that one occasionally shows up as a shoulder; in the previously reported [5] examples (compounds **4**) this splitting is not observed. Only the high frequency absorption of **8** and the low frequency absorption of **4** fall outside the typical ranges, probably because of specific conjugation effects. It may be of interest to note – for comparison – that simpler cyclobutenones show [10] a carbonyl band in the same region (1741–1758 cm^{-1}) as the examined 3,7-dehydrotropones.

The electronic spectra (see table) are expected to be particularly sensitive in showing up conjugation. 2-*t*-Butyl-3,7-dehydrotropone (**5**), the representative example for the 3,7-dehydrotropone system in this work, has a strong absorption maximum at 233 nm ($\varepsilon = 21600$), a triplet of weaker maxima at 275, 282 and 293 nm ($\varepsilon = 4500$, 4700 and 3200) and a shoulder at about 317 nm ($\varepsilon = 100$). The last mentioned absorption is reminiscent of that usually found in fulvenes [11]. In the 6-bromo-derivative **6**, the same pattern is observed, with bathochromic shifts of 5 to 12 nm. 2-Phenyl-3,7-dehydrotropone (**7**) shows a similar spectrum if it is assumed that the single maximum (267 nm) has weakened ($\varepsilon = 11500$) and been shifted by +23 nm, whereas the triplet (325, 335 and 347 nm) and the shoulder (415 nm) have increased in intensity ($\varepsilon = 12000$–17000 and 570) and been shifted by +40 to 50 and

[8]) In [5] the alternating charge densities at C(4), C(5), and C(6) of 2-dialkylamino-3,7-dehydrotropones (**4**) referred to in the middle of p. 1171 should be opposite in sign to those quoted and the charge densities mentioned further below on that page are meant to be *positive* charge densities.

+98 nm, both shifts probably arising from additional conjugation with the phenyl group. The UV.-spectra of the 2-dialkylamino-3,7-dehydrotropones (**4**) exhibit a completely different pattern indicating that the electron pair on the amino group is indeed involved in the delocalization over the 3,7-dehydrotropone system of **4**.

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Experimental Part

General. The abbreviations and the spectral data notations have been described previously [12]. All compounds gave elemental analyses within 0.3% of the calculated values, with the exception of **14** and **17** which were not entirely pure and thus not analyzed.

The mass spectra, ^{1}H-NMR.-, ^{13}C-NMR.-spectra and IR.-spectra were measured in our laboratories for mass spectrometry (under Prof. *M. Hesse*), for nuclear magnetic resonance (under Prof. *W. von Philipsborn* with Mr. *W. Schwotzer*) and for micro-analysis (under Mr. *H. Frohofer*), respectively. Elemental analyses were performed in the last mentioned laboratory.

7-exo-*Bromo*-7-endo-t-*butyl-bicyclo*[*3.2.0*]*hept-2-en-6-one* (**9**) was prepared in 73% yield according to [6], except that benzene as a solvent was found to be preferable to hexane and that addition of the reagents at 0° was followed by 2 h reflux.

4-exo,7-exo-*Dibromo*-7-endo-t-*butyl-bicyclo*[*3.2.0*]*hept-2-en-6-one* (**10**). A suspension of 18.25 g (75 mmol) of 7-*exo*-bromo-7-*endo*-t-butyl-bicyclo[3.2.0]hept-2-en-6-one (**9**) and 13.5 g (75 mmol) of N-bromosuccinimide in 200 ml of carbon tetrachloride was heated over a light bulb for 15 min. After removal of the solid the solvent was evaporated giving 24 g of a yellow oil which showed essentially the same ^{1}H-NMR.-spectrum as pure **10**. The oil was dissolved in pentane and left in the cold to yield 17 g (73%) of **10**, m.p. 40–43°, after recrystallization from pentane, m.p. 42–43.5°. – IR. (KBr): 2997*m*, 2985*m*, 1792*s*(sh) and 1785*s* (C=O), 1600*w*, 1220*m*, 1045*m*, 785*m*, 772*m*, 708*m*, 650*m*, 640*m*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 6.21 ($d \times d \times d$, $J_{1,3} = 1.6$, $J_{2,3} = 5.5$, $J_{3,4} = 2.2$, 1H, H–C(3)); 6.09 ($d \times d \times d \times d$, $J_{1,2} = 2.3$, $J_{2,4} = 0.8$, $J_{2,5} = 0.8$, 1H, H–C(2)); 5.10 ($d \times d \times d \times d$, $J_{1,4} = 3.0$, $J_{4,5} = 0.8$, 1H, H–C(4)); 4.71 ($d \times d \times d$, $J_{1,5} = 6.5$, 1H, H–C(5)); 4.14 ($d \times d \times d \times d$, 1H, H–C(1)); 1.18 (*s*, 9H, *t*-Bu). – $C_{11}H_{14}Br_2O$ (322.05).

From the mother liquors of the crystallization was isolated about 1% of 2,4-exo,6-exo-*tribromo*-6-endo-t-*butyl-bicyclo*[*3.2.0*]*hept-2-en-7-one* (**11**), identical with the product described below.

2,4-exo-6-exo-*Tribromo*-6-endo-t-*butyl-bicyclo*[*3.2.0*]*hept-2-en-7-one* (**11**). A mixture of 7.3 g (30 mmol) of 7-*exo*-bromo-7-*endo*-t-butyl-bicyclo[3.2.0] hept-2-en-6-one (**9**) and 18.8 g (60 mmol) of N-bromosuccinimide in 250 ml of carbon tetrachloride was heated over a light bulb for 2 h. After cooling the succinimide was removed by filtration and washed with 50 ml of chloroform. The combined solutions were washed twice with water, dried over $MgSO_4$, and evaporated to dryness yielding a dark brown oil which slowly crystallized. The crystals were washed with ether yielding 6.8 g (56%) of **11**, m.p. 135–137°. Recrystallization from pentane/ether gave an analytical sample, m.p. 136.8–137.4°. – IR. (KBr): 2975*w*, 1785*s* and 1775*m*(sh) (C=O), 1597*s*, 1370*m*, 1180*m*, 1052*m*, 900*s*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 6.22 ($d \times d \times d$, $J_{1,3} = 1.8$, $J_{3,4} = 2.5$, $J_{3,5} = 0.8$, 1H, H–C(3)); 5.37 ($d \times d \times d$, $J_{1,4} = 3.3$, $J_{4,5} = 0.7$, 1H, H–C(4)); 4.80 ($d \times d \times d$, $J_{1,5} = 6.7$, 1H, H–C(1)); 4.08 ($d \times d \times d$, 1H, H–C(5)); 1.17 (*s*, 9H, *t*-Bu). – $C_{11}H_{13}Br_3O$ (400.952).

4-exo-*Bromo*-7-exo-*chloro*-7-endo-*phenyl-bicyclo*[*3.2.0*]*hept-2-en-6-one* (**13**) *and* 4-exo-*bromo*-6-exo-*chloro*-6-endo-*phenyl-bicyclo*[*3.2.0*]*hept-2-en-7-one* (**14**). A mixture of 6.55 g (30 mmol) of 7-*exo*-chloro-7-*endo*-phenyl-bicyclo[3.2.0]hept-2-en-6-one (**12**) [7], 5.5 g (31 mmol) of N-bromosuccinimide and a catalytic amount of benzoyl peroxide in 90 ml of carbon tetrachloride was heated over a light bulb for 10 h. Having removed the succinimide the solvent was evaporated yielding a brown oil which according to NMR. consisted of a 77:23 mixture of the ketones **13** and **14**. When the mixture was left in the cold with pentane 5.07 g (57%) of **13** crystallized, m.p. 71–73°,

after recrystallization from pentane, m.p. 73.5–75.5°. – IR. (KBr): 1783 *s* (C=O), 1595 *w*, 1448 *m*, 1342 *m*, 1218 *s*, 1040 *m*, 1020 *m*, 835 *m*, 780 *s*, 768 *s*, 700 *s*, 693 *s*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 7.2–7.5 (*m*, 5H, C_6H_5—C(7); 6.05 ($d \times d \times d$, $J_{1,3} = 1.6$, $J_{2,3} = 5.3$, $J_{3,4} = 2.2$, 1H, H—C(3)); 5.58 ($d \times d \times d \times d$, $J_{1,2} = 2.3$, $J_{2,4} = 0.8$, $J_{2,5} = 0.8$, 1H, H—C(2)); 5.12 ($d \times d \times d \times d$, $J_{1,4} = 3.0$, $J_{4,5} = 0.8$, 1H, H—C(4)); 4.66 ($d \times d \times d$, $J_{1,5} = 6.0$, 1H, H—C(5)); 4.28 ($d \times d \times d \times d$, 1H, H—C(1)). – $C_{13}H_{10}BrClO$ (297.58).

The residue of the mother liquor of the crystallization was subjected to preparative TLC. to yield a small amount of **14**, after recrystallization from pentane, m.p. 93–94°. – IR. (KBr): 1798 *s*(sh), 1792 *s*, 1592 *w*, 1490 *w*, 1448 *m*, 1040 *m*, 848 *m*, 783 *m*, 758 *m*, 708 *m*, 695 *m*, 687 *w*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 7,29 *s* with broad base, 5H, C_6H_5—C(6)); 5.83 (*s* with broad base, 2H, H—C(2) and H—C(3)); 4.87 ($d \times d \times m$, $J_{1,5} = 6$, $J \sim 3$, 1H, H—C(1)); 4.45–4.50 (doublet-like *m*, 1H, H—C(4)); 3.88 (*d*, $J = 6$, 1H, H—C(5)). This product decomposed on standing even at low temperature.

4-exo-Bromo-7,7-dichloro-2,3-benzo-bicyclo[3.2.0]hept-2-en-6-one (**17**). A mixture of 2.27 g (10 mmol) of 7,7-Dichloro-2,3-benzo-bicyclo[3.2.0]hept-2-en-6-one (**16**) [8] and 1.81 g (2% excess) of N-bromosuccinimide in 30 ml of carbon tetrachloride was heated over a light bulb for 1 h. After cooling the succinimide was filtered off and the filtrate evaporated to dryness yielding 3.07 g (100%) of crude **17** as a yellow oil which did not crystallize. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 7.45 (*s* with broad base, 4H, C_6H_4—C(2)); 5,68 (*s* with very fine splitting, 1H, H—C(4)); 4.85–4.45 (*m* with a finely split strong peak at 4.75, 2H, H—C(1) and H—C(5)).

2-t-Butyl-3,7-dehydrotropone (**5**). To a stirred solution of 3.22 g (10 mmol) of 4-*exo*-7-*exo*-dibromo-7-*endo*-*t*-butyl-bicyclo[3.2.0]hept-2-en-6-one (**10**) in 50 ml of methylene chloride at 5° 2.2 g (10% excess) of triethylamine in 10 ml of methylene chloride was added slowly. The mixture was then stirred for 15 min and washed with dilute HCl and water. After drying over $MgSO_4$ the orange solution was evaporated under reduced pressure at –10°. The residue was washed with pentane yielding 820 mg (51%) of **5** as a slightly buff-colored powder, m.p. 65° (effervescence and darkening). – IR. (KBr): 3010 *w*, 2965 *s*, 2940 *m*, 2910 *w*, 2873 *m*, 1760 *vs*, 1722 *vs*, 1660 *s*, 1599 *s*, 1560 *w*, 1462 *m*, 1456 *m*, 1370 *s*, 1363 *m*, 763 *s*, 720 *s*. IR. ($CHCl_3$): 3010 *w*, 2973 *m*, 2937 *w*, 2908 *w*, 2885 *w*, 1755 *vs*, 1735 *s*, 1697 *w*, 1613 *m*, 1605 *m*]sh), 1463 *m*, 1370 *m*, 1352 *m*, 1180 *m*, 853 *m*. – ^{1}H-NMR (60 MHz, $CDCl_3$): 7.83 ($d \times d$, $J = 4.0$, 2.0, 1H, H—C(5)); 6.85 (*d*, $J = 4.0$, 1H, H—C(4)); 6.39 (*d*, $J = 2.0$, 1H, H—C(6)); 1.45 (*s*, 9H, *t*-Bu). – ^{13}C-NMR. (25.2 MHz, $CDCl_3$): 189.8 (*s*, C(1)); 174.2, 169.0 and 163.3 (3 *s*, C(2), C(3) and C(7)); 157.2 (*d*, C(5)); 114.4 and 111.7 (2 *d*, C(4) and C(6)); 35.5 (*s*, quaternary carbon of *t*-Bu); 26.8 (*q*, methyl carbons of *t*-Bu). The chemical shifts are taken from a proton-noise decoupled spectrum, the multiplicity (only ^{1}J couplings are considered) from an off-resonance experiment. – UV. (ethanol): 293 (3200), 282 (4700), 275 (4500), 233 (21600), 375 (100, sh). – MS. : 160 (38, *M*), 145 (12, *M* – CH_3), 131 (27, *M* – HCO), 118 (12), 117 (100, *M* – CO – CH_3), 116 (24), 115 (48), 102 (13), 91 (45, tropylium), 89 (10), 77 (12), 75 (12), 74 (12), 65 (13), 63 (19), 51 (21), 50 (16). – $C_{11}H_{12}O$ (160.217).

When a 2.3 molar solution of pure **5** in deuteriochloroform was prepared at –20°, evolution of a gas was observed when the solution approached RT. The ^{13}C-NMR.-spectrum of such a solution showed the presence of a new species which will be dealt with in a future publication.

6-Bromo-2-t-butyl-3,7-dehydrotropone (**6**). 2 g (5 mmol) of 2,4-*exo*,6-*exo*-tribromo-6-*endo*-*t*-butyl-bicyclo[3.2.0]hept-2-en-7-one (**11**) in 50 ml of methylene chloride at 0° and 1.1 g (10% excess) of triethylamine in 10 ml of methylene chloride were treated for 2 h and worked-up as above: 370 mg (31%) of **6**, yellow solid, m.p. 82° (effervescence and darkening). – IR. (KBr): 2962 *m*, 2945 *w*, 2925 *w*, 2895 *w*, 2860 *w*, 1764 *s*, 1735 *s*, 1608 *m*, 1595 *w*, 1192 *m*, 1090 *m*, 863 *m*, 792 *m*, 756 *m*. IR. ($CHCl_3$): 2960 *m*, 2930 *w*, 1768 *vs*, 1738 *vs*, 1610 *ms*, 1600 *m*(sh), 1458 *m*, 1365 *m*, 1338 *m*, 1279 *s*, 1090 *s*, 861 *s*. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 7.50 (*d*, $J = 4.4$, 1H, H—C(5)); 6.78 (*d*, $J = 4.4$, 1H, H—C(4)); 1.40 (*s*, 9H, *t*-Bu). – UV. (ethanol: 299 (3300), 288 (4700), 280 (4300), 244 (20300), 255 (16500), 387 (270, sh). – MS.: 240 and 238 (each 10, *M*), 159 (23, *M* – Br), 144 (24, *M* – Br – CH_3), 132 (11), 131 (100, *M* – Br – CO), 130 (24), 129 (24), 117 (11), 116 (95, *M* – Br – CO – CH_3), 115 (78), 91 (49, tropylium). – $C_{11}H_{11}BrO$ (239.118).

2-Phenyl-3,7-dehydrotropone (**7**). 1.49 g (5 mmol) of 4-*exo*-bromo-7-*exo*-chloro-7-*endo*-phenyl-bicyclo[3.2.0]hept-2-en-6-one (**13**) in 40 ml of methylene chloride at 5° and 1.1 g (10% excess) of

triethylamine in 5 ml of methylene chloride were treated for 15 min and worked-up as above omitting the final washing with pentane: 810 mg (90%) of **7**, rusty-brown powder, m.p. 53° (dec.). – IR. (KBr): 3105*w*, 3090*w*, 3060*w*, 1760*m*(sh), 1738*vs*, 1725*m*(sh), 1603*s*, 1595*w*(sh), 1533*m*, 1450*m*, 1378*s*, 1365*s*, 1183*s*, 835*s*, 800*s*, 750*s*, 685*s*. IR. ($CHCl_3$): 3070*w*, 3030*w*, 3015*m*, 1760*s*(sh), 1740*vs*, 1605*m*, 1595*m*(sh), 1450*w*, 1382*m*, 1363*m*, 1178*m*, 1068*w*, 1048*w*, 832*w*. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 8.33–8.06*m*, 2H, 2 × *o*-H of H_5C_6—C(2)); 7.68–7.50 (*m*, 3H, 2 × *m*-H and *p*-H of H_5C_6—C(2)); 7.88 (*d* × *d*, *J* = 4.0 and 2.0, 1H, H—C(5)); 6.95 (*d*, *J* = 4.0, 1H, H—C(4)); 6.46 (*d*, *J* = 2.0, 1H, H—C(6)). – UV. (ethanol): infl. 347 (12500), 335 (16800), infl. 325 (14500), 267 (11500), 225 (11800), 210 (9900), 415 (570, sh). – MS.: 180 (17, *M*), 153 (14), 152 (100, *M* – CO), 151 (21), 126 (37, *M* – CO – C_2H_2), 102 (13), 99 (18), 98 (29), 87 (24), 86 (24), 85 (13), 76 (22), 75 (34), 74 (59), 63 (34), 62 (30), 61 (24), 53 (11), 52 (12), 51 (49), 50 (55), 49 (12). – $C_{13}H_8O$ (180.207)

2-Chloro-4,5-benzo-3,7-dehydrotropone (**8**). 917 mg (3 mmol) of 4-*exo*-bromo-7,7-dichloro-2,3-benzo-bicyclo[3.2.0]hept-2-en-6-one (**17**) in 20 ml of carbon tetrachloride at –10° and 670 mg of triethylamine in 5 ml of carbon tetrachloride were treated for 15 min and worked-up as above. The residue was purified by preparative TLC and crystallized from pentane: 57 mg (10%) of **8**, yellow needles, m.p. 99–100°. – IR. (KBr): 1845*w*, 1802*s*, 1760*vs*, 1623*s*, 1597*m*, 1299*m*, 1176*s*, 1099*m*, 1083*s*, 923*m*, 873*m*, 838*m*, 757*s*, 753*s*, 740*s*. IR. (CCl_4): 3075*w*, 3042*w*, 1845*m*, 1805*vs*, 1780*vs*, 1670*w*, 1624*ms*, 1597*m*, 1538*m*, 1468*w*, 1302*m*, 1177*s*, 1101*s*, 1080*s*, 1017*m*, 873*s*, 833*m*, – ^{1}H-NMR. (100 MHz, $CDCl_3$): 7.97 (*d* × *m*, *J* = 7.2, 1H, 1 × H of C_6H_4—C(4)); 7.60–7.09 (*m*, 3 H, 3 × H of C_6H_4—C(4)); 6.55 (br.*s*, 1H, H—C(6)). – MS.: 190 and 188 (14 and 43, *M*), 162 and 160 (26 and 79, *M* – CO), 125 (31, *M* – CO – Cl), 75 (11), 74 (10). – $C_{11}H_5ClO$ (188.607).

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