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129. 2-Dialkylamino-3,7-dehydrotropone[1])

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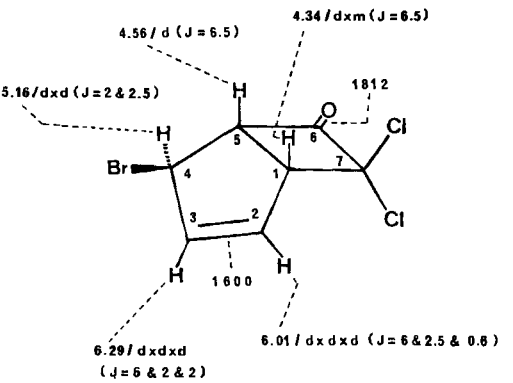
(7. V. 74)

Zusammenfassung. Behandlung des durch N-Brom-succinimid aus 7,7-Dichlor-bicyclo[3.2.0]hept-2-en-6-on erhaltenen 4-*exo*-Brom-7,7-dichlor-bicyclo[3.2.0]hept-2-en-6-ons (**1**) mit Lithium-diisopropylamid ergab 2-Diisopropylamino-3,7-dehydrotropon (**2**). Auf gleiche Weise wurde mit Lithium-dimethylamid das entsprechende 2-Dimethylamino-3,7-dehydrotropon (**3**) hergestellt. Die Strukturen von **2** und **3** ergeben sich aus den Spektraleigenschaften, welche auch die starke π-Elektronendelokalisierung im 2-Amino-dehydrotropon-System widerspiegeln.

The general significance of the concept of 1,4-dehydroaromaticity has recently been reviewed by *Bergman* [1]. Also discussed there are attempts towards the synthesis of seven-membered 1,4-dehydroaromatic systems, which so far have been without success [2]. We report here the preparation of two stable derivatives of



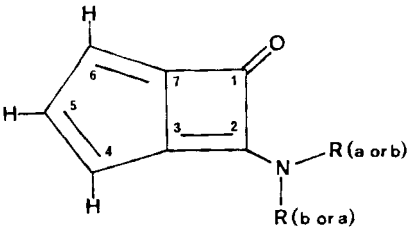
IR.- and ^{1}H-NMR.-spectral data of 4-exo-*bromo-7,7-dichloro-bicyclo[3.2.0]hept-2-en-6-one* (**1**)
(IR. spectrum in cm^{-1}, NMR.: δ-values in ppm and J-values in Hz)

[1]) The systematic name is 7-dialkylamino-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.

3,7-dehydrotropone. It is the first example[2]) of a small ring dehydroannulenone, which – on account of its angle compression strain – must remain coplanar.

Allylic bromination of 7,7-dichloro-bicyclo[3.2.0]hept-2-en-6-one [3] with N-bromo-succinimide yielded 50% of 4-*exo*-bromo-7,7-dichloro-bicyclo[3.2.0]hept-2-en-6-one (**1**), m.p. 81°. The spectral properties are summarised on the formula in the figure. The *exo*-configuration of Br–C(4), expected from the steric preference of *exo*-attack, is confirmed by the near-zero coupling between H–C(4) and H–C(5). Molecules of this type prefer a conformation with the carbonyl group 'folded in' [4], where the torsional angle between *endo*-H–C(4) and H–C(5) is about 90°.

When compound **1** was treated with three mol-equivalents of lithium diisopropylamide for 10 min at 0° and the crude product purified over alumina and by sublimation, a 33% yield of the yellow 2-diisopropylamino-3,7-dehydrotropone (**2**), m.p. 100°, was isolated. Some of its spectral data are summarised and interpreted in the table.



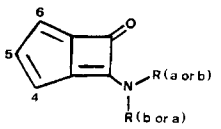
2 R = isopropyl
3 R = methyl

The structure of **2** is supported by the following arguments: The mass spectrum (M^+ 203 *m/e*) and the elemental analysis indicate a molecular formula of $C_{13}H_{17}NO$. A highly conjugated system is suggested by the UV.-absorptions (ethanol) at 252 (33100), 304 (14000) and 345–355 (1200) nm (ε). In the IR.-spectrum ($CHCl_3$) the two most intense bands are at 1730 and at 1630 cm^{-1}. The first of these (1730 cm^{-1}) is attributed to the stretching vibration of the carbonyl group which is subjected to two opposing effects, namely 1) a four-membered ring strain and 2) a π-electron delocalisation over the ring and involving the nitrogen. The second intense absorption (1630 cm^{-1}) is probably the stretching band of a double bond strongly polarised due to the same delocalisation.

The ^{1}H-NMR.-spectrum is particularly revealing. It shows the signals (two septetts at $\delta = 5.25$ and 3.99 ppm, as well as two doublets at $\delta = 1.55$ and 1.45 ppm) for two non-equivalent isopropyl groups. This indicates slow rotation around the C(2)–N bond, which agrees with the postulated delocalisation. The three remaining signals ($\delta = 7.51$, 6.48 and 6.40 ppm) are in the vinyl proton region and show the ABM-pattern ($J_{AM} = 3.6$ and $J_{BM} = 3.2$ Hz) characteristic for three vicinal hydrogens on an unsaturated five-membered ring. The large chemical shift difference ($\Delta\delta = ca.$

[2]) *Note added in proof*: In a recent preliminary communication *R. Breslow, M. Oda & T. Sugimoto* (J. Amer. chem. Soc. *96*, 1639 (1974)) reported the preparation of 3,6-dehydrotropone (there named bicyclotropone or cyclobutadienocyclopentadienone).

Spectral properties[a]) *of 2-diisopropylamino-* (**2**) *and 2-dimethylamino-3,7-dehydrotropone* (**3**)



		R = isopropyl		R = methyl	
		2		**3**	
IR. ($CHCl_3$)	C=O	1730 vs		1740	
	C=C	1630 vs		1660	
UV. (C_2H_5OH)		252	(33100)	250	(49500)
		304	(14000)	299	(17700)
		345–355	(1200)	340–350	(1200)
^{1}H-NMR. ($CDCl_3$)	NR(a)	5.25/*sept.*	(6.5)	3.53/*s*	
		1.55/*d*	(6.5)		
	NR(b)	3.99/*sept.*	(6.5)	3.20/*s*	
		1.45/*d*	(6.5)		
	H–C(4)	6.48/*d*	(3.6)	6.47/*d*	(3.6)
	H–C(6)	6.40/*d*	(3.2)	6.38/*d*	(3.2)
	H–C(5)	7.51/*d* × *d* (3.6, 3.2)		7.48/*d* × *d* (3.6, 3.2)	

[a]) The numerical values for UV. in nm (ε), for IR. and NMR. see Fig. 1.

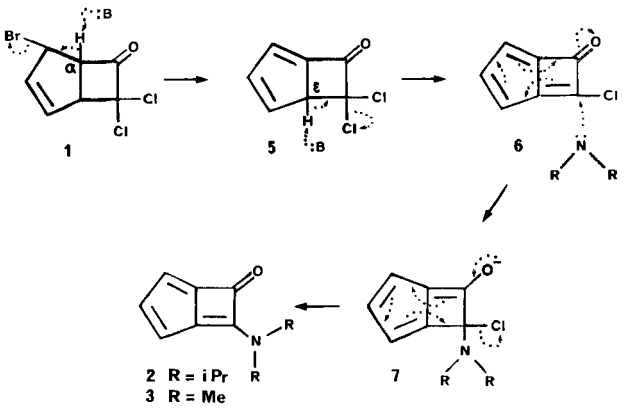
1.1 ppm) between H–C(5) on the one hand and H–C(4) and H–C(6) on the other shows that the above mentioned π-electron delocalisation induces alternating charge densities, with C(4) being positive, C(5) negative and C(6) again positive.

In the proton-noise decoupled ^{13}C-NMR.-spectrum there are eleven signals, four clearly weaker than the others. The four signals of low intensity at $\delta = 169.6$, 168.1, 158.9 and 144.9 ppm are assigned to the carbon atoms C(1), C(2), C(3) and C(7), their weak intensity being due to the long relaxation time characteristic for carbon atoms carrying no hydrogen. Comparison with the ^{13}C-NMR.-spectrum of 6-dimethylaminofulvene [5] enables the assignment of C(2) to one of the high frequency signals at $\delta = 169.6$ or 168.1 ppm, in which region the carbonyl carbon C(1) would also be expected. Thus the signals at $\delta = 158.9$ and 144.9 ppm are due to C(3) and C(7). The remaining high frequency signal at $\delta = 145.6$ ppm may be attributed to C(5) on the basis of the relatively high charge density postulated from the ^{1}H-NMR.-spectrum. Carbon atoms C(4) and C(6) must appear at $\delta = 108.9$ and 106.6 ppm, which is in accord with their relatively low charge densities. The differentiation of C(1) from C(2) (169.6, 168.0 ppm), C(3) from C(7) (158.9, 144.9 ppm) and C(4) from C(6) (108.9, 106.6 ppm) is not possible from the fully decoupled spectrum. The non-equivalence of the N-isopropyl groups is confirmed by the presence of the four quadriligant carbon signals at $\delta = 50.1$, 49.3 ppm (2 × CH) and 21.1, 19.5 ppm (2 × CH_3).

The mass spectrum exhibits the loss of an isopropyl group (160 *m/e*) followed by propylene, giving rise to the base peak at 118 *m/e*.

Treatment of the bromo-dichloro-ketone **1** with lithium dimethylamide afforded the lemon coloured 2-dimethylamino-3,7-dehydrotropone (**3**), m.p. 112°, in 10% yield. Its spectral properties, summarised in Table 1, are practically identical with those of the 2-diisopropylamino-derivative (**2**), with the exception of the two ^{1}H-NMR.-singlets due to the non-identical methyl groups in **3**.

A plausible mechanism for the formation of **2** and **3** from **1** in the presence of lithium dialkylamide is depicted in the reaction *Scheme*.



Two consecutive dehydrohalogenations involving abstractions of protons, activated due to their α- (H–C(α) in the case of **1**) and doubly vinylogous α-positions (H–C(ε) in the case of **5**), could lead to 2-chloro-3,7-dehydrotropone (**6**) which, in the presence of excess dialkylamide, would undergo nucleophilic attack with subsequent elimination of chloride ion. The latter process has its analogy in the conversion of 2-chloro-tropone to 2-dimethylamino-tropone [6].

Further studies on the properties of the unique ring system **2** and **3** are in progress.

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* and by *Sandoz* AG Basel. We thank the members of our research team for interesting discussions on this problem.

Experimental. – The abbreviations used in the following text have been described previously [7].

4-exo-Bromo-7,7-dichloro-bicyclo[3.2.0]hept-2-en-6-one (**1**). A suspension of 5,12 g (0.029 mol) N-bromo-succinimide in 5 g (0.028 mol) 7,7-dichloro-bicyclo[3.2.0]hept-2-en-6-one [3] and 150 ml carbon tetrachloride was heated over a light bulb for 2.25 h. Removal of the solid and evaporation of the solvent left an oil which crystallised on triturating with hexane as buff coloured plates (3.6 g; 50% yield), m.p. 79–81°. Recrystallisation from warm hexane gave *4-exo-bromo-7,7-dichloro-bicyclo[3.2.0]hept-2-en-6-one* (**1**) as colourless plates m.p. 80–81°. – IR. ($CHCl_3$): 1812 s (C=O); 1600 w (C=C); 1345 s; 1273 m; 1172 m; 1146 m; 1111 w; 1068 w; 1037 s; 1070 s; 972 s; 940 s; 855 m; 826 s. – ^{1}H-NMR. (100 MHz; $CDCl_3$): δ = 6.29/*d*×*d*×*d* (*J* = 6, 2, 2), 1 pr (H—C(3)); 6.01/*d*×*d*×*d* (*J* = 6, 2.5, 0.6), 1 pr (H—C(2)); 5.16/*d*×*d* (*J* = 2, 2.5), 1 pr (H—C(4)); 4.56/*d* (*J* = 6.5), 1 pr (H—C(5)); 4.34/*d*×*m* (*J* = 6.5), 1 pr (H—C(1)). The material obtained by concentrating the combined mother liquors of the above crystallisations set to a light brown

semi-solid on standing. Its ^{1}H-NMR-spectrum showed that it contained mostly the same product (**1**) with only minor impurities.

$C_7H_5BrCl_2O$ (255.94) Calc. C 32.94 H 1.96% Found C 32.96 H 2.06%

2-Diisopropylamino-3,7-dehydrotropone (**2**). Lithium diisopropylamide (10% solution in hexane; 6 mmol) was added dropwise with stirring to a solution of 0.50 g (2 mmol) 4-*exo*-bromo-7,7-dichloro-bicyclo[3.2.0]hept-2-en-6-one (**1**) in 15 ml tetrahydrofuran at 0°. After 10 min water was added and the deep red solution extracted with chloroform. A solution of the resulting red gum in chloroform was filtered through a 15 g aluminium oxide column, to yield 0.26 g of an orange semi-solid mass. Further purification by sublimation at 75–80°/10^{-3} Torr followed by recrystallisation from warm *n*-hexane gave 0.133 g (33%) *2-diisopropylamino-3,7-dehydrotropone* (**2**) as yellow prisms, m.p. 99–100°. – UV. (EtOH): Max. 252 (33100); 304 (14000); 345–355 (1200). – IR. ($CHCl_3$): 2980 m; 2937 m; 1730 vs (C=O); 1630 vs (C=C); 1478 m; 1466 m; 1458 m; 1389 m; 1375 m; 1341 s; 1300 s; 1192 w; 1154 m; 1126 m; 1040 m; 998 w; 970 w; 913 w; 880 w. – ^{1}H-NMR. (100 MHz; $CDCl_3$): δ = 7.51/*d* × *d* (J = 3.2, 3.6), 1 pr (H–C(5)); 6.48/*d* (J = 3.6), 1 pr (H–C(4) or H–C(6)); 6.40/*d* (J = 3.2), 1 pr (H–C(6) or H–C(4)); 5.25/*sept.* (J = 6.5), 1 pr (H–C(a)); 3.99/*sept.* (J = 6.5), 1 pr (H–C(b)); 1.55/*d* (J = 6.5), 6 pr (2 × CH_3–C(b)); 1.45/*d* (J = 6.5), 6 pr (2 × CH_3–C(b)). – ^{13}C-NMR. (25.2 MHz, proton-noise decoupled; $CDCl_3$): δ = 169.6 weak (C(1) or C(2)); 168.1 weak (C(2) or C(1)); 158.9 weak (C(3) or C(7)); 145.6 (C(5)); 144.9 weak (C(7) or C(3)); 108.9 (C(4) or C(6)); 106.6 (C(6) or C(4)); 50.1 (C(a)); 49.3 (C(b)); 21.1 (2 × *C*–C(a)); 19.5 (2 × *C*–C(b)). – MS.: 203 (16) (M^+); 160 (13); 120 (10); 118 (100); 90 (10); 63 (9); 43 (12); 41 (11).

$C_{13}H_{17}NO$ (203.27) Calc. C 76.81 H 8.43 N 6.89% Found C 76.73 H 8.43 N 7.15%

2-Dimethylamino-3,7-dehydrotropone (**3**). To a stirred solution at 0° of (0.03 mol) lithium dimethylamide in 10 ml tetrahydrofuran under nitrogen was added 2.56 g (0.01 mol) 4-*exo*-bromo-7,7-dichloro-bicyclo[3.2.0]hept-2-en-6-one (**1**) in 10 ml tetrahydrofuran. After addition of ice-water, the mixture was extracted with chloroform to yield 3 g of a dark brown oil. Purification was affected by chromatography firstly on alumina ($CHCl_3$) and then on silica gel ($CHCl_3$) thereby removing the red-brown polymeric material present. The resultant 145 mg (10%) pale yellow solid was recrystallised from methylene dichloride/hexane giving *2-dimethylamino-3,7-dehydrotropone* (**3**) as lemon coloured needles, m.p. 111–112°. – UV. (EtOH): 250 (49500); 299 (17700); 340–350 (1200). – IR. ($CHCl_3$): 3000 w; 2930 m; 2850 w; 1792 w; 1740 vs (C=O); 1660 vs (C=C); 1486 m; 1455 m; 1424 m; 1415 sh; 1360 w; 1308 s; 1040 w; 995 m; 910 w; 840 w. – ^{1}H-NMR. (100 MHz; $CDCl_3$): δ = 7.48/*d* × *d* (J = 3.6, 3.2), 1 pr (H–C(5)); 6.47/*d* (J = 3.6), 1 pr (H–C(4) or H–C(6)); 6.38/*d* (J = 3.2), 1 pr (H–C(6) or H–C(4)); 3.53/*s*, 3 pr (CH_3(a)); 3.20/*s*, 3 pr (CH_3(b)). – MS.: 147 (46) (M^+); 133 (10); 132 (100); 117 (31); 104 (26); 77 (18); 72 (94); 63 (17); 28 (41).

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