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THE INFLUENCE OF HETEROATOM SUBSTITUENTS ON THE STABILITY OF TROPYLIUM IONS1)

Baldur Föhlisch* and Rüdiger Braun
Institut für Organische Chemie, Biochemie und Isotopenforschung der Universität Stuttgart, Pfaffenwaldring 55, D-7000 Stuttgart 80

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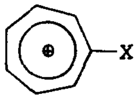
A recent MINDO/3 calculation of some substituted tropylium ions (**1**) suggests that substituents R = NH_2, OH, OCH_3, F, Cl, CH_3, CN "seem to provide no conjugative stabilization" of the ion2). The influence of substituents on the positively charged tropylium system is believed to be approximately the same as on uncharged benzene2). According to these calculations, hydroxytropylium ion has the lowest heat of formation, followed by methoxy- and fluorotropylium ions. Surprisingly the amino substituent is predicted to be pyramidal and orthogonal to the ring and therefore can provide no efficient stabilization of the carbenium ion.



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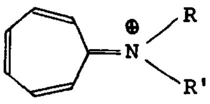
1	X	ΔH_f^o	$\Delta\Delta H_f^o$
		(calc.,	Kcal/mol)2)
a	H	195.6	0
b	OH	133.7	- 61.9
c	OCH_3	145.0	- 50.6
d	F	148.3	- 47.3
e	Cl	191.2	- 4.4
f	NH_2	191.4	- 4.2



2

Solution chemistry, however, indicates, that the amino group as well as alkylamino- and dialkylamino groups exert a powerful stabilising effect on the tropylium ion: alkylamino- and dialkylaminotropylium salts can be prepared from the corresponding (di)alkylaminocycloheptatrienes by dehydrideation with an unsubstituted tropylium salt3,4). UV and pmr spectra resemble those of tropone and are therefore in agreement with a large contribution of the cycloheptatrienylidene-imonium structure **2**3,4).

A scale of the relative thermodynamic stability in solution has been established for some carbenium ions based upon the definition of the pK_{R^+} -values[5]. With the heterosubstituted tropylium ions **1b**-**f**, however, this treatment cannot be applied because of their propensity to hydrolyse to tropone. Therefore we have tried to determine a scale of stability by examination of the equilibrium shown in equation (**1**)[6].

(**1**)

1 **3** **4** **5**

The pmr spectra[7] were taken for equimolar amounts (0.2 mmol) of (substituted) tropylium salt **1** (perchlorate or fluoroborate) and (substituted) cycloheptatriene (**3**)[8], dissolved separately in 0.5 ml trideuterioacetonitrile (probe temperature 35°C, Varian T 60). The solutions of **1** and **3** were then combined in a single nmr tube and the spectra were recorded immediately and repeated after 4-5 hr. A developing red colouration of the mixture indicates the beginning hydride transfer. The last measurement was after 3 days; in that time most solutions had turned black. The position of the equilibrium, which was reached in 4 hr, could be determined by integration of the peaks of the tropylium ions (**1** and **5**). Since the more complex signals of the cycloheptatrienes (**3** and **4**) overlapped in most cases the relative concentration of the cycloheptatrienes could not be determined ; therefore the evaluation of an equilibrium constant was not possible.

However, the conversion of the tropylium ions shows a clear trend (Table 1). The dehydrideation of 7-dimethylaminocycloheptatriene and methoxycycloheptatrienes with **1a** was described by other investigators in preparative work several years ago[3,4,9]. We have found, that dimethylaminotropyliumtetrafluoroborate does not react with methoxycycloheptatrienes. The solution of the components in CD_3CN retains its yellow colour and the pmr is unchanged. On the other hand, the hydrogen of 7-dimethylaminocycloheptatriene is transfered quantitatively to methoxy- or methylthiotropylium ion within 3 hr. These results clearly demonstrate the superior stability of the dimethylaminotropylium ion, in accord with the resonance structure **2**. All other combinations of tropylium ions and cycloheptatrienes (Entries 4 - 11) form equilibrium mixtures but with different extent of conversion. Whereas chlorotropyliumperchlorate abstracts hydrogen effectively from cycloheptatriene, fluorocycloheptatriene acts as a hydride donor versus unsubstituted tropylium ion. Apparently fluorine stabilises the tropylium ion, whereas chlorine has a destabilising effect. The relative degree of conversion with methoxy- and methylthiotropylium salts and cycloheptatriene indicates that the methoxy stabilises the tropylium ion more than the methylthio group[9]. However, the combination of methylthiotropylium salt with methoxycycloheptatrienes or methoxytropylium salt with methylthiocycloheptatrienes gives no clear results because of side reactions which obscure the pmr spectra. Starting with the first combination an equilibrium mixture of 50:50 between ions **1c** and **1h** was obtained.

Table 1. Dehydrideation of cycloheptatrienes by tropylium ions (eq. 1).

Experiment	Tropylium ion (**1**)	X	Anion $Z^{\ominus}$	Cyclohepta-triene (**3**)	Y	Degree of conversion to **5** [%]
1	**1c**	$(CH_3O-$	ClO_4	**3b**	$(CH_3)_2N-$	100
2	**1g**	$(CH_3)_2N-$	BF_4	**3c**	CH_3O-	0
3	**1h**	CH_3S-	ClO_4	**3b**	$(CH_3)_2N-$	100
4	**1e**	Cl-	ClO_4	**3a**	H-	75
5	**1a**	H-	BF_4	**3d**	F-	71
6	**1a**	H-	BF_4	**3c**	CH_3O	75
7	**1c**	CH_3O	ClO_4	**3a**	H-	16
8	**1a**	H-	BF_4	**3e**	CH_3S-	25
9	**1h**	CH_3S-	ClO_4	**3a**	H-	60
10	**1c**	CH_3O	ClO_4	**3e**	CH_3S-	50
11	**1h**	CH_3S-	ClO_4	**3c**	CH_3O-	50

Our results demonstrate that the stabilising effect of tropylium ion substituents is in the order

$$(CH_3)_2N- \gg CH_3O \sim CH_3S \sim F > H > Cl.$$

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Footnotes and References:

1) Tropylium ions and tropilidenes, VI. Part V: B.Föhlisch, Ch.Fischer, E. Widmann and E.Wolf, Tetrahedron 34, 533 (1978).

2) M.J.S.Dewar and D.Landman, J.Am.Chem.Soc. 99, 7439 (1977).

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5) D.Bethell and V.Gold, Carbonium Ions, p. 60, Academic Press, London 1967.

6) The equilibrium between tropylium ion (**1a**) and methylcycloheptatrienes was investigated by K.Conrow, J.Am.Chem.Soc. 83, 2343 (1961). It was concluded that methyltropylium ion is 3.7 kcal/mole more stable than **1a**, a value which is in rather good agreement with the MINDO/3 calculation ($\Delta\Delta H_f^o$ = 5.6 kcal/mole)[2].

7) pmr values are found in the references cited[8] and in K.H.Harmon, in Carbonium ions (Edit. G.A.Olah and P.v.R.Schleyer), Vol. 4, p. 1579, Wiley-Interscience 1973.

8) Cycloheptatriene (**3a**), from Deutsche Shell Chemie, was rectified prior to use. The other educts were prepared by procedures published in the following references: **1a**-BF_4: K.Conrow, Org.Syntheses 43, 101 (1963); **1c**-ClO_4, **1e**-ClO_4, **1i**-ClO_4: B.Föhlisch and E.Haug, Chem.Ber. 104, 2324 (1971); **1h**-BF_4: E.Haug and B.Föhlisch, Chem.Ber. 104, 2338 (1971); 7-dimethylaminocycloheptatriene (**3b**): W.v.E.Doering and L.H.Knox, J.Am.Chem.Soc. 79, 352 (1957); equilibrium mixture of 1-, 2- and 3-methoxycycloheptatriene (70:7:23) (**3c**): E.Haug and B.Föhlisch, Chem.Ber. 104, 2670 (1971); mixture of 1-, 2- and 3-fluorocycloheptatriene (21:26:53) (**3d**): E.Müller, H.Kessler, H.Fricke and W.Kiedaisch, Liebigs Ann.Chem. 675, 63 (1964); equilibrium mixture of 1-, 2- and 3-methylthiocycloheptatriene (66:4:30) (**3e**): in analogy to **3c**, B.Föhlisch and R.Braun, unpublished work.

9) E.Weth and A.S.Dreiding, Proc.Chem.Soc.[London] 1964, 59, made brief mention of the dehydrideation of 1- + 3-methoxycycloheptatriene by **1a**.