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THE RELATION BETWEEN BRIDGEHEAD REACTIVITY AND ELECTRONIC EFFECTS

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Dedicated to Prof. Dr. Ch. Rüchardt on the occasion of his 60th birthday.

ABSTRACT. — Electronic effects on bridgehead reactivity examined by means of UV/VIS and NMR spectroscopic methods lead to the conclusion that bridgehead reactivity is influenced both by angle strain and by electronic effects. In most cases both effects influence the reactivity in the same direction. Electronic effects are especially important when only a small change in bridgehead bond angles occurs during the reaction. This is given in highly strained bridgehead systems.

Introduction

Bridgehead reactivity[1] is a convenient mechanistic tool[2-5] for the investigation of geometries of transition states[6-9]. For example, the main experimental support for the planarisation of the reaction center during S_N1 reactions derives mainly from this effect[9]. The effect is well established for normal sized ring systems, although there are exceptions. For instance, the μ-triquinyl system is discussed to react in solvolysis reactions 10^9 times more slowly than expected from calculated bridgehead strain[10] (but see for a further discussion ref.[11, 12]).

Moreover, with small ring systems — highly strained bridgeheads — solvolysis reactions proceed unexpectedly fast[3, 13]. Finally, the 4-homocubyl carbenium ion could be established as an intermediate in solvolysis reactions[14], but a classical ion is expected to be very highly strained and should resist the planarisation of the bridgehead. We think that the electronegativity of the bridgehead carbon atom — electron donating of withdrawing properties in ground and transition state — plays an important part, especially in small ring systems, and that this effect must be added to the influence of bridgehead strain. This possible influence has been already mentioned by Bentley and Roberts[15]. Thus, we sought a simple system which gave experimental information about bridgehead electronegativity.

Results

A sensitive probe for electronic effects is the absorption wavelength of donor-acceptor dyes 1 or 2, in which a donor D is conjugated to an acceptor A by a π-system X[16] (see also ref.[17]).

$$D-X-A \qquad D-X-A-X-D$$

$$1 \qquad\qquad 2$$
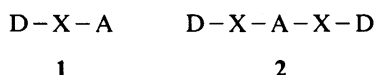
The absorption wavelength of these systems depends strongly upon the donor function of D and is thus sensitive to electronic properties of substituents on D.

We used O-picrylethers as chromophors of type 1 with the oxygen as a donor and a nitro group as an acceptor. In order

3

8   9   10

11   12   13

14   15   16
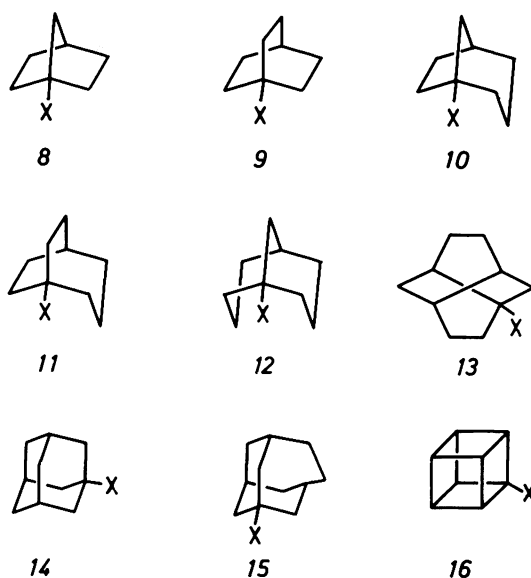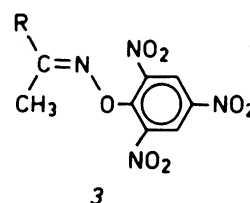
to minimize specific interaction the brideghead carbon under test has to be moved away from the oxygen, but should be linked to it by a group which transmits electronic effects. These conditions are fulfilled by the oximpicrates 3, the synthesis of which is well established[18-23]. For the UV/VIS measurements we used anti-methylketoximpicrates with bridgehead substituents R[23] which can be prepared according to literature procedure[23, 24] from the corresponding bridgehead carboxylic acid by the reaction with methyllithium to the methyl ketone and further with hydroxylamine to the anti-methylketoxime. The methylketoxime can be converted to the anti-methylketoximpicrate with picrylchloride and purified

by low temperature crystallisation. The shift of these UV/VIS absorption spectra as a function of the bridgehead substituent, given in Table I, is small, but can be obtained quantitatively by a precise spectrometer. From λ_{max} of the absorption spectra the molar energy E_T of excitation can be calculated according to equation (1).

$$E_T = 28\,590\ [\text{kcal} \times \text{nm} \times \text{mol}^{-1}]/\lambda_{max} \tag{1}$$

The E_T values should be used in linear free energy relationships rather than λ_{max}. Another measure for electronic effects is the ^{1}H-NMR chemical shift of the methyl singlet of 3. The methyl group is far enough away from the substituent R so that there cannot be a notable interference with anisotropic effects. These σ values are given also in Table I as well as the kinetic data of the Beckmann rearrangement for the mentioned groups[22, 23]. These k_1-values are a good measure of electronic effects, for the migrating group carries a large positive charge in the transition state, which is only slightly planarized[23].

Discussion

Firstly, the sensitivity of the spectra of 3 to electronic effects of R was tested. To the end, oximpicrates with primary, secondary, tertiary and increasingly branched tertiary groups R were examined (see Table I, 1 ... 4 and 5 ... 7). The spectra changed in the expected manner from methyl to tert-butyl and to more branched tertiary substituents: the higher the electron donating ability of R the longer the wavelength of absorption of 3 (smaller E_T values). Parallel to this long wavelength shift in the UV-spectra of 3 there is an upfield shift of the methyl singlet in the ^{1}H-NMR spectrum. Both these effects are accompanied by a large rate enhancement for the Beckmann rearrangement.

Table I. – Absorption spectra of bridgehead and other methylketoximpicrats (3) — comparison with ^{1}H-NMR and kinetic data from Beckmann rearrangement.

Nr.	Substituent R in 3	λ_{max} [a] [nm]	E_T [b] [kcal/mol]	δ [c] [ppm]	$k_1 \cdot 10^5$ [d] [s^{-1}]
1	CH$_3$	285.1	100.28	2.17	< 0.1
2	C$_2$H$_5$	288.4	99.13	2.12	0.347
3	i-C$_3$H$_7$	289.1	98.89	2.10	11.4
4	t-C$_4$H$_9$	290.3	98.55	2.02	51.7
5	2,2-Dimethylpropyl	290.1	98.55		1.32
6	1,1,2,2-Tetramethyl-propyl	290.6	98.38		888
7	1,1-Dipropylbutyl	291.1	98.21		909
8	1-Bicyclo[2.2.1]heptyl	292.6	97.71	2.15	4.72
9	1-Bicyclo[2.2.2]octyl	292.2	97.84	2.02	51.5
10	1-Bicyclo[3.2.1]octyl	291.9	97.84	2.10	87.5
11	1-Bicyclo[3.2.2]nonyl	292.1	97.88	2.02	239
12	1-Bicyclo[3.3.1]nonyl	292.2	97.84	2.10	902
13	1-Twistyl	293.9	97.28		88.4
14	1-Adamantyl	292.3	97.81	2.04	520
15	1-Homoadamantyl	293.4	97.44	2.04	1 550
16	1-Cubyl	300.4	95.17	2.03 '	126
17	4-Homocubyl	302.8	94.42	2.02	192

[a] Absorption wavelength of 3 in cyclohexane; [b] Molar energy of excitation of 3 in cyclohexane; [c] ^{1}H-NMR chemical shift of the methyl singlet of 3 in CCl$_4$; [d] First order rate constant for the Beckmann rearrangement of 3 in 1,4-dichlorobutane at 80° C (see ref.[22-23]).

With bridgeheads the trend of the effect is similar, but not so pronounced as with the simple aliphatic groups. The 1-bicyclo-[3.2.1]octyl bridgehead derivative (nr. 10) absorbs at short wavelengths (electron withdrawing) and has a low field shift of the methyl singlet in the ^{1}H-NMR spectrum. On the other hand, the 1-homoadamantyl derivative[27-29] (nr. 15) has a long wavelength absorption and an upfield shift for the methyl singlet. The migration tendencies of these groups (k in Table I) also show a corresponding behaviour. The other bridgehead derivatives give roughly similar results. An exception is the 1-bicyclo[2.2.1]heptyl derivative (nr. 8) which has a low reactivity in the Beckmann rearrangement and a downfield shift of the methyl singlet, but the absorption wavelength is unexpectedly high. An explanation for this effect cannot be given so far. The spectroscopic data of the 1-cubyl and 4-homocubyl derivative (nr. 16 and 17) are especially interesting, for these systems are unexpectedly reactive in the Beckmann rearrangement[23]. They give a long wavelength UV absorption and a highfield shift of the methyl singlet which suggests electron donating properties.
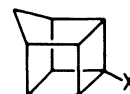
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The spectral shifts in 3 give information about ground state properties of bridgehead electronic effects. For reaction kinetics the transition state must also be taken into account, but some of the electronic effects will have a similar influence there as in the ground state. Deviations in the comparison of spectral data with kinetic data can be understood this way. The unusual reactivity of 1-cubyl and 4-homocubyl bridgehead have been explained in terms of a vertical stabilisation[30] — it is interesting that this effect can also be found in the spectral shifts.

The measurements indicate that electronic effects play an important part in bridgehead reactivity and must be taken into account as well as angle strain effects. This is all the more important when geometric changes during the reaction are small. Fortunately, in most cases both effects influence the reactivity in the same direction.

Acknowledgements

Experimental section

For the preparation and purification of the anti-methylketoximpicrates see ref.[22, 23]. The UV/VIS-spectra were measured with 1 cm quartz cuvettes at 20° C in cyclohexane in order to prevent specific interactions with the solvent and to avoid Chapman rearrangement. The spectrometer — MIT 20/L from Bruins — had a resolution and an accuracy of 0.02 nm and was calibrated with holmiumoxide glass[24] directly before and after each run. The extinctions of the samples at maximum wavelength were between 0.7 and 1.0 (4-homocubyl and 1-cubyl) derivative: 0.02 ... 0.1). The maximum wavelength was localized by the use of Mathias' rule[25, 26].

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