

NITROGEN BRIDGEHEAD COMPOUNDS PART 22¹. REACTION OF 2,3a,6a-TRI-
AZAPHENALENIUM SALTS WITH NUCLEOPHILES

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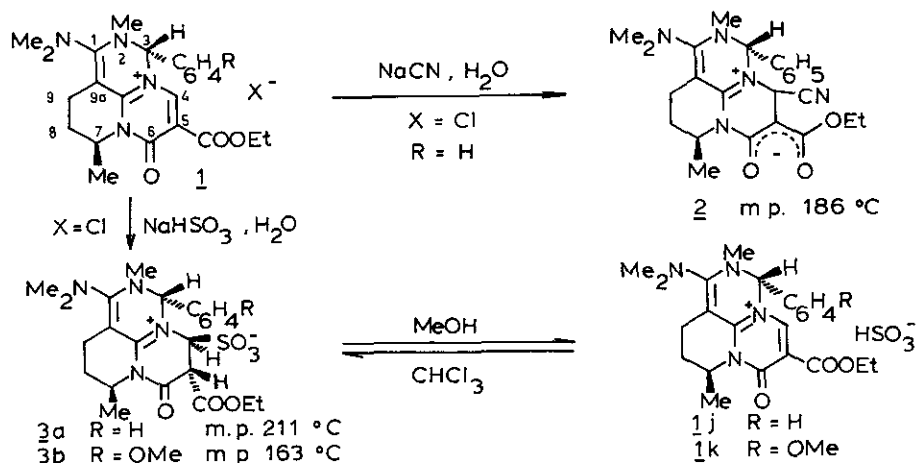
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Abstract - Novel 2,3a,6a-triazaphenalenium chlorides were allowed to react with different nucleophiles. Beside anion exchange Michael addition took place with CN^- and HSO_3^- anions affording tricyclic betaines.

We have earlier reported¹ on a facile synthesis of 2,3a,6a-triazaphenalenium chlorides **1a**. Studying the chemical behaviour of this new type of quaternary ring system we were interested first of all in their reactions with nucleophiles. The quaternary heterocycles can undergo various types of reactions affording many derivatives of the same heterocycle. It is rather common, however, that a new type of heterocycle is formed because of ring transformation².

We have investigated the reactions of compound **1a** with common nucleophiles in solutions. In the case of Br^- , I^- , BF_4^- , ClO_4^- , SCN^- , OCN^- , and N_3^- ions only the exchange of anions were observed as all quaternary salts of type **1b-i** but **1f** have poor solubility in water therefore they can be precipitated with the appropriate sodium salts from the solution of **1a** (yield 60-85%). The **1f** nitrate is fairly soluble in water hence it can be prepared by AgNO_3 from aqueous solution of **1a** after filtration of AgCl and evaporation of the solvent (yield 90%).

According to their triazaphenalenium structure these salts (**1b-i**) exhibit the same UV, IR and NMR spectra as **1a** (chloride) does. However we have observed an anomalous phenomenon in their ¹H nmr spectra: depending on the anion the H3, H4 and NMe signals show remarkable upfield shifts; the largest ones are caused by complex anions such as BF_4^- and ClO_4^- (Table 1). We suppose that these shifts should be induced by the differences in the anisotropy of the anions and in the strength of the ionic linkage together. The importance of the latter can be studied when the anion remains the same but solvents with different solvation properties are applied (Table 1). Protic solvents can considerably stabilise cations so the methanol and water weakening the strength of the ionic linkage because of strong solvation compared to chloroform cause the same upfield shifts as the change in anions from chloride to perchlorate does. In the case of 2,6-di-tert-butyl-1-methylpyridinium salts similar effects of solvents and anion exchanges were reported³. The UV and ¹³C nmr spectra of compounds **1a-i** do not show changes in different solvents mentioned in Table 1 excluding covalent addition of methanol or water reported on many heterocyclic cations to occur⁴.



On the other hand smooth addition takes place on the C4-C5 double bond with cyanide and hydrosulfite ions yielding $\underline{2}$ ⁵ and $\underline{3a}$, $\underline{3b}$ ⁶, respectively. The cyanide and hydrosulfite adducts of $\underline{1}$ are well-defined crystalline compounds which are easily precipitated from the aqueous solution of $\underline{1a}$ by the appropriate sodium salts. Since their formations like other Michael additions are reversible processes, they can easily lose cyanide or hydrosulfite ion in acidic media affording the starting compound $\underline{1}$.

Table 1. Characteristic ^1H nmr chem. shifts of $\underline{1a-i}$ salts (R=H)

Compounds	x^-	mp. °C	H4	H3	NMe	NMe ₂	solvent
$\underline{1a}$	Cl^-	232	9.73	8.34	3.80	3.19	CDCl_3
$\underline{1b}$	Br^-	178	9.51	7.97	3.73	3.21	CDCl_3
$\underline{1c}$	I^-	240	9.51	7.84	3.37	3.26	CDCl_3
$\underline{1d}$	OCN^-	195	9.21	7.50	3.64	3.23	CDCl_3
$\underline{1e}$	N_3^-	173	9.10	7.30	3.68	3.25	CDCl_3
$\underline{1f}$	NO_3^-	232	9.00	7.30	3.48	3.20	CDCl_3
$\underline{1g}$	SCN^-	242	9.00	7.10	3.64	3.26	CDCl_3
$\underline{1h}$	BF_4^-	246	8.60	6.78	3.27	3.22	CDCl_3
$\underline{1i}$	ClO_4^-	191	8.62	6.72	3.47	3.22	CDCl_3
$\underline{1a}$	Cl^-	232	8.78	6.84	3.40	3.23	CD_3OD
$\underline{1a}$	Cl^-	232	8.70	6.58	3.43	3.23	D_2O

The changes in the ^{13}C nmr spectra clearly indicate the disappearance of C4-C5 double bond in $\underline{1}$: the C4 and C5 at 148.9 and 107.0 ppm in $\underline{1a}$ ¹ are shifted to 42.1 and 68.9 ppm in $\underline{2}$ and to 71.4 and 46.2 ppm in $\underline{3b}$ (Table 2). These values can well be estimated by the additivity rules except for C5 in $\underline{2}$ the negative charge of which is delocalised. This delocalisation can well be demonstrated by the

Table 2. ^{13}C nmr chemical shifts, JEOL FX-100 solvent= CDCl_3 $\delta(\text{TMS}) = 0$ ppm

Com- pounds	C1	Me-2	C3	C4	C5	C6	C7	C8	C9	C9a	C9b	CN-4
$\underline{2}$	151.9	42.0	77.5	42.1	68.9	159.6	50.8	27.1	18.3	85.9	155.9	118.5
$\underline{3b}$	159.7	43.5	77.7	71.4	46.2	162.0	46.2	26.6	18.5	86.4	160.4	

comparison of the respective bond lengths of 2 to those of 3a in which the C5 atom is of pure sp^3 character. On the basis of the X-ray analysis of 2 and 3a the C5-C6 and C5-C25 bonds are shorter while the C6-O26 and C25-O28 carbonyl bonds are longer in 2 than in 3a in agreement with the enolate-type resonance structures of 2. (Fig. 2.) Moreover, the X-ray analysis of 3a⁷ revealed that the addition is stereospecific being the sulfo and ethoxycarbonyl groups in trans position (Fig. 2), and the H4-C4-C5-H5 dihedral angle is 86° in accordance with the $J_{4,5} = 1$ Hz coupling constant⁶.

It is fairly surprising that the positive charge of the heterocycles remains unaffected during the addition and the products 2 and 3a, 3b are internal salts (betaines) which bear negative charge on the C5 atom or the sulfo group respectively. Although the positive charge is extensively delocalised among the four N atoms one should expect a pseudo-type addition with strong nucleophiles in analogy with other quaternary pyrido[1,2-a]pyrimidines⁸. In this respect the C1 and C9b atoms should be the most suitable sites for nucleophilic attack. It is interesting, however, that the adducts 3a, 3b show the same solvent dependence toward the equilibrium covalent molecule (COV) \rightleftharpoons ion pairs (IP) as the pseudobases do⁹.

Generally the equilibrium (COV) \rightleftharpoons (IP) is sensitive to the following four parameters: stability of the cations, stability of the anions, polarity of the solvent and temperature. As solvent polarity is increased systems are attained in which the free energy difference between ionic and covalent structures is small¹⁰. This is the case with 3a and 3b which are stable in chloroform solution but dissociate to an equilibrium mixture when diluting with methanol in nmr tube.

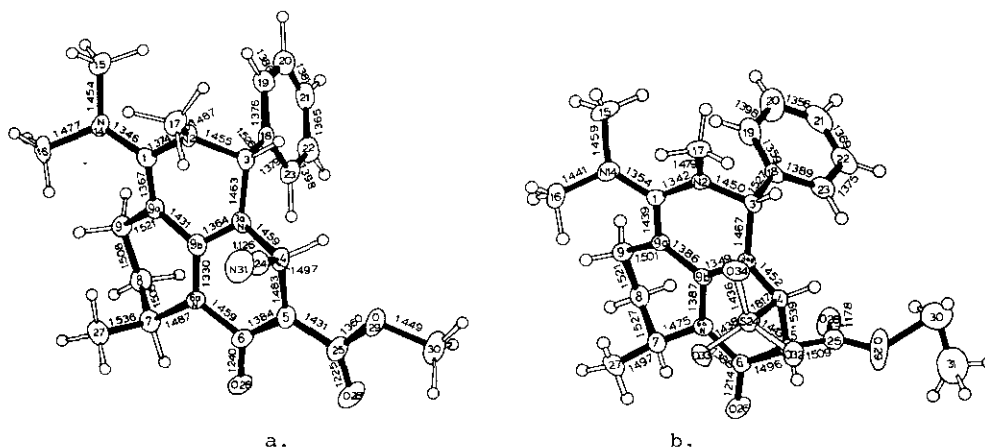
On the other hand even with such stable anion as chloride there is a slight tendency toward covalent bonding, at least in solid state¹¹. The detailed investigation of the four parameters affecting the equilibrium (COV) \rightleftharpoons (IP) is in progress.

REFERENCES & NOTES

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- 5 2: yield 61%, UV (CH_2Cl_2) λ_{max} 336 nm ($\lg \epsilon$ 3.82), 250 (3.89), 1H nmr ($CDCl_3$) 1.33 (t 3H OEt), 1.18 (d 3H Me-7), 1.7-2.8 (m 4H CH_2 -8,9), 3.06 s (6H NMe_2), 3.27 (s 3H NMe), 4.17 (q 2H OEt), 5.40 (m 1H H7), 5.65 (s 1H H3), 5.77 (s 1H H4), 7.23 (m 5H Ar)
- 6 3b: yield 80%, UV (CH_2Cl_2) λ_{max} 360 nm ($\lg \epsilon$ 4.25), 278 (4.11), 1H nmr ($CDCl_3$) 1.07 (t 3H OEt), 1.33 (d 3H Me-7), 1.7-2.8 (m 4H CH_2 -8,9), 3.02 (s 6H NMe_2), 3.52 (s 3H NMe), 3.78 (s 3H OMe), 4.22 (q 2H OEt), 4.46 (d 1H H5 $J=1$ Hz), 4.88 (d 1H H4 $J=1$ Hz), 4.92 (m 1H H7), 6.08 (s 1H H3), 6.82 (d 2H Ar), 7.10 (d 2H Ar), 1k: 1H nmr (CD_3OD) 1.32 (t 3H OEt), 1.27 (d 3H Me-7), 1.7-3.1 (m 4H CH_2 -8,9), 3.23 (s 6H NMe_2), 3.47 (s 3H NMe), 3.85 (s 3H OMe), 4.27 (q 2H OEt), 6.90 (s 1H H3), 8.83 (s 1H H4), 6.88 (d 2H Ar), 7.11 (d 2H Ar).

- 7 The X-ray analysis of 2 and 3a: recrystallization from methanol resulted in single crystals of the methyl ester, $C_{23}H_{25}N_5O_3$, $a = 9.702(5)$, $b = 9.219(3)$, $c = 15.249(7) \text{ \AA}$, $\beta = 120.81(5)^\circ$, s.g. Pc, $Z = 4$, $R = 0.046$ for 1306 refl. ($I \geq \sigma(I)$). 3b: $C_{23}H_{30}N_4O_6S$, $a = 12.686(1)$, $b = 16.524(2)$, $c = 12.405(2) \text{ \AA}$, $\beta = 113.60(1)^\circ$, s.g. $P2_1/c$, $Z = 4$, $R = 0.057$ for 3092 refl. ($I \geq 2\sigma(I)$). The intensities were collected for 2 and 3a on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated MoK_α radiation. The structures were solved by direct methods and refined using the SDP ENRAF-NONIUS program package with local modifications on a PDP 11/34 minicomputer. Relevant data are deposited¹.
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- 11 An analogy in the crystal structures of 2, 3a and 1 has been found; namely the directions of C4-CN and C4-SO₃ bonds are exactly the same and they are trans to the phenyl group. The chloride anion in 1 also lies on this axis, trans to phenyl. This position should indicate some kind of ionic interaction with C4 the electron deficiency of which may be considerable for resonance causes. Moreover the interaction is reflected in the C4-Cl⁻ distance -3.3 \AA - which is within the sum of Van der Waals radii by 0.2 \AA .

Figure 2.



ORTEP diagram of the structure of 2(a) and 3a(b) showing atomic numbering and bond distances (\AA). E.s.d.s are in the range of 0.004-0.008 \AA except for the disordered atoms of the ethoxycarbonyl group in 3a.

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