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A REVERSIBLE DOUBLE SMILES REARRANGEMENT THROUGH INTERMEDIATE FORMATION OF TWO TAUTOMERIC MEISENHEIMER SPIRO-COMPLEXES

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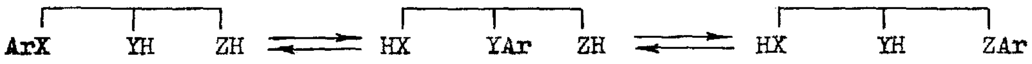
Abstract: A reversible double Smiles rearrangement in the system of 1-methylamino-3-picryloxy-2-propanol - 3-N-methyl-N-picrylamino-1,2-propandiol proceeds through intermediate formation of two tautomeric Meisenheimer spiro-complexes.

The Smiles rearrangement proceeds as an intramolecular migration of an aryl group, activated as a rule by electron-withdrawing substituents, from one nucleophilic center to another through the intermediate formation of a Meisenheimer spiro-complex, more often with a five-membered heterocycle. The direction of the migration is determined by the relative nucleophilicities of the centers and the thermodynamical stabilities of the forming compounds[1].

Until recently the possibility of arylotropic migration along a chain of three nucleophilic centers has not been investigated.



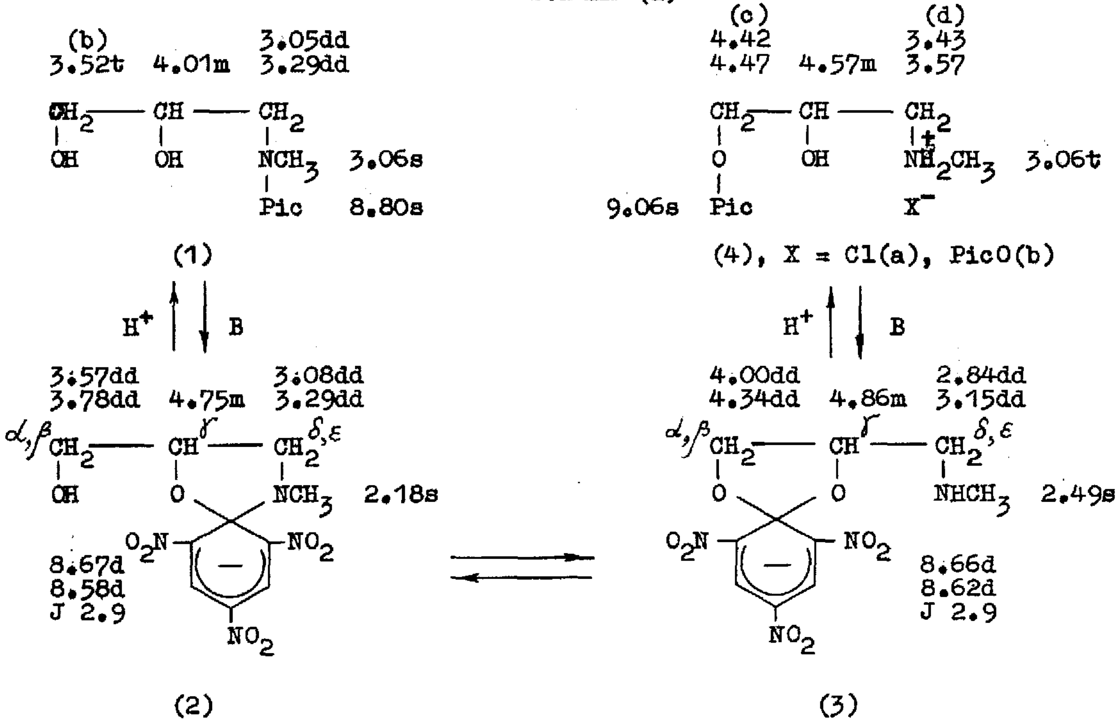
$$\mathrm{ArX\quad YH\quad ZH} \rightleftharpoons \mathrm{HX\quad YAr\quad ZH} \rightleftharpoons \mathrm{HX\quad YH\quad ZAr}$$

Such migration suggests the formation of two isomeric Meisenheimer spiro-complexes with five-membered heterocycles, which are in equilibrium with one another.

We have brought about such a migration in the case of picryl derivatives of 3-methylamino-1,2-propandiol. 3-N-Methyl-N-picrylamino-1,2-propandiol (1) was prepared by condensation of the initial aminoalcohol with picryl chloride.

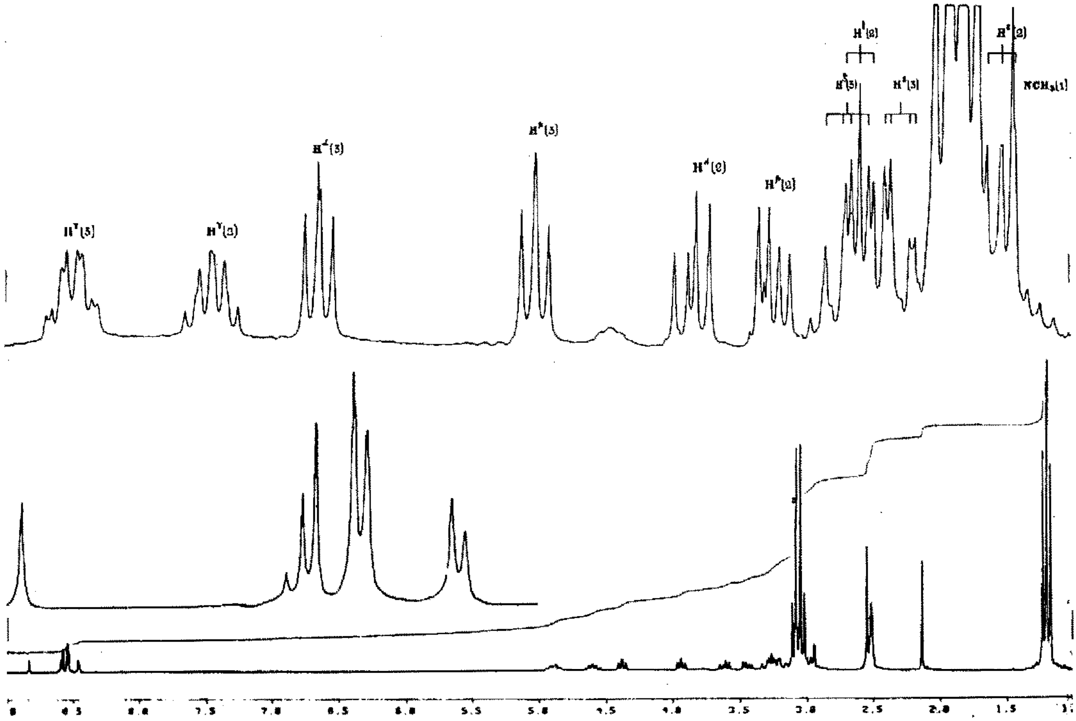
A dark-red K-salt of the spiro-complex (2) was formed as a result of treatment of picramide (1) with t-BuOK in a benzene - t-BuOH solution. It was characterized by the NMR data given in the scheme. Changes taking place in the NMR spectrum after treatment of the picramide (1) solution in acetone-d_6 with 1 eq. of t-BuOK or Et_3N proved the formation of the same complex. Shifts to higher fields of the picryl proton signals which are detected in the spectrum of (2) as two doublets, and also of the N-CH_3 group, and the opposite shift of the methine proton signal to lower fields are similiar to the shifts observed as a result of the formation of Meisenheimer spiro-complexes with the five-membered oxazolidine cycle[2]. It confirms the structure of complex (2). This complex was stable in acetone-d_6 at 20°C, but in DMSO-d_6 the signals of complex (3) gradually appeared (see below), and in a week the ratio of (2):(3) became about 10:1. 1-Methylamino-3-picryloxy-2-propanol hydrochloride (4a) was isolated by quick acidification of the solution of complex (2) with concentrated HCl. Treatment by silver picrate resulted in the corresponding picrate (4b). The addition of 2 eq. of Et_3N to the solution of (4) in acetone-d_6 or DMSO-d_6 resulted in the formation of the spiro-complex (3) with a five-membered dioxolane ring. In the NMR spectrum protons of the picryl cycle became non-equivalent, and their signals shifted to higher fields. The multiplet of methine proton shifted to lower fields and in comparison with (4), the shielding of the signals near the nitrogen atom due to the formation of a free N-methylamino group took place. With time the intensity of spiro-complex (3) signals decreased, and the signals of complex (2) could be seen in the spectrum. Rearrangement of (3) $\longrightarrow$ (2) proceeded much more quickly in acetone-d_6 than in DMSO-d_6. In the first case after the addition of Et_3N to compound (4) there was an equal proportion of complexes (3) and (2) in the mixture in 5 minutes and in 30 minutes the equilibration practically completly shifted to complex (2). In the DMSO-d_6 solution the first traces of complex (2) appeared in an hour. In 24 hours the ratio (3):(2) reached 1:1 (Figure), and in a week it was approximately 3:7 and weak signals of the compound (1) appeared. An intermediate, 3-methylamino-2-picryloxy-1-propanol, through which it may be supposed the conversion of complex (2) into complex (3) and vice versa is realized was not registrated. Rearrangement of (4) $\longrightarrow$ (1) took place on addition of

SCHEME (a)



	J_{gem}		J_{vic}			J_{gem}		J_{vic}	
	CH_2O	CH_2N	CH_2O	CH_2N		CH_2O	CH_2N	CH_2O	CH_2N
(1)	(b)	-13.5	4.8(b)	7.6 3.9	(4b)	-9.5(c)	(d)	4.5(c) 4.5(c)	(d)
(2)	-10.7	-8.0	6.7 5.0	6.7 6.7	(3)	-5.9	-12.2	7.5 7.5	7.8 4.3

(a) NMR data (250 MHz) are given in δ-scale for solutions in acetone-d_6, J – in Hz. (b) A_2-part of degenerated system A_2X with splitting on the OH group. (c) AB-part of the system ABX. (d) Broad multiplets.



a base to the solution of the compounds (4a,b) followed by slow acidification with dilute HCl and during the melting of these compounds.

Possibility for the mutual conversion of (1) $\rightleftharpoons$ (4) through the formation of a Meisenheimer spiro-complex with a six-membered 1,3-perhydrooxazine cycle or an according intramolecular mechanism, though not completly excluded, seems unlikely.

References and Notes

1. W.E.Truce, E.M.Kreider and W.W.Brand, Org.React., 18, 99 (1970).
2. C.F.Bernasconi and R.H.de Rossi, J.Org.Chem., 38, 500 (1973); C.F.Bernasconi, R.H.de Rossi and C.L.Gehringer, J.Org.Chem., 38, 2838 (1973); S.Sekiguchi and T.Shijioma, Bull.Chem.Soc.Japan, 46, 693 (1973); V.N.Drozd, V.N.Knyazev and V.M.Minov, Zh.Org.Chim., 13, 396 (1977).
3. All new synthesized compounds showed satisfactory elemental analysis. M.p.: (1) 133-134°C (EtOAc-hexane 7:3), (4a) 157-159°C (dil. HCl-ethanol), (4b) 135-137°C (precipitation from nitromethane by ether).

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