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TAUTOMERIC REARRANGEMENTS AND INTRAMOLECULAR DIELS-ALDER REACTIONS OF DICYANOVINYL AND (CYANOIMINO)ALKYL GROUPS IN THE TROPOLONE SERIES

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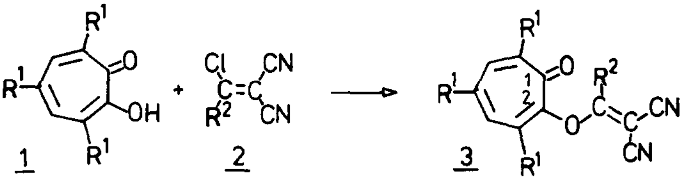
Summary: At room temperature the O-dicyanovinyl tropolones 3 and the O-(cyanoimino)alkyl tropolones 5 show a rapid degenerate O,O-migration of the dicyanovinyl and (cyanoimino)alkyl groups. By heating 3 and 5 in boiling toluene the Diels-Alder adducts 7 and 8 are formed.

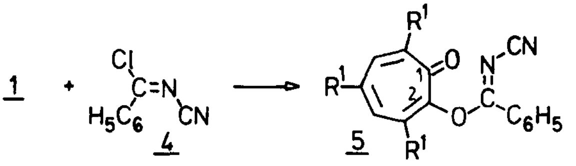
Degenerate tautomeric rearrangements of hydrogen and other atoms or functional groups have been studied intensively during the last 25 years[1]. A high migratory aptitude is shown by the acyl group in enol esters of 1,3-diketones and related systems[2]. Due to a rather favourable geometric arrangement the acylotropic tautomerism is exceptionally rapid in O-acyl tropolones[3]. As the electronic properties of an acyl group are similar to those of a dicyanovinyl or a (cyanoimino)alkyl group[4], we have studied the degenerate tautomeric rearrangement in some O-dicyanovinyl tropolones 3 and O-(cyanoimino)alkyl tropolone 5.

Stirring tropolone 1 with 2-chloro-alkylidene malonitrile 2[5] in CH_2Cl_2 at room temperature in the presence of 1 mol of triethylamine and 0.1 mol of 4-dimethylamino pyridine[6] leads to the formation of 3c and 3g (method a). 3a-b and 3d-f are best prepared from thallium(I) troponolate[7] and 2 in toluene between 0-65°C (method b). The O-(cyanoimino)alkyl tropolones 5 have been obtained from 1 and 4[8] by method a). The yields indicated refer to pure recrystallised products[9].



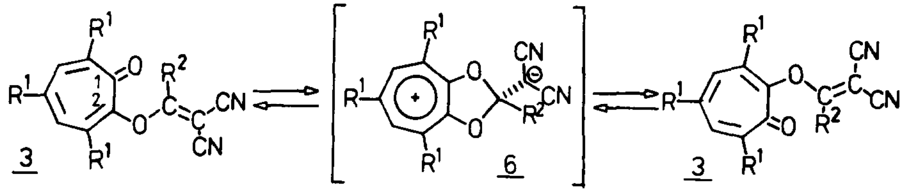
3	R^1	R^2	mp [°C]	yield [%]
a	H	H	122	57
b	H	CH_3	127	66
c	H	C_6H_5	172 (dec.)	74
d	H	CN	111	15

3	R^1	R^2	mp [°C]	yield [%]
e	CH_3	H	151-152	69
f	CH_3	CH_3	138	49
g	CH_3	C_6H_5	140-141	57

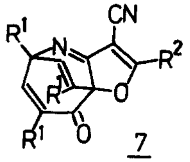


5	R^1	mp [°C]	yield [%]
a	H	137	46
b	CH_3	110	64

The ^{1}H and ^{13}C NMR spectra of 3 at room temperature clearly show, that the dicyanovinyl group is migrating rapidly between both oxygens of the tropolone ring. The same is true for the (cyanoimino)alkyl group in 5. The dipolaric intermediate of this degenerate rearrangement for the tropolone ethers 3 can be formulated as 6. In the ^{13}C NMR spectra of 3a-3d and 5a both carbon atoms 1 and 2 have one common broad signal around 0°C, which sharpens between room temperature and 80°C. Similarly both methyl groups adjacent to the oxygen atoms in the tropolone ring of 3e-g and 5b give only one common singulet at room temperature (δ = 2.33-2.38ppm)[10]. The ^{13}C NMR data of 3a ($[D_6]$DMSO at 40°C) may be considered representative for the structures 3 and 5: δ = 175.6ppm (^1J = 202 Hz, C-8); 168.5 (C-1, -2); 135.3 (C-4, -5, -6); 132.9 (C-3, -7); 111.0 (9-CN); 66.4 (^2J = 11.6 Hz, C-9).



By heating 3g in boiling toluene for 5 minutes, a new isomeric compound is formed in nearly quantitative yield. This has been identified by X-ray crystallography (see fig. 1) as the intramolecular Diels-Alder adduct 7d: One of the cyano groups undergoes a 1,4-cycloaddition to the tropolone ring. The Diels-Alder reaction is facilitated by methyl substituents in the 7-membered ring (R^1 = CH_3) and a phenyl group in the side chain. Not all O-dicyanovinyl tropolones 3 form Diels-Alder adducts on heating: 3a and 3d decompose before any cyclisation occurs. Of the O-(cyanoimino)alkyl tropolones 5 only 5b gave the cyclised product 8.



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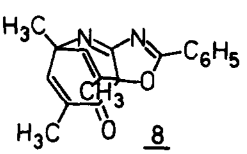


8

	R^1	R^2	mp [°C]	yield [%]	r.t. [min]
7a	H	CH_3	170	66	480
7b	H	C_6H_5	185	76	180
7c	CH_3	CH_3	132	83	220
7d	CH_3	C_6H_5	178	95	5
8	-	-	145	87	160

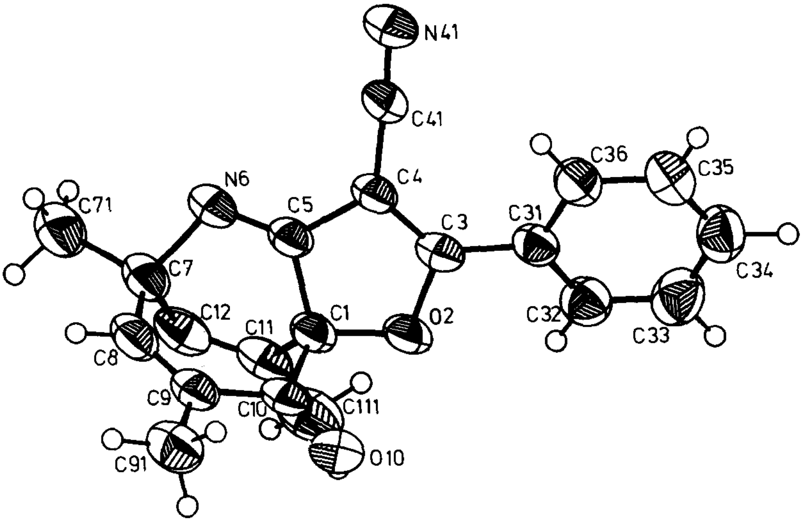
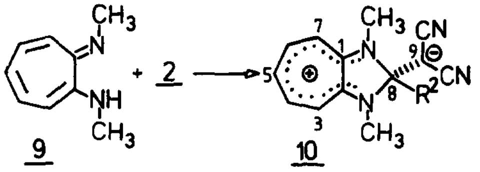


Fig. 1: ORTEP plot of 7d

The 2-chloro-alkylidene malonitriles 2 condense also with the aminotroponeimine 9[11] to form N-substituted products. In these cases, however, no degenerate N,N-migration of the dicyanovinyl group is observed. Instead the dipolaric structure 10 is obviously the most stable one along the reaction coordinate. This is mainly supported by the ^{13}C NMR data for 10a ($[D_6]$DMSO at 20°C), which show an extreme high field shift for C-8 and C-9 as compared to 3a, large shift differences between the ring carbon atoms and a rather low field signal for the cyano groups: δ = 153.6ppm (C-1, -2); 142.6 (C-4, -6); 124.9 (9-CN); 124.2 (C-5); 112.3 (C-3, -7); 92.5 (^1J = 161 Hz, C-8); 29.9 (CH_3); 21.3 (C-9). Further evidence is given in the IR spectra by the CN stretching vibrations, which are unusually intense and shifted to rather low wave numbers: for 10a 2170 and 2130cm^{-1}, for 3a 2220cm^{-1}.



10	R^2	mp [°C]
a	H	171
b	C_6H_5	230 (dec.)

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References and Notes

1 For reviews see: a) V.I.Minkin, L.P.Olekhnovich and Yu.A.Zhdanov, Molecular Design of Tautomeric Systems, Rostov on Don University Publishing House, Rostov on Don (USSR) 1977 [Chem.Abstr. 90, 38481d (1979)] ; b) V.I.Minkin, L.P.Olekhnovich and Yu.A.Zhdanov, Acc.Chem.Res. 14, 210 (1981).

2 a) V.I.Minkin, L.P.Olekhnovich, Yu.A.Zhdanov. V.V.Kislev, M.A.Voronov and Z.N.Budarina, Dokl.Akad.Nauk SSSR 204, 1363 (1972); b) K.Hartke, D.Krampitz and W.Uhde, Chimia 27, 209 (1973); c) E.Wachsen and K.Hartke, Chem.Ber. 108, 683 (1975); d) E.Wachsen and K.Hartke, Chem.Ber. 108, 138 (1975); e) A.Mannschreck and H.Dvorak, Tetrahedron Lett. 1973, 547.

3 a) S.Masamune, A.V.Kemp-Jones, J.Green and D.L.Rabenstein, J.Chem.Soc., Chem.Commun. 1973, 283; b) V.I.Minkin, L.P.Olekhnovich, Yu.A.Zhdanov, Z.N.Budarina and V.P.Metlushenko, Tetrahedron Lett. 1974, 563; c) V.I.Minkin, L.P.Olekhnovich, Yu.A.Zhdanov, Z.N.Budarina, V.P.Metlushenko and I.B.Orenshtein, Zh.Org.Khim. 13, 777 (1977); d) L.P.Olekhnovich, N.I.Borisenko, Z.N.Budarina, V.P.Metlushenko, Yu.A.Zhdanov and V.I.Minkin, Zh.Org.Khim. 18, 1785 (1982).

4 K.Wallenfels, K.Friedrich, J.Rieser, W.Ertl and H.K.Thieme, Angew.Chem. 88, 311 (1976); Angew.Chem.Int.Ed.Engl. 15, 261 (1976).

5 For a preparation see: K.Hartke and L.Peshkar, Pharm.Zentralhalle Dtschl. 107, 348 (1968). K.Friedrich, Angew.Chem. 79, 980 (1967); Angew.Chem.Int.Ed.Engl. 6, 959 (1967). C.L.Dickinson, D.W.Wiley and B.C.McKusick, J.Am.Chem.Soc. 82, 6132 (1960).

6 G.Höfle, W.Steglich and H.Vorbrüggen, Angew.Chem. 90, 602 (1978); Angew.Chem. Int.Ed.Engl. 17, 569 (1978).

7 W.H.Nelson and M.J.Aroney, Inorg.Chem. 1973, 132.

8 Prepared from methyl N-cyano-thiobenzimidate with 2 moles of SO_2Cl_2.

9 All new compounds mentioned in this paper showed a correct elemental analysis.

10 More details of the kinetics will be given in the full paper.

11 R.W.Brasen, H.E.Homquist and R.E.Benson, J.Am.Chem.Soc. 83, 3125 (1961). N.Soma, J.Nakazawa, T.Watanabe, Y.Sato and G.Sunagawa, Chem.Pharm.Bull. (Tokyo) 13, 819 (1965).

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