Tetrahedron Letters No. 7, pp 563 - 566, 1974. Pergamon Press. Printed in Great Britain.

ACYLOTROPIC TAUTOMERISM. EXCEPTIONALLY RAPID AND REVERSIBLE MIGRATIONS OF ACYL GROUPS IN TROPOLONE DERIVATES.

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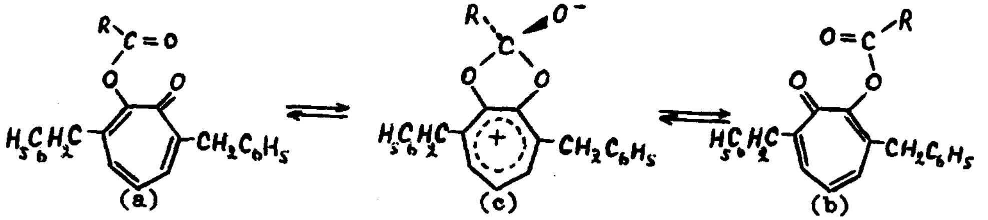
(Received in UK 30 July 1973; accepted for publication 11 January 1974)

Rapid and reversible migrations of various acyl and aroyl groups between two oxygen centers have been revealed recently in the O-derivatives of the 2,4-pentanedione enol forms [1-4]. Similar rearrangements have been qualified earlier as a new acylotropic type of tautomerism [5]. Recently the first examples of acylotropic tautomerism have been found also for the tropolone derivatives[4,6].

Now we wish to report some new data concerning this acylotropic system with exceptionally fast isomerisation rates (NMR time scale).



(I) R = CH_3 $T_c = -110^{\circ}$[8] $k_c = 21\ sec^{-1}$ $G^{\ddagger}_{c} = 8$ kcal/mole

(II) R = OCH_3 $T_c = -51^{\circ}$[8] $k_c = 21\ sec^{-1}$ $G^{\ddagger}_{c} = 11$ kcal/mole

At room and higher temperatures methylene groups of 2-acetoxy-3,7-dibenzyl tropone (I) and 2-carbomethoxy-3,7-dibenzyl tropone (II) give rise to one single peak. Only one common signal can be observed also for protons of both phenyl groups in each of these compounds at the condition mentioned.

In the initial 3,7-dibenzyl tropolone (III) a completely analogous spectral picture is observed, which is due to the rapid proton migrations preserved up to the minimum temperatures obtained (-130°). Consequently, the rapid exchange of the acyl group positions (a)$\rightleftharpoons$(b) occurs in (I) and (II).

On cooling, the common methylene singlet first broadens and below the coalescence temperature separates into two distinct AB quartets. Accordingly, one common phenyl proton signal gives rise to two distinct singlets. This spectral behaviour is identical for both (I) and (II) and is connected, obviously, with the freezing of the acyl migration. Diastereotopic methylene protons are possible only for a non-planar structure of the acyloxy tropone portion of molecules (I) and (II).

X-ray studies have shown the seven-membered ring of tropolonyl p-chlorobenzoate (R = p-C_6H_4Cl) and other tropolone derivates to be essentially planar, whilst the exocyclic oxygen of tropolonyl p-chlorobenzoate was markedly out of plane of the heptagon [7]. This nonplanarity may be considered as a possible cause for the diastereotopic behavior of methylene groups. However, hindering of acyl group rotation resulting in a sufficient rigid skew conformation appears a somewhat more favourable explanation, when comparison with 2-methoxy-3,7-dibenzyl tropone (IY) is made.

The spectrum of this compound is not susceptible to temperature variations at -100° to 180°. Two distinct singlets from the non-equivalent methylene and phenyl groups have been observed over this temperature range without detectable broadening. These observations strongly suggest that the declination of the carbonyl oxygen from the molecular plane, if it does take place, is too small to be responsible for the diastereotopic behaviour of methylene proton. Table I summarizes some data of the PMR spectra compounds (I)-(IY).

The reversible and non-catalyzed acyl rearrangements studied are more rapid than the earlier known ones [1-4,10]. This result may be rationalized by inspection of ($\sigma+\pi$) CNDO/2 electronic distribution at the transition structure (c) and by comparison with that for acylated enol of 2,4-pentanedione [4]. The carbonyl carbon at (c) possesses the highest positive charge, whose value determines the (a)$\rightleftharpoons$(b) migration rate [4].

TABLE I

COMPOUND Number	COMPOUND Name	T°C [a]	$\mathrm{C\underline{H}_2}$,p.p.m. [b]	$\mathrm{C_6\underline{H}_5}$,p.p.m.	$\mathrm{C\underline{H}_3}$, p.p.m.
(I)	2-acetoxy-3,7-dibenzyl tropone [d]	35 -I20	3.83 (3.93, 3.88), (3.82, 3.75) [c]	7.IO 7.I2, 7.I9	2.I9 2.29
(II)	2-carbomethoxy-3,7-dibenzyl tropone [e]	25 -I00	3.87 (3.9I, 3.88), (3.8I, 3.76) [c]	7.I2 7.I4, 7.II	3.70 3.73
(III)	3,7-dibenzyl tropolone [d]	-II0	4.03	7.I4	-
(IV)	2-methoxy-3,7-dibenzyl tropone [f]	I80	3.93, 3.87	7.08, 7.04	3.64

[a] Two temperatures - one is for a rapid exchange and the other is for a slow one - are quoted if the rearrangements are observed.

[b] Chemical shifts in -scale relative to TMS.

[c] The inner AB-quartet peaks are given. The outer peaks have very small intensities. The values of J_{AB} coupling constants were estimated by approximate formulae from relative intensities of inner peak [9]. Both J_{AB} coupling constants are of about 20 Hz.

[d] In CS_2 - acetone(d_6) (4:I) solution.

[e] In CS_2 - CH_2Cl_2 (3:I) solution.

[f] In perchlorobutadiene solution.

3,7-Dibenzyl tropolone (III) was synthesized by the literature method [II] and their derivates (I),(II),(IV) were prepared from (III) by usual procedures. PMR spectra have been registered by means of the Tesla BS-407 C spectrometer (80 MHz.).

Further studies of acyl group migrations in tropolone and dithio tropolone derivates are now in progress.

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