Temperature-dependent Carbon-13 Nuclear Magnetic Resonance Spectra of Tropolone Acetate

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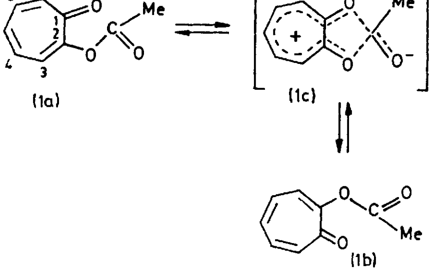
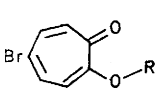
Summary Temperature-dependent ^{13}C n.m.r. spectra of tropolone acetate prove that degenerate rearrangement of the acetate proceeds rapidly at low temperatures.

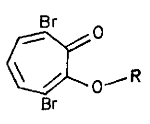
There are good reasons to believe that tropolone acetate (**1a**)[1] would readily undergo isomerization under ordinary, uncatalysed conditions, as indicated by equilibrium (**1a**) ⇌ (**1b**),[2] and some results do suggest the fluxional nature of tropolone derivatives.[3] We present unambiguous evidence to prove that the rearrangement does indeed proceed very rapidly even at low temperatures.



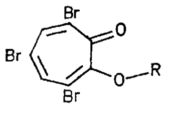
(1a) (1c) (1b)



(2a) R = COMe
(2b) R = H



(3a) R = COMe
(3b) R = H



(4a) R = COMe
(4b) R = H

^1H N.m.r. spectra (100 MHz) of (**1a**) measured in various solvents were found to be temperature-dependent over the range 203—298 K and the ring protons exhibited either deceptively simple or complex absorptions in a rather narrow range of field [δ (Me_4Si) 7·3—7·9, in dimethylformamide (DMF) and acetone; δ 6·2—7·5 in toluene]. Obviously the complexity of the tightly coupled 5-spin system makes analysis of these temperature-dependent spectra nearly impossible. As expected, ^{13}C n.m.r. spectroscopy offers unique advantages in solving this kind of problem.[4] Thus, the proton-decoupled ^{13}C n.m.r. spectrum (22·63 MHz) of (**1a**) in [$^2H_7$]DMF at 203 K showed 9 singlets at δ 178·3 (A), 168·0 (B), 157·5 (C), 139·5 (D), 137·5 (E), 134·1 (F), 132·1 (G), 128·1 (H), and 19·7 (I) downfield from Me_4Si. Chemical shifts[5] and off-resonance proton decoupled spectra clearly assign signals A, B, C, and I to C-1, -8, -2, and -9, and the temperature-dependence of three pairs of signals A and C (465 Hz apart), D and H (256 Hz), and E and G (121 Hz) (see below) shows that these signals are due to C-1 and -2 as assigned already, C-6 and -4, and C-7 and -3,† respectively, signal F thus being due to C-5. Upon warming, signals D, E, G, and H broadened extensively around 230 K, A and C coalesced completely around 240 K, and finally at 323 K the spectrum consisted of only three absorptions centred approximately at δ 167 (C-1, -2, and -8), 134 (C-3, -4, -5, -6, and -7), and 19·8 (C-9). The above temperature-dependent spectra are readily treated as the composition of three sets of two-site exchange problem[6] and spectra measured at more than 10 temperatures between 203 and 263 K were compared with computer-simulated ones with appropriate T_2 values. $\Delta G^\ddagger$ for the migration process of the acetyl group of (**1a**) is *ca.* 10·8 ($+0{\cdot}002T$) kcal mol^{-1} in this temperature range. The coalescence temperature was only slightly dependent on the polarity of solvent (DMF *vs.* $CDCl_3$), a result normally unexpected from the highly polarized character of the supposed intermediate (**1c**). With these findings, it is not surprising that the acetates (**2a**), (**3a**), and (**4a**) of a few selected ring-substituted tropolones show only averaged

† The C-7 and C-3 assignments could be reversed.

chemical shifts [δ (H-3) = δ(H-7); δ(H-4) = δ(H-6)] and coupling constants ($J_{3,4} = J_{6,7}$; $J_{4,5} = J_{5,6}$) in their ^{1}H n.m.r. spectra (room temperature) in a manner similar to the corresponding tropolones (**2b**), (**3b**), and (**4b**).

The above results raise a question as to the generality of the acyl migration in similar systems, such as the enol acetate of acetylacetone, MeCO·CH:C(OAc)Me, whose temperature-dependent ^{1}H n.m.r. spectra readily demonstrated that signals from the two methyl groups coalesce around 300 K and that the process requires an activation energy higher than that of (**1a**) as expected.[7]

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[2] For review of the tropolone chemistry, see T. Nozoe, *Pure Appl. Chem.*, 1971, **28**, 239.

[3] M. Yasunami and K. Takase, Japan Chem. Soc., 24th Annual Meeting Abstract 1971, No. 3, p. 1315 (Suita, Japan). Acetylation of a 4-substituted tropolone invariably provided a single crystalline derivative.

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