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The Solid-Phase ^{13}C NMR Spectra of Several Tropolone Derivatives

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The solid-phase ^{13}C NMR spectra of *o*-, *m*-, and *p*-hydroxytropolones were measured. In the solid state, the hydrogen shift between the C-1 and C-2 oxygens was frozen under the NMR time-scale; the major tautomer of the *o*-hydroxytropolone was shown to the 2,7-dihydroxytropone form, which was parallel to the previous assignment deduced from the IR spectroscopy. In addition, the solid-phase ^{13}C NMR of *o*-bromotropolone showed it to be 7-bromo-2-hydroxytropone.

It is well-known that the tropolones undergo rapid tautomerism in solution and their ^{13}C NMR spectra usually reveal averaged signals. However, in the solid state, this tautomerism is inhibited, e.g., parent tropolone exhibited six resolved lines.[1,2]

Recently, we have investigated the [1,9] sigmatropic acetoxyl migration of several polyacetoxytropones, including hexaacetoxytropone (**1**) and 2,3-diacetoxytropone (**2**), and elucidated the concerted nature of the process by means of a kinetic analysis.[3] In the case of **2**, apparently no acetotropic rearrangement has been detected in respect of high-temperature ^{13}C NMR; this was explained in terms of the thermodynamic stability of the symmetrical 2,7-diacetoxytropone structure (**2a**) over 2,3-diacetoxy isomer (**2b**). Even tri-, tetra-, and pentaacetoxytropones, the acetotropic equilibria were operative between tautomers having the carbonyl group at the inner positions. In this connection, the prototropy in the tropolone system seems to be worth investigating by means of solid-phase NMR measurement, since the NMR in solution represent the equilibrated structures by hydrogen exchange.

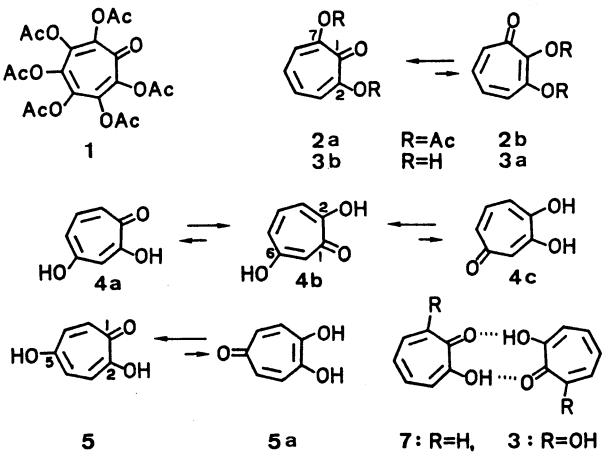
We wish to describe the investigations with *o*-hydroxytropolone (**3**), *m*-hydroxytropolone (**4**), and *p*-hydroxytropolone (**5**); these dihydroxytropones may constitute interesting tautomeric systems. Additionally included are the solid state and solution NMR behaviors of *o*-bromotropolone (**6**), being a point in dispute with its major tautomer in solution.

Experimental

The solid-phase ^{13}C NMR spectra were measured with a JEOL GX 270 spectrometer at 67.8 MHz, using the technique of high-power ^{1}H decoupling CP/MAS with a cross-polarization time of 2 ms. Chemical shifts were expressed by external reference to the Me_4Si. The actual reference compound was adamantame (methine carbon signal at δ=29.5). The samples, *o*-hydroxytropolone,[4] *m*-hydroxytropolone,[5] and *p*-hydroxytropolone,[6] *o*-bromotropolone[7] and their methyl ethers were prepared by known methods.

Results and Discussion

The ^{13}C NMR Spectra of *o*-, *m*-, and *p*-Hydroxytropolones. In the NMR of **3**, six lines appeared; its lowest signal at δ=168.1 was ascribable to a carbon having a pronounced carbonyl nature and the next two low-field signals, at δ=160.8 and 159.8, to carbons having the hydroxy nature. Superficially, the appearance of two separated hydroxy-bearing carbon signals together with exhibiting six lines favored the unsymmetrical 2,3-dihydroxytropone structure (**3a**), but the chemical shift of the lowest signal was considerably higher than that of tropolone (**7**), δ=177.5. If the magnetic non-equivalence arises from the arrangement in crystals, an alternative symmetrical 2,7-dihydroxytropone structure (**3b**) should be equally probable. This was the case from the ^{13}C NMR chemical shift comparisons between **3** and 2,3-dimethoxytropone (**8**) and 2,7-dimethoxytropone (**9**).[8] Thus, the solid-state ^{13}C NMR of **9** disclosed two separated methoxy carbon signals as well as six aromatic carbon signals, of which the magnetic non-equivalence should come from the molecular arrangement in the lattice. According to the X-ray crystallograhic analysis,[9] the tropolones are known to exist in the dimeric form with intermolecular hydrogen bondings between the α-hydroxyenone moiety; in the case of **3**, such a dimeric structure makes two kinds of hydroxyl groups, one is intermolecularly hydrogen-bonded and another isolated. The chemical shifts of **3** resembled those of **9** more closely than those of **8**. Therefore, the predominant tautomer of **3** must be 2,7-dihydroxytropone (**3b**), as being parallel to the previous result of the IR spec-



Scheme 1.

troscopy by Ikegami.[10] From these results, the signals of **3** were assigned as shown in Table 1 and the substituent effect of a hydroxyl group at C-7 was obtained to be +26.1. Furthermore, the solid-state NMR of its diacetate, *o*-diacetoxytropone (**2**),[3] exists as the symmetrical 2,7-diacetoxytropone (**2a**), which was also an exclusive tautomer in solution. Under similar conditions 2-acetoxytropones generally exist as equilibrated mixtures resulting from the [1,9] sigmatropic acetyl migration.[3]

In the case of **5**, separated seven line signals and the chemical shift of the carbonyl carbon, 173.5, eliminated the alternative 4,5-dihydroxytropone structure (**5a**).[11] From this result, the substituent effect of a hydroxyl group at C-5 was estimated to be 29.6, which was similar to the value (+26.1) obtained in **3** and that reported for a hydroxyl group of the benzenoid.[12]

On the other hand, the NMR spectrum of **4** showed considerably low-field shifted carbon signals for enolic carbons, at 164.6 and 170.3, together with a carbonyl carbon signal at 176.1. The appearance of a signal at 164.6, being appropriate for C-2 of the tropolone ring and the chemical shift of the carbonyl carbon, 176.1 eliminated the 3,4-dihydroxytropone structure (**4c**). While the substituent effect of a hydroxyl group was estimated to be +37.6 for **4a** and +28.6 for **4b**, the latter was in accord to those obtained for **3** and **5**. Thus, the major isomer of *m*-hydroxytropolone was assigned to be 6-hydroxytropolone (**4b**). The data were shown in Table 1. Consequently, α-hydroxy keto structures must be a more favorable contribution than others, and all of **3**, **4**, and **5** exist as frozen forms under the conditions for solid-phase NMR measurements.

The Tautomeric Form of *o*-Bromotropolone. According to the solid-state ^{13}C NMR spectra, the major tautomer of *o*-bromotropolone (**6**) in the solid state is indeed 7-bromo-2-hydroxytropone (**6b**). The spectrum of **6** disclosed five lines, among which, the

Table 1. Solid-Phase ^{13}C NMR of *o*-, *m*-, and *p*-Hydroxytropolones and Their Derivatives

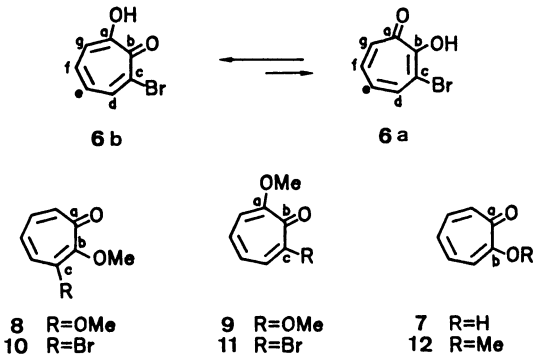
Compd	Position							
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	
7	177.5	165.4	113.0	133.7	128.1	141.7	133.7	
	(171.7)[a]	(171.7)	(123.9)	(137.5)	(128.2)	(137.5)	(123.9)	
Δδ	−5.8	+6.3	+10.9	+3.8	+0.1	−4.2	−9.8	Σ=+1.3
3	168.1	160.8	123.2	130.1	130.1	121.5	159.8	
	(169.8)	(161.8)	(122.1)	(130.3)	(130.3)	(122.1)	(161.8)	
Δδ	+1.7	+1.0	−1.1	+0.2	+0.2	+0.6	+2.0	Σ=+5.6
8	(180.7)	(154.5)	(158.6)	(127.8)	(129.7)	(140.5)	(133.2)	
9	162.9	173.0	161.7	112.0	127.0	127.0	115.4	
	(161.7)	(173.7)	(161.7)	(114.1)	(125.7)	(125.7)	(114.1)	
Δδ	−1.2	+0.7	0	+2.1	−1.3	−1.3	−1.3	Σ=−2.3
4	176.1	164.6	112.0	136.2	123.4	170.3	113.9	
	(174.7)	(168.4)	(114.7)	(138.1)	(121.5)	(169.3)	(115.8)	
Δδ	−1.4	+3.8	+2.7	+1.9	−1.0	−1.9	+1.9	Σ=+6.0
5	173.5	162.1	121.5	120.4	157.7	134.4	134.7	
	(169.4)	(169.4)	(127.5)	(126.4)	(160.9)	(126.4)	(127.5)	
Δδ	−4.1	+7.3	+6.0	+6.0	+3.2	−8.0	+7.2	Σ=+17.6

a) The figures shown in the parentheses were those measured in $CDCl_3$ solutions.

Table 2. Solid-Phase ^{13}C NMR of *o*-Bromotropolones and Its Related Derivatives

Compd	Position							
	C-a	C-b	C-c	C-d	C-e	C-f	C-g	
7	177.5	165.4	113.0	133.7	128.1	141.7	133.7	
12	(180.1)[a]	(165.0)	(112.2)	(132.4)	(127.6)	(136.3)	(136.3)	
6	162.6	172.9	127.5	139.2	127.5	139.2	119.5	
	(165.7)	(170.9)	(129.8)	(142.7)	(126.4)	(137.4)	(120.1)	
Δδ	+3.1	−2.0	+2.3	+3.5	−1.1	−1.8	+0.6	Σ=+4.6
11	162.8	171.7	136.7	136.7	126.0	136.7	114.3	
	(162.6)	(173.6)	(137.5)	(139.9)	(125.3)	(133.3)	(112.6)	
Δδ	−0.2	+1.9	+0.8	+3.2	−0.7	−3.4	−1.7	Σ=−0.1
10	178.7	163.0	130.2	137.9	130.2	137.9	137.9	
	(179.6)	(163.3)	(128.4)	(138.4)	(128.6)	(135.1)	(138.2)	
Δδ	+0.9	+0.3	−1.8	+0.5	−1.6	−2.8	+0.3	Σ=−4.2
Δδ(**7**—**12**)	+2.6	−0.4	−0.8	−1.3	−0.5	−5.4	+2.6	|Σ|=13.6
Δδ(**6**—**11**)	+0.2	−1.2	+9.2	−2.5	−0.5	−2.5	−5.2	|Σ|=21.3
Δδ(**6**—**10**)	+5.8[b]	+0.4[b]	+2.7	−1.3	+2.7	−1.3	+18.4	|Σ|=32.5

a) The figures shown in the parentheses were those measured in $CDCl_3$ solutions. b) These values were differences between C-a of **6b** and C-b of **10** and between C-b of **6b** and C-a of **10**, respectively.



Scheme 2.

highest signal at δ=119.5 could be ascribable to the α-carbon of the hydroxyl group. This fact clarified its stable tautomer to be **6b** in the solid state.

To date, the major tautomer of **6** has been disputed; 3-bromo-2-hydroxytropone form (**6a**) was proposed by H. Sugiyama et al. on the basis of ^{1}H NMR chemical shift considerations in terms of the anisotropic effect from the bromine substituent in $CDCl_3$;[13] later, however, Bagli et al. claimed it to be **6b** on the basis of observing the triplet carbonyl carbon signal which spin-coupled to two β-protons in the ^{13}C NMR spectrum.[2] When the ^{1}H NMR spectrum of **6** was compared with isomeric 3-bromo-2-methoxytropone (**10**) and 7-bromo-2-methoxytropone (**11**), much better resemblance was observed between **6** and **10**, in favor of the H. Sugiyama's conclusion. However, the ^{13}C NMR of **6** in solution resembled **11** rather than **10**. This apparent contradiction called further careful investigation for the predominant tautomer of **6** in solution: Table 2 shows the solid-phase ^{13}C NMR of **6**, its two methyl ethers, **10** and **11**, together with reference compounds, unsubstituted tropolone, **7** and 2-methoxytropone (**12**). For the ^{13}C NMR spectra of **6**, **10**, and **11**, the chemical shifts measured in $CDCl_3$ solutions and as the solid state were parallel and showed agreement within 3.5 ppm in each other. In addition, the chemical shift of carbonyl carbon of **6** is closely related to that of **11**. By extending this to all carbons, the summations of the absolute values of the chemical shift differences for each carbon signals gave smaller $|\Delta\delta|$ in **6**—**11** (21.3) than **6**—**10** (32.5). The $|\Delta\delta|$ between **7** and **12** is 13.6. Furthermore, when we observed multiplicities of the carbonyl carbon signals, following the Bagli's procedure, **10** showed a doublet signal (J=11 Hz) while **11** showed a triplet signal (J=9.5 Hz). Consequently, **6** must predominantly exist as **6b**, 7-bromo-2-hydroxytropone form in solution and in the solid phase.

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