A ^{13}C nuclear magnetic resonance study of the reversible substituent migration in several 2-acyl and 2-silyl derivatives of tropolone. Troponoid-IV[1]

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The energy barrier for the reversible substituent migration was determined for a number of 2-acyl and 2-silyl derivatives of tropolone. The energy barrier is found to be dependent on the nature of the migrating group. Asymmetric monosubstitution on the ring shifts the equilibrium in favor of one dynamic isomer. In the two cases studied (3-bromotropolone and 3-bromotropolone acetate) it is found that the equilibrium is shifted towards the isomer bearing the bromine atom at the 7-position.

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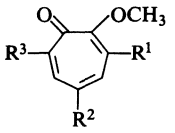
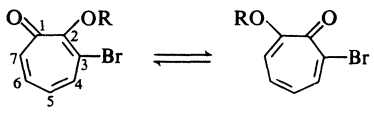
Nous avons mesuré la barrière énergétique pour le processus de migration réversible du substituent en position 2 de quelques dérivés acylés et silylés de la tropolone. La nature du groupe migrateur modifie l'énergie d'activation autant dans le cas des dérivés acylés que dans le cas des dérivés silylés. La présence d'une substitution asymétrique sur le cycle déplace l'équilibre vers un seul isomère dynamique. Dans les deux cas étudiés (bromo-3-tropolone et acétate de bromo-3-tropolone) nous avons montré que l'équilibre favorise l'isomère portant l'atome de brome à la position 7.

Parallel to other studies on the pharmaceutical activity of tropone and tropolone derivatives (1), we have recently reported on the additivity of substituent effects on ^{13}C nmr chemical shifts for a number of 2-methoxytropone derivatives **1** and have shown that ^{13}C nmr is quite useful to distinguish between various isomers in the 2-methoxytropone family (2). A more challenging task involves the identification of the dynamic isomer favored by nonsymmetric tropolones and tropolone derivatives for which the 2-substituent is capable of rapid migration at room temperature of the type illustrated by **2***a* ⇌ **2***b*.



1

R^1, R^2, R^3 = H, Br, CH_3, OCH_3, $CH_2CO_2CH_3$



R = H : **2***a* **2***b*
R = Ac: **3***a* **3***b*

It is well known that tropolone acetate undergoes rapid intramolecular acetyl migration at room temperature (**4***a* ⇌ **4***b*) for which $\Delta G^{\ddagger}$ is 10.8 kcal/mol (3*a*). The nonaveraging spectrum can be recorded below −60°C for which the correct line assignment was published in a previous paper in this series (3*b*). A similar exchange process has been observed in substituted tropolone acetates such as 3,7-dibenzyltropolone acetate for which $\Delta G^{\ddagger}$ was found to be 8 kcal/mol (4).

While investigating rearrangements of trialkylsilyl groups bonded to electronegative elements, Reich and Murcia (5) noted that the room temperature ^{13}C nmr spectrum of 2-(2-butyldimethylsiloxy)tropone contains only 4 lines, indicating a fast exchange of the trialkylsilyl group between the two oxygen atoms on the tropolone ring (**5***a* ⇌ **5***b*). In addition, they reported line broadening at about −70°C, but the slow exchange spectrum was not observed. Nevertheless, the authors estimated that $\Delta G^{\ddagger}$ for the silyl group migration is about 8.2 kcal/mol. A similar observation was reported by Hobson and co-workers (6) who prepared the trimethylsilyl ethers of tropolone (**6**) and 3-bromotropolone (**7**) and studied their ^1H nmr spectra down to −95°C. No significant change was observed for solutions of both trimethylsilyl ethers in toluene-d_8, thus indicating a significantly lower energy barrier for the exchange process.

Very few studies concerned with the identifica-

[1]Troponoid III is ref. 1.

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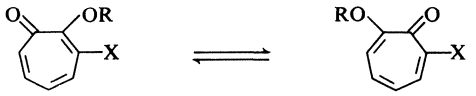
tion of the major isomer adopted by unsymmetrically substituted tropolones have been reported in the literature. In 1968, Sugiyama (7) used ^1H coupling constants and chemical shifts arguments to suggest that the 3-Br form (**2***a*) is favored relative to **2***b*.



R = Ac; X = H : **4***a* **4***b*

R = $-Si(CH_3)_2CH(CH_3)_2$; X = H : **5***a* **5***b*

R = TMS; X = H : **6***a* **6***b*

R = TMS; X = Br: **7***a* **7***b*

R = TBDMS; X = H : **8***a* **8***b*

R = COPh; X = H : **9***a* **9***b*

In the present work, we report the $\Delta G^{\ddagger}$ value for **6** as well as for other rapidly equilibrating 2-substituted tropolone derivatives. A quantitative description of the dynamic features of these compounds will be presented and extended to nonsymmetric derivatives such as **2** and **3**. Our results show clearly that the published conclusion (7) for **2** is wrong.

Results and discussion

The partial 22.63 MHz ^{13}C nmr spectra of 2-trimethylsiloxytropone (**6**) at several temperatures are shown in Fig. 1. The room temperature spectrum is almost identical to that of the 2-(2-butyldimethylsilyl) derivative investigated by Reich and Murcia (5). At −109°C, the signals of C-3,7 and C-5 overlap but significant broadening is not yet observed. Maximum broadening takes place at −139°C, the coalescence temperature, below which a slow exchange spectrum can be recorded. At −155°C, the low field region of the spectrum of **6** contains 7 lines, one for each carbon of the tropolone ring. The splitting pattern of the C-3,7 signal is represented in Fig. 1. A $\Delta G^{\ddagger}$ of 5.7 kcal/mol was calculated at the coalescence temperature. This value is much lower than the 10.8 kcal/mol determined for the acetate derivative and it suggests that migration of a silyl group is easier than migration of an acyl group. The chemical shifts and $\Delta G^{\ddagger}$ values for all compounds investigated are summarized in Table 1.

In order to test the sensitivity of this barrier to the size of the migrating silyl group we have prepared 2-*tert*-butyldimethylsiloxytropone **8** and have studied its ^{13}C nmr (20 MHz) spectrum as a function of temperature. Again the room temperature spectrum contains 4 lines and is similar to the

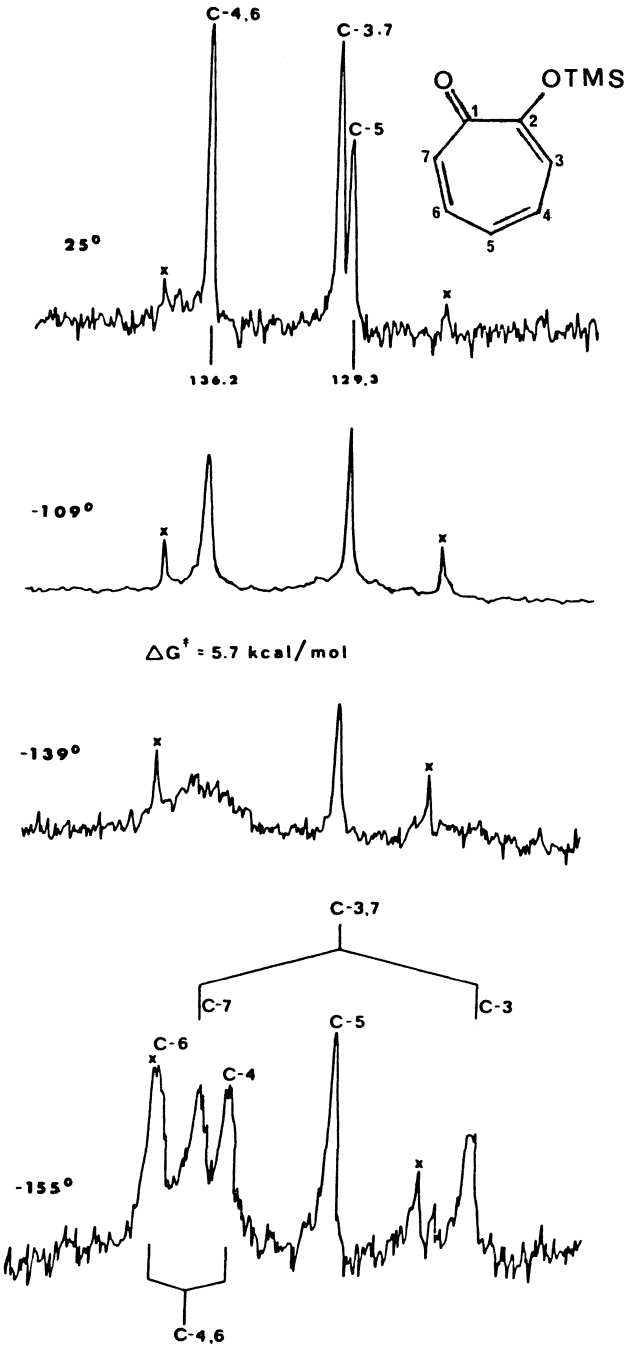


FIG. 1. The partial 22.63 MHz ^{13}C nmr spectra of **6** in $CHFCl_2$ at several temperatures (x denotes tropolone impurity). Flip angle = 30°; SW = 6024 Hz; data size = 8K.

spectra of **5** and **6**. As the temperature is lowered to −80°C, broadening occurs; maximum broadening is observed at −104°C, the coalescence temperature for carbons 3 and 7, and finally a well-resolved slow exchange spectrum is recorded at −130°C. A

TABLE 1. Carbon-13 chemical shifts for ring carbons and dynamic parameters for compounds **2**, **3**, **6**, **8–10**

Compound	Solvent	T (°C)	C-1	C-2	C-3	C-4	C-5	C-6	C-7	Δν (Hz)	T_c (°C)	$\Delta G^{\ddagger}$ (kcal/mol)
6	$CHFCl_2$	25	—	—	129.9	136.2	129.3	136.2	129.9	312.3	−139	5.7
		−155	181.5	163.6	122.6	135.0	129.9	138.5	136.4	(C-3, 7)		
8	$CHFCl_2$	25	—	—	130.9	136.8	130.1	136.8	130.9	255.6	−104	7.3
		−130	181.9	165.2	124.5	135.6	130.3	139.0	136.7	(C-3, 7)		
9	$CHFCl_2$	25	—	—	134.2	134.5	134.5	134.5	134.2	110.8	−23	11.5
		−80	180.2	158.9	129.4	132.7	135	138.2	140.9	(C-4, 6)		
10	$CHFCl_2$	25	—	—	136.7	138.9	129.0	138.9	136.7	42.65	−43	10.9
		−100	171.8	153.1	132.8	138.7	130.2	140.8	142.8	(C-4, 6)		
3	$CHFCl_2$	25	—	—	129.7	132.8	131.7	140.6	141.6			
		−97	174.0	155.5	129.6	133.5	132.9	141.9	142.9	—	—	—
2	$CDCl_3$	25	170.8	166.0	120.1	137.1	126.0	142.3	129.3	—	—	—
Tropolone	$CDCl_3$[a]	25	172.6	172.6	123.5	137.6	128.1	137.6	123.5	—	—	—
	Solid[b]	25	177.5	165.4	113.0	133.7	128.1	141.7	133.7			

[a] Values taken from ref. 10*b*.
[b] Values taken from ref. 10*a*.

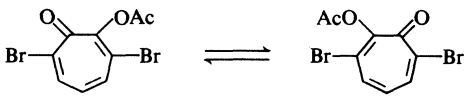
$\Delta G^{\ddagger}$ value of 7.3 kcal/mol can be calculated for **8**, indicating that increasing the size of the migrating silyl group raises the energy barrier of the process.

Studies on the lability of *O*-silyl derivatives of *cis* enols of 1,3-diketones (8) have shown that the energy barrier of the migration process is lowered as the polarity of the migrating group increases, presumably because an increase in the electron withdrawing ability of the substituent results in a greater positive charge on silicon and facilitates the use of a d-orbital in achieving the transition state. These results are consistent with a mechanism involving the formation of a five-coordinated silicon intermediate of the type proposed by Reich and Murcia (5). It appears, however, that polarity effects alone cannot account for the 1.6 kcal/mol difference in $\Delta G^{\ddagger}$ observed between **6** and **8** and that steric effects must also contribute to the energy required for the activation process.

Figure 2 illustrates the 100 MHz ^{13}C nmr spectrum of tropolone benzoate (**9**) recorded at 20° and −80°C. The room temperature spectrum contains only five signals while there are nine nonequivalent sites on the molecule: four belong to the tropolone ring and five to the benzoate group. Distinguishing between these two types of signals is straightforward since the latter remain unaffected by the temperature change. The slow exchange spectrum of **9** recorded at −80°C contains all 12 expected lines. The assignment of the tropolone carbons in Fig. 2 (and Table 1) respects the order of chemical shifts found for tropolone acetate and 2-methoxytropone (2). The phenyl carbons are assigned directly by comparison with the chemical shifts observed for methyl benzoate. Only the C-5 and C-12 lines cannot be assigned unambiguously because of their proximity.

From the coalescence temperature of −23°C observed for C-4,6 at 20 MHz for this compound, a $\Delta G^{\ddagger}$ of 11.5 kcal/mol is calculated. This value is 0.7 kcal/mol higher than what has been observed for tropolone acetate **4**, indicating that migration of an acetyl group is easier than migration of a benzyl group. A similar behaviour has been observed for *O*-acyl derivatives of the *cis* enols of 1,3-diketones in which replacement of acyl by benzyl raises the energy barrier from 15.4 kcal/mol to 16.3 kcal/mol (9).

The potential influence of ring substituents on the energy barrier of acetyl migration suggested from the published ^1H dnmr results for 3,7-dibenzyltropolone acetate (4) was investigated further through analysis of the variable temperature spectra of 3,7-dibromotropolone acetate (**10**).



10*a* **10***b*

Under ordinary recording conditions, the room temperature 20 MHz ^{13}C nmr spectrum of **10** shows only three signals instead of five for the unsaturated carbons. Assignments are straightforward from intensity and chemical shifts considerations: there is an intense line at 138.9 ppm which is due to the equivalent C-4 and C-6 carbons and a less intense line at 129.0 ppm which is due to C-5. The weak line observed at 136.7 ppm is due to the nonprotonated C-3,7 carbons. At −100°C, the low field region of

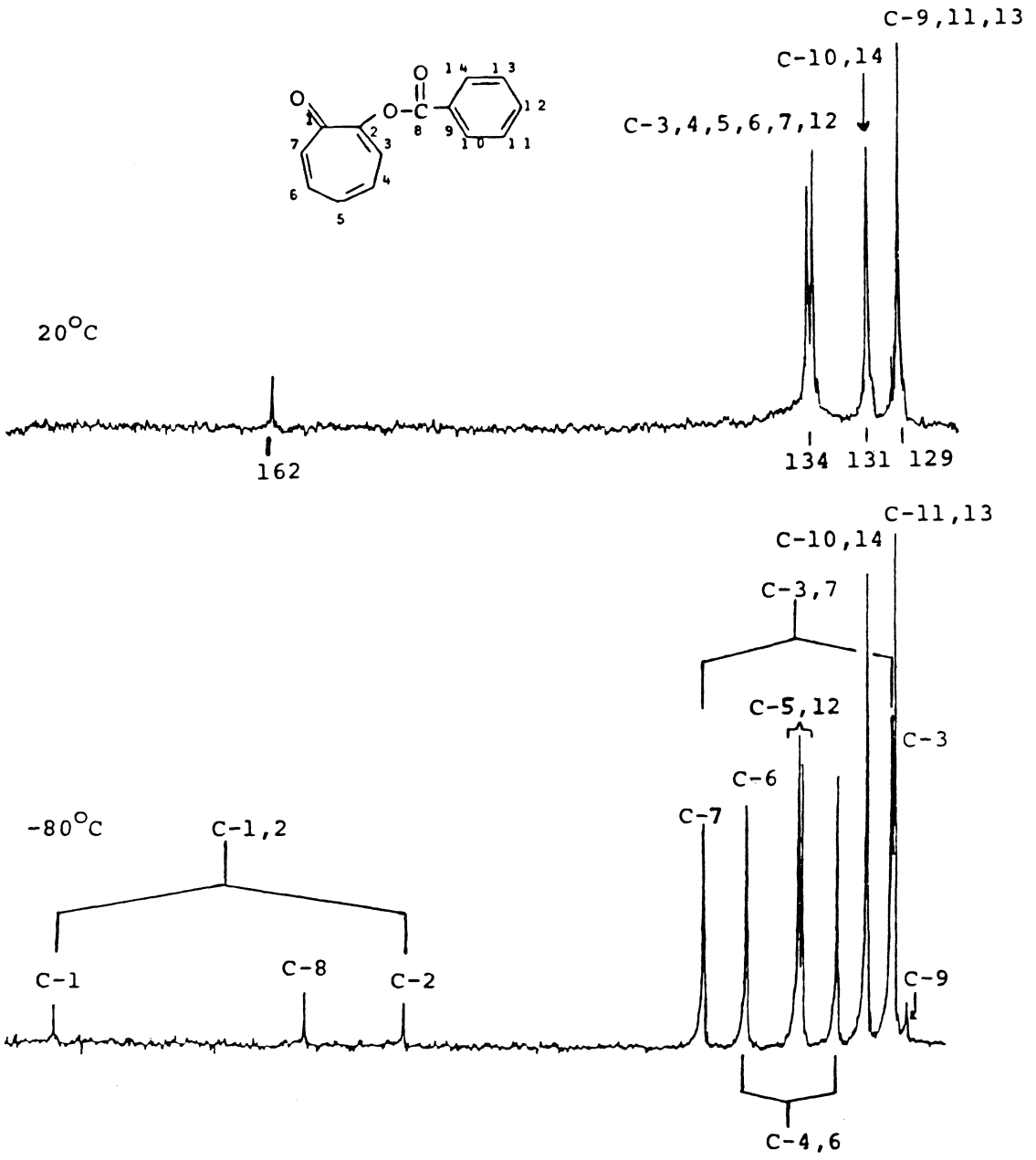


FIG. 2. The 100 MHz ^{13}C nmr spectra of **9** in $CHFCl_2$ at 20°C and −80°C. Flip angle = 25°; SW = 8064 Hz; data size = 8K.

the spectrum of **10** contains all expected 8 lines: the C-4,6 line has split into a doublet with components at 140.8 and 138.7 ppm while the C-3,7 line has also split into a doublet with components at 142.8 and 137.8 ppm. The C-1,2 line and the C-8 carbonyl line which were not observed at room temperature are now visible in the slow exchange spectrum: C-1 and C-2 appear at 171.8 and 153.1 ppm respectively.

A $\Delta G^{\ddagger}$ of 10.9 kcal/mol for the acetyl migration process is calculated at the coalescence temperature of −43°C observed for the C-4,6 signal. This value is very similar to that observed for tropolone acetate, indicating little influence of the two adjacent bromine substituents on the energy barrier of the migration process.

At this point it should be mentioned that the energy barrier for tautomerization in tropolone itself is too low for it to be amenable to an

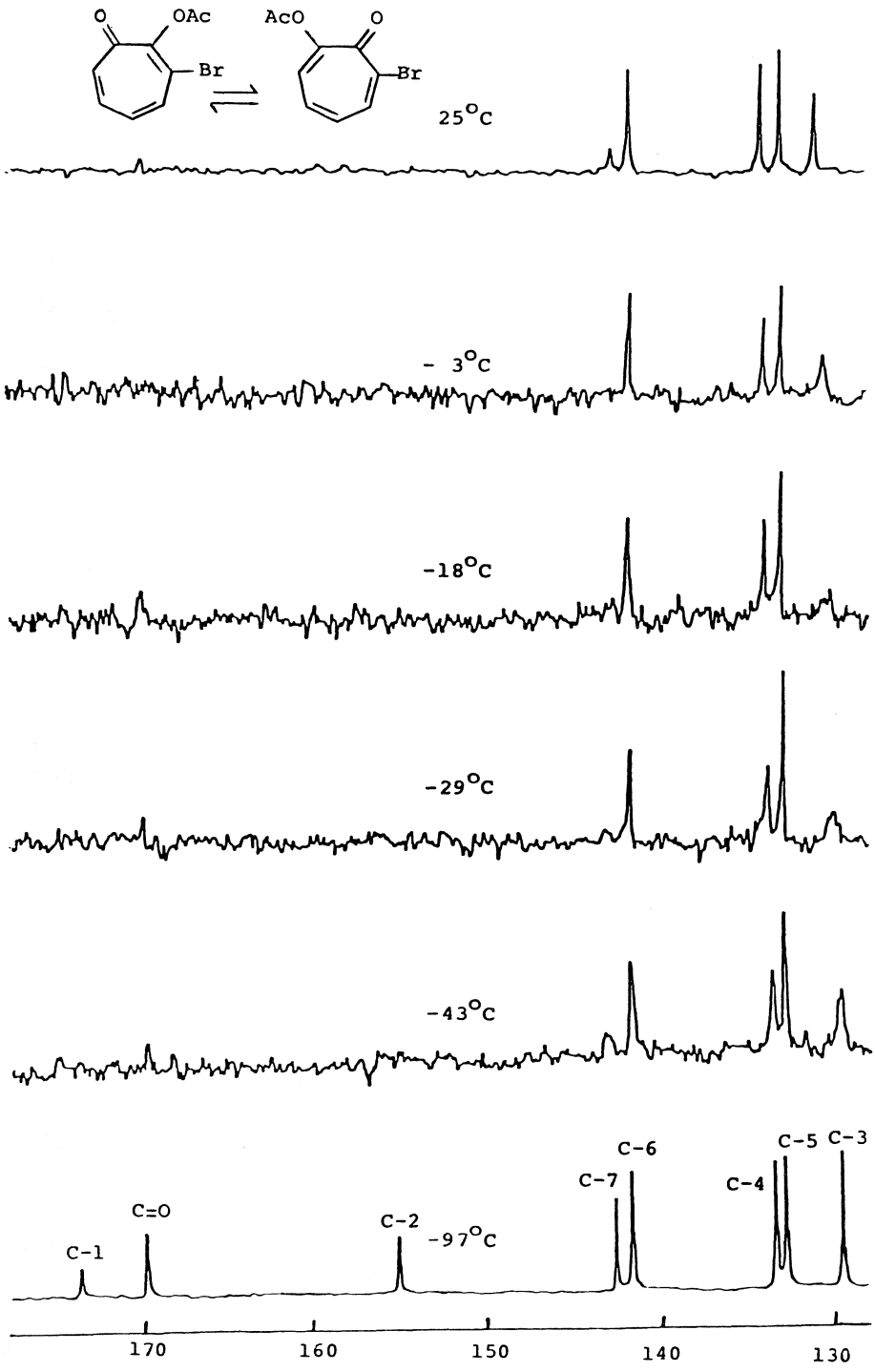


FIG. 3. The 20.15 MHz ^{13}C nmr spectra of **3** in $CHFCl_2$ at several temperatures. Flip angle = 35°; SW = 6024 Hz; data size = 8K.

investigation in solution by dynamic nmr techniques and our efforts to determine $\Delta G^{\ddagger}$ for tautomerization by nmr have failed. On the other hand, the 25 MHz ^{13}C nmr spectrum of tropolone in the solid state has recently been recorded by Fyfe (*10a*); it contains 7 lines, indicating that proton exchange is slow in the solid state. The chemical shifts of all 7 nonequivalent carbons in tropolone

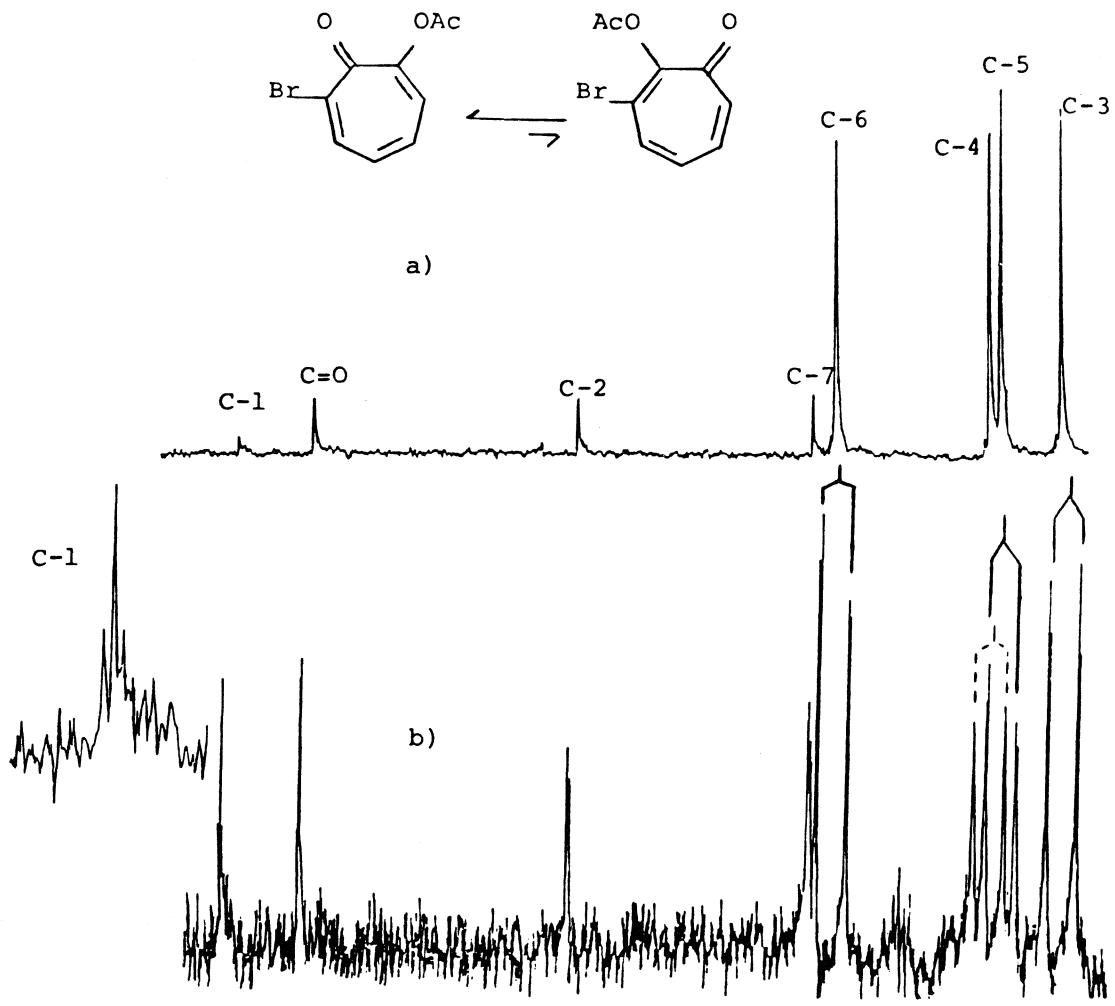


FIG. 4. The 100 MHz ^{13}C nmr spectra of **3** in $CHFCl_2$ at −80°C; (a) broad band decoupling; (b) gated decoupling. Flip angle = 25°; SW = 10 000 Hz; data size = 8K.

obtained from that spectrum are given in Table 1. When averaged, these chemical shifts closely match those observed in $CDCl_3$ solution (10*b*).

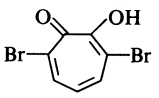
We now turn our attention to unsymmetrical, singly substituted derivatives at C-3 or C-7, such as **2** and **3**.

Figure 3 illustrates the variable temperature 20 MHz ^{13}C nmr spectra of **3** in CHF_2Cl solution. It is immediately apparent that no major changes are observed in the spectrum as the temperature is lowered. At −97°C, the acetyl migration process should be slow and indeed the line broadening observed at intermediate temperatures for the smaller 142.9 and 129.6 ppm lines clearly indicates that the process has been slowed down (11). This absence of new signals suggests that the molecule exists predominantly in only one form. The total absence of weak signals at low temperature and the line broadening phenomenon at intermediate temperatures show that if a minor isomer existed it would account for less than 2% in the **3***a* ⇌ **3***b* equilibrium (11). There thus remains the task of identifying the nature of this predominant isomer, namely that which bears the bromine atom at the 3-position (**3***a*) or at the 7-position (**3***b*).

Our earlier work (2) suggested that substituent effects on ^{13}C chemical shifts might allow the determination of the structure of the favored isomer of **3**. Unfortunately the required substituent parameters are not available for the 2-acetoxy derivative but only for the 2-methoxy derivative. Predicted chemical shifts for **3***a* and **3***b* lead to the suggestion that **3***b* is more compatible with the observed spectrum of **3**. On the other hand, no obvious convergence is observed when this method is applied to **2**.

Because carbon–proton coupling constants through three bonds ($^3J_{CH}$) offered an alternate probe for locating the position of the bromine atom, proton coupled ^{13}C nmr spectra were recorded and analysed. It is well known (12) that in aromatic systems the magnitude of $^1J_{CH}$ coupling constants is close to 160 MHz while $^2J_{CH}$ are smaller (<3 Hz) and frequently nonresolved. Values for $^3J_{CH}$, on the other hand, usually range from 7 to 11 Hz and lead to clearly recognizable patterns in fully coupled ^{13}C nmr spectra (12); they therefore constitute a convenient method for determining the number of protons β to a given carbon.

The 20 MHz ^{13}C nmr coupled spectrum of 3,7-dibromopolone (**11**) shows that the averaged C-1,2 signal appears as a doublet ($^3J_{CH}$ = 8.8 Hz) because these equivalent carbons are coupled to only one β proton which constitutes a mean of H-6 and H-4. Similarly, the averaged C-1,2 signal in the coupled spectrum of 5-bromotropolone (**12**) appears as a triplet ($^3J_{CH}$ = 9.8 Hz) since both carbons are at all times coupled to two β protons. These results suggest that in the case of the nonsymmetric compounds **2** and **3**, if the 3-Br form was predominant, the C-1 signal should appear as a doublet (coupling with H-6) and the C-2 signal as a triplet (coupling with H-7 and H-4), while the reverse should be observed if the 7-Br form was predominant.



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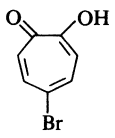

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The 100 MHz coupled ^{13}C nmr spectrum of **3** at −80°C (Fig. 4) clearly shows that the C-1 signal appears as a triplet ($^3J_{CH}$ = 9.8 Hz) thereby proving unambiguously that **3***b* is the major isomer adopted by this molecule. In this case, the C-2 signal revealed additional coupling to $^3J_{CH}$ and is therefore of little use. Similarly, the room temperature 100 MHz coupled ^{13}C nmr spectrum of **2** shows that the C-1 signal is a triplet ($^3J_{CH}$ = 8.3 Hz) and the C-2 signal is a doublet ($^3J_{CH}$ = 11.1 Hz), thus confirming that the 7-Br form is also favored by this molecule. This conclusion disproves the earlier claim (7), based on the interpretation of ^1H nmr parameters, that **2***a* should be the more favored form.

Experimental

Melting points are uncorrected and were determined using a Büchi melting point apparatus. The vpc analyses and separations were carried out on a Varian-Aerograph model 920 instrument using helium as carrier gas.

The variable temperature ^{13}C nmr spectra were recorded in the FT mode with Bruker WP-80, WH-90, or WH-400 instruments operating respectively at 20.15, 22.63, and 100.0 MHz and equipped with a Bruker variable temperature accessory. Unless otherwise mentioned, all ^{13}C spectra were recorded with proton noise decoupling for solutions in dichlorofluoromethane (100–150 mg in 2.2 mL of solution) containing TMS and about 19% of CD_2Cl_2 (for locking purposes) in standard 10 mm tubes which had been degassed and sealed. In the case of 20.15 MHz and 22.63 MHz spectra, temperatures were measured accurately with a calibrated copper–constantan thermocouple placed inside a solvent-containing dummy nmr tube. A precision of ±1°C is expected. $CDCl_3$ solutions containing TMS were used for samples studied only at room temperature. Coupled spectra were recorded using the gated decoupling technique with the decoupler on for 15 s and then switched off 0.005 s before the pulse.

The rate constants were estimated at the coalescence temperature using the equation $k = \pi\Delta\nu/\sqrt{2}$. The free energy values ($\Delta G^{\ddagger}$) were calculated from standard equations (13) using a transmission coefficient of one-half.

Synthesis of compounds

Monobromotropolone acetate (3)

To a solution of monobromotropolone (**2**) (14) (9.64 g, 48 mmol) in chloroform (12 mL) and pyridine (4.8 mL) was added a solution of acetyl chloride (4.08 mL) in chloroform (8 mL) with cooling. The mixture was stirred for 3 h at room temperature, diluted with chloroform, washed with water, and dried. The solvent was removed to yield the crude acetate. The product was purified by column chromatography to yield the pure product (5.2 g, 44.5%), mp = 72–74°C; *m/e*: 244/242 (M^+), 202/200 ($M - COCH_2)^+$, 174/172 [$M - (COCH_3 + CO)$]$^+$.

2-Trimethylsiloxytropone (6)

Tropolone (0.50 g, 4.1 mmol), pyridine (3 mL), hexamethyldisiloxane (2.7 mL), and chlorotrimethylsilane (1.54 mL, 12.3 mmol) were allowed to react at room temperature for 15 min. The mixture was decanted and 100 μL samples of the resulting clear solution were analysed and separated by gas chromatography. A yellow oil (250 mg) still containing tropolone impurities was obtained after separation on a SE-30 5% column (5 ft × ¼ in.). The ^1H nmr spectrum was similar to that already published (6) and the ^{13}C nmr data in Table 1 and Fig. 1 confirm the structure; *m/e*: 194 (M^+), 179 ($M - CH_3)^+$.

2-tert-Butyl dimethylsiloxytropone (8)

Tropolone (0.5 g, 4.1 mmol), *tert*-butyldimethylsilyl chloride (1.88 g, 12.5 mmol), and pyridine (1 mL) in hexane (13 mL) were stirred for 3 h and then refluxed for 15 h. The solution was filtered and the residue washed with hexane. Evaporation of the filtrate under reduced pressure gave 0.53 g (55%) of a pale beige solid, mp = 45°C. The structure of this compound was characterized by ^{13}C nmr (Table 1); *m/e*: 221 ($M - CH_3)^+$, 179 [$M - (CH_3)_3C$]$^+$.

Tropolone benzoate (9)

This compound was prepared according to the method reported by Doering and Knox (15). Yield 42.2%, mp = 130°C (lit. (15) yield 31%; mp 130°C).

3,7-Dibromotropolone (11)

A solution of tropolone (20 g, 160 mmol) in methanol (200 mL) was cooled between −10° and −15°C. Bromine (58 g, 360 mmol) was then added over a period of 30 min while keeping the temperature at −15°C. After the addition, the bath was removed and the reaction mixture was allowed to reach room temperature. Excess bromine was blown out with a stream of nitrogen. The crude product which precipitated was filtered to give a mixture (32.6 g) of 3,7-dibromo and 3,5,7-tribromotropolone.

Recrystallization from methanol gave the pure product (15.6 g, 30.3%), mp = 153–155°C (lit. (16) mp 159–160°C); *m/e*: 278/280/282 (M^+, 100%), 250/252/254 [$(M - CO)^+$, 75%], 199/201 [$(M - Br)^+$, 5%]. *Anal.* calcd. for $C_7H_4O_2Br_2$: C 30.04, H 1.44; found: C 30.23, H 1.5. A second crop (16.9 g), also free of tribromo impurity, was obtained on concentration of the solution. Total yield: 43.7%.

*3,7-Dibromotropolone acetate (**10**)*

To a solution of 3,7-dibromotropolone (1.68, 60 mmol) in chloroform (1.5 mL) and dry pyridine (0.6 mL) was added dropwise a solution of acetyl chloride (0.54 mL, 6.6 mmol) in chloroform (1 mL). The mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with chloroform, washed with water, dried, and the solvent was removed to yield the crude product (1.71 g). This was purified by filtering through silica gel to yield the pure product (0.64 g, 33%), mp = 110–112°C; *m/e*: 320/322/324 $(M)^+$, 277/279/271 $(M - COCH_3)^+$, 249/251/253 $[M - (COCH_3 + CO)]^+$.

*5-Bromotropolone (**12**)*

To a suspension of 5-aminotropolone (17) (5 g, 36.5 mmol) in water (34 mL) was added hydrobromic acid 48% (222 mL, 1168 mmol). The mixture was cooled to −10°C and stirred for 15 min. Sodium nitrite (2.5 g) in water (17.2 mL) was added to the mixture over 5 min. The temperature was maintained at −10°C for 1.5 h. The mixture was then allowed to warm up to room temperature over one hour, heated to 45°C for one hour, and then cooled to room temperature. The mixture was then poured on crushed ice (400 g), filtered, and the solid washed with water. The crude solid (3.5 g) was dissolved in chloroform and filtered. The filtrate was treated with charcoal, dried over magnesium sulfate, and filtered. The solvent was removed and the residue (12.7 g) crystallized from chloroform–hexane to yield 1.8 g (24.5%) of pure product, mp = 189–190°C (lit. (18) mp 188°C); *m/e*: 200/202 (M^+, 60%), 172/174 [$(M - CO)^+$, 100%], 93 $[(M - (CO + Br)]^+$, 10%].

Acknowledgements

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1. J. F. Bagli, T. Bogri, B. Palameta, R. Martel, W. Robinson, T. Pugsley, and W. Lippmann. J. Med. Chem. **22**, 1186 (1979).
2. J. F. Bagli, T. Bogri, B. Palameta, and M. St-Jacques. Can J. Chem. **57**, 1949 (1979).
3. (*a*) S. Masamune, A. V. Kemp-Jones, J. Green, D. L. Rabenstein, M. Yasunami, K. Takase, and T. Nozoe. J. Chem. Soc. Chem. Commun. 283 (1973); (*b*) J. F. Bagli and M. St-Jacques. Can J. Chem. **56**, 578 (1978).
4. V. I. Minkin, L. P. Olekhnovich, Y. A. Zhdanov, Z. N. Budarina, and V. P. Metlushenko. Tetrahedron Lett. 563 (1974).
5. H. J. Reich and D. A. Murcia. J. Am. Chem. Soc. **95**, 3418 (1973).
6. R. M. Harrison, J. D. Hobson, and A. W. Midgley. J. Chem. Soc. Perkin Trans. I, 2403 (1976).
7. H. Sugiyama. Sci. Rep. Tohoku Univ. **20**, 34 (1968).
8. (*a*) J. J. Howe and T. J. Pinnavaia. J. Am. Chem. Soc. **91**, 5378 (1969); (*b*) T. J. Pinnavaia, W. T. Collins, and J. J. Howe. J. Am. Chem. Soc. **92**, 4544 (1970).
9. V. I. Minkin, L. P. Olekhnovich, Y. A. Zhdanov, V. V. Kiselev, M. A. Voronov, and Z. N. Budarina. J. Org. Chem. USSR, **9**, 1319 (1973).
10. (*a*) C. Fyfe. Personal communication of data presented at the 21st Experimental NMR Conference, Tallahassee, Florida, March 16–20, 1980; (*b*) L. Weiler. Can J. Chem. **50**, 1975 (1972).
11. (*a*) F. A. L. Anet and V. J. Basus. J. Am. Chem. Soc. **95**, 4424 (1973); (*b*) N. Okazawa and T. S. Sorensen. Can J. Chem. **56**, 2737 (1978).
12. F. W. Wherli and T. Wirthlin. Interpretation of carbon-13 nmr spectra. Heyden, New York, NY. 1976.
13. F. A. L. Anet, P. J. Degen, and J. Krane. J. Am. Chem. Soc. **98**, 2059 (1976).
14. T. Toda, H. Kubota, and T. Nozoe. Nippon Kagaku Zasshi, **88**, 1234 (1967); Chem. Abstr. **68**, 101342x (1968).
15. W. von E. Doering and L. H. Knox. J. Am. Chem. Soc. **73**, 828 (1951).
16. T. Nozoe, Y. Kitahara, and K. Yamane. Proc. Jpn. Acad. **27**, 18 (1951).
17. T. Nozoe and S. Seto. Proc. Jpn. Acad. **27**, 188 (1951); Chem. Abstr. **46**, 4522 (1952).
18. J. W. Cook, A. R. M. Gibb, and R. A. Raphael. J. Chem. Soc. 2244 (1951).