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Stereochemistry of 10-Alkyl-9-arylthioxanthenium Salts[1]

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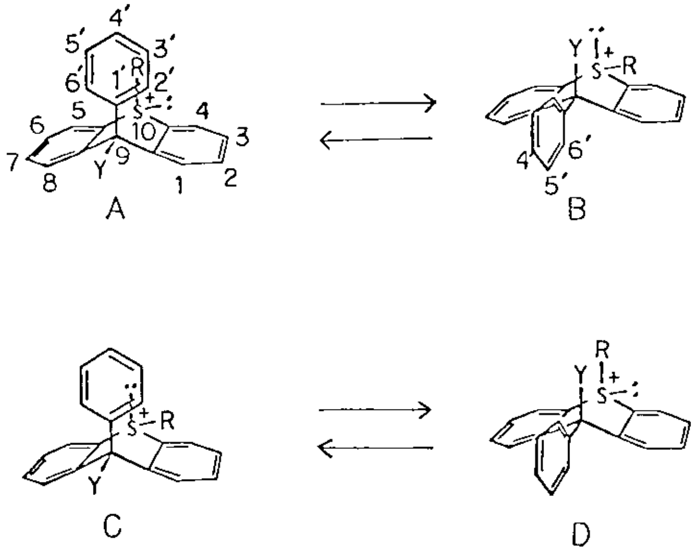
Abstract -- The stereochemistry of 10-alkyl-9-arylthioxanthenium salts was studied in detail by the nmr spectroscopy. The conformation was elucidated.

Although the number of reports on the stereochemistry of sulfur heterocycles is increasing, stereochemical studies of 10-substituted 9-arylthioxanthenium salts are little known.

In this communication we wish to report the stereochemistry of 10-alkyl-9-arylthioxanthenium salts. 10-Alkyl-9-arylthioxanthenium salts were synthesized to study 1,4-ylides, 9,10-disubstituted 10-thiaanthracenes and the conformations were determined by the detailed investigation of their nmr spectra.[2,3] The nmr spectral data were summarized in Table I.

Four isomers (A - D) are possible for 9-arylthioxanthenium salts from conformational and configurational view points in analogy with 9-arylthioxanthene 10-oxides.[2,4] Conformation of the 9-aryl group was determined by the facts that the



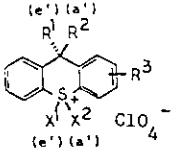
A

B

C

D

Table I. NMR Spectral Data of 10-Alkyl-9-arylthioxanthenium Salts in CF_3CO_2H[a)]



Compd No.	R^1[b)]	R^2[b)]	R^3	X^1	X^2	$H_{1,8}$	$H_9(W_{1/2}Hz)$	Me_{10} (CH_2)	other absorptions	preferred conformation
1	H	Ph	H	-:	Me	--[c)]	5.71(2.4)	2.70	6.77-7.08($H_{2',6'}$), 7.11-7.42($H_{3',4',5'}$)	A
2	Ph	H	H	-:	Me	6.99-[d)]	5.62(2.6)	3.39		D
3	H	Ph	4-Me	-:	Me	--[c)]	5.87(2.8)	2.64	6.86-7.17($H_{2',6'}$), 7.26-7.55($H_{3',4',5'}$)	A
4	Me	Ph	H	-:	Me	--[c)]	--	2.51	6.60-6.92($H_{2',6'}$), 7.09-7.37($H_{3',4',5'}$)	A
5	Me	Ph	H	Me	-:	--[c)]	--	3.51	6.76-7.10($H_{2',6'}$), 7.10-7.40($H_{3',4',5'}$)	C
6	Me	Ph	H	-:	Et	--[c)]	--	(2.66)	6.59-6.94($H_{2',6'}$), 7.07-7.40($H_{3',4',5'}$)	A
7	Ph	Me	H	-:	Et	6.97-7.50[e)]	--	(3.71)		D
8	Ph	Pr^i	H	Me	-:	7.00-7.44	--	3.62	7.37(9-C_6H_5)	B
9	Ph	CH_2	H	-:	CH_2	7.26-[d)]	--	(3.67)		D
10	Mes	H	H	-:	Me	6.96-7.57[f)]	6.12(3.9)	3.29	1.29($Me_{6'}$), 2.44($Me_{4'}$), 2.60($Me_{2'}$)	D
11	Mes	H	3-Me	-:	Me	6.80-[d)]	6.04(3.7)	3.23	1.27($Me_{6'}$), 2.40($Me_{4'}$), 2.52($Me_{2',3}$)	D
12	Mes	H	3-Me	Me	-:	6.80-[d)]	5.94(3.9)	3.60	1.00-2.80($Me_{2',6'}$), 2.36($Me_{4'}$)	B
13	Dur	H	H	-:	Me	7.16-7.45	6.26(3.7)	3.27	1.19($Me_{6'}$), 2.18($Me_{2'}$), 2.49($Me_{3',5'}$)	D
14	Dur	H	4-Me	-:	Me	7.01-7.46	6.29(3.3)	3.27	1.23($Me_{6'}$), 2.22($Me_{2'}$), 2.50($Me_{3',5'}$)	D
15	H	C_6F_5	H	Me	-:	--[c)]	6.39(3.7)	3.63		C
16	C_6F_5	H	H	Me	-:	7.32-7.67	6.38(4.6)	3.48		B

a) Chemical shifts (δ) are reported in parts per million downfield from Me_4Si. b) Pr^i = isopropyl; Mes = mesityl; Dur = 2,3,5,6-tetramethylphenyl. c) The upfield shifts of $H_{1,8}$ were not observed. d) The downfield side of the absorption was obscured by the absorption of the other aromatic protons. e) The absorption of 9-phenyl protons was included. f) The absorption of $H_{3',5'}$ was included.

anisotropic effect of 9-aryl group in the pseudoequatorial (e') position caused the upfield shift of the proximal peri protons (H_1 and H_8) and that the thioxanthene ring shielded the protons or the substituents of 9-aryl group in the pseudoaxial (a') position. Conformation of the 10-alkyl group was determined by the fact that the 10a'-alkyl group was affected by the anisotropic effect of the thioxanthene ring and the signal of the 10a'-alkyl group appeared in the upper field than that of the 10e'-one.

In conformers A and C, the 9-aryl group is a'. Therefore, protons of the 9-aryl group especially $H_{2'}$ and $H_{6'}$ should be shielded by the thioxanthene ring. Compound 5 showed the signals of $H_{2',6'}$ and $H_{3',4',5'}$ at δ 6.76 - 7.10 and 7.10 - 7.40, respectively. The upfield shift of the protons of 9-aryl group was observed in compounds 1, 3, 4, 5 and 6. Additionally, since the 9-aryl and 10-alkyl groups occupy the a' array in the conformer A, the aryl group shields the 10-alkyl group. Consequently, the definitive upfield shift of 10-alkyl group could be observed in compounds 1, 3, 4 and 6. Fig. 1 depicts the difference of chemical shifts of 10-methyl groups between compounds 4 (conformer A) and 5 (conformer C). Compound 1 showed the methyl signal at quite a high field (δ 2.70) and the signals of $H_{2',6'}$ and $H_{3',4',5'}$ at δ 6.77 - 7.08 and 7.11 - 7.42, respectively. The assignment of 9-phenyl protons was drawn from the spectrum of the corresponding 9-pentadeuteriophenyl derivative as shown in Fig. 2.

Fig. 1

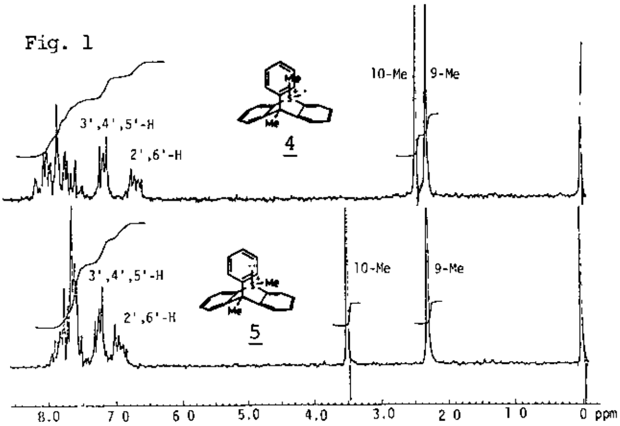
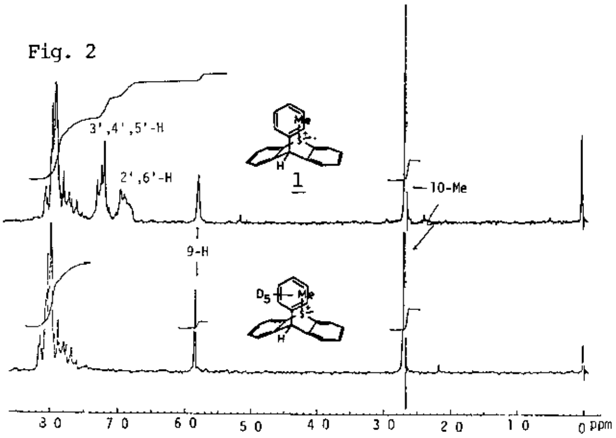
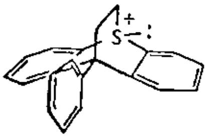


Fig. 2



In conformers B and D in which the 9-aryl group takes the e' array, H_1 and H_8 of the thioxanthene ring should be shielded by the 9-aryl group. The upfield shift of H_1 and H_8 was observed in compounds

2, 7 - 14 and 16. In compound 8, since a bulkier isopropyl group occupies the 9a'-conformation and the 9-phenyl group is in the e'-conformation, the upfield shift of H_1 and H_8 was observed. Compound 9 has a bridged 9,10-ethano group which takes the 9a'- and 10a'-conformations.



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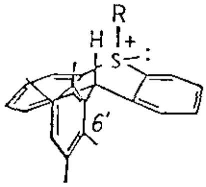

When the 9-aryl group having the methyl groups at 2'- and 6'-positions was substituted at 9-position the rotation about C_9-$C_{1'}$ bond was hindered and the 6'-methyl group was packed just under the thioxanthene ring and hence affected by the anisotropy of the thioxanthene ring. Therefore, the signal of the 6'-methyl group appeared at quite a high field (δ 1.00 - 1.29).

Other things which were revealed by the stereochemical studies are: The absorptions of 10a'- and 10e'-methyl groups appear at higher than δ 3.39 and lower than δ 3.48, respectively. Compounds such as 3 and 14 having a methyl group at 4-position took the 10a'-conformation. The half-height width ($W_{1/2}$) of the 9e'-proton was smaller than that of the 9a'-position. The stereoisomers isolated were not the conformers by ring inversion but the conformers by pyramidal inversion.

References

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2. Compounds in Table I were synthesized in a similar way described for 10-methylthioxanthenium salt by Andersen et al. (K. K. Andersen, M. Cinquini, and N. E. Papanikolaou, J. Org. Chem., 1970, 35, 706). All new compounds gave satisfactory elemental analyses.
3. M. Hori, T. Kataoka, and H. Shimizu, Chemistry Lett., 1974, 1073; M. Hori, T. Kataoka, H. Shimizu, and S. Ohno, Tetrahedron Lett., 1978, 255.
4. M. Hori, T. Kataoka, H. Shimizu, and S. Ohno, Heterocycles, 1979, No. 11 in press.

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