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NEW REARRANGEMENT OF 1,4-YLIDIC THIAANTHRACENES VIA RADICALS[1)]

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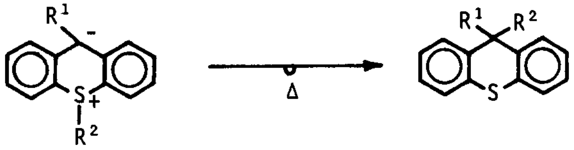
In the preceding paper,[2)] we reported on the synthesis and properties of a stable and crystalline cyclic sulfur 1,4-ylide, 9-cyano-10-methyl-10-thiaanthracene (**1a**), which on heating undergoes thermal Stevens-type 1,4-rearrangement to give 9-cyano-9-methylthioxanthene (**2a**) in an excellent yield, although unstable 9,10-disubstituted 10-thiaanthracenes (**1b**) do the rearrangement to yield the corresponding 9,9-disubstituted thioxanthenes (**2b**)[3)] easily even at room temperature.



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a: R^1= CN ; R^2= CH_3

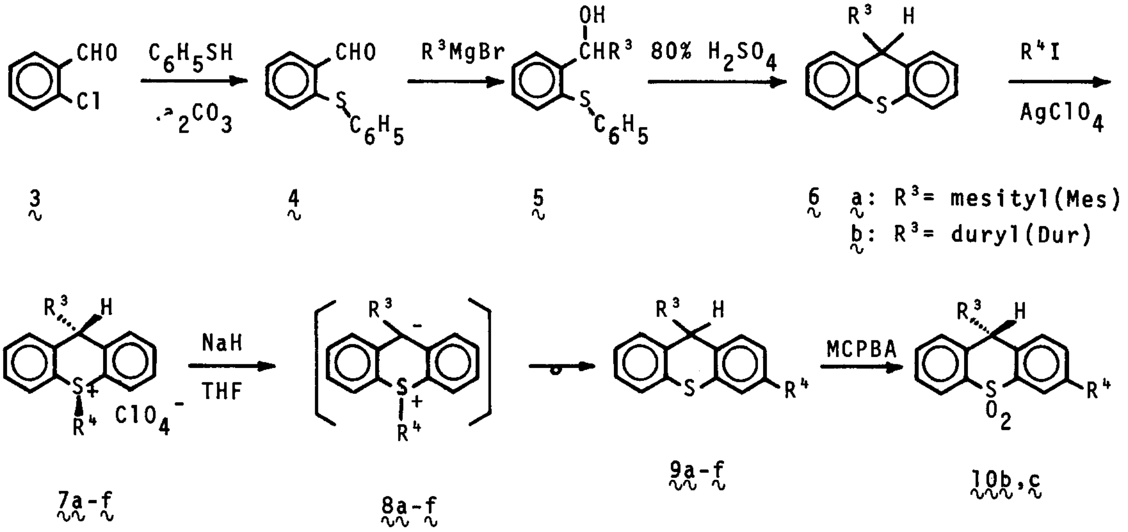
b: R^1= H, C_6H_5
R^2= alkyl, aryl

In this communication, we wish to report the new rearrangement reaction, via radical intermediate, of the new type of cyclic sulfur 1,4-ylides, 10-alkyl-9-mesityl-(**8a**-**c**) and 9-duryl-10-thiaanthracenes (**8d**-**f**) having sterically hindered substituents at 9-position which may play effectively a role to prevent the 10-alkyl group to rearrange to 9-position of **8**.

o-Chlorobenzaldehyde (**3**) was allowed to react with thiophenol in HMPA in the presence of Na_2CO_3 to give o-phenylthiobenzaldehyde (**4**)[4)] in 90 % yield. Treatment of **4** with mesityl or durylmagnesium bromide followed by cyclization using 80 % H_2SO_4 afforded 9-mesitylthioxanthene (**6a**), mp 156-158° (lit.[3c)] mp

155-157°) in 95 % yield or 9-durylthioxanthene (6b) with colorless needles (from CH_2Cl_2- n-hexane), mp 178-179° in 91 % yield : NMR ($CDCl_3$) δ 1.95 (6H, br.s($W_{1/2}$=0.39 ppm), $C_{2',6'}$-Me), 2.33 (6H, s, $C_{3',5'}$-Me), 5.52 (1H, br.s, C_9-H), and 6.66-7.60 (9H, m, ArH), respectively. Thioxanthenes (6) were alkylated with alkyl halides-$AgClO_4$ in 1,2-dichloroethane to give the corresponding thioxanthenium perchlorates (7)[5] (see Table).

Treatment of thioxanthenium salts (7) with NaH in THF under nitrogen atmosphere at room temperature gave orange-yellow solutions of 1,4-ylides (8). After



Scheme I

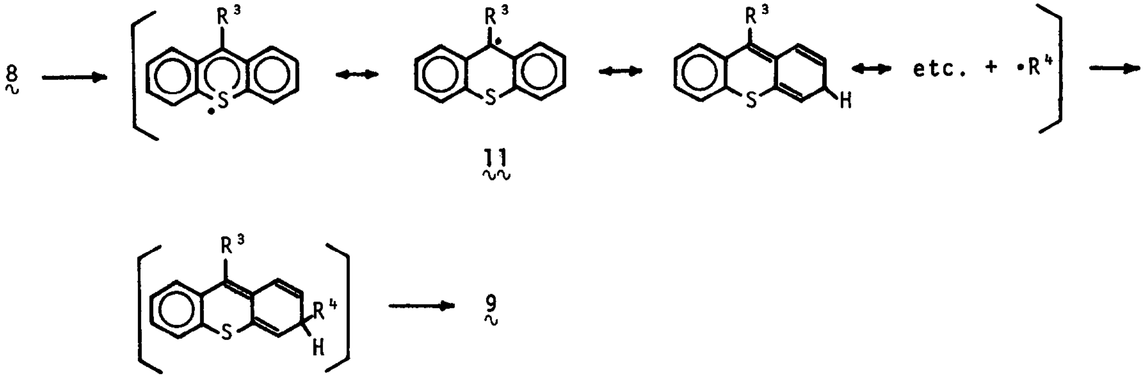
Table. Yields and Melting Points of 10-Alkyl-9-arylthioxanthenium Perchlorates (7) and 3-Alkyl-9-arylthioxanthenes (9)

	R^3	R^4	7, Yield(%)	mp(°C(decomp.))	9, Yield(%)	mp(°C)
a	Mes	Me	94	209-216	68	134-136
b	Mes	Et	93	181-183	63	- *
c	Mes	n-Pr	93	170-174	66	- *
d	Dur	Me	97	215-217	67	155-157
e	Dur	Et	93	191-192	65	145-147
f	Dur	n-Pr	91	185-187	66	130-132

* Oily 3-alkyl-9-arylthioxanthenes (9b and 9c) were oxidized by m-chloroperbenzoic acid (MCPBA) to give the corresponding crystalline sulfones (10).[5,7]

changing the orange-yellow color to dark brown, 3-alkyl-9-arylthioxanthenes (**9**)9) were isolated in 63-68 % yields. The results were also shown in Table. The structural assignments of **9** were based on the spectral data6) and further confirmed by the comparison of the melting points and the spectral data with those of authentic samples.

ESR spectra were observed for the rearrangement reactions described above. The spectra were quite similar to that of a known 9-pentadeuterophenylthioxanthyl radical,8) indicating the formation of 9-arylthioxanthyl radicals during the rearrangement of **8** to **9**. Thus, this new rearrangement reaction might be explained by a mechanism involving the radical intermediate (**11**) in the solvent cage as shown below. And the direction of alkyl migration is explained in terms of the effective blocking of the reaction site (1- or 9-position) by the 9-bulky substituents.



Scheme II

Further studies on the application of this new 1,4-rearrangement reaction to other ylides are now in progress.

REFERENCES AND FOOTNOTES

1) A part of this work was presented at a) 8th Congress of Heterocyclic Chemistry, Kyoto, Japan, Oct., 1975, Abstracts of Papers p. 119 by M. Hori, T. Kataoka, H. Shimizu, S. Ohno, K. Narita, and H. Aoki ; b) 7th International Symposium on Organic Sulfur Chemistry, Hamburg (Federal Republic of Germany), July, 1976, Abstracts of Papers p. 172 by M. Hori, T. Kataoka, H. Shimizu, S. Ohno, M. Okitsu, H. Matsushita, and T. Miyasako.

2) M. Hori, T. Kataoka, H. Shimizu, S. Ohno, and K. Narita, Tetrahedron Letters, submitted for publication.

3) a) M. Hori, T. Kataoka, and H. Shimizu, *Chemistry Letters*, 1117 (1974); b) G. H. Senkler, Jr., J. Stackhouse, B. E. Maryanoff, and K. Mislow, *J. Amer. Chem. Soc.*, **96**, 5648 (1974); c) B. E. Maryanoff, J. Stackhouse, G. H. Senkler, Jr., and K. Mislow, *J. Amer. Chem. Soc.*, **97**, 2718 (1975); d) F. Ogura, W. D. Hounshell, C. A. Maryanoff, W. J. Richter, and K. Mislow, *J. Amer. Chem. Soc.*, **98**, 3615 (1976); e) H. Pirelahi, Y. Abdoh, and A. Afzali, *Tetrahedron Letters*, 4609 (1976).

4) G. Jacques, *Ger. Patent*, 2165260 (1972) (*C. A.* **77**, 114271j (1972)).

5) In the Scheme I, dotted and thick lines drawn in the figure of compounds (**7**) and (**10**) indicate pseudo-equatorial and pseudo-axial bonds, respectively. Detailed discussion on the stereochemistry of **7** and **10** will be described in the separated report in the near future.

6) NMR data (ppm) of **9** in $CDCl_3$; **9a**: 2.06 (6H, s, $C_{2',6'}$-Me), 2.30 (3H, s, C_3-Me), 2.39 (3H, s, $C_{4'}$-Me), 5.41 (1H, br.s, C_9-H), 6.69 (1H, d, J=8.6 Hz, C_1-H), and 6.69-7.56 (8H, m, ArH). **9b**: 1.21 (3H, t, J=7.0 Hz, $CH_2C\underline{H}_3$), 2.07 (6H, s, $C_{2',6'}$-Me), 2.39 (3H, s, $C_{4'}$-Me), 2.61 (2H, q, J=7.0 Hz, $CH_2C\underline{H}_3$), 5.42 (1H, br.s, C_9-H), 6.72 (1H, d, J=8.7 Hz, C_1-H), and 6.69-7.55 (8H, m, ArH). **9c**: 0.92 (3H, t, J=6.4 Hz, $CH_2CH_2C\underline{H}_3$), 1.64 (2H, m, $CH_2C\underline{H}_2CH_3$), 2.05 (6H, s, $C_{2',6'}$-Me), 2.39 (3H, s, $C_{4'}$-Me), 2.56 (2H, t, J=7.7 Hz, $C\underline{H}_2CH_2CH_3$), 5.41 (1H, br.s, C_9-H), 6.59-7.58 (8H, m, ArH), and 6.71 (1H, d, J=8.3 Hz, C_1-H). **9d**: 1.89 (6H, br.s($W_{1/2}$=0.45 ppm), $C_{2',6'}$-Me), 2.30 (9H, s, $C_{3,3',5'}$-Me), 5.47 (1H, br.s, C_9-H), 6.60 (1H, br.d, J=8.8 Hz, C_1-H), and 6.60-7.50 (7H, m, ArH). **9e**: 1.22 (3H, t, J=7.5 Hz, $CH_2C\underline{H}_3$), 1.94 (6H, br.s($W_{1/2}$=0.6 ppm), $C_{2',6'}$-Me), 2.33 (6H, s, $C_{3',5'}$-Me), 2.62 (2H, q, J=7.5 Hz, $C\underline{H}_2CH_3$), 5.51 (1H, br.s, C_9-H), 6.69 (1H, d, J=7.8 Hz, C_1-H), 6.90 (1H, d.d, J=7.8, 1.6 Hz, C_2-H), and 6.68-7.60 (6H, m, ArH). **9f**: 0.91 (3H, t, J=7.3 Hz, $CH_2CH_2C\underline{H}_3$), 1.62 (2H, m, $CH_2C\underline{H}_2CH_3$), 1.30-2.79 (6H, br.s, $C_{2',6'}$-Me), 2.30 (6H, s, $C_{3',5'}$-Me), 2.53 (2H, t, J=7.8 Hz, $C\underline{H}_2CH_2CH_3$), 5.47 (1H, br.s, C_9-H), 6.62 (1H, d, J=8.7 Hz, C_1-H), 6.82 (1H, d.d, J=8.7, 1.3 Hz, C_2-H), and 6.53-7.47 (6H, m, ArH).

7) **10b** : colorless rhombs (CH_2Cl_2-MeOH), mp 201-204°, NMR ($CDCl_3$) δ 1.28 (3H, t, J=7.0 Hz, $CH_2C\underline{H}_3$), 1.36 (3H, br.s, $C_{6'}$-Me), 2.40 (3H, s, $C_{4'}$-Me), 2.45 (3H, br.s, $C_{2'}$-Me), 2.76 (2H, q, J=7.0 Hz, $C\underline{H}_2CH_3$), 5.91 (1H, br.s, C_9-H), 6.77-7.74 (7H, m, ArH), 8.11 (1H, d, J=1.6 Hz, C_4-H), and 8.17-8.40 (1H, m, C_5-H); IR (KBr) ν cm^{-1} 1303 and 1158 (SO_2). **10c**: colorless needles (CH_2Cl_2- pet. ether), mp 162-164°, NMR ($CDCl_3$) δ 0.95 (3H, t, J=6.6 Hz, $CH_2CH_2C\underline{H}_3$), 1.35 (3H, s, $C_{6'}$-Me), 1.69 (2H, m, $CH_2C\underline{H}_2CH_3$), 2.40 (3H, s, $C_{4'}$-Me), 2.45 (3H, s, $C_{2'}$-Me), 2.70 (2H, t, J=7.7 Hz, $C\underline{H}_2CH_2CH_3$), 5.91 (1H, br.s, C_9-H), 6.75-7.70 (7H, m, ArH), 8.08 (1H, d, J=1.5 Hz, C_4-H), and 8.13-8.42 (1H, m, C_5-H); IR (KBr) ν cm^{-1} 1035, 1300, and 1162 (SO_2).

8) M. Hori, T. Kataoka, Y. Asahi, and E. Mizuta, *Chem. Pharm. Bull.*, **21**, 1692 (1973).

9) All new compounds had satisfactory analytical data to support the assignment.