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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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A. L. Ternay Jr.^a; Bobbie E. South^a; R. Mckellar^a; W. W. Lam^a

^a Center for Medicinal Chemistry Research, Department of Chemistry, The University of Texas at Arlington, Arlington, Texas, U.S.A.

To cite this Article Ternay Jr., A. L. , South, Bobbie E. , Mckellar, R. and Lam, W. W.(1992) 'RING FLATTENING IN THIANTHRENE SULFONIUM BIS(CARBOMETHOXY)METHYLIDES', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 73: 1, 63 – 66

To link to this Article: DOI: 10.1080/10426509208034432

URL: <http://dx.doi.org/10.1080/10426509208034432>

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RING FLATTENING IN THIANTHRENE SULFONIUM BIS(CARBOMETHOXY)METHYLIDES

A. L. TERNAY, JR., BOBBIE E. SOUTH, R. McKELLAR and W. W. LAM

*Center for Medicinal Chemistry Research, Department of Chemistry, The
University of Texas at Arlington, Arlington, Texas 76019, U.S.A.*

(Received August 1, 1992; in final form September 10, 1992)

Bis(carbomethoxy)methylides derived from thianthrene 5,5-dioxide and 2,7-dichlorothianthrene 5,5-dioxide exhibit hindered S^+-C^- bond rotation. Variable temperature NMR studies are described for these ylides as well as 9,9-dimethylthioxanthenium bis(carbomethoxy)methylide. With coalescence temperatures of $\approx 30^\circ\text{C}$ (200 MHz), all have $\Delta G^\ddagger \approx 15$ kcal/mol.

Key words: Thianthrene; ylide; conformation; NMR

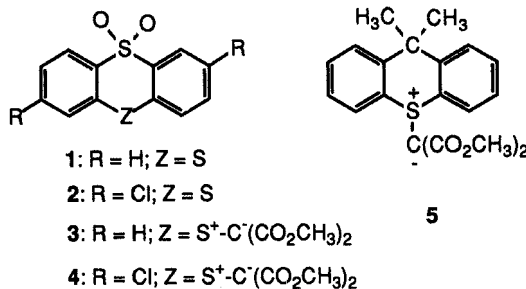
INTRODUCTION

We have reported that sulfonium bis(carboalkoxy)methylides derived from thialogs of 9,10-dihydroanthracene (e.g., thianthrenes) exist with the methylide carbon in either the pseudo-axial (a') or pseudo-equatorial (e') geometry. So long as the a' position is accessible, e.g., by central ring inversion, the bis(carboalkoxy)methylide fragment undergoes rapid S^+-C^- bond rotation and both carboalkoxy groups are isochronous. However, if the bis(carboalkoxy)methylide fragment is locked into the e' position then bond rotation is prevented and the carboalkoxy groups are anisochronous.¹ This suggests that the methylide fragment should be a useful conformational probe and, furthermore, may be used to indicate when ring distortion (flattening) is present.²

In order to extend the value of the methylide fragment as a probe of sulfur-containing heterocycles, we now report on the proton NMR spectra of sulfonium ylides of thianthrenes where ring distortion is likely.

RESULTS AND DISCUSSION

Thianthrene and 2,7-dichlorothianthrene were converted to thianthrene 5,5-dioxide (1) and 2,7-dichlorothianthrene 5,5-dioxide (2), respectively. The reaction of these monosulfones with dimethyl diazomalonate afforded the corresponding dioxide-monoylides, 10-bis(carbomethoxy)methylidethianthrenium 5,5-dioxide (3) and 2,7-dichlorothianthrenium 10-bis(carbomethoxy)methylidethianthrenium 5,5-dioxide (4) in good yield. Aside from anticipated differences due to the presence of chlorine, spectroscopic data for 3 and 4 were quite similar. The salient feature of their ^1H nmr spectra was two broad singlets (3H/3H), found at 3.77 and 3.55 δ for 3 and at 3.79 and 3.62 δ for 4. That both ylides had similar geometries was supported by a common ^{13}C chemical shift for their methylide carbons (49.9 δ) and by the presence of two $^{13}\text{C}=\text{O}$ resonances (165 and 166 δ) for each.³



Taken together, these data demand an environment for the methyllide fragment intermediate between that found in the a' and e' arrays and lead us to conclude that these heterocyclic systems are flatter than are related monoylides of thioxanthene or the trans-diyliide of thianthrene.^{4,5}

Variable temperature ¹H NMR studies were conducted from 21°C to 36°C for **3**, and from 20°C to 45°C for **4**. The methoxy protons of the former coalesced at 32°C, while those of the latter coalesced at 33°C. For **3**, the Δν_{max} and T_c were 47.38 Hz and 305.0 K, respectively, leading to a value for ΔG_{c‡} of 15.04 kcal mol⁻¹. Similarly, for **4** the Δν_{max} and T_c were 35.14 Hz and 306.0 K, respectively, leading to a value of 15.28 kcal mol⁻¹.⁶ The ΔG_{c‡}'s, based upon the total line shape analysis^{7,8} were found to be 15.07 and 15.29 kcal mol⁻¹, respectively.

The effect of temperature on rate constants was analyzed with the aid of the Arrhenius equation. The activation enthalpy (ΔH‡) and entropy (ΔS‡) were calculated assuming a negligible change in the activation volume. These results indicate that the activation parameters are virtually identical for **3** and **4** (E_a ≈ 15.3 kcal/mol; ΔH‡ ≈ 14.5 kcal/mol; ΔS‡ = -1.5 e.u. Related parameters⁹ for a series of eight 2-substituted thioxanthonium bis(carbomethoxy)methylides (H, Br, Cl, Me, F, OMe, C(O)Me, C(O)OMe) are similar, consistent with a flattened geometry for these rings.¹⁰

Finally, in order to determine that electron delocalization to either sulfonyl or carbonyl groups was not confounding the data, 9,9-dimethylthioxanthonium bis(carbomethoxy)methylide (**5**) was prepared and observed to behave similarly, i.e., exhibit two broadened OCH₃ signals at 25°C.¹¹ A VT ¹H NMR experiment (25–35°C) indicated a coalescence temperature of 32°C, suggesting a geometry similar to that of these others.

In summary, we conclude that (a) sulfonium ylides derived from these various heterocycles¹² have flattened structures with the methyllide carbon occupying the more e' of the two positions associated with tricoordinated sulfur and (b) interactions with the proximal aryl ("peri") hydrogens leads to an intermediate rate of S⁺—C⁻ rotation.

EXPERIMENTAL¹³

Thianthrenium 10-Bis(carbomethoxy)methylide 5,5-Dioxide (3): Into a 25 mL one-necked flask there was placed thianthrene 5,5-dioxide (135 mg; 0.544 mmol), anhydrous toluene (7 mL) and anhydrous copper (II) sulfate (10 mg). The temperature of the reaction mixtures was raised to about 95°C and then dimethyl diazomalonate (103 mg; 0.605 mmol) was added with stirring. After refluxing for 3 h

and then cooling to room temperature, the resulting solid¹⁴ was removed by filtration and washed sequentially with water (15 mL) and hexane (15 mL). Drying *in vacuo* overnight afforded 135 mg of thianthrenium 10-bis(carbomethoxy)methylide 5,5-dioxide (**3**) as a white solid, mp 223.5–224.5°C dec. Recrystallization (ethanol; 33 mL) yielded 104 mg (0.260 mmol, 47.8%) of fine white crystals, mp 246°C dec, which was homogeneous on TLC.

The mass spectrum of **3** showed the following major peaks: 377.9 (M^+ , 84), 346.9 (44), 318.9 (75), 275.0 (67), 255.1 (53), 248.0 (80), 212.0 (36), 200.0 (79), 184.0 (100), 171.0 (49), 152.1 (41), 139.1 (33) and 59.0 (40). The IR spectrum (KBr) showed absorptions at 1732, 1706, 1659, 1436, 1329 (SO_2), 1300, 1170 (SO_2), 1088 and 1037 cm^{-1} .

Anal. Calcd for $C_{17}H_{14}O_6S_2$: C, 53.96; H, 3.37

Found: C, 54.02; H, 3.71

2,7-Dichlorothianthrene 10-Bis(carbomethoxy)methylide 5,5-Dioxide (4): Into a 50 mL three-necked flask there was added 2,7-dichlorothianthrene 5,5-dioxide (0.50 g; 1.6 mmol), anhydrous toluene (10.0 mL), anhydrous copper sulfate (6.0 mg; 0.036 mmol) and (0.30 g; 1.9 mmol) of dimethyl diazomalonate. The reaction mixture was heated to 100°C and, after 3 h cooled to room temperature. The resulting solid was removed by filtration, washed with hexane, and then suspended in water. The resulting pale yellow solid was isolated by filtration and dried *in vacuo* overnight to afford 0.44 g of crude product, mp 194–197°C.

A column was packed¹⁵ and 0.40 g of this crude mixture was separated by flash chromatography. The first fraction, collected after eluting with 160 mL of chloroform, afforded 0.27 g (0.60 mmol, 38% yield) of 2,7-dichlorothianthrenium 10-bis(carbomethoxy)methylide 5,5-dioxide, **4**, mp 214–216°C.

The mass spectrum of **4** exhibited the following major peaks: 448.0 (40), 445.9 (M^+ , 65), 386.9 (52), 344.9 (48), 342.8 (73), 324.9 (36), 322.9 (49), 317.9 (54), 315.9 (66), 268.0 (43), 254.0 (42), 252.0 (62) and 59.1 (100). The IR spectrum (KBr) showed absorptions at 1736, 1701, 1661, 1653, 1570, 1436, 1337 (SO_2), 1240, 1171 (SO_2), 1113 and 1091 cm^{-1} .

Anal. Calcd for $C_{17}H_{12}Cl_2O_6S_2$: C, 45.64; H, 2.71

Found: C, 45.28; H, 2.65

9,9-Dimethylthioxanthene: To a stirred suspension of 2.12 g (10.0 mmol) of thioxanthone, 8 mg of benzoic acid and 20 mL of benzene there was added, dropwise and with stirring, 15 mL (30 mmol) of a 2.0 M solution of trimethylaluminum in toluene.¹⁶ The reaction mixture then was heated to 60–70°C, maintained there for 30 min and finally poured into 100 mL of 1 M hydrochloric acid.¹⁷ The aqueous phase was separated, extracted with methylene chloride (2 × 25 mL) and the extracts combined with the benzene/toluene solution. After drying (calcium chloride), the solvents were removed to afford 2.34 g of crude product. Vacuum distillation afforded 2.09 g (9.23 mmol; 92.3 % yield) of the desired product which was converted to the ylide without further purification.¹⁸ The 1H NMR ($CDCl_3$) exhibited an aryl multiplet (6.8–7.5 δ ; 8H) and a methyl singlet (1.6 δ ; 6H).

9,9-Dimethylthioxanthenum Bis(carbomethoxy)methylide (5): A mixture of 9,9-dimethylthioxanthene (1.93 g; 8.53 mmol), dimethyl diazomalonate (1.42 g; 8.98 mmol), anhydrous toluene (18 mL) and anhydrous copper sulfate (68 mg) was heated to 95–100°C and maintained there for 3 h. Upon cooling to room temperature, the resulting mixture was extracted with methylene chloride, the extract dried (magnesium sulfate) and the solvent removed under reduced pressure to afford 3.47 g of a light yellow solid. This solid was suspended in chloroform and a small amount of insoluble residue removed by filtration. The chloroform was removed to yield a yellow oil which, with the addition of toluene, afforded 2.08 g of colorless crystals, mp 199–200.5°C. A second crop raised the final yield of **5** to 2.53 g (7.10 mmol; 83.2% yield), mp 199–200°C.¹⁹

Anal. Calcd for $C_{20}H_{20}O_4S$: C, 67.39; H, 5.66

Found: C, 67.28; H, 5.70

The 1H NMR ($CDCl_3$; 200 MHz) exhibited the following signals: 7.70 δ (4H, dd); 7.50 δ (2H, dd); 7.38 δ (2H, dd); 3.81 δ (3H, brd s); 3.37 δ (3H, brd s); 2.08 δ (3H, s); 1.48 δ (3H, s).

ACKNOWLEDGEMENT

This research was graciously supported by The Robert A. Welch Foundation through grant Y-484.

FOOTNOTES AND REFERENCES

1. (a) A. L. Ternay, Jr. and W. W. Lam, *Phosphorous, Sulfur and Silicon*, in press, and references cited herein; (b) M. Kluba, J. Harwood, P. K. Casey and A. L. Ternay, Jr., *J. Heterocyclic Chem.*, **22**, 1261 (1985); (c) A. L. Ternay, Jr., J. C. Baack, S. S. C. Chu, V. Napoleone, G. Martin and C. Alfaro, *J. Heterocyclic Chem.*, **19**, 833 (1982).
2. A flattened central ring leads to geometries between a' and e' and with an intermediate rotation rate.
3. 50.3 MHz; CDCl₃; 25°C.
4. In addition to Reference 1, see: J. Galloy, W. H. Watson, D. Craig, C. Guidry, M. Morgan, R. McKellar, A. L. Ternay, Jr. and G. Martin, *J. Heterocyclic Chem.*, **20**, 399 (1983).
5. For a related discussion of sulfonium salts see: M. Oki and Y. Yamada, *Bull. Chem. Soc. Jpn.*, **61**, 1181 (1988).
6. The free energy of activation (ΔG^\ddagger) were obtained using the Eyring equation, $\Delta G^\ddagger = 4.575 T_c [9.972 + \log_{10}(T_c/\Delta\nu_{\max})]$. ΔG^\ddagger = free energy of activation in cal mol⁻¹; T_c = temperature of coalescence; $\Delta\nu_{\max}$ = maximum chemical shift difference (Hz) at very slow exchange; M. Oki, *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*, VCH: Florida, 1985, p. 407.
7. (a) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **1956**, **25**, 1228; (b) H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **1953**, **21**, 1688; (c) H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **1953**, **21**, 279; (d) F. Bloch, *Phys. Rev.*, **1946**, **70**, 460.
8. Using the NMCXCH program provided by Nicolet Magnetics.
9. $T_c \approx 310$ K, $\Delta G^\ddagger \approx 15$ Kcal mol⁻¹: A. L. Ternay, Jr. and R. McKellar, manuscript in preparation.
10. The X-ray structure of 2-chlorothioxanthone reveals an angle of fold of 173.5°: A. L. Ternay, in *IUPAC Organic Sulfur Chemistry*, R. Kh. Freidlina, Pergamon Press, New York, 1981, pp. 175–188.
11. 3.37 and 3.80 δ (200 MHz/CDCl₃/25°C).
12. In general, it appears that *gem*-disubstituted systems are flattened relative to their less-substituted analogs.
13. Reactions were conducted under nitrogen. Melting points are uncorrected and chemical shifts referenced to internal TMS. TLC's were on silica gel with chloroform eluent and iodine visualization.
14. Some white solid had formed after refluxing for 1 h.
15. The column (length: 4.5 cm; diameter: 2.0 cm) was packed with 15 g of 200–325 mesh silica gel using chloroform.
16. Addition was exothermic and accompanied by various color changes.
17. CAUTION: The quench was quite exothermic and accompanied by significant foaming.
18. An earlier, different preparation of this compound produced an oil which solidified after several months: A. L. Ternay, Jr., L. Ens, J. Herrmann and S. Evans, *J. Org. Chem.*, **34**, 940 (1969). The present scheme affords much improved yields.
19. The melting point was unchanged when the sample was cooled and remelted in a closed capillary tube.