Tetrahedron Letters No. 3, pp 215 - 218, 1976. Pergamon Press. Printed in Great Britain.

[2 + 4]CYCLOADDITION OF THIOPHOSGENE WITH ANTHRACENES

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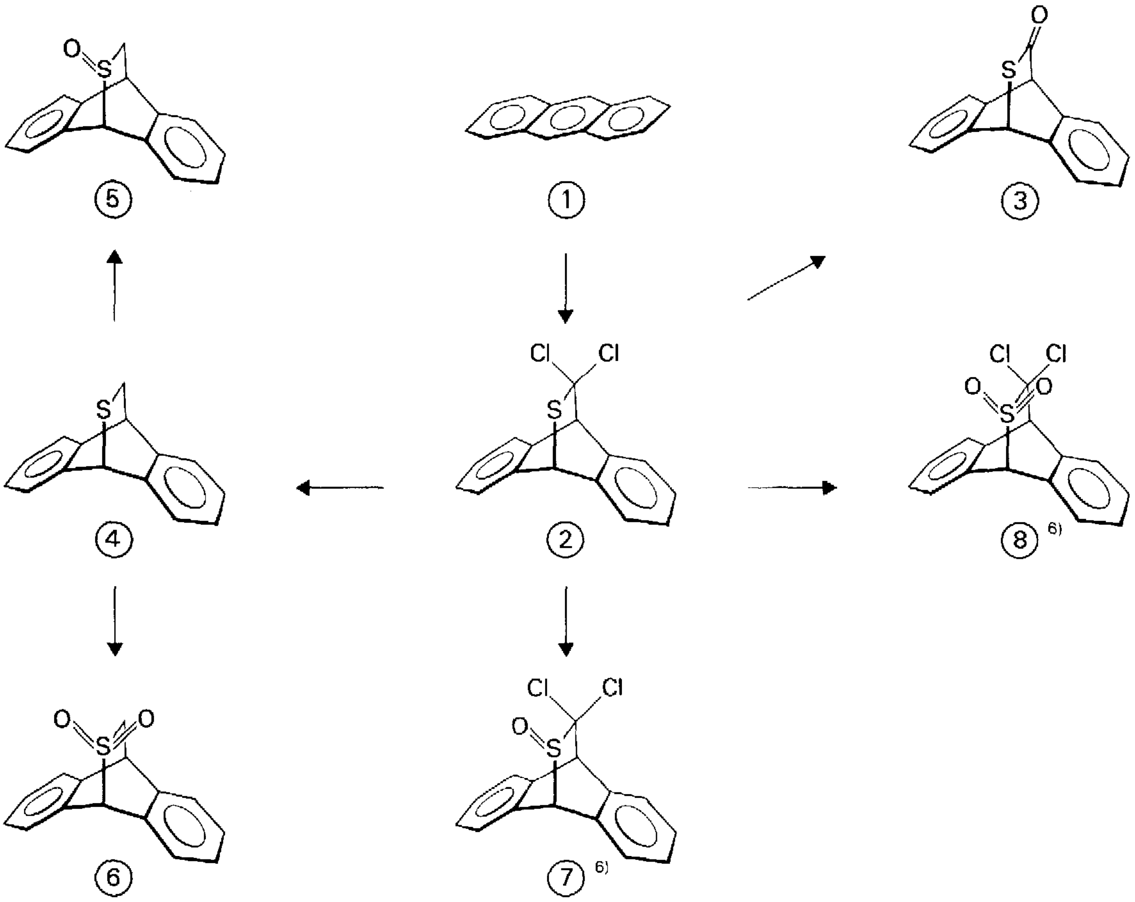
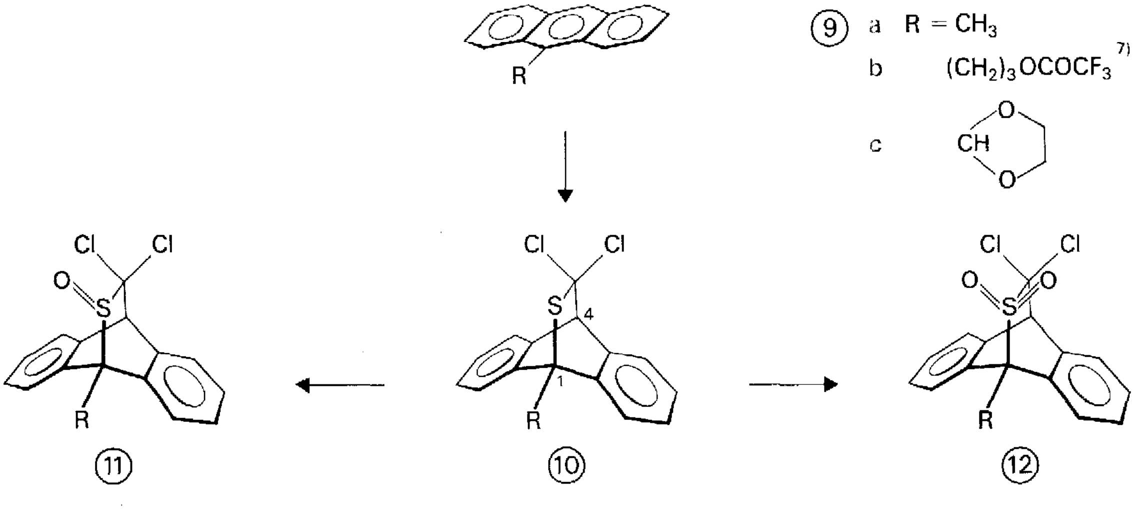
(Received in UK 21 November 1975; accepted for publication 4 December 1975)

Thiophosgene is known to react as dienophile in [2 + 4]cycloadditions with reactive dienes such as cyclopentadiene1), cyclohexadiene2) and 1,4-diphenyl-1,3-butadiene3). We report here the Diels-Alder addition of thiophosgene to anthracene ① and three of its 9-substituted derivatives ⑨ .

When 53.4 g (0.3 moles) of anthracene ① , 72 g (0.63 moles) of thiophosgene and 760 ml of xylene were heated at 90° for 6 hours, the resulting mixture evaporated and the residue crystallized from ether, the bridged sulfide ② 4) was obtained in 60% yield5), mp 133-5° dec., δ (CDCl$_3$) ppm: 5.19 (1H, s), 5.28 (1H, s). ② is stable in the absence of water but solvolyses rapidly in hydroxylic solvents. Hydrolysis of ② with silicagel-water-dioxane at 25° during 48 hours afforded the thiolactone ③ , mp 135-7° → 208-15° (mp of anthracene) from ether-petrolether, 64% yield, ν (CH$_2$Cl$_2$): 1695 cm^{-1} (C=O), δ (CDCl$_3$) ppm: 5.20 (1H, s), 5.55 (1H, s). The unsubstituted thioether ④ was formed in 18% yield by reduction of ② with lithium aluminum hydride for 1.5 hours in refluxing ether, mp 161-5° from ether δ (CDCl$_3$) ppm: 2.95 (2H, d, J 3 Hz), 4.73 (1H, t, J 3 Hz), 5.05 (1H, s). Sodium metaperiodate oxidation in water-acetone at 25° for 3 hours converted ④ into the sulfoxide ⑤ , mp (159)-209° (gradual decomposition) from ether, 52% yield, δ (CDCl$_3$) ppm: 2.30 (1H, dd, J_1 12.5 Hz, J_2 3 Hz), 3.48 (1H, dd, J_1 12.5 Hz, J_2 3 Hz), 4.67 (1H, t, J 3 Hz), 5.67 (1H, s). Treatment of ④ during 2 hours in methylene chloride with an excess of m-chloroperbenzoic acid lead to the sulfone ⑥ , mp 296-8° from methanol, 72% yield, δ (DMSO-d$_6$): 3.04 (2H, d, J 3 Hz), 4.85 (1H, t, J 3 Hz), 5.82 (1H, s). ② was further characterized by oxidation with m-chloroperbenzoic acid to the recently published and independently synthesized dichlorosulfoxide ⑦ and dichlorosulfone ⑧ 6).





⑨ a R = CH_3

b $(CH_2)_3OCOCF_3$ 7)

c CH O O

TABLE 1: Cycloaddition products ⑩ , corresponding sulfoxides ⑪ and sulfones ⑫

R	reaction conditions	mp, solvent of crystallisation and yield of		
	⑨ → ⑩	sulfide ⑩	sulfoxide ⑪ 9)	sulfone ⑫ 10)
CH_3	0.104 moles (9a) , 0.194 moles $CSCl_2$, 100 ml xylene, 25°, 2 hours	dec. on heating, xylene, 65%	195-7° dec., tetrahydrofurane-petrolether, 87%	206-8°, ether-petrolether, 55%
$(CH_2)_3OCOCF_3$ 7)	0.12 moles (9b) , 0.24 moles $CSCl_2$, 300 ml xylene, 50°, 17 hours	147-50° dec. xylene-petrolether, 62%	183-6°, tetrahydrofurane, 81%	205-7° dec., tetrahydrofurane-petrolether, 85%
 11)	0.013 moles (9c) , 0.014 moles $CSCl_2$, 35 ml xylene, 90-100°, 3 hours	225-6° dec., toluene, 73%	215-220°, tetrahydrofurane-petrolether, 84%	284-6°, tetrahydrofurane-chloroform, 43%

TABLE 2: ^{1}H-nmr spectral parameters for ⑩ , ⑪ and ⑫

R	sulfide ⑩	sulfoxide ⑪	sulfone ⑫
CH_3	$CDCl_3$ 1H, s, 5.14 ppm 3H, s, 2.24 ppm	$CDCl_3$ 1H, s, 5.01 ppm 3H, s, 2.30 ppm	$CDCl_3$ 1H, s, 5.00 ppm 3H, s, 2.34 ppm
$(CH_2)_3OCOCF_3$	$CDCl_3$ 1H, s, 5.15 ppm		$CDCl_3$ 1H, s, 5.00 ppm
	$CDCl_3$ 1H, s, 6.16 ppm (acetal-H) 1H, s, 5.14 ppm	DMSO-d_6 1H, s, 5.98 ppm (acetal-H) 1H, s, 5.51 ppm	DMSO-d_6 1H, s, 6.20 ppm (acetal-H) 1H, s, 5.59 ppm

Cycloaddition experiments of thiophosgene with 9-substituted anthracenes (9a) , (9b) and (9c) revealed a remarkable regiospecificity and occurred in case (9a) already at 25° (table 1). The cycloaddition products are assigned structure ⑩ with the sulfur atom attached to the tertiary carbon atom of the starting anthracenes ⑨ . The structural proof is based on the absence of a substantial shift of the $H-C_4$-proton upon transforming the primary sulfide adducts ⑩ into the corresponding sulfoxides ⑪ and sulfones ⑫ (table 2). Comparison of the ^{13}C nmr spectra ($CDCl_3$) of (10a) (C_1 54.3, C_4 64.7, CH_3 15.8) and (11a) (C_1 68.7, C_4 61.3, CH_3 13.5) furnishes an independent proof of this structural assignment: The ^{13}C chemical shift difference between (11a) and (10a) amounts to 14.4 ppm for C_1 (substituent effect of SO vs. S, cf. lit. 12)) and to -3.4 and -2.3 ppm for C_4 and CH_3 respectively (γ-effect of the O-atom).

Acknowledgement: We thank Miss Felicitas Widmer for skilled and efficient technical assistance. The encouragement and interest of Dr. A.R. Gagneux is gratefully acknowledged.

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