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THE SYNTHESIS OF 1,4-SELENATHIAFULVENES

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The first examples (18 and 19) of 1,4-selenathiafulvenes are described. These compounds were prepared by a Wittig-type synthesis from the appropriate aldehydes and 1,3-selenathiolyl phosphonium salts (9 and 11) in methanol, using KOH as the base. The same reaction conditions also afforded a number of 1,4-dithiafulvenes, the Wittig synthesis of which has previously been achieved only under aprotic conditions.

Protonation of phenylethynylthiolate ion (1) or of phenylethynylselenolate ion (2) affords, according to the exact conditions used, convenient syntheses of either the E or the Z isomer of 2,6-diphenyl-1,4-dithiafulvene (3) or of 2,6-diphenyl-1,4-diselenafulvene (4), respectively.[1a,b,c] This type of synthesis is not applicable, however, to the preparation of the corresponding 1,4-selenathiafulvenes, which we required for a comparative physical organic study. We now report the synthesis of the first 1,4-selenathiafulvenes by the use of phosphorane intermediates.

Alkylation of 4-phenyl-1,3-selenathiole-2-thione (5)[2] with methyl fluorosulfonate gave the corresponding S-methyl fluorosulfonate salt 6 (98%), mp 180° (dec).[3] Reduction of the latter by sodium borohydride in ethanol gave crystalline selenathiole 7 (70%), mp 82°, which was converted by fluoroboric acid - acetic anhydride into 4-phenyl-1,3-selenathiolium fluoroborate (8, 50%), mp 155° (dec). Reaction of the latter with triphenylphosphine in methylene chloride (1 h, rt) gave the corresponding phosphonium salt 9 (90%), mp 170°. In a similar manner, the known 1,3-selenathiolium fluoroborate (10)[4] was treated with triphenylphosphine to give the corresponding phosphonium salt 11 (74%), mp 158°.

The Wittig-type synthesis of a number of 1,4-dithiafulvenes from a variety of carbonyl components and the phosphoranes (12 and 13) derived from the corresponding 1,3-dithiolyl phosphonium salts 14 and 15 has been reported.[5,6] Phosphorane 12 was generated and used only at -78° under aprotic conditions;[5] the presumably more stable phosphorane 13 was generated also aprotically under similar conditions, although it could be trapped even at room temperature by the most reactive carbonyl components.[6]

We have now found that the selenathiolylidene phosphoranes 16 and 17 may be readily generated and trapped in methanol at room temperature, using potassium hydroxide as the base. Thus, addition of methanolic potassium hydroxide at room temperature to a methanolic solution of fluoroborate 9 containing benzaldehyde afforded a readily separable mixture of E-3,6-diphenyl-1,4-selenathiafulvene (18a, 50%), mp 205° and its Z-isomer 18b (30%), mp 127°. By analogy with the corresponding isomeric dithiafulvenes and diselenafulvenes,[1b,c] 18b was rapidly converted to 18a by a trace of mineral acid. Under similar reaction conditions a solution of fluoroborate 11 and cinnamaldehyde afforded the selenathiafulvene 19 (75%, mp 110°).

Further investigation revealed that the previously studied 1,3-dithiolylidene phosphoranes 12 and 13 could also be generated by potassium hydroxide in methanol at room temperature and trapped by a variety of aromatic aldehydes. As shown in Table 1, fulvenes 20, 21 and 22-24 were prepared from phosphonium salts 14 and 15, respectively.

Dithiafulvene 22. To a mixture of cinnamaldehyde (0.150 g) and phosphonium salt 15 [5] (0.508 g) in absolute methanol (7 cc) was added methanolic potassium hydroxide (0.5 ml; 20%) with swirling. The mixture warmed up and fulvene 22 crystallized immediately. It was filtered after addition of 5 cc more methanol, washed with water and methanol successively and dried. The product was practically pure at this stage. Recrystallization from methanol furnished fulvene 22 as red crystals, mp 126° (lit.[6] mp 126°). The mother-liquor of crystallization furnished a second crop (0.07 g). Total yield of 22 was 93%.

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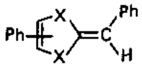
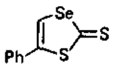
$Ph\text{-}C{\equiv}C\text{-}X^{\ominus}$

1: X = S
2: X = Se



3: X = S
4: X = Se



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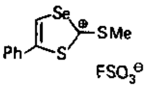

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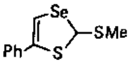

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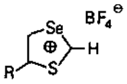
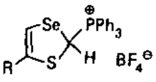
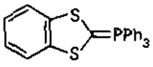


8: R = Ph
10: R = H



9: R = Ph
11: R = H



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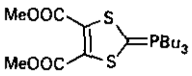

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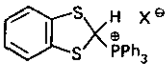

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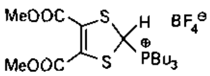

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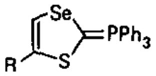
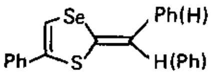


16: R = Ph
17: R = H



18a: *E* isomer
18b: *Z* isomer

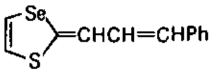


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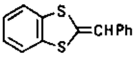
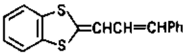
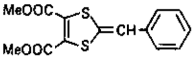
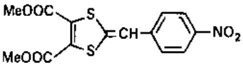
Table 1. 1,4-Dithiafulvenes Synthesized by the Wittig Reaction.

Wittig reagent	*Aldehyde*	*1,4-Dithiafulvene*	*Mp (° C)*		*Yield (percent)*
			Observed	*Literature*	
14	PhCHO	 **20**	132	132[5]	84
	$PhCH=CHCHO$	 **21**	148	148[5]	80
15	PhCHO	 **23**	90	91[6]	80
	p-$O_2NC_6H_4CHO$	 **24**	158	—	87

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(c). I. Lalezari, A. Shafiee and M. Yalpari, *J. Org. Chem.*, 1973, **38**, 338.

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3. Extreme caution is necessary in the handling of methyl fluorosulfonate due to its extremely toxic nature.

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