Tetrahedron Letters No. 41, pp 3695 - 3698, 1976. Pergamon Press. Printed in Great Britain.

SYNTHESIS OF 1,4-BENZODITHIAFULVENES VIA WITTIG REACTION

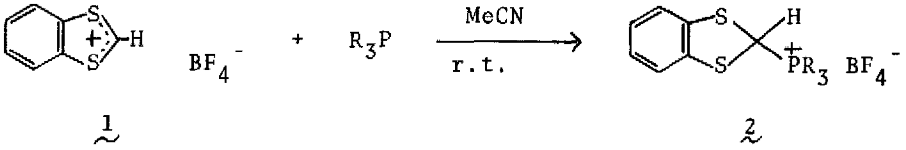
Kiyofumi Ishikawa, Kin-ya Akiba,* and Naoki Inamoto
Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Tokyo 113, Japan

(Received in Japan 1 July 1976; received in UK for publication 23 August 1976)

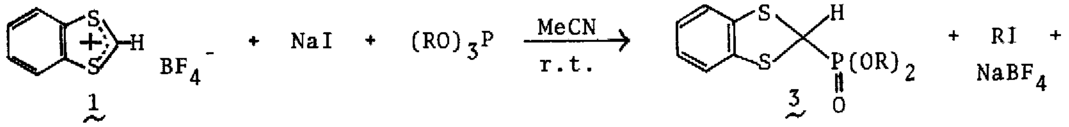
There has been no general synthetic method of 1,4-dithiafulvenes, although those with electron-withdrawing groups on the exo-methylene can be prepared by condensation of 2-methylthio-1,3-dithiolylium salts with malonates$^{1)}$ and some of them were obtained among photolysis products of 1,2,3-thiadiazoles.$^{2)}$ Hartzler reported the formation of 1,3-dithiol-2-ylidenetributylphosphoranes in situ by addition of activated acetylenes to a mixture of tributylphosphine and carbon disulfide and subsequent Wittig reaction of the phosphoranes.$^{3)}$ Very recently Miles et al. reported the intermediacy of the same kind of phosphorane during desulfurization of 4,5-dicyano-1,3-dithiole-2-thione with tertiary phosphines.$^{4)}$ To our knowledge, only these two special cases are reported to date on this type of phosphorane and their Wittig reaction.

We report here the synthesis of phosphonium salts and phosphonates from 1,3-benzodithiolylium tetrafluoroborate and their general use in Wittig reaction to afford 1,4-benzodithiafulvenes.

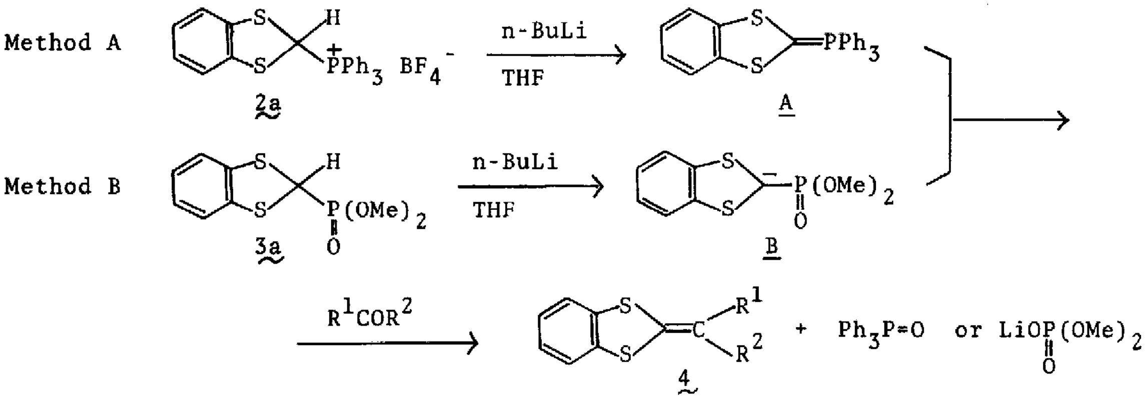
1,3-Benzodithiolylium tetrafluoroborate (1), obtained easily on a preparative scale,$^{5)}$ reacted with phosphines in acetonitrile at room temperature for 2 hr to give the corresponding phosphonium salts (2) in high yields [2a: R=Ph, 87%, mp 211.5-212.5°C (dec.); 2b: R=n-Bu, 90%, mp 166.5-168.0°C].



Also, 1 reacted with trialkyl phosphite in the presence of an equimolar amount of sodium iodide to give dialkyl 1,3-benzodithiolylphosphonate (3) [3a: R=Me, 93%, mp 121.5-122.5°C; 3b: R=Et, 90%, mp 115.0-116.0°C].



Both 2 and 3 were deprotonated with n-butyllithium in THF at -78°C and the resulting anions (A and B) reacted with carbonyl compounds to give 1,4-benzodithiafulvenes (4) at low temperature. Typical examples are shown below.



Method A: To a suspension of phosphonium salt (2a, 2.0 mmol) in THF (50 ml) was added n-butyllithium in hexane (1.5 ml, 2.3 mmol) at -78°C under nitrogen with stirring. Stirring was continued for 2.0-2.5 hr to give a dark red solution of the phosphorane (A). p-Tolualdehyde (2.0 mmol) was added and stirring was continued for 5-10 min at -78°C, when red color of A changed to yellow one of the product (4b). The mixture was allowed to get warm to room temperature and THF was evaporated under reduced pressure. The residue was extracted with dichloromethane (30 ml ×3) after addition of water (50 ml). The residue, after evaporation of the solvent, was separated by dry column chromatography (silica gel; carbon tetrachloride) to give 4b (1.5 mmol, 75%) and triphenylphosphine oxide (1.5 mmol, 74%).

Method B: To a solution of phosphonate (3a, 2.0 mmol) in THF (20 ml) was added n-butyllithium in hexane (1.5 ml, 2.3 mmol) at -78°C under nitrogen with stirring. p-Tolualdehyde (2.0 mmol) was added to the yellow solution of B after 10 min and the mixture was stirred for 10 min at -78°C. After the same work-up as above, **4b** (1.88 mmol, 94%) was obtained after evaporation of dichloromethane.

Yields and mp of **4** are shown in the Table. Method B is superior to method A for synthetic purpose by the following reasons: i) easier handling of **3** than **2**, because **2** may dissociate to some extent in solution, ii) shorter reaction time, iii) no need of chromatographic separation, the resulting phosphoric acid being soluble in water, and iv) no by-production of dibenzotetrathiafulvalene, which is the case in method A when the reaction is carried out at higher temperature (0°C).

Table Yields and mp of 1,4-Benzodithiafulvenes (**4**)

	R^1	R^2	Method	Yield	mp (°C)
a)	p-$MeOC_6H_4$	H	A	77 (75)*	144.5-145.5
b)	p-MeC_6H_4	H	A	75 (74)	149.5-151.0
			B	94	
c)	Ph	H	A	74 (72)	133.0-134.5
d)	p-ClC_6H_4	H	A	82	190.0-190.8
e)		H	A	78 (80)	148.0-149.0
f)		H	B	95	72.0- 73.0
g)	$(CH_2)_4$		B	96	105.5-107.0
h)	$(CH_2)_5$		B	98	96.0-97.5
i)	p-MeC_6H_4	Me	B	92	80.0-81.0
j)	p-ClC_6H_4	p-ClC_6H_4	B	95	113.0-114.0

* Numerical values in parentheses show yields of triphenylphosphine oxide.

It should be noted that extraordinarily rapid Wittig reaction was observed in both methods A and B as compared with usual reaction conditions.[6)] Moreover, B reacted with cycloalkanones, acetophenone, and even benzophenone at low temperature in contrast to 1,3-dithiacyclohexylidenetrimethoxyphosphorane which did not react with those ketones mentioned above by heating at 60°C for 24 hr.[7)]

The reason for rapid reaction can be ascribed at least to two factors, i.e., i) contribution of anti-aromaticity (8π electrons) to A and B, endorsing strong nucleophilicity and ii) contribution of pseudo-aromaticity (dithiolylium) to the product, lowering the energy of the transition state, because that of Wittig reaction has been shown to lie at the decomposition of the betaine.[8)]

The research on this subject is currently in progress.

Acknowledgement: We are grateful for partial support of this research to Grant-in aid (No. 164135) administered by Ministry of Education.

References and Notes

1) E. Campaigne and R. D. Hamilton, *J. Org. Chem.*, **29**, 1711 (1964).

2) K.-P. Zeller, H. Meier, and E. Müller, *Ann. Chem.*, **766**, 32 (1972);
W. Kirmse and L. Horner, *Ann. Chem.*, **614**, 4 (1958).

3) H. D. Hartzler, *J. Am. Chem. Soc.*, **93**, 4961 (1971).

4) M. G. Miles, J. S. Wager, J. D. Wilson, and A. R. Siedle, *J. Org. Chem.*, **40**, 2577 (1975). However, Scherowsky and Weiland [*Chem. Ber.*, **107**, 3155 (1974)] could not detect the same kind of phosphorane as ours (A) in desulfurization of 1,3-benzodithiole-2-thione with triethyl phosphite.

5) J. Nakayama, K. Fujiwara, and M. Hoshino, *Chem. Lett.*, **1975**, 1099.

6) A. Maercker, *Org. Reactions*, **14**, 270, John Wiley & Sons, Inc., N. Y., 1965.

7) E. J. Corey and G. Märkl, *Tetrahedron Lett.*, 1967, 3201;
F. A. Carey and J. R. Neergaard, *J. Org. Chem.*, **36**, 2731 (1971).

8) D. E. Bissing and A. J. Speziale, *J. Am. Chem. Soc.*, **87**, 2683 (1965);
A. J. Kirby and S. C. Warren, "*The Organic Chemistry of Phosphorus*", Reaction Mechanism in Organic Chemistry, Monograph 5, Elsevier Pub. Co., London, 1967.

9) All **2**, **3** and **4** gave correct elemental analysis and reasonable IR and NMR. All **4** showed parent peak as the base peak in MS, except **4a** (257, M^+-15) and **4e** (128, $M^{+}-$ ).
NMR ($CDCl_3$); **3a**: δ 3.63 (d, J_{POCH} = 10.4 Hz, 6H), 4.75 (d, J_{PCH} = 5.8 Hz, 1H), and 6.7-7.3 (m, 4H); **3b**: δ 1.23 (t, J = 6.9 Hz, 6H), 4.20 (dq, $J_{HH} \doteqdot J_{POCH}$ = 6.9 Hz, 4H), 4.92 (d, J_{PCH} = 5.4 Hz, 1H), and 6.9-7.4 (m, 4H).