

BENZYNE-INDUCED FRAGMENTATION REACTIONS OF 1,3-DITHIOLANES

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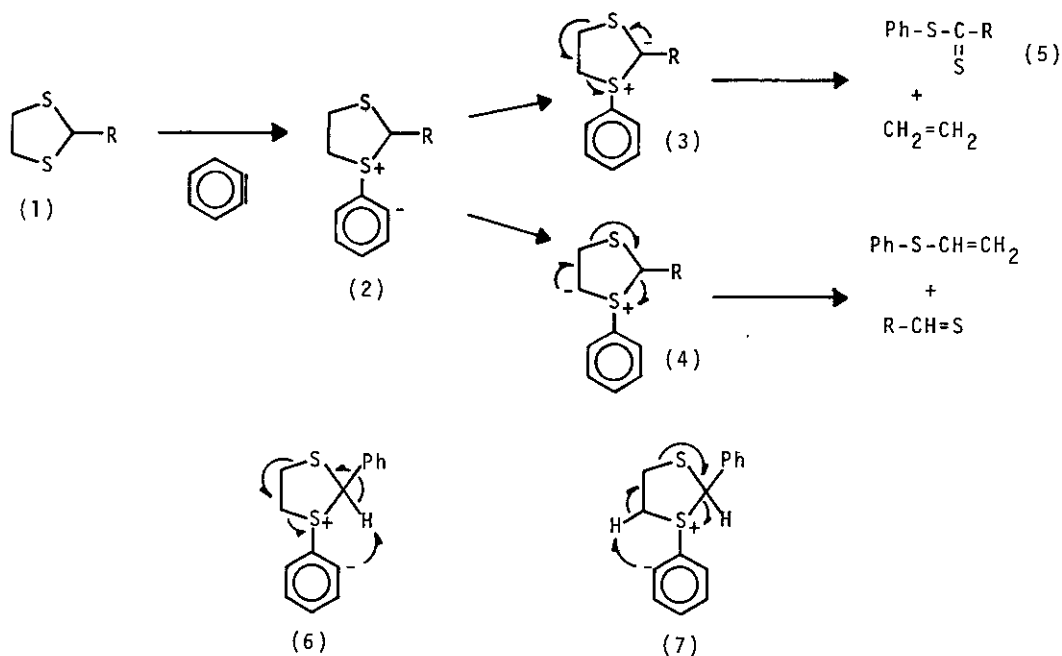
Abstract — 2-Monosubstituted 1,3-dithiolanes, on reaction with benzyne, undergo two types of fragmentation, one of which gives phenyl vinyl sulfide and thioaldehydes (corresponding aldehydes as the final products) and the other gives phenyl dithiocarboxylates and ethylene. Meanwhile, 2,2-disubstituted 1,3-dithiolanes undergo the sole fragmentation yielding phenyl vinyl sulfide and thioketones.

Recently, the base-promoted fragmentation of 1,3-dithiolanes, whose chemistry dates back to 1931,¹ has been extensively studied by two groups^{2,3} from both synthetic and mechanistic points of view. We report here the benzyne-induced fragmentation of 1,3-dithiolanes.

Benzyne is generated by heating 2-carboxybenzenediazonium chloride in boiling 1,2-dichloroethane in the presence of propylene oxide as hydrogen chloride scavenger.⁴ Thus, refluxing a mixture of 2-phenyl-1,3-dithiolane (1; R=Ph, 10 mmol), 2-carboxybenzenediazonium chloride (11 mmol), propylene oxide (3 ml) in 1,2-dichloroethane (100 ml) for 1 h afforded phenyl vinyl sulfide (17%), diphenyl sulfide (5%),⁵ phenyl dithiobenzoate (5; R=Ph, 23%), and a variable yield of benzaldehyde (5-20%) with 22% recovery of the starting dithiolane.

Reaction of benzyne with sulfides generally yields sulfonium ylides via the initial formation of betaine intermediates,⁶ and also a limited number of fragmentation reactions of cyclic sulfonium ylides are known.⁷ In the light of these facts, the present results may best be rationalized as follows. The betaine (2; R=Ph) produced from the dithiolane and benzyne gives ylides (3, R=Ph) and (4, R=Ph) competitively, and then the former ylide undergoes a novel fragmentation to give phenyl dithiobenzoate (5, R=Ph) and ethylene, while the latter ylide

undergoes one to give phenyl vinyl sulfide and thiobenzaldehyde (thiobenzaldehyde must be hydrolyzed to benzaldehyde under the conditions⁸). However, we cannot rule out the possibility that the fragmentation reactions occur directly from the betaine (2) via the transition state such as (6) and (7).



In a similar way, a variety of 2-substituted 1,3-dithiolanes (1) were allowed to react with benzyne. Phenyl dithiocarbonyl sulfides (5) and phenyl vinyl sulfide summarized in Table 1 were obtained in every case (in most cases the formation of the corresponding aldehydes was also observed). These results clearly show that

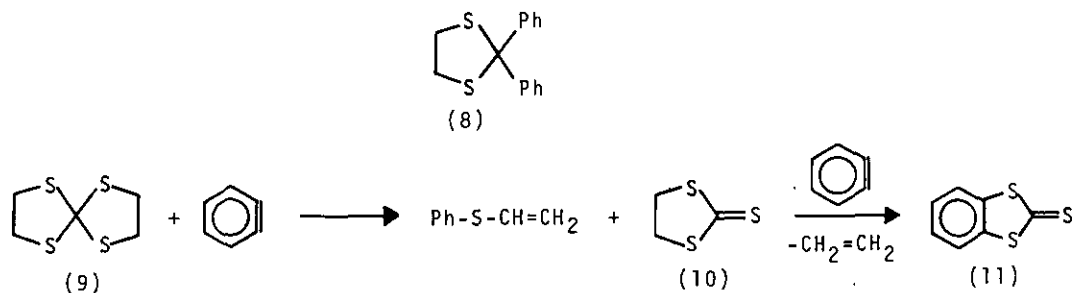
Table 1 Reaction of Benzyne with 2-Monosubstituted 1,3-Dithiolanes (1)

R	yield of (5, %)	mp of (5, °C)	yield of phenyl vinyl sulfide (%)	R	yield of (5, %)	mp of (5, °C)	yield of phenyl vinyl sulfide (%)
C ₆ H ₅	23	60-60.5	17	<i>o</i> -ClC ₆ H ₄	9	57	9
<i>p</i> -CH ₃ C ₆ H ₄	29	83-84	11	1-naphthyl	29	78.5-79	21
<i>p</i> -CH ₃ OC ₆ H ₄	34	82.5-83.5	15	2-thienyl	22	36-37	7
<i>p</i> -ClC ₆ H ₄	25	94-95	9	CH ₂ CH ₃	9	(70/0.2) ^a	39
<i>m</i> -ClC ₆ H ₄	23	48-50	9	CH ₂ CH ₂ CH ₃	9	(95/1.5) ^a	39

^a Boiling points (°C/mmHg; distillation with Kugelrohr).

the reaction is quite general and two types of fragmentation reactions are consistently operative. The reaction developed here also provides a method for preparation of (5) from aldehydes (all of (1) are easily prepared by condensation of aldehydes with 1,2-ethanedithiol in excellent yields).^{9,10}

2,2-Diphenyl-1,3-dithiolane (8) having no hydrogen at the 2-position, on reaction with benzyne, underwent the sole fragmentation to give phenyl vinyl sulfide (54%) and benzophenone (14%).^{8,11} Although no thiocarbonyl compounds could be isolated in the foregoing reactions, the reaction of the spiro-compound (9) with benzyne permitted isolation of ethylene trithiocarbonate (10, 15%) and 1,3-benzodithiole-2-thione (11, 5%) along with phenyl vinyl sulfide (36%) with 59% recovery of (9). It is known that benzyne reacts with (10) to give (11) with elimination of ethylene.¹²



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4. B. H. Klanderma and T. R. Criswell, J. Org. Chem., 1969, 34, 3426.
5. Separate experiment showed that diphenyl sulfide originates from reaction of phenyl vinyl sulfide with benzyne.
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7. E. Block, 'Reactions of Organosulfur Compounds,' Academic Press, New York, 1978, p. 117.
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11. It is known that thiobenzophenones react with an intermediate in benzyne formation from 2-carboxybenzenediazonium chloride (benzenediazonium-2-carboxylate) to give benzoxathianones; D. C. Dittmer and E. S. Whitman, J. Org. Chem., 1969, 34, 2004; H. Tokunaga, T. Kawashima, and N. Inamoto, Bull. Chem. Soc. Jpn., 1972, 45, 2220. No benzoxathianone was found in the product mixture in the present case.
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Received, 6th February, 1984