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CARBON-SULFUR BOND CLEAVAGE BY BENZYNE GENERATED FROM 2-CARBOXYBENZENEDIAZONIUM CHLORIDE

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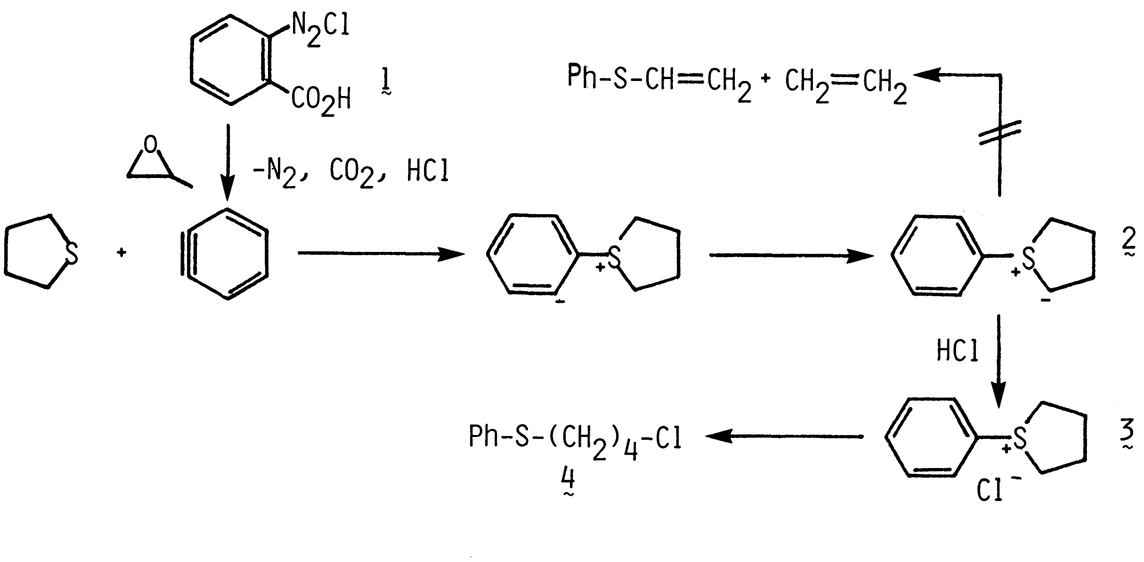
The reaction of cyclic sulfides with benzyne generated from 2-carboxybenzenediazonium chloride affords ω-chloroalkyl phenyl sulfides in good yields. A similar type of reaction was also observed with acyclic sulfides.

In our continuing interest in the fragmentation of the cyclic sulfonium ylides produced by the reaction of benzyne with cyclic sulfides,[1-3] we investigated the reaction of thiolane with benzyne generated from 2-carboxybenzenediazonium chloride (1).[4] In the light of our own results with 1,3-dithiolanes[2] and 1,3-oxathiolanes[3] and also the result of the reaction of tetrafluorobenzyne with thiolane,[5] the ylide 2 resulting from this reaction is expected to undergo the fragmentation leading to phenyl vinyl sulfide and ethylene. However, heating 1 (11 mmol) and thiolane (10 mmol) with propylene oxide (5 ml, HCl scavenger) in refluxing 1,2-dichloroethane (100 ml) for 45 min unexpectedly afforded 4-chlorobutyl phenyl sulfide (4) in 63% yield, no expected phenyl vinyl sulfide being formed. This indicates that the fragmentation of 2 is not so fast that 2 is captured by HCl produced from 1 despite the use of propylene oxide as the HCl scavenger, and the resulting sulfonium chloride 3 collapses to yield the final product 4. Heating 1 and thiolane in the absence of propylene oxide in refluxing 1,2-dichloroethane also gives 4 in 65% yield.[6]

In a similar way a series of cyclic and acyclic sulfides were allowed to react with benzyne generated from 1 in either the presence or absence of propylene oxide (Table 1). Thietane, thiolane, and thiane all react with benzyne generated from 1



to afford the corresponding ω-chloroalkyl phenyl sulfides in good yields regardless of the presence or absence of propylene oxide (Runs 1-6). Acyclic sulfides also undergo the same alteration (Runs 7-13). The use of **1** in excess (2.8 equiv.) cleaves the aliphatic carbon-sulfur bond exclusively to afford diphenyl sulfide and alkyl chlorides (Runs 11 and 12). In the reaction with benzyl cetyl sulfide, both the benzyl and cetyl carbon-sulfur bonds are cleaved, though the cleavage of the former bond predominates (Run 13). The only exception is observed in the reaction of bis(3-methyl-2-propenyl) sulfide, which provides the product derived from the rearrangement of the ylide intermediate in agreement with the reported result (Run 14).[7)]

We therefore conclude that, in case of the succeeding reactions (fragmentation, rearrangement, etc.) of the ylides being slow, they are captured by HCl produced from **1** to provide the sulfonium chlorides from which the final products are formed. The net result means that **1** acted on sulfides as a Ph^+Cl^- equivalent.

The couple of **1** and propylene oxide has been employed as one of the most convenient benzyne sources since 1965.[4)] However, the present result shows that propylene oxide does not operate as the HCl scavenger when more HCl-sensitive species is present. We must therefore keep this point in mind in using this couple as the benzyne source.

Table 1. Reaction of Cyclic and Acyclic Sulfides with Benzyne Generated from **1**[a)]

Run	Sulfides	Propylene oxide	Products (Yield/%)
1	thietane	with	$Ph\text{-}S\text{-}(CH_2)_3\text{-}Cl$ (70)
2	thietane	without	$Ph\text{-}S\text{-}(CH_2)_3\text{-}Cl$ (70)
3	thiolane	with	$Ph\text{-}S\text{-}(CH_2)_4\text{-}Cl$ (63)
4	thiolane	without	$Ph\text{-}S\text{-}(CH_2)_4\text{-}Cl$ (65)
5	thiane	with	$Ph\text{-}S\text{-}(CH_2)_5\text{-}Cl$ (79)
6	thiane	without	$Ph\text{-}S\text{-}(CH_2)_5\text{-}Cl$ (70)
7	$Ph\text{-}S\text{-}C_{16}H_{33}$	with	Ph-S-Ph (88), $C_{16}H_{33}Cl$ (85)
8	$Ph\text{-}S\text{-}C_{16}H_{33}$	without	Ph-S-Ph (93.5), $C_{16}H_{33}Cl$ (87.5)
9	$Ph\text{-}S\text{-}CH_2Ph$	with	Ph-S-Ph (94), $PhCH_2Cl$ (78)
10	$Ph\text{-}S\text{-}CH_2Ph$	without	Ph-S-Ph (85), $PhCH_2Cl$ (84)
11	$C_{16}H_{33}\text{-}S\text{-}C_{16}H_{33}$	with	Ph-S-Ph (93.5), $Ph\text{-}S\text{-}C_{16}H_{33}$ (6), $C_{16}H_{33}Cl$ (86)
12	$PhCH_2\text{-}S\text{-}CH_2Ph$	with	Ph-S-Ph (89), $PhCH_2Cl$ (65.5)
13	$PhCH_2\text{-}S\text{-}C_{16}H_{33}$	with	$PhSC_{16}H_{33}$ (74), $PhCH_2Cl$ (65), $PhSCH_2Ph$ (8), $C_{16}H_{33}Cl$ (11)
14	$S(CH_2\text{-}CH{=}CMe_2)_2$	with	$CH_2{=}CH\text{-}CMe_2\text{-}CH(SPh)\text{-}CH{=}CMe_2$ (50)

a) 1.1 Equiv. of **1** was used except Runs 11 and 12 where 2.8 equiv. of **1** was used. The solvent used is 1,2-dichloroethane except Run 12 where dichloromethane was used.

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