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SOMMELET REARRANGEMENT OF SULFONIUM SALTS

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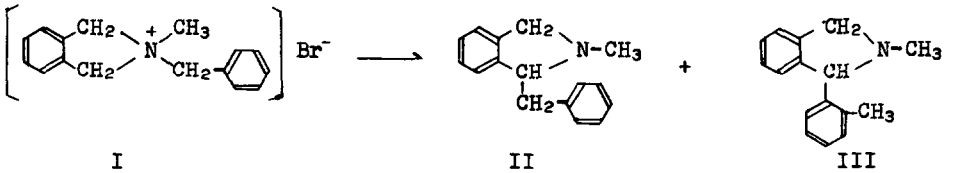
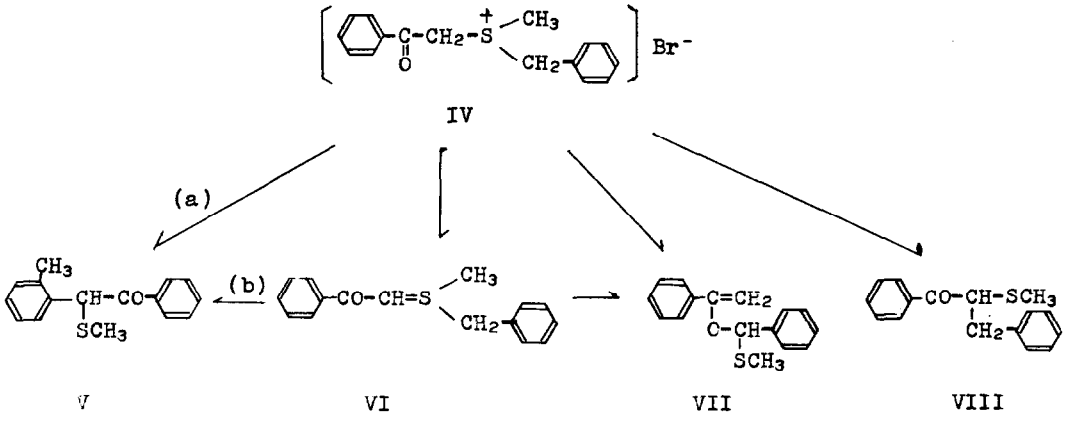
The Stevens and the Sommelet rearrangements of ammonium salts have been extensively studied. Wittig and Streib[1] found decreasing yields of Sommelet rearrangement product (III) and increasing yields of Stevens product (II) as the temperature increased, when the ammonium salt (I) was treated with bases. An interpretation is given for the temperature dependence of the product distribution.[2]



I II III

Similar rearrangements have been observed with sulfonium salts. Ratts and Yao[3] investigated the rearrangement of the sulfonium salt (IV) as a function of reaction conditions and base concentration[4].



IV

V VI VII VIII

The amount of base is one of the factors controlling whether the Stevens or the Sommelet rearrangement occurs in the reaction of tribenzylsulfonium salt[5].

The base concentration dependence of the product distribution, however, has

not been widely studied, therefore, we reexamined the reaction of I[1] and IV[3].

We found that in general these product distributions are dependent on concentration of base, however, independent on equivalent amounts of base. The results obtained are shown in TABLE 1 and 2 (the ratio of the products was determined by nmr analysis).

TABLE 1

The ratio of the products, II and III

Reaction condition	II	III
3% Na in ethanol at 80°C*	90	10
10% Na in ethanol at 80°C*	50	50
10% phenyl lithium in ether at 25-35°C	15	85

*The products were contaminated with unidentified materials.

TABLE 2

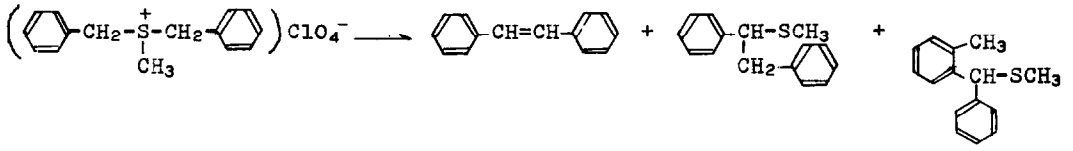
Yields(%) of the products, V and VII

Reaction condition*	V	VII
5% Na	3	78
10% Na	48	32
15% Na	69	trace

*IV was treated with ten equivalents of sodium methoxide in methanol at 60-65°C for 2hr.

It can be seen from TABLE 1 and 2 that base concentration is also one of the important factors for the products distribution. The salt IV gave pure sulfide V (bp 178°/6; sulfone, mp 137-139°C), when IV was treated with 35% sodium methoxide(=15% Na) in methanol at 60-65°C for 2hr (condition A). The ylide VI also gave V (30% yield) under the condition A.

The ratio of the Sommelet (XII : bp 148-149°C/6; sulfone, mp 94-96°C) to the Stevens (XI : bp 185°C/27; sulfone, mp 117-119°C) rearrangement product was increased as the concentration of base was raised, when the perchlorate (X)[9] was treated with sodium hydroxide aqueous solution.

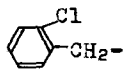
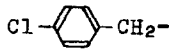
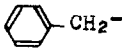
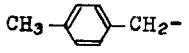
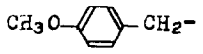
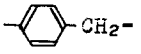


X XI XII

Aqueous solution of benzyldimethylsulfonium chloride (IX) gave increasing yields (from trace to 87% yield) of the Sommelet rearrangement product[6] and decreasing yields (from 100% yield to trace) of the benzyl alcohol[7] as the concentration of base was raised, when IX was treated with sodium hydroxide.

In the similar manner, sulfonium perchlorates gave substitution products and Sommelet rearrangement products, when perchlorates were treated with sodium methoxide. Some examples of the reactions are shown in TABLE 3.

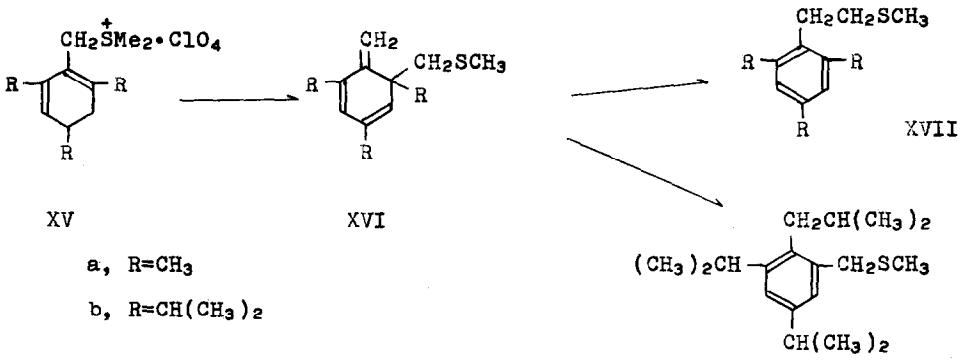
TABLE 3 Yields(%) of products

(R-SMe_2)X	X=ClO_4*		X=Cl**		
R-	$ROCH_3$	Rearr.***	ROH	R_2O	Rearr.***
	11	85	13	0	64
	29	56	4	7	70
	60	40	3	50	35
	82	15	11	36	33
	84	3	-	-	-
	only dinitrostilbene was isolated[8]				

*perchlorate was treated under the condition A.
**2.5M sulfonium chloride aqueous solution (0.1 mole) was treated with 30% sodium hydroxide aqueous solution (0.2 mole).
***Sommelet rearrangement product.

Pure Sommelet rearrangement products can be isolated from the reaction of IX or X and potassium tert-butoxide in tert-butanol.

When both ortho positions are occupied, sulfonium salts gave exo-methylene-cyclohexadiene derivatives (XVI) (90-95% yield) by the reaction of potassium tert-butoxide in tert-butanol. The cyclohexadienes undergo thermal isomerization to aromatic products as ammonium salts[10]. In the case of XVIb, main product (80% yield) was XVIII (bp 135-137°C/3; sulfone, mp 105-107°C), while XVIa gave XVIIa (bp 160-165°C/26; sulfone, mp 154-156°C).



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