

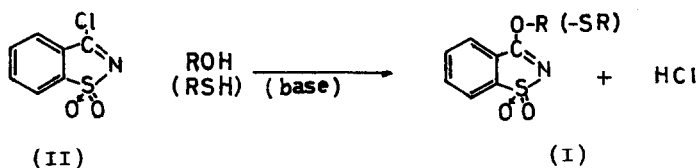
CHAPMAN-MUMM REARRANGEMENT OF PSEUDO-
SACCHARINETHERS ⁺

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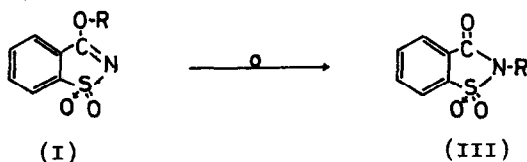
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Pseudosaccharinethers ^{1) 2)} (I) and thioethers ³⁾ are conveniently prepared from pseudosaccharinchloride (II) and the corresponding alcohols or thiols respectively ⁴⁾.



Compounds of type (I) can be cleaved by treatment with ammonia in an inert solvent (e.g. dioxane). We employed the reagent (II) for protecting the alcohol functions of various steroids, terpene alcohols and others. Examples are given in table 1. We noticed, that pseudosaccharinethers will rearrange on heating in a CHAPMAN-MUMM type reaction ^{5) 6)} to the corresponding N-substituted saccharine derivatives (III) in appreciable yields.

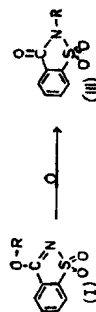


Very likely the reaction proceeds via a four center mechanism ⁵⁾. The same rearrangement under the conditions of electron impact seems to precede mass spectrometric fragmentation ⁷⁾. The CHAPMAN-MUMM rearrangement is apparently the main reaction in cases, where olefin formation via a six-membered cyclic mechanism ⁸⁾ is unfavourable for steric reasons.

Reactions of pseudosaccharinchloride (II) with salts of different acids produced the N-acylated derivatives of saccharin exclusively ^{9) 10)}. From

⁺ Reactions with pseudosaccharinchloride, Part V.

TABLE 1



Compound R	mp.	Temperature of Rearrangement	Compound after Rearrangement	mp.	analysis				
					% C	% H	% N	% S	
Ia 1) R = CH ₃ C ₈ H ₇ NO ₃ S	186°	190° (sealed tube)	IIIa yield: 92 %	132°	calcd. found Ia IIIa	48.77 48.76 48.50	3.58 3.60 3.48	7.11 6.90 7.01	16.26 16.04
Ib 1) R = C ₂ H ₅ C ₉ H ₉ NO ₃ S	219°	220°	IIIb	96°	calcd. found Ib IIIb	51.17 50.75 51.19	4.30 4.27 4.36	6.46 6.41	15.20 15.10
Ic R=menthyl (1-) C ₁₇ H ₂₃ NO ₃ S	124°	180° (sublimat. flask)	(elimination reaction)		calcd. found Ic	63.50 63.38	7.21 7.28	4.36 4.33	9.98 9.83
Id R=cholestryl C ₃₄ H ₄₉ NO ₃ S	208°	200° (sublimat. flask)	IIIc yield: 55 %	165- 167°	calcd. found Id IIIc	74.02 74.15 74.07	8.95 9.06 8.72	2.54 2.63 2.50	5.83 5.82 5.60
Ie R = CD ₃ C ₈ H ₄ D ₃ NO ₃ S	186°	197° (sealed tube)	IIIe yield: 88 %	133, 5°	calcd. found Ie IIIe	47.99 48.04	5.02 3.54	7.00 7.12 7.05	16.03 15.91 15.97
If R=α-pyridone C ₁₂ H ₈ N ₂ O ₃ S	183°				calcd. found If	55.38 55.27	3.10 3.50	10.76 10.59	
Ig SR=S-n-butyl C ₁₁ H ₁₃ NO ₂ S ₂	94°	no rearrangement			calcd. found Ig	51.75 51.64	5.13 5.28	5.48 5.48	25.12 24.98

the reaction of tetraalkylammoniumpicrate with pseudosaccharinchloride we obtained - among other products - the N-picryl derivative (mp. 263 - 264°, lit. cit. mp. 262° C) ¹¹⁾.

The reaction of pseudosaccharinchloride with α -pyridone yielded the pseudosaccharin- α -pyridoneether (table 1, substance If) as indicated by complete absence of a carbonyl group in the infrared. The rearrangement of pseudosaccharinethers (I) does not occur spontaneously. The substances were either heated above melting point in a sealed tube or in a sublimation flask at oil pump vacuum.

The reaction can be followed kinetically by high temperature NMR. The rearrangement of the N-methylether (c.f. subst. Ia ¹⁾ table 1) at 200° was practically complete after 70 minutes.

Only the pseudosaccharin-methylether (Ia) so far could be rearranged by treatment with lithiumiodide in acetone. On addition of ethyliodide to the same experiment N-methyl-ether and N-ethylether were formed side by side. N-substituted saccharine derivatives (III) can be considered as protected amines.

Pseudosaccharinchloride is capable of cleaving trialkylphosphites with formation of the corresponding pseudosaccharin alkylether. In addition trialkylphosphate was identified from the reaction by V.P.C., IR-spectroscopy and elemental analysis. All the products described were checked by IR, NMR and mass spectrometry. Purity was checked by thin layer chromatography or gas chromatography.

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