

## Letters to the Editor

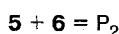
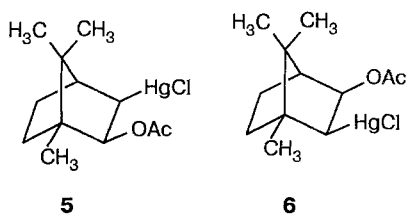
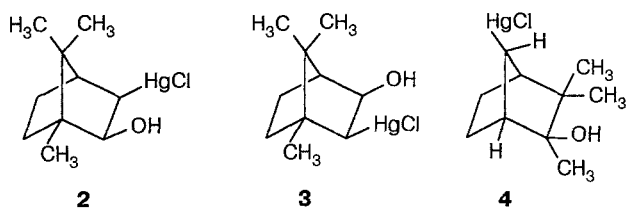
### Ion pairs and solvated ions in the reactions of mercury salts with alkenes

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The occurrence of salt effects in the solvomercuration of alkenes has been observed previously.<sup>1</sup> However, no special investigations of these effects have been performed.



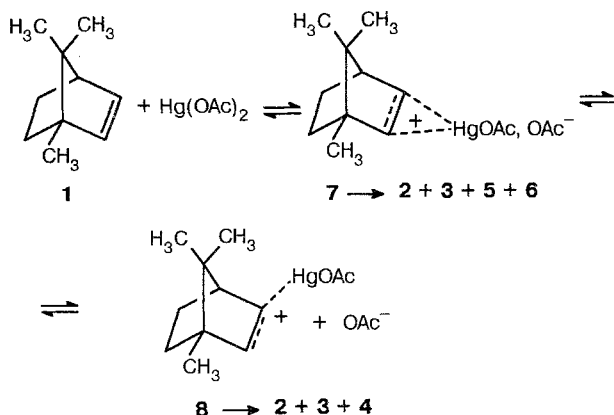
We studied the effect of CH<sub>3</sub>COONa on the reaction of bornylene (**1**) with Hg(OCOCH<sub>3</sub>)<sub>2</sub> with respect to the reaction rate and composition of the products (**2–6**).

It was found that even the addition of small amounts of CH<sub>3</sub>COONa strongly decreases the second-order reaction rate constant and very significantly alters the composition of the products. The presence of the additive results in a drastic decrease in the amount of the rearranged product (**4**) (from 17 to 3 %). Moreover, reversal of the regiochemistry of solvomercuration occurs, and adducts (**5**, **6**) are formed (Table 1).

**Table 1.** Effect of the addition of CH<sub>3</sub>COONa on the reaction rate and composition of products

[CH <sub>3</sub> COONa] /M	<i>k</i> · 10 <sup>2</sup> /L mol <sup>-1</sup> s <sup>-1</sup>	Yield (%)				
		P <sub>1</sub>	(2:3)	<b>4</b>	P <sub>2</sub>	(5:6)
0	3.65	83	(61:39)	17	0	—
0.001	1.00	60	(56:44)	10	30	(65:35)
0.005	0.53	45	(47:53)	6	49	(58:42)
0.01	0.40	41	(42:58)	5	54	(56:44)
0.015	0.33	38	(37:63)	6	56	(57:43)
0.100	—	34	(33:67)	3	63	(55:45)

The data obtained imply that the reaction proceeds *via* at least two intermediates (**7**, **8**). In the absence of salts, the products are predominantly formed from solvated ion **8**. In the presence of the salt, the products are probably formed from ion **8** and ion pair **7** due to the effect of the common ion.



If the maximum concentrations of the salt are used ( $\sim 0.015\text{ M}$ ), then the  $7 \rightleftharpoons 8$  equilibrium is shifted toward ion pair **7**, and the reaction rate constant no longer depends on the additive concentration. In this case, the reaction products are formed from ion pair **7**. The regiochemical data and the composition of the reaction products indicate that ion pair **7** has a more symmetric structure than ion **8**.

The reaction rate was determined from changes in the concentration of  $\text{Hg}(\text{OCOCH}_3)_2$  measured by the known procedure.<sup>2</sup> The composition of the reaction products after their demercuration with  $\text{NaBH}_4$  or sodium amalgam was analyzed by GLC.

## References

1. I. C. Ambidge, S. K. Dwight, C. M. Rynard, and T. T. Tidwell, *Can. J. Chem.*, 1977, **55**, 3086.
2. S. Fukuzumi and J. K. Kochi, *J. Am. Chem. Soc.*, 1981, **103**, 2783.

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## Interaction of 3-amino-2-carbamoyl-5,6-trimethylene- and 3-amino-2-carbamoyl-5,6-hexamethylenethieno[2,3-*b*]pyridines with acetic anhydride

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3-Amino-2-carbamoylthieno[2,3-*b*]pyridines substituted at the pyridine ring are used for synthesizing 4-oxopyrido[2',3':5,4]thieno[2,3-*d*]pyrimidines.<sup>1</sup>

We have found that the direction of the reaction of 5,6-polymethylene-3-amino-2-carbamoylthieno[2,3-*b*]pyridines with acetic anhydride depends on the size of the polymethylene cycle. Refluxing 3-amino-2-carbamoyl-5,6-hexamethylenethieno[2,3-*b*]pyridine (**1a**) with acetic anhydride results in 2-methyl-4-oxopyrido[2',3':5,4]thieno[2,3-*d*]pyrimidine (**2**), which exists in two tautomeric forms (**2a** and **2b**) in the ratio 2:1 (Scheme 1).

The reaction starting from 3-amino-2-carbamoyl-5,6-trimethylenethienopyridine (**1b**) proceeds in another direction and unexpectedly affords 3-acetylamino-2-cyanothieno[2,3-*b*]pyridine (**3**). The latter was also obtained by an independent synthesis from 3-amino-2-cyano-5,6-trimethylenethieno[2,3-*b*]pyridine (**4**). Obviously, the reaction follows this path due to increased strain in the thienopyridine unit, violation of the coplanar state of the aromatic thieno[2,3-*b*]pyridine bicycle, and a change in the electronic conjugation in the

