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ENHANCEMENT OF THE EFFICIENCY OF SILVER(I) PROMOTED REARRANGEMENTS IN MOLTEN EUTECTICS[1]

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The Ag^+ ion plays a special role in organic synthesis because of its ability to catalyze highly specific rearrangements of strained molecules.[2] Invariably, these processes are second-order reactions showing a kinetic dependence on the concentrations both of substrate and silver salt.[3,4] In those instances where isomerization is slow, common practice has been to employ several molar equivalents of silver salt, preferably in a polar, high boiling solvent system (e.g., water-dioxane combinations), sometimes with recourse to sealed tube conditions.[5,6] Although the Ag^+ can be recovered as silver chloride, such methodology is wasteful since the subsequent conversion of AgCl to usable $AgNO_3$ incurs losses, requires additional reagents, and is time consuming. In an effort to obviate the need for recycling while simultaneously enhancing the overall rates of the rearrangement reactions, we have developed new methodology involving the use of low melting silver salt eutectics as both reaction media and catalysts. The exceptional promise of our findings is described herein.

A search of the literature revealed that at least ten binary or ternary silver salt eutectics are available in the temperature range $82^\circ < \text{f.p.} < 193^\circ$ (Table I).[7] When fused, these salt mixtures are transformed into ionic liquids, the physicochemical properties of which are fully compatible with their intended application as solvents. Thus, such molten salts are not only completely dissociated into ions (although likely aggregated rather than randomly distributed) providing a previously unattainable concentration of Ag^+, but they also possess high thermal stability, low vapor pressure, low viscosity, and excellent thermal conductivity.[8] Moreover, the catalytic activity of these materials was expected to persist indefinitely. Finally, the resolidified melt was anticipated to be immiscible with the products of isomerization, which should accordingly be readily isolated.

Scrutiny of the results obtained with the $AgNO_3$:KNO_3:AgCl (59:38:3) eutectic mixture (number 3, Table I) shows the fused electrolyte procedure to be a decided improvement over existing methodology (Table II). In each example studied, the products were recovered quan-

Table I. Silver Salt Eutectic Data

		Salts			Mole fractions		
No.	Mp, ^{o}C	A	B	C	A	B	C
1	82.2	$AgNO_3$	$TlNO_3$	----	0.48	0.52	----
2	82.5	$AgNO_3$	$TlNO_3$	----	0.52	0.48	----
3	113	$AgNO_3$	KNO_3	AgCl	0.59	0.38	0.03
4	119	$AgNO_3$	KNO_3	AgBr	0.61	0.37	0.02
5	131	$AgNO_3$	KNO_3	----	0.62	0.38	----
6	158	$AgNO_3$	AgCl	AgBr	0.77	0.06	0.18
7	161	$AgNO_3$	AgBr	----	0.74	0.26	----
8	173	$AgNO_3$	$LiNO_3$	----	0.76	0.24	----
9	188	AgCl	TlCl	KCl	0.56	0.37	0.07
10	193	$AgNO_3$	AgCl	---	0.75	0.25	----

titatively. This feature is a direct consequence of the simple workup procedure which consists of crushing the cooled solid mass and extracting the snoutane isomer with an organic solvent (CH_2Cl_2 was most commonly employed). Except for the carbomethoxy norsnoutane example, the products were judged to be pure by ^{1}H NMR spectroscopy at this stage. Removal of the organic solvent in vacuo returns the eutectic for apparently indefinite re-use when light has been excluded.

Since much shorter reaction times are required, the yields for compounds with low stability are greatly improved. Perhaps of greater importance to the success of this molten salt methodology is a less obvious factor. When $AgNO_3$ and $AgClO_4$ are heated at elevated temperatures in protic or aprotic solvents for prolonged periods of time, these solutions *sometimes* develop an acidic nature for reasons which are not clearly understood.[9] When generated, these low levels of acidity can cause decomposition of the product and/or starting material. In the eutectic solvents, this complication has not been encountered.

Sublimation of more volatile substrates from the molten salt has been noted on occasion. Although we have not examined the suitability of lower melting eutectics to minimize the rate of volatilization, it has been found that merely conducting the rearrangement in a closed vessel with intermittent shaking obviates the minor difficulty.

In our experience, ionic liquids are the best solvents for effecting the isomerizations surveyed in Table II. The money- and time-saving features, as well as the almost trivial na-

Table II. Experimental Findings

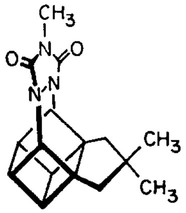
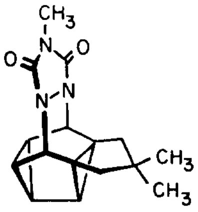
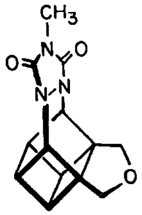
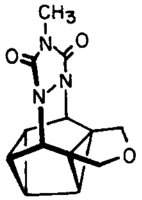
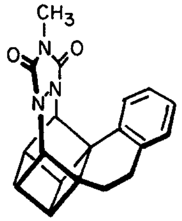
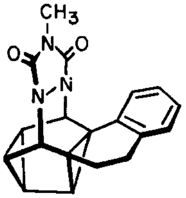
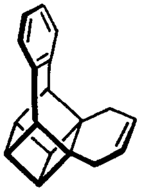
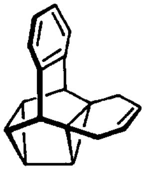
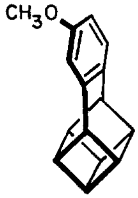
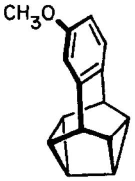
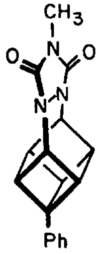
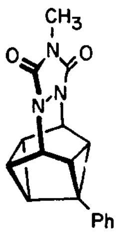
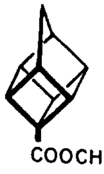
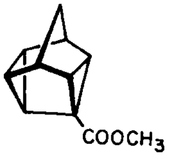
Starting material	Product	Conditions previously employed	Eutectic conditions[a]
		(a) 10 eq $AgClO_4$, C_6H_6, reflux, 3 days (0%)[b] (b) 5 eq $AgNO_3$, dioxane-H_2O (3:1), 130°, 84 hr (20% conversion)[b]	130°, 16 hr (100%)
		30 eq $AgNO_3$, dioxane-H_2O (4:1), 130°, 4 days (65%)[c]	150-160°, 3 hr (92-95%)
		30 eq $AgNO_3$, dioxane-H_2O (4:1), 130°, 36 hr (80%)[d]	130°, 5 hr (100%)
		6.5 eq $AgNO_3$, dioxane-H_2O, 60°, 12 hr (100%)[e]	130°, 45 min (100%)
		-----------	130°, 3 hr (100%)
		15 eq $AgNO_3$, methanol-H_2O (4:1), reflux, 20 hr (96%)[f]	130°, 4 hr (100%)

Table II (continued)

Starting material	Product	Conditions previously employed	Eutectic conditions[a]
		eq $AgClO_4$, C_6H_6, 123° 12 hr (55%)[g]	130°, 12 hr (75% conversion; all starting material recovered)

[a] The conditions employed consisted in mixing 6-10 parts of eutectic number 3 (Table I) with the starting material, with or without magnetic stirring. At no time was a two-phase system observed, although on occasion the melt took on a cloudy appearance. Since the eutectic components are essentially insoluble in methylene chloride, contamination of the final products with salt is not significant. [b] A. K. Sharma, unpublished work. [c] Reference 6a. [d] Reference 6b. [e] G. Kretschmer, unpublished work. [f] Reference 5a. [g] Reference 4b.

ture of the experimental procedure, argue additionally for broad application of this technique in the present and related applications.

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Footnotes and References

(1) Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. 36. For Part 35, see P. Bischof, R. Gleiter, R. T. Taylor, A. R. Browne, and L. A. Paquette, *J. Org. Chem.*, in press. Part 34 is R. T. Taylor and L. A. Paquette, *ibid.*, **43**, 242 (1978).

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