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Sequential Rearrangements via Bridged Carbocations

Sir:

Sequential rearrangements of alicyclic carbocations reveal structural and stereochemical preferences which were labeled "Memory Effects".[1] These phenomena were explained in terms of twisted ions separated by rotational barriers,[1] bridged ions (σ delocalization), and ion pairs.[2] Stereochemical control by ion pairing has been convincingly demonstrated,[2] but no unequivocal case of a sequential rearrangement via bridged ions appears to be known. We report here on sequential rearrangements involving phenonium ions.[3-5]

Scheme I

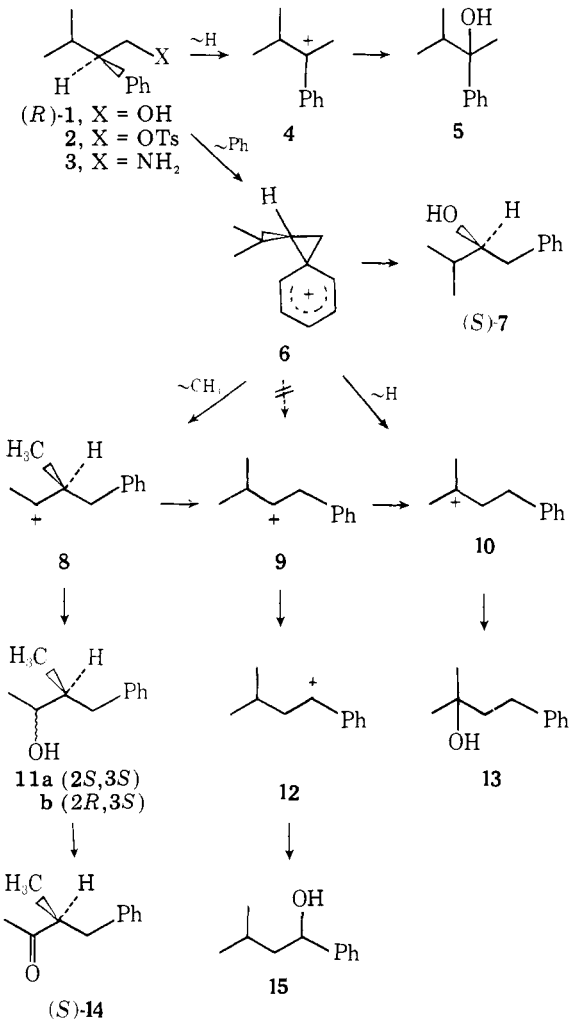
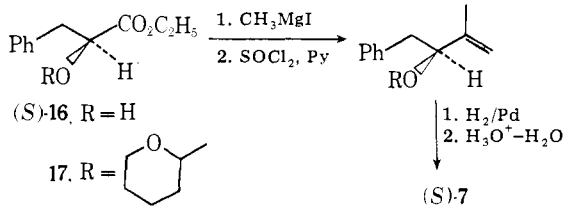


Table I. Products of the Solvolysis of **2** (Water–Dioxane, 4:1, 80 °C) and of the Deamination of **3** (0.03 M in $HClO_4$, pH 3.5, 25 °C)

	Alkenes	5	7	11a	11b	13	15	1
(*R*)-**2**	12.1	1.3	52.9	7.7	9.9	9.2		3.2
(*R*)-**3**	2.5	17.5	47.6	2.5	3.1	6.7	12.8	3.7
[2-^{2}H]-**3**	4.3	13.4	48.6	2.1	3.5	6.9	13.5	5.6

Scheme II



The tosylate **2** of (−)-(*R*)-3-methyl-2-phenyl-1-butanol[6] (**1**) was solvolyzed in aqueous dioxane at 80 °C in the presence of 2,6-lutidine (Scheme I, Table I). The major product, 3-methyl-1-phenyl-2-butanol (**7**), arises by a 1,2-phenyl shift. **7**, isolated from the solvolysis products by GLC, $[\alpha]^{24}_D$ −51.3° (*c* 1.95, CCl_4), was optically pure (±3%) as estimated by NMR in the presence of a chiral shift reagent[7] and by GLC of its *N*-trifluoroacetylprolyl ester.[9] The absolute configuration of (−)-**7** was established as *S* by correlation with (*S*)-2-hydroxy-3-phenylpropionic acid[10] as shown in Scheme II.[11] The complete inversion of configuration associated with the phenyl shift suggests formation of **7** from the phenonium ion **6** rather than from the open 3-methyl-1-phenyl-2-butyl cation **9**.

2-Methyl-4-phenyl-2-butanol (**13**), the product of a sequential Ph,H shift, was formed in the solvolysis of **2**, but 3-methyl-1-phenyl-1-butanol (**15**) was not obtained. The absence of **15** constitutes additional evidence against the open cation **9** which would be expected to undergo 1,2-H shifts to give **10** and **12** with comparable case. When **9** was generated by nitrous acid deamination of 1-benzyl-2-methylpropylamine, **13** and **15** were produced in a 2.3:1 ratio.

3-Methyl-4-phenyl-2-butanol (**11**) originates from **2** by a sequential Ph,CH_3 shift. The mixture of diastereoisomers **11a,b** was oxidized to give (+)-(*S*)-3-methyl-4-phenyl-2-butanone (**14**) of 83% optical purity. The configuration of **14** has been established by correlation with 2-methyl-3-phenylpropionic acid.[12] As some racemization was likely to occur during the oxidation of **11**, the enantiomeric purities of **11a** (95 ±3%) and **11b** (95 ± 3%) were determined by GLC of their (*S*)-2-acetoxypropionates.[13] The stereochemistry of the **2** → **11** transformation (displacement of phenyl by methyl with almost complete inversion) indicates that **11** arises via phenonium ion **6**, methyl acting as an internal nuclophile.[14]

The nitrous acid deamination[16] of **3** was studied for comparison with **2**. Again, **7**, $[\alpha]^{24}_D$ −52.0° (*c* 2.57, CCl_4), **11a** (enantiomeric purity by GLC, 98 ± 2%), and **11b** (enantiomeric purity, 99 ± 1%) were produced with complete inversion. The most significant feature distinguishing deamination from solvolysis is the formation of substantial quantities of **15**. The reaction path leading to **15** was explored with the aid of [2-^{2}H]-**3** (Scheme III). The label was completely recovered in fragment A (*m/e* 107) of **15**, establishing an isopropyl shift as the exclusive source of **15**. A sequential Ph,H shift involving the open cation **9** would have placed the label at C-2 of **15**.

$$Ph{=}{=}CH{=}{=}OH^+$$
A

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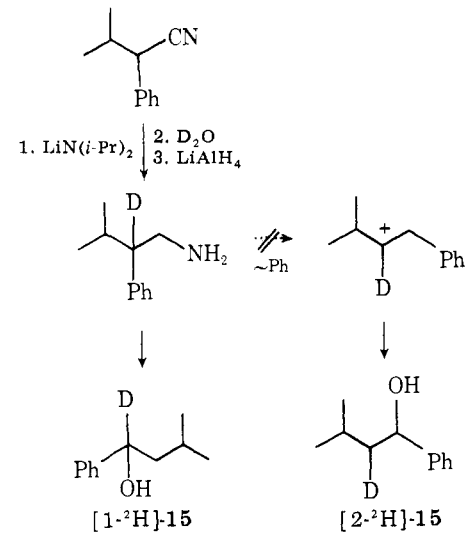
Scheme III



Both deamination and solvolysis induce sequential rearrangements which are regio- and stereospecific.[18] The widely different reaction conditions exclude ion pairing as a possible cause of the observed stereochemistry. Phenyl, isopropyl, and hydrogen shifts compete efficiently in the deamination of **3**, whereas the tosylate **2** reacts predominantly by phenyl migration. These variations conform with previous experience[19] and are readily understood in terms of an increased demand for anchimeric assistance in tosylate solvolysis.

Our results demonstrate that phenonium ions can undergo sequential rearrangements in competition with attack by external nucleophiles, although the driving force for such processes is not obvious. The regioselectivity of sequential rearrangements provides an additional criterion for distinguishing open and bridged ions.

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Lithium Ion Promotion in the Synthesis of Novel Dinuclear Iron–Carbyne Complexes

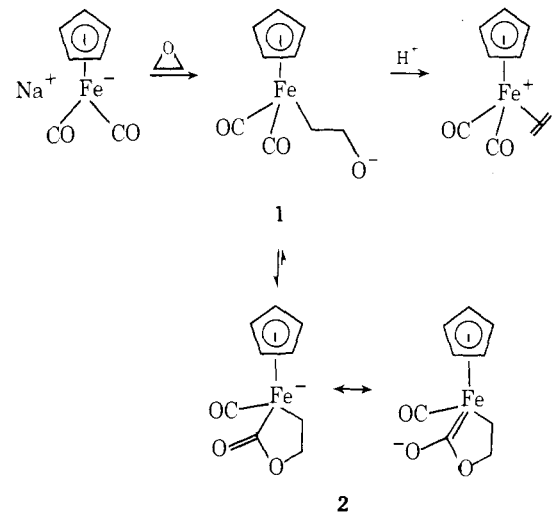
Sir:

The importance of ion pairing in intra- and intermolecular reactions of organometallic salts has recently been emphasized.[1] These interactions are now shown to play an important role in the synthesis of a new class of stereochemically dynamic binuclear iron–carbyne complexes.

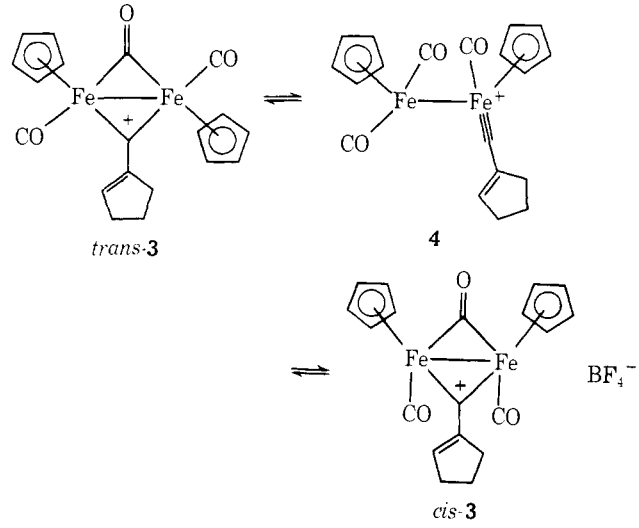
Earlier, we reported the conversion of epoxides to Fp(olefin) cations (Fp ≡ η^5-$C_5H_5Fe(CO)_2$) by the sequence outlined in Scheme I.[2] In these reactions, the anionic intermediate (**1**) has been shown to exist preferentially in the lactone form (**2**).[3]

The use of FpLi in place of FpNa in these reactions results in a marked increase in the rate of epoxide ring opening, but for acyclic epoxides the overall course of reaction is unchanged.[4] However, the behavior of cyclopentene oxide is

Scheme I



Scheme II



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