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A *para*-SOMMELET-HAUSER REARRANGEMENT[a]

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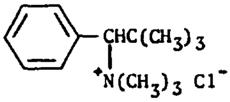
Renewed interest has recently been focused on the Stevens Rearrangement of Quaternary Ammonium Salts(1). In particular, the possibility of ion-pair involvement in the rearrangement mechanism has been proposed(2). Such a mechanism was initially proposed by Stevens(3) but disregarded in the intervening years(4). Cram(5) and Bumgardner(6) have proposed that the closely related Sommelet-Hauser *ortho* rearrangement(4a,7) of benzyl quaternary ammonium salts might also involve an ion-pair mechanism. However, the absence of any *para* rearrangement has recently been used as an argument against ion-pair involvement in the latter rearrangement(8). In the following we report the observation of such a *para* rearrangement.

When N,N,N-trimethyl-α-phenylneopentyl ammonium chloride(I) is allowed to react with



(I)

a variety of bases under numerous reaction conditions *p*-dimethylaminomethylneopentyl benzene (V) is found in the basic products in yields of 0-9% (see Table I). Control runs have demonstrated that this product does not come from further rearrangement of the *ortho*

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TABLE I

para-Rearrangement of N,N,N-Trimethyl-α-Phenylneopentyl Ammonium Chloride at 87-90°C.

	Base	Solvent	base/subst.	t(hrs.)	% V	% decomp.**
1	$NaNH_2$	NH_3 (ℓ)*	2.1	6	0.8	75
2	KOMe	MeOH	1.2	41	0	10
3	t-butOK	t-butOH	1.6	43	0.5	70
4	t-butOK	DMSO	1.1	41	3	75
5	t-butOK	$c\text{-}C_6H_{10}$	1.1	50	9	50
6	n-but Li	$n\text{-}C_6H_{14}$	4.6	43	8	--

* -33°C
**Percent decomposition of the quaternary ammonium salt

rearrangement product or the other basic products. (The major products of the reactions are N,N-dimethyl-α-phenylneopentylamine, o-dimethylaminomethylneopentylbenzene, and α-dimethylaminomethylneopentylbenzene. The marked dependence of product ratios on reaction conditions will be considered in a full report of this work.)

We believe that this represents the first example of a para-Sommelet-Hauser Rearrangement of a quaternary ammonium salt[b]. Molecular models indicate that the S_ni' mechanism proposed for the ortho rearrangement(4a) cannot operate in this system and suggest that an ion pair intermediate (III) may be involved. Both the immonium cation and the benzyl anion are expected to be reasonable intermediates in this system. The isolation of neopentylbenzene(IV) from the non-basic reaction product is consistent with this mechanistic picture.

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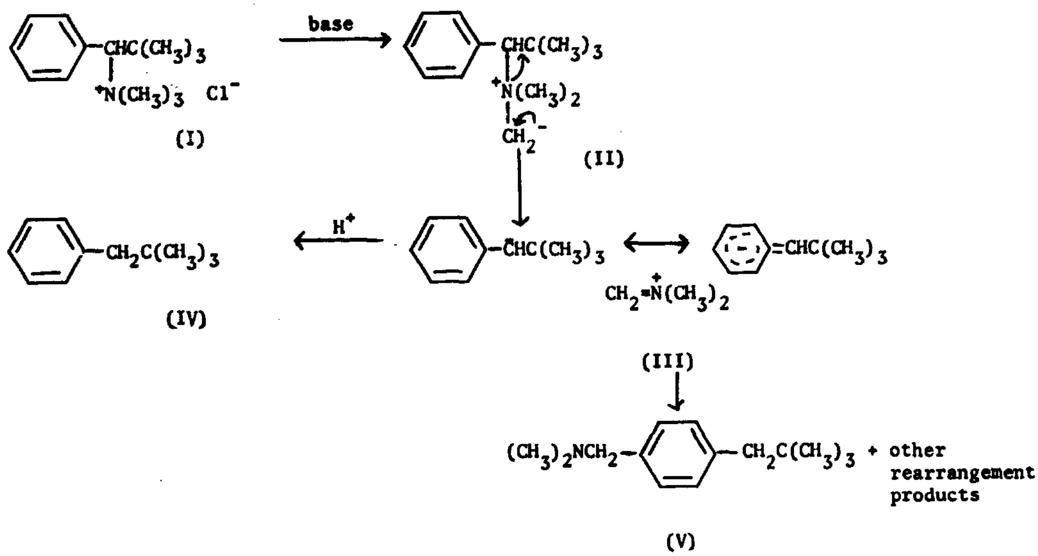
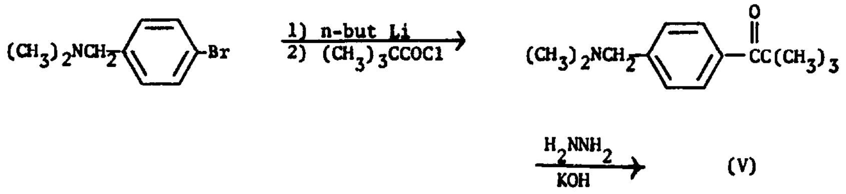
b) Recently, the possibility that a related para rearrangement might proceed via a sulfonium salt has been suggested(9).



A previous attempt to support an ion-pair mechanism by trapping the intermediate was unsuccessful(8) and our preliminary investigations have been similar. However, we do not believe that these results eliminate such an ion-pair intermediate (III). A tight ion-pair which leads to intramolecular rearrangement products or, collapses with solvent without returning to the ion-pair would be consistent with the data. The data of Table I also suggest that (V) is favored in less polar solvents. As the solvent polarity increased ion-pair separation and collapse with solvent or base leads to relatively lower yields of (V).

The structure of (V) was established by its nuclear magnetic resonance spectrum [singlets at 0.9 p.p.m. (9), 2.2 p.p.m. (6), 2.5 p.p.m. (2), and 3.4 p.p.m. (2); and an AA'BB' quartet at 7.0-7.4 p.p.m. (4)--all chemical shifts are downfield from internal T.M.S.], infrared spectrum (typical para-substitution pattern in the region 1600-2000 cm^{-1})(10), and ultraviolet spectrum [typical benzenoid absorption 251-268 mμ: λ_{max}256 (ε=437-Ethanol)]. In addition, (V) was synthesized by a Wurtz-Fittig reaction of *p*-chloro-N,N-dimethylbenzylamine and neopentyl chloride, as well as the scheme indicated below. The spectral properties and gas chromatography retention time of the synthesized material were identical with



the rearrangement product.

N,N,N-trimethyl-α-phenylneopentyl ammonium chloride (I) was prepared from α-phenylneopentylamine(11) by Eschweiler-Clarke methylation(12) followed by methyl iodide quaternization and silver chloride halide exchange. Recrystallization from abs. ethanol-ethyl ether gave white crystals, m.p. 205°C d. (uncor.). The nuclear magnetic resonance spectrum showed singlets at 1.3 p.p.m. (9), 3.5 p.p.m. (9), 5.4 p.p.m. (1) and a broad multiplet at 7.2-7.9 p.p.m. (5).

All compounds involved in these studies had satisfactory C, H, and N analysis.

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