HYDROXIDE ION INITIATED REACTIONS IN PHASE TRANSFER CATALYSIS . I. ISOMERIZATION OF ALLYLBENZENE. Marc Halpern, Minda Yonowich-Weiss, Yoel Sasson and Mordecai Rabinovitz* Department of Organic Chemistry, Institute of Chemistry and Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem,

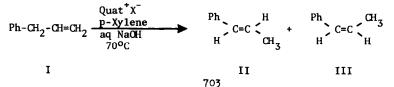
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<u>Abstract</u>: Allylbenzene ($pK_a^{\mathcal{X}}$ 34) was isomerized to trans and cis β -methylstyrene under phase transfer catalysis conditions. Several half lives of this reaction were measured under various conditions.

Phase transfer catalysis has been established as a widespread synthetic technique¹. Hydroxide ion initiated reactions (alkylations, carbene additions, deuterium exchange, etc.) performed under PTC conditions provide unique advantages in the laboratory and in industry^{2,3}. It is therefore surprising that no systematic study of the various factors involved in such reactions has been published in light of the known anomalous behavior of PTC systems involving the hydroxide ion, e.g. the success of TEBA (triethylbenzyl ammonium chloride) in such reactions⁴ vs. the failure of TEBA in S_N² reactions involving softer anions⁵. In addition, prior to this report, no anionic reaction induced by the hydroxide ion under PTC conditions of a substrate of pK_a greater than 23 (fluorene) has been reported⁶.

We wish to report the successful isomerization of allylbenzene (I) $(pK_a^{3} 34)^7$ to <u>trans</u>-(II) and <u>cis</u>-(III) β -methyl styrene by the hydroxide ion under liquid-liquid PTC conditions, and we wish to present some kinetic data of this reaction.

Allylbenzene (500 µl) was mixed with a solution of 5 mol % PT catalyst in p-xylene (2.00 ml). Aqueous NaOH was introduced into the system preheated to 70° C and magnetically stirred in a multireaction Pierce magnetic stirring/heating unit. The conversion of allylbenzene to <u>trans</u>- and <u>cis</u>- β -methyl styrene was followed by GC analysis. The results are summarized in the Table.



| Quat | Counterion | [NaOH] | t ₁ (min) ^a |
|-------------------------|-----------------|--------|-----------------------------------|
| Adogen 464 ^b | C1 ⁻ | 50% | 12 |
| Adogen 464 | C1 ⁻ | 40% | 53 |
| тна ^с | Br | 50% | 66 |
| TPA ^d | Br ⁻ | 50% | 82 |

Table: CONDITIONS AND RESULTS OF THE ISOMERIZATION OF ALLYLBENZENE

(a) reactions were carried out to at least 98% conversion;(b) tri-caprylmethylammonium;(c) tetrahexylammonium;(d) tetrapentylammonium.

The marked increase of the half life of the reaction by a factor of 4.5 when decreasing the hydroxide ion concentration by 20% indicates that no simple extraction constant governs the behavior of the system. This enhanced reactivity may be due to a combination of two factors: (1) a large salting out effect of the quat into the organic phase at high aqueous phase ionic strength, (2) decreased hydration of the attacking hydroxide ion due to the reduced availability of water molecules to accompany the hydroxide ion into the organic phase.

At constant hydroxide ion concentration in systems containing the same counterion, homologous quats (THA and TPA) probably demonstrate behavior consistent with their relative extraction constants.

Further investigation of hydroxide ion initiated reactions under PTC conditions is being carried out.

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