

Friedel-Crafts Rearrangements of 1,2-Diarylethanes*

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The transalkylation of 2-arylethyltoluenes (intermolecular shift of 2-arylethyl groups) in benzene or toluene with $\text{AlBr}_3 \cdot \text{HBr}$ has been shown to proceed by a mechanism involving the hydride abstraction in the side chain. Under these conditions, 1,2-diphenyl-1-*o*-tolylethane in benzene was converted immediately to 1,1,2-triphenylethane, which was then cleaved gradually to 1,2-diphenylethane with a minor amount of diphenylmethane. This observation provides strong support for the above mechanism.

In a series of investigation on the Friedel-Crafts reaction, we have studied the $\text{AlBr}_3 \cdot \text{HBr}$ -induced rearrangement reactions of 1,2-diarylethanes (2-arylethyltoluenes) in benzene or toluene solution at 50°C.^{1,2)} When an isomer of 1,2-ditolylethanes (DTE) was treated in toluene, the composition of the isomers changed with time and after a period the equilibrium was reached (Fig. 1). Further, 1,2-diphenylethane (DPE) in toluene was slowly converted to 1-phenyl-2-tolylethanes (PTE) and DTE in the several constant distribution ratios of the

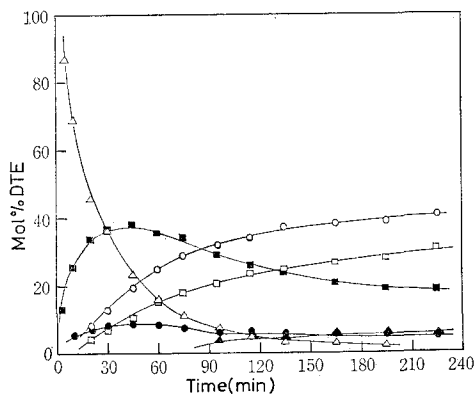


Fig. 1. Isomerization of 1,2-di-*o*-tolylethane in toluene at 50°C: Initial concentrations of reactants, $[o, o' \text{-DTE}] = [\text{AlBr}_3] = 0.08 \text{ mol/l}$; equilibrium isomer mixture contains about 42% *m, m'*- (○), 35% *m, p'*- (□), 12% *o, m'*- (■), 7% *p, p'*- (▲), and 4% *o, p'*-DTE (●) together with a trace of *o, o'*-isomer (△).

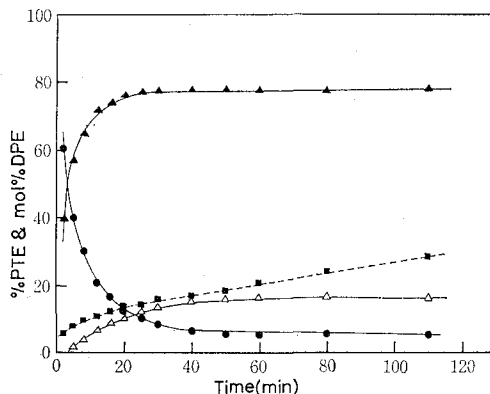


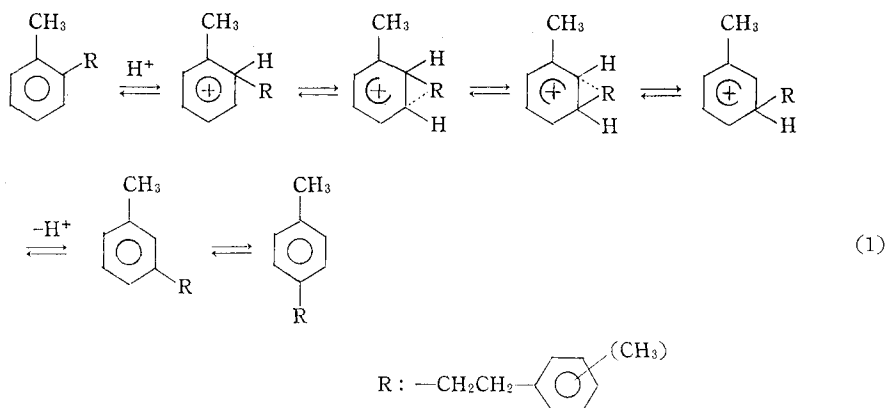
Fig. 2. Rearrangement of 1-phenyl-2-*o*-tolylethane in benzene at 50°C: Initial concentrations of reactants, $[o \text{-PTE}] = [\text{AlBr}_3] = 0.08 \text{ mol/l}$; isomer distribution is normalized for PTE, *o*- (●), *m*- (▲), and *p*-PTE (△); transalkylated product, DPE (■), is given in mole %.

* A part of this work was previously reported: Refs. 1 and 2.

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isomers. When the reaction was started from any of PTE isomers in benzene, initially the PTE isomer mixture attained the constant distribution, and then DPE produced by the accompanying transalkylation of the 2-phenylethyl group to benzene increased gradually (Fig. 2). Under the same conditions, PTE in toluene were transalkylated to DTE as slowly as in benzene, showing the several constant distributions of the isomers of PTE and DTE.

On the basis of these results, it was concluded that the positional isomerization of 2-arylethyltoluenes proceeded mainly by an intramolecular 1,2-shift³⁾ of 2-arylethyl groups (Eq. 1) which was much faster than an intermolecular



mechanism. Further, a carbonium ion chain alkylation-dealkylation mechanism⁴⁾ was preferred for transalkylation (intermolecular alkyl group transfer), since a displacement ($\text{S}_{\text{N}}2$ -type) mechanism⁵⁾ could not explain why the transalky-

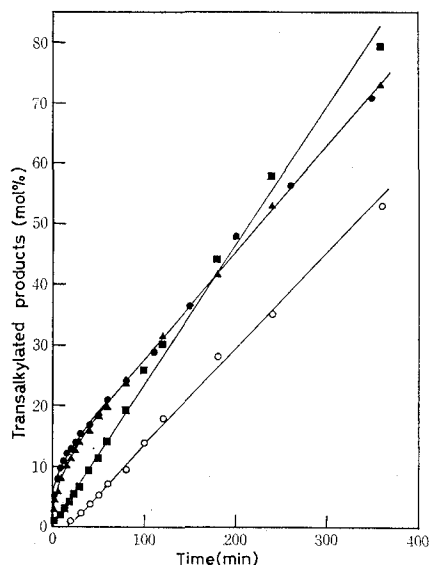
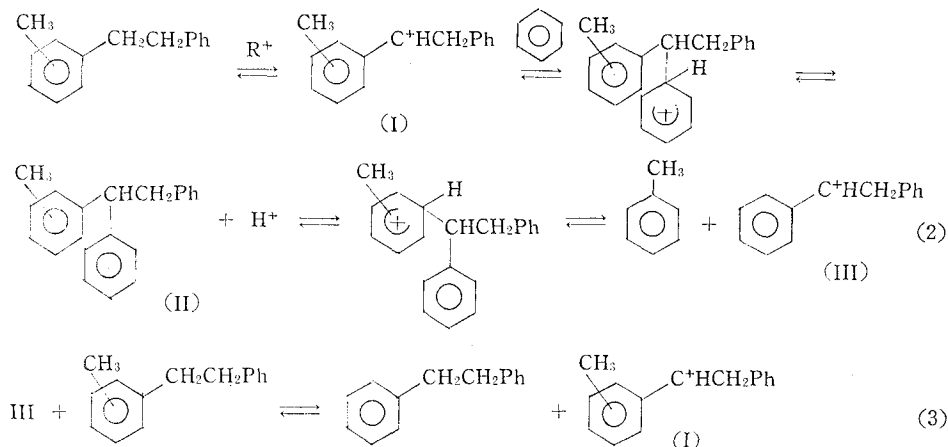


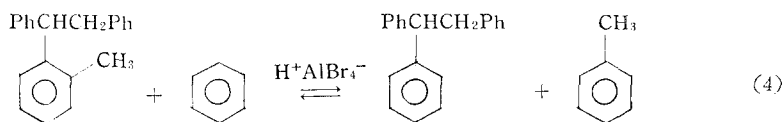
Fig. 3. Transalkylation of PTE in benzene or toluene at 50°C: Transalkylated products; DPE from *o*- (●), *m*- (■), or *p*- (▲) PTE in benzene; DTE from *o*-PTE (○) in toluene.

lation showed the zero-order dependence on the concentration of the reactant as shown in Fig. 3.²⁾ The intermolecular rearrangement mechanism for the reaction of PTE in benzene is illustrated in Eqs. 2 and 3. In this mechanism, the hydride abstraction at the α -position of the side chain initiates the carbonium ion chain process. The resulting cation (I) reacts with benzene to form 1,1,2-triaryl-



ethane (II), which undergoes rapid breakdown by acid to toluene and a cation (III) similar to I. The hydride transfer between III and another molecule of PTE regenerates I. The rate of this chain reaction depends on the steady state concentration of the arylalkyl cation such as I or III. Hence, the transalkylation proceeds at a constant rate after the constant distribution of PTE isomers is attained. This mechanism led us to inquire as to whether the intermediate (II) reacted rapidly under the experimental conditions.

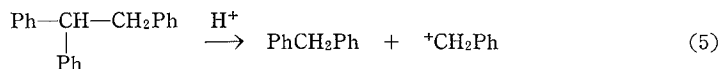
In order to clarify this point, a solution of 1,2-diphenyl-1-*o*-tolylethane in benzene was treated with aluminum bromide and hydrogen bromide at 50°C. Aliquots were periodically taken out from the reaction mixture and analyzed by gas chromatography. Even when the first aliquot was withdrawn, *i.e.*, as early as 30 seconds after initiation, the diphenyltolylethane was converted completely to 1,1,2-triphenylethane (TPE) and toluene together with a minor amount of DPE. No starting material was found. The amount of DPE increased gradually in the course of the reaction. Therefore, the following reaction is considered to



be much faster than the transalkylation of PTE in benzene. Streitwieser and Downs have already demonstrated that 1,1-di-*p*-tolylethane in benzene containing gallium bromide and hydrogen bromide is converted immediately to 1,1-diphenylethane and toluene.⁶⁾ It has been also reported that 1,1,2-triarylethane or 1,1,2,2-tetraarylethane in benzene yields DPE by the action of $\text{AlCl}_3 \cdot \text{HCl}$.⁷⁾ Thus for the proposed mechanism the exchange of the aromatic rings constitutes a necessary reaction sequence.

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Small amounts of other products were also detected by gas chromatography, among which only diphenylmethane (DPM) was formed in quantities enough to be identified. The amount of DPM increased with reaction time. This probably arises from the fragmentation⁸⁾ of TPE. A small quantity of DPM was also



found in the reaction mixture of the rearrangement of PTE in benzene.²⁾ The identification of DPM in both reactions adds strong support for the suggestion that the transalkylation process involves the *gem*-diarylethane-type intermediate, since the formation of DPM is not explicable by the S_N2-type mechanism.

In conclusion, the transalkylation of 2-arylethyltoluenes in aromatic hydrocarbon solvents is considered to proceed by the mechanism which involves the hydride transfer.

EXPERIMENTAL

Diphenylmethane⁹⁾ and 1,1,2-triphenylethane^{10,11)} were prepared as described in the literatures. 1,2-Diphenyl-1-*o*-tolylethane (mp 61–2°C from petroleum ether) was obtained by hydrogenation¹¹⁾ of 1,2-diphenyl-1-*o*-tolylethylene (mp 74.5–75.0°C from petroleum ether) which was prepared according to the procedure similar to those of Adkins and Zartman.¹⁰⁾ The structure of these compounds was checked by spectroscopic methods (IR spectra with a Hitachi EPI-S2 Spectrophotometer and NMR spectra with a Varian T-60 Spectrometer). The preparation and the purification of other materials were mentioned previously.^{1,2)} The experiment was carried out in the same equipment and in the same manner as the earlier studies. To a 200-ml. flask was added 50 ml. of benzene solution containing 2.13 g. (0.008 mole) of aluminum bromide. The flask was then placed into a constant temperature bath (50±0.1°C). Through the stirred solution, hydrogen bromide was passed for saturation. To this solution was added 50 ml. of benzene solution containing 2.18 g. (0.008 mole) of 1,2-diphenyl-1-*o*-tolylethane. At specific times, 4-ml. portions of the reaction mixture were withdrawn. Each sample was quenched with ice-water and the organic layer was separated, dried over anhydrous sodium sulfate, and examined by gas chromatography (with a Hitachi Perkin-Elmer model F6 gas chromatograph). A Z-45 Golay capillary column (coated with SE-30 silicone oil gumrubber) was used with a hydrogen flame ionization detector. For lower boiling products, a BDS-90 Golay column was also employed.

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