

Friedel-Crafts Aralkylation III.* The Reaction of Benzene with 2-Phenylethyl-1,1-d₂ and 2-(*p*-Chlorophenyl)-ethyl-1,1-d₂ chlorides

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The $\text{AlCl}_3\cdot\text{CH}_3\text{NO}_2$ -catalyzed phenethylation of benzene with 2-phenylethyl-1,1-d₂ and 2-(*p*-chlorophenyl)-ethyl-1,1-d₂ chlorides in nitromethane solution has been investigated. In the unreacted chlorides, 1,2-aryl migration was observed and the amounts of 2-arylethyl-2,2-d₂ chlorides formed increased with reaction time. The same extent of the migration was also observed in absence of benzene.

McMahon *et al.*¹⁾ found that the Friedel-Crafts reaction of toluene with 2-phenylethyl-1-C¹⁴ chloride gave β -tolylethylbenzene in which about 52% of the carbon-14 was contained in the α -position, while the chloride recovered had no isotope position rearrangement, and proposed a mechanism involving a stabilized phenonium type intermediate. One of the authors^{2,3)} has proposed a displacement mechanism not involving the phenonium ion intermediate on the basis of the kinetic study of the $\text{AlCl}_3\cdot\text{CH}_3\text{NO}_2$ -catalyzed phenethylation of benzene and toluene with 2-arylethyl chlorides in nitromethane solution, in which the linear relationships with Hammett's σ was obtained but not with Brown's σ^+ constants. However, aryl migration from 2- to 1-carbon atom via the phenonium ion may occur independently of the phenethylation.

In order to clarify this point, we carried out a study of the reaction of 2-phenylethyl-1,1-d₂ and 2-(*p*-chlorophenyl)-ethyl-1,1-d₂ chlorides with benzene in nitromethane solution at 50°C. Aluminum chloride dissolved in the solvent was used as the catalyst. In both cases, the mole ratio of benzene: $\text{ArCH}_2\text{CD}_2\text{Cl}$: AlCl_3 in the solution was 11.4 : 1 : 1. The 2-arylethyl chloride recovered was analyzed by NMR spectroscopy.

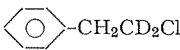
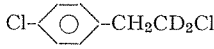
The NMR spectra of the 2-arylethyl chloride recovered showed a significant absorption (δ , 3.6, singlet) in addition to that (δ , 3.03, singlet) for 2-protons of 1,1-d₂ chloride. If only one deuterium at 1-position was replaced by hydrogen, the spin-spin splitting would be observed. However, the aliphatic protons always appeared as singlets. Hence the absorption is attributable to 1-protons of 2-arylethyl-2,2-d₂ chloride (see Experimental part), indicating that the aryl group migrates from 2- to 1-position to some extent. The amounts of 2,2-d₂ chlorides contained in the recovered chlorides are summarized in Table I. They increased gradually with reaction time. Further, when 2-phenylethyl-1,1-d₂ chloride was treated under the same conditions as those of the phenethylation except

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Table 1. The Extent of 1,2-Aryl Migration in the Recovered 2-Arylethyl Chloride (50°C)

Starting material	Rearranged chloride %	Reaction time (hrs.)
	16	1
	21*	2*
	24	2
	28	3
	7	2
	8	3
	10	4.5

* In the absence of benzene.

without benzene, the same extent of the migration was also observed. The present study is not entirely conclusive since the extent of 1,2-aryl migration in the product can not be determined yet. However, the above observations could be explained also by the consideration that the phenethylation and the migration would occur independently, that is, they have no common intermediate in the rate-determining steps.

EXPERIMENTAL **

Benzene, nitromethane, and 2-phenylethyl chloride were purified as described previously.²⁾ The preparation of 2-(*p*-chlorophenyl)-ethyl chloride was also reported.²⁾ Lithium aluminum deuteride was obtained from Merck Co. Aluminum chloride was sublimed before use. 2-Phenylethanol-1,1-d₂ was prepared by treating ethyl phenylacetate with lithium aluminum deuteride in diethyl ether, b.p. 109–10°C/18 mmHg, NMR, δ 2.83 ppm (2H, s).⁴⁾ In the same manner, 2-(*p*-chlorophenyl)-ethanol-1,1-d₂ was prepared from ethyl *p*-chlorophenylacetate, b.p. 139°C/18 mmHg, NMR, δ 2.81 ppm (2H, s). The alcohols thus obtained were converted to the corresponding chlorides by treatment with thionyl chloride. 2-Phenylethyl-1,1-d₂ chloride, b.p. 85–6°C/23 mmHg, NMR, δ 3.03 ppm (2H, s). 2-(*p*-Chlorophenyl)-ethyl-1,1-d₂ chloride, b.p. 115–6°C/24 mmHg, NMR, δ 3.01 ppm (2H, s).

The procedures of phenethylation were almost identical with those of the previous investigations. Parts of the reaction mixture were withdrawn periodically. Each part was quenched with ice-water, extracted with ether, and the upper layer was separated. Then the unreacted 2-arylethyl chloride was obtained by distillation under reduced pressure. The purity of the recovered chloride was checked by gas chromatography and then analyzed by NMR spectroscopy using a Varian T-60 Spectrometer. The NMR spectrum of recovered 2-phenylethyl chloride showed two resonance peaks at 3.03(s) and 3.65 ppm(s). The latter peak was attributable to 1,1-2H of 2-phenylethyl-2,2-d₂

** All of the boiling points are uncorrected. The NMR spectra were measured in CDCl₃, using tetramethylsilane as an internal standard.

Table 2. NMR Spectra of 2-Arylethyl Chlorides (in CDCl_3)

2-Arylethyl chloride	Chemical shift, δ (ppm)	
	1-position	2-position
 -CH ₂ CD ₂ Cl	—	3.03 (s)
 -CH ₂ CH ₂ Cl	3.65 (t)	3.02 (t)
Cl-  -CH ₂ CD ₂ Cl	—	3.01 (s)
Cl-  -CH ₂ CH ₂ Cl	3.63 (t)	3.00 (t)

chloride. For 2-(p-chlorophenyl)-ethyl chloride, the absorption at 3.62 ppm(s) was assigned to 1,1-protons of 2,2-d₂ chloride. The absorption data for 1- and 2-protons are summarized in Table 2. The amount of the rearranged chloride was determined by integrating these absorption peaks. The accuracy of measurements was checked by analyses of samples of known compositions and found to be within the limit of 6% relative error.

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