

Metalation of Toluene and Cumene with Alkali Metal–Crown Ether Complexes

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Abstract—Metalation of toluene and isopropylbenzene with alkali metal–crown ether complexes led to the corresponding α -metalated alkylbenzenes. Treatment of the latter in succession with solid carbon dioxide, water, and hydrochloric acid gave carboxylic or dicarboxylic acids in 65–78% yield. Metalation of isopropylbenzene with sodium or potassium crown ether complexes above 90°C was accompanied by cleavage of the polyether ring with formation of organometallic compounds which then reacted with isopropylbenzene to produce 2-sodio(potassio)-2-phenylpropane and open-chain oligoether.

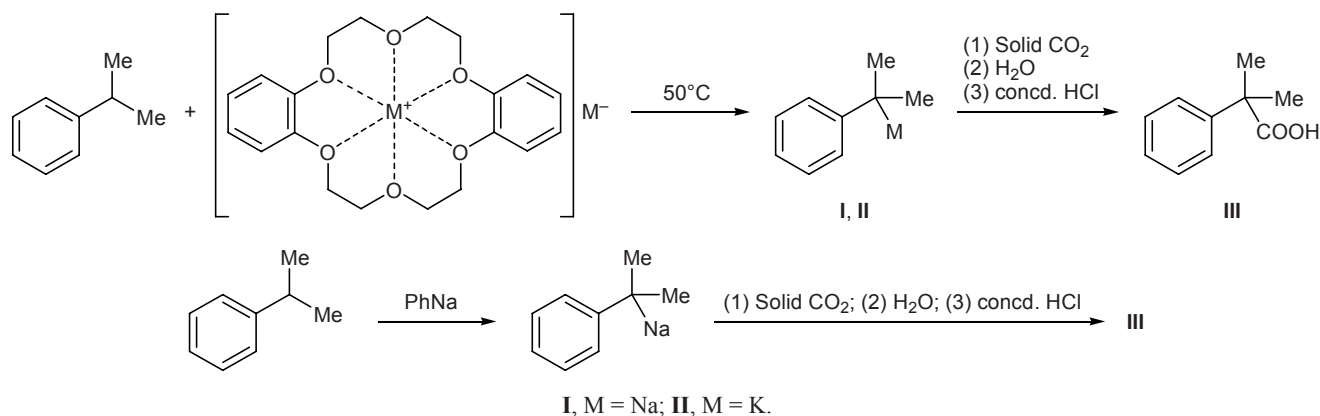
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Replacement of a benzylic hydrogen atom via metalation of alkylaromatic hydrocarbons with sodium or potassium is undoubtedly very important from the synthetic viewpoint. However, there are almost no published data on the direct substitution of hydrogen in benzylic or other positions by the action of alkali metals. The most widely known classical procedure for metalation of alkylaromatic hydrocarbons is based on reactions with alkali metal hydrocarbyls [1]; it was applied more or less successfully to hydrocarbons and their derivatives. A disadvantage of this procedure is that it requires preliminary preparation of alkyl- or arylsodium or -potassium. On the other hand, the

yields are often not high. A limited number of relevant examples have been reported.

We studied substitution of benzylic hydrogen atom in alkylaromatic hydrocarbons by alkali metals in the presence of crown ethers (CE). It is known that CEs react with sodium and potassium in hydrocarbons to produce ultradispersed colloidal systems [2–8]. Such systems are formed as follows. At a temperature below 0°C, macrocyclic ligand knocks out an alkali metal cation from the crystal lattice to give complex $[\text{KE} \cdot \text{M}^+] \text{M}^-$ [2], where M^- is alkali metal anion. Further studies have shown that, apart from $[\text{KE} \cdot \text{M}^+] \text{M}^-$ complexes, complexes with the $[\text{KE} \cdot \text{M}^+] \text{M}_7^-$ composi-

Scheme 1.



tion are also formed, where M_7 ion is a nanoparticle [3, 4, 7]. Taking into account strong basicity of alkali metal anions [5–7], we examined replacement of the α -hydrogen atom in toluene and cumene (isopropylbenzene) by an alkali metal via generation of the above complexes using these hydrocarbons as reaction medium. Dispersion of alkali metal in isopropylbenzene in the presence of dicyclohexyl-18-crown-6, dibenzo-15-crown-5, or dibenzo-18-crown-6 on heating resulted in replacement of hydrogen at the tertiary carbon atom by alkali metal as shown in Scheme 1.

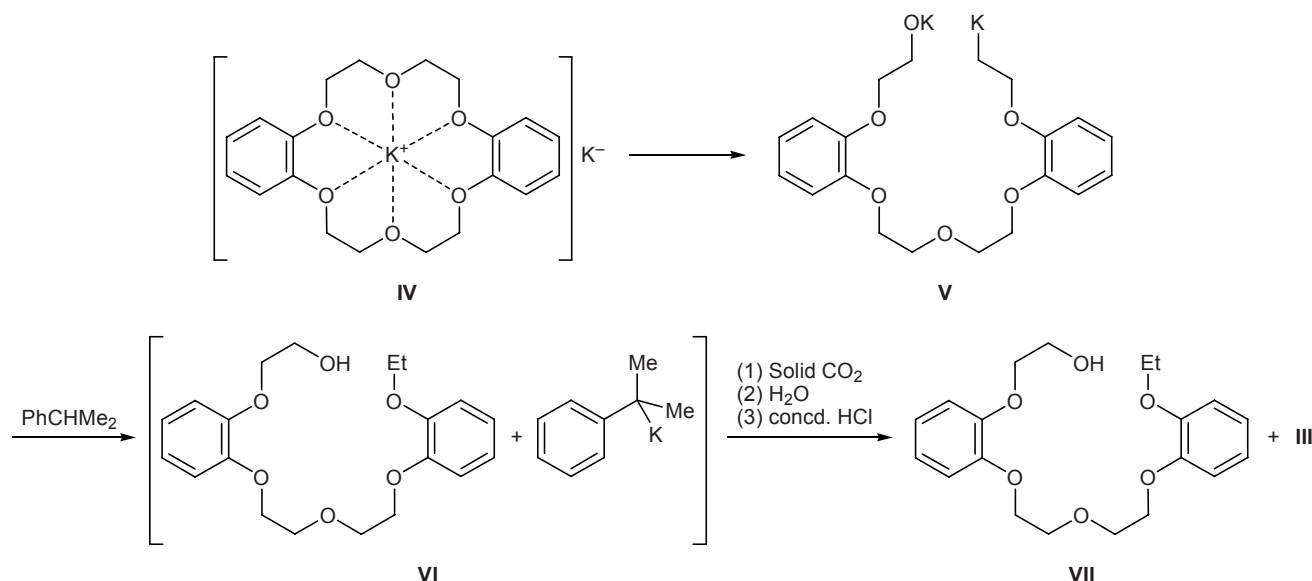
The formation of α -substituted sodium and potassium derivatives **I** and **II** is confirmed by the isolation of 2-methyl-2-phenylpropionic acid **III** after treatment of the reaction mixture with solid carbon dioxide, followed by careful dilution with water under nitrogen and acidification with concentrated hydrochloric acid (pH 2). Recrystallization of the brown–grey precipitate from petroleum ether gave a dark grey sample with mp 76–77°C, which was additionally purified by reprecipitation from aqueous alkali with concentrated hydrochloric acid. The pure product had mp 78°C which coincided with that reported for 2-methyl-2-phenylpropionic acid (**III**) [9]. No replacement of α -hydrogen atom was observed in the absence of CE even when alkali metal was dispersed using a high-speed stirrer (up to 10000 rpm) on heating.

Acid **III** was also synthesized by independent method from isopropylbenzene and preliminarily prepared phenylsodium [9]. As might be expected, metalation of isopropylbenzene with phenyl sodium gave

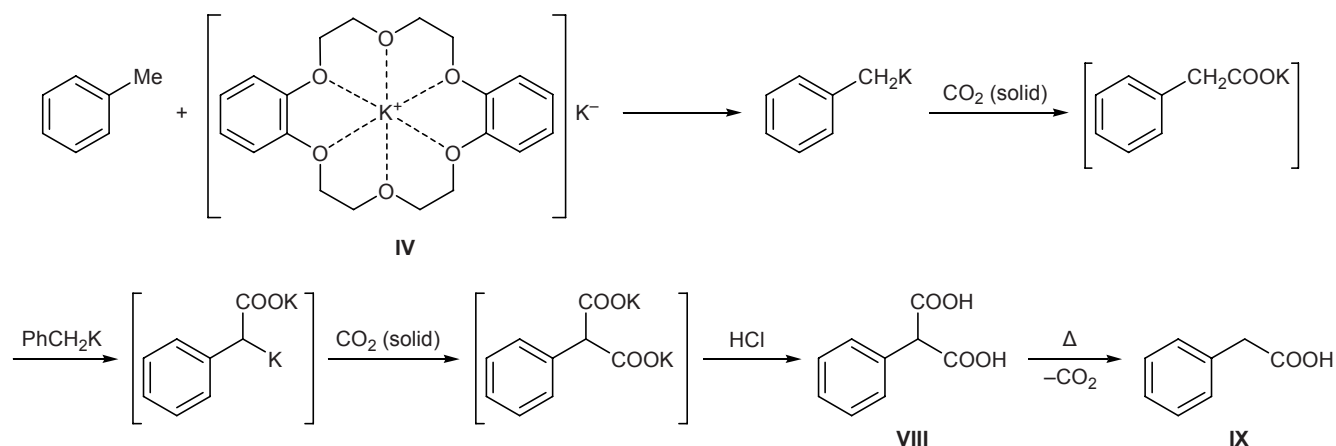
organosodium derivative, and treatment of the latter in succession with solid carbon dioxide, water, and concentrated hydrochloric acid afforded acid **III** which was identical to a sample obtained by metalation of isopropylbenzene with sodium in the presence of crown ether. The melting point of acid **III** coincided with that given in [1], and no depression of the melting point was observed on mixing samples prepared by different methods. The structure of **III** was also confirmed by the IR and ^1H NMR spectra. The IR spectrum contained a strong absorption band at 1701 cm^{-1} due to carboxy group; the phenyl group gave rise to absorption bands at $3032\text{ (C-H}_{\text{arom}})$ and 1589 cm^{-1} (C=C_{arom}), and bands at 758 and 698 cm^{-1} indicated the presence of a monosubstituted benzene ring. In the ^1H NMR spectrum of **III**, protons in the two methyl groups resonated as a six-proton narrow multiplet centered at $\delta 1.19$ ppm, multiplet at $\delta 7.1$ ppm (5H) was assigned to aromatic protons, and carboxy proton appeared as a singlet at $\delta 8.6$ ppm (1H).

We found that dibenzo-18-crown-6 and dibenzo-15-crown-5 are optimal crown ethers for the metalation with potassium and sodium, respectively. The reaction direction depends on the temperature. The benzylic hydrogen atom is replaced by potassium or sodium in the presence of crown compounds below 60°C. Above 90°C, the predominant process is exchange metalation of alkylaromatic hydrocarbons involving cleavage of the polyether ring in complex **IV**. Presumably, organopotassium compound **V** is formed as intermediate which metalates isopropylbenzene (Scheme 2). This follows from the result of successive treatment of the

Scheme 2.



Scheme 3.



reaction mixture with solid carbon dioxide, water, and hydrochloric acid, which gave a mixture of 2-methyl-2-phenylpropionic acid (**III**) and 2-(2-{2-[2-(2-ethoxyphenoxy)ethoxy]ethoxy}phenoxy)ethanol (**VII**). Acid **III** was isolated by neutralization with aqueous alkali and subsequent reprecipitation by acidification. The white crystalline substance which did not dissolve in alkaline solution was recrystallized from petroleum ether (mp 65–67°C). Its structure was determined on the basis of its elemental composition and IR and ^1H NMR spectra. The IR spectrum contained an absorption band at 3437 cm^{-1} , corresponding to stretching vibration of hydroxy group, and in the ^1H NMR spectrum we observed signals typical of hydroxy, aromatic, and methylene protons. These data were consistent with structure **VII**.

Unlike isopropylbenzene, metalation of toluene with potassium in the presence of dibenzo-18-crown-6 and subsequent treatment of the reaction mixture in succession with solid carbon dioxide, water, and concentrated hydrochloric acid gave phenylmalonic acid (**VIII**) as the major product. Its formation may be illustrated by Scheme 3. The physical constants of phenylmalonic acid (**VIII**) obtained according to Scheme 3 fully coincided with those reported in [10]. On heating above 155°C acid **VIII** underwent decarboxylation to give phenylacetic acid (**IX**).

EXPERIMENTAL

The IR spectra were recorded in the range from 4000 to 400 cm^{-1} on a Specord M80 spectrometer from samples prepared as KBr pellets. The ^1H NMR spectra were measured on a Bruker-300 instrument (300 MHz) using D_2O and DMSO as solvents and tetramethylsilane as internal reference. Toluene and cumene of

chemically pure grade (Merck), dibenzo-18-crown-6, and benzo-15-crown-5 (Cherkassy, Ukraine) were commercial products.

Phenylmalonic acid (VIII). A mixture of 0.39 g (0.01 mol) of potassium and 50 ml of toluene was heated to 75°C in a nitrogen atmosphere, and the resulting potassium melt was dispersed using a high-speed stirrer (10 000 rpm) so that the size of metal particles did not exceed $25\text{ }\mu\text{m}$. The fine suspension of potassium in toluene thus obtained was cooled to -5°C , and 3.6 g (0.01 mol) of dibenzo-18-crown-6 was added. The mixture spontaneously warmed up under stirring at room temperature. The blue solution turned dark brown at $55\text{--}60^\circ\text{C}$. The mixture was stirred for 3 h at 75°C , cooled, and poured onto solid carbon dioxide taken in a large excess. It was then carefully quenched with water, the aqueous phase was acidified with hydrochloric acid, and the precipitate was filtered off and dried. The product was additionally purified by dissolution in aqueous alkali and subsequent precipitation with concentrated hydrochloric acid; the precipitate was filtered off and dried. Yield 0.67 g (75%), mp 153°C [10]. On heating above 160°C , compound **VIII** was converted almost quantitatively into phenylacetic acid with mp 76°C [1].

2-Methyl-2-phenylpropionic acid (III). *a.* Acid **III** was synthesized as described above for compound **VIII** using 0.78 g (0.02 mol) of metallic potassium and 7.2 g (0.02 mol) of dibenzo-18-crown-6 in 100 ml of isopropylbenzene. Acid **III** was purified by reprecipitation from an alkaline solution with hydrochloric acid. Yield 1.15 g (78%), mp 78°C [1]. IR spectrum, ν , cm^{-1} : 1589 ($\text{C}=\text{C}_{\text{arom}}$); 3032 ($\text{C}-\text{H}_{\text{arom}}$); 1701 ($\text{C}=\text{O}$); 758, 698 ($\delta\text{C}-\text{H}_{\text{arom}}$). ^1H NMR spectrum, δ , ppm: 1.19 m (6H, CH_3), 7.1 m (5H, C_6H_5), 8.6 s (1H, COOH).

b. Cumene, 50 ml, was added under stirring to a black suspension of 10.05 g (0.1 mol) of phenylsodium (prepared preliminarily from chlorobenzene and metallic sodium according to the procedure described in [1]), maintaining the temperature at 25–30°C. The mixture was stirred for 1.5 h at 112°C, cooled to room temperature, and poured onto solid carbon dioxide taken in a large excess. Excess carbon dioxide was removed, the residue was carefully quenched with water, the aqueous phase was neutralized with concentrated hydrochloric acid, and the precipitate was filtered off. The product was additionally purified by dissolution in aqueous alkali and subsequent precipitation with concentrated hydrochloric acid; the precipitate was filtered off and dried. Yield 5.7 g (35%), mp 78°C. No depression of the melting point was observed on mixing with a sample of **III** prepared as described in a.

c. A mixture of 0.47 g (0.02 mol) of metallic sodium and 75 ml of isopropylbenzene was heated to 108°C under nitrogen, and the resulting sodium melt was dispersed using a high-speed stirrer (10 000 rpm). The fine sodium suspension was cooled to –6°C, and 5.36 g (0.02 mol) of benzo-15-crown-5 was added. The mixture spontaneously warmed up to room temperature and turned blue and then (at 60°C) dark brown. The mixture was stirred for 3 h at 60°C, cooled, and slowly poured onto solid carbon dioxide taken in a large excess. The mixture was carefully quenched with water under nitrogen, the aqueous phase was neutralized with concentrated hydrochloric acid, and the precipitate was filtered off and dried. The product was additionally purified by reprecipitation from aqueous alkali with concentrated hydrochloric acid; the precipitate was filtered off and dried. Yield 1.24 g (38%), mp 78°C.

2-(2-{2-[2-(2-Ethoxyphenoxy)ethoxy]ethoxy}-phenoxy)ethanol (VII). A mixture of 30 ml of cumene, 3.9 g (0.1 mol) of finely dispersed potassium, and 1.8 g (5 mmol) of dibenzo-18-crown-6 was heated to 112–115°C under stirring and was stirred for 1.5 h at that temperature. The mixture was cooled to room tem-

perature and slowly poured onto solid carbon dioxide taken in a large excess. It was then carefully quenched with water under nitrogen, the aqueous phase was acidified with hydrochloric acid, and the grey-brown precipitate was filtered off. Recrystallization of the product from petroleum ether gave 4.5 g (28%) of acid **III** as brown crystals. Compound **VII** (it did not dissolve in aqueous alkali) was purified by recrystallization from petroleum ether. Yield 0.64 g (36%), white crystals, mp 65°C. ¹H NMR spectrum, δ, ppm: 7.12 m (8H, H_{arom}), 1.3 t (3H, CH₃CH₂O), 3.5–3.8 m (14H, OCH₂), 4.5 s (1H, OH). Found, %: C 66.21; H 7.24. C₂₀H₂₆O₆. Calculated, %: C 66.3; H 7.18.

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