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Syntheses of Aromatic Dicarbamates and Their *N,N'*-Dihydroxymethyl Derivatives

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In previous papers,[1-3] aromatic monocarbamates, their *N*-monohydroxymethyl carbamates, and *N,N'*-methylenebis(carbamates) were synthesized. This paper will deal with the syntheses of aromatic dicarbamates and their *N,N'*-dihydroxymethyl derivatives.

p-Xylylene dicarbamate (Ia) and 4,6-dimethyl-*m*-xylylene dicarbamate (IIIa) were synthesized by the method of Kraft[4]:

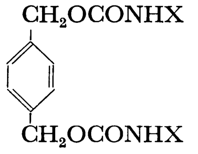
$$\text{R-(CH}_2\text{OH)}_2 + 2\text{C}_2\text{H}_5\text{OCONH}_2 \xrightarrow{\text{Al(OC}_3\text{H}_7)_3} \text{R-(CH}_2\text{OCONH}_2)_2 + 2\text{C}_2\text{H}_5\text{OH}$$

(Ia, IIa)

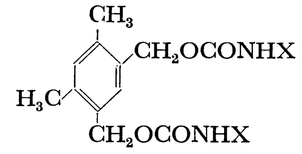
These dicarbamates (Ia, IIa) react with 2 mol of formaldehyde, in the presence of potassium hydroxide as a catalyst, to form *N,N'*-dihydroxymethyl derivatives (Ib, IIb):

$$\underset{\text{(Ia, IIa)}}{\text{R-(CH}_2\text{OCONH}_2)_2} + 2\text{CH}_2\text{O} \xrightarrow{\text{OH}^-} \underset{\text{(Ib, IIb)}}{\text{R-(CH}_2\text{OCONHCH}_2\text{OH)}_2}$$

From the analytical data, the structures of these products were determined to be as follows:



Ia (X=H)
Ib (X=CH$_2$OH)



IIa (X=H)
IIb (X=CH$_2$OH)

Experimental

The melting points are uncorrected. The IR spectra were recorded with a KBr disk on a JASCO Model IR-S infrared spectrometer. The NMR spectra were recorded on a Japan Electron Optics 60 MHz spectrometer in d_6-DMSO (*ca.* 10%); the δ values (ppm) were given against tetramethylsilane as an internal standard.

Preparation of p-*Xylylene Dicarbamate (Ia).* To 53.5 g (0.60 mol) of ethyl carbamate (recrystallized from benzene) in a 300 m*l* four-necked flask fitted with a stirrer, a thermometer, a condenser, and a 30 cm asbestoslagged column, we added 34.5 g (0.25 mol) of *p*-xylylene glycol (mp 115—116°C, from methanol) and 160 m*l* of ethylbenzene. The reaction mixture was heated at 110°C in an oil bath to remove any water in the reagents and was then cooled to 100°C. Subsequently, aluminum isopropoxide (about 10 g) was added and the reaction temperature was held at 134—137°C. The reaction mixture was subsequently stirred for 15 hr. The ethanol-ethylbenzene azeotropic mixture was removed through the column. The crude product thus obtained was recrystallized from DMF to give 28.3 g (50.5%) of a white powder melting at 211—213°C. IR (cm^{-1}): 3430—3230 (ν(NH$_2$), *etc.*), 1700 (ν(C=O)), 1620 (δ(NH$_2$)). NMR (ppm): 7.27 (s, 4H, C_6H_4–), 6.5 (s, 4H, –NH$_2$), 4.93 (s, 4H, –CH$_2$–). Found: C, 53.70; H, 5.53; N, 12.36%. Calcd for $C_{10}H_{12}N_2O_4$: C, 53.56; H, 5.4; N, 12.5%.

*Preparation of 4,6-Dimethyl-*m*-xylylene Dicarbamate (IIa).* To 49.0 g (0.55 mol) of ethyl carbamate we added 33.2 g (0.20 mol) of 4,6-dimethyl-*m*-xylylene glycol and 160 m*l* of ethylbenzene. The reatcion mixture was stirred for 11 hr at 135°C and then treated as has been described above. Mp 199—200°C. Yield, 14.0 g (27.7%). IR (cm^{-1}): 3427—3207 (ν(NH$_2$), *etc.*), 1687 (ν(C=O)), 1605 (δ(NH$_2$)). NMR (ppm): 7.22 and 7.02 (s, each one proton, C_6H_2–), 6.5 (s, 4H, –NH$_2$), 4.93 (s, 4H, –CH$_2$–), 2.23 (s, 6H, –CH$_3$). Found: C, 57.38; H, 6.40; N, 11.12%. Calcd for $C_{12}H_{16}N_2O_4$: C, 57.12; H, 6.41; N, 11.10%.

Reaction Product of Ia with Formaldehyde. A mixture of Ia (5.6 g, 0.025 mol), paraformaldehyde (2.0 g, 0.067 mol), dioxane (30 m*l*), and water (15 m*l*) was stirred at 74°C and pH 11.4 for 80 min, and then to the reaction mixture we added 200 m*l* of water. The solid thus formed was filtered and recrystallized from methanol-water to afford Ib as a white powder; 2.9 g (40.8%); mp 172—173°C. A test with a Tollens reagent was positive. IR (cm^{-1}): 3317 (ν(NH), ν(OH)), 1695 (ν(C=O)), 1530 (ν(CN)+δ(NH)). NMR (ppm): 7.8 (t, 2H, –OH), 7.29 (s, 4H, C_6H_4–), 5.5 (t, 2H, –NH–), 5.0 (s, 4H, –CH$_2$OC–), 4.43 (t, 4H, –N–CH$_2$O–). Found: C, 50.94; H, 5.84; N, 9.66%. Calcd for $C_{12}H_{16}N_2O_6$: C, 50.69; H, 5.68; N, 9.86%.

Reaction Product of IIa with Formaldehyde. A mixture of IIa (2.1 g, 0.008 mol), paraformaldehyde (0.8 g, 0.025 mol), dioxane (30 m*l*), and water (15 m*l*) was stirred at 70°C and pH 13.2 for 30 min and then treated as has been described above. Mp 145—147°C. Yield, 0.57 g (18.3%). A test with a Tollens reagent was positive. IR (cm^{-1}): 3250 (ν(NH), ν(OH)), 1690 (ν(C=O)), 1530 (ν(CN)+δ(NH)). NMR (ppm): 7.8 (t, 2H, –OH), 7.23 and 7.0 (s, each one proton, C_6H_2–), 5.5 (t, 2H, –NH–), 4.97 (s, 4H, –CH$_2$OC–), 4.45 (t, 2H, –N–CH$_2$O–), 2.24 (s, 6H, –CH$_3$). Found: C, 53.67; H, 6.68; N, 8.82%. Calcd for $C_{14}H_{20}N_2O_6$: C, 53.85; H, 6.47; N, 8.97%.

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