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NOTE

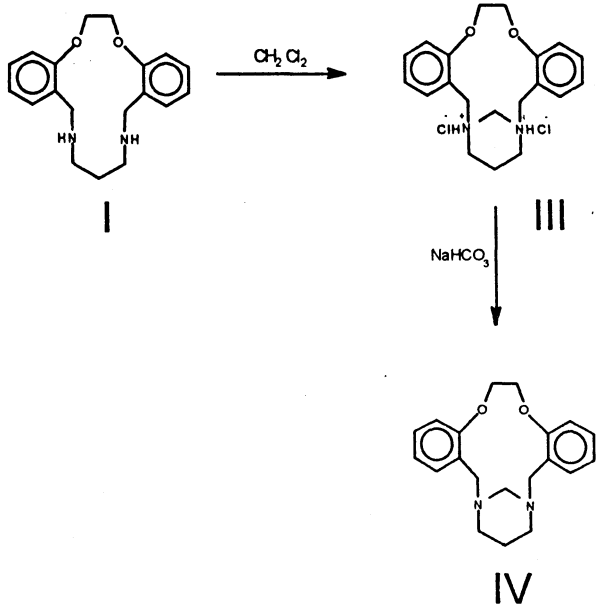
Reaction of Methylene Chloride with Some Aza-crown Ethers

DEEB MARJI* and KHAMIS ABBAS
Chemistry Department
Yarmouk University, Irbid, Jordan

Two aza-crown ethers, dibenzo-1, 4-dioxa-8, 12-diaza-cyclopentadeca-5, 14-diene (DBA_2) and N-phenyl-aza-15-crown-5 (PhA 15C5) were reacted with methylene chloride at room temperature to produce two new crown ethers. It is belived that the crown ethers activate the methylene chloride through complexation which then acts as a methylating agent.

It is well known that crown ethers can complex with neutral molecules such as CH_3CN, urea and DMSO.[1–3] Previous studies reported the activation of DMSO by crown-ethers where DMSO acts as methylating agent.[3] Recently, it has been published that diaza-18-crown-6 reacted with ethylene chloride to form a new kryptand.[4] The ethylene chloride acts as an ethylating agent and can supply the crown with CH_2—CH_2 unit. This result prompted us to investigate the reaction of methylene chloride with two aza-crown ethers.

When crown-ether I was dissolved in methylene chloride at room temperature, a colourless precipitate (III) was formed after a few days. The reaction is shown in scheme A.



I III IV

Scheme A

Sodium bicarbonate solution (5%) was added to neutralize the hydrochloric acid and to liberate the free crown which dissolved in methylene chloride. The methylene chloride layer was separated, the solvent was evaporated to give a white powder (IV).

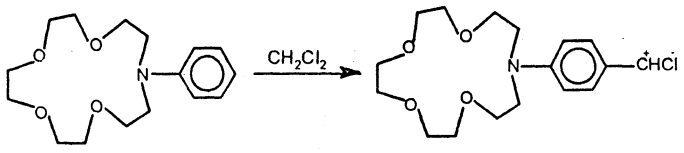
The powder was identified as follows: m.p. 127–128°C. The IR spectrum (KBr disc) shows the characteristic bands at 1598 cm^{-1} ν(C=C aromatic), 1255 cm^{-1} ν(C—N), 1235 cm^{-1} characteristic of crow- ether ν(C—O—C). The UV spectrum (methanol solution) shows two bands at 260 and 195 nm. The NMR spectrum in CD_3CN (solution) shows signal at; 1.81 ppm (2 H, m); 2.8 p pm (4H, t); 3.2 ppm (2H, S); 3.6 ppm (4H, S); 4.2 ppm (4 H, S); and 6.8–7.3 (8H, m) due to the aromatic moiety.

The mass spectrum shows the following peaks, m/e: 324 (m^+); 323 (base peak); 254 ($C_{16}H_{16}NO_2$); 217 ($C_{13}H_{17}N_2O$); 107 (C_7H_7O) and 70 (C_4H_8N). The fragmentation pattern is in agreement with the proposed structure.

The elemental asnalysis for the proposed structure shows: C (calcd. 74.0, found 74.1%); N (calcd. 8.73, found 8.64%) and H (calcd. 7.40, found 7.47%).

The above results clearly support the proposed structure(III).

On the other hand, when PhA15C5 (II) was dissolved in methylene chloride at room temperature, a blue colour was developed after several days; evaporation of the solvent left a gummy blue solid. The reaction is shown is Scheme B.



II V

Scheme–B

The blue colored compound is believed to be a quinone imonium-cation type (V) and it was precipitated with KPF_6 solution to give a blue crystalline product identified as follows:

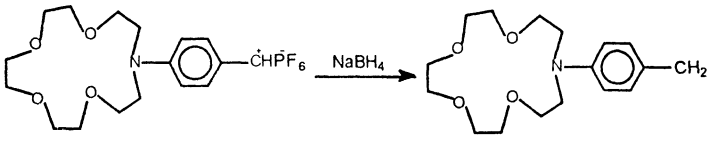
IR (KBr disc ν_{max}) 1600, 1345 and 1130 cm^{-1}, UV-visible (MeOH, λ_{max}) 600, 583 and 260 nm. ^1H NMR δ3.7 and 6.6–7.3 (m, 9H).

Mass spectrum m/e 602 ($M^+ + 1$) for $C_{33}H_{49}N_2O_8$; 308 for $C_{17}H_{26}NO_4$ and 295 for $C_{16}H_{25}NO_4$.

The above reults obatained are in complete agreement with those obtained for the quinone-imonium cation obtained from the reaction of dimethyl sulfoxide with PhA15C5.[3, 5]

Further characterization step was carried out by reduction of the quinone-immonium cation with sodium borohydride to produce new crown-ether (VI) as shown in Scheme C.

The crown(VI) was characterized by IR, mass spectrum, ^1H NMR and UV spectrum. The results agree with that reported for compound (VI).[5]



Scheme C

The above results give a clear conclusion that the methylene chloride reacts with aza-crown ethers and can provide a CH_2 unit.

At this stage we believe that the crown ether ring plays a role by activating methylene chloride through complexation to produce an active species acting as a methylating agent.

However, further work is needed in order to investigate the mechanism of reaction.

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