

EXPERIMENTAL

Reaction of 2,3-dichloro-*p*-dioxane with tetrahydrofuran. A mixture of 300 ml. (3.7 moles) of tetrahydrofuran, 157 g. (1 mole) of 2,3-dichlorodioxane and 5 g. of zinc chloride was refluxed for 3.5 hr. The initial reaction was slightly exothermic. (The reaction was complete in 45 min. when 20 g. of zinc chloride was used.) The progress of the reaction was followed by the increase in the boiling point of the reaction solution from an initial 75° to a constant 95°. The excess tetrahydrofuran was distilled at 200 mm. pressure. To the remaining solution was added 400 ml. of carbon tetrachloride and then it was washed 6 times with 300 ml. of water. The carbon tetrachloride layer was distilled at reduced pressure to give 43% yield of 2,3-di(4'-chlorobutoxy)-*p*-dioxane; b.p., 165° at 0.7 mm.; n_D^{25} 1.4725; d_{25} 1.18. The 64 g. of very viscous dark residue was discarded.

Anal. Calcd. for $C_{12}H_{22}O_4Cl_2$: C, 47.82, H, 7.33, Cl, 23.6. Found: C, 47.74; H, 7.47; Cl, 23.3.

Reaction of 2,3-dichloro-*p*-dioxane with 4-chlorobutanol. A mixture of 235 g. (1.5 moles) of 2,3-dichloro-*p*-dioxane, 390 g. (3.5 moles) of 4-chloro-1-butanol and 200 ml. of benzene was refluxed for 16 hr. The HCl was allowed to escape through the condenser as it formed. The dissolved HCl, benzene and excess 4-chloro-1-butanol were distilled at reduced pressure followed by 254 g. (57% yield) of 2,3-di(4'-chlorobutoxy)-*p*-dioxane; n_D^{25} 1.4718, d_{25} 1.18.

Reaction of 2,3-dichlorotetrahydrofuran with tetrahydrofuran. One mole of 2,3-dichlorotetrahydrofuran was added to 3 moles of tetrahydrofuran in which 20 g. of freshly fused $ZnCl_2$ was dissolved. The reaction was exothermic and vigorous at 65–85°. After 10 min. heat was applied and the reaction was maintained at reflux temperature (90–93°) for an additional 15 min. The material was water washed, dried with Na_2SO_4 and then distilled at reduced pressure to give a 53% yield of 2-(4'-chlorobutoxy)-3-chlorotetrahydrofuran; b₁ 107°, b₂₀ 144° (lit.⁷ b₂₀ 145–155°); n_D^{24} 1.4700; d_{24} 1.19.

Anal. Calcd. for $C_8H_{14}Cl_2O_2$: C, 45.09; H, 6.62; Cl, 33.27. Found: C, 45.57; H, 6.87; Cl, 32.7.

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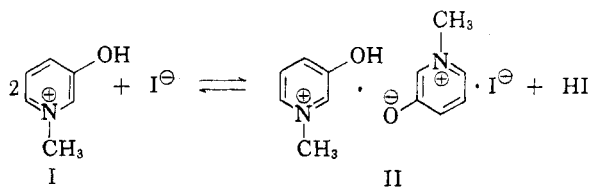
An Unusual Dimeric Quaternary Complex from 1-Methyl-3-hydroxypyridinium Iodide

KENNETH MECKLENBORG¹ AND MILTON ORCHIN

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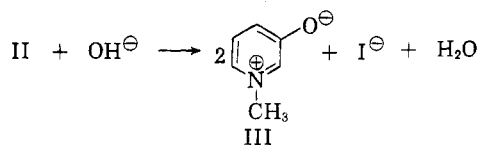
When 3-hydroxypyridine and methyl iodide were refluxed in acetone solution in an attempt to prepare the known 1-methyl-3-hydroxypyridinium iodide (I), a small quantity of crystalline insoluble material precipitated. This was filtered and the mother liquor worked up to secure the desired quaternary compound (I). The insoluble material melted at 179–181° and was obviously different from I, m.p. 114–116°. The higher melting, less-soluble material gave a test for iodide. Ultimate analysis indicated its formula as $C_{12}H_{18}IN_2O_2$ which corresponds to twice the sum of I less a molecule of hydrogen iodide. The relation between the two compounds may thus be represented as follows:

(1) Taken in part from this author's Ph.D. dissertation. Present address, Research Laboratories, Standard Oil of Indiana, Whiting, Ind.



The new compound, II, is written as a complex without specifying the bonding between the two ring moieties. That a complex with the composition of II exists was substantiated by the following.

Treatment of an acetone solution of I with excess triethylamine gave II and triethylamine hydroiodide. The total weight of solid material corresponded to that expected by the removal of a mole of HI. Treatment of pure II with excess HI regenerated I. II gave a positive ferric chloride test. Titration of II with base gave the expected neutral equivalent:



The preparation and titration of I has been reported previously² and the equivalence point at which the zwitter ion, III, is presumed to exist was given as lying between pH of 7 and 9. The titration of II gave a similar equivalence point. The ultraviolet spectrum of II should vary with pH. In base, II should exist as III and in strong acid, II should exist as I. The ultraviolet spectrum of II in base at pH 9.7 showed a long wave-length maximum essentially identical with that previously reported for III; however the intensity was approximately twice that of III as required by the stoichiometry above. Similarly, the spectrum of II in acid solution showed the long wave-length maximum reported for I except for the two-fold increase in intensity.

Compound III has been reported³ to exist as an oil, boiling at 300° (1–2 mm). In an attempt to convert II to III, II was treated with silver carbonate. Silver iodide precipitated and a white, iodide-free, semisolid was isolated. This was rather unstable and could not be purified.

No attempt was made to elaborate the structure of the complex II although possible "charge-transfer" complexes⁴ may be of interest in this connection.

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Isolation with preparation of II. During the quaternization of 3-hydroxypyridine with methyl iodide by the known pro-

(2) S. A. Harris, T. J. Webb, and K. Folkers, *J. Am. Chem. Soc.*, **62**, 3198 (1940).

(3) R. R. Williams, *Ind. Eng. Chem.*, **13**, 1107 (1921).

(4) E. M. Kosower and J. C. Burbach, *J. Am. Chem. Soc.*, **78**, 5838 (1956).

cedure a small amount of solid separated. This later proved to be II. It was more convenient to prepare II from the normal and more soluble product, 1-methyl-3-hydroxypyridinium iodide (I). For this purpose there was added dropwise to an acetone solution of I, m.p. 114–116°, triethylamine until precipitation on addition ceased. The solid was collected, washed with acetone, and recrystallized from methanol-ether. The sample for analysis⁶ had m.p. 179–181°.

Anal.: Calcd. for $C_{12}H_{15}IN_2O_2$: C, 41.63; H, 4.37; N, 8.09; I, 36.66. Found: C, 41.95; H, 4.36; N, 7.99; I, 36.50.

The compound gave a dark red color with ferric chloride solution. It was soluble in polar solvents, but insoluble in ether, acetone, and ethyl acetate. It gave a precipitate with silver nitrate solution. When a solution of 1.00 g. of I in 20 ml. of acetone was treated dropwise with 2.0 g. of triethylamine, 0.63 g. of precipitate was formed, m.p. 179–181°, no depression when mixed with II. Evaporation to dryness of the mother liquor gave 0.57 g. of residue, which on extraction with acetone and evaporation of the solvent, gave 0.26 of a white powder, m.p. 179–180°, no depression when mixed with authentic triethylamine hydroiodide, but m.p. 140–160°, when mixed with II.

Titration of II. Potentiometric titration of an aqueous solution of II with 0.05N NaOH gave a sharp break (0.02 ml.) between pH 7.8 and 8.4. The neutral equivalent calculated from this consumption of alkali was 344.4 ± 2.0 . Calcd. for $C_{12}H_{15}IN_2O_2$: 346.2.

Ultraviolet spectra of II. The spectra determinations were made with a Beckman DU quartz spectrophotometer using water as a solvent. At pH 2.1, a solution of II gave maxima at 288 $m\mu$, $\epsilon = 11,800$ and 225 $m\mu$, $\epsilon = 21,300$. At pH 9.7 maxima were at 320 $m\mu$, $\epsilon = 10,500$ and 248 $m\mu$, $\epsilon = 16,000$. From the literature curves,¹ the comparable figures secured with I were, at pH 2.1, 288 $m\mu$, $\epsilon = 5700$ and at pH 10.2, 320 $m\mu$, $\epsilon = 5,200$.

Attempted preparation of III. To 1.0 g. of II in methanol there was added freshly prepared silver carbonate until no further precipitation of silver iodide occurred. The mixture was heated to boiling and filtered. Ether was added to the filtrate until it became turbid. Cooling in an ice-salt bath gave a silvery crystalline mass melting at 10–20° to a clear oil. The oil gave a negative test with silver nitrate solution. Attempted distillation of the oil at 1 mm. gave extensive decomposition. On standing in air, the oil turned brown. The spectrum of the freshly prepared oil in water (pH 7.6) showed maxima at 319 and 248 $m\mu$. Heating II with triethanolamine at 150° gave triethanolamine hydroiodide, m.p. 173–174, no depression with a sample prepared from triethanolamine and hydrogen iodide. No product could be isolated from the mother liquor.

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APPLIED SCIENCE DEPARTMENT
UNIVERSITY OF CINCINNATI
CINCINNATI, OHIO

(5) Geller Laboratories, Bardonia, New York.

Hydrogenolysis of 1-Nitronaphthalene by Complex Metal Hydrides

H. J. SHINE AND MEILING TSAI¹

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A number of reports have appeared in recent years on hydrogenolysis by complex metal hy-

drides.² Most of these have concerned the hydrogenolysis of carbon-oxygen bonds, such as in alcohols, ketones, esters, and amides. The hydrogenolysis of halogen compounds has been reported also,^{2,3} while two reports on the hydrogenolysis of an aliphatic nitro group have appeared.^{4,5}

We are now able to add to these examples of the reactions of complex metal hydrides the hydrogenolysis of an aromatic nitro group. This occurred during attempts to convert 1-nitronaphthalene to the azonaphthalene. Although some nitrobenzenes are reduced to the azobenzenes by lithium aluminum hydride⁶ and nitrobenzene to azoxybenzene by sodium borohydride,⁷ 1-nitronaphthalene behaves quite differently. Numerous attempts to prepare 1,1'-azonaphthalene from 1-nitronaphthalene by the action of lithium aluminum hydride, sodium-, potassium-, and lithium borohydride have proved, for the most part, unsuccessful. A small amount of the azocompound was obtained from some experiments with lithium aluminum hydride, while in other experiments with this hydride no azocompound could be isolated. No azonaphthalene was found in experiments with the other hydrides even though the red color of the solutions during reduction suggested the presence of azocompound. In all of the reductions some naphthylamine was formed along with large amounts of tars. In all experiments with sodium- and potassium borohydride small amounts of naphthalene were also obtained. Although there was usually a faint smell of naphthalene during the working-up of the products from lithium aluminum hydride reductions, it was possible to isolate the naphthalene in only one experiment with this hydride; this was in the case of reduction by reverse addition. There is no doubt that the naphthalene was formed as a result of reaction during these experiments; the nitronaphthalene used was well purified.

The course of the hydrogenolysis is not clear. There is some indication that the tarry products obtained in the reductions lead partly to naphthalene on treatment with dilute hydrochloric acid. Thus, we suspect that naphthalene may arise

(1) From the M. S. thesis of Miss Meiling Tsai, Texas Technological College, 1958.

(2) N. G. Gaylord, *Reduction with Complex Metal Hydrides*, Interscience Publishers, Inc., New York, N. Y., 1956, pp. 979–91.

(3) W. E. Rosen, V. P. Toohey, and A. C. Shabica, *J. Am. Chem. Soc.*, **80**, 935 (1958).

(4) H. J. Backer, *Rec. trav. chim.*, **64**, 844 (1949), obtained a small amount of $CH_2(SO_2CH_3)_2$ from the action of lithium aluminum hydride on $O_2NCH(SO_2CH_3)_2$.

(5) R. Adams and W. Moje, *J. Am. Chem. Soc.*, **74**, 5557 (1952), obtained a 60% yield of bis-2-(1,4-naphthalenedibenzene-sulfonamido)methane by the action of lithium aluminum hydride on bis-2-(1,4-naphthalenedibenzene-sulfonamido)nitromethanol.

(6) Reference 2, p. 773.

(7) C. E. Weill and G. S. Panson, *J. Org. Chem.*, **21**, 803 (1956).