cymene or dipentene. The mixture was heated for 10 hr. and the evolved water (0.6 ml., 100%) was collected in a Dean-Stark trap. Dimethylurea was soluble in the boiling solution and, on cooling, white crystals separated. The yield was 8.5 g. (91%). After three recrystallizations from alcohol the m.p. remained at 197°. The mixed melting point of a 1:1 mixture of the products by both methods was undepressed.

Anal. Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 10.00. Found: C, 73.21; H, 6.08; N, 9.94.

On refluxing VI (1.42 g., 0.005 mole) for 8 hr. in dipentene (35 ml.), water (0.09 ml., 100%) distilled and was collected in a Dean-Stark trap. On cooling and recrystallizing from alcohol 1.31 g. (98%) of white needles of III, m.p. 215°, was obtained. The hydantoin, III, could also be obtained directly by refluxing for 1.5 hr. a mixture of benzil (2.10 g.), methylurea (0.74 g.), and dipentene (75 ml.)[7] until no more water distilled. The methyl group of III was shown to be in the 3-position by preparing III from I by the methylation procedure of Klosa.[8] The mixed melting point of III prepared by both methods was undepressed.

Formation of IV *from* V. Compound V (9.93 g., 0.03 mole) was refluxed in dipentene (200 ml.) and, after 30 min., the theoretical volume of water (0.6 ml.) had collected in the water trap. Further heating for 60 min. yielded no more water. After cooling to 0° the crystalline solid was filtered, washed with alcohol, and dried in air. The yield was 9.2 g. (98.5%). Three recrystallizations from alcohol gave IV, m.p. 197°. The mixed-melting point of this compound with that prepared by the method of Biltz was undepressed.

Attempt to form IV *from* V *by the action of base.* One g. of V, sodium hydroxide (0.5 g.), and isopropyl alcohol (50 ml.) were refluxed for 30 min., then poured into water (200 ml.). Addition of concentrated hydrochloric acid to *p*H 4 produced a flocculent white precipitate which was filtered and recrystallized from dilute alcohol to yield 0.6 g., m.p. 150°, corresponding with benzilic acid. The mixed melting point with authentic benzilic acid was undepressed.

Attempts to react benzil with phenylurea, etc. In place of dimethylurea in the procedure for the preparation of V the following compounds were employed: phenylurea, 1,3-diphenylurea, 1,3-diphenylthiourea, and 1,3-diphenylguanidine. In each case no evidence of any reaction was obtained and the original compounds were quantitatively recovered. Fusion of benzil with diphenylurea, in 1:1 molar ratio at 205°, as in the preparation of IV, yielded a yellow product which after recrystallization from alcohol melted at 95° (benzil). Similar results were obtained using diphenylthiourea and diphenylguanidine.

Ultraviolet absorption spectra of I, IV, *and* V. Spectral determinations were carried out in the standard manner using a Beckman spectrophotometer, Model DU, and matched 1-cm. quartz cells. Spectral measurements were made from 220 to 300 mμ. Comparison of the spectrum of I showed it to be very similar to that of IV, and quite different from that of V.

Acknowledgment. The author thanks Mr. R. E. Wilde[9] for the preparation of compound I and for the spectral determinations.

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(7) Using xylene a 10-hr. reflux time was required.

(8) J. Klosa, *Arch. Pharm.*, 285, 274 (1952).

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Cleavage of Tetrahydrofuran by 2,3-Dichloro-*p*-dioxane and 2,3-Dichlorotetrahydrofuran Using Zinc Chloride as a Catalyst

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Reported in the literature are many examples of tetrahydrofuran ring cleavage with a number of different compounds. Those containing an active halogen break the furan ring and bring about the formation of 4-halobutoxy derivatives. Some that have been used are the hydrogen halides,[1–3] acid chlorides[4,5] and methyl iodide.[6] Reppe and Kroper[7] claim that during the chlorination of tetrahydrofuran to 2,3-dichlorotetrahydrofuran a small amount of 2-(4′-chlorobutoxy)-3-chlorotetrahydrofuran is formed. They report that this comes from the reaction between 2,3-dichlorotetrahydrofuran and 4-chlorobutanol-1 which is formed during the chlorination of tetrahydrofuran by the action of HCl on tetrahydrofuran. No references were found where an alpha halo ether was used to cleave tetrahydrofuran.

Tetrahydrofuran was opened with 2,3-dichloro-*p*-dioxane to give 2,3-di(4′-chlorobutoxy)-*p*-dioxane in 40 to 43% yields. It was also opened with 2,3-dichlorotetrahydrofuran to give 2-(4′-chlorobutoxy)-3-chlorotetrahydrofuran in 53% yield. These reactions were carried out in anhydrous systems in which there appeared to be no HCl present to cleave the tetrahydrofuran. The amount of catalyst (zinc chloride) was varied from 5 to 20 g. per mole of alpha chloroether. The only effect noted was a slightly higher reaction rate at the higher catalyst concentration. There was no reaction when no catalyst was used.

The 2,3-di(4′-chlorobutoxy)-*p*-dioxane prepared by a more conventional method[8] using 4-chlorobutanol had the same physical properties and infrared spectrum as when prepared using tetrahydrofuran.

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(2) N. D. Scott, U. S. Patent 2,491,834; *Chem. Abstr.*, 44, 2542h (1950).

(3) F. Codignola and M. Piacenze, Italian Patent 424,590; *Chem. Abstr.*, 43, 4284b (1949).

(4) M. E. Synerholm, *Org. Syntheses*, Coll. Vol. III, 187 (1955).

(5) S. B. McFarlane and J. Lomartire, U. S. Patent 2,513,504; *Chem. Abstr.*, 44, 8944a (1950).

(6) A. Muller, E. Funder-Fritzsche, A. Müller, E. Funder-Fritzche, W. Konar, and E. Rintersbacker-Wlasak, *Monatsh.*, 84, 1206 (1953).

(7) W. Reppe and H. Kroper, German Patent 703,956; *Chem. Abstr.*, 36, 10506 (1942).

(8) C. L. Butler and L. H. Cretcher, *J. Am. Chem. Soc.*, 54, 2987 (1932).

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^{26} 1.4718, d_{26} 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; b_5 107°, b_{20} 144° (lit.[7] b_{20} 145–155°); n_D^{24} 1.4700; d_{24} 1.19.

Anal. Calcd. for $C_8H_{14}Cl_2O_2$: C, 45.09; 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

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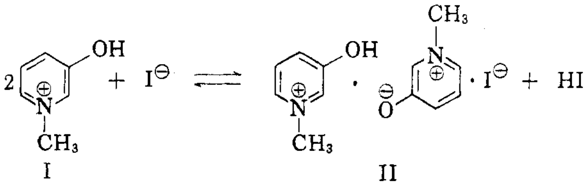
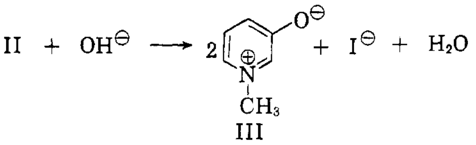
When 3-hydroxypyridine and methyl iodide were refluxed in actone solution in an attempt to prepare the known 1-methyl-3-hydroxypyridinium iodide (I), a small quantity of crystalline insoluble material precipitated. This was filtered and the mother liquor worked up to secure the desired quaternary compound (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 $C_{12}H_{15}IN_2O_2$ 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:



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 previously[2] and the equivalence point at which the zwitter ion, III, is presumed to exist was given as lying between *p*H of 7 and 9. The titration of II gave a similar equivalence point. The ultraviolet spectrum of II should vary with *p*H. In base, II should exist as III and in strong acid, II should exist as I. The ultraviolet spectrum of II in base at *p*H 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 reported[3] 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" complexes[4] may be of interest in this connection.

EXPERIMENTAL

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

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

[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).