# ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

## Organic Compounds of Uranium. VII. Uranyl Alkoxides and Dithiocarbamates

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Several uranyl dialkyldithiocarbamates, uranyl ethoxide and a compound thought to be uranyl *t*-butoxide are described.

Among the uranium compounds prepared in this Laboratory during our search for derivatives suitable for isotope separation were several uranyl compounds. They were non-volatile for all practical purposes and, therefore, were examined only in a preliminary way. Several uranyl dialkyldithiocarbamates, uranyl ethoxide and a compound thought to be uranyl *t*-butoxide were reasonably well characterized and are described in this paper.

The reactions between aqueous solutions of uranyl acetate and potassium dialkyldithiocarbamates generally gave uranyl dialkyldithiocarbamates as dark red crystalline precipitates. These compounds, with the exception of the one prepared from dimethylamine, were readily soluble in hot ethanol from which they separated as brilliant red needles when the solutions were cooled. On the basis of uranium and sulfur analyses, the crystals contained from four to six moles of ethanol of crystallization. Uranyl dithiocarbamates were mentioned but not described by Delepine.[1] More recently Albers and co-workers[2] have described a series of uranyl dithiocarbamates, but their compounds appear to differ in a number of ways from those reported here.

Uranyl ethoxide was obtained by treating a solution of anhydrous uranyl chloride in absolute ethanol with sodium ethoxide. It was isolated as a yellow-brown crystalline solid readily soluble in ethanol or anhydrous ether. It retained three moles of ethanol of association even after being heated at 200° under 0.004 mm. pressure for 1 hr. The compound was very easily hydrolyzed by water.

An interesting uranium derivative of *t*-butyl alcohol was obtained in two ways from uranium(IV) *t*-butoxide. When the latter was heated under greatly reduced pressure, a red sublimate was obtained. This was partially soluble in petroleum ether to form a red solution that deposited red crystals when it was evaporated. The second procedure consisted of passing dry air or oxygen through a petroleum ether solution of uranium(IV) *t*-butoxide. The solution changed from green through brown to red and deposited ruby-red crystals when partially evaporated. This compound was distinctly different from the brown uranium(V) *t*-butoxide[3] which, incidentally, remained unchanged when exposed to oxygen. The new compound was soluble in absolute ethanol but was recovered apparently unchanged after heating the ethanol solution and then evaporating the solvent. Thus, it differed from uranium(VI) *t*-butoxide which, when heated with excess ethanol, was converted to uranium(VI) ethoxide.[4] Unfortunately, the red solid was not fully characterized. On the basis of a number of uranium analyses, one possible formula for the compound appears to be $UO_2(OC_4H_9\text{-}t)_2\cdot 4\ t\text{-}C_4H_9OH$. It may be related to the uranyl diisoamyloxide mentioned by Albers and co-workers[5] as a ruby-red compound soluble in benzene but not isolated in crystalline form.

### Experimental

**Uranyl Dithiocarbamates.**—The preparation of uranyl diethyldithiocarbamate is illustrative of the method used to synthesize the compounds in Table I.

To a mixture of 7.6 g. (0.10 mole) of carbon disulfide and 25 ml. of water, containing 5.6 g. (0.10 mole) of potassium hydroxide, was added dropwise with stirring and cooling 7.3 g. (0.10 mole) of diethylamine. The resulting solution of potassium diethyldithiocarbamate was filtered with suction and added with stirring to a solution of 21.2 g. (0.05 mole) of uranyl acetate dihydrate and 10 g. (0.10 mole) of potassium acetate in 800 ml. of water. A red precipitate was formed immediately. After a few minutes the precipitate was collected, washed with water and allowed to dry in the air. The yield of dark red powder was 20 g. It was recrystallized from 150 ml. of hot 95% ethanol from which it separated as brilliant dark red crystals. The yield was 17 g. of product containing four moles of alcohol of crystallization.

The compound obtained from dimethylamine was a dark red solid, insoluble in ethanol or other common organic solvents.

**Uranyl Ethoxide.**—Anhydrous uranyl chloride was prepared by heating the hydrated compound in a glass tube through which was passed a slow current of dry hydrogen chloride. After the moisture had been driven off, the material was removed from the tube, powdered and again placed in the tube. A mixture of hydrogen chloride and chlorine gas was passed slowly through the tube, and the contents fused by gradually heating to dull redness. The material was powdered and stored in a tightly stoppered bottle. The uranyl chloride was insoluble in anhydrous ether. It dissolved readily in absolute ethanol with the evolution of heat. An aliquot of the ethanol solution was analyzed, and the ratio of chlorine to uranium was found to be 2.000.

To a solution of 21.5 g. (0.063 mole) of $UO_2Cl_2$ in 50 ml. of absolute ethanol was added a solution made by dissolving 2.67 g. (0.116 g. atom) of sodium in 50 ml. of absolute ethanol. The alcohol was removed by heating under reduced pressure, and the residue was heated at 200° under 0.004 mm. for 1 hr. The dry residue was extracted with 100 ml. of anhydrous ether, the ether extract was centrifuged and the clear yellow solution was evaporated leaving uranyl ethoxide as a yellow-brown crystalline solid. It apparently contained alcohol of crystallization and was very easily decomposed by water.

*Anal.* Calcd. for $UO_2(OC_2H_5)_2\cdot 3C_2H_5OH$: U, 47.79. Found: U, 47.80, 48.05.

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(1) M. Delepine, *Bull. soc. chim. France*, [4] **3**, 643 (1908).

(2) H. Albers and S. Lange, *Ber.*, **85**, 278 (1952).

(3) R. G. Jones, E. Bindschadler, G. Karmas, G. A. Martin, Jr., J. R. Thirtle, F. A. Yeoman and H. Gilman, THIS JOURNAL, **78**, 4289 (1956).

(4) R. G. Jones, E. Bindschadler, D. Blume, G. Karmas, G. A. Martin, Jr., J. R. Thirtle, F. A. Yeoman and H. Gilman, *ibid.*, **78**, 6030 (1956).

(5) H. Albers, M. Deutch, W. Krastinat and H. von Osten, *Ber.*, **85**, 278 (1952).

TABLE I

URANYL DIALKYLDITHIOCARBAMATES, $UO_2(R_2NCS_2)_2 \cdot XC_2H_5OH$

| R | Empirical formula | Ethanol of crystln., moles | Yield, % | M.p., °C. | Uranium, % Calcd. | Uranium, % Found | Sulfur, % Calcd. | Sulfur, % Found |
|---|---|---|---|---|---|---|---|---|
| $C_2H_5$ | $C_{18}H_{44}N_2O_6S_4U$ | 4 | 24 | Dec. | 31.7 | 30.9 | 17.1 | 17.4 |
| Piperidyl | $C_{24}H_{56}N_2O_8S_4U$ | 6 | 30 | >250 | 28.4 | 29.3 | | |
| $CH_2=CHCH_2$ | $C_{26}H_{44}N_2O_8S_4U$ | 6 | 14 | 156 | 27.1 | 27.3 | 14.5 | 14.4 |
| $C_3H_7$ | $C_{25}H_{50}N_2O_8S_4U$ | 6 | 13 | 186 | 26.9 | 27.2 | 14.5 | 15.4 |
| $n$-$C_4H_9$ | $C_{30}H_{72}N_2O_8S_4U$ | 6 | 13 | 154 | 24.9 | 24.9 | 13.4 | 14.3 |
| $i$-$C_4H_9$ | $C_{30}H_{72}N_2O_8S_4U$ | 6 | 14 | 188 | 24.9 | 24.9 | 13.4 | 13.5 |
| $s$-$C_4H_9$ | $C_{30}H_{72}N_2O_8S_4U$ | 6 | 18 | 194 | 24.9 | 24.8 | 13.4 | 13.4 |

**Uranyl *t*-Butoxide.**—A solution of uranium(IV) *t*-butoxide[6] in petroleum ether (b.p. 28–38°) was allowed to stand in the presence of dry air for three days. During this time the solution changed color from bright green to bright red. When the red solution was allowed to evaporate slowly, hard red crystals were obtained. The same red compound was formed when dry oxygen was slowly bubbled through a solution of uranium(IV) *t*-butoxide in petroleum ether. The solution changed from green to brown and finally red, and upon evaporation a red crystalline solid was obtained.

When uranium(IV) *t*-butoxide was heated under greatly reduced pressure, a red sublimate was obtained. This was partially soluble in petroleum ether, and when the resulting solution was evaporated, it deposited a red crystalline solid.

Unfortunately, no carbon and hydrogen analyses were carried out. Six uranium analyses on samples prepared by each of the above processes gave values in the range 32.0–32.4% uranium. Calcd. for $UO_2(OC_4H_9)_2 \cdot 4C_4H_9OH$: U, 32.02.

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[6] R. G. Jones, G. Karmas, G. A. Martin, Jr., and H. Gilman, THIS JOURNAL, **78**, 4285 (1956).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

# The Metalation of 1-Methyl-, 1-Benzyl- and 1-Phenylimidazole with *n*-Butyllithium

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1-Methyl-, 1-benzyl- and 1-phenylimidazole are metalated in the 2-position with *n*-butyllithium in yields above 65%. 1-Methylimidazole was found to give a small amount of metalation in the 5-position. Dimetalation of 1-phenylimidazole followed by carbonation gave in low yield a cyclic ketone, 4-oxoimidazo[1,2-a]indoline, a new heterocyclic ring system. The 2-lithioimidazoles from metalation were converted to a variety of derivatives.

The metalation of heterocyclic ring systems by organolithium reagents is frequently a useful method of placing substituents in positions not available in substitution by most reagents. The metalation in the 2-position of thianaphthene[1] and N-substituted indoles,[2] the 1-position of phenothiazine,[3] the 4-position of dibenzofuran[4] and phenoxathiin[5] are examples of monosubstitution of positions not reached by other substitution reactions. We have extended our examination of the metalation of heterocyclic ring systems to some N-substituted imidazoles.

Imidazole and its N-substituted derivatives undergo nitration, chlorination, bromination and sulfonation in the 4- and/or 5-positions. In the case of chlorination and bromination, 2-substitution occurs after substitution of the 4- and 5-positions. At least three reactions, however, allow substitution preferentially in the 2-position. These are iodination, hydroxymethylation and diazo coupling.[6]

The strong tendency for metalation to occur at positions adjacent to the hetero atom in heterocyclic rings is well-established.[7] There are few reports, however, of metalation of monocyclic systems containing two hetero atoms. The metalation of thiazole[8] and 4,5-dimethylthiazole[9] in the 2-position with phenyllithium and the metalation of 1-phenyl-3-methylpyrazole with *n*-butyllithium in the 5-position[10] appear to be the only recorded examples.

Metalation of 1-methylimidazole with an equivalent of *n*-butyllithium followed by carbonation produced mainly 1-methyl-2-imidazolecarboxylic acid (32% yield) and a small amount (1.5% yield) of the 5-acid. The structure of the 5-acid was indicated by comparison of the melting point of the picrate of the acid and the picrate of the methyl ester with values given by Hubball and Pyman[11] and also by comparison of the picrate of the methyl ester with an authentic sample prepared from methyl 1 - methyl - 2 - mercapto - 5 - imidazolecarboxylate. 1-Methyl-2-imidazolecarboxylic acid has not been reported previously. Its structure was proved by two lines of evidence. First the picrate of the methyl ester of 1-methyl-4-imidazolecarboxylic acid, m.p. 171–172°, has been described by Hubball and Pyman,[11] while the picrate of the methyl

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[2] D. A. Shirley and P. A. Roussel, *ibid.*, **75**, 375 (1953).

[3] H. Gilman, D. A. Shirley and P. R. Van Ess, *ibid.*, **66**, 625 (1944).

[4] H. Gilman, F. W. Moore and O. Baine, *ibid.*, **63**, 2479 (1941).

[5] H. Gilman, M. Van Ess, H. B. Willis and F. J. Webb, *ibid.*, **62**, 2606 (1940).

[6] K. Hofmann, "Imidazole and its Derivatives," Part 1, Interscience Publishers, Inc., New York, N. Y., 1953.

[7] H. Gilman and J. W. Morton in R. Adams, ed., "Organic Reaction," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 258–304.

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[9] M. Erne and H. Erlenmeyer, *Helv. Chim. Acta*, **31**, 652 (1948).

[10] H. R. Snyder, F. Verbanc and D. B. Bright, THIS JOURNAL, **74**, 3246 (1952).

[11] W. Hubball and F. L. Pyman, *J. Chem. Soc.*, 21 (1928).