color, granular, and irregular in shape. They melted at 127–128° and were probably an impure acid chloride. Upon digestion with concentrated aqueous ammonia they formed a product which, upon crystallization from alcohol, gave yellow plates possessing no definite melting-point and charring at about 290°. They were not analyzed. The residue, which was insoluble in alcohol, was recrystallized several times from water and then analyzed. The results obtained indicate that one of the two methyl groups, $CH_3$, present in the original salt, was oxidized to the corresponding carboxyl group, CO.OH, but it yet remains to be shown which one of them it was. We are hoping to determine this point in the near future. Tentatively it is assumed to be that methyl group which is in the first position (1). Upon this assumption the salt obtained was the acid potassium salt of 1-carboxy-3-methyl-2,6-dinitrobenzene-4-sulphonic acid and contains one molecule of water of crystallization. The analysis gave 11.04 per cent. potassium, 5.00 per cent. water, 9.00 per cent. sulphur, against 11.08 per cent. potassium, 4.97 per cent. water, 8.83 per cent. sulphur required by theory.

The *acid barium salt* was obtained by adding barium carbonate to the hot solution of the acid potassium salt, filtering, and adding hydrochloric acid to the filtrate. Upon coooling there separated yellow plates containing three molecules of water of crystallization. The analysis gave 15.59 per cent. barium, 12.68 per cent. water, compared to 16.06 per cent. barium, 12.62 per cent. water calculated according to theory.

The *neutral barium salt* was prepared by adding barium carbonate to the hot solution of the acid potassium salt and filtering. It separated in light yellow plates containing no water of crystallization. The analysis gave 30.98 per cent. barium against 30.90 per cent. barium required by theory.

The *neutral strontium salt* was formed by adding strontium carbonate to the hot solution of the acid potassium salt and filtering. It separated in almost white, square crystals containing no water of crystallization. The analysis gave 21.81 per cent. strontium against 22.08 per cent. required by theory.

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# CONCERNING α-DINAPHTHYL SELENIDE AND TELLURIDE.

BY R. E. LYONS AND G. C. BUSH.

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Some years ago, while collecting and tabulating material for the comparative study of the periodic relationship in the oxygen family, especially in the organic combinations of sulphur, selenium and tellurium, we were led to undertake the synthesis of certain aromatic compounds of selenium and tellurium necessary to fill in the blank spaces in the chart. The work was not completed because of our separation. The compounds prepared in this connection are as yet unreported and may be described as follows:

*1. α-Dinaphthyl Selenide,* $(C_{10}H_7)_2Se$.—Krafft and Lyons[1] prepared phenyl telluride by heating together mercury diphenyl and metallic tellurium. We undertook the preparation of α-dinaphthyl selenide in an analogous manner from α-dinaphthyl mercury and selenium:

$$(C_{10}H_7)_2Hg + 2Se = HgSe + (C_{10}H_7)_2Se.$$

A mixture of 4.5 grams α-dinaphthyl mercury, m. p. 242°, and 1.58 grams finely powdered selenium, contained in a small Anschütz flask, was kept in a Wood's metal bath at 190° under a pressure of 16 mm. for about 12 hours. A temperature above 200° was found unfavorable, causing the dinaphthyl mercury to split into mercury and naphthalene. When cool, the mixture was distilled with steam to remove the naphthalene and the residue extracted with ether. Evaporation of the extracts gave 1.7 grams, or 54 per cent. of the theoretical amount of the dinaphthyl selenide. The product crystallized from absolute alcohol, in which it is moderately soluble, in fine, faintly yellow, glittering leaflets, which melted at 114°. Neither treatment with charcoal nor crystallization from other solvents, as ether or amyl alcohol, gave a colorless product. Exposure to air and light effects rapid decomposition of the selenide.[2]

$(C_{10}H_7)_2Se$, Calculated: C, 72.28; H, 4.18.
Found: C, 72.20; H, 4.11.

The selenium in the compound was determined by the method of Lyons and Shinn.[3] 0.3816 gram required 45.7 cc. *N*/10 sodium thiosulphate. Calculated, 23.73; found, 23.65 per cent. Se.

*2. α-Dinaphthyl Selenide Dibromide,* $(C_{10}H_7)_2Se.Br_2$.—When the theoretical quantity of bromine was slowly added to a warm alcoholic solution of the selenide and the mixture allowed to stand for several hours the dinaphthyl selenide dibromide separated out in the form of dirty white needles. The yield was practically quantitative. The bromide is soluble in amyl alcohol, but was more readily crystallized from carbon disulphide as white, delicate needles which melted at 183° with decomposition.

Calculated for $(C_{10}H_7)_2Se.Br_2$: Br, 32.45.
Found: Br, 32.31.

Diphenyl selenium oxide[4] and diphenyl tellurium oxide[5] have been ob-

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[1] *Ber.*, **27**, 1769.

[2] All selenium and tellurium compounds described in this paper are so affected in varying degrees.

[3] THIS JOURNAL, **24**, 1087.

[4] *Ber.*, **26**, 2819.

[5] *Ibid.*, **27**, 1770.

tained by treating the respective bromides with dilute solutions of sodium hydroxide. The treatment of α-dinaphthyl selenide dibromide with solutions of sodium hydroxide of varying concentration at different temperatures failed to produce the desired dinaphthyl selenium oxide, $(C_{10}H_7)_2SeO$. Boiling with 15 per cent. sodium hydroxide solution produced no change in the substance. A 25 per cent. solution of the alkali was without action at room temperature, but at about 90° the bromine was removed. That oxygen did not take its place was shown by the recovery of dinaphthyl selenide from the reaction mixture.

3. *α-Dinaphthyl Selenide Dichloride*, $(C_{10}H_7)_2Se.Cl_2$.—A current of dry chlorine gas passed into an ether solution of the dinaphthyl selenide produced immediately a heavy, white, amorphous precipitate of dinaphthyl selenide dichloride. The chloride is insoluble in alcohol, ether, chloroform, benzene, ligroin, carbon disulphide and amyl alcohol; easily soluble in xylene, from which it crystallizes in colorless prisms melting at 130°.

Calculated for $(C_{10}H_7)_2Se.Cl_2$: Cl, 17.53.
Found: Cl, 17.40.

4. *α-Dinaphthyl Telluride*, $(C_{10}H_7)_2Te$.—This compound was obtained by heating together molecular quantities of α-dinaphthyl mercury and tellurium according to the method successfully used in the preparation of phenyl telluride and α-dinaphthyl selenide,

$$(C_{10}H_7)_2Hg + 2Te = HgTe + (C_{10}H_7)_2Te.$$

A mixture of 4.5 grams dinaphthyl mercury and 2.5 grams powdered tellurium, contained in a small Anschutz flask, attached to a vacuum pump, was kept at 190–198° and 16.5 mm. pressure for about 8 hours. After cooling, the solidified mass was distilled with steam to effect the removal of the naphthalene which had collected in the upper portion of the flask. The residue was then extracted with ether, the ether solution quickly filtered and evaporated, to avoid excessive separation of tellurium. The solid residue was purified by crystallization from much alcohol. Three crystallizations of the telluride from alcohol gave glittering brownish yellow leaflets which melted at 126.5°. The yield of the crude product was 53 per cent. of the theoretical. Excessive or prolonged heating of the reaction mixture brings about a secondary change resulting in the formation of a yellow product which melts at about 190° and imparts to alcohol, ether, carbon disulphide and other solvents a very pronounced fluorescence. The product was tellurium-free and was not further examined.

$(C_{10}H_7)_2Te$, Calculated: C, 63.33; H, 3.69.
Found: C, 63.23; H, 3.49.

The tellurium was determined by decomposition of the substance with red fuming nitric acid in a Carius tube, reducing the tellurous acid in hydrochloric acid solution with sodium bisulphite, collecting the precipitate on a weighed Gooch filter, drying at 105°, and weighing.

Calculated for $(C_{10}H_7)_2Te$: Te, 32.98.
Found: Te, 32.79.

5. *α-Dinaphthyl Telluride Dibromide*, $(C_{10}H_7)_2Te.Br_2$.—The addition of bromine to an ether or alcoholic solution of α-dinaphthyl telluride gave immediately a heavy yellow precipitate of dinaphthyl telluride dibromide. The precipitate was washed with ether and crystallized from carbon disulphide, in which it is sparingly soluble, as sparkling, lemon-yellow granules, which melted with decomposition at 244°. If the bromine is added to an exceedingly dilute, warm, alcoholic solution of the telluride and the mixture be allowed to stand for several hours, fine yellow crystals of the bromide separate, which, after washing and drying, melt at 244°.

Calculated for $(C_{10}H_7)_2Te.Br_2$: Br, 29.57.
Found: Br, 29.67.

6. *α-Dinaphthyl Telluride Dichloride*, $(C_{10}H_7)_2Te.Cl_2$.—When a current of dry chlorine is passed into an ether solution of α-dinaphthyl telluride a heavy white precipitate of the chloride is formed. The chloride is insoluble in all of the ordinary solvents, but is sparingly soluble in xylene, from which it crystallizes in glittering, colorless granules, melting at 265°.

Calculated for $(C_{10}H_7)_2Te.Cl_2$: Cl, 15.74.
Found: Cl, 15.83.

7. *Diphenyl Telluride Dichloride*, $(C_6H_5)_2Te.Cl_2$, was prepared by passing dry chlorine gas into an ether solution of diphenyl telluride[1] and purified by recrystallization from xylene, in which it is very readily soluble. Long, white prisms, melting at 160°.

Calculated for $(C_6H_5)_2Te.Cl_2$: Cl, 20.24.
Found: Cl, 20.36.

8. *β-Dinaphthyl Selenide Dichloride*, $(C_{10}H_7)_2Se.Cl_2$, was prepared by the action of dry chlorine gas upon the selenide in ether solution. By recrystallization from carbon disulphide it was obtained in almost colorless leaflets, melting at 146°.

Calculated for $(C_{10}H_7)_2Se.Cl_2$: Cl, 17.53.
Found: Cl, 17.60.

From the time of Doebereiner the similarity of sulphur, selenium and tellurium compounds has been a subject of comment. There is, in general, a pronounced similarity in methods of formation, in deportment and in the effect of substituents in the compounds of these elements with organic radicals. The changes in the physical constants, *e. g.*, boiling-point, melting-point, to be observed in a comparison of sulphides, selenides

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[1] *Ber.*, **27**, 1769.

[2] *Ibid.*, **27**, 1767.

and tellurides of like radicals, are usually gradual and progressive with the increase in magnitude of the atomic weights. Data concerning the compounds described in this paper and some related compounds, previously reported,[1] are placed in the following tables:

| Sulphides. | B. p. (16 mm.). | Selenides. | B. p. (16 mm.). | Tellurides. | B. p. (16 mm.). |
|---|---|---|---|---|---|
| $(C_5H_5)_2S$ | 157° | $(C_6H_5)_2Se$ | 167° | $(C_6H_5)_2Te$ | 182° |
| $C_6H_5.SH$ | 172° | $C_6H_5.SeH$ | 183° | ...... | .... |
|  | M. p. |  | M. p. |  | M. p. |
| $(C_6H_5)_2S.S$ | 60° | $(C_6H_5)_2Se.Se$ | 63.5° | ...... | .... |
| $(C_6H_5)_2SO$ | 70.5° | $(C_6N_5)_2SeO$ | 114° | $(C_6H_5)_2TeO$ | 187° |
| $\alpha$-$(C_{10}H_7)_2S$ | 110° | $\alpha$-$(C_{10}H_7)_2Se$ | 114° | $\alpha$-$(C_{10}H_7)_2Te$ | 126.5° |
| $\beta$-$(C_{10}H_7)_2S$ | 151° | $\beta$-$(C_{10}H_7)_2Se$ | 138.5° | ...... | .... |
| ($o$-$CH_3.C_6H_4)_2S$ | 64° | ($o$-$CH_3.C_6H_4)_2Se$ | 62° | ($o$-$CH_3.C_6H_4)_2Te$ | 38° |
| ($p$-$CH_3.C_6H_4)_2S$ | 57° | ($p$-$CH_3.C_6H_4)_2Se$ | 69° | ($p$-$CH_3.C_6H_4)_2Te$ | 64° |
| $(C_6H_4Cl)_2S$ | 88° | $(C_6H_4Cl)_2Se$ | 96° | ...... | .... |
| $(C_6H_4Br)_2S$ | 109.5° | $(C_6H_4Br)_2Se$ | 115.5° | ...... | .... |

The Halogen Addition Products.

| Chlorides. | M. p. | Bromides. | M. p. |
|---|---|---|---|
| $(C_6H_5)_2S.Cl_2$ | .... | $(C_6H_5)_2S.Br_2$ | .... |
| $(C_6H_5)_2Se.Cl_2$ | 183° | $(C_6H_5)_2Se.Br_2$ | 148° |
| $(C_6H_5)_2Te.Cl_2$ | 160° | $(C_6H_5)_2Te.Br_2$ | 203° |
| $\beta$-$(C_{10}H_7)_2S.Cl_2$ | .... | $\beta$-$(C_{10}H_7)_2S.Br_2$ | .... |
| $\beta$-$(C_{10}H_7)_2Se.Cl_2$ | 146° | $\beta$-$(C_{10}H_7)_2Se.Br_2$ | 161° |
| $\beta$-$(C_{10}H_7)_2Te.Cl_2$ | .... | $\beta$-$(C_{10}H_7)_2Te.Br_2$ | .... |
| $\alpha$-$(C_{10}H_7)_2S.Cl_2$ | .... | $\alpha$-$(C_{10}H_7)_2S.Br_2$ | .... |
| $\alpha$-$(C_{10}H_7)_2Se.Cl_2$ | 130° | $\alpha$-$(C_{10}H_7)_2Se.Br_2$ | 183° |
| $\alpha$-$(C_{10}H_7)_2Te.Cl_2$ | 265° | $\alpha$-$(C_{10}H_7)_2Te.Br_2$ | 244° |
| ($p$-$CH_3.C_6H_4)_2S.Cl_2$ | .... | ($p$-$CH_3.C_6H_4)_2S.Br_2$ | .... |
| ($p$-$CH_3.C_6H_4)_2Se.Cl_2$ | 177° | ($p$-$CH_3.C_6H_4)_2Se.Br_2$ | 162° |
| $p$-$CH_3.C_6H_4)_2Te.Cl_2$ | .... | ($p$-$CH_3.C_6H_4)_2Te.Br_2$ | 201° |
| ($o$-$CH_3.C_6H_4)_2Se.Cl_2$ | 152° | ($o$-$CH_3.C_6H_4)_2SeBr_2$ | 84° |
| ($o$-$CH_3.C_6H_4)_2Te.Cl_2$ | .... | ($o$-$CH_3.C_6H_4)_2Te.Br_2$ | 182° |

Consideration of the rather limited number of these compounds now available shows that the change in boiling and melting point generally, but not always, varies directly with the magnitude of the atomic weight. The first known and simpler compounds of these elements, *e. g.*, the phenyl compounds, conform to this and exhibit differences which are strikingly constant. However, examination of all of the data given in the above tables shows that the change does not follow a rigid or fixed rule. In some instances the changes are very abrupt and out of proportion to the difference between the atomic weights; in other instances the change is the reverse of the expectation and is without plausible explanation, *e. g.*, *o*-tolyl sulphide, selenide and telluride show the melting-points 64°, 62° and 38°, respectively. The melting-point decreases as the atomic weight increases and the drop from 62° to 38° is abrupt.

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[1] *Ber.*, **26**, 2818; **27**, 1764; **28**, 1670.

The changes are even more erratic and irregular in the halogen addition products. An extreme case is found in the *o*-tolyl selenide dichloride and dibromide melting at 152° and 84°, respectively. The halogen substitution products, thus far reported, exhibit differences which are more nearly constant than is observed among the halogen addition products.

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(CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.)

# HYDRAZONES OF AROMATIC HYDROXYKETONES. ALKALI-INSOLUBLE PHENOLS.

## SECOND PAPER.

BY HENRY A. TORREY AND H. B. KIPPER.

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Although it is a very general rule, so general indeed that it is almost universal, that phenols are soluble in aqueous alkalies, there are certain substances of this class that are marked exceptions. The work described in this paper consists of an extension of the list of such compounds, and some investigation of the conditions to which this alkali-insolubility is due. While studying the phenylhydrazones of certain hydroxy aceto- and benzophenones, it was found, as mentioned in an earlier paper,[1] that when the free hydroxyl was in the ortho position with reference to the substituted ketone group, the substance was insoluble in strong aqueous alkalies. Substances showing this characteristic property have been obtained and studied by others. O. Anselmino[2] studied the phenylhydrazones of homosalicylaldehydes and obtained alkali-insoluble compounds similar to ours. Liebermann[3] first discussed in detail the alkaline insolubility of benzene azonaphthol, which was later studied by Goldschmidt and R. Brubacher,[4] McPherson[5] and Hantzsch and Farmer.[6] St. v. Kostanecki has obtained certain nitrogen-free phenols which are insoluble in alkalies; thus A. Cornelson and St. v. Kostanecki[7] report that 2-hydroxy-benzaldiacetophenone,

$$HOC_6H_4CH(CH_2COC_6H_5)_2,$$

is insoluble in warm dilute sodium hydroxide, although it does dissolve in hot 15 per cent. potassium hydroxide, and St. v. Kostanecki and R. v. Salis[8] state that 2-ethoxybenzalresacetophenonmonoethyl ether,

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[1] THIS JOURNAL, 29, 77.

[2] *Ber.*, 35, 4099.

[3] *Ibid.*, 16, 2858.

[4] *Ibid.*, 24, 2306.

[5] *Ibid.*, 28, 2418.

[6] *Ibid.*, 32, 3100.

[7] *Ibid.*, 29, 242.

[8] *Ibid.*, 32, 1030.