When petroleum ether (Skellysolve B) was added to this clear ether solution, an oily product separated. After the mixture had been allowed to stand overnight, the oil had not crystallized but crystalline material was present throughout the solution. This crystalline material, when carefully separated from the oil, gave a negative Legal (nitroprusside) test. The oil was crystallized from a mixture of alcohol and water. After two recrystallizations, 350 mg. (19%) of product was obtained. The compound crystallizes as needles, which contain 1.5 moles of water of crystallization. The melting point depends upon the rate of heating, but ordinarily the compound melts at 145–150° after preliminary sintering. For analysis it was dried over calcium chloride at 75° and 10 mm.

Anal. Calcd. for $C_{37}H_{52}O_{14}\cdot 1.5H_2O$: C, 59.4; H, 7.4. Found: C, 59.4; H, 7.4.

Periplogenin-(3)-β-*d*-glucoside.—The viscous oil obtained on deacetylation was crystallized initially from ethyl acetate saturated with water, and recrystallized from 95% alcohol–ether. It crystallized as fine needles containing two waters of crystallization and melted at 195–200° (dec.). For analysis it was dried over calcium chloride at 75° and 10 mm.

Anal. Calcd. for $C_{29}H_{44}O_{10}\cdot 2H_2O$: C, 59.2; H, 8.2. Found: C, 59.5; H, 8.0.

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RECEIVED MAY 8, 1947

Pyrolysis of Diketene

BY J. T. FITZPATRICK

There is considerable evidence in favor of the Boese–Wilson[1] vinylaceto-β-lactone structure for diketene.[1–5] However, on pyrolysis this structure would be expected to give allene and carbon dioxide as well as the previously observed product, ketene.[1,3] It has now been found that significant amounts of these by-products are present in ketene made in a "ketene lamp"[1] with a Nichrome filament. The amount of impurities depends on both the temperature and the condition of the filament. A filament which had been used for some time gave a product containing 13% allene and carbon dioxide in approximately equal amounts; after thorough cleaning with nitric acid the filament gave only 8% by-products. When a used filament was operated at a voltage lower than usual, the by-products accounted for more than 18% of the reacted diketene.

The diketene used was commercial material which had been redistilled in the laboratory; it boiled at 62° at 75 mm., and froze at −6.5 to −7.0°; its purity was estimated to be well over 99%. It was cracked in a ketene lamp with a filament made of approximately 14 ft. of no. 22 B. and S. gage Nichrome wire. The rate of cracking was 320–350 g./hour with 75 volts, or 50–55 g./hour with 55 volts on the filament. After passing through a partial condenser to remove unreacted diketene, the products were condensed and weighed in tared traps cooled with liquid air. The material was vaporized from these traps and passed through 0.25% aqueous sulfuric acid at 50–55° to remove the ketene. The small amount of residue which did not vaporize at room temperature was considered to be unreacted diketene. The blow-off gas from the absorber was again collected in tared traps and weighed. Samples of this condensate were analyzed in the mass spectrograph by the South Charleston Works Laboratory of this Company. A typical analysis was: carbon dioxide, 53.9%; allene, 45.1%; acetone, 0.4%; and trifling amounts of other compounds, including 0.1% ketene. Lack of a reaction with silver nitrate solution showed the absence of methylacetylene, which is nearly indistinguishable from allene in the mass spectrograph.

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RECEIVED JUNE 16, 1947

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[1] Boese, *Ind. Eng. Chem.*, **32**, 16 (1940).

[2] Hurdis and Smyth, THIS JOURNAL, **65**, 89 (1943).

[3] Rice and Roberts, *ibid.*, **65**, 1677 (1943).

[4] Taufen and Murray, *ibid.*, **67**, 754 (1945).

[5] Bauer, Bregman and Wrightson, paper presented before the Division of Physical Chemistry of the American Chemical Society at the Atlantic City meeting, April, 1946.

Selenenyl Sulfur Compounds

BY OLAV FOSS

Twiss, Jones and Hadley[1] reported the reactions of *o*-nitrobenzeneselenenyl bromide[2] with mercaptobenzthiazole and thiocarbonyl salts. We have found that *o*-nitrobenzeneselenenyl bromide reacts rapidly with sodium or potassium thiocyanate, di-O-alkylmonothiophosphates,[3] thiosulfonates, and sulfinates, to give *o*-nitrobenzeneselenenyl thiocyanate, di-O-alkylmonothiophosphates, thiosulfonates and sulfinates, respectively. The general procedure consists in dissolving 1 g. of the bromide in 3–4 ml. of ethyl acetate and 5 ml. of methanol, and adding a slight excess of the thio salt or sulfinate, dissolved in 10 ml. of methanol. The product thereon crystallizes out rapidly (in the case of di-O-alkylmonothiophosphates after addition of some water). Potassium *o*-nitrobenzeneselenenyl thiosulfate was obtained by reaction of the bromide, dissolved in benzene, with a slight excess of potassium thiosulfate in the double amount of water. The crystals are stable, and have a yellowish green color. The di-O-ethylmonothiophosphate was obtained as a yellowish green oil. Among the compounds prepared are these in Table I.

TABLE I

Compound (R = *o*-nitrophenyl)	M. p., °C. (uncor.)	Selenium, % Calcd.	Found
$RSeSCN$	107[a]	30.5	30.4
$RSeSPO(OCH_3)_2$	79[b]	23.1	23.1
$RSeSPO(OC_2H_5)_2$	Oil	21.3	21.5
$RSeS_2O_2CH_3$	96[b]	25.3	25.3
$RSeS_2O_2C_2H_5$	90[b]	24.2	24.0
$RSeS_2O_2C_6H_5$	147[c]	21.1	21.3
$RSeS_2O_2C_6H_4CH_3$-*p*	148[c]	20.3	20.2
$RSeS_2O_2C_6H_4Br$-*p*	169[c]	17.4	17.1
$RSeSO_2C_6H_5$	109[d]	23.1	23.1
$RSeSO_2C_6H_4CH_3$-*p*	118[d]	22.2	22.0
$RSeSO_2C_6H_4CH_3$-*o*	95[e]	22.2	22.2
$RSeSO_2C_6H_4Br$-*p*	126[c]	18.8	18.7
$RSeS_2O_3K$	*ca.* 190[d] dec.	22.4	22.4

[a] Crystallized from carbon tetrachloride. [b] Crystallized from carbon disulfide. [c] Crystallized from benzene. [d] Crystallized from ethanol. [e] Crystallized from methanol.

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[1] Twiss, Jones and Hadley, British Patent 441,653 (1936).

[2] Behaghel and Seibert, *Ber.*, **66**, 708 (1933).

[3] Foss, *Acta Chemica Scandinavica*, **1**, 8 (1947).