TABLE I

ACTION OF GRIGNARD REAGENTS ON OXAZOLIN-5-ONES

Oxazolin-5-one Derivs.	Grignard Reagent	Product	M.p.,[a] °C.	Yield, %	Color with H_2SO_4	Formula	Analysis Carbon Calc'd	Analysis Carbon Found	Analysis Hydrogen Calc'd	Analysis Hydrogen Found	Analysis Nitrogen Calc'd	Analysis Nitrogen Found
IIIa	Methyl	IVa	118	65	Red	$C_{18}H_{19}NO_2$	76.87	76.68	6.76	6.56	4.98	4.78
IIIa	Phenyl	IVb	156	73	Orange-red	$C_{28}H_{23}NO_2$[b]	82.96	82.75	5.68	5.48	3.46	3.27
IIIa	*p*-Tolyl	IVc	185	62	Red	$C_{30}H_{27}NO_2$	83.14	82.94	6.23	6.13	3.23	3.18
IIIb[c]	Methyl	IVd	104	58	Orange	$C_{19}H_{21}NO_3$	73.31	73.24	6.75	6.47	4.50	4.32
IIIb	Phenyl	IVe	106	63	Orange	$C_{29}H_{25}NO_3$	80.00	79.68	5.74	5.66	3.22	2.98
IIIb	*p*-Tolyl	IVf	146	56	Orange	$C_{31}H_{29}NO_3$	80.34	80.21	6.26	5.98	3.02	2.94

[a] All melting points are uncorrected. [b] Active H, Calc'd: 0.49. Found: 0.42. Mol. wt.: 405. Found (micro-Rast) 391. [c] Henze, Whitney, and Eppright, *J. Am. Chem. Soc.*, **62**, 567 (1940).

EXPERIMENTAL

Action of Grignard reagents on 2-phenyl-4-arylidene-2-oxazolin-5-ones (III). The following illustrates the procedure: To an ethereal solution of phenylmagnesium bromide (prepared from 0.9 g. of magnesium, 8 g. of bromobenzene, and 40 ml. of dry ether) was added a suspension of 1 g. of IIIa[6] in 30 ml. of benzene. The reaction mixture was refluxed (steam-bath) for two hours, set aside at room temperature overnight, and then decomposed with a cold, saturated aqueous ammonium chloride solution. The reaction mixture was extracted with ether; the ethereal layer was dried (Na_2SO_4) and allowed to evaporate slowly. The oily residue was washed several times with hot petroleum ether (b.p. 40–60°). The solid (IVa), so obtained, was crystallized from benzene, m.p. 156°. A mixture of benzene and petroleum ether (b.p. 50–60°) was used as a solvent for the products IVb–f.

Action of phenylmagnesium bromide on ethyl α-benzoylaminocinnamate. A solution of 1 g. of ethyl α-benzoylaminocinnamate[6] in 40 ml. of dry benzene was treated with phenylmagnesium bromide as described above. The oily residue that was obtained after the evaporation of the ethereal solution was washed several times with petroleum ether (b.p. 50–60°) and was crystallized from benzene, m.p. 156°. It was identified as IVb (m.p. and mixture m.p., and color reaction with sulfuric acid).

Behavior of 2-phenyl-4-benzylidene-2-imidazolin-5-one (VIII) *toward:* (*a*) *Methylmagnesium iodide.* To an ethereal solution of methylmagnesium iodide (prepared from 1 g. of magnesium, 7 g. of methyl iodide, and 40 ml. of dry ether) was added a suspension of 1 g. of VIII[7] in 30 ml. of dry benzene. The reaction mixture was worked up in the usual manner and the solid obtained upon evaporation of the ethereal extract was crystallized from acetone, m.p. 188°. Yield, *ca.* 77%.

Anal. Calc'd for $C_{17}H_{16}N_2O$: C, 77.27; H, 6.06; N, 10.61. Found: C, 77.13; H, 5.87; N, 10.53.

Compound IXa is difficultly soluble in benzene and alcohol, and almost insoluble in aqueous sodium hydroxide solution (10%). It gives an orange color when treated with sulfuric acid.

(*b*) *Phenylmagnesium bromide.* A suspension of 1 g. of VIII in 40 ml. of dry benzene was treated with phenylmagnesium bromide as described for IIIa. The solid residue, obtained by evaporation of the ether extract, was crystallized from benzene, m.p. 216°.

Anal. Calc'd for $C_{22}H_{18}N_2O$: C, 80.98; H, 5.52; N, 8.59; Mol. wt., 326. Found: C, 80.77; H, 5.31; N, 8.24; Mol. wt. (micro-Rast), 311.

Compound IXb is difficultly soluble in boiling alcohol and benzene. It is almost insoluble in aqueous sodium hydroxide solution (10%) and gives an orange color with sulfuric acid.

Action of hydrochloric acid and glacial acetic acid on IVb. A suspension of 0.5 g. of IVb in 20 ml. of glacial acetic acid and 10 ml. of hydrochloric acid (*sp. gr.* 1.18) was refluxed for 15 minutes. Compound IVb dissolved gradually giving a yellow solution. Compound V, which separated during the reflux period was filtered off, washed with water, and recrystallized from alcohol, m.p. 186°. The yield is almost quantitative.

Anal. Calc'd for $C_{28}H_{21}NO$: C, 86.82; H, 5.42; N, 3.62. Found: C, 86.67; H, 5.24; N, 3.55.

V is soluble in boiling benzene and acetic acid, readily soluble in cold chloroform. It is almost insoluble in aqueous sodium hydroxide solution (10%) and gives an orange-red color with sulfuric acid.

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[6] Erlenmeyer, *Ann.*, **275**, 11 (1893).

[7] Williams and Ronzio, *J. Am. Chem. Soc.*, **68**, 647 (1946).

The Preparation of 2-Methylthianaphthene and 2-Methylselenonaphthene and Their Ultraviolet Absorption Spectra

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The purpose of our investigations was the preparation of selenonaphthene with an alkyl group in α-position and the comparison of its spectrum with the spectra of the basic compound and the sulfur analog. As far as we are aware investigations of this compound have not been reported.

The synthesis of 2-methylthianaphthene (I) was carried out by the method of Hansch and Blondon[1] except that the 2-methyl-3-acetoxythianaphthene was isolated and the resulting ketone was subjected to a Clemensen reduction. The 2,3-dihydro-2-methylthianaphthene then was dehydrogenated by boiling with sulfur. We subjected our compound to this treatment so as to prove that the compound

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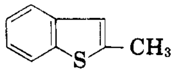
[1] C. Hansch and W. Blondon, *J. Am. Chem. Soc.*, **70**, 1561 (1948).

obtained here was identical with that obtained by the different methods.

From o,o'-diselenodibenzoic acid,[2] a new compound, the α-(o-carboxyphenylseleno)propionic acid was prepared, and from this the selenium analog (II) was synthesized by a ring closure method in which the 2-methyl-3-oxoselenonaphthane was reduced with sodium amalgam. The reduction was carried out following the method used for 3-selenonaphthenol.[3]



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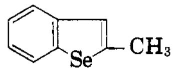

II

The ultraviolet absorption spectrum from 200 mμ for 2-methylthianaphthene (Fig. 1) was determined in heptane. Maxima were found at 297.5, 288, 259.5, and 229.5 mμ (log ε: 3.34, 3.27, 3.89, and 4.47, resp.), minima at 295, 283.5, and 246.5 mμ (log ε: 2.88, 3.18, and 3.76, resp.) and inflexions at 291, 281, and 264 mμ. For comparison the spectrum of thianaphthene is given in Fig. 1. It can be seen that the curve of the methyl derivative is very similar to that of the thianaphthene. The curve shows a slight bathochromic shift and some variation in intensity. These changes are due to the hyperconjugation of the methyl group.

Similarly, the spectrum of 2-methylselenonaphthene closely resembles the spectrum of selenonaphthene. Fig. 2 shows the observed maxima at 304, 295.5, 262, and 238 mμ (log ε: 3.73, 3.53, 3.85, and 4.47, resp.), minima at 300.5, 281, 256, and 218 mμ (log ε: 3.35, 3.21, 3.82, and 3.82 resp.) and inflexions at 292.5, 288, and 253 mμ. Here also the slight bathochromic shift can be observed which is due to the hyperconjugation of the methyl group.

Comparing the two methyl derivatives it is obvious that a considerable resemblance exists between the sulfur and selenium compounds. This fact fits in with the regularity according to which the spectrum of a selenium compound shows a bathochromic shift compared with the spectrum of the corresponding sulfur compound, the spectra otherwise being of the same structure.

The spectra were measured also in ethyl alcohol. The curves obtained here are in close agreement with those measured in heptane. The slight difference between the spectra in the two solvents is due to the effects of the polarity of ethyl alcohol.

EXPERIMENTAL

α-(o-Carboxyphenylmercapto)propionic acid. The reduction of o,o'-dithiodibenzoic acid was carried out with iron filings,[4] then an equivalent amount of α-bromopropionic acid, neutralized with sodium carbonate, was added. Yield: 83%, m.p. 195°, from water.

2-Methyl-3-acetoxythianaphthene. After the ring closure the mixture obtained was neutralized with the calculated amount of sodium hydroxide. It was extracted with ether and the residue was cooled in ice to give yellowish-white needles, m.p. 39–42°; yield, 76–80%.

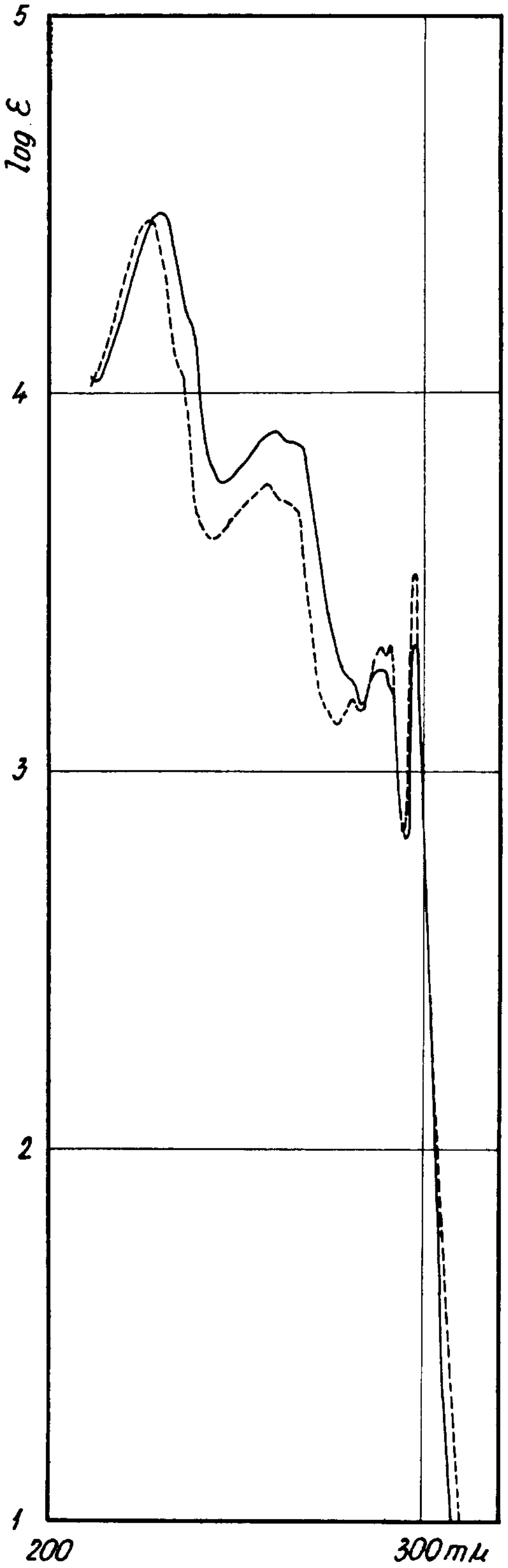

FIG. 1.—ULTRAVIOLET ABSORPTION SPECTRA IN HEPTANE. 2-Methylthianaphthene (————); thianaphthene (- - - - - -).

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[2] R. Lesser, R. Weiss, *Ber.*, **46**, 2640 (1913).

[3] G. Komppa and G. A. Nyman, *J. prakt. Chem.*, [2], **139**, 229 (1934).

[4] H. E. Fierz-David, L. Blangey, *Farbenchemie*, 8 Aufl, Springer, Wien, 1952, p. 323.

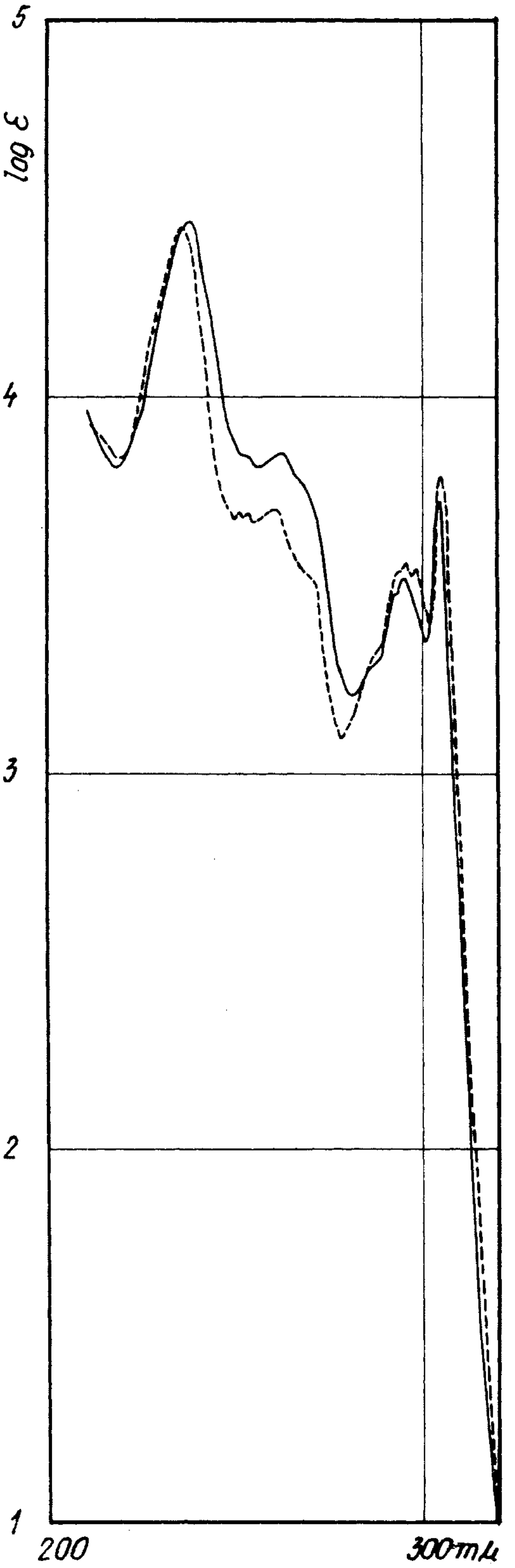

FIG. 2.—ULTRAVIOLET ABSORPTION SPECTRA IN HEPTANE. 2-Methylselenonaphthene (————); selenonaphthene (- - - - - - -).

2,3-Dihydro-2-methylthianaphthene. 2-Methyl-3-oxothianaphthane (20.52 g., 0.125 mole) was dissolved in 54 ml. of toluene, then 54 g. of amalgamated zinc suspended in 40 ml. of water was added. During stirring the mixture was acidified with 44 ml. of acetic acid; then there was added 94 ml. of hydrochloric acid under reflux. This was repeated four times in every hour with 25.6 ml. of hydrochloric acid. After six hours the toluene portion was separated, washed with water, and dried over calcium chloride. The toluene was distilled and the residue was fractionated in a vacuum; b.p. 111–125°/18 mm.

2-Methylthianaphthene. 2,3-Dihydro-2-methylthianaphthene (8.5 g.) was heated for three hours at 220° with 1.82 g. of sulfur, and then was steam-distilled from a dilute alkaline solution to give white needles from ethanol, m.p. 51–52°.

Anal. Calc'd for C_9H_8S: C, 72,93: H, 5.44. Found: C, 72.25; H, 5.41.

The *picrate* of this substance had m.p. 108.5°.

α-(o-Carboxyphenylseleno)propionic acid. o,o'-Diselenodibenzoic acid (5.2 g., 0.013 mole) was dissolved in a solution of 2.6 g. of sodium hydroxide. It was heated and stirred for a half hour with 4 g. of zinc dust, then was filtered and to the clear solution was added an equivalent amount of α-bromopropionic acid neutralized with sodium carbonate. After short warming it was acidified with hydrochloric acid. Yield, 5.1 g. (72%), m.p. 212–213°, from a methanol-water mixture. The substance was soluble in most organic solvents.

Anal. Calc'd for $C_{10}H_{10}O_2Se$: C, 43.97; H, 3.69, Found: C, 43.83; H, 3.70.

2-Methylselenonaphthene. A mixture of 4 g. (0.014 mole) of α-(*o*-carboxyphenylseleno)propionic acid, 1.7 g. of anhydrous potassium acetate, and 4.4 ml. of acetic anhydride was heated to 115°. Carbon dioxide gas evolved and after subsidence of the gas evolution the temperature was raised to 135–140° and the mixture was kept at that temperature for 20 minutes. Then it was cooled and made alkaline with a solution of 10 g. of potassium hydroxide and refluxed for an hour. The solution was acidified with phosphoric acid and steam-distilled. The resulting oil was extracted with ether.

The 2-methyl-3-oxoselenonaphthane thus obtained was dissolved in dil. ethanol and 48 g. of amalgam, containing 4 per cent sodium, was added. Next day the solution was warmed, the ethanol was distilled off and the solution acidified with dil. hydrochloric acid. Hydrogen selenide gas was evolved and the separated oil was steam-distilled. The resulting red-brown crystals were steam-distilled once more to remove the traces of selenium. Yield: 0.8 g. (28.2%). It formed white, bright plates from methanol and was soluble in most organic solvents, insoluble in water. It sublimes in a vacuum, m.p. 63°.

Anal. Calc'd for C_9H_8Se: C, 55.4; H, 4.13. Found: C, 55.98; H, 4.60.

This compound gives a *picrate* in form of golden-yellow needles from ethanol. M.p. 118.5°. When dried in a vacuum it decomposes.

The spectra were determined with a Beckman quartz spectrophotometer Model DU in silica cells of 1 cm. thickness.

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2-Pyrrolidone

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Catalytic hydrogenation of an alkyl 3-cyanopropionate over Raney nickel gives good yields of 2-pyrrolidone when carried out in the presence of ammonia.