

1-Naphthyllithium and Silicon Compounds.—Perylene was isolated from several mixtures resulting from the separate treatment of silicon tetrachloride, ethyl silicate and hexachlorodisilane with 1-naphthyllithium. In all cases the 1-naphthyllithium was made in the conventional manner from the bromide and lithium.

A typical run is described. 1-Naphthyllithium (0.26 mole) in 400 ml. of ether was added to 17.9 g. (0.086 mole) of ethyl silicate and refluxed overnight. The ether was replaced with benzene, the solution filtered and the filtrate was concentrated to about 50 ml. and allowed to crystallize. The yellow solid, m.p. 190–210°, after two crystallizations from benzene melted at 268–269° and showed no depression of m.p. when mixed with perylene. The yield from this run was 2.1%.

Similar runs using silicon tetrachloride gave yields of perylene from 1.2 to 2.6%, and with hexachlorodisilane,

2.2 and 2.4%. The evidence is, therefore, that the silicon compounds play no significant part in the formation of perylene.

Summary

The hydrocarbon, perylene, has been isolated from several reaction mixtures involving 1-naphthyllithium and 1-naphthylmagnesium bromide. The formation of perylene from the 1-naphthyl-metallic compounds may be due in part to a free radical mechanism and also to a cyclodehydrogenation of 1,1'-binaphthyl by means of organolithium compounds. Experiments are presented in support of this latter mechanism.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Characterization of Sulfonic, Sulfinic, Phosphonic and Some Other Acids as Thallous Salts

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It has been suggested² that thallous sulfonates may be reagents of choice in the characterization of some sulfonic acids. Several advantages of the thallous salts as derivatives of the sulfonic acids were detailed in a previous contribution.² The present report extends the scope of the reaction to other types of acids, and also further defines certain limitations in the usefulness of the reaction.

Although the thallous arylsulfonates meet the requirements for good derivatives, the thallous alkylsulfonates appear to be less satisfactory derivatives.

The arylsulfinic acids appear to be conveniently characterized as thallous salts.

The aromatic thiols give excellent derivatives, but the aliphatic thiols give salts having insufficiently sharp melting points. Moreover, the thallous mercaptides are evidently unstable, decomposing on standing in the dark in tightly stoppered vials. However, the quantitative formation of the highly colored thallous mercaptides suggests their use as extremely sensitive qualitative tests for the detection of mercaptans.

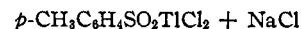
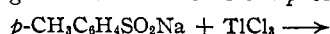
Both arylphosphonic acids and arylphosphinic acids are readily characterized by this method. Either the mono- or the di-thallous salts of the phosphonic acids provide derivatives with good melting points.

Nitromethane and nitroethane readily form monothallous salts, but only the latter has a definite decomposition point.

2,4,6-Trinitrobenzoic acid gives a crystalline monothallous salt, melting with decomposition at 160–163°, which decarboxylates smoothly in boiling pyridine solution giving 1,3,5-trinitrobenzene and thallous oxalate. Thallous 2,4,6-trinitroben-

zoate reacts further with a second equivalent of thallous hydroxide giving a blood-red complex of uncertain composition. 1,3,5-Trinitrobenzene was found likewise to react with one, two and three equivalents of thallous hydroxide giving complexes of rather indefinite composition which explode on heating.

Thallium trichloride reacts with sodium *p*-toluenesulfinate and with *p*-toluenesulfinic acid to give thallium dichloride *p*-toluenesulfinate.



However, the interesting observation was made that this compound did not eliminate sulfur dioxide with the formation of a carbon-metal linkage, as has been observed with some related mercury compounds.³

Experimental

Two general procedures have been mentioned² for the preparation of thallous sulfonates. These procedures were used for the thallous salts described in Table I. The most important point in their preparation is the recrystallization solvent. In most cases it was desirable to evaporate the solution of salt almost to dryness and then recrystallize the salt from ethanol-water mixtures since most of them are very soluble in water and much less soluble in ethanol.

Thallium Dichloride *p*-Toluenesulfinate.—On mixing 0.1 mole each of sodium *p*-toluenesulfinate and thallium trichloride dissolved in a minimum of water, there was an immediate precipitate accompanied by an odor of *p*-toluenesulfonyl chloride. The precipitate was filtered, washed, and dried giving 36 g. (84%) of the salt, which melted at 203–205° (dec.).

Anal. Calcd. for C₇H₇O₂Cl₂STl: Tl, 47.4. Found: Tl, 47.6.

2,4,6-Trinitrobenzoic Acid and Two Equivalents of Thallous Hydroxide.—In order to determine whether the red precipitate transiently encountered in the preparation

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(3) Peters, *Ber.*, **38**, 2567 (1905); Kharasch, *THIS JOURNAL*, **48**, 610 (1921); Loudon, *J. Chem. Soc.*, 823 (1933).

TABLE I
 THALLOUS SULFONATES, SULFINATE, PHOSPHONATES, ETC.

Thallos salt	M. p., °C. ^a	Yield, %	Formula	Tl analyses, %	
				Calcd.	Found
Benzenesulfonate	185-187	94	C ₆ H ₅ O ₃ STl	56.5	56.3
β-Naphthalenesulfonate	234-236	92	C ₁₀ H ₇ O ₃ STl	49.7	49.5
Dodecylsulfonate ^b	143-144	53	C ₁₂ H ₂₅ O ₃ STl	45.1	44.6
p-Toluenesulfinate	154-156	89	C ₇ H ₇ O ₂ STl	56.7	56.3
Phenylphosphonate (mono)	200-201	86	C ₆ H ₅ O ₂ PTl	56.5	56.3
Phenylphosphonate (di) ^c	317-320	79	C ₆ H ₅ O ₃ PTl	72.5	72.3
Diphenylphosphinate ^d	203-205	82	C ₁₂ H ₁₀ O ₂ PTl	48.5	48.3
Nitromethane	Dec.	85	CH ₂ O ₂ NTl	76.8	76.6
Nitroethane ^e	80-82 (dec.)	81	C ₂ H ₅ O ₂ NTl	73.4	73.2
Methylmercaptide ^f	136-140 (dec.)	100	CH ₃ STl	80.9	80.5
Ethylmercaptide	Dec.	100	C ₂ H ₅ STl	76.8	76.4
n-Butylmercaptide	84-90	100	C ₄ H ₉ STl	69.4	69.1
Thiophenolate	258-260	99	C ₆ H ₅ STl	65.2	65.0
p-Thiocresolate	178-180	99	C ₇ H ₇ STl	62.3	62.0
Thio-β-naphtholate	165-168	97	C ₁₀ H ₇ STl	56.2	55.9
2,4,6-Trinitrobenzoate	160-163	93	C ₇ H ₃ O ₆ N ₃ Tl	44.3	44.1

^a All melting points were taken on a Fisher-Johns type block, uncorrected. ^b The melting point of this compound was not sharp. After two recrystallizations from 95% ethanol, the crystals sintered at 125° before melting at 143-145°. ^c This compound showed a transition point at 260° when examined under a hot-stage microscope, melting and immediately resolidifying. The compound then melted to a clear phase at 317-320°. ^d A mixed melting point with monothallos phenylphosphonate was depressed to 140-150°. ^e This salt appeared to be extremely resistant to detonation by mechanical shock. ^f The canary yellow precipitate of thallos mercaptide obtained with the volatile aliphatic mercaptans is so delicate a test that the vapor present in the air was sufficient to give a precipitate with solutions of thallos hydroxide three or four feet distant. The mercaptides and thiophenolates were obtained from absolute methanol or ethanol solutions.

of thallos 2,4,6-trinitrobenzoate actually contained more than one equivalent of thallium, 0.02 mole of 1.04 N thallos hydroxide³ was added to 0.01 mole of 2,4,6-trinitrobenzoic acid in 75 ml. of methanol. A heavy red precipitate formed after the addition of the first equivalent of base. After prolonged shaking, filtering, and drying, 5.6 g. of product was obtained. The compound exploded on heating. Analysis showed that nearly two atoms of thallium were present in the molecule, but no satisfactory agreement for any definite compound was indicated.

Anal. Calcd. for C₇H₃O₆N₃Tl₂: Tl, 61.7. Found: Tl, 59.4.

1,3,5-Trinitrobenzene and Thallos Hydroxide.—Equivalent amounts of 1,3,5-trinitrobenzene and thallos hydroxide were reacted in a manner similar to the previous experiment. The red precipitate did not melt but exploded on heating.

Anal. Calcd. for C₆H₃O₇N₃Tl: Tl, 46.9. Found: Tl, 41.1.

The products of reaction of trinitrobenzene with two and three equivalents of thallos hydroxide, respectively, likewise showed approximate but not stoichiometric amounts of thallium to be present.

Anal. Calcd. for C₆H₃O₈N₃Tl₂: Tl, 62.5. Found: Tl, 56.8. Calcd. for C₆H₃O₉N₃Tl₃: Tl, 70.0. Found: Tl, 62.5.

Decarboxylation of Thallos 2,4,6-Trinitrobenzoate.—A suspension of 0.01 mole of this salt in 25 ml. of pyridine was boiled until a microcrystalline precipitate was deposited, during which time the color of the solution changed from an intense green to a pale brown. On filtering off the precipitate and diluting the clear filtrate, 1.4 g. (67%) of 1,3,5-trinitrobenzene was obtained melting at 120-122°.

The crystalline precipitate was found to contain all the thallium of the original thallos 2,4,6-trinitrobenzoate in the monovalent state. It was soluble in hot water, in-

soluble in cold water and hot pyridine, and nitrogen-free, melting at 320° with decomposition.

Anal. Calcd. for C₆O₄Tl₂: Tl, 82.5. Found: Tl, 82.7.

Although thallos oxalate has been reported,⁴ no record could be found of its melting or decomposition point. An authentic sample was prepared. It was found to melt at 315-320° with decomposition and to be identical with that obtained on pyrolysis of thallos 2,4,6-trinitrobenzoate in solubility, analysis and pyrolytic behavior.

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Summary

The thallos salts have been found to be well crystallized and easily prepared derivatives of the arylsulfonic, sulfinic, phosphonic and phosphinic acids, as well as for the thiophenols. However, they are of limited use for alkylsulfonic acids and of little value for mercaptans and the simple nitroalkanes.

Thallos 2,4,6-trinitrobenzoate, which also melts sharply, is pyrolyzed smoothly to 1,3,5-trinitrobenzene and thallos oxalate.

2,4,6-Trinitrobenzoic acid and 1,3,5-trinitrobenzene unite with more than one equivalent of thallos hydroxide giving red insoluble complexes.

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