	Solanine-s		Solancarpine	
	Crystal form	M. p., °C.	Crystal farm	M. p., °C.
Gluco-alkaloid	Plates	286 (dec.) (Romeo) 275–280 (dec.) (Oddo)	?	288–289 (dec.)
Agluco-alkaloid	Plates	200 (Oddo) 216–219 (A. and B.)	Plates	197–198
Sulfate	Needles ⟶ plates	? (dec.)	Plates	293–294 (dec.)
Nitrate[a]	Needles	269 (dec.)	Needles	271–272 (dec.)
Hydrochloride	Needles	309.5 (dec.)	Needles	313–314 (dec.)
Hydrobromide	Needles	283 (dec.)	Needles	307–308 (dec.)
Hydriodide[a]	Needles	283–284 (dec.)	Needles	283–284 (dec.)
Picrate	Needles	144–145 (dec.)	Needles	148–149 (dec.)
Oxalate[a]	Needles	238 (dec.)	Needles	238–239 (dec.)
Tartrate[a]	Needles	222 (dec.)	Needles	224–225 (dec.)

(The salts are those of the agluco-alkaloid.) [a] New derivatives.

ably with the rate of heating (in the case of the sulfate by over 100°) which may explain discrepancies in the decomposition points.

DEPARTMENT OF CHEMISTRY L. H. BRIGGS
AUCKLAND UNIVERSITY COLLEGE
AUCKLAND, NEW ZEALAND

RECEIVED MAY 13, 1937

THE PEROXIDE EFFECT IN THE HALOGENATION OF AROMATIC SIDE CHAINS

Sir:

Extensive investigations of bromination of toluene [an extensive literature review of this subject is given by Van der Laan, *Rec. trav. chim.*, **26**, 1 (1907); see also Ref. *a*] indicate that the following factors influence the rate of substitution in the side chain: (1) light, (2) temperature, (3) concentration of bromine, (4) non-metallic catalysts. In an effort to correlate these diverse observations, we undertook an investigation of the effect of peroxides on the bromination of toluene and other aromatic molecules containing side chains. It appeared reasonable that a chain reaction involving bromine atoms might provide a mechanism in harmony with the recorded facts.

We can now state that, as far as brominations in the dark are concerned, peroxides exert a more pronounced effect on the rate of side chain substitution than any of the factors cited above. In this respect our experience with the bromination of toluene is most instructive. In the dark at 25° in the presence of three mole per cent. of ascaridole (on the bromine basis) (other toluene-soluble peroxides are equally effective) the bromination of toluene takes place in about half an hour and the product is over 98% benzyl bromide. Furthermore, the rate of nuclear substitution is increased tremendously by peroxides.

Table I is a summary of some of our results. It is to be noted that the decreased proportion of benzyl bromide in the bromination mixture (as the ratio of toluene to bromine is decreased) is in accord with the postulated bromine atom mechanism.

TABLE I

THE PEROXIDE EFFECT IN THE BROMINATION OF TOLUENE IN THE DARK AT 25°

Moles % Ascaridole	Air	Toluene/Bromine in moles	Reaction time	Monobromide %	Benzyl bromide in product, %	Remarks
3	Present	20	25 min.	85	98	Complete reaction
3	Present	10	1 hour	70	90	HBr evolution ceased
3	Present	5	3 hours	56	30	Incomplete
3	Present	2	3 hours	56	11	Incomplete
None	Present	10	4 days	60	10	Incomplete
None	Absent	10	4 days	56	11	Incomplete
		25	3 weeks	100	36	
None	Present	16	3 weeks	100	20	Complete
None	Present	8	3 weeks	100	10	(Br_2 disappeared)
None	Present	4.7	3 weeks	100	8	

[a] Holleman and Polak, *Rec. trav. chim.*, **27**, 435 (1908).

The reaction of bromine with *p*-chlorotoluene in the presence of peroxides is rather slow at room temperature, but goes to completion in several hours on the water-bath. The product is exclusively *p*-chlorobenzylbromide. Experiments with *o*- and *p*-cyanotoluene at 100° indicate a definite accelerating effect by peroxides.

Examination of the effect of impurities led to the discovery of the remarkable inhibiting effect of very small amounts of alcohols on the rate of bromination in the peroxide catalyzed reaction.

The side-chain chlorination of toluene is accelerated by peroxides.

The study of the effects herein described is being extended to the bromination of aliphatic molecules, and to aromatic compounds containing side chains. A study is also under way to determine whether peroxides will affect the

ortho, para ratio in the halogenation of aromatic compounds.

GEORGE HERBERT JONES
CHEMICAL LABORATORY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

M. S. KHARASCH
E. MARGOLIS
P. C. WHITE
F. R. MAYO

RECEIVED JUNE 18, 1937

OPTICAL MEASUREMENT OF THE THICKNESS OF A FILM ADSORBED FROM A SOLUTION

Sir:

A single layer of molecules deposited from a water surface on a built-up film produces [I. Langmuir, V. J. Schaefer and D. Wrinch, *Science*, **85**, 76–80 (1937); K. B. Blodgett and I. Langmuir, *Phys. Rev.*, **51**, 964 (1937)] a perceptible change in the color given by interference of light from the top and bottom of the film.

We can condition the surface of the built-up film to enable it to adsorb organic or inorganic substances from solution, and determine the dimensions of adsorbed molecules by the change in color.

Dipping the film into a solution containing a second substance reactive to the first, a second adsorbed film can be formed. Sometimes successive alternating layers can be built.

One method of conditioning a plate is to deposit upon it an A-layer of stearic acid from a water surface and to bring it into an aluminum chloride solution (10^{-3} molar). After washing, it is ready to adsorb many organic substances which contain polar groups.

For example a drop of a 1% solution of egg albumin is applied to the wet plate which is then washed and dried. The apparent increase in thickness is equivalent to 2 barium stearate layers (50 Å.). With Stanley's tobacco virus protein we obtain a maximum thickness of 12 stearate layers equivalent to 300 Å.

A surface conditioned by a monolayer of egg albumin deposited from a water surface takes up an adsorbed film of tobacco protein having a maximum thickness of only 5 stearate layers. This may be the thickness of molecules lying flat on the surface. Adsorbed films of other proteins on aluminized surfaces give films of from 2 to 8 stearate layers. As these are not always proportional to the cube root of the molecular weight, some protein molecules seem to be non-spherical.

It facilitates the formation of a complete layer to apply the protein in successive stages, washing and drying the plate after each addition of the protein, probably because of consolidation by surface tension.

The molecular dimension (normal to the surface) of adsorbed molecules in a film which is only 70% complete may be determined by filling the interstices between molecules with hexadecane after covering with 4 barium stearate layers to render the surface non-wettable by oil.

Coöperating with Dr. Harry Sobotka we have conditioned a surface by deposition of a monolayer of cholesterol (18 Å.). This surface takes digitonin from aqueous solution giving an adsorbed film of 36 Å. Another layer of cholesterol can be deposited and a second adsorbed film of digitonin, etc. These multilayers give accurate measurement of molecular dimensions.

With Dr. E. F. Porter, we have adsorbed diphtheria toxin on a plate conditioned by aluminum chloride obtaining a monofilm of 36 Å. On dipping the plate into diphtheria antitoxin, there was an increase in thickness of 75 Å. Successive alternating layers of toxin-antitoxin can be built up indefinitely.

Not only the thickness but many other properties of adsorbed films can be measured such as contact angles with various liquids, solubilities, adsorbing power for substances in solution, refractive index, etc.

We believe the methods outlined are useful for detecting and identifying minute amounts of substances of biological interest and for studying the structure, reactivities and other properties of these substances.

GENERAL ELECTRIC COMPANY
SCHENECTADY, N. Y.

IRVING LANGMUIR
VINCENT J. SCHAEFER

RECEIVED JUNE 2, 1937

PHENOXYPYRIDINE

Sir:

Thanks to Professor Chichibabin, my attention has been called to some inaccuracies in a recent article by Renshaw and Conn [THIS JOURNAL, **59**, 297 (1937)], where the statement is made: "A number of 2-pyridyl ethers were prepared by heating 2-bromopyridine with the alkali salts of alcohols and phenols . . .," and farther on: "This is a more satisfactory method than that reported by Chichibabin [*J. Russ. Phys.-Chem. Soc.*, **50**, 502 (1918)] for the preparation of 2-phenoxypyridine, the only alpha-substituted pyridine reported in the literature."