thermostated cell holder. The temperature was maintained at 30.0 ± 0.05°.

Solutions of diphenyldiazomethane and benzoic acids (about 0.1 *M*) in absolute alcohol were thermostated for at least an hour, then pipeted into a small flask, mixed and transferred to a spectrophotometer cell. Optical density readings were taken at 525 mμ using ethyl alcohol as a standard at two-minute intervals over a period equivalent to at least two half-lives. Zero-time was taken as the time of mixing of the solutions. The optical density readings were plotted on semi-logarithmatic paper and the pseudo-unimolecular rate constants of the reactions obtained from the slopes of the best straight line through the experimental points. A plot of the data for a typical run using benzoic acid is shown in Fig. 3. Since the acid concentrations were several times those of the diphenyldiazomethane the reactions appeared to be unimolecular. However, the slopes of the curves were strictly dependent on the concentration of acid and the final rate constants (k_2) were calculated by dividing the pseudo-unimolecular constants by the corresponding acid concentrations. The reaction rates were shown to be insensitive to the intensity of the light used in the spectrophotometer. The rate data for the various benzoic acids are summarized in Table IV.

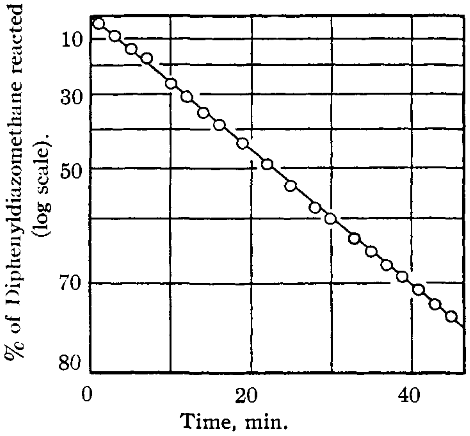

Fig. 3.—Rate of reaction of diphenyldiazomethane with benzoic acid in ethyl alcohol at 30°.

TABLE IV

RATE CONSTANTS FOR THE REACTION OF SUBSTITUTED BENZOIC ACIDS WITH DIPHENYLDIAZOMETHANE IN ABSOLUTE ALCOHOL AT 30°

Substituent	Concn. of acid, mole/l.	Half-life, min.	k_2, l./mole-min.
p-NH_2–	0.0289	89.7	0.268
p-CH_3–	.0289	31.2	0.770
None	.0284	23.5	1.04
p-$(CH_3)_3Si$–	.0287	23.0	1.05
m-$(CH_3)_3Si$–	.0293	22.1	1.07
p-Br–	.0284	13.0	1.88
m-Br–	.0286	9.65	2.51
m-NO_2–	.0287	4.70	5.15
p-OH–	.0284	45.9	0.533[a]

[a] The σ-constant calculated for the *p*-OH group from this rate constant is −0.341.

Summary

Trimethylsilyl groups attached to benzene rings have been shown by dipole moment studies to be slightly electron-releasing. The relative reactivities of the carboxyl groups in *m*- and *p*-trimethylsilylbenzoic acids indicate that the electrical influence of the trimethylsilyl group is different in kind from that of alkyl groups.

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NOTES

Formation of the Chloroiodate(I) Ion from the Reaction of Iodide and Thionyl Chloride

BY WILLIAM B. BROWNELL AND L. CARROLL KING

During the course of an investigation of the reactions of certain quaternary pyridinium iodides it was noted that thionyl chloride acting directly on the salts converted the iodide ion to chloroiodate(I) with appearance of free sulfur. The reaction may be formulated as

$$2SOCl_2 + 2I^- \longrightarrow 2ICl_2^- + SO_2 + S$$

The identity of the anion was established by analysis and in two cases by direct comparison with known cycloammonium quaternary salts containing the chloroiodate(I) anion.

The reaction of thionyl chloride with potassium iodide was reported by Rao.[1] The reaction of dry hydrogen iodide with thionyl chloride was reported by Besson[2]; neither author observed the chloroiodate(I) ion in the reaction products.

Compounds containing the chloroiodate(I) ion have been prepared by the reaction of iodine monochloride with a quaternary ammonium

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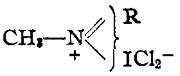
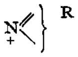
[1] Rao, *Proc. Indian Acad. Sci.*, **11A**, 185 (1940); *C. A.*, **34**, 7200 (1940).

[2] Besson, *Compt. rend.*, **123**, 884 (1896); *Chem. Zentr.*, **68**, I, 12 (1897).

TABLE I


$CH_3—\overset{+}{N}R\ ICl_2^-$

	Yield, %	M. p., °C.[a]	Formula	Iodine, %[b] Calcd.	Iodine, %[b] Found	Total halogen[e] Calcd.	Total halogen[e] Found
Pyridinium	73	87–89[c]	$C_6H_8Cl_2IN$	43.5	43.8	10.3	10.1
α-Picolinium	49	92–93	$C_7H_{10}Cl_2IN$	41.5	41.0	9.82	9.67
Quinolinium	56	112–113[d]	$C_{10}H_{10}Cl_2IN$	37.2	36.9	8.77	8.63
Isoquinolinium	82	72–73	$C_{10}H_{10}Cl_2IN$	37.2	36.7	8.77	8.53
Quinaldinium	64	109–110	$C_{11}H_{12}Cl_2IN$	35.8	35.4	8.43	8.23

[a] Melting points are uncorrected. [b] Iodine was determined by titration with standard thiosulfate after addition of potassium iodide. The amount of iodine found was divided by two to obtain the iodine in the chloroiodate(I) ion. [c] Bally, ref. 4, reports a m. p. of 90°. [d] Ostermayer, ref. 3, reports a m. p. of 112°. [e] The total halogen was determined by the Volhard method using dilute alcohol for a solvent. In the presence of alcohol all the halogen in the ion was readily converted to silver halide. The numbers in the table represent milliequivalents of halogen per gram of compound.

chloride,[3] by the reaction of chlorine with a quaternary ammonium iodide,[4] and by the reaction of a quaternary ammonium chloride with potassium iodate in concentrated hydrochloric acid.[5]

The general applicability of thionyl chloride for the preparation of compounds containing the chloroiodate(I) ion was demonstrated by treating several quaternary iodides with this reagent. The compounds prepared, and their analyses, are summarized in the accompanying table. These substances are yellow or orange crystalline solids stable in air. They are slightly soluble in water first forming an oil which slowly enters solution. The resulting solutions liberate iodine color on standing. A drop of a saturated sodium bicarbonate when added to the chloroiodate(I) solution caused the appearance of iodine color. Iodine color was also liberated by addition of potassium iodide, sodium thiosulfate or sodium bisulfite. An excess of the latter two reagents removed the iodine color.

Experimental

The following example describes the general method for carrying out the reaction.

Methylpyridinium Chloroiodate (I).—Ten cc. of thionyl chloride, purified according to the method described by Fieser,[6] was added to 5 g. of dry methylpyridinium iodide. The reaction was vigorous and was accompanied by the initial formation of a dark tar which quickly entered solution. The excess thionyl chloride was removed by distillation *in vacuo*, the residue[7] was dissolved in 15 cc. of hot glacial acetic acid and the solution filtered to remove sulfur. After cooling the yellow crystalline product was separated, washed with cold acetic acid and finally with ether. The yield was 4.8 g. (73%) melting at 87–89°. The melting point was not depressed when the substance was mixed with a sample of authentic methylpyridinium chloroiodate (I), prepared according to Bally.[4]

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[3] Ostermayer, *Ber.*, **18**, 591 (1885).

[4] Bally, *Ber.*, **21**, 1772 (1888).

[5] Zincke and Lawson, *Ann.*, **240**, 124 (1887).

[6] Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 381.

[7] When this residue was shaken with benzene, sulfur separated from the crude oil.

L-Arabinose from Heartwood of Western Red Cedar (*Thuja plicata*)[1]

BY ARTHUR B. ANDERSON[2] AND H. ERDTMAN[3]

Free L-arabinose appears to be a common constituent of the heartwood of many conifers. It has been isolated from a great variety of pine heartwoods, especially from species belonging to the Diploxylon series (generally possessing leaves in bundles of three or two.[4,5] The amount present is generally small. The heartwood of pines belonging to the *Haploxylon* sub-group (generally having five leaves in a bundle) always appears to contain pinitol, sometimes in surprisingly large quantities, which renders the isolation of the sugars more difficult.

While investigating the extractives from the heartwood of western red cedar,[6] a yield of 1.29 g. of a sugar melting at 151–153° was obtained from 470 g. of wood. The material reduced Fehling solution and gave a strong pentose reaction with phloroglucinol and hydrochloric acid. This crude sugar has been identified as L-arabinose.

Experimental

Four hundred and seventy grams of western red cedar heartwood sawdust was extracted with acetone in a Soxhlet extractor for eight hours. The dark-red acetone extract was evaporated and the resulting residue extracted several times with ethyl ether. Several hundred ml. of water was added to the ether insoluble portion of the extract, heated on a steam-bath with stirring and charcoal (Darco) added. This was filtered and the resulting aqueous solution concentrated to a sirup under vacuum on a water-bath. The sirup was triturated with one volume of absolute ethanol and placed in a desiccator containing calcium chloride for about twenty-four hours or until the first crystals appeared and then placed in an ice-chest for several days to ensure complete crystallization. The solid was filtered and the precipitate washed with absolute ethanol and finally absolute ether. The resulting white

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[1] The work by A. B. A. was carried on while on the staff of the Forest Products Laboratory, Madison, Wisconsin, and the authors wish to thank the U. S. Forest Products Laboratory for permission to publish this work.

[2] Present address: Oregon Lumber Co., Res. Lab., Portland, Ore.

[3] Royal Institute of Technology, Stockholm, Sweden.

[4] Erdtman, *Svensk, Papperstidni*, **46**, 228 (1943).

[5] Lindstedt, unpublished observations.

[6] Anderson and Sherrard, THIS JOURNAL, **55**, 3813 (1933).