2,3-Diphenyl-X-methylpyrido(2,3)pyrazines.—These were prepared by the condensation of the above 2,3-diaminopicolines with benzil following the procedure of Chichibabin and Kirsanow.[6] The yields of pure product after recrystallization from ethanol were about 30%.

2,3-Diphenyl-8-methylpyrido(2,3)pyrazine.—M. p. 143–144°. *Anal.*[5] Calcd. for $C_{20}H_{15}N_3$: N, 14.14. Found: N, 14.00.

2,3-Diphenyl-7-methylpyrido(2,3)pyrazine.—M. p. 160–161°. *Anal.*[5] Calcd. for $C_{20}H_{15}N_3$: N, 14.14. Found: N, 14.15.

2,3-Diphenyl-6-methylpyrido(2,3)pyrazine.—M. p. 169–170°. *Anal.*[5] Calcd. for $C_{20}H_{15}N_3$: N, 14.14. Found: N, 14.00.

3- and 5-Nitro-2-picolinols.—These were prepared by the reaction of the corresponding nitro-2-aminopicolines with nitrous acid at 0° following the usual procedure. The products were purified by recrystallization from water to give nearly quantitative yields.

TABLE I

3- AND 5-NITRO-X-METHYL-2-PYRIDINOLS

Nitro	Methyl	M. p., °C.	N Anal.,[5] % Calcd. for $C_6H_5O_3N_2$	N Anal.,[5] % Found
5	3	234–235	18.18	18.26
5	4	189–190	18.18	18.17
5	6	235–236	18.18	18.20
3	4	234–235	18.18	18.09
3	5	253–255	18.18	18.11
3	6	223–224	18.18	18.21

3-Amino-5-methyl-2-pyridinol.—Low pressure catalytic reduction of 5.0 g. (0.033 mole) of 3-nitro-5-methyl-2-pyridinol dissolved in 100 ml. of ethanol using palladium-on-charcoal catalyst gave 3.8 g. (80%) of this compound, m. p., after recrystallization from benzene, 119–120°. *Anal.*[5] Calcd. for $C_6H_8ON_2$: N, 22.58. Found: N, 22.63.

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RECEIVED DECEMBER 2, 1949

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(6) Chichibabin and Kirsanow, *Ber.*, **60**, 766 (1927).

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Oxonium Salts of Khellin

New compounds believed to be oxonium salts have been prepared by direct treatment of khellin[1] with sulfuric and hydrochloric acids.

Khellin Sulfate.—Powdered khellin (0.5 g.) in 1 cc. 98% sulfuric acid turned orange and then formed an orange-red viscous solution. On the addition of 50 cc. of ethyl acetate an orange solid separated which was filtered off, washed and dried; yield 0.7 g. Crystallization from ethyl acetate gave orange plates which melted at 210° with decomposition to a violet liquid. The solid was stable for a long time but decomposed almost quantitatively in aqueous solution or in dilute ammonia at room temperature to give khellin. This oxonium compound is practically insoluble in dry organic solvents, *e.g.*, benzene and toluene.

Anal. Calcd. for $C_{14}H_{12}O_5$, H_2SO_4: C, 46.9; H, 3.9; S, 8.9. Found: C, 46.7; H, 4.01; S, 8.9.

Khellin Hydrochloride.—Powdered khellin (0.5 g.) was dissolved in hot absolute alcohol and after cooling externally with ice, hydrogen chloride was passed into the solution. An orange color immediately developed, followed by the precipitation of yellow needles which were filtered off, washed with a little absolute alcohol, saturated with hydrogen chloride and then dried at room temperature. This substance melted at 98° decomposing to a red liquid. In aqueous solution it decomposed to khellin; yield, 0.4 g.

Anal. Calcd. for $C_{14}H_{12}O_5$, HCl; Cl, 11.9. Found: Cl, 12.1.

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RECEIVED MAY 31, 1949

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(1) Khellin has been isolated from *Ami Visnaga* (*cf.* Späth and Gruber, *Ber.*, **71B**, 106–113 (1938).

3-Amino-4-ethyl-, 3-Amino-4-*t*-butylbenzoic Acids and 4-Bromo-3-*t*-butylaniline

The two amino acids were prepared from *p*-ethyl and *p*-*t*-butylbenzoic acids by nitration and reduction. 3-Nitro-4-ethylbenzoic acid so obtained[1] (90.5%) melted at 157.5–158.3° (lit.,[2] 155–156°), the *t*-butyl analog (90.7%) at 162.7–163.2° (lit.,[3] 161°).

Reduction was carried out according to the general procedure of Jacobs and Heidelberger.[4] A solution of 0.40 mole of the 3-nitro-4-alkylbenzoic acid in dilute ammonium hydroxide was added dropwise during a few minutes to a vigorously stirred, boiling solution of 780 g. (2.8 moles) of ferrous sulfate crystals in 1 l. of water. The mixture was then immediately treated with concentrated ammonium hydroxide, added dropwise at the rate of about 200 ml. an hour, while heating and vigorous stirring was maintained. Water lost by evaporation was made up from time to time by washing down the sides of the beaker with water. Addition of ammonium hydroxide was continued until the boiling solution became strongly ammoniacal and the mixture was then filtered hot. The cake was washed thoroughly by removing it from the filter, heating and stirring it with about 500 ml. of water containing 100 ml. of concentrated ammonium hydroxide, and then refiltering. The combined filtrates, which were dark in color, were concentrated to about 1 l., boiled with decolorizing charcoal, and refiltered. The warm filtrate was made barely acidic with acetic acid, resulting in the immediate separation of a solid precipitate or of an oil which solidified upon stirring. After cooling, this amino-acid was removed by filtration and dried at 105°. The amino-acids were purified further by recrystallization from boiling water. 3-Amino-4-ethylbenzoic acid was obtained in 73% yield, m. p. 149.4–149.7°.

Anal. Calcd. for $C_9H_{11}O_2N$: C, 65.43; H, 6.71; N, 8.48. Found: C, 65.78; H, 6.66; N, 8.66.

The *t*-butyl analog (75%) melted at 154–155°.

Anal. Calcd. for $C_{11}H_{15}O_2N$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.50; H, 7.64; N, 7.47.

4-Bromo-3-*t*-butylaniline.—*t*-Butylbenzene was converted to the 2,4-dinitro derivative (72%) m. p. 62.3–63.0° (lit.,[5] 61–62°), which was partially reduced to 4-amino-2-nitro-*t*-butylbenzene (97%), m. p. 56.6–57.7° (lit.,[5] 55°) and deaminated by diazotization and hypophosphorus acid to *o*-nitro-*t*-butylbenzene, b. p. 118° (12 mm.) (lit.,[5] 114–115° 10 mm.). Reduction gave 78% of *o*-*t*-butylaniline, b. p. 103–105° (11 mm.) (lit.,[5] 102° (10 mm.)). This material (34.5 g.) was boiled in 100 ml. of glacial acetic acid for three hours to convert it to *o*-*t*-butyl-acetanilide. After cooling, an equivalent of bromine was added dropwise over half-an-hour with shaking at room temperature. After standing an additional half-hour, the mixture was poured into a liter of water containing enough bisulfite to destroy any excess bromine. The precipitate of crude 2-*t*-butyl-4-bromoacetanilide was collected and hydrolyzed without further purification by

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(1) Kloeppel, *Ber.*, **26**, 1733 (1893).

(2) Aschenbrandt, *Ann.*, **216**, 221 (1882).

(3) Kelbe and Pfeiffer, *Ber.*, **19**, 1726 (1886).

(4) Jacobs and Heidelberger, THIS JOURNAL, **39**, 1435 (1917).

(5) Shoesmith and Mackay, *J. Chem. Soc.*, 2336 (1928).

boiling in an equal mixture of ethanol and concentrated hydrochloric acid for eighteen hours. (The methyl and ethyl homologs required only three hours under the same conditions.) After saturation with hydrogen chloride, the crystalline platelets of amine hydrochloride were separated and converted to amine by shaking with 20% sodium hydroxide solution and ether. The ether extract on distillation gave 37% of **2-*t*-butyl-4-bromoaniline**, a colorless oil, b. p. 146–147° (9 mm.), n^{23}D 1.5811.

Anal. Calcd. for $C_{10}H_{14}BrN$: C, 52.64; H, 6.19; Br, 35.03; N, 6.14. Found: C, 53.03; H, 6.20; Br, 34.40; N, 6.23.

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Aryl Esters of Substituted Benzenesulfonic Acids

The esters of benzenesulfonic acid listed in the table were prepared by the Hinsberg[1] method with slight variations. One mole of the arylsulfonyl chloride and one mole of the phenol were heated together with stirring at 60–70°. One mole of dilute sodium hydroxide solution (0.7 *N*) was added during a half-hour period, keeping the temperature at 60–80°. The reaction mass was heated for an additional hour at 60–80°. As the reaction proceeded, the ester precipitated and crystallized. The slurry was cooled, filtered, and washed with water. The dried crystals were purified by repeated crystallizations from ethyl alcohol containing a little benzene.

TABLE I

Compound	Crude yield, %	Chlorine, % Found	Chlorine, % Calcd.	Sulfur, % Found	Sulfur, % Calcd.	M. p., °C.[a]
p-Chlorophenyl *m*-nitrobenzenesulfonate	87.0	11.24	11.30	10.27	10.22	104–105
p-Bromophenyl *p*-bromobenzenesulfonate	93.0	40.53 Br	40.76 Br	8.04	8.18	121–122
p-Chlorophenyl *p*-bromobenzenesulfonate[b]	96.5	10.23 Cl	10.11 Cl	9.47	9.22	109–110
p-Bromophenyl *p*-chlorobenzenesulfonate[c]	88.5	10.17 Cl	10.11 Cl	8.94	9.22	95.5–97.5
2,4-Dichlorophenyl *p*-chlorobenzenesulfonate	94.5	31.79	31.51	9.58	9.50	118–119
2,4,5-Trichlorophenyl *p*-chlorobenzenesulfonate	92.0	37.56	38.12	8.80	8.62	130–131
2,4,6-Trichlorophenyl *p*-chlorobenzenesulfonate	96.4	38.14	38.12	8.72	8.62	97–98
2,3,4,6-Tetrachlorophenyl *p*-chlorobenzenesulfonate	83.0	44.37	43.61	7.72	7.88	123–124
Pentachlorophenyl *p*-chlorobenzenesulfonate	93.0	48.80	48.25	7.34	7.27	146.5–147.5
p-Tolyl *p*-chlorobenzenesulfonate	97.5	12.80	12.54	11.56	11.34	76–77
o-*s*-Butylphenyl *p*-chlorobenzenesulfonate	88.2	10.87	10.91	9.79	9.87	60–61.5
p-*t*-Butylphenyl *p*-chlorobenzenesulfonate	93.7	11.04	10.92	9.82	9.87	92–93
o-Allylphenyl *p*-chlorobenzenesulfonate	89.0	11.58	11.48	10.29	10.38	58–59
2-Biphenylyl *p*-chlorobenzenesulfonate	92.5	10.31	10.28	9.32	9.30	85.5–86.5
p-Methoxyphenyl *p*-chlorobenzenesulfonate	95.3	12.11	11.87	10.73	10.73	90–91

[a] Uncorrected. [b] Br calcd. 22.99; found 22.95. [c] Br calcd. 22.99; found 22.92.

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[1] Hinsberg, *Ber.*, **23**, 2962 (1890).

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Some New Glycol Trichloroacetates

We have prepared several new glycol trichloroacetates which may serve as model substances for carbohydrate trichloroacetates. Two methods were used. The first method consisted of the direct reaction of the glycol with trichloroacetic acid in the absence of a catalyst and either with or without the presence of a water entrainer. The second method employed trichloroacetyl chloride in the presence of pyridine. This method was suitable for the preparation of mixed esters.

An attempt was made to determine whether the trichloroacetyl group acts as a neighboring group in the displacement of the *p*-toluenesulfonoxy group from a position *trans* to it on the cyclohexane ring, under conditions similar to those employed by Winstein and co-workers.[1] Although a first order reaction was observed, the products were not isolated.

All melting points are corrected and the micro-analyses were performed by Mrs. C. F. Spencer.

Ethylene Glycol Bis-trichloroacetate.—Ethylene glycol (5.6 ml., 0.1 mole) and trichloroacetic acid (32.7 g., 0.2 mole, Dow Chemical Co.) were distilled slowly at atmospheric pressure until the temperature had reached 125° and about 3.5 ml. of distillate (largely water) had collected. The residue, which crystallized on cooling, was mixed with some cold water, and the solid (17.6 g., m. p. 40–41°) removed by filtration. After recrystallization from an ethanol-water mixture, 50% recovery of a product melting at 41–42° was obtained. The substance was very soluble in most organic solvents including alcohols, hydrocarbons, ethers, and chlorinated hydrocarbons. It was difficultly soluble in hot water. The compound was also prepared by the reaction of trichloroacetyl chloride and ethylene glycol in pyridine. It is probable that the ester undergoes hydrolysis with some ease.

Anal. Calcd. for $C_6H_4O_4Cl_6$: C, 20.40; H, 1.13; Cl, 60.34; sapon. equiv., 353. Found: C, 20.34; H, 1.18; Cl, 60.60; sapon. equiv., 324.

***trans*-1,2-Cyclohexanediol Bis-trichloroacetate.**—*trans*-1,2-Cyclohexanediol[2] (11.6 g., 0.1 mole) and pyridine (32 ml., 0.4 mole) were mixed and trichloroacetyl chloride[3] (36.4 g., 0.2 mole) was slowly added with sufficient cooling to keep the temperature in the range of 60–70°. The mixture was then allowed to stand overnight at room temperature. It was then shaken with 200 ml. of water, and the yellow oil which separated crystallized on refrigeration, yield 37.2 g., 91%. The crude product (m. p. 59–61°) was recrystallized from an alcohol-water mixture to a constant melting point of 60–61°.

Anal. Calcd. for $C_{10}H_{10}O_4Cl_6$: C, 29.48; H, 2.46; Cl, 52.33; sapon. equiv., 407. Found: C, 29.40; H, 2.55; Cl, 52.09; sapon. equiv., 402.

***trans*-1,2-Cyclohexanediol Monotrichloracetate.**—*trans*-1,2-Cyclohexanediol[2] (11.5 g., 0.1 mole) and trichloroacetic acid (16.4 g., 0.1 mole, Dow Chemical Co.) and benzene (100 ml.) were heated under reflux in an all-glass

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[1] Winstein, Hanson and Grunwald, THIS JOURNAL, **70**, 812 (1948).

[2] "Org. Syn.," **28**, 35 (1948).

[3] Prepared from trichloroacetic acid and benzoyl chloride according to the method of Brown, THIS JOURNAL, **60**, 1352 (1938).