dry benzene was added dropwise with stirring 5 g. (0.033 mole) of *m*-nitrostyrene while dry hydrogen bromide gas was bubbled through the solution. The solution turned dark red. Addition took 0.5 hr. and the passage of hydrogen bromide was continued for 2.5 hr. more. The reaction mixture was then poured into ice water and the benzene layer was separated, washed three times with dilute sodium bicarbonate solution and three times with water, dried over calcium chloride, and concentrated. The residue was distilled at 0.6 mm. and collected in two fractions, b.p. 110–115° and 115–130°. Both fractions solidified on standing in the refrigerator, m.p. 40.5–41.5° and 38–41°, combined yield 5.3 g. (70%). Recrystallization raised the m.p. to 42–43°.

Anal. Calcd for $C_8H_8BrNO_2$: C, 41.76; H, 3.50. Found: C, 41.84; H, 3.47.

α-(m-Nitrophenyl)ethyl alcohol. The above bromide (1.5 g.) was boiled for 24 hr. with a solution of 4.0 g. lead nitrate in 60 ml. of water. Upon cooling the organic material solidified. It was extracted into ether and the ether layer dried over calcium chloride and concentrated. The residue crystallized when chilled in Dry Ice–acetone and, upon recrystallization, melted at 59–60°. The mixture melting point with an authentic sample of α-(*m*-nitrophenyl)ethyl alcohol, m.p. 60–61° (lit.[8] m.p. 62.5), prepared by reduction of *m*-nitroacetophenone with sodium borohydride in methanol, was 60–61.5°.

α-(p-Nitrophenyl)ethyl bromide. (a) *By addition of hydrogen bromide to p-nitrostyrene.* Five grams of *p*-nitrostyrene was subjected to procedure (b) described above for *m*-nitrostyrene. The product was distilled at 0.6 mm. and collected in four fractions: (1) b.p. below 100° (1.0 g.); (2) b.p. 100–126° (1.0 g.); (3) b.p. 126–135° (2.5 g.); (4) 135–138° (1.0 g.). Fractions 2, 3, and 4 solidified upon cooling in Dry Ice–methanol and upon recrystallization from petroleum ether melted at 33–34°. Further recrystallization raised the melting point to 35.0–35.5°.

The infrared spectrum of fraction 1 above indicated it to be mainly recovered *p*-nitrostyrene (characteristic bands at 922 and 987 cm.$^{-1}$). Fractions 2–4 were mainly α-(*p*-nitrophenyl)-ethyl bromide containing decreasing amounts of *p*-nitrostyrene as an impurity; thus the yield of the bromide was *ca.* 4.5 g. or 73% based on 4 g. of starting material consumed. A careful inspection was made for the presence of β-(*p*-nitrophenyl)ethyl bromide in fractions 3 and 4, since a comparison sample of this bromide, m.p. 67.0–69.5° (lit.[10] m.p. 69–70.5°) was available from the preparation of *p*-nitrostyrene. The β-bromide has a characteristic infrared band at 1263 cm.$^{-1}$ which is absent in the α-isomer. Comparison of the infrared spectra of fractions 3 and 4 with spectra of synthetic mixtures of the isomeric bromides indicated that the addition product of *p*-nitrostyrene and hydrogen bromide contained less than 5% of the β-bromide. This conclusion was confirmed by the NMR spectra of fractions 3 and 4 which were identical with that of the pure α-bromide and did not show the complex multiplet due to the methylene protons which appears in the spectrum of the pure β-bromide. A mixture of 95% α- and 5% β-bromide clearly showed this multiplet in between the methyl doublet and the methine quartet of the α-bromide.

(*b*) *By photobromination of p-nitroethylbenzene.*[12] Eleven grams of *p*-nitroethyllbenzene was brominated in carbon tetrachloride using a 500-watt tungsten projector lamp as light source.[12] The product, 12.9 g. (77%) boiled at 107–114°/0.3–0.4 mm. (lit.[12] b.p. 152–153°/5 mm.) and solidified on cooling (not previously reported.[12]) Recrystallization from petroleum ether gave material melting at 35.0–35.5°; mixture melting point with addition product of *p*-nitrostyrene and hydrogen bromide, 35.0–35.5°.

Controls. Attempted addition of hydrogen bromide to o-nitrostyrene. The attempted addition of hydrogen bromide to *p*-nitrostyrene in pentane, in high-boiling petroleum ether at 90–100° and in acetic acid in a sealed tube failed, *p*-nitrostyrene being recovered. Treatment of β-(*p*-nitrophenyl)-ethyl bromide with aluminum bromide in benzene under the conditions of the addition reaction led to recovery of starting material in over 73% yield. Distillation of a mixture of 2.0 g. of α-bromide and 0.4 g. of β-bromide at 0.6 mm. returned 0.75 g. material of b.p. 120–126° and 0.95 g. of b.p. 126–128°. Both fractions were shown, by NMR spectroscopy, to contain about 15–20% β-bromide.

Attempted addition of hydrogen bromide to *o*-nitrostyrene in the presence of aluminum bromide in varying proportions gave only unchanged *o*-nitrostyrene or intractable high-boiling materials. A dark-colored complex appeared to form between the olefin and the catalyst in benzene solution.

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[12] H. B. Hass and M. L. Bender, *J. Am. Chem. Soc.*, 71, 3482 (1949) following the procedure of W. M. Cumming, I. V. Hopper, and T. S. Wheeler, *Systematic Organic Chemistry*, 4th ed., Constable and Co., Ltd., London, England, 1950, p. 358.

Ylides from *o*-Xylylene Dipyridinium Salts

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In the course of our attempts to prepare 4,5,6,7-tetrachloroisoindoline derivatives,[1,2] we have studied the reaction of tetrachloro-*o*-xylylene dipyridinium salts (IIc and IId) with methylamine. The preparation of 3,4,5,6-tetrachloro-*o*-xylylene dipyridinium dibromide (IIc) from Ic, as of *o*-xylylene dipyridinium dibromide (IIa) itself from Ia, was straightforward. In contrast, the preparation of 3,4,5,6-tetrachloro-*o*-xylylene dipyridinium di-*p*-toluenesulfonate (IId) from Id (with *p*-toluenesulfonyl chloride in pyridine), unlike the preparation of *o*-xylylene dipyridinium di-*p*-toluenesulfonate (IIb) from Ib, was complex. The yield of IId was low, even in the presence of excess *p*-toluenesulfonyl chloride, and the monopyridinium salts IIIa and IIIb were isolated as by-products.[3]

Treatment of the dibromide IIc or the di-*p*-toluenesulfonate IId with aqueous methylamine gave no isoindoline. Instead, methylamine abstracted a proton from a benzyl carbon atom, and generated the corresponding ylide (IVb or IVc, respectively) in 85% yield. Aqueous ammonia or aqueous potassium hydroxide generated IVb from

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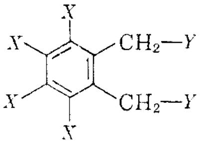
[1] W. E. Rosen, V. P. Toohey, and A. C. Shabica, *J. Am. Chem. Soc.*, 79, 3167 (1957).

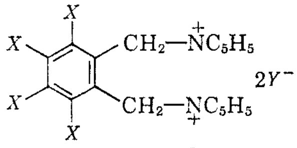
[2] W. E. Rosen, V. P. Toohey, and A. C. Shabica, *J. Am. Chem. Soc.*, 80, 935 (1958).

[3] Treatment of the pyridine-insoluble monopyridinium tosylate IIIa with excess *p*-toluenesulfonyl chloride in pyridine for seven days gave a 94% yield of dipyridinium *dichloride* (IIe).

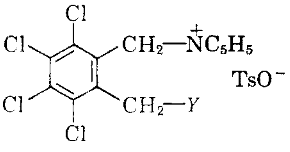
IIc in the same yield. Syntheses involving this type of pyridinium salt ylide (C-betaine) as intermediate are well known[4,5] but the ylide itself is usually not isolated. In the case of IVb or IVc, the four chlorine atoms on the benzene ring apparently stabilize the benzyl carbanion by inductive withdrawal.[1,2,6] Treatment of 3,4,5,6-tetrachloro-*o*-xylylene dipyridinium dibromide (IIc) with *strong* base (sodium methoxide in methanol) gave a 79% yield of a bromine-free red solid, whose structure is probably either the quinolizinium ylide V (*via* path a) or the benzobutene ylide VI (*via* path b). We favor structure V because the infrared spectrum in carbon disulfide solution showed a medium absorption band at 742 cm.$^{-1}$, consistent with an α-substituted pyridine derivative (749 cm.$^{-1}$) but not with an unsubstituted pyridine (701 cm.$^{-1}$).[7] Consistent with the ylide formulation was the hypsochromic shift of the ultraviolet absorption spectrum in acidic solution and the isolation of a bromide salt after treatment with hydrobromic acid.



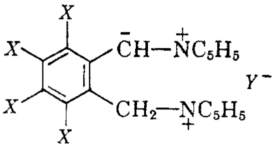
Ia. X = H; Y = Br
b. X = H; Y = OH
c. X = Cl; Y = Br
d. X = Cl; Y = OH



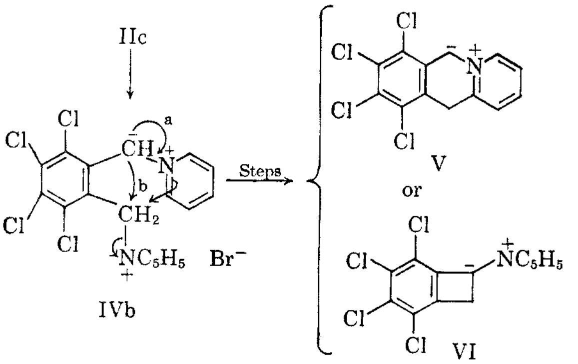
IIa. X = H; Y = Br
b. X = H; Y = TsO
c. X = Cl; Y = Br
d. X = Cl; Y = TsO
e. X = Y = Cl



IIIa. Y = OH
b. Y = Cl



IVa. X = H, Y = Br
b. X = Cl, Y = Br
c. X = Cl, Y = TsO



IVb

V

VI

The ultraviolet absorption spectrum of 1-benzylpyridinium chloride has been reported[8] to remain "essentially the same in neutral, basic, and acidic solutions." We have confirmed this observation and found that the statement applies as well to the corresponding bromide salt. In basic solutions of IIc and IId (and also with IIIa), broad weak bands at *ca.* 330 mμ and 450 mμ were generated, as expected from the ready formation of the ylides IVb and IVc. Surprisingly, basic solutions of IIa and IIb also generated these long wave length bands. In fact, from a solution of IIa in methanolic sodium methoxide, two deeply colored products were isolated which had analyses consistent with the monoylide IVa and the corresponding diylide.

EXPERIMENTAL[9]

Preparation of o-xylylene-α,α'-dipyridinium dibromide (IIa) *from Ia.* Addition of 1.30 g. of *o*-xylene dibromide (Ia) to 4.0 ml. of dry pyridine with swirling gave 2.01 g. (96.9%) of solid product, m.p. 227–229°. One crystallization from methanol–ethyl acetate gave colorless prisms, m.p. 228–231°; λ_{max} 254–56 mμ (sh., ε 7,690), 260 (8,040), 266–269 (sh., 5,930); λ_{min} 234 mμ (ε 3,710); λ^{base}_{max} 259–262 mμ (ε 4,670), 324–334 (2,100), 436–463 (815); λ^{base}_{min} 240–242 mμ (ε 3,820), 286–290 (1,500), 403–412 (700).

Anal. Calcd. for $C_{18}H_{18}Br_2N_2$ (422.29): C, 51.21; H, 4.30; N, 6.64. Found: C, 51.23; H, 4.28; N, 6.34.

Preparation of o-xylylene-α,α'-dipyridinium di-p-toluenesulfonate (IIb) *from Ib. p*-Toluenesulfonyl chloride (5.73 g., 0.03 mole) was added to a −5° solution of 1.38 g. (0.01 mole) of *o*-xylylene-α,α'-diol (Ib) in 25 ml. of dry pyridine. The solution, after standing at 0° for 18 hours, was poured into 100 ml. of water and washed twice with 100-ml. portions of ether. The aqueous solution was stripped to dryness at reduced pressure, leaving 10.00 g. of viscous yellow oil. After standing in air for several days, the oil deposited 2.85 g. of sticky white crystals, which were recrystallized from methanol-ethyl acetate to give 1.70 g. of pyridinium *p*-toluenesulfonate, m.p. 119–121°.

A 2.93-g. aliquot of the remaining yellow oil was dissolved in 15 ml. of methanol and diluted with 400 ml. of ethyl acetate, giving 1.34 g. (54%) of pale yellow crystals, m.p. (s142) 149–153° dec. The crystals were recrystallized to give long white prisms of *o*-xylylene-α,α'-dipyridinium di-*p*-toluenesulfonate (IIb), m.p. 161–162° (yellow melt); λ_{max} 217 mμ (ε 35,000), 227 (sh., 18,600), 255–258 (sh., 8,340), 261 (8,500), 268 (sh., 6,060); λ_{min} 236–238 mμ (ε 4,250); λ^{base}_{max} 226–228 mμ (sh., ε 22,700), 256–259 (plateau, 5,300), 262 (5,410), 268 (sh., 4,470), 320–354 (1,990), 439–457 (740); λ^{base}_{min} 239–242 mμ (ε 4,440), 288–292 (1,430), 400–406 (590). The infrared spectrum showed absorption at 1012, 1035, 1123, and 1158 cm.$^{-1}$, typical of ionic *p*-toluenesulfonate.

Anal. Calcd. for $C_{32}H_{32}O_6N_2S_2$ (604.76): C, 63.55; H, 5.33; N, 4.63. Found: C, 63.26; H, 5.52; N, 4.46.

Preparation of 3,4,5,6-tetrachloro-o-xylylene-α,α'-dipyridinium dibromide (IIc) *from* Ic. When 1.30 g. of 3,4,5,6-tet-

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(4) F. Kröhnke, *Angew. Chem.*, **65**, 605 (1953).

(5) O. Westphal and K. Jann, *Ann.*, **605**, 8 (1957).

(6) The ability of even one chlorine atom to increase the acidity of the benzyl hydrogen was demonstrated by C. H. DePuy and R. E. Leary, *J. Am. Chem. Soc.*, **79**, 3705 (1957).

(7) H. Shindo and N. Ikekawa, *Pharm. Bull.* (*Japan*) **4**, 192 (1956).

(8) A. G. Anderson, Jr., and G. Berkelhammer, *J. Org. Chem.*, **23**, 1109 (1958).

(9) Melting points were taken on an electrically heated aluminum block in open capillaries and are uncorrected. Analytical samples were dried at waterpump vacuum over Drierite at 75° for 3–5 hr. Ultraviolet absorption spectra were taken in 95% ethanol, unless otherwise specified; spectra labeled "base" were taken in 0.1*N* potassium hydroxide in 95% ethanol; spectra labeled "acid" were taken in 0.1*N* hydrochloric acid in 95% ethanol. Infrared spectra were taken as Nujol mulls.

rachloro-*o*-xylylene-α,α'-dibromide[2] (Ic) was swirled with 10 ml. of dry pyridine, it dissolved completely before IIc began to precipitate. One crystallization of the crude IIc from methanol–ethyl acetate gave 1.16 g. (64%) of off-white prisms, m.p. 202–207° dec.; $\lambda_{\max}$ 220 mμ (sh., ϵ 54,200), 239–243 (sh., 15,700), 256–259 (plateau, 8,550), 266 (sh., 6,530), 290–292 (1,370), 302 (1,300), 322 (sh., 400); $\lambda_{\min}$ 285 mμ (ϵ 1,250), 297 (1,190); $\lambda_{\max}^{\text{base}}$ 234–238 mμ (sh., ϵ 16,100), 258–264 (sh., 5,270), 268–270 (sh., 4,070), 285–287 (2,120), 296–297 (2,470), 325–334 (2,740), 442–448 (680); $\lambda_{\min}^{\text{base}}$ 282–283 mμ (2,050), 288 (2,080), 304–306 (2,300), 406–412 (573). The ultraviolet absorption spectrum in 0.1*N* sodium methoxide in methanol was the same as the "base" curve.

Anal. Calcd. for $C_{18}H_{14}N_2Cl_4Br_2.H_2O$ (578.00): C, 37.40; H, 2.79; N, 4.85. Found: C, 37.26; H, 3.40; N, 4.82.

Preparation of 3,4,5,6-tetrachloro-o-xylylene-α,α'-dipyridinium di-p-toluenesulfonate (IId), *and 3,4,5,6-tetrachloro-o-xylylene-α-ol-α'-pyridinium p-toluenesulfonate* (IIIa) *from* Id. A solution of 2.76 g. of 3,4,5,6-tetrachloro-*o*-xylylene-α,α'-diol[2] (Id) and 5.73 g. (50% excess) of *p*-toluenesulfonyl chloride in 25 ml. of dry pyridine was allowed to stand at room temperature for 25 hr. The white crystalline precipitate was collected and slurried with 50 ml. of water. The white, water-insoluble crystals were dried, giving 2.45 g. (33%) of 3,4,5,6-tetrachloro-*o*-xylylene-α,α'-dipyridinium di-*p*-toluenesulfonate (IId), m.p. 242–244° dec. One crystallization from methanol-ethyl acetate afforded 1.48 g. of fine white needles of IId, m.p. 245–247° dec.; $\lambda_{\max}$ 218–220 mμ (ϵ 72,200), 229 (sh., 38,800), 240 (sh., 15,750), 242–246 (sh., 13,580), 254–261 (plateau, 8,340), 268–270 (sh., 6,050), 291–292 (928), 302 (965), 320–355 (plateau, 190); $\lambda_{\min}$ 283–285 mμ (ϵ 715), 297 (798); $\lambda_{\max}^{\text{base}}$ 235–242 mμ (sh., ϵ 14,210), 256 (sh., 5,650), 261 (5,230), 267 (sh., 4,400), 286 (1,870), 296 (2,160), 330–333 (2,620), 450–459 (822); $\lambda_{\min}^{\text{base}}$ 260 mμ (ϵ 5,200), 282 (1,810), 287 (1,860), 303 (2,020), 411–420 (745). The infrared spectrum showed strong absorption at 1014, 1038, 1125, and 1158 cm.$^{-1}$, typical of ionic *p*-toluenesulfonate groups.

Anal. Calcd. for $C_{32}H_{28}O_6N_2Cl_4S_2 \cdot H_2O$ (760.57): C, 50.53; H, 3.98; N, 3.68. Found: C, 50.99, H, 3.87; N, 3.64.

The aqueous solution of the water slurry precipitated 0.16 g. (2%) more IId, m.p. 243–246° dec., on standing overnight. The solution was evaporated to dryness *in vacuo*, leaving 2.75 g. of yellow oil. Two crystallizations of this oil from methanol-ethyl acetate gave 1.71 g. (33.6%) of pale yellow prisms of 3,4,5,6-tetrachloro-*o*-xylylene-α-ol-α'-pyridinium *p*-toluenesulfonate (IIIa), m.p. 185° dec.; $\lambda_{\max}$ 214–220 mμ (plateau, ϵ 55,600), 239–243 (sh., 14,700), 258–260 (pleateau, 6,360), 291 (870), 302 (885), 322–356 (plateau, 100); $\lambda_{\min}$ 285 mμ (ϵ 688), 297 (720); $\lambda_{\max}^{\text{base}}$ 236–240 mμ (ϵ 14,100), 256 (sh., 5,280), 260 (sh., 4,950), 270 (sh., 3,680), 296–298 (2,210), 332–338 (2,640), 442–456 (885); $\lambda_{\min}^{\text{base}}$ 281–283 mμ (ϵ 1,890), 302–304 (2,090), 412–424 (850). Infrared absorption due to ionic *p*-toluenesulfonate anion appeared at 1012, 1035, 1120, and 1151 cm.$^{-1}$

Anal. Calcd. for $C_{20}H_{17}O_4NCl_4S \cdot H_2O$ (527.27): C, 45.56; H, 3.63. Found: C, 45.81; H, 3.65.

When twice as much *p*-toluenesulfonyl chloride (0.06 mole) was used, 38.8% IId, m.p. 238–241° dec. (28.8% m.p. 244–246° dec., after one recrystallization) and 28.7% IIIa, m.p. 180–186° dec., were isolated.

Preparation of IId *from* Id *at 0°; isolation of* IIIa *and 3,4,5,6-tetrachloro-o-xylylene-α-chloride-α'-pyridinium p-toluenesulfonate* (IIIb). To a solution of 2.76 g. (0.01 mole) of 3,4,5,6-tetrachloro-*o*-xylylene-α,α'-diol (Id) in 25 ml. of dry pyridine chilled to −10° was added 5.73 g. (0.03 mole) of *p*-toluenesulfonyl chloride. After standing at 0° for 25 hr., the precipitated white solid was washed three times with 15-ml. portions of water and dried, leaving 1.59 g. (21.5%) of IId, m.p. (s 230) 238–240° dec. The water washings were evaporated *in vacuo* to 1.29 g. of yellow semisolid; crystallization from methanol-ethyl acetate gave a few percent of crude IId plus 0.13 g. (2.5%) of the monopyridinium salt (IIIa), m.p. 181–186° dec. The red pyridine mother liquors were diluted with 100 ml. of ice-cold water, washed with 100 ml. of ether, acidified with concentrated hydrochloric acid, and extracted three times with chloroform. The chloroform extracts were evaporated *in vacuo* to 0.36 g. (7%) of yellow solid. Two crystallizations from acetone gave analytically pure 3,4,5,6-tetrachloro-*o*-xylylene-α-chloride-α'-pyridinium *p*-toluenesulfonate (IIIb), m.p. 185–187°; a mixed melting point with IIIa depressed to 170°. The infrared spectrum showed strong absorption bands at 1011, 1032, 1121, and 1173 cm.$^{-1}$ characteristic of ionic *p*-toluenesulfonate. In chloroform solution, the ionic *p*-toluenesulfonate bands absorbed at 1009, 1029 (weak), 1121, and 1158 cm.$^{-1}$

Anal. Calcd. for $C_{20}H_{16}O_3NCl_5S$ (527.71): C, 45.52; H, 3.06; Cl, 33.60; S, 6.08. Found: C, 45.59; H, 3.18; Cl, 33.87; S, 6.24.

Preparation of 3,4,5,6-tetrachloro-o-xylylene-α,α'-dipyridinium dichloride (IIe) *from* IIIa. A suspension of 0.53 g. (1.0 millimole) of 3,4,5,6-tetrachloro-*o*-xylylene-α-ol-α'-pyridinium *p*-toluenesulfonate (IIIa) in 10 ml. of dry pyridine containing 0.57 g. (3.0 mmoles) of *p*-toluenesulfonyl chloride was allowed to stand at room temperature, with occasional swirling, for 7 days. The off-white solid was separated, giving 0.44 g. (93.6%) of product m.p. 173–193° dec. Its infrared spectrum showed no ionic *p*-toluenesulfonate. One crystallization from water-acetone gave white crystals, m.p. 162–172° (resolidified), 192–196° dec.

Anal. Calcd. for $C_{18}H_{14}N_2Cl_6 \cdot 2H_2O$ (507.10): C, 42.63; H, 3.58; N, 5.52. Found: C, 43.02; H, 3.80; N, 5.35.

Preparation of 3,4,5,6-tetrachloro-o-xylylene-α-pyridinium-ylide-α'-pyridinium bromide (IVb) *from* IIC. (*a*) *With methylamine.* When 0.50 g. of 3,4,5,6-tetrachloro-*o*-xylylene dipyridinium dibromide (IIc) was added to 5 ml. of 25% aqueous methylamine, the solution turned red-orange and red solid separated. After 24 hr., the red rust-colored solid was collected, washed with water, and dried, giving 0.35 g, (85%) of product which darkened and softened above 200°, but did not melt to 300°; $\lambda_{\max}$ 237 mμ (sh., ϵ 16,860), 254–256 (plateau, 8,050), 269 (sh., 7,720), 287 (sh., 3,900), 298 (sh., 3,460), 350–353 (1,760), 376 (1,710), 398 (1,380), 422 (1,240); $\lambda_{\min}$ 337–341 mμ (ϵ 1,740), 369 (1,700), 391 (1,310), 412 (1,070). The infrared spectrum was the same as the ylide IVc (minus those bands due to ionic tosylate).

Anal. Calcd. $C_{18}H_{13}N_2Cl_4Br$ (479.06): C, 45.12; H, 2.74; N, 5.85; Cl + Br, 46.29. Found: C, 45.68; H, 3.02; N, 6.19; Cl + Br, 44.23.

A slurry with hot dimethylformamide and thorough washing with acetone gave a red solid.

Anal. Found: C, 44.99; H, 3.09; N, 5.90.

(b) *With aqueous ammonia.* To a light yellow solution of 2.00 g. of 3,4,5,6-tetrachloro-*o*-xylylene-α,α'-dipyridinium dibromide (IIc) in 4 ml. of warm water was added 0.8 ml. of 29% aqueous ammonia. The solution turned red, and red solid separated after about 1 min. After the suspension had stood at room temperature for 2 hr., the red solid was collected, washed once with water, and dried *in vacuo* at 60° for 4 hr., giving 1.51 g. (88%) of the ylide (IVb), softening at 220° and darkening, but not melting to 300°.

Anal. Found: C, 45.09; H, 2.90; N, 6.15; Br + Cl, 45.56.

(c) *With aqueous potassium hydroxide.* One milliliter of 30% aqueous potassium hydroxide was added to a stirred solution of 2.00 g. of IIc in 4 ml. of water. The red solid which separated was collected, washed with water, and methanol, and dried, giving 1.38 g. (83.4%) of IVb, darkening but not melting to 300°.

Anal. Found: C, 45.04; H, 2.67.

Preparation of 3,4,5,6-tetrachloro-o-xylylene-α-pyridinium-ylide-α'-pyridinium p-toluenesulfonate (IVc) *from* IId. Five milliliters of 25% aqueous methylamine was added to a solution of 1.00 g. of 3,4,5,6-tetrachloro-*o*-xylylene-α,α'-dipyridinium di-*p*-toluenesulfonate (IId) in 2 ml. of methanol. The solution turned dark red, and an oil which separated became solid on swirling. After standing at room temperature for 24 hr., the rust-colored solid was collected, washed with water, and dried, giving 0.65 g. (86.5%) of IVc, m.p. 203–

207° dec.; λ_{max} 261 mμ (sh., ε 5,480), 268 (sh. 4,560), 295 (2,470), 342–345 (2,420), 450–459 (1,520); λ_{min} 288 mμ (ε 2,360), 302–308 (2,230), 412 (1,290). The infrared spectrum showed absorption typical of ionic *p*-toluenesulfonate.

Anal. Calcd. for $C_{25}H_{20}O_3N_2Cl_4S$ (570.35): C, 52.65; H, 3.53; N, 4.91; Cl, 24.87. Found: C, 52.37; H, 3.70; N, 5.33; Cl, 25.31.

A small sample was crystallized from dimethylformamide and washed well with acetone. After the orange crystals had dried over Drierite *in vacuo* at 75° for 6 hr., they were further dried at 75° under a stream of dry nitrogen for 6 hrs.

Anal. Found: C, 52.42, H, 3.99; N, 5.01; Cl, 24.23.

Preparation of 7,8,9,10-tetrachloro-6,11-dihydrobenzo[*b*]-*quinolizinium betaine* (V) *from* IIc. A solution of 0.50 g. (0.89 millimole) of 3,4,5,6-tetrachloro-*o*-xylylene dipyridinium dibromide (IIc) in 30 ml. of methanol was added dropwise over 25 min. to a stirred solution of 0.50 g. (9.2 mmoles) of sodium methoxide in 40 ml. of methanol. The first drop turned the sodium methoxide solution pale yellow, and further addition caused color intensification from yellow to orange to red-orange. After 5 min. more stirring, the solution was stripped to dryness, and the red solid was slurry-washed with 25 ml. of water and dried. The 0.23 g. (79.3%) of red solid darkened above 200° but did not melt to 300°; λ_{max} 236 mμ (sh., ε 15,000), 267 (sh., 5,300), 354–360 (2,850), 378 (sh., 2,480), 447 (1,670), 472–474 (sh., 1,340); λ_{min} 308–312 mμ (ε 2,070), 437 (1,660); λ_{max}^{base} 360 mμ (ε 3,320), 378 (sh., 2,970), 410–412 (sh., 2,100), 446–450 (sh., 1,920), 472 (sh., 1,570); λ_{min}^{base} 300–303 mμ(ε 2,380); λ_{max}^{acid} 256 mμ (sh., ε 9,490), 267 (9,630), 297 (sh., 3,820), 375 (1,570), 399 (1,400), 420 (1,180); λ_{min}^{acid} 251 mμ (ε 9,230), 342–344 (1,340), 387 (1,330), 411 (1,120).

Anal. Calcd. for $C_{13}H_7NCl_4$ (319.04): C, 48.94; H, 2.21; N, 4.39. Found: C, 48.63; H, 2.41; N, 4.57.

The brick red solid was soluble in 48% hydrobromic acid, and in 36% or 3.6% hydrochloric acid.

A solution of 0.13 g. of V in 2.0 ml. of 48% hydrobromic acid was filtered and stripped to dryness. The residue was thoroughly dried, giving a brown solid which darkened but did not melt to 320°. The neutral ultraviolet absorption curve was the same as that of V in acid solution; λ_{max} 235 mμ (sh., ε 14,000), 256–257 (8,250), 266–268 (8,250), 296 (sh., 3,500), 312 (sh., 2,420), 376 (1,930), 399 (1,620), 423 (1,320).

Anal. Calcd. for $C_{13}H_8BrCl_4N.H_2O$ (417.98): C, 37.36; H, 2.41. Found: C, 37.14; H, 2.83.

Probable preparation of o-xylylene-α-pyridinium-ylide-α′-pyridinium bromide (IVa) *and o-xylylene dipyridinium diylide from strong base treatment of* IIa. A solution of 3.00 g. (7.1 mmoles) of *o*-xylylene dipyridinium dibromide (IIa) in 20 ml. of methanol was added to a stirred solution of 3.84 g. (71 mmoles) of sodium methoxide in 30 ml. of methanol. The dark red solution was further stirred for 2 hr., and the dark purple-brown solution was stripped to dryness at reduced pressure. The residue was slurried with water, collected, and dried, giving 2.00 g. of brown solid decomposing 130–135°. The brown solid was swirled with 30 ml. of hot methanol and filtered. The insoluble material was washed again with hot methanol, leaving a small amount of brown solid (IVa) which darkened but did not melt to 300°. The material was too insoluble in alcohol to give a distinct ultraviolet absorption curve, but addition of hydrogen chloride caused a general hypsochromic shift.

Anal. Calcd. for $C_{18}H_{17}BrN_2$ (341.27): C, 63.35; H, 5.02; N, 8.21. Found: C, 63.81; H, 5.12; N, 8.47.

The methanol solution of the original slurry was diluted with an equal volume of water, and the precipitated solid was collected and dried: dec. 262–270°.

Anal. Calcd. for $C_{18}H_{16}N_2 \cdot 2H_2O$ (296.37): C, 72.95; H, 6.80; N, 9.45. Found: C, 71.70; H, 6.14; N, 9.01.

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Equilibrium Constants for the Hydrolysis of Some *N*-Aryl-D-glucosylamines

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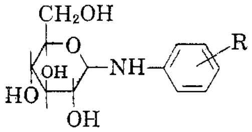
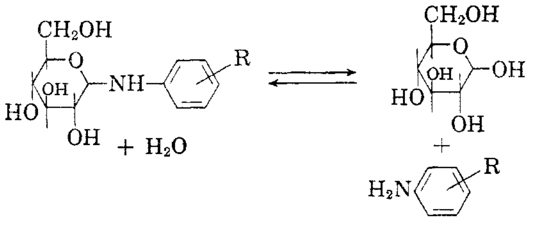
The relative stabilities of the *N*-aryl-D-glucosylamines in aqueous solutions have been studied by only a few workers.[1,2,3] Their results indicated that the extent of hydrolysis increased as the *p*H of the solution decreased and as the base strength of the parent aromatic amine increased.

The present work was concerned with the determination of the equilibrium constants for the hydrolysis of *N*-phenyl-(I), *N*-*p*-tolyl-(II), *N*-*m*-tolyl-(III), *N*-*p*-chlorophenyl-(IV), and *N*-*p*-nitrophenyl-D-glycosylamine (V). All of these compounds were prepared according to methods previously reported in the literature. The equilibrium constants for reaction I in aqueous ethanol were determined by polarimetric analysis of the solutions.



I. R = H
II. R = *p*-CH_3
III. R = *m*-CH_3
IV. R = *p*-Cl
V. R = *p*-NO_2



(I)

When dissolved in aqueous ethanol, *N*-phenyl-D-glucosylamine (I) underwent mutarotation and hydrolysis. The mutarotation caused a decrease while the slower hydrolysis reaction caused an increase in specific rotation. At a *p*H of 10.5 or greater, only the mutarotation reaction was observed and after fifty hours the specific rotation was constant at −71°. At a *p*H of 6.8, both reactions were noted and an extrapolation of the hydrolysis curve back to time zero indicated a specific rotation of −71°. In solutions of *p*H 5.4 or less, only the hydrolysis reaction was detected, apparently because mutaro-

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