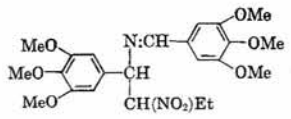
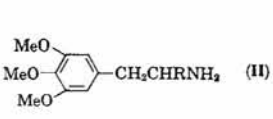
6-nitroacetanilides (alkyl and m.p. given): Me, 172.5–3.5°; iso-Pr, 125.5–6°; *tert*-Bu, 212°. The acetanilides were hydrolyzed and the following 2,4-dialkyl-6-nitroanilines obtained (alkyl and m.p. given): Me, 71°; iso-Pr, 66.5–7.5°; *tert*-Bu, 89.5°. These compds. were diazotized and reduced with either EtOH or H_3PO_2 to 2,4-dialkylanilines (alkyl, m.p., % yield by redn. with EtOH, and % yield by H_3PO_2 redn. given): Me, 71.5°, 51, 84; iso-Pr, — (b_5 129.5), —, 78; *tert*-Bu, 119–19.5°, 40, 80. 3,5-(*tert*-Bu)$_2$C$_6$H$_3$NO$_2$ (1.5 g.) reduced with 4 g. Raney Ni gave 3,5-(*tert*-Bu)$_2$C$_6$H$_3$NH$_2$, m. 54°. M. Oki

Cyclopropylcarbinyllithium. Peter T. Lansbury and Victor A. Pattison (State Univ. of New York, Buffalo). *J. Am. Chem. Soc.* **85**(12), 1886–7(1963); cf. *CA* **58**, 3292*e*. Cyclopropylcarbinyl chloride and NaI in dry Me_2CO gave cyclopropylcarbinyl iodide (I), b_{150} 88–90°. To 1 millimole EtLi at −70° was added 1 millimole I, the whole kept 2 hrs. at −70° and 2 millimoles BzH added; gas-liquid partition chromatography of the reaction mixt. indicated 3% PhEtCHOH, 17% cyclopropylmethylphenylcarbinol and 80% CH_2:$CHCH_2CH_2PhCHOH$. Harry L. Yale

Psychotomimetic agents related to mescaline. A. T. Shulgin (Dow Chem. Co., Walnut Creek, Calif.). *Experientia* **19**(3), 127–8(1963)(in English). The widely studied pharmacology of mescaline prompted the synthesis of higher homologs. All of the amines were prepd. by the $LiAlH_4$ redn. of the corresponding nitrostyrenes, which in turn were prepd. by the ammonia-catalyzed condensation of the appropriate nitroalkane with 3,4,5-trimethoxybenzaldehyde, in AcOH. With $PrNO_2$ in AcOH, the product was 3,4,5-trimethoxybenzonitrile, and substitution of iso-PrOH for the acidic solvent led to the unexpected formation of the Schiff base (I), m. 151.5–2.0°. Hydrolysis of I gave trimethoxybenzaldehyde and after neutralization, 1-(3,4,5-trimethoxyphenyl)-2-nitrobutylamine. Replacement of the ammonia catalyst with a secondary amine led to a proper nitrostyrene. The following homologs (II) of mescaline were ob-



(I)

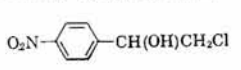


(II)

tained (R, m.p.% yield of the intermediate nitrostyrene, m.p. of picrate of II, m.p. of HCl of II, and % yield of II given): Me, 93–4°, 50, 171–3°, 208–9°, 62; Et, 72–3°, 29, 177–81°, 192–3°, 52; Pr, 82.5–3.5°, 32, 182–4°, 214–18°, 65; Bu, 73–4°, 34, 168–70°, 182–4°, 45; Am, 54–5°, 24, 162–3°, 155–8°, 50; hexyl, 51–2°, 21, 149–51°, 132–4°, 53; heptyl, 43–4°, 19, 148–9°, 112–16°, 19; nonyl, 46–7°, 16, —, —, 0. B. K. Wasson

Schmidt reaction. Richard F. Stockel and David M. Hall (Clemson Coll., Clemson, S. Car.). *Nature* **197**, 787–8(1963). Aromatic carboxylic acids are converted to the corresponding amines with polyphosphoric acid and excess NaN_3 at room temp. The results were (acid, amine, and % yield given): BzOH, $PhNH_2$, 71.2; *p*-$O_2NC_6H_4CO_2H$, *p*-$O_2NC_6H_4NH_2$, 48.2; *p*-MeO-$C_6H_4CO_2H$, *p*-$MeOC_6H_4NH_2$, 79.7; mesitoic acid, mesidine, 90.6. Evidently the acids with electron-donating groups give better yields and have faster rates. No by-products were formed. V. N. Gupta

Synthesis of *p*-aminostyrene. V. G. Sinyavs'kii, A. I. Turbina, and M. Ya. Romankevich. *Dopovidi Akad. Nauk Ukr. RSR* **1962**(12), 1622–4. Starting with I, the title synthesis was conducted in 3 steps. To 180 g. I in 300 ml. MeOH at 35–40° was added with stirring over 1–1.5 hrs. 50 ml. 40% aq. NaOH. After filtering, washing, and crystg. from aq. MeOH, 116 g. II, m. 86.5–7.5°, was obtained. Three ways were proposed to convert II into *p*-aminophenylethanol (III). (*a*) A mixt. of 80 g. Zn dust, 8 g. $CaCl_2$, and 400 ml. H_2O was boiled with stirring for 1 hr., II (20 g.) was added portionwise, boiling continued for another hr., Na_2CO_3 added, the mixt. filtered, washed with MeOH, and distd. *in vacuo*. The fraction b_{4-6} 233–8° was collected with a yield of 7.1 g., m. 107.5–108°. (*b*) II (66 g.) was mixed with 1.2 g. Na_2CO_3, 4 g. Raney Ni, and 200 ml. thiophene-free benzene and hydrogenated in an autoclave with 36 l. H at 50–60° and 100–150 atm. The resulting resinous material was dissolved in MeOH, filtered, and the residue distd. at 230–40°/5–10 mm. to give 33.1 g. III, m. 107–8°. (*c*) Platinized C (20%) was used instead of Raney Ni. A mixt. of 36.7 g. III and 35 g. KOH was heated in a N atmosphere (8–10 mm.). *p*-Aminostyrene was distd. together with H_2O, extd. with ether, dried over KOH, filtered, and redistd. to give 26.7 g. *p*-$H_2NC_6H_4CH$:CH_2, b_{8-10} 115–17°.



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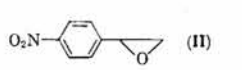


(II)

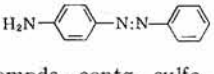
N. Jasinczuk

Action of bromine on thioformanilide. M. B. Antia and Mirs I. Pandit (Holkar Coll., Indore, India). *Vikram, J. Vikram Univ.* **5**, No. 1, 106–7(1961). Satd. Br–H_2O (100 ml.) stirred into 7 g. HCSNHPh in 20 ml. ice-H_2O pptd. 4-BrC_6H_4N:CBr_2 (I), m. 115°. Addn. of further Br–H_2O to the filtrate pptd. 2,4,6-$Br_3C_6H_2NH_2$, m. 121°. I (2 g.) boiled in 6*N* HCl until dissolved, then cooled pptd. 4-$BrC_6H_4NH_3Cl$, m. >217°. J. A. Giles

Halo and thiocyanato thiosemicarbazides and thiosemicarbazones and their behavior in paper chromatography. II. D. Goeckeritz and R. Pohloudek-Fabini (Ernst-Moritz-Arndt-Univ., Greifswald, Ger.). *Pharmazie* **17**, 679–85(1962); cf. *ibid.* 515. The paper chromatographic sepn. of halo- and thiocyanatoanilines, phenyl isothiocyanates, phenylthiocarbamic acid *O*-Me esters, phenylthiosemicarbazides, and phenylthiosemicarbazones is reported. The following R_f values were detd. using paper impregnated with Me_2NCHO: *p*-$RC_6H_4NH_2$ (mobile phase cyclohexane-benzene 3:1) (R and R_f given): H, 0.42; F, 0.35; Cl, 0.46; Br, 0.48; I, 0.52; NCS, 0.19. *p*-$RC_6H_4NH_2$ (xylene): H, 0.60; F, 0.58; Cl, 0.69; Br, 0.72; I, 0.73; NCS, 0.60. *p*-$RC_6H_4NHCSOMe$ (cyclohexane): H, 0.42; F, 0.40; Cl, 0.61; Br, 0.60; I, 0.60; NCS, 0.22. *p*-$RC_6H_4NHCSOMe$ (xylene): H, 0.90; F, 0.86; Cl, 0.90; Br, 0.91; I, 0.90; NCS, 0.89. *p*-$RC_6H_4NHCSOMe$ (nonane): H, 0.13; F, 0.12; Cl, 0.21; Br, 0.22; I, 0.21; NCS, 0.04. *p*-RC_6H_4NCS (nonane): H, 0.88; F, 0.88; Cl, 0.90; Br, 0.90; I, 0.90; NCS, 0.69. *p*-$RC_6H_4NHCSNHNH_2$ (xylene-benzene 1:1): H, 0.24; F, 0.27; Cl, 0.44; Br, 0.48; I, 0.52; NCS, 0.38. *p*-$RC_6H_4NHCSNHNH_2$ (xylene): H, 0.12; F, 0.10; Cl 0.23; Br, 0.23; I, 0.24; NCS, 0.18. *p*-$RC_6H_4NHCSNHN$:$CHEt$ (octane): F, 0.05; Cl, 0.11; Br, 0.13; I, 0.13; NCS, 0.02. *p*-$RC_6H_4NHCSNHN$:$CHPr$ (octane): F, 0.12; Cl, 0.21; Br, 0.22; I, 0.21; NCS, 0.05. *p*-$RC_6H_4NHCSNHN$:$CHCHMe_2$ (octane): F, 0.14; Cl, 0.24; Br, 0.24; I, 0.24; NCS, 0.06. *p*-$RC_6H_4NHCSNHN$:$CH(CH_2)_4Me_2$ (octane): F, 0 32; Cl, 0.43; Br, 0.44; I, 0.39; NCS, 0.14. *p*-$RC_6H_4NHCSNHN$:-CMe_2 (octane): F, 0.06; Cl, 0.11; Br, 0.12; I, 0.11; NCS, 0.02. *p*-$RC_6H_4NHCSNHN$:$CMePr$ (octane): F, 0.27; Cl, 0.40; Br, 0.40; NCS, 0.12. *p*-$RC_6H_4NHCSNHN$:C_6H_{10} (C_6H_{10}-cyclohexylidene) (octane): F, 0.17; Cl, 0.26; Br, 0.27; I, 0.27; NCS, 0.07. *p*-$RC_6H_4NHCSNHN$:$CHPh$ (cyclohexane): F, 0.19; Cl, 0.25; Br, 0.30; I, 0.24; NCS, 0.10. *p*-RC_6H_4-$NHCSNHN$:$CHC_6H_4CHMe_2$-*p* (cyclohexane): F, 0.56; Cl, 0.69; Br, 0.69; I, 0.65; NCS, 0.38. *p*-$RC_6H_4NHCSNHN$:$CHCH$:-$CHPh$ (cyclohexane): F, 0.23; Cl, 0.26; Br, 0.34; I, 0.30; NCS, 0.14. *p*-$RC_6H_4NHCSNHN$:$CH(CH_2)_2Ph$ (cyclohexane): F, 0.35; Cl, 0.44; Br, 0.49; I, 0.45; NCS, 0.22. The following *p*-RC_6H_4-NHCSOMe (R and m.p. given) were prepd. by refluxing solns. of *p*-RC_6H_4NCS (0.01 mole) in 4 ml. MeOH for 1 hr. and crystg. the ppt. obtained on cooling from petr. ether: H, 92–3°; F, 64–5°; Cl, 92–3°; Br, 101–2°; I, 112–13°; NCS, 137–8°. E. Ciganek

Advances of chemistry of aromatic diazo compounds. B. I. Belov and V. V. Kozlov (G. V. Plekhanov Inst. National Econ., Moscow). *Uspekhi Khim.* **32**, 121–53(1963). A review with 196 references through 1961, covering methods of diazotization, properties of the diazo compds., kinetics and mechanism of diazotization, and conversion of diazo compds. by substitution and redn., and formation of hetero-org. compds. G. M. Kosolapoff

Polarographic investigation of some azo compounds. Istvan Rusznak, Ferenc Peter, and Gyula Palyi (Tech. Univ., Budapest). *Acta Chim. Acad. Sci. Hung.* **35**, 199–204(1963)(in English). Twelve para derivs. of azobenzene were studied in order to det. the correlation between the structure and half-wave potential. Measurements were carried out in solns. of pH 3.52, 6.51, and 9.81 contg. 10% EtOH and 90% buffer (Britton-Robinson). The compds. tested and the half-wave potentials (v.) observed were: 4-aminoazobenzene (I), −0.195, −0.410, and −0.650; 2,4-diaminoazobenzene, −0.260, −0.445, and −0.685; 3-methyl-4,6-diaminoazobenzene, −0.310, −0.590, and −0.770; 3,3′-dimethyl-4-aminoazobenzene, −0.235, −0.480, −0.665; 4-aminoazobenzene-3,4′-disulfonic acid, −0.160, −0.375, no wave; 2′-hydroxy-2,4-diaminoazobenzene-5′-sulfonic acid, −0.280, −0.460, −0.700; 3,2′-dimethyl-4-aminoazobenzene-5,4′-disulfonic acid, −0.165, −0.375, −0.635; 5-methyl-2′-hydroxy-3′,5′-dinitro-2,4-diaminoazobenzene, no wave, −0.535, −0.890; 4-(dimethylamino)azobenzene-4′-sulfonic acid, −0.180, −0.370, −0.615; 4-(dimethylamino)azobenzene-2′-carboxylic acid, −0.135, −0.350, −0.540; 4-(phenylamino)azobenzene-3′-sulfonic acid, −0.170, −0.410, −0.625; 4-(2,4-dinitrophenylamino)azobenzene-4′-sulfonic acid, −0.170, −0.350, −0.555. The above half-wave potential values were at pH 3.52, 6.51, and 9.81, resp. Based on the above data, the following generalizations were made: (1) mols. contg. two α-Me groups, two NH_2 groups, or one Me and one NH_2 group, are more difficultly reducible than 4-amino-



(I)

azobenzene; (2) compds. contg. sulfo, carboxy, and phenylamino groups are more easily reducible than 4-aminoazobenzene.