months *cis.trans*-II had darkened somewhat and had rearranged to a form which had m.p. −4°. Redistillation gave the pure *trans,trans*-II, b.p. 80° (2 mm.), $n^{20}D$ 1.555, m.p. −3 to −1°.

Anal. Calcd. for $C_8H_{16}N_2$: N, 19.97. Found: N, 19.91, 19.95.

This rearrangement could be carried out much more rapidly by adding traces of acids or water. In 24 hr. at room temperature or 3 hr. at 65–70° in the presence of 1 drop of water or acetic acid, the melting point of II (10 g.) rose from < −70° to −4°. Prolonged room temperature storage of *trans,trans*-II led to resinification.

2,2,4,11,13,13-Hexamethyl-6,9-bis-(dimethylamino)-6,8-tetradecadiene. Method G.—Hexane (50 g.) and 50% sodium dispersion[3] in xylene (4 g.) were heated to reflux, the source of heat was removed and compound I (14 g., 0.10 mole) was added dropwise. Thereafter, 2,2,4,11,13,13-hexamethyl-6,9-bis-(dimethylamino)-7-tetradecyne (136 g., 0.37 mole) was added during 39 minutes. The reaction mixture was stirred and heated for an additional 2.5 hr. Distillation under reduced pressure gave (a), 10 g., b.p. 68–187° (4 mm.), $n^{20}D$ 1.5420; and (b), 131 g., b.p. 187–192° (4 mm.), $n^{20}D$ 1.4986. Cut a was chiefly II while cut b represented a 94.5% yield of the desired product in high purity as judged by its ultraviolet spectrum (ϵ_{max} 21,900 at 295 mμ).

Dimerization of 1,4-Bis-(dimethylamino)-1,3-butadiene. —A mixture at I (150 g., 1.07 mole), xylene (150 ml.) and potassium metal (0.75 g., 0.02 mole) dissolved in 1-octanol (4.25 g.) was stirred and heated under reflux for 5 hr. Dis-

tillation under reduced pressure gave the product (126 g., 84%), b.p. 72–132° (0.2 mm.). Redistillation (powdered potassium hydroxide in the pot) of a combination of products from several such runs gave a series of fractions at 1.0 mm. whose physical properties indicated that a mixture of dimeric materials was present.

Hydrogenation of 1,4-Bis-(dimethylamino)-2-butyne Dimer.—The once-distilled dimer, b.p. 115–118° (0.15 mm.), $n^{19}D$ 1.5220–1.5250, prepared as above (133 g., 0.475 mole), ethanol (30 ml.) and Raney nickel (10 g. of catalyst rinsed with ethanol) were hydrogenated at 170 atm. and 110–116° during 8.5 hr. Dimethylamine (0.227 mole) was recovered in the processing. Distillation and redistillation of selected cuts gave 8.5 g. of liquid, b.p. 81–90° at 0.20 mm., $n^{20}D$ 1.4693. (*Anal.* Calcd. for $C_{14}H_{31}N_3$: N, 17.41; mol. wt., 241. Found: N, 17.46; mol. wt., 253) along with some solid material m.p. after recrystallization from heptane 104–105.5°.

Anal. Calcd. for $C_{16}H_{36}N_4$: C, 67.60; H, 12.68; N, 19.72; mol. wt., 284. Found: C, 67.76; H, 12.57; N, 19.04; mol. wt., 277.[12]

The same solid was obtained in low yields by hydrogenation in ethanol solution at 3 atmospheres in the presence of platinum oxide catalyst.

(12) By a modified Menzies–Wright ebulliometric procedure; W. E. Barr and V. J. Anhorn, "Scientific and Industrial Glass Blowing and Laboratory Techniques," Instrument Publishing Co., Pittsburgh, Pa., 1949, p. 284.

Philadelphia, Penna.

Chemistry of 1,4-Diamino-1,3-butadienes. II. A New Synthesis of N-Substituted Pyrroles[1]

By Marian F. Fegley, Newman M. Bortnick and Charles H. McKeever

N-Substituted pyrroles have been prepared by interaction of 1,4-bis-(dimethylamino)-1,3-butadiene and primary amines in the presence of an acidic catalyst.
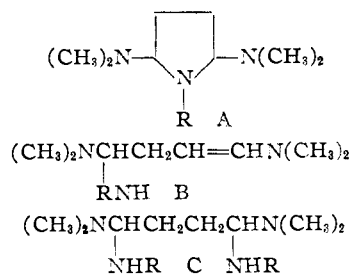
Primary amines have been found to react with 1,4-bis-(dimethylamino)-1,3-butadiene (I)[2] in the presence of catalytic amounts of acids. The unstable cyclic addition product II was formed with evolution of heat when I and aniline were mixed in the presence of a trace of acetic acid.

$C_6H_5NH_2$ + $(CH_3)_2NCH=CHCH=CHN(CH_3)_2$ ⟶
I
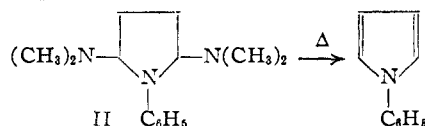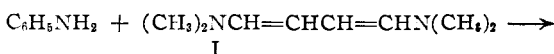
When II was distilled at atmospheric pressure, a low yield of N-phenylpyrrole was isolated together with dimethylamine, aniline, I and polymeric products.

The reaction of benzylamine with I required the addition of more acetic acid for its initiation than was the case with aniline and I. Ultraviolet spectroscopic assay[2] of an equimolar mixture showed that 85% of I had disappeared. Thus, a 1:1 addition product must have constituted a major portion of the mixture. It seems likely that products hav-

(1) Given in part at the 124th Meeting of the American Chemical Society, Chicago, Ill., September 9, 1953.

(2) M. F. Fegley, N. M. Bortnick and C. H. McKeever, This Journal, in press.

ing the structures A–C were all in equilibrium with the starting materials.

Distillation of the reaction mixture gave a 40% yield of N-benzylpyrrole.

n-Butylamine failed to react with I in the presence of acetic acid. Addition of a few drops of concentrated hydrochloric acid led to evolution of dimethylamine and formation of N-*n*-butylpyrrole. This observation has formed the basis for a general procedure for the preparation of N-substituted pyrroles (Table I).

The mixtures of primary amine and I were treated with acid while a stream of inert gas was used to sweep out the dimethylamine as it was liberated. The reaction mixtures were treated with solid potassium carbonate and then distilled to isolate the pyrroles. In some experiments, removal

TABLE I

PYRROLES PREPARED BY TRANSAMINATION

N-Substituted pyrrole	Boiling point °C.	Mm.	$n^{20}D$	Reactants, moles I	Amine	Reaction conditions Time, hours	Temp., °C.	$(CH_3)_2$-NH liberated, moles	Yield, %	Nitrogen, % Found	Calcd.
CH_3-[a]	114		1.4855[k]	0.57	3.2	5.5	27-44	..	46	16.7	17.3
n-C_4H_9-[b]	170-171		1.4730	.33	1.04	4	47-90	0.70	64	11.2	11.4
$(CH_3)_3C$-	74-79	42	1.4722	.5	1.0	9.5	30-45	1.1	16	10.9	11.4
$(CH_3)_3CCH_2C(CH_3)_2$-	58-59	1.5	1.4790	.1	.23	{2 / 0.5}	{50-70 / 90}[j]	.20	66	8.0	7.8
$(CH_3)_3CCH_2CH(CH_3)CH_2CH_2$-	93-94	4.3	1.4686	.1	.22	{3 / 1}	{50-70 / 80-90}[j]	.17	67	7.4	7.2
n-$C_{18}H_{37}$-	172-174	1	Solid	.11	.20	3	55-80	.21	47	4.5	4.4
CH_2=CH—CH_2-[c]	63	36	1.4933[l]	.25	.53	5	27-60	.5	67	12.9	13.1
$(CH_2)_5CH$-[d]	62-63	1	1.5111	.53	.76	4.75	30-75	.73	70.5	9.4	9.4
-CH_2-CH_2-[i]	M.p. 107.5-108[i]		....	.5	.5	5.5	60	.97	{24 }54 / 30}	{17.4 / 24.8}	{17.5 / 25.4}
NH_2-CH_2-CH_2-[e,i]	50	1[i]	1.5188								
NH_2-$(CH_2)_6$-	91-120		1.4920	.35	.40	{2 / 1.75}	{30 / 80}[j]	.6	17	16.8	16.9
HO-CH_2-CH_2-	210-215		1.5162	.3	.51	6.5	30-65	.3+	38	12.7	12.6
CH_2=CH-O-CH_2-CH_2-	100	20.5	1.5000	.25	.57	4.5	55-65	.46	57	10.4	10.2
HO-CH_2-CH_2-NH-CH_2-CH_2-	109-113	65	1.5218	.60	.88	14	50	.94	48	18.4	18.2
$O(CH_2CH_2)_2N$-$CH_2CH_2CH_2$-	162.5-163	19.5	1.5092	.25	.46	7	53	.47	75	14.4	14.4
CH₂—CH₂ / HN\C/N—CH₂CH₂- (C=O)	198	4	Solid	.14	.23	0.5	68	.28	50	23.5	23.5
	M.p. 114-115.5										
C_6H_5-[g]	220-225		Solid	.21	.51	9	30-55	.2	5	..	..
C_6H_5-CH_2-[h]	67-68	0.35	1.5655[m]	.6[n]	1.0	6+	70	1.1	42.5	..	..

[a] N. D. Zelinsky and J. K. Jurjew, Ber., 62, 2589 (1929), gave $n^{21}D$ 1.4858; G. Ciamician and M. Dennstedt, Ber., 17, 2951 (1884), gave b.p. 114-115° (747.5 mm). [b] T. Reichstein, Helv. Chim. Acta, 10, 389 (1927), gave b.p. 53-54 (11 mm.); L. C. Craig and R. M. Hixon, THIS JOURNAL, 53, 187 (1931), gave b.p. 165-180° (atm.); N. Elming and N. Clauson-Kaas, Acta Chem. Scand., 6, 867 (1952), gave $n^{25}D$ 1.4700, b.p. 52-53° (9 mm.). [c] G. Ciamician and M. Dennstedt, Ber., 15, 2581 (1882), gave b.p. 105° (48 mm.). [d] H. Adkins and L. G. Lundsted, THIS JOURNAL, 71, 2964 (1949), reported b.p. 114° (19 mm.), $n^{25}D$ 1.5140. [e] O. Klamerth and W. Kutscher, Chem. Ber., 85, 444 (1952), gave b.p. 75-78° (12 mm.). [f] Recryst. from petroleum ether (30-60°). [g] N. Elming and N. Clauson-Kaas, Acta Chem. Scand., 6, 867 (1952), gave b.p. 131-133° (30 mm.) and m.p. 57-59°; A. Pictet and P. Crepieux, Ber., 28, 1905 (1895), gave b.p. 234°; M. Kottnitz, J. prakt. Chem., [2] 6, 148 (1872), gave m.p. 62°. [h] Yu. K. Yur'ev, V. A. Tronova, N. A. L'vova and Z. Ya. Bukshpan, J. Gen. Chem. (U.S.S.R.), 11, 1128 (1941), C. A., 37, 4071 (1943), gave $n^{20}D$ 1.5839, b.p. 132-133° (13 mm.). [i] Both products were isolated from a single run. [j] The reaction was started at the lower temperature and completed at the higher temperature. [k] At 23.5°. [l] At 23°. [m] At 24°. [n] $[O(CH_2CH_2)_2NCH=CH]_2$.

of excesses of the amine reactant was accomplished by washing an ether solution of the reaction mixture with cold dilute hydrochloric acid solution, with water and then with dilute sodium hydroxide solution. Drying and distillation gave pure samples.

The method worked well for primary amines of proper basicity ($K_b \geq 10^{-7}$). Neither the presence of -OH, -NH₂, CH₂=CHCH₂-, CH₂=CHO-, cyclic urea groups nor branching at the carbon atom bearing the amino group interfered with pyrrole formation.

The reaction failed when aminoacetonitrile, α-aminoisobutyronitrile or 2-aminopyridine was employed. The low yield obtained when aniline was employed was not improved with subsequent study. Only polymeric material resulted when the reaction of ammonia with I was investigated.

Experimental[3]

Reaction of Aniline with 1,4-Bis-(dimethylamino)-1,3-butadiene (I).—A mixture of aniline (9.3 g., 0.10 mole) and I (14.0 g., 0.10 mole) was treated with glacial acetic acid (6 drops) whereupon an exothermic reaction ensued. The tem-

(3) All temperatures are uncorrected. Elemental analyses were carried out by the analytical laboratories of the Rohm & Haas Co.

perature was kept below 60° with cooling until the entire reaction mixture solidified. The temperature rose to 65-70°. The crude addition product was crystallized from diethyl ether or petroleum ether (30-60°) by cooling to −70°, m.p. 71-73°. The infrared absorption spectrum showed no absorption bands corresponding to the stretching of C=C, C≡N or N-H bonds. The normal monosubstituted aromatic bands at 3100, 3060, 3030, 1603 and 1508 cm.⁻¹ were in evidence. The product decomposed on standing at room temperature; this fact accounts for the poor analysis shown below.

Anal. Calcd. for $C_{14}H_{22}N_2$: N, 18.0. Found: N, 16.8.

A batch of material prepared as above and then treated with potassium carbonate (1 g.) was distilled at atmospheric pressure. Dimethylamine was evolved, considerable tar remained in the pot and from the distillate was obtained aniline (5 g.) and a fraction, b.p. 225-250° (1 + g.). Redistillation of the latter gave 0.5 g., b.p. 80-90° (1 mm.), which froze in the receiver. Two recrystallizations from 30-60° petroleum ether gave N-phenylpyrrole, m.p. 60-61°.

Reaction of Benzylamine with I.—Benzylamine (5.35 g., 0.05 mole) and I (7.00 g., 0.05 mole) were treated with glacial acetic acid (3 drops). A mildly exothermic reaction ensued; the temperature rose to 53° before falling slowly to room temperature. From the ultraviolet absorption spectrum of the mixture, 85% of I had disappeared. All efforts to isolate a pure sample of the addition product failed. The reaction mixture was distilled at atmospheric pressure. The cut (3 g., 40% yield), b.p. 225-260°, m.p. 13°, was redistilled to give the analytical sample, 1.5 g.,

b.p. 80-100° (1 mm.), 246° (760 mm.), m.p. 15°, n^{20}D 1.569.

Anal. Calcd. for $C_{11}H_{11}N$: N, 8.9. Found: N, 8.9.

N-Methylpyrrole.—A mixture of 40% aqueous methylamine (219 g., 3.2 moles). 1 (80 g., 0.57 mole), glacial acetic acid (15 drops) and concentrated hydrochloric acid (9 drops) was heated slowly with stirring to 44°, then the heat source was removed. After 30 minutes at that temperature, the mixture became homogeneous. The mixture was maintained at 44° for another hour then allowed to stand at room temperature overnight. The reaction mixture was cooled in an ice-bath and acidified by the careful addition of 18% hydrochloric acid. The mixture was thrice extracted with ether and the combined organic layers were dried over anhydrous potassium carbonate, filtered and distilled to give the product, 21 g. (46% yield), b.p. 114°, $n^{23.5}$D 1.4855.

N-Cyclohexylpyrrole.—Cyclohexylamine (75 g., 0.75

mole) and I (75 g., 0.53 mole) were treated with acetic acid (9 drops) and concentrated hydrochloric acid (5 drops) while nitrogen was swept slowly through the stirred mixture. The vent gas from the condenser was passed through a scrubber which contained 350 ml. of 2.8 N hydrochloric acid solution. After the mixture was heated at 70 ± 5° for 4 hr., 1.0 mole of dimethylamine had been liberated. Potassium carbonate (1 g.) was added and distillation of the reaction mixture gave (a) b.p. 53-60° (17 mm.), 17 g., n^{20}D 1.4589 (recovered amine); (b) b.p. 60° (17 mm.) to 62° (1 mm.), 8.5 g., n^{20}D 1.5060 (intermediate cut, contained product contaminated with 10% recovered amine); (c) b.p. 62-63° (1 mm.), 48 g., n^{20}D 1.5111; (d) residue, 18 g., polymeric.

Anal. (Cut c) Calcd. for $C_{10}H_{15}N$: N, 9.4. Found: N, 9.4.

PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES, AND FLORIDA STATE UNIVERSITY]

Correlation of Solvolysis Rates. VIII. Benzhydryl Chloride and Bromide. Comparison of mY and Swain's Correlations[1]

BY S. WINSTEIN, ARNOLD H. FAINBERG AND E. GRUNWALD

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In this paper are reported rates of solvolysis of benzhydryl chloride and bromide and the correlation of these and other data in the literature by means of the mY relation. The dispersion of log k vs. Y plots into separate lines for each solvent pair, observed previously with t-butyl, α-phenylethyl and neophyl halides, is even more marked with the benzhydryl halides. The contributing causes of such dispersion include structural limitations of the mY relation with respect to variation of both the R and X parts of RX. The leaving group specificity is especially marked with F, fluorides tending to be very fast in carboxylic acid solvents. Ion pair return, which depresses the observed solvolysis rate below the ionization rate by variable amounts depending on the nature of the solvent, contributes to the observed dispersion in some cases. Swain and Mosely's conclusion that the solvolysis of t-butyl chloride is not limiting and that gradation of mechanism continues far past t-butyl as structure is varied so as to make solvolysis more nearly limiting is based to a large extent on the solvolytic behavior in the series n-BuBr, t-BuCl, $(C_6H_5)_3CF$. In the view of Swain and Mosely, the unusually high rate of solvolysis of trityl fluoride in acetic acid is caused by the change in structure of the R part of RX from t-Bu to $(C_6H_5)_3C$. In our view, it is caused instead by the change of X in RX from Cl to F. Examination of $(k_{ROH}/k_{AcOH})Y$ values for a whole group of substances supports the designation of t-butyl chloride solvolysis in the common solvents as limiting. The relations between Grunwald and Winstein's two-parameter, Swain, Dittmer and Kaiser's three-parameter and Swain, Mosely and Bown's four-parameter correlations of solvolysis rates are discussed and the numerical fits obtained are compared.

The three preceding papers of this series[2-4] were concerned with the correlation of the rates of solvolysis of t-butyl, α-phenylethyl and neophyl halides by the linear free energy relationship[5] 1.

$$\log k = \log k_0 + mY \qquad (1)$$

A marked dispersion of the data into separate lines, one for each solvent pair, was noted. In this paper we examine new data for benzhydryl chloride and bromide and related data from the literature which show this dispersion to an even greater degree.

The point of view adopted in this paper is somewhat different from that of 1948.[5a] In the original mY treatment,[5a] the intent was to separate the total effect of solvent change into a variable Y, characteristic of the solvent, and a variable m, characteristic solely of RX. With the limited data then available, this approach succeeded for

aliphatic compounds. However, the data for α-phenylethyl and benzhydryl chloride could not be fitted to the Y values for the aliphatic compounds in all of the solvent pairs with a single value of m. This was, of course, a manifestation of dispersion[2-4,5d] of lines and was recognized as a limitation of the mY relationship. It was handled by introducing a second set of Y values with which it was possible to correlate the data for both compounds and which was recommended for general use with α-aryl derivatives. The parameter m was still considered constant for any one RX.

As more data became available,[2-4,5d,6] the limitations of the original mY treatment became more and more apparent, and the pattern of dispersed lines evolved. To fit the data in the next higher approximation, m is a function of both RX *and* of the solvent pair.[2-4,5d] Since the burden of accounting for the structural limitations of the original mY treatment[5a] has thus been shifted on to m, there is no advantage in retaining more than one set of Y values. The set based on t-butyl chloride[5c] has therefore been used in this paper.

On the basis of the new findings, the use of sol-

(1) Research sponsored by the Office of Ordnance Research, U. S. Army.

(2) A. H. Fainberg and S. Winstein, THIS JOURNAL, 79, 1597 (1957).

(3) A. H. Fainberg and S. Winstein, *ibid.*, 79, 1602 (1957).

(4) A. H. Fainberg and S. Winstein, *ibid.*, 79, 1608 (1957).

(5) (a) E. Grunwald and S. Winstein, *ibid.*, 70, 846 (1948); (b) S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, 73, 2700 (1951); (c) A. H. Fainberg and S. Winstein, *ibid.*, 78, 2770 (1956); (d) S. Winstein, Discussion at 13th National Organic Chemistry Symposium of the American Chemical Society, Ann Arbor, Mich., June 17, 1953.

(6) L. Wilputte-Steinert and P. J. C. Fierens, *Bull. soc. chim. Belges*, 64, 277, 287, 299, 308 (1955).