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Chemistry of 1,4-Diamino-1,3-butadienes. III. Transamination with Secondary Amines[1]

BY MARIAN F. FEGLEY, NEWMAN M. BORTNICK, CHARLES H. MCKEEVER AND FLORENCE B. FARNUM

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Transamination occurred when 1,4-bis-(dimethylamino)-1,3-butadiene was treated with secondary amines in the presence of acidic catalysts. The reaction products have the *trans,trans*-structure. The physical and spectral properties of five isomeric pairs of 1,4-diamino-1,3-butadienes are described and discussed.

We have examined the reaction of secondary amines with 1,4-bis-(dimethylamino)-1,3-butadiene (I)[2] in the presence of acidic catalysts. As was the case in the corresponding reaction of I with primary amines,[3] the basicity of the secondary amines governed the nature of the products which could be isolated.

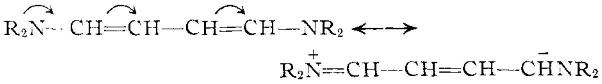
An exothermic reaction occurred when N-methylaniline was mixed with I in the presence of acetic acid. Distillation of the reaction mixture in an attempt to effect elimination of dimethylamine led to recovery of most of the N-methylaniline and formation of a polymeric residue.

Stronger acids were required to initiate a reaction between stronger bases, such as pyrrolidine, and I. Transamination[4] was achieved by simply heating the mixture under reduced pressure or passing a stream of nitrogen through the reaction mixture. The 1,4-bis-(disubstituted-amino)-1,3-butadienes shown in Table I were obtained in this manner. The product from di-(2-ethylhexyl)-amine was not obtained analytically pure. In that instance an intermediate cut was obtained which analyzed well for 1-dimethylamino-4-di-(2-ethylhexyl)-amino-1,3-butadiene.[5]

When morpholine was a reactant, transamination proceeded especially easily because the product crystallized as it formed. Both weak acids (formic acid, phenol) and strong acids (sulfuric acid, aluminum chloride) served as catalysts. A transamination occurred on standing for several days even in the absence of added catalyst. However, the product was 1,4,4,-trimorpholino-*x*-butene. This compound lost morpholine on heating above its melting point (78–83°) and gave 1,4-dimorpholino-1,3-butadiene. Attempts to prepare 1,1,4,4-tetramorpholinobutane failed.

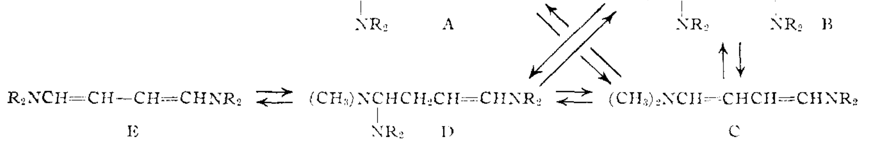
These transamination products are geometrical isomers of the 1,4-diamino-1,3-butadienes prepared previously by means of sodium-catalyzed rearrangement of the corresponding 2-butynes.[2] Table II shows a comparison of the properties of pairs I-V. The isomers obtained in the presence of acid catalysts uniformly have (1) higher boiling points, (2) higher melting points, (3) higher indices of refraction and (4) higher molar extinction coefficients at (5) lower maxima in the ultraviolet range. The infrared spectra of I isomers have been interpreted[2] to indicate *cis,trans* geometry for the sodium-catalyzed rearrangement product and *trans,trans* geometry for the product obtained from it by acid-catalyzed isomerization. By analogy, the transamination products II-V have *trans,trans* geometry.[6]

Replacement of a hydrogen atom by a dialkylamino group at C_1 in butadiene has been shown[7] to produce a large bathochromic shift and an observable hyperchromic displacement owing to π-p conjugation. Replacement of an additional hydrogen atom at C_4 by another dialkylamino group produces little additional change in either position of maximum absorption or molar extinction coefficient. Thus, only one of the two dialkylamino groups takes part in the spectral conjugation, and the second amino group must not exert an important damping effect.



$$R_2\ddot{N}\cdots CH{=}CH{-}CH{=}CH{-}NR_2 \longleftrightarrow R_2\overset{+}{N}{=}CH{-}CH{=}CH{-}\overset{-}{C}HNR_2$$

Our observation that the *cis,trans* isomers of



$$\begin{tikzcd}
I \arrow[r, shift left] & (CH_3)_2N\underset{\substack{| \\ NR_2}}{C}HCH_2CH{=}CHN(CH_3)_2 \ \text{A} \arrow[l, shift left] \arrow[r, shift left] \arrow[dr, shift left] & (CH_3)_2N\underset{\substack{| \\ NR_2}}{C}HCH_2CH_2\underset{\substack{| \\ NR_2}}{C}HN(CH_3)_2 \ \text{B} \arrow[l, shift left] \arrow[dl, shift left] \arrow[d, shift left] \\
R_2NCH{=}CH{-}CH{=}CHNR_2 \ \text{E} \arrow[r, shift left] & (CH_3)N\underset{\substack{| \\ NR_2}}{C}HCH_2CH{=}CHNR_2 \ \text{D} \arrow[l, shift left] \arrow[r, shift left] \arrow[ur, shift left] & (CH_3)_2NCH{=}CHCH{=}CHNR_2 \ \text{C} \arrow[l, shift left] \arrow[u, shift left] \arrow[ul, shift left]
\end{tikzcd}$$

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[1] Presented in part at the 124th Meeting of the American Chemical Society, Chicago, Ill., September 9, 1953, and in part at the 128th Meeting of the American Chemical Society, Minneapolis, Minn., September 16, 1955.

[2] M. F. Fegley, N. M. Bortnick and C. H. McKeever, THIS JOURNAL, **79**, 4140 (1957).

[3] M. F. Fegley, N. M. Bortnick and C. H. McKeever, *ibid.*, **79**, 4144 (1957).

[4] We believe that a complex equilibrium was established involving I and species of the types A-E. Removing dimethylamine from the reaction mixture shifted this equilibrium toward E.

[5] Footnote 4, compound C.

[6] N. J. Leonard and R. R. Sauers, *J. Org. Chem.*, **21**, 1187 (1957), have recently reported the preparation of 1,4-di-(1-pyrrolidino)-1,3-cyclohexadiene and the corresponding 1,4-di-(1-piperidino) analog. These compounds must have *trans,trans* geometry and are constrained to the "cisoid" conformation by inclusion in a ring. The presence of bands at 1633 cm.$^{-1}$ and two near 800 cm.$^{-1}$ is in accord with absorption bands present in the spectrum of *t-t*-I at 1623(s), at 790(m) and at 854(m) cm.$^{-1}$. Data in the ultraviolet range show no parallelism, perhaps because the "aminobutadiene" absorption bands are masked by the intense bands characteristic of the corresponding *p*-phenylenediamines which easily form on exposure of the 1,3-cyclohexadiene derivatives to air.

[7] (a) K. Bowden, E. A. Braude, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 45 (1946). (b) K. Bowden, E. A. Braude and E. R. H. Jones, *ibid.*, 948 (1946). (c) E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, Chapter 4.

TABLE I

trans,trans-1,4-BIS-(DIALKYLAMINO)-1,3-BUTADIENES PREPARED BY TRANSAMINATION

	$(R_2N—CH=CH—)_2$ R_2N-	M.p. or b.p. (mm.), °C.	n^{t}D	*t*, °C.	Reactants I, mole	Reactants Amine, moles	Reaction conditions Time., hr.	Reaction conditions Temp., °C.	Amine liberated moles	Yield, %	Nitrogen, % Found	Nitrogen, % Calcd
II	$(C_2H_5)_2N$-	77 (0.15)	1.5403	25	0.75	2.2	40	27–41	1.4	10	14.5	14.3
III	*n*-$(C_4H_9)_2N$-	148–157 (0.03)	1.5089	24	.25	0.58	7.5	60	..	49	9.2	9.1
IV	C_4H_8N-[a]	94–97	....	..	.37	1.0	18	30–50	0.84	72	14.4	14.6
V	C_4H_8ON-[b]	139–141	....	..	.25	0.69	4	30–65	.50	89	12.5	12.5
VI	$CH_2=CHOCH_2CH_2N(CH_3)$-	150–157 (0.1)	1.5400	20	.4	1.01	8	46	.76	32	11.1	11.1
VII	$(C_6H_5CH_2)N$-	136–137.5	....	..	.164	0.33	3	50	.26	6	6.4	6.3

[a] N-Pyrrolidyl. [b] N-Morpholyl.

TABLE II

COMPARISON OF 1,4-DIAMINO-1,3-BUTADIENES (*cis,trans* AND *trans,trans* FORMS)

	$(R_2NCH=CH—)_2$, R_2N-	Catalyst	B.p., °C.	(mm.)	M.p., °C.	n^{20}D	U.v. absorption spectrum (in 2,2,4-trimethylpentane) Max., mμ	ϵ_{max}	Assignment
I	$(CH_3)_2N$-	Na	205	760	<−100	1.5500	294	19,300	*c,t*
	$(CH_3)_2N$-	H^+	215	760	−4	1.5569	287.5	23,200	*t,t*
II	$(C_2H_5)_2N$-	Na	77	1.0	.....	1.5221[d]	292.5	19,400	*c,t*
	$(C_2H_5)_2N$-	H^+	77	0.15	.....	1.5403[d]	287.5	23,350	*t,t*
III	$(C_4H_9)_2N$-	Na	142–146	0.35	.....	1.5020	300	20,400	*c,t*
	$(C_4H_9)_2N$-	H^+	148–157	0.03	.....	1.5089[e]	292.5	23,900	*t,t*
IV	C_4H_8N-[a]	Na[b]	125–132	0.3		1.5988	306	19,320	*c,t*
					91–98		300	22,600	*t,t*
	C_4H_8N-[a]	H^+	.....	....	94–97		300	22,555	*t,t*
V	C_4H_8ON-[c]	Na	160–163	3.0	70–74	1.5555[d]	289	(14,620)[f]	*c,t*
	C_4H_8ON-[c]	H^+			140	.....	284	28,000	*t,t*
	$CH_2=CHCH=CH_2$						217	21,000[g]	
	$(C_2H_5)NCH=CHCH=CH_2$						281	24,000[g]	
							277.5	27,000[h]	

[a] N-Pyrrolidyl. [b] Both isomers were isolated from the sodium-catalyzed rearrangement mixture owing to the great ease of isomerization of the *cis,trans* to the *trans,trans* form. The latter crystallized and was removed by filtration. [c] N-Morpholyl. [d] At 25°. [e] At 24°. [f] As normally carried out, the *trans,trans* isomer usually was obtained. In the course of recrystallization, exposure to the atmosphere permitted the facile isomerization of the initially formed *cis,trans* isomer to occur. In one experiment, the reaction mixture was distilled and the distillate was examined without further purification to give the result shown here. The index of refraction shown was for the super-cooled liquid. [g] Reference 7a. [h] This work.

this series show absorption in the ultraviolet range at longer wave lengths and with lower intensities than the corresponding *trans, trans* isomers, agrees with a similar observation of Nichols, Herb and Riemenschneider[8] for the spectral properties of the corresponding $\Delta^{9,11}$- and $\Delta^{10,12}$-octadecadienoic acid isomers.

Although it is usual for *trans* isomers to show absorption in the ultraviolet range at longer wave lengths than the corresponding *cis* isomers,[7c] this relationship has been found to be reversed in the case of the piperylenes[8] and of the azo-benzenes.[9] It may be that the usual observed relationship is a consequence of steric hindrance in most of the examples cited[7c] and that the normal spectral relationships between *cis* and *trans* isomers are those observed in this work.[10]

In this connection we tried to ascertain whether the 1-diethylamino-1,3-butadiene examined by Bowden, Braude, Jones and Weedon[7a] had the *cis* or *trans* structure by study of the infrared absorption spectrum. Our repetition of their work led to a product which had the spectral properties[11] in the ultraviolet range shown in Table II. The infrared absorption spectrum of our product was consistent with its 1-amino-1,3-butadiene structure. Extension of the *cis,trans* correlations obtained for the 1,4-bis-(dimethylamino)-1,3-butadiene isomers[2] could not be made because a terminal methylene group is present in this case. Bonds at 923 and 993 cm.$^{-1}$, arising from the wagging out of plane of the vinyl hydrogen atoms, complicated the region of the spectrum in which the *trans*-hydrogen band usually falls. Since it is well known that *cis* hydrogen bands are extremely variable and unpredictable,[12] the determination of geometric structure cannot be made from the infrared data.

Experimental[13]

***trans,trans*-1,4-Bis-(dibutylamino)-1,3-butadiene.**—A mixture of I (35 g., 0.25 mole), dibutylamine (75 g., 0.58

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(8) P. L. Nichols, S. F. Herb and R. W. Riemenschneider, THIS JOURNAL, **73**, 247 (1951); *cf.* R. R. Allen, *J. Org. Chem.*, **21**, 143 (1956); D. Holme, E. R. H. Jones and M. C. Whiting, *Chem. & Ind.*, 928 (1956).

(9) A. Burawoy, *J. Chem. Soc.*, 1865 (1937); A. H. Cook, D. G. Jones and J. B. Polya, *ibid.*, 1315 (1939).

(10) G. N. Lewis, T. T. Magel and D. Lipkin, THIS JOURNAL, **62**, 2973 (1940).

(11) It is interesting that the spectral relationships between our sample of 1-diethylamino-1,3-butadiene and that of Bowden, *et al.*,[7a] parallel those for the *cis,trans* and *trans,trans* 1,4-diamino-1,3-butadienes. However, in the absence of a direct comparison, no conclusion should be drawn in this regard.

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 42.

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

mole), acetic acid (10 drops) and concentrated hydrochloric acid (5 drops) was stirred at 54 ± 4° at 65 ± 5 mm. pressure for 7.5 hr. Treatment with potassium carbonate (1 g.) and distillation under reduced pressure gave: cut (a) b.p. 123–145° (0.04 mm.), 11 g., $n^{20}\mathrm{D}$ 1.5180, N, 11.3; cut (b) b.p. 145–148° (0.04 mm.), 32 g., $n^{24}\mathrm{D}$ 1.5082, N, 9.3; cut (c) b.p. 148–157° (0.03 mm.), 5.5 g., $n^{24}\mathrm{D}$ 1.5089, N, 9.1; residue, 7.7 g. Cuts b and c were the desired product (49% yield). Cut a is chiefly the desired product probably contaminated with 1-dibutylamino-4-dimethylamino-1,3-butadiene.

***trans,trans*-1,4-Dimorpholino-1,3-butadiene**—A mixture of I (35 g., 0.25 mole), morpholine (60 g., 0.69 mole), acetic acid (10 drops) and concentrated hydrochloric acid (5 drops) was heated to 60° during 3 hr. and maintained one hour at that temperature, by which time 0.39 mole of dimethylamine was evolved (flushed with nitrogen into a scrubber containing standard acid solution). To facilitate stirring, pentane (50 ml.) was added. The mixture was refluxed for an additional hour at which point 0.50 mole of dimethylamine had been evolved. The product was separated by filtration. The filtrate was evaporated to dryness, washed twice with pentane and dried. The combined crops weighed 50 g. (89% yield), m.p. 117–121°. One recrystallization from diethyl ether raised the melting point to 138–139.5° (75% recovery in first crop) and a second recrystallization gave the analytical sample (see Table I for data).

1,1,4-Trimorpholino-*x*-butene.—Nitrogen was bubbled through a mixture of I (21 g., 0.15 mole) and morpholine (30 g., 0.34 mole) for 4 days. The solid (19.5 g., m.p. 62–72°) which formed was separated by filtration and recrystallized from ether to give the product, m.p. 78–83°, resolidified at 90° and melted again over a wide range beginning at 115°.

Anal. Calcd. for $C_{16}H_{29}O_3N_3$: N, 13.5. Found: N, 13.5.

The ultraviolet absorption spectrum showed a maximum at 284 mμ with an intensity which increased as the test solution was allowed to stand and was initially about 10% that of *trans,trans*-1,4-dimorpholino-1,3-butadiene. On heating at 50–60° for two days the product decomposed to a mixture of a solid and a liquid. The solid was recrystallized from diethyl ether, m.p. 136–139°. Melting and mixed melting point determinations showed it to be *trans,trans*-1,4-dimorpholino-1,3-butadiene. The filtrate was treated with phenyl isothiocyanate to give the morpholinophenylthiourea, m.p. and mixed m.p. 131–132°.

PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE ROHM & HAAS CO.]

Chemistry of the 1,4-Diamino-1,3-butadines. IV. The Diels–Alder Reaction[1]

BY MARIAN F. FEGLEY, NEWMAN M. BORTNICK AND CHARLES H. MCKEEVER

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1,4-Bis-(disubstituted-amino)-1,3-butadienes gave the Diels–Alder reaction with dienophiles bearing electron-withdrawing groups attached to the double bond. *cis,trans* and *trans,trans* forms gave isomeric adducts. The adducts lost secondary amine on heating to give the corresponding aromatic derivatives.

cis,trans-1,4-Bis-(dimethylamino) -1,3- butadiene (Ia)[2] has been found to undergo the Diels–Alder reaction with dienophiles bearing electron-withdrawing groups attached to the double bond. Thus, fumaronitrile, acrylonitrile and ethyl acrylate each gave adducts. A reaction occurred but no pure product was isolated when diethyl fumarate was heated with Ia. Maleic anhydride and butyl vinyl ether gave polymeric products. Methacrylonitrile, styrene and vinyl acetate failed to react with Ia.

trans,trans-1,4-Bis-(dimethylamino)-1,3-butadiene (Ib)[2] gave an adduct (IIb) with fumaronitrile which was not identical with that (IIa) obtained from Ia and fumaronitrile. Similarly, the corresponding two forms of 1,4-dipyrrolidino-1,3-butadiene[3] gave different adducts. Their ultraviolet and infrared spectra were consistent with their formulation as isomeric 3,6-bis-(dimethylamino)-4-cyclohexene-1,2-dicarbonitriles.

Examination of molecular models of Ia and Ib showed that both can assume the "cisoid" conformation required for participation in the Diels–Alder reaction.[4] The cyclohexene derivatives obtainable from each of these are IIa and IIb, respectively (Fig. 1, R— = CH_3—). We cannot say whether compound IIa has the structure A_1 or A_2.[5]

All of the adducts prepared from fumaronitrile were found to be unstable; phthalonitrile was isolated when the adducts were heated. This ease of aromatization finds a parallel in the observations of Langenbeck, Godde, Weschky and Schaller[6] that interaction of 1-piperidino-1,3-butadiene and *p*-benzoquinone gave traces of 1,4-naphthoquinone. Similarly, interaction of 1,4-naphthoquinone and 1-diethylamino-1,3-butadiene gave anthraquinone.

When ethyl 2,5-bis-(dimethylamino)-3-cyclohexenecarboxylate was heated with a trace of sulfuric acid at 160–195°, ethyl benzoate was obtained in 20% yield. Similarly, benzonitrile was obtained in low yield when the corresponding 2,5-bis-(dimethylamino)-3-cyclohexenecarbonitrile was heated with sulfuric acid.

Experimental[7]

***cis,trans* (or *trans,cis*)-3,6-Bis-(dimethylamino)-4-cyclohexene-*cis,trans*-1,2-dicarbonitrile.**—A mixture of *cis,trans*-1,4-bis-(dimethylamino)-1,3-butadiene (14 g., 0.10 mole), fumaronitrile (7.8 g., 0.10 mole) and benzene (30 g.) was warmed to 50° and stirred for 30 minutes. Within 5 minutes an exothermic reaction ensued. The temperature rose to 76° in 17 minutes. After standing overnight at room temperature, the benzene was evaporated under reduced

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(1) Given in part at the 128th Meeting of the American Chemical Society, Minneapolis, Minn., September 16, 1955.

(2) M. F. Fegley, N. M. Bortnick and C. H. McKeever, THIS JOURNAL, **79**, 4140 (1957).

(3) M. F. Fegley, N. M. Bortnick, C. H. McKeever and F. Farnum, *ibid.*, **79**, 4734 (1957).

(4) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

(5) Both isomers were isolated by K. Alder and W. Vogt, *Ann.*, **571**, 137 (1951), in their study of the products from the reaction of fumaryl chloride with *cis,trans*-1,4-dimethyl-1,3-butadiene. Compare also K. Alder, *et al.*, **571**, 87, 108, 153, 157 (1951).

(6) W. Langenbeck, O. Godde, L. Weschky and R. Schaller, *Ber.*, **75**, 232 (1942).

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