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., $n^{20}\text{D}$ 1.5180, N, 11.3; cut (b) b.p. 145–148° (0.04 mm.), 32 g., $n^{24}\text{D}$ 1.5082, N, 9.3; cut (c) b.p. 148–157° (0.03 mm.), 5.5 g., $n^{24}\text{D}$ 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

RECEIVED APRIL 6, 1957

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).

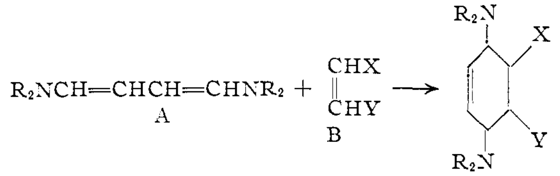
[4] K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

[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 fumaroyl 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.

DIELS–ALDER ADDUCTS DERIVED FROM 1,4-BIS-(DIALKYLAMINO)-1,3-BUTADIENES



A		B		M.p. or b.p. (mm.), °C.	Nitrogen, %		Yield of adduct, %
R_2N–	Structure[a]	X	Y		Theory	Found	
$(CH_3)_2N$–	*t–t*	CN	CN[b]	136–137.5	25.7	25.5	46
	c–t			145.5–147.5	25.7	25.4	55
C_4H_8N–[f]	*t–t*	CN	CN[b]	157.5–159	20.7	20.6	. .
	c–t			195–196.5	20.7	20.5	. .
C_4H_8ON–[g]	*t–t*	CN	CN[b]	197–197.5	18.5	18.4	50
$(CH_3)_2N$–	*c–t*	H	CN	110–112 (0.5)[c]	21.7	21.2	30[d]
$(CH_3)_2N$–	*c–t*	H	$COOC_2H_5$	103–107 (1.0)[e]	11.7	11.8	21

[a] *c–t* = *cis,trans*; *t–t* = *trans,trans*. [b] Fumaronitrile. [c] $n^{20}D$ 1.4986. [d] Foreruns contained $(CH_3)_2NCH_2CH_2CN$ (picrate m.p. 154–155°; mixed m.p. with authentic sample which had m.p. 156.5–157.5°, 155–156.5°). [e] $n^{20}D$ 1.4848. [f] N-Pyrrolidyl. [g] N-Morpholyl.

pressure and the solid residue was washed twice with ethanol and pressed dry on porous plate (12 g., m.p. 139–142°). Recrystallization from ethanol gave the pure product, m.p. 145.5–147.5°, neut. equiv. 110 (calcd. for $C_{12}H_{18}N_4$, 109).

cis,cis-**3,6-Bis-(dimethylamino)-4-cyclohexene**-*cis,trans*-**1,2-dicarbonitrile**.—A mixture of *trans,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. A mildly exothermic reaction which ensued within 5 minutes maintained the temperature at 51–52° during the next 15 minutes. The mixture was allowed to stand overnight at room temperature. Benzene was evaporated under reduced pressure, the solid was filtered, washed twice with ethanol and pressed dry on porous plate (10.2 g., m.p. 135–137°). Two recrystallizations from ethanol gave the pure product, m.p. 136–137.5°, neut. equiv. 110 (calcd. for $C_{12}H_{18}N_4$, 109).

The fumaronitrile adducts were less stable when dissolved in ethanol than when dissolved in benzene. Recrystallizations were carried out quickly to avoid large losses.

cis,trans- (or *trans,cis*)-**3,6-Di-(1-pyrrolidino)-4-cyclohexene**-*cis,trans*-**1,2-dicarbonitrile**.—A mixture of *cis,trans*-1,4-dipyrrolidino-1,3-butadiene[2] (3.3 g., 0.0172 mole), fumaronitrile (1.4 g., 0.018 mole) and benzene (15 ml.) was heated to boiling, then allowed to cool. The precipitate was recrystallized from ethanol, m.p. 195–196.5°, neut. equiv. 134 (calcd. for $C_{16}H_{22}N_4$, 135). Phthalonitrile (m.p. and mixed m.p. 139–141°) was isolated upon distillation of a reaction mixture prepared as above.

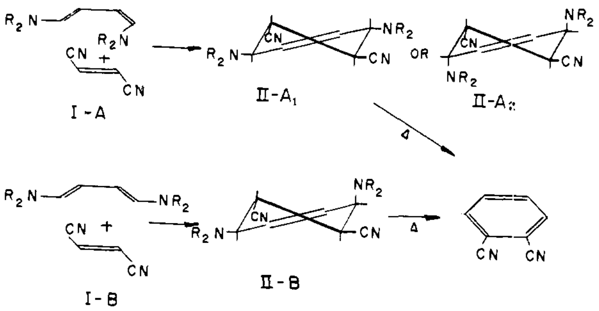


Fig. 1.

cis,cis-**3,6-Di-(1-pyrrolidino)-4-cyclohexene**-*cis,trans*-**1,2-dicarbonitrile**.—A mixture of *trans,trans*-1,4-dipyrrolidino-1,3-butadiene[4] (4.0 g., 0.0208 ml.), fumaronitrile (1.6 g., 0.205 mole) and benzene (20 ml.) was warmed to 80° then allowed to cool. The mixture was reheated to 80° and again allowed to cool. The mixture was allowed to stand at room temperature for 1 week. The solid which separated was recrystallized from ethanol, m.p. 157.5–159°, neut. equiv., 133 (calcd. for $C_{16}H_{22}N_4$, 135).

Phthalonitrile (m.p. and mixed m.p. 139–141°) was isolated upon distillation of a reaction mixture prepared as above.

PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Dithioacetals of D-Glucuronic Acid and 2-Amino-2-deoxy-D-galactose

BY M. L. WOLFROM AND K. ONODERA[1]

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Thioacetals and acetylated thioacetals of D-glucuronic acid and of 2-amino-2-deoxy-D-galactose have been prepared in crystalline form. D-Glucurono-3,6-lactone diethyl dithioacetal reacts with methanolic hydrogen chloride to yield a crystalline dehydration product.

Dithioacetals of reducing sugars have been utilized for sugar identification since their discovery by Fischer.[2] Aldoses may be identified conveniently as their acetylated dithioacetals.[3] Simultaneous hydrolysis and thioacetal formation ("mercaptolysis") has been useful in the elucidation of oligosaccharide and polysaccharide structures[4–6] especially when followed by reductive desulfurization.[7,8] Thioacetals of D-galacturonic acid have

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[1] National Science Foundation Research Associate under Grant NSF-G584 to The Ohio State University; recipient of a travel grant from The Rockefeller Foundation.

[2] E. Fischer, *Ber.*, **27**, 673 (1894).

[3] M. L. Wolfrom and J. V. Karabinos, THIS JOURNAL, **67**, 500 (1945).

[4] M. L. Wolfrom, J. C. Sowden and E. N. Lassettre, *ibid.*, **61**, 1072 (1939).

[5] C. Araki and S. Hirase, *Bull. Chem. Soc. Japan*, **26**, 463 (1953).

[6] A. N. O'Neill, THIS JOURNAL, **77**, 6324 (1955).

[7] M. L. Wolfrom and J. V. Karabinos, *ibid.*, **66**, 909 (1944).

[8] R. U. Lemieux and M. L. Wolfrom, *Advances in Carbohydrate Chem.*, **3**, 355 (1948).