

bath at 145° for 1 hr. longer than necessary for the complete dissolution of paraformaldehyde. A portion of the resulting cooled oil could then be transferred to the n.m.r. tube.

Materials 4 and 8.—Equimolar amounts of the amide and paraformaldehyde were treated at 100° for 1 hr. longer than necessary for complete dissolution of the paraformaldehyde. The resulting products were colorless and yellow oils.

Material 6.—Equimolar amounts of *N*-methylbenzamide and paraformaldehyde containing 0.05% by weight of dry potassium carbonate were heated at 140–160° for 1 hr. longer than necessary for complete dissolution of the paraformaldehyde. On cooling, a salve-like material was obtained, which necessitated measuring its n.m.r. spectra at ca. 55° in order to obtain satisfactory resolution.

B. Aqueous Conditions. Materials 10, 11, 13 and 14.—The method of Vail⁸ was followed, wherein a fresh 20% solution of formaldehyde was prepared by dissolving the appropriate amount of paraformaldehyde in water in a pressure flask at 60–70° (pH 8–9 maintained by a trace of sodium bicarbonate). To this solution was added the appropriate amount of amide, and the mixture was heated in a closed glass vessel with an oil bath for 2 hr. at 60°. The n.m.r. spectra of the cooled clear solution was then obtained.

Vapor Phase Chromatography of Mixtures 2, 4, and 7.—A known amount of material 2 (20 μ l.) was passed through a chro-

matography column at 200° (15% butenediol succinate on Chromosorb P-2). The amount of *N*-methylacetamide recovered in this mixture as determined by the area of the amide peak was 70.5% by weight of the injected mixture. The calculated amount of changed and unchanged *N*-methylacetamide in material 2 was 71%.

In similar fashion, 75% of *N*-methyl α -chloroacetamide was recovered from material 7 *vs.* the calculated amount of 78%, while 70% of *N*-methylformamide was recovered from 4 *vs.* the calculated 66%.

Preparation of IV.—The procedure was based upon the method given by Walter,⁶ wherein an excess of acetic anhydride was added to material 2 and stirred at 20–25° for 3 days, then heated to 40° for 6 hr. The excess acetic anhydride and acetic acid were then removed under vacuum and the resulting mixture was distilled to give product at 45° (0.05 mm.); n_D^{25} 1.4470. This material was further purified by passing a portion of it through a v.p.c. column at 200° (previously described) and recovering, at the appropriate retention time, the purified product, n_D^{25} 1.4445, with infrared and n.m.r. spectra identical to that given by Walter.

Acknowledgment.—The authors wish to express their appreciation to Dr. C. C. Tung for stimulating discussions during the course of this work.

A Novel Elimination Reaction of *o*-Acylaminobenzenesulfonamides

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Received March 27, 1963

The action of heat on some *o*-acylaminobenzenesulfonamides has been shown to give the corresponding acylaminobenzenes in addition to the expected benzothiadiazines. The dependence of the reaction on various structural factors was investigated. A mechanism for the reaction is proposed.

In connection with another program¹ we have been engaged in the synthesis of various 3-substituted 2*H*-1,2,4-benzothiadiazine 1,1-dioxides utilizing the known method² of fusing the appropriately substituted *o*-acylaminobenzenesulfonamides. During the course of the preparation of 3-(α -cyclohexyl)benzyl-6,7-dichloro-2*H*-1,2,4-benzothiadiazine 1,1-dioxide [II, R

= CH(C₆H₁₁)C₆H₅], another product was isolated in approximately the same yield as the benzothiadiazine (35–37%). This additional compound did not contain sulfur and was shown to be α -cyclohexyl-3,4-dichloro- α -phenylacetanilide [III, R = CH(C₆H₁₁)C₆H₅] by comparison with an authentic sample. Careful examination of the fusion products of other substituted *o*-acylaminobenzenesulfonamides showed that the reaction is a general one and that the yield of the acylaminobenzene varies markedly with the structure of the acyl group. The yields of benzothiadiazine and acylaminobenzene obtained from the fusion of a number of substituted *o*-acylaminobenzenesulfonamides are given in Table I. It is apparent from these results that the yield of the acylaminobenzene (III) is greatest in those

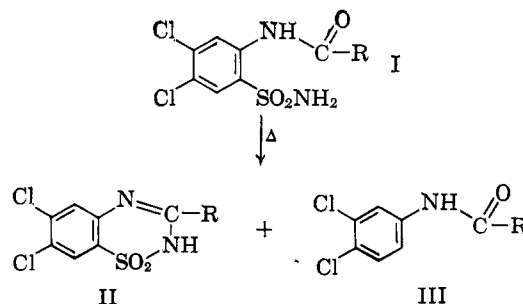
TABLE I
YIELDS OF BENZOTHIADIAZINES (II) AND ACYLAMINO BENZENES (III) OBTAINED FROM VARIOUS *o*-ACYLAMINO BENZENESULFONAMIDES (I)

R	% Yield of		Total
	II	III	
<i>n</i> -C ₃ H ₇	87	0.9	88
<i>i</i> -C ₃ H ₇	89	3.0	92
<i>sec</i> -C ₄ H ₉	79	0.6	80
CH(C ₂ H ₅) ₂	65	24	89
C ₆ H ₅	87	5.4	92
CH(<i>n</i> -C ₃ H ₇)C ₆ H ₅	47	26	73
C(CH ₃) ₃	80	13	93
CH(C ₆ H ₅) ₂	73	17	90
CH(C ₆ H ₁₁)C ₆ H ₅ ^a	35	37	72
CH(C ₆ H ₁₁) ₂	54	38	92

^a In the corresponding example where the chlorine atoms on the phenyl nucleus of I are replaced by hydrogen (*i.e.*, compound V) the yields of benzothiadiazine and acylaminobenzene were 38% and 14%, respectively.

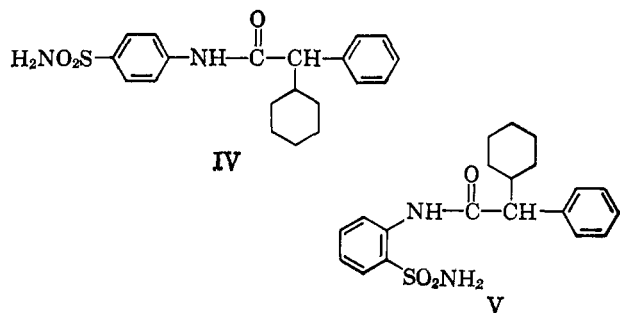
(1) J. G. Topliss, M. H. Sherlock, H. Reimann, L. M. Konzelman, E. P. Shapiro, B. W. Petterson, H. Schneider, and N. Sperber, *J. Med. Chem.*, **6**, 122 (1963); J. G. Topliss, L. M. Konzelman, E. P. Shapiro, and N. Sperber, paper in preparation.

(2) A. Ekblom, *Bihang, K. Svenska Vet. Akad. Handl.*, **27** (II), 3 (1902); *Beilstein*, **27**, 571; J. H. Freeman and E. C. Wagner, *J. Org. Chem.*, **16**, 815 (1951); F. C. Novello, S. C. Bell, E. L. A. Abrams, C. Ziegler, and J. M. Sprague, *ibid.*, **25**, 970 (1960).



cases where the group R has a high steric requirement.

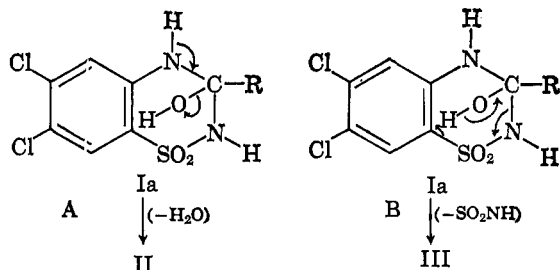
Evidence that the *ortho* relationship of the acylamino and the sulfamoyl groups is necessary for the elimination to take place was obtained by subjecting IV to



the standard reaction conditions; no product could be found corresponding to loss of the sulfamoyl group from this compound.

That the chlorine atoms do not play a decisive role in the reaction was demonstrated by fusion of V which gave results qualitatively similar to those for I [$R = \text{CH}(\text{C}_6\text{H}_{11})\text{C}_6\text{H}_5$].

The substantial yields of III in the fusion reaction, and the high over-all conversion of I to II and III, together with the evidence of the importance of the *ortho* relationship of the acylamino and sulfamoyl groups for loss of the sulfamoyl group, provide a good indication that III is formed by a concerted mechanism. We view the reaction as first proceeding to a cyclic intermediate Ia from which either water or sulfimide is eliminated according to one of two pathways, A³ and B. With bulkier R groups steric effects apparently



render pathway B more competitive with the normally favored pathway A.

It is interesting to note that treatment of I [$R = \text{CH}(\text{C}_6\text{H}_{11})\text{C}_6\text{H}_5$] with dilute sodium hydroxide at 100° furnished II [$R = \text{CH}(\text{C}_6\text{H}_{11})\text{C}_6\text{H}_5$] in 88% yield with no detectable quantity of III [$R = \text{CH}(\text{C}_6\text{H}_{11})\text{C}_6\text{H}_5$]. For the same R group a 37% yield of III and a 35% yield of II was obtained by heating I at 250°.

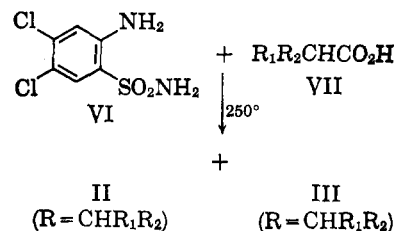
Loss of the sulfamoyl group was also observed in the three examples investigated when 2-amino-4,5-dichlorobenzenesulfonamide (VI) was heated with a carboxylic acid VII at 250° to give the amide III ($R = \text{CHR}_1\text{R}_2$) and the benzothiadiazine II ($R = \text{CHR}_1\text{R}_2$). Yields of the amide III ($R = \text{CHR}_1\text{R}_2$) were somewhat higher (Table II) both in absolute terms and in proportion

Table II
YIELDS OF BENTHODIAZINE (II) AND ACYLAMINO BENZENE (III)
FROM THE REACTION OF VI WITH VII

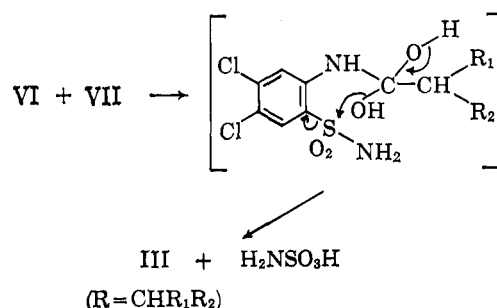
R	% Yield of		
	II	III	Total
$\text{CH}(\text{C}_6\text{H}_5)_2$	46	30	76
$\text{CH}(\text{C}_6\text{H}_{11})\text{C}_6\text{H}_5$	39	54	93
$\text{CH}(\text{C}_6\text{H}_{11})_2$	45	54	99

(3) The elimination may be equally well considered to involve the hydrogen atom at position 2 to give the tautomeric form of II.

to the benzothiadiazine II ($R = \text{CHR}_1\text{R}_2$) obtained, than for the corresponding cases proceeding from the intermediate I. These results indicate that the reac-



tion between VI and VII does not proceed entirely through an amide I (reaction intermediate Ia), but that the reaction probably proceeds, in part, through an alternate mechanism such as the one shown.



The various acylaminobenzenesulfonamides used in this investigation were prepared by reaction of the appropriate acid chloride with the aminobenzenesulfonamide in refluxing benzene or toluene. The constants for these intermediates are listed in Table III. The position of the acyl group was established from infrared data. The compounds exhibited amide carbonyl absorption bands in the range $5.96 \pm 0.02 \mu$ comparable with the amide carbonyl absorption bands, $6.00 \pm 0.03 \mu$ shown by the corresponding acylaminobenzenes (III) and clearly distinguishable from the carbonyl absorptions of acylsulfonamides which appear at lower wave lengths.⁴ Authentic samples of the acylaminobenzenes were prepared from the aniline and the appropriate acid chloride in refluxing benzene (or toluene) as solvent or in pyridine solution at steam bath temperature (Table IV). Constants for the benzothiadiazines synthesized appear in Table V.

Experimental⁵

Acylaminobenzenesulfonamides (I).—A solution of the acid chloride⁶ (1.1 mole ratio) was added to a stirred, refluxing suspension of the benzenesulfonamide in benzene⁷ (ca. 20 ml. of benzene per gram of sulfonamide). The reaction mixture was refluxed for 4 hr.⁸ and then concentrated by distillation whereupon hexane was added (20 ml. per gram of sulfonamide) and the solu-

(4) J. G. Topliss, *J. Org. Chem.*, **27**, 654 (1962).

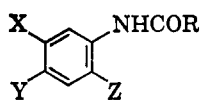
(5) Melting points were determined on a Thomas Hoover capillary melting point apparatus and infrared spectra from Nujol mulls.

(6) Prepared by refluxing the acid with a slight excess of thionyl chloride in benzene (ca. 5 ml. of benzene per gram of thionyl chloride).

(7) In the case of $R = \text{CH}(\text{C}_6\text{H}_{11})_2$, the acid chloride was prepared in the usual manner from dicyclohexylacetic acid and thionyl chloride in benzene. Excess thionyl chloride and benzene were then distilled, toluene (15 ml. per gram of acid) added and nitrogen passed through the solution for 1 hr. to remove dissolved gases. This solution of the acid chloride was added to a suspension of the sulfonamide in toluene and treated as in the general method.

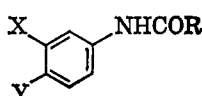
(8) In a few instances the hot benzene solution was filtered at this point to remove a small amount of insoluble material.

TABLE III



R	X	Y	Z	M.p., °C.	Recrystn. solvent	Molecular formula	—% Chlorine—		—% Nitrogen—		—% Sulfur—	
							Calcd.	Found	Calcd.	Found	Calcd.	Found
<i>n</i> -C ₃ H ₇	Cl	Cl	SO ₂ NH ₂	154–156	MeOH–H ₂ O	C ₁₀ H ₁₂ Cl ₂ N ₂ SO ₂	22.78	23.00	9.00	9.28		
<i>i</i> -C ₃ H ₇	Cl	Cl	SO ₂ NH ₂	159–160	MeOH–H ₂ O	C ₁₀ H ₁₂ Cl ₂ N ₂ SO ₂	22.78	23.00	9.00	8.95		
<i>sec</i> -C ₄ H ₉	Cl	Cl	SO ₂ NH ₂	157–159	MeOH–H ₂ O	C ₁₁ H ₁₄ Cl ₂ N ₂ SO ₂	21.80	21.94	8.62	8.66		
CH(C ₂ H ₅) ₂	Cl	Cl	SO ₂ NH ₂	151–152	MeOH–H ₂ O	C ₁₂ H ₁₆ Cl ₂ N ₂ SO ₂	20.90	20.92	8.26	8.27		
C ₅ H ₉	Cl	Cl	SO ₂ NH ₂	165–167	MeOH–H ₂ O	C ₁₂ H ₁₄ Cl ₂ N ₂ SO ₂	21.03	20.81	8.31	8.16		
CH(<i>n</i> -C ₃ H ₇)C ₅ H ₉	Cl	Cl	SO ₂ NH ₂	166–168	MeOH–H ₂ O	C ₁₆ H ₂₂ Cl ₂ N ₂ O ₃ S	18.03	17.82	7.12	7.06	8.15	8.22
C(CH ₃) ₃	Cl	Cl	SO ₂ NH ₂	132–133	MeOH–H ₂ O	C ₁₁ H ₁₄ Cl ₂ N ₂ O ₃ S	21.74	21.75	8.59	8.80	9.83	9.77
CH(C ₆ H ₅) ₂	Cl	Cl	SO ₂ NH ₂	200–202	MeOH	C ₂₀ H ₁₆ Cl ₂ N ₂ O ₃ S	16.29	16.50			7.36	7.27
CH(C ₆ H ₁₁)C ₆ H ₅	Cl	Cl	SO ₂ NH ₂	171–172	MeOH–H ₂ O	C ₂₀ H ₂₂ Cl ₂ N ₂ O ₃ S	16.07	16.00	6.35	6.00	7.26	7.48
CH(C ₆ H ₁₁) ₂	Cl	Cl	SO ₂ NH ₂	170–172	MeOH–H ₂ O	C ₂₀ H ₂₈ Cl ₂ N ₂ O ₃ S	15.85	15.80	6.26	5.96	7.17	7.15
CH(C ₆ H ₁₁)C ₆ H ₅	H	H	SO ₂ NH ₂	154–156	MeOH–H ₂ O	C ₂₀ H ₂₄ N ₂ O ₃ S			7.52	7.07	8.61	8.28
CH(C ₆ H ₁₁)C ₆ H ₅	H	SO ₂ NH ₂	H	246–247	Acetone– C ₆ H ₆ –Et ₂ O	C ₂₀ H ₂₄ N ₂ O ₃ S			7.52	7.35	8.61	8.77

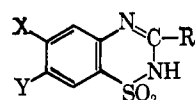
TABLE IV



R	X	Y	M.p., °C.	Recrystn. solvent	Molecular formula	—% Carbon—		—% Hydrogen—		—% Chlorine—		—% Nitrogen—	
						Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
<i>n</i> -C ₃ H ₇ ^a	Cl	Cl	79–81 ^c	C ₆ H ₁₄ –C ₆ H ₆	C ₁₀ H ₁₁ Cl ₂ NO					30.55	30.43	6.04	5.96
<i>i</i> -C ₃ H ₇ ^a	Cl	Cl	135–136 ^d	C ₆ H ₆	C ₁₀ H ₁₁ Cl ₂ NO					30.55	30.28	6.04	5.89
<i>sec</i> -C ₄ H ₉ ^a	Cl	Cl	112–114 ^e	C ₆ H ₆	C ₁₁ H ₁₃ Cl ₂ NO					28.81	28.65	5.79	5.82
CH(C ₂ H ₅) ₂ ^a	Cl	Cl	126–127 ^f	C ₆ H ₆ –Petr. ether	C ₁₂ H ₁₅ Cl ₂ NO					27.26	27.10	5.38	5.20
C ₅ H ₉ ^a	Cl	Cl	134–135	C ₆ H ₆	C ₁₂ H ₁₃ Cl ₂ NO					27.46	27.60	5.43	5.40
CH(<i>n</i> -C ₃ H ₇)C ₅ H ₉ ^b	Cl	Cl	138–139	C ₆ H ₁₄ –C ₆ H ₆	C ₁₆ H ₂₁ Cl ₂ NO	61.15	61.38	6.74	6.89	22.56	22.41		
C(CH ₃) ₃ ^b	Cl	Cl	149–150 ^g	MeOH–H ₂ O	C ₁₁ H ₁₃ Cl ₂ NO	53.68	53.41	5.23	5.31				
CH(C ₆ H ₅) ₂ ^b	Cl	Cl	181–182	MeOH–H ₂ O	C ₂₀ H ₁₅ Cl ₂ NO	67.43	67.63	4.24	4.46	19.91	20.08		
CH(C ₆ H ₁₁)C ₆ H ₅ ^b	Cl	Cl	220–222	MeOH–H ₂ O	C ₂₀ H ₂₁ Cl ₂ NO	66.30	66.34	5.84	6.18	19.57	20.08		
CH(C ₆ H ₁₁) ₂ ^b	Cl	Cl	194–195	CHCl ₃ – C ₆ H ₁₄	C ₂₀ H ₂₇ Cl ₂ NO	65.21	65.50	7.39	7.66	19.25	18.77		
CH(C ₆ H ₁₁)C ₆ H ₅ ^b	H	H	195–196	C ₆ H ₆	C ₂₀ H ₂₃ NO	81.86	82.01	7.90	8.00			4.77	4.57

^a Prepared using pyridine as solvent. ^b Prepared using benzene as solvent. ^c C. W. Huffman and S. E. Allen [*J. Agr. Food Chem.*, **8**, 298 (1960)] report m.p. 76.6–77.9°. ^d Ref. *c* m.p. 134.6–135.2°. ^e N. E. Good [*Plant Physiol.* **36**, 788 (1961)] reports m.p. 112–113°. ^f Ref. *c* m.p. 124.2–125.8°. ^g Ref. *e* m.p. 145–146°.

TABLE V



R	X	Y	M.p., °C.	Recrystn. solvent	Molecular formula	—% Chlorine—		—% Nitrogen—		—% Sulfur—	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
<i>n</i> -C ₃ H ₇	Cl	Cl	306–308	MeOH–H ₂ O	C ₁₀ H ₁₀ Cl ₂ N ₂ SO ₂					10.93	11.12
<i>i</i> -C ₃ H ₇	Cl	Cl	338–339	MeOH–acetone	C ₁₀ H ₁₀ Cl ₂ N ₂ SO ₂					9.56	9.68
<i>sec</i> -C ₄ H ₉	Cl	Cl	285–286	MeOH–acetone	C ₁₁ H ₁₂ Cl ₂ N ₂ SO ₂	23.07	22.80	9.12	9.27		
CH(C ₂ H ₅) ₂	Cl	Cl	237–238	MeOH	C ₁₂ H ₁₄ Cl ₂ N ₂ O ₂ S	22.08	21.92	8.72	9.02		
C ₅ H ₉	Cl	Cl	>360	MeOH–acetone– dimethyl- formamide	C ₁₂ H ₁₂ Cl ₂ N ₂ O ₂ S	22.21	22.42	8.78	8.86		
CH(<i>n</i> -C ₃ H ₇)C ₅ H ₉	Cl	Cl	211–214	Acetone–C ₆ H ₁₄	C ₁₆ H ₂₀ Cl ₂ N ₂ O ₂ S	19.52	19.45	7.71	7.80		
C(CH ₃) ₃	Cl	Cl	359–360	MeOH–acetone	C ₁₁ H ₁₂ Cl ₂ N ₂ O ₂ S	23.08	23.20	9.12	9.14		
CH(C ₆ H ₅) ₂	Cl	Cl	292–294	MeOH–acetone	C ₂₀ H ₁₄ Cl ₂ N ₂ O ₂ S	17.00	16.91			7.68	7.55
CH(C ₆ H ₁₁)C ₆ H ₅	Cl	Cl	272–273	MeOH	C ₂₀ H ₂₀ Cl ₂ N ₂ O ₂ S	16.75	16.72	6.62	6.70	7.57	7.38
CH(C ₆ H ₁₁) ₂	Cl	Cl	273–276	MeOH–acetone	C ₂₀ H ₂₆ Cl ₂ N ₂ O ₂ S	16.51	16.80			7.47	7.44
CH(C ₆ H ₁₁)C ₆ H ₅	H	H	276–278	MeOH	C ₂₀ H ₂₂ N ₂ O ₂ S			7.91	7.97	9.04	9.00

tion was chilled. Filtration gave crude product in yields of 75–95%. One recrystallization usually gave product of high purity in an over-all yield of 60–90%. (Table III).

Acylaminobenzenes (III).—One method used for the preparation of authentic samples of these compounds was essentially equivalent to that described for the preparation of compounds of type I.

In an alternate procedure, the aniline and the acid chloride (1:2 mole ratio) in pyridine (minimum volume about 3 ml. per gram of the aniline) were heated on a steam bath for 1 to 2 hr., and the reaction mixture was chilled and then poured into 10% aqueous hydrochloric acid (*ca.* 30 ml. per gram of starting aniline). If a solid precipitated, it was collected, washed with 10% hydro-

chloric acid and water, and dried. If an oil resulted, it was extracted with ether and the ether solution washed with water and dried (sodium sulfate). Evaporation of the ether gave an oil which could be crystallized from petroleum ether. Crude product was obtained in yields of 40–95%. After recrystallization over-all yields were 35–85% (Table IV).

Conversion of Acylaminobenzenesulfonamides (I) to II and III.—I (10–20 g.) was heated at 240–250° for 1–2 hr. The crude reaction mass was extracted with boiling benzene⁹ and filtered hot giving crude II as the insoluble portion. The benzene solution was concentrated and chromatographed on an alumina column (10 g. of alumina per gram of I). III was eluted with benzene and additional II was obtained by elution with chloroform. The products of the reaction were further purified by recrystallization where necessary (Tables I, IV and V).

Reaction of 2-Amino-4,5-dichlorobenzenesulfonamide (VI) with Substituted Acetic Acids VII.—An equimolar mixture of 2-amino-4,5-dichlorobenzenesulfonamide and the appropriate substituted acetic acid was heated at 240–250° for 1.5 hr. The crude reaction mixture was extracted with hot benzene (100 ml.

(9) With $R = CH(n-C_2H_5)C_6H_5$, complete solution in benzene was effected.

per gram of VI) giving II as the insoluble portion. The benzene solution was concentrated and chromatographed on an alumina column (10 g. of alumina per gram of I). III was eluted with benzene and additional II was obtained by elution with chloroform. The products of the reaction were further purified by recrystallization where necessary (Tables II, IV and V).

3-(α -Cyclohexyl)benzyl-6,7-dichloro-2H-1,2,4-benzothiadiazine 1,1-Dioxide.—A solution of I [$R = CH(C_6H_{11})C_6H_5$] (6.1 g.) and sodium hydroxide (1.1 g.) in water (100 ml.) was refluxed for 16 hr., cooled, and acidified with concentrated hydrochloric acid to give crude product (5.7 g.). This was extracted with boiling benzene (300 ml.) giving II [$R = CH(C_6H_{11})C_6H_5$] (5.1 g., 88%), m.p. 268–270°, as the insoluble portion. The benzene solution was concentrated and chromatographed on an alumina column (60 g. of alumina). No III [$R = CH(C_6H_{11})C_6H_5$] was isolated.

Acknowledgment.—The authors are indebted to Drs. P. J. L. Daniels and C. H. Robinson for helpful discussions and to Mr. E. Conner of the Physical and Analytical Chemical Research Department, Schering Corporation, for the microanalyses.

The Configuration of Paromose¹

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Received April 25, 1963

The diamino-hexose (paromose) in the antibiotic paromomycin is shown to be 2,6-diamino-2,6-dideoxy-L-idose. The alkaline degradation of 1,1-bis(alkylsulfonyl)hexitol derivatives was extended to 2,6-diacetamido-2,6-dideoxyhexitol derivatives and afforded 5-acetamido-5-deoxy-L-xylofuranose and the isomeric 5-acetamido-5-deoxy-L-xylopyranose. Deamination of methyl tetra-O-acetylparomobiosaminide dihydrochloride followed by acid hydrolysis gave L-galactose and D-ribose. The hexose is shown to be derived from the diamino-hexosyl moiety by acetate participation followed by inversion at C-2 and C-3.

Previous communications² from these laboratories have dealt with the structure of the antibiotic paromomycin.³ The configuration at C-2 in the 2,6-diamino-2,6-dideoxyhexose (paromose) in paromomycin was established as being "D-glycero."² The total configuration of paromose has now been established; the sugar is shown to be 2,6-diamino-2,6-dideoxy-L-idose.

The 2,6-diamino-2,6-dideoxyhexose in Neomycin B has been suggested to possess the L-ido stereochemistry^{4,5} on the basis of optical rotation data of periodate oxidation products and biogenetic considerations. The 2,6-diamino-2,6-dideoxy hexose in Neomycin C was assigned the D-gluco stereochemistry⁶ and the assignment was confirmed by the synthesis of 2,6-diamino-2,6-dideoxy-D-glucose.^{7,8}

(1) Preliminary communication; Abstracts of Papers of the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963, p. 19C.

(2) T. H. Haskell, J. C. French, and Q. R. Bartz, *J. Am. Chem. Soc.*, **81**, 3480, 3481, 3482 (1959). The previously reported $[\alpha]_D$ for the *p*-nitrophenylhydrazone of N,N'-diacetylparomose is in error. The corrected value is $[\alpha]_D^{25} + 72.2^\circ$ (c 0.5, in 50% methanol-water).

(3) Parke, Davis & Company, U. S. Patent 2,916,485 (December 8, 1959).

(4) (a) K. L. Rinehart, Jr., and A. D. Argoudelis, Abstracts of the 17th National Organic Symposium, Bloomington, Ind., June 25–29, 1961, p. 96; (b) Abstracts of the 1st Interscience Conference on Antimicrobial Agents and Chemotherapy, New York, N. Y., October 31–November 2, 1961.

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(6) K. L. Rinehart, Jr., P. W. K. Woo, and A. D. Argoudelis, *ibid.*, **80**, 6461 (1958).

(7) H. Weidmann and H. K. Zimmermann, Jr., *Angew. Chem.*, **72**, 750 (1960).

The degradation of the hexoses,⁹ 2-amino-2-deoxyhexoses¹⁰ and 3-amino-3-deoxyhexoses,¹¹ to the lower pentose by reaction of the respective 1,1-bis(alkylsulfonyl) derivatives with aqueous ammonia has been shown. In the case of 2-amino-2-deoxy sugars, the reaction was studied in detail with 2-acetamido-2-deoxy-D-glucose diethyl dithioacetal and a mechanism was proposed for the degradation.¹⁰ Thus, peroxypropionic acid oxidation of the dithioacetal derivative afforded 2-amino-1,1-bis(ethylsulfonyl)-2-deoxy-D-glucitol peroxypropionate which was degraded to D-arabinose in aqueous ammonia. With 3-acetamido-3-deoxy-D-allose¹¹ and 3-acetamido-3-deoxy-D-altrose¹¹ derivatives, degradation to the lower pentose occurred during the oxidation of the respective dithioacetals with peroxypropionic acid under nonalkaline conditions.

Alkaline degradation of N,N'-diacetyl-1,1-bis(alkylsulfonyl)paromitol derivatives afforded 5-acetamido-5-deoxy-L-xylofuranose¹² (I) and 5-acetamido-5-deoxy-L-xylopyranose (II) thus providing the configuration at the remaining asymmetric carbon atoms in paromose. The success of the reaction with 2,6-diamino-2,6-dideoxyhexose derivatives constitutes an important extension of the degradation. Furthermore, the degradation was possible with N-acetylated 1,1-bis-

(8) K. L. Rinehart, Jr., M. Hichens, K. Streigler, K. R. Rover, T. P. Culbertson, S. Tatsuoka, S. Horii, T. Yamaguchi, H. Hitomi, and A. Miyake, *J. Am. Chem. Soc.*, **83**, 2964 (1961).

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