tone as a viscous cloudy liquid, $[\eta]^{25}_{TFE} = 0.50 \pm 0.01$ dl/g. After 2 months at room temperature, the polyester crystallized into a tough white waxy material, mp 29–30°, by the hot-stage polarizing microscope. An X-ray diagram at −14° indicated sharp lines and a high degree of crystallinity (see Table I for *d* spacings); $[\alpha]^{25}_{450}$ +8.78° (*c* 1.068, TFE). The infrared spectrum of this material showed the characteristic absorption of an ester group at 1740 and 1170 cm^{-1}.

Anal. Calcd for $(C_7H_{12}O_2)_n$: C, 65.59; H, 9.44. Found: C, 64.62; H, 9.40; ash, 1.143; after substracting the ash: C, 65.37; H, 9.43.

6. Poly-(±)-γ-methyl-ε-caprolactone. The same general procedure described above was used except that aluminum triisobutyl was added as the pure liquid and the polymerization run in bulk. From 5.2 g (0.041 mole) of (±)-γ-methyl-ε-caprolactone,[9] 0.15 g (7.58×10^{-4} mole) of aluminum triisobutyl, and 9 mg (5×10^{-4} mole) of water was obtained 3.03 g (58.2%) of poly-(±)-γ-methyl-ε-caprolactone as a viscous glassy material, $[\eta]^{25}_{TFE} = 0.76 \pm 0.01$ dl/g. The infrared spectrum of this material was identical with that of poly-(*R*)-(+)-γ-methyl-ε-caprolactone.

Anal. Calcd for $(C_7H_{12}O_2)_n$: C, 65.59; H, 9.44. Found: C, 65.01; H, 9.18; ash, 1.154; after subtracting the ash: C, 65.64; H, 9.39.

7. (*R*)-(+)-Ethyl 6-Acetoxy-5-methylhexanoate (III). (*R*)-(−)-δ-Methyl-ε-caprolactone,[9] $[\alpha]^{25}D$ −36.11° (*c* 0.46, $CHCl_3$), 1.0 g (0.0078 mole), was allowed to stand for 3 days at room temperature in 35 ml of ethanol saturated with hydrogen chloride. The ethanol and hydrogen chloride were then removed under vacuum. To the remaining oil, 10 ml of ether, 5 ml of pyridine, and 3 g of acetyl chloride in 5 ml of ether were added, and the resulting mixture was stirred and refluxed overnight. At the end of this time, 10 ml of water was added, and the ethereal phase was extracted with cold 10% sulfuric acid followed by saturated sodium bicarbonate solution. After drying over molecular sieves for 12 hr, the ether was removed on a rotating evaporator and the remaining oil distilled through a microdistillation apparatus yielding 1.2 g (71.3%) of (*R*)-(+)-ethyl 6-acetoxy-5-methylhexanoate, bp 81° (0.2 mm), $[\alpha]^{25}_{350}$ −15.91° (*c* 0.314, TFE), $n^{25}D$ 1.4283.

Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 61.08; H, 9.32. The infrared spectrum showed the characteristic ester absorptions at 1740 (s) and 1240 cm^{-1} (s).

8. (*R*)-(+)-Ethyl 6-Acetoxy-3-methylhexanoate (IV). The same procedure as for (*R*)-(+)-ethyl 6-acetoxy-5-methylhexanoate was used.

From (*R*)-(−)-β-methyl-ε-caprolactone,[9] $[\alpha]^{25}D$ −32.18° (*c* 1.24, $CHCl_3$), $n^{25}D$ 1.4583, 1 g (0.0078 mole), was obtained 0.6 g (35.5%) of (*R*)-(+)-ethyl 6-acetoxy-3-methylhexanoate, bp 84° (0.2 mm), $[\alpha]^{25}_{350}$ +29.78° (*c* 0.460, TFE), $n^{25}D$ 1.4294.

Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 61.09; H, 9.38.

The infrared spectrum showed the characteristic ester absorptions at 1740 (s) and 1240 cm^{-1} (s).

Acknowledgment. Acknowledgment is given to Professor Murray Goodman of this department for the use of the Bendix-Ericcson ultraviolet spectropolarimeter.

The Solvolysis of Alkyl Diazotates. II. Stereochemistry and Internal Return in the 2-Octyl System[1]

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Abstract: The deamination of optically active 2-octylamine in aqueous nitrous acid affords racemic 2-octanol. Active 2-octylamine was converted to octane-2-diazotate by a series of reactions believed to preserve optical purity. Decomposition of the active diazotate in aqueous base afforded 2-octanol with 16% net inversion. Hydrolysis in the presence of ether (or pentane) afforded 2-octanol with 46% (38%) net inversion. Under either purely aqueous or ether–water conditions, acidic hydrolysis of the diazotate afforded more completely racemized alcohol. Hydrolysis of the diazotate in H_2O^{18} showed that *ca.* 40% of the derived 2-octanol had retained the original diazotate oxygen; for hydrolysis under ether–water conditions, the corresponding datum was *ca.* 38%. The extent of hydride-shifted (3- and 4-) octanols was determined for the various deaminations, and was largest for nitrous acid deamination of the amine. Hydrolysis of the active diazotate under ether–water conditions showed little stereochemical response to increasing hydroxide ion concentration. The results are discussed in terms of octane-2-diazotic acid as an important intermediate in the diazotate hydrolysis. In such reactions, it is suggested that a free 2-octyl cation is largely bypassed. In the presence of acid, it is suggested that much diazotic acid escapes to free diazonium and/or carbonium ions. The deamination (aqueous nitrous acid, pH 4) of active 2-butyl- and α-phenylethylamines was reinvestigated during the course of this work. The principal product was, in each case, the corresponding alcohol, formed with 22 and 14% net inversion, respectively.

We have recently shown that N-alkyl-N-nitrosourethans are cleaved to alkyl diazotates (I) by the action of ethereal potassium *t*-butoxide (eq 1).[1]

$$\mathrm{RN(NO)COC_2H_5} + t\text{-}\mathrm{C_4H_9O^-K^+} \longrightarrow t\text{-}\mathrm{C_4H_9OCOC_2H_5} + \underset{\mathrm{I}}{\mathrm{RN{=}NO^-K^+}}\downarrow \quad (1)$$

Hydrolysis of the diazotates occurs almost instantaneously in aqueous base, affording diazoalkanes and/or nitrogen and products commonly associated with carbonium ions (eq 2 and 3). Partition of the diazotic acid

$$\mathrm{RN{=}NO^-K^+ + H_2O} \rightleftharpoons \underset{\mathrm{II}}{\mathrm{RN{=}NOH}} + \mathrm{K^+OH^-} \quad (2)$$

$$\mathrm{II} \xrightarrow{-N_2,\,-OH^-} \text{products of } R^+ \qquad \mathrm{II} \xrightarrow{-H^+,\,-OH^-} R{=}N_2 \quad (3)$$

(1) Part I: R. A. Moss, *J. Org. Chem.*, **31**, 1082 (1966).

(II) was found to be dependent on the structure of R. In particular, if R was secondary, less than 3% of diazoalkane was formed. The entire sequence was formally equivalent to nitrous acid deamination of RNH_2 (since II is generally considered to be an intermediate in that process[2]) but was unique in proceeding rapidly in *strong aqueous base.*

We have now studied the stereochemistry of hydrolysis of an optically active diazotate under various conditions of basicity and solvent, and in H_2O^{18}. We believe that the results, which follow, make an interesting contribution to our knowledge of the transient intermediates which intervene in these mechanistically complex reactions.

Results

The 2-Octyl System. 2-Octylamine was converted to N-2-octylurethan.[3] The urethan was nitrosated with ethereal nitrogen tetroxide.[4] The resulting N-nitroso-N-2-octylurethan was characterized by relation of its nmr spectrum to that of N-2-octylurethan.[5]

Treatment of ethereal N-nitroso-N-2-octylurethan with 2 equiv of potassium *t*-butoxide at −30 to −15° for 25 min led to the formation of a thick yellow slurry. No gas evolution was observed. The rapid addition of water triggered immediate evolution of 90–95% of the theoretical gas content (N_2) within 5 sec. From the product mixture, there could be isolated by vpc 33% of a mixture of 1- and 2-octene, 25% 2-octanol, 3% 2-octanone, and 75% of a carbonate mixture consisting mainly of di-*t*-butyl carbonate and ethyl *t*-butyl carbonate. *Trace* amounts of 3- and 4-octanol (see below) were also present. The observation that no gas (nitrogen) evolution occurred during the basic cleavage of the nitrosourethan, coupled with the observation of quantitative and immediate gas evolution upon hydrolysis, shows that no octanol or octyl carbonate could have been formed during the cleavage step. Therefore, all octanol products must have arisen during the hydrolysis step. The intermediacy of octane-2-diazotate in the above sequence is supported by the high yield of carbonates (product of alkoxide attack at the nitrosourethan acyl carbon), by vacuum distillation isolation of carbonates from the nitrosourethan–butoxide slurries *prior* to the addition of water (in which case quantitative gas evolution is still observed, and the final product mixture contains all of the usual products *except* carbonates), by analogy to our previous results,[1,6] and by analogy to earlier studies.[7]

Substitution of deuterium oxide in the hydrolysis of octane-2-diazotate led to 2-octanol which contained less than 3% carbinyldeuterium (nmr, mass spectral analysis). This excludes 2-diazooctane as a significant precursor of the 2-octanol. The diazo compound was similarly *excluded as an octanol precursor* under the even more alkaline hydrolysis conditions described below. In these latter cases, however, some 2-diazooctane may have formed (15%), as indicated by less than quantitative gas evolution and a light orange coloration of the ethereal product mixtures.[8]

Stereochemical and Related Studies. 2-Octylamine was resolved by the method of Mann and Porter,[9] affording *l*-2-octylamine of greater than 97% optical purity.[10] Conversion to the urethan and nitrosation were readily accomplished. Since none of the reactions used to convert 2-octylamine to N-nitroso-N-2-octylurethan involved making or breaking bonds at the asymmetric carbon, and since cleavage of the nitrosourethan involved a very high degree of butoxide attack at acyl carbon, it was reasonable to believe that octane-2-diazotate was produced with essentially complete optical integrity.

Decompositions of the active diazotate were effected under several conditions. The active 2-octanol product (shown by control experiments to be optically stable under *all* conditions employed) was isolated by vpc. Product purity was established by rechromatography (capillary and packed column) and infrared spectroscopy. Optical purity was established by standard polarimetric techniques. The results appear in Table I; further details appear in the Experimental Section.

The stereochemical results may be summarized as follows. (a) Hydrolysis of octane-2-diazotate in water leads to about 16% inverted 2-octanol (runs 18, 21). (b) Hydrolysis in the two-phase system, water–ether, leads to about 46% inverted 2-octanol (runs 1, 2). Similar results, 38% inversion, are observed in the two-phase system, water–pentane (runs 14, 15). (c) Increasing the hydroxide ion concentration in the water quench leads to little stereochemical change in the water–ether system (runs 5, 6) and to some enhancement of inversion in the water–pentane system (runs 16, 17). (d) Acidic aqueous quenches lead to significantly more racemized 2-octanol, both in ether–water and pure water systems (runs 8–12, and 22, 23). (e) Temperature effects are small (runs 3, 4, 20). (f) The ether distillation and solvent replacement procedures do not significantly affect the results in and of themselves (run 13).

(2) Recent discussions of amine–nitrous acid deamination appear in: (a) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. I, W. A. Benjamin, Inc., New York, N. Y., 1965; (b) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961; (c) J. H. Ridd, *Quart. Rev.* (London), **15**, 418 (1961).

(3) N. Bortnick, L. S. Luskin, M. D. Hurwitz, and A. W. Rytina, *J. Am. Chem. Soc.*, **78**, 4358 (1956).

(4) E. H. White, *ibid.*, 77, 6008 (1955).

(5) R. A. Moss, *Tetrahedron Letters*, 711 (1966).

(6) These results are complementary to those of Jones' group: W. M. Jones, D. L. Muck, and T. K. Tandy, Jr., *J. Am. Chem. Soc.*, **88**, 68 (1966); W. M. Jones and D. L. Muck, *ibid.*, **88**, 3798 (1966). Whether the base attacks at nitroso N or acyl C depends on the type of substrate (urea or urethan), type of alkoxide (especially the cation), and solvent. Our system appears optimal in all factors which favor acyl attack. (See the data and discussion in Jones and Muck, cited immediately above.) We have found it necessary, however, to use 2 equiv of butoxide/equiv of the nitrosourethan. Use of less than 2 equiv leads to less than 100% gas evolution upon hydrolysis, and the formation of traces of N-2-octylurethan. We presently have no explanation for this phenomenon. In order to ensure the completeness of reaction 1, all our studies have been carried out with the requisite excess of butoxide. There was thus 1 equiv of alkoxide present at hydrolysis.

(7) A. Hantzsch and M. Lehmann, *Ber.*, **35**, 897 (1902); F. W. Bollinger, F. N. Hayes, and S. Siegel, *J. Am. Chem. Soc.*, **72**, 5592 (1950); M. S. Newman and A. Kutner, *ibid.*, **73**, 4199 (1951); R. Huisgen and J. Reinertshofer, *Ann.*, **575**, 174 (1952); G. Nischk and E. Müller, *ibid.*, **576**, 232 (1952); C. D. Gutsche and H. E. Johnson, *J. Am. Chem. Soc.*, 77, 109 (1955); D. E. Applequist and D. E. McGreer, *ibid.*, **82**, 1965 (1960); E. Müller, H. Haiss, and W. Rundel, *Ber.*, **93**, 1541 (1960); T. K. Tandy, Jr., and W. M. Jones, *J. Org. Chem.*, **30**, 4257 (1965).

(8) Experiments in the neopentyl diazotate system provide evidence that the partition described in ref 3 is dependent on $[OH^-]$: R. A. Moss, unpublished results.

(9) F. G. Mann and J. W. G. Porter, *J. Chem. Soc.*, 456 (1944).

(10) $\alpha^{24}D$ −2.58° (*l* 0.5 dm, neat). F. G. Mann and J. Reid, *ibid.*, 3384 (1950) report $\alpha^{19}D$ −2.66° (*l* 0.5 dm, neat) for sodium-dried amine. Our amine was not so treated. Traces of water are known to lower $\alpha^{19}D$ to −2.55°.[11] Allowing for temperature and drying corrections, our amine was very close to 100% optically pure.

(11) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **78**, 5597 (1956).

Table I. Stereochemistry of Hydrolysis of Active Octane-2-diazotate

Run	Conditions[a]	Quench,[b] equiv	Net inversion,[c] %
1, 2	A	H_2O	44, 48
3, 4	A′	H_2O	36, 40
5	A	0.5 KOH	49
6	A	2.2 KOH	48
7	A	2 H_2O[d]	42
8, 9	A	1.0 HCl	33, 35
10, 11, 12	A	2.0 HCl	23, 23, 24
13	B	1.0 KOH	44
14, 15	C	1.0 KOH	40, 36
16, 17	C	2.2 KOH	42, 53
18	D	1.0 KOH	16
19	D	1.0 KOH–D_2O	24
20	D′	1.0 KOH	20
21	D	1.0 KOH	17
22	D	1.0 HCl	11
23	D	2.0 HCl	11

[a] Octane-2-diazotate was prepared from 10.0 mmoles of optically active N-nitroso-N-2-octylurethan and 20.0 mmoles of (sublimed) potassium *t*-butoxide, in 45 ml of dry ether at −30°. After 25 min, the "quench" was carried out by rapid addition of 4.4 ml of water. Conditions: A, 4.4 ml of water was added to the diazotate–ether slurry at −15°; A′, as previously, but at +25°; B, the ether solvent and the various carbonates were removed by distillation under reduced pressure (1 mm), ambient temperature (the distillation was begun 25 min after addition of the nitrosourethan to the butoxide; the reduced pressure was maintained for 1 hr; fresh ether was then added, and a normal quench was carried out at −15°); C, the ether was distilled off as before (it was replaced with dry pentane; quenching was effected at −15°); D, the ether was distilled off as before (quenching was effected in the absence of an organic phase, at −15°); D′, as under D, but at +25°. [b] Number of equivalents based on mmoles of potassium *t*-butoxide used in the cleavage of the nitrosourethan. [c] By comparison of the isolated 2-octanol with the starting 2-octylamine. [d] 8.8 ml of water was added as a quench, rather than 4.4 ml.

For comparison, active 2-octylamine was deaminated at pH 4 with sodium nitrite and aqueous perchloric acid. Some time ago, Hughes, Ingold, and co-workers reported that nitrous acid deamination of active 2-octylamine, 2-butylamine, and α-phenylethylamine afforded the corresponding alcohols with "racemization and inversion."[12] Quantitative data were not presented.[13]

Wiberg reported that active 2-butylamine afforded 2-butanol with 22% net inversion.[14] Later, Streitwieser, calculating from data obtained in 1905, reported that α-phenylethylamine afforded α-phenylethyl alcohol with 6–12% net inversion.[15] Until recently,[16] these reports appear to have been the only stereochemical investigation of aqueous nitrous acid deamination of secondary acyclic carbinamines. Because they lacked either quantitative data, adequate controls, and/or high efficiency methods of product purification and identification, we also reinvestigated the 2-butylamine and α-phenylethylamine deaminations. The results appear in Table II; the details appear in the Experimental Section.

Control experiments were performed for each system. Active product alcohol, related olefins, and ketone were added to a foreign amine which was then deaminated under the standard conditions. The usual work-up procedure gave back the original alcohol with unaltered activity. Data in Table II indicate that the original reports concerning 2-butylamine and α-phenylethylamine are essentially correct, but that the 2-octylamine, contrary to previous reports,[12] deaminates with essentially complete racemization. Vpc analysis of the 2-octylamine deamination product mixture revealed the presence of 1- and 2-octenes (20%), 2-octanol (27%), and 2-octanone (2%). Also present were 3- and 4-octanol to the extent of 6% of the yield of 2-octanol. The ratio of 3- to 4-octanol was *ca.* 3.

Table II. Stereochemistry of Deamination of Some Acyclic Secondary Carbinamines in Aqueous Nitrous Acid, pH 4, *Ca.* 25°

R in $RCH(NH_2)CH_3$	Net inversion,[a] %
C_2H_5	22
C_6H_5	14
c-C_3H_5	0–5[b]
n-C_6H_{13}	0–2

[a] Based on isolated alcohol. [b] Reference 16.

Finally, we summarize some other results which were obtained in the diazotate study. (a) Attempts to quench ethereal octane-2-diazotate slurries with either *saturated* aqueous potassium hydroxide or potassium fluoride (18–20 *M*) led to no gas evolution over 5–10 min. Subsequent dilution with water afforded the usual quantitative gas evolution. (b) Quenches of ethereal octane-2-diazotate slurries with saturated aqueous sodium azide (*ca.* 7 *M*) led to standard product results. 2-Octyl azide formed only to 0.1 the extent of 2-octanol. Similar results were observed with ether-free diazotate. (c) In ethereal diazotate hydrolysis, 3- and 4-octanol formed only to the extent of 1–1.4% of the yield of 2-octanol. The corresponding yield of isomeric octanols was five to six times greater in the nitrous acid deamination of 2-octylamine (see above). The yield of 3- and 4-octanol was intermediate under condition D of Table I. (d) Most importantly, quenching of octane-2-diazotate with H_2O^{18} demonstrated that significant retention of the orginal diazotate oxygen had occurred in the formation of product 2-octanol. Pertinent results appear in Table III.

Table III. Hydrolysis of Octane-2-diazotate in H_2O^{18} [a]

Run	Conditions[b]	Atom % O^{18} in product 2-octanol[c]
1	A	12.40, 12.96, 12.30
2	A	15.65, 15.51, 15.47
3	B	12.70, 12.73

[a] Purchased from Yeda Research and Development Co., Rehovoth, Israel. The scale of the reaction was 3 mmoles of the diazotate to *ca.* 65 mmoles of water. We estimate that dilution of the O^{18} pool by O^{16} exchanged from the diazotate could have lowered the effective average O^{18} by no more than 0.5%. [b] Condition A: as in Table I, but the scale of the reaction was reduced. The water was 22.60% O^{18}. Condition B: the ether was removed after 25 min, and the quench was effected with H_2O^{18} at −15°. The water was 21.4% O^{18}. [c] Analyses by West Coast Technical Service, San Gabriel, Calif., by the method of D. Rittenberg and L. Ponticorvo, *Intern. J. Appl. Radiation Isotopes*, **1**, 208 (1956). The analysis was checked with good agreement, in run 3, by direct mass spectral examination of the 2-octanol.

From the data in Table III it may be estimated that, in water–ether, a mean minimum of *ca.* 38% of the

(12) P. Brewster, F. Hiron, E. D. Hughes, C. K. Ingold, and P. A. D. S. Rao, *Nature*, **166**, 179 (1950).

(13) In a private communication (May 27, 1966), Professor Ingold informed us that the original data have not, unfortunately, been located among the effects of the late Dr. Hughes.

(14) K. B. Wiberg, Ph.D. Thesis, Columbia University, New York, N. Y., 1950.

(15) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957), footnote 16.

(16) M. Vogel and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 2262 (1966).

2-octanol derives its oxygen directly from the diazotate. In the pure water case, the corresponding datum is *ca.* 40%.

Discussion

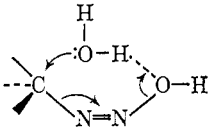
Huisgen[17] and Streitwieser[15,18] have indicated the inherent difficulty in attempts to create a comprehensive mechanism for the amine–nitrous acid deamination reaction. In Streitwieser's phrasing, "The great stability of the leaving nitrogen molecule implies that the activation energy required for the decomposition of an aliphatic diazonium ion is rather small, perhaps of the order of 3–5 kcal/mole. Consequently, the range of energies required for a number of competing reactions is compressed . . . ."[15] General acceptance of this viewpoint is reflected in the plethora of intermediates postulated for deamination reactions. A principal part of the problem involves deciding how much product arises *via* diazonium species, *bypassing* free carbonium ions, and how much product arises *via* carbonium ions, and, moreover, how any such partition depends on structure and conformation, solvent, etc.[19] Evidence bearing on this problem is difficult to obtain and product distribution in any given deamination must be regarded as a sum of various pathways, peculiar to the particular reaction under study, and not mechanistically relevant in and of itself. Stereochemical studies of nitrous acid deamination are a case in point.

For the primary carbinamine, 1-amino-1-butane-1-*d*, a high degree of inversion attends deamination in acetic acid, and it has been proposed that most of the diazonium ions go directly to product *via* an SN2-like mechanism, bypassing the primary carbonium ion.[18] Secondary carbinamine data are more complex. Nitrous acid deamination of α-methylallylamine in acetic acid has been partitioned into two pathways; the one which bypasses a normal allylic carbonium ion produces highly inverted α-methylallyl acetate.[20] The secondary systems gathered in Table II deaminate with low net inversion, and the data can be interpreted to represent an unequal partition between diazonium ion and carbonium ion pathways with the latter favored. Whiting's evidence for shorter diazonium ion lifetime in secondary as compared to primary systems is consistent with the foregoing.[21] Little data for acyclic tertiary carbinamines is at hand. What there is suggests that aqueous deamination leads to racemization, presumably *via* the carbonium ion.[22]

In turning to the present study, consider first the contrast between aqueous nitrous acid deamination of 2-octylamine which, at pH 4, leads to racemized 2-octanol (Table II) and the hydrolysis of octane-2-diazotate which, at pH >14, leads to 16% net inverted 2-octanol (Table I, runs 18 and 21). From the H_2O^{18} data (Table III), the diazotate hydrolysis involves about 40% return of original oxygen during alcohol formation. Return of OH has been demonstrated in deamination reactions carried out in nonaqueous solvents,[19,23,24] but an attempt to demonstrate its existence in the aqueous $HNO^{18}{}_2$ deamination of cyclohexylamine limited its importance to less than 10%.[25] Actual participation of the return pathway was probably considerably less than 10%, since several side reactions might have accounted for the O^{18} incorporation observed in the product cyclohexanol.[25] Our observation appears to be the first direct evidence for substantial hydroxide return during diazotic acid decomposition in water. Since the return process most likely occurs with net retention (see below), the portion of alcohol formation *not* involving return must occur with more than 16% net inversion.[26]

More importantly, it appears that the combination of hydroxide return data and stereochemical data severely limits the possible role of free carbonium ion intermediates in these deaminative diazotate hydrolyses. Consider again the 2-octanol formed by octane-2-diazotate hydrolysis. If the hydroxide return process (40%) went with complete stereochemical retention, which is not likely (see below), other pathways to alcohol would have involved a minimum of 56% inversion (since 16% net inversion is actually observed). Only 4% of octanol-yielding decompositions could then have involved free carbonium ion intermediates, which would be expected to yield alcohol with racemization *and* loss of the original diazotate oxygen. The hydrolysis data are consistent with the interpretation that octane-2-diazotic acid (formed *via* protonation of the diazotate) may decompose with hydroxide return (*possibly via* an intimate diazonium ion–hydroxide ion pair, and mainly with stereochemical retention), with inverting incorporation of solvent, and with some racemization. Since it is likely that hydroxide return occurs with some *inversion* (see below) one might estimate that the latter process, racemization, which could represent escape of diazotic acid to solvated diazonium ions and/or carbonium ions, could occur to about 20%. (This estimate is based on the assumption of 60% net retention in the hydroxide return process.[27,28])

In principle, then, we are suggesting that, in these strongly basic diazotate hydrolyses, the most important nitrogen-containing intermediate is the diazotic acid itself, and that its leaving group, N=NOH, has considerable integrity. Furthermore, the evidence suggests that much of the transformation of diazotic acid to alcohol bypasses free carbonium ion intermediates. On the other hand, in nitrous acid deamination, the leaving group might more properly be considered to be



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(17) R. Huisgen and C. Rüchardt, *Ann.*, **601**, 1 (1956).
(18) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2888 (1957).
(19) J. G. Traynham and M. J. Yang, *ibid.*, **87**, 2394 (1965).
(20) D. Semenow, C.-H. Shih, and W. G. Young, *ibid.*, **80**, 5472 (1958).
(21) H. Maskill, R. M. Southam, and M. C. Whiting, *Chem. Commun.*, 496 (1965); M. C. Whiting, *Chem. Brit.*, **2**, 482 (1966).
(22) C. L. Arcus, J. Kenyon, and S. Levin, *J. Chem. Soc.*, 407 (1951).
(23) T. Cohen and E. Jankowski, *J. Am. Chem. Soc.*, **86**, 4217 (1964).
(24) E. H. White and J. E. Stuber, *ibid.*, **85**, 2168 (1963).
(25) D. L. Boutle and C. A. Bunton, *J. Chem. Soc.*, 761 (1961).
(26) At present we cannot estimate the significance of processes such as i which would lead to retention *and* O^{18} incorporation. In view of the lack of direct evidence for such a pathway, we will omit it from further consideration here.
(27) E. H. White and F. W. Bachelor, *Tetrahedron Letters*, 77 (1965); E. H. White and C. A. Aufdermarsh, Jr., *J. Am. Chem. Soc.*, **83**, 1179 (1961).
(28) See, for example, ref 19, 23, and 24. See also the report of chloride return with net retention in an alkyl diazochloride decomposition: H. Felkin, *Compt. Rend.*, **236**, 298 (1953).

N_2, and the most important nitrogen-containing species, a diazonium ion.

This view accounts for the increased importance of return pathways in basic diazotate hydrolysis. Furthermore, relative to free diazonium ions, the diazotic acid decompositions may involve a somewhat poorer leaving group, with a greater shielding effect, leading to greater net inversion in the competitive, solvent-incorporating, alcohol-forming reaction.[29]

In support, note that hydrolysis of octane-2-diazotate with acidic water leads to more completely racemized 2-octanol (Table I, runs 22 and 23). Protonation of N_2OH should be competitive with decomposition and would at least partially convert the diazotic acid to a diazonium ion. The observation of less isomerized octanol in basic diazotate hydrolysis, as compared to the acidic deamination of 2-octylamine, also speaks for the importance of pathways which avoid free diazonium ion–carbonium ion intermediates in the basic diazotate hydrolysis.[21]

An extraordinary aspect of the data in Table I is the enhancement of inversion observed when the diazotate is hydrolyzed in the presence of an organic phase. Hydrolysis in water leads to 16% inversion, but hydrolysis in the presence of ether (or pentane) affords 2-octanol which is 46% (or 38%) inverted. Under ether–water conditions, about 38% of the diazotic acid molecules collapse with return of the original OH (Table III). If return occurred with complete stereochemical retention, the maximum total inversion could be 62%. Since the observation of 46% net inversion (Table I, runs 1 and 2) demands 73% total inversion, hydroxide return must involve less than complete retention. Such a result is in keeping with the demonstration of "intramolecular inversion" pathways in the decomposition of diazonium ion pairs.[24,27] No doubt, though less than complete, retention is quite dominant in the return process.[27,28] If this is so, then the overlap of hydroxide return and stereochemical inversion data leave little room for the intervention of a free carbonium ion in the ether–water diazotate hydrolysis. This is in contrast to diazotate hydrolysis in the absence of an organic phase (see above) where the carbonium ion could account for a significant portion of the product 2-octanol.

The concept of a diazotic acid (the N_2OH leaving group of which has considerable integrity) as a key intermediate in the ether–water or pentane–water diazotate hydrolyses is not only useful in explaining the stereochemical and O^{18} data, but also accounts for the pronounced increase in racemization upon acidic hydrolysis of the diazotate (Table I, runs 8–12), again explicable as a diversion of the diazotic acid to free diazonium ions and carbonium ions. Failure to observe the formation of appreciable amounts of 2-octyl azide upon hydrolysis of the ethereal diazotate with saturated sodium azide solution, lack of stereochemical response to hydrolysis with more concentrated aqueous hydroxide, and minimal formation of 3- and 4-octanol are also consistent with a diazotic acid (or intimate diazonium hydroxide ion pair) which unimolecularly decomposes with hydroxide return or inverting solvent collapse.

It remains to consider the possible origins of the ether or pentane effect. Although we have developed several consistent explanations, we believe that it is presently premature to offer them. Whatever the exact origin of the effect, the enhanced inversion in these two-phase "basic deaminations" is a unique result of possibly wide utility. We intend to seek this effect in other systems.

(29) This interpretation derives from the comments of Ridd[2c] (see pp 438–439). The increased inversion is also consistent with the kind of S_N2 mechanism suggested by Streitwieser.[15,18] Importance of a classical kind of S_N2 displacement in the diazotic acid decomposition seems ruled out by the azide and hydroxide variation experiments described above. Inverting solvent attack might also occur directly on an intimate diazonium hydroxide ion pair. For related suggestions, see: R. A. Sneen, J. V. Carter, and P. S. Kay, *J. Am. Chem. Soc.*, **88**, 2594 (1966), and references therein.

Experimental Section

Diazotate Studies. 2-Octylamine was converted to N-2-octylurethan with ethyl chloroformate.[3] The urethan had bp 80–81° (0.35 mm) and $n^{23}D$ 1.4385;[30] infrared (10% CCl_4): 1725 cm^{-1}; nmr (10% CCl_4): 4.7 (broad), 4.03 (quartet, J = 7.0 cps). 3.6 (broad multiplet), and 1.31–0.89 (numerous absorptions, including a sharp triplet at 1.21, J = 7.0 cps).[31] Approximate area ratios were 1:2:1:19.

N-2-Octylurethan was nitrosated by White's method,[4] as adapted by Moss.[1] The N-nitroso-N-2-octylurethan was a golden oil, obtained in 95% yield; infrared (10% CCl_4): 1740 cm^{-1}; nmr (10% CCl_4): 4.47 (quartet, J = 7.0 cps), 4.8 (broad quartet, J = *ca.* 7 cps), and 1.21–0.88 (numerous absorptions, including a sharp triplet at 1.46, J = 7.0 cps).[32]

The nitrosourethan (693 mg, 3.0 mmoles) in 10 ml of dry ether was injected through a septum into a well-stirred, N_2-covered, cooled (−30°) slurry of 672 mg (6.0 mmoles) of potassium *t*-butoxide (M.S.A. Research Corp.) in 10 ml of dry ether. No gas evolution was observed over 25 min. Then, with the temperature at −15°, 1.3 ml of water was injected. Within 5 sec, 70 ml (91%) of gas evolved. The reaction was exothermic (temperature rose to +5°). The gas volume was corrected for this effect. The ethereal phase was separated; the aqueous phase (pH 13.6) was extracted with 10 ml of ether. The combined ether solutions were washed twice with 10-ml portions of water, and then dried over $MgSO_4$. Filtration and concentration (rotary evaporator) afforded 640 mg of yellow oil.

Vpc analysis on a Carbowax 20M column (16 ft, 3/8 in., 15% Carbowax 20M on 70/80 Anakrom ABS, Aerograph A-90-P instrument, injector temperature 200°, column temperature 140°, helium pressure 20 psig) revealed three major components and several minor components. These are discussed in order of elution. Component a was a mixture of 1- and 2-octenes, identified by comparison of retention time and infrared and nmr spectra with those of an authentic mixture. Component b was a mixture of (trace) diethyl, ethyl *t*-butyl, and di-*t*-butyl carbonates, identified by vpc and spectral comparisons with an authentic mixture. We have described this mixture and its origin previously.[1] Component c was 2-octanone (vpc, infrared, nmr). Component d was 2-octanol (vpc, infrared, nmr). Programming the column temperature to 200° eluted trace components (less than 3%) identified as higher carbonates (ethyl 2-octyl, *t*-butyl 2-octyl) by infrared and nmr; the identity of two other trace components is unclear. Yields were determined for a–d against an 1-octanol standard after calibrating the thermal conductivity detector for relative response for each component. The yields, based on N-nitroso-N-2-octyl-

(30) Lit.[3] bp 88–90° (0.5 mm) and $n^{25}D$ 1.4371.

(31) In parts per million downfield from internal TMS; determined on Varian A-60 equipment. Assignments of importance: 4.7, NH; 4.03, OCH_2; 3.6, CHN; 1.21, urethan methyl.

(32) Assignments of importance are: 4.47, OCH_2; 4.8, CHN; 1.46, urethan methyl. With reference to the nmr spectrum of the urethan,[31] deshielding of 0.44, 1.2, and 0.25 ppm for the OCH_2, CHN, and urethan methyl protons, respectively, attended the introduction of the nitroso group. These observations serve as definitive characterization. See ref 5, in which the nmr spectra of ten N-alkylurethans and their N-nitroso derivatives are discussed. N-Nitroso-N-2-octylurethan was reasonably stable when stored at −10°. The purity of the nitrosourethan was also established by nmr[5] and was >98%. Samples of the nitrosourethan were reexamined from time to time so as to guard against decomposition (*Anal.* Calcd for $C_{11}H_{22}N_2O_3$: C, 57.37; H, 9.63; N, 12.17. Found: C, 57.30; H, 9.83; N, 11.86).

urethan, were a, 33%; b, 75%; c, 3%; d, 25%. 3- and 4-octanol appeared as a lower retention time shoulder on the 2-octanol peak. This shoulder was never collected during preparative work. (The combined yield of isomeric octanols was 1.4% of the yield of 2-octanol. The ratio of 3-octanol to 4-octanol was about 3.0.)

The foregoing experiment was repeated, except that instead of being hydrolyzed at the end of the 25-min reaction period, the ethereal slurry was warmed to 25°. The reaction vessel was connected to a vacuum system (maintained at 1 mm) for 1 hr. At the end of this time, fresh ether was added to the solid remaining in the reaction vessel and hydrolysis was carried out as previously described. Quantitative gas evolution was observed. In the oil remaining after work-up of the product mixture, all the components described above, *except* the carbonates, b, were observed. The carbonates could be recovered from the ether which had been distilled off and collected in a cold trap.

Analysis of collected 2-octanol in the D_2O experiments was by nmr and/or mass spectroscopy. Such analyses were carried out for all types of hydrolyses conditions described in Table I and always revealed less than 3% carbinyl deuterium.

Optically Active Diazotate Studies. 2-Octylamine was resolved *via* the tartrate salt, affording *l*-2-octylamine of close to 100% optical purity.[9-11] *l*-2-Octylurethan was then prepared as described for the racemic material. Our sample of greatest rotation had $\alpha^{20}D$ −2.24° (*l* 0.5 dm, neat) and was prepared from amine which had $\alpha^{25}D$ −2.60° (*l* 0.5 dm, neat). It was about 98.5% optically pure.[9-11,33] In some preparations of the active urethan, 2-octylamine of *ca.* 20% optical purity was used. The urethan rotation was in proper ratio. The infrared spectrum of the active urethan was identical with that of the racemic material. Nitrosation of the active urethan, as above, afforded active N-nitroso-N-2-octylurethan of proper spectral properties. Its rotation was not accurately determined due to its yellow color, which made difficult readings of αD. The approximate αD was −160 to −210°.

The results of decompositions of octane-2-diazotate derived from the active nitrosourethan are gathered in Table I. In a typical run, 2.31 g (10.0 mmoles) of the nitrosourethan in 20 ml of dry ether was cleaved with 2.24 g of potassium *t*-butoxide (20.0 mmoles) in 25 ml of dry ether. Quenching was effected with 4.4 ml of water. Various quench conditions are detailed in Table I. Work-up and collection of 2-octanol were as described above. The rotation of the octanol product was determined on a neat sample.[33] Active 2-octanol was optically stable to *all* conditions described in Table I. Octanol isolated in each run was homogeneous to rechromatography in general. (In some cases, several per cent of 2-octanone intruded (vpc) and rotations were corrected. These corrections were very minor.) Isolated 2-octanol also showed a proper infrared spectrum. Two typical optical results are described; others were analogously obtained.

Table I, Run 1. 2-Octylamine, $\alpha^{25}D$ −2.58° (97% optically pure[9,11]), was converted to the urethan ($\alpha^{23}D$ −2.18°). The urethan was nitrostated, and the nitrosourethan was converted to octane-2-diazotate. Decomposition of the diazotate with water gave 2-octanol, $\alpha^{25}D$ +1.73° (43% optically pure[34]). This result corresponds to 44% *net* inversion, based on starting amine.

Table I, Run 13. 2-Octylamine, $\alpha^{23}D$ +0.55° (21% optically pure), was converted to the urethan ($\alpha^{24}D$ +0.46°) which ultimately afforded 2-octanol, $\alpha^{23}D$ −0.35°. After correction for 3% contamination by 2-octanone, this corresponds to an optical purity of 9.1% and net inversion of 44% for the reaction sequence.[35]

Water (O^{18}) Decompositions. These decompositions were carried out on 3.0 mmoles of octane-2-diazotate obtained from the nitrosourethan as described above. Details of the quench conditions and analytical results appear in Table III. H_2O^{18} was certified 22.60% O^{18} by Yeda Co. and was used immediately upon opening the sealed ampoule (runs 1 and 2). Run 3 was carried out with H_2O^{18} which was reanalyzed at the time of use (see Table III). Octanol was isolated in the usual manner (*via* vpc) and then subjected to a final rechromatography. Final product (30 mg, homogeneous to vpc) was immediately sealed into a dry ampoule. All transfers were effected with dry Hamilton syringes.

Nitrous Acid Deaminations. a. 2-Octyl System. To a 10% aqueous solution of 1.94 g (15.0 mmoles) of 2-octylamine at 23°, in a three-necked flask fitted with a dropping funnel, pH meter electrodes, and a stirring bar, was added 1.7 ml of 60% aqueous perchloric acid. A 10% aqueous solution of 2.07 g (30.0 mmoles) of sodium nitrite was added. Further perchloric acid solution was then added dropwise, with stirring, until nitrogen evolution began (pH 5.31). The pH was adjusted to *ca.* 4.0, and the evolved gas was collected in a gas buret. After 4 hr, the pH was 4.1, and 370 ml (99%) of gas had evolved. The solution was extracted twice with 50-ml portions of ether. Combined ether was washed once with 50 ml of water and dried over $MgSO_4$. After filtration and stirring of the solvent, 1.27 g of yellow oil remained. Vpc on the previously described Carbowax column revealed components: a, a mixture of 1- and 2-octene; b, 2-octanone; c, 2-octanol. Product identities were established by vpc, infrared, and nmr comparisons with authentic materials. The yields were determined as in the diazotate decompositions, and were 20, 2, and 27%, respectively. A short retention time shoulder on the 2-octanol (not collected in preparative runs) was resolved on a 0.25-in. Carbowax column and shown to be a mixture of 3- and 4-octanols, ratio 3:1, and, in total, *ca.* 6% of the 2-octanol. Traces of materials with retention times greater than c were observed but were not identified.

The above procedure was applied to *l*-2-octylamine, and the product 2-octanol was collected and studied in the polarimeter. Three experiments with amine having $\alpha^{24}D$ −2.58° (optical purity 97+%) gave alcohol with $\alpha^{28}D$ +0.01, +0.02, and 0.00°. The collected 2-octanol had traces of 3-octanol (2%, capillary vpc).

As a control, a mixture of 1.04 g (12.0 mmoles) of *neopentylamine*, 390 mg (3.0 mmoles) of *d*-2-octanol, $\alpha^{25}D$ +3.81°, 38.4 mg (0.3 mmoles) of 2-octanone, and 168 mg (1.5 mmoles) each of 1- and 2-octene were treated under the above conditions until 98% of the theoretical nitrogen evolution had occurred. Isolation of the 2-octanol as before afforded material having $\alpha^{21}D$ +3.80°.

b. α-Phenylethyl System. The deamination of α-phenylethylamine, as described for 2-octylamine, afforded 35% α-phenylethyl alcohol, 2% styrene, and 2% acetophenone. The products were identified by vpc, infrared, and nmr. α-Phenylethylamine was resolved by the method of Theilaker and Winkler.[36] Two runs were made with a sample having $\alpha^{28}D$ −10.55° (56.0% optically pure[37]). They afforded alcohol with $\alpha^{29}D$ +1.76 and +1.64° (8.15 and 7.60% optically pure[38]). A third run with amine having $\alpha^{24}D$ −8.48° (optical purity 44.7%[39]) afforded alcohol with $\alpha^{23}D$ +1.32° (optical purity 6.04%[40]). The data correspond to net inversions of 14.5, 13.6, and 13.5%, respectively. The isolated α-phenylethyl alcohol was homogeneous to vpc, and had a proper infrared spectrum. A control mixture with active α-phenylethyl alcohol, styrene, acetophenone, and neopentylamine was carried through the deamination procedure and returned alcohol of unaltered activity.

c. 2-Butyl System. Active 2-butylamine was prepared from active 2-methyl-1-butanol (Aldrich Chemical Co.), *via* 2-methylbutanoic acid, as described by Wiberg.[14] Our material had $\alpha^{24}D$ +2.04° (76.0% optically pure[41]). Deamination of this material as described for 2-octylamine afforded a product mixture which, on the Carbowax preparative column, at 75°, revealed several minor peaks (unidentified) and 2-butanol (16% yield). 2-Butanol was homogeneous to rechromatography, had a proper infrared spectrum, and showed $\alpha^{24}D$ −0.91° (17.1% optically pure[42]). The result corresponds to 22.5% net inversion.[43] Two other runs gave net inversions of 22.7 and 23.4%. An appropriate control experiment (as described for the other systems, except that isopropylamine was used here) demonstrated the optical stability of active 2-butanol under deamination conditions.

(33) *All rotations* were measured with a Rudolph polarimeter using a 100 μl, 0.5-dm cell. Blank readings were taken. Ten readings were made in each determination. Readings are considered accurate to ±0.02°.

(34) Based upon $\alpha^{23}D$ +16.08° (*l* 2 dm, neat), for 100% purity.[11]

(35) Details of all observed rotations are contained in the Ph.D. Dissertation of S. M. Lane, Rutgers University, 1968, and will be available from University Microfilms, Ann Arbor, Mich.

(36) W. Theilaker and H.-G. Winkler, *Ber.*, **87**, 690 (1954).

(37) Based upon $\alpha^{26}D$ +37.7° (*l* 1 dm, neat), D. J. Cram, L. K. Gaston, and H. Jaeger, *J. Am. Chem. Soc.*, **83**, 2183 (1961). See also ref 36.

(38) Based upon $\alpha^{28}D$ −21.6° (*l* 0.5 dm, neat), N. Kornblum and H. E. De LaMare, *ibid.*, **74**, 3079 (1952). See also: R. L. Burwell, Jr., A. D. Shields, and H. Hart, *ibid.*, **76**, 908 (1954).

(39) Based upon $\alpha^{25}D$ −37.95° (*l* 1 dm, neat), N. Kornblum, L. Fishbein, and R. A. Smiley, *ibid.*, 77, 6261 (1955).

(40) Based upon $\alpha^{25}D$ 43.7° (*l* 1 dm, neat), ref 38 (Burwell, *et al.*).

(41) Based upon $\alpha^{20}D$ +5.38° (*l* 1 dm, neat), L. G. Thomé, *Ber.*, **36**, 582 (1903).

(42) Based upon $\alpha^{25}D$ −10.67° (*l* 1 dm, neat), P. J. Leroux and H. J. Lucas, *J. Am. Chem. Soc.*, **73**, 41 (1951); see also J. Kenyon, H. Phillips, and V. P. Pittman, *J. Chem. Soc.*, 1072 (1935).

(43) All amine–alcohol systems considered here have similar rotational signs for antipodes of the same relative configuration.[16]

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Partial Hydrolysis and Acetolysis of Cellotriose-1-C^{14} [1]

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Abstract: The chemical preparation and purification of cellotriose-1-C^{14} is described. Starting with inert cellotriose, the reaction sequence involved an oxidation to the aldonic acid followed by a Ruff degradation, cyanohydrin addition using sodium cyanide-C^{14}, hydrolysis of the resulting nitrile, lactonization, and subsequent reduction with sodium amalgam. The resulting cellotriose-1-C^{14}, after purification, was used in a series of experiments wherein the ratio of the hydrolysis rates of the two glycosidic bonds within the molecule was determined. The ratio was measured using 14.2 *N* (50%) sulfuric acid at 30° and 0.5 *N* sulfuric acid at both 90 and 120°; in all cases the ratio of the hydrolysis rate of the bond at the nonreducing end of the molecule (k_2) to that at the reducing end (k_1) was 1.5. At 120° in 0.5 *N* sulfuric acid, the hydrolysis rate of cellotriose ($k_1 + k_2$) was 0.126 min^{-1}. Thus k_1 = 0.050 min^{-1} and k_2 = 0.076 min^{-1}. When cellotriose-1-C^{14} underwent acetolysis, however, the ratio of cleavage rates was reversed, and a threefold preference was observed for cleaving the glycosidic bond at the reducing end of the molecule.

The hydrolysis of glycosides in acidic solution is a reaction well known to the organic chemist. From the numerous studies available concerning this reaction, it is evident that among conformationally stable glycosides, rate of hydrolysis depends on the structure of the glycone; inductive effects in the aglycone have but little effect on rate.[3] Recent critical reviews and interpretations[4-7] on this subject conclude that the major rate-controlling factors are steric diequatorial intramolecular interactions within the glycone. When the cellotriose molecule, which is composed of three β-D-glucopyranose units linked 1→4, is examined in the light of this conclusion, it is apparent that the two glycosidic bonds within the molecule are different. The prediction would be made that the rate of hydrolysis of the glycosidic bond at the nonreducing portion of the molecule, which is controlled by a D-glucopyranose structure, would be faster than that at the reducing end, the rate of which is controlled by a more bulky glycone containing two D-glucopyranose residues. It would also be expected that the rate of hydrolysis of the glycosidic bond at the nonreducing end of cellotriose would approximate that of cellobiose.

This communication reports a series of experiments wherein the above conclusions and predictions were tested. The experiments involved the measurement of the rate of hydrolysis of cellotriose in 0.5 *N* sulfuric acid at 120°, and measurement, under the same conditions, of the ratio of the hydrolysis rates of the two glycosidic bonds within the molecule. This ratio was also measured in 0.5 *N* sulfuric acid at 90° and in 14.2 *N* (50.0%) sulfuric acid at 30°. In order to measure the ratio of the two rate constants, it was necessary to employ a cellotriose molecule labeled specifically at one end.

The compound used was cellotriose-1-C^{14}, that is, the trisaccharide in which the reducing unit was D-glucose-1-C^{14}. It was synthesized from inert cellotriose obtained by a previously described method,[8] using essentially the procedures developed by Isbell, *et al.*, in their synthesis of specifically labeled disaccharides.[9] It was purified by acetylation and chromatographed on silica gel. The resulting crystalline acetate was deacetylated and the sugar further purified by preparative paper chromatography. The final cellotriose-1-C^{14} preparation, after dilution and crystallization, contained less than 0.5% of radiochemical contamination by mannose, glucose, and cellobiose. That it contained negligible epimer, which could have been produced during the cyanohydrin addition, was verified by the finding of insignificant quantities (less than 1%) of radioactive mannose in total hydrolysates of the material.

Labeled cellotriose was partially hydrolyzed to give a maximum yield of cellobiose in excess of 20%; ap-

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