Nitrosobenzene and Azoxybenzene with Cyclohexane.—To gain additional information concerning the decomposition of nitrosobenzene to phenyl radical and NO and its conversion to azoxybenzene, we carried out the reactions of nitrosobenzene and azoxybenzene with cyclohexane at 600°. As phenyl radical prefers to abstract hydrogen from cyclohexane rather than add to the aromatic ring of benzene at 600°,[7] some of the phenyl radicals generated from nitrosobenzene should be converted to benzene. This should facilitate the conversion of nitrosobenzene to azoxybenzene and its subsequent decomposition to aniline. The data from these reactions are shown in Table V. Aniline indeed was formed as a major product from nitrosobenzene; product distributions from both nitrosobenzene and azoxybenzene with cyclohexane were more nearly the same than those from the corresponding reactions with benzene.

This study shows that the thermal chemistry of nitrosobenzene is quite complex. Dissociation of nitrosobenzene to azoxybenzene and nitrobenzene or to phenyl radicals and NO depends on temperature and the nature of the hydrocarbon used as a reagent.

(7) A. I. Feinstein, E. K. Fields, and S. Meyerson, *J. Org. Chem.*, **35**, 303 (1970).

Registry No.—Nitrosobenzene, 586-96-9; azoxybenzene, 495-48-7; benzene, 71-43-2; benzene-d_6, 1076-43-3; cyclohexane, 110-82-7.

Acknowledgment.—We acknowledge with thanks the assistance of S. Meyerson of Standard Oil of Indiana and D. K. Albert of the American Oil Company for mass spectrometric and gas chromatographic analyses.

The Basic Hydrolysis of Solubilized Octane-2-diazotate. Dissection of Conservation and Exchange Pathways[1,2]

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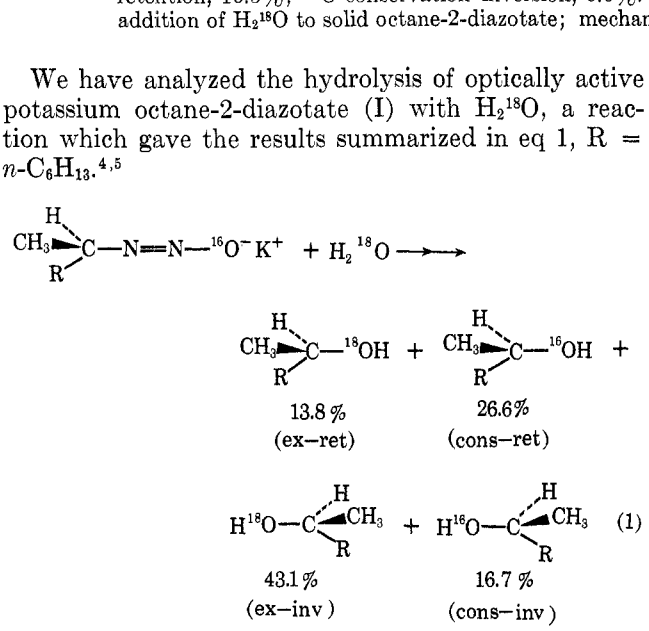
Solubilized optically active octane-2-diazotate (^{16}O) in hexamethylphosphoric triamide–dicyclohexyl-18-crown-6 was hydrolyzed by slow addition to $H_2{}^{18}O$. The resultant 2-octanol was attributed to four product-forming pathways: ^{18}O-incorporation–retention, 18.9%; ^{18}O-incorporation–inversion, 58.5%; ^{16}O-conservation–retention, 16.5%; ^{16}O-conservation–inversion, 6.0%. The results are compared to those obtained upon direct addition of $H_2{}^{18}O$ to solid octane-2-diazotate; mechanisms are discussed.

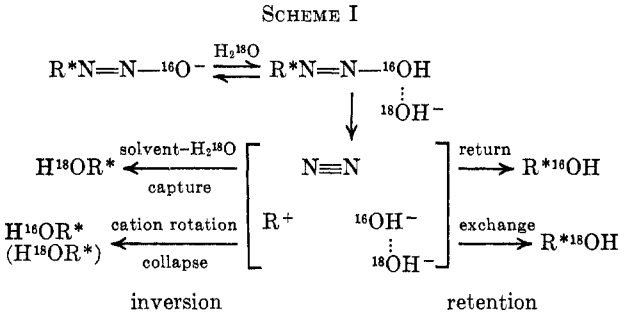
We have analyzed the hydrolysis of optically active potassium octane-2-diazotate (I) with $H_2{}^{18}O$, a reaction which gave the results summarized in eq 1, R = n-C_6H_{13}.[4,5]



Solvent incorporating (exchange) inversion was the predominant pathway (ex-inv product), but substantial conservation of the original diazotate oxygen was also observed. The exchange pathways afforded 2-octanol with 76% overall *inversion*, whereas the conservation pathways afforded 2-octanol with 61% overall *retention*. This pattern, exchange with inversion and conservation with retention, was also observed in the ethanolysis of potassium 1-phenylethanediazotate.[2]

We proposed[4] a mechanism in which $H_2{}^{18}O$ and $^{16}OH^-$ competed for 2-octyl cation in a nonsymmetrically hydrated ion pair (see Scheme I). This mechanism

SCHEME I



was an adaptation of White's "counterion hypothesis," which has worked well for deaminative processes in nonaqueous solvents.[6]

The previous hydrolyses of I[4,5] involved the addition of water to the solid salt. The ensuing reactions were very rapid on the normal time scale, and the results could have reflected local inhomogeneities in the reac-

(1) Alkyl Diazotates. IX.[2]

(2) Part VIII: R. A. Moss and M. J. Landon, *J. Amer. Chem. Soc.*, **92**, 5755 (1970).

(3) (a) Fellow of the Alfred P. Sloan Foundation; to whom correspondence should be addressed at Rutgers University. (b) National Science Foundation Undergraduate Research Participant, summer 1970. (c) Colgate-Palmolive Research Center.

(4) R. A. Moss, D. W. Reger, and E. M. Emery, *J. Amer. Chem. Soc.*, **92**, 1366 (1970).

(5) R. A. Moss and S. M. Lane, *ibid.*, **89**, 5655 (1967).

(6) E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, pp 440–483. This excellent review includes a definitive statement of the "counterion hypothesis," as well as elegant illustrations of its applicability.

tant system, particularly if the rate of decomposition of protonated I were comparable to the rate of solution and hydration of I. That is, bimolecular reactions of octane-2-diazotic acid (or ion pairs derived therefrom), in local, abnormally high concentrations could have accounted for some of the cons–inv product of eq 1. It seemed unlikely that such reactions occurred between truly dissolved, solution-equilibrated octane-2-diazotic acid, because the stereochemical outcome of the overall reaction was not sensitive to the addition of such strong nucleophiles as hydroxide and azide.[5]

To gain perspective on this problem, we have prepared apparent solutions of I in hexamethylphosphoric triamide (HMPT) containing the macrocyclic polyether, dicyclohexyl-18-crown-6.[7] "Inverse" hydrolyses of I were carried out by slow addition of these solutions to water. Here we present the results of these studies, which refine and extend our earlier work.[4,5]

Results

Stereochemistry.—A clear, dark orange solution of optically active I[4,5] in HMPT[8] was decomposed by slow addition to a large excess of vigorously stirred water (200 ml). Nitrogen evolution was 87% of the theoretical quantity. The gc-isolated 2-octanol product was converted to a mixture of diastereomeric *d*- and *l*-2-octyl L-acetyllactate esters,[4] which was assayed by gc.[9] The analysis indicated that the 2-octanol had been 30.02% optically pure *d* enantiomer. Since the original I derived from *l*-2-octylamine of 95% optical purity, the overall stereochemical result for I → 2-octanol was 31.6% net inversion. A second, analogous experiment gave a stereochemical result of 31.2% net inversion.[10]

These results should be compared with those for the direct addition of water to solid I, in which 20% net inversion was found.[4,5] (For a discussion of errors in the stereochemical data, see the Experimental Section.)

Oxygen Conservation.—A solution of 0.61 mmol of I in 5 ml of HMPT, containing also 1.58 mmol of the crown ether[7] and 0.82 mmol of potassium *tert*-butoxide, was slowly added to 2.5 ml of water which was 20.82 atom % ^{18}O (D normalized), with the evolution of 88% of the theoretical amount of nitrogen.

Mass spectral examination of the isolated 2-octanol revealed 14.83 atom % ^{18}O, which indicated that the I → 2-octanol conversion had occurred with 29% of ^{16}O (original oxygen) conservation. A duplicate experiment gave 2-octanol containing 15.74 atom % ^{18}O, indicative of 24% ^{16}O conservation.

These results are to be contrasted to those for the direct addition of $H_2{}^{18}O$ to solid I, in which *ca.* 40% of ^{16}O conservation was observed.[4,5]

Stereochemical Dissection of Oxygen Conservation and Exchange.—The above experiments demonstrated that the I–HMPT inverse hydrolysis occurred with somewhat more overall inversion and less ^{16}O conservation than did the direct addition of water to I. In order to obtain a clearer picture of the origins of these overall changes, we hydrolyzed optically active I–HMPT with $H_2{}^{18}O$, converted the isolated 2-octanol to the diastereomeric 2-octyl L-acetyllactate esters, and determined the $^{16}O/^{18}O$ ratio of each ester. A display of the results is given in Table I.

TABLE I

2-OCTANOL FROM THE INVERSE HYDROLYSIS OF HMPT-DISSOLVED OPTICALLY ACTIVE I WITH $H_2{}^{18}O$[a]

Σ^{18}O in ROH, atom %		Stereochemistry (gc) Retained 2-octanol, %	Inverted 2-octanol, %	Atom % ^{18}O in resolved ROH: *l*-ROH (retention)	*d*-ROH (inversion)
Found	Calcd				
15.21[b]	16.07	36.35	63.65	11.46[c]	18.70[c–e]

[a] Conditions: 5.83 mmol of I (derived from *l*-2-octylurethane[4,5] of 94% optical purity) in 10 ml of HMPT, containing 12.9 mmol of the crown ether[7] and 6.1 mmol of potassium *tert*-butoxide, was added to 5 ml of $H_2{}^{18}O$ (20.82 atom % ^{18}O, D normalized). [b] Measured directly on the isolated 2-octanol, before its conversion to the L-acetyllactates. [c] Measured on the appropriate 2-octyl L-acetyllactate. [d] Dilution of the ^{18}O pool by ^{16}O exchanged from I could have lowered the effective average ^{18}O by no more than 0.3 atom %. [e] We estimate all reading errors for mass spectral data to be less than 1%.

The (gc) stereochemical data for this run correspond to a stereochemical course of 29% net inversion for the I → 2-octanol conversion, in reasonable agreement with the 31.4% (average) result (above). However, this determination was less precise than the former cases; see the Experimental Section. The overall ^{18}O incorporation observed in the unresolved 2-octanol, 15.21 atom %, agrees well with the 15.28 atom % (average) ^{18}O incorporation (above). The deviation of *back-calculated* total ^{18}O in the unresolved 2-octanol from the observed value (5.7% deviation) is somewhat larger than in our previous work.[4] In particular, we consider the ^{18}O analyses of the octyl L-acetyllactates to be more accurate than the ^{18}O analyses of 2-octanol. With the esters, there is no interference between ^{16}O and ^{18}O analogous ions; this is a minor problem in the 2-octanol analyses in the *m/e* 43, 45, 47 series. Moreover, the 2-octanol is sensitive to oxidation, which affords 2-octanone, complicating the analysis. The esters are not subject to this problem. Since the mechanistic analysis of the present experiment (see below) uses only the $^{18}O/^{16}O$ data determined on the esters, we feel that the isotope distribution data of Table I are acceptable. Further remarks about the mass spectral analyses can be found in the Experimental Section.

The data of Table I can be processed[4] to permit the construction of Table II, in which a percentage is assigned to each of the four octanol-forming pathways summarized in eq 1. A correction was made for the 6% of racemic I which had been present, and which contributed 2.2% to the 2-octanol enantiomers formed with ^{18}O exchange and 0.8% to the 2-octanol enantiomers formed with ^{16}O conservation (based on total octanol = 100%, and on the results of the $H_2{}^{18}O$ hydrolyses of racemic I, above). Table II also includes analogous results for the direct addition of $H_2{}^{18}O$ to solid, optically active I.[4]

(7) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

(8) 3.04 mmol in 25 ml of HMPT. Also present were 7.10 mmol of the crown ether[7] and 3.11 mmol of potassium *tert*-butoxide.

(9) E. Gil-Av, R. Charles-Sigler, G. Fischer, and D. Nurok, *J. Gas Chromatogr.*, **4**, 51 (1966); H. C. Rose, R. L. Stern, and B. L. Karger, *Anal. Chem.*, **38**, 469 (1966).

(10) A control experiment, in which I–HMPT–crown ether was added to D_2O, gave 2-octanol with only 0.5% of one carbon-bound D (mass spectrum). The importance of 2-diazooctane as a 2-octanol precursor was therefore negligible. It is of greater importance in the direct additions (up to 8%).[4,5]

TABLE II

STEREOCHEMISTRY OF EXCHANGE AND CONSERVATION PATHWAYS IN OCTANE-2-DIAZOTATE → 2-OCTANOL

Run	Σ^{18}O exchange[a,b]	Stereochemistry[a,c] Ret	Stereochemistry[a,c] Inv	Σ^{18}O conservation[a,b]	Stereochemistry[a,c] Ret	Stereochemistry[a,c] Inv
Direct addition[d]	58.4	13.8	43.1	41.6	26.6	16.7
HMPT–I inverse[e]	73.0	18.9	58.5	27.0	16.5	6.0[f]

[a] Per cent of total 2-octanol product. [b] Calculated from atom % ^{18}O (^{16}O) in the unresolved 2-octanol. [c] Calculated from the atom % ^{18}O (^{16}O) in the 2-octyl acetyllactates. That, *e.g.*, (13.8 + 43.1) ≠ 58.4, indicates the "give" in the data, since the two sides of the inequality were derived from independent experimental measurements. The agreement is less satisfactory in the second run (see above). [d] $H_2{}^{18}O$ added to solid I, ref 4. [e] HMPT–I–crown ether added to $H_2{}^{18}O$, this work. [f] A discussion of probable error in these data can be found in the Experimental Section.

Discussion

The HMPT–I inverse addition procedure enhances *both* the ex–ret and ex–inv pathways (eq 1), as compared to the "direct" hydrolysis procedure. However, both exchange pathways are augmented in proportion, and the overall stereochemistry of this pathway remains constant (*ca.* 76% inversion, 24% retention). The overall contribution of exchange or solvent incorporating pathways increases from 58% (direct addition) to 73% (inverse addition).

In contrast, *both* ^{16}O conservation pathways, cons–ret and cons–inv (eq 1), are suppressed in the inverse addition. The latter is most strongly affected, and, as a result, the stereochemistry of the ^{16}O conservation pathway changes from 61% retention, 39% inversion (direct addition) to 73% retention, 27% inversion (inverse addition).

Although the stereochemistry of the exchange process did not change, whereas the stereochemistry of the conservation process moved toward greater retention, the increased importance of the total exchange process is the dominant factor in determining the *overall* stereochemical change, which therefore moves from *ca.* 20% (direct addition) to *ca.* 30% *net* inversion (inverse addition).

The competitive processes which afford the products of eq 1 have been discussed in terms of Scheme I,[4] in which the cons–inv product was pictured as arising from cation rotation within the ion pair followed by collapse.[6] It is precisely this product, however, which is most dramatically suppressed on changing the experimental procedure from direct to inverse addition. It is therefore tempting to conclude that a significant portion of this product arose *via* bimolecular reactions of (^{16}O) octane-2-diazotic acid (or of $^{16}OH^-$ and octane-2-diazotic acid) present in local, abnormally high concentrations during the addition of water to solid I. These pathways should mainly yield cons–inv 2-octanol, and ought to decrease in importance when HMPT–I is slowly added to water.[11]

Bimolecular, inverting displacements by nucleophiles on RN=NX (X = OH, halide, –OOCR′) are not common, but they are not unknown. They certainly contribute in the decomposition of RN=NX (R = *sec*-alkyl) in poor solvents such as pentane.[6,12] We have also observed this type of reaction in the ethereal acetylation of butane-2-diazotate.[13]

Interestingly, White observed that "in the decomposition of the nitrosoamide of 1-phenylethylamine in which a benzylic cation is formed, the displacement could not be detected. . . ."[6,12] In this light, and in contrast to the present results for the hydrolysis of I, we recall our study of the ethanolysis of optically active 1-phenylethane-1-diazotate, in which the conservation product (1-phenylethanol) formed with *ca.* 73% net retention and the exchange product (1-phenylethyl ethyl ether) formed with *ca.* 30% net inversion.[2] These stereochemical results, for a reaction which most likely involved a benzylic cation, were essentially independent of experimental procedure, whether ethanol was added to the solid diazotate or a solution of the diazotate in HMPT–crown ether was added to ethanol.[2]

Assuming, then, that the present experiments with HMPT–I have obviated bimolecular reactions of octane-2-diazotic acid, the results, fitted to Scheme I, can be compared to other, related work. For example, conservation pathways in the acetolysis of *N*-(1-phenylethyl)-*N*-nitroso-2-naphthamide led to 1-phenylethyl 2-naphthoate with 81% retention and 19% inversion.[14] Compare with 73% retention and 27% inversion for the ^{16}O conservation pathways in the HMPT inverse hydrolysis of I (above). In contrast, however, exchange pathways in the former reaction led to 1-phenylethyl acetate with 56% retention and 44% inversion. This net retention is markedly different from the 76% inversion, 24% retention which characterizes the ^{18}O exchange pathways in the hydrolysis of I. The variance of stereochemical course in the exchange pathways of the two reactions can be understood in terms of (1) the much greater medium nucleophilicity in the hydrolysis of I, (2) the inferior stability of the 2-octyl cation, and (3) greater competitive ability of front-side (retention) exchange processes[6] (acetate for 2-naphthoate) in the less nucleophilic medium of the nitrosoamide decomposition.

These factors would combine to favor greater inverting displacement in the basic hydrolysis of I, as opposed to the acetolysis of *N*-(1-phenylethyl)-*N*-nitroso-2-naphthamide (*i.e.*, of 1-phenylethyl diazo-2-naphthoate).

A search of the literature reveals that the stereochemical aspects of the conservation process, as now determined in the inverse HMPT–I hydrolysis, are similar to those of other conservation processes which involve different alkyl groups, gegenions, and solvents; see Table III. Indeed, this remarkable resemblance, maintained over a diversity of reactants, suggests both the fundamentality of the processes being examined, and that the inverse HMPT–I hydrolysis has probably obviated most of the bimolecular reactions of octane-2-diazotic acid.

Finally, we note the possibility that the change from direct to inverse hydrolysis of I may not have eliminated

(11) In the presence of an ethereal phase, the *direct* hydrolysis of solid I affords *ca.* 21% cons–inv 2-octanol, but only 15% cons–ret 2-octanol. This net inversion in the conservation process has been tentatively attributed to "bimolecular displacement reactions occurring with inversion (and ^{16}O conservation), possibly between RN=N–^{16}OH molecules extracted into the organic phase."[4]

(12) E. H. White, *J. Amer. Chem. Soc.*, **77**, 6014 (1955).

(13) R. A. Moss and K. M. Luchter, *J. Org. Chem.*, in press.

(14) E. H. White and C. A. Aufdermarsh, Jr., *J. Amer. Chem. Soc.*, **83**, 1179 (1961).

TABLE III
STEREOCHEMISTRY OF THE CONSERVATION PATHWAYS OF SOME DEAMINATIVE REACTIONS

$$RN{=}NX \xrightarrow{\text{solvent}} N_2 + RX$$

R	X	Solvent	% retention	% inversion	Ref
$C_6H_5CHCH_3$	$OOCC_{10}H_7$	CH_3COOH	81	19	*a*
$C_6H_5CHCH_3$	OH	CH_3COOH	79	21	*b*
$C_6H_5CHCH_3$	OH	C_2H_5OH	87	13	*c*
$C_6H_5CHCH_3$	OC_2H_5	CH_2Cl_2	82	18	*c*
$C_2H_5CHCH_3$	OOC_6H_5	CH_3COOH	68	32	*d*
		Compared to			
$C_6H_{13}CHCH_3$	^{16}OH	HMPA-$H_2{}^{18}O$	73	27	*e*

[a] Reference 14. [b] R. Huisgen and C. Rüchardt, *Ann.*, **601**, 21 (1956). [c] Reference 2. [d] Reference 12. [e] This work.

all bimolecular reactions of octane-2-diazotic acid, and that some of the 6% of cons–inv 2-octanol still arises in this way. On the face of it, this seems unlikely, because the experimental procedure maintains a low concentration of the diazotic acid during its decomposition.

It could be argued that decomposition of protonated I is so rapid that it competes with the diffusive processes which equilibrate each drop of HMPT–I newly added to the water. Again, we doubt this. But, if the point is pressed, a curious logical impasse develops. If protonated I is held not to have been equilibrated before significant decomposition occurred, then neither can the HMPT be said to have dispersed. In view of the basic and nucleophile-potentiating character of HMPT,[15] the observed decrease in cons–inv 2-octanol might then be revealing less about possible bimolecular reactions of octane 2-diazotic acid during "direct" addition, than about a specific HMPT solvent effect during "inverse" addition. Indeed, we cannot completely rule out the possibility that a general HMPT solvent effect is at least partly responsible for the diminution in cons–inv 2-octanol. For, in the inverse addition, optically active I–$H_2{}^{18}O$ experiment, we were forced to use conditions which gave a *final* HMPT/H_2O mole ratio of ~0.2.

A referee has suggested that "a temperature effect may also be involved in view of the exothermic reaction that results on addition of water to the diazotate." It is true that temperature cannot be so easily controlled during the "direct" as opposed to the "inverse" hydrolysis. However, we suspect that the "exothermicity effect" is likely to be small, because a deliberate 40° temperature variation has only a small effect on the stereochemistry of the diazotate decomposition.[5] Moreover, the direct hydrolysis[4] was carried out at −20°, to allow for the exothermicity of the reaction; the inverse hydrolysis was done at 0°.

In conclusion, although the four pathways which, *via* Scheme I, lead to the four 2-octanols of eq 1, might be somewhat redistributed in other solvent systems, it seems likely that none would disappear entirely, and that their competition, an example of the deaminative counterion hypothesis,[6] is as germane in aqueous as it is in nonaqueous solvent systems.

Experimental Section

Stereochemical Runs.—Optically active octane-2-diazotate (potassium) (prepared from *l*-2-octylamine of 95% optical purity) was made as previously described.[4,5] A typical experiment, commencing with the optically active *N*-nitroso-*N*-2-octylurethane,[4,5] is described in order to illustrate how the HMPT–I solutions were prepared.

Potassium *tert*-butoxide (0.69 g, 6.15 mmol) was placed in a dry, nitrogen-filled, 50-ml, three-neck flask. After the addition of 11 ml of dry ether, the contents of the flask was magnetically stirred and cooled to −30°. A solution of 0.70 g (3.04 mmol) of optically active *N*-nitroso-*N*-2-octylurethane in 11 ml of dry ether was injected through a septum. The solution was stirred for 45 min at −30 to −20°. No gas evolution was observed. At the end of this period, the solvent was removed with a mechanical pump; the temperature was allowed to rise to *ca.* 25° during "drying."

A solution of 2.64 g (7.10 mmol) of dicyclohexyl-18-crown-6[7] (Du Pont Co., purified grade) in 25 ml of HMPT (distilled from CaH_2) was injected, and stirring produced a clear orange solution within 10 min. The solution was transferred by syringe to an addition funnel and then added, with stirring, over 30 min, to 200 ml of water at 0°. The reaction vessel was connected to a gas buret, and 87% of the theoretical gas evolution was observed during the addition process.

The product mixture was extracted with 150 ml of ether and then with four 100-ml portions of ether. The combined ethereal extracts were backwashed with water (two 100-ml portions), and then allowed to stand over $MgSO_4$ for 12 hr. Filtration and removal of solvent (rotary evaporator) gave 3.54 g of an oil, from which 55 μl of 2-octanol was isolated by iterative gc on a 5 ft × 0.25 in., 5% Carbowax on 45/60 Gas-Chrom P column. The operating conditions follow: injector, 215°; column, 90°; detector, 210°; helium head pressure, 20 psig.

After conversion of the 2-octanol to its L-acetyllactate diastereomers,[4] final analysis was carried out by gc on a 24 ft × 0.25 in., 10% 1,2,3-tris(2-cyanoethoxy)propane on 45/60 Gas-Chrom R column. The operating conditions follow: injector, 260°; column, 160°; detector, 240°; helium head pressure, 30 psig. Integration of the diastereomer peaks was by cut-and-weigh of Xerox copies of the original trace. Four copies were used for each trace, and three traces were obtained. The overall optical purity thus determined for the isolated 2-octanol was 30.02 ± 1.13%.[16] The diastereomer derived from *d*-2-octanol predominated. Taking account of the 95% optical purity of the initial amine, the stereochemical result was 31.6% net inversion.

A duplicate experiment gave 29.70 ± 0.97%[16] optically pure *d*-2-octanol, or 31.2% net inversion.

$H_2{}^{18}O$ Runs.—A similar procedure was used to prepare a solution of 0.61 mmol of racemic octane-2-diazotate in 5 ml of HMPT and 0.59 g (1.58 mmol) of the crown ether. This solution was slowly injected into 2.5 ml of Miles Laboratories' 20.82 atom % ^{18}O, D-normalized water. The precautions used in handling this water are discussed in our previous work.[4,5]

Nitrogen evolution was 88% of theory. The product mixture was poured into 50 ml of ether; the ether layer was separated and allowed to stand over $MgSO_4$ for at least 12 hr.[10] 2-Octanol was isolated by gc[17] of the (stripped) product mixture. Mass spectral analysis for $^{16}O/^{18}O$ on a consolidated Model 21-104 instrument, equipped with an electron multiplier, employed (principally) *m/e* 45 and 47. Corrections for natural heavy isotope abundances were made, based on the fragmentation pattern of the normal compound. There was 14.83 atom % of ^{18}O in the product 2-octanol. A second experiment afforded 2-octanol containing 15.74 atom % of ^{18}O.

Stereochemical ^{18}O Exchange Run.—This run was carried out as before, using 94% optically pure octane 2-diazotate and water which was 20.82 atom % ^{18}O, D normalized. Details appear in Table I.

The derived *d*- and *l*-2-octyl-L-acetyllactates were isolated by gc on the tris(2-cyanoethoxy)propane column and analyzed for $^{16}O/^{18}O$ by mass spectroscopy. Ions *m/e* 133 and 135[18] were principally employed. Corrections were made, based on the fragmentation pattern of the normal esters. The ester derived from *d*-2-octanol contained, per oxygen atom, 18.70 atom % ^{18}O. The ester derived from *l*-2-octanol contained 11.46 atom % ^{18}O.

(15) H. Normant, *Russ. Chem. Rev.*, **39**, 457 (1970); A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

(16) This error is the average deviation from the mean value of optical purity of the three gc traces. Within the analysis of each trace, deviation from the mean value of optical purity was smaller, *ca.* ±0.6%.

(17) On a 7 ft × 0.25 in. 5% Carbowax on 80/100 Chromosorb P column, 105°.

(18) These ions correspond to protonated acetyllactic acid: F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1967, p 137.

In contrast to our previous experience in determining 2-octanol optical purity by the gc-diastereomer method, the results in this run were imprecise. Thus, although the Xerox cut-outs of each of three traces were mutually consistent (four copies per trace, average deviations 1.30, 1.71, 1.13%), the final (uncorrected) optical purities obtained were 22.24, 32.72, and 26.94%. The average value was 27.30 ± 3.61%. The stereochemical course of the reaction was therefore 27.30/0.94 ~ 29% net inversion.

Although we cannot account for the poor precision in this stereochemical determination, we can show that the results in Table II, which partly rest upon this determination, are relatively unaffected. Thus, using the lower, uncorrected, net inversion limit of (27.30 − 3.61) = 23.69%, we calculate a final 2-octanol distribution of ex–ret, 20.00; ex–inv, 56.74; cons–ret, 17.40; and cons–inv, 5.85%. The final values corresponding to the higher, uncorrected, net inversion of 30.91% afford a distribution of 17.88, 60.21, 14.73, and 6.23%, respectively. These limiting values are very similar to the distribution shown in Table II, which is based on the average, uncorrected, net inversion of 27.30%.

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Reactions of Diazo Compounds with Tetrasubstituted 1,3-Cyclobutanediones and the Corresponding Dithiones. Isolation of Bis-Δ^3-1,3,4-thiadiazolines from the Dipolar Addition of Diazomethane to the Dithiones and Their Thermal Decomposition into Diepisulfides

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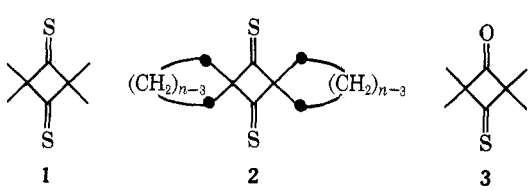
Tetramethyl-1,3-cyclobutanedithione (**1**), dispiro[4.1.4.1]dodecane-6,12-dithione (**2**, n = 5), and dispiro-[5.1.5.1]tetradecane-7,14-dithione (**2**, n = 6) on treatment with diazomethane at 0° lead to novel stereoisomeric bis-Δ^3-1,3,4-thiadiazolines **12**, **13** (n = 5), and **13** (n = 6), respectively. These bis adducts are reasonably stable and on thermolysis readily undergo loss of nitrogen to yield stereoisomeric mixtures of diepisulfides **17**, **18** (n = 5), and **18** (n = 6). Treatment of **1** with diphenyldiazomethane leads to the cis and trans diepisulfides **21**. Treatment of the diones **1** (S = O) and **2** (n = 4, 5, or 6; S = O) with ethanolic–ethereal diazomethane leads to the ring-expanded diones **22** and **23** (n = 4, 5, or 6), respectively. The relative ease of ring expansion stands in the order: **2** (n = 4; S = O) >>>> **2** (n = 5; S = O) > **1** (S = O) > **2** (n = 6; S = O). The possible reasons for this order are discussed.

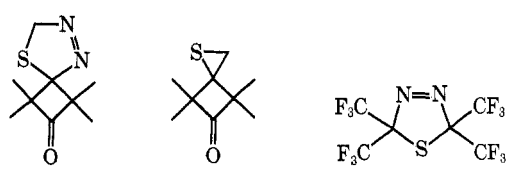
As part of a program designed to contrast the chemistry of –C=O and –C=S linkages, we have recently begun a study of various reactions of tetrasubstituted 1,3-cyclobutanedithiones **1** and **2** (n = 5 or 6) and the corresponding diones **1** (S = O) and **2** (n = 4, 5, or 6; S = O). This report deals with the reaction of diazomethane with dithiones **1** and **2** (n = 5 or 6) and diones **1** (S = O) and **2** (n = 4, 5, or 6; S = O).



1 **2** **3**

In general most simple aliphatic and alicyclic thiones are unstable in the monomeric state.[3] As a consequence, their chemistry and reactivity have not been fully investigated. The dithiones **1**[4] and **2** (n = 6)[5] and the monothione **3**[4a] have been prepared recently and join the ranks of such non-enethiolizable thiones as thiocamphor,[6] thiofenchone,[7] and adamantanethione[8] in possessing stable thione groups. Hexafluorothioacetone has been reported to undergo dimerization on standing for several hours.[9]

The reaction of several aliphatic thioketones with diazomethane (0°, ether) led to the corresponding episulfides along with methylthioalkenes (from the enethiol). In the case of diisopropyl thioketone only the episulfide was formed; in none of the cases was any thiadiazoline intermediate isolated.[10] Recently the reaction of **3** has been reported to lead to the unstable Δ^3-1,3,4-thiadiazoline **4** (tentatively characterized by ir and nmr spectroscopy).[11] The thiadiazoline **4** readily loses nitrogen to yield the episulfide **5**. Bis-



4 **5** **6**

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