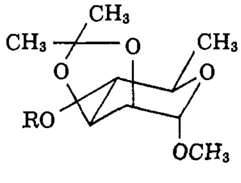
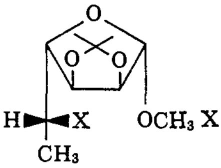
Formation of IIa results from inversion at C-4 and retention (or double inversion) at C-5 of Ia, while formation of IIIa is a result of inversions at both C-4 and C-5. Separation of the IIa–IIIa mixture was effected *via* their crystalline brosylates.



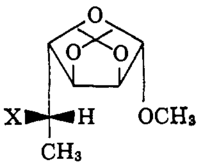
α-D-*manno*

Ia, R = Mes
b, R = Tos
c, R = Bros
d, R = H



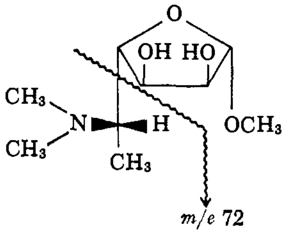
α-D-*talo*

IIa, X = OH
b, X = OBros
c, X = $C_6H_5CO_2$
d, X = OCH_3
e, X = NH_2
f, X = phthalimido

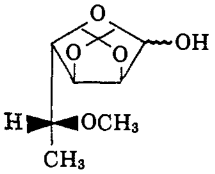


β-L-*allo*

IIIa, X = OH
b, X = OBros
c, X = OTos
d, X = N_3
e, X = NH_2
f, X = $N(CH_3)_2$



IV, β-L-*allo*



V, D-*talo*

The configurations of IIa and IIIa were determined as follows. Hydrogenation with Raney nickel of brosylate IIb, mp 85–86°, afforded IIa as an oil which was purified through its benzoate derivative IIc, mp 93–94°, $[\alpha]^{27}\text{D}$ 35.6° (*c* 0.92). Saponification of IIc and distillation gave pure IIa, $[\alpha]^{27}\text{D}$ 57.5 (*c* 1.27). Acid hydrolysis and phenylhydrazine treatment converted IIa to the osazone of 6-deoxy-D-talose,[7] mp 171–173°. In addition, the physical constants of IIa and c agreed with those reported for their L counterparts.[7] In much the same way, brosylate IIIb, mp 142–143°, was hydrogenated to give pure IIIa, $[\alpha]^{27}\text{D}$ 81.5° (*c* 0.84), and, again, IIIa gave the osazone of 6-deoxy-L-allose, mp 183–184°. The physical constants reported for the counterparts of IIIa,c[8] and the osazone[7,8] agree. Interconversion of IIa and IIIa with acetate ion in DMF and the synthesis of nitrogen derivatives with nucleophiles in DMF indicated that displacement reactions at C-5 of the furanose derivatives proceeded without further rearrangement. This result was, however, strictly dependent on reaction conditions (see below).

From brosylate IIb, amine IIIe (HCl), mp 233–234°, was prepared *via* azide IIId. Reductive methylation of IIIe gave the dimethylamino derivative IIIf (HCl), mp 155–156°. An nmr spectrum ($CDCl_3$) of the free base IIIf clearly revealed that the N–C–H proton, a broad multiplet at δ 2.34, was adjacent to the C-methyl group. Also, a mass spectrum of compound IV (picrate mp 194–195°) revealed an intense peak at *m/e* 72.[9]

The D-*talo* amine IIe (HCl), mp 183–184°, and phthalimido derivative IIf, mp 158–159°, were also prepared from IIIb by displacements in DMF. Lithium azide displacements in DMF attempted on the pyranose 4-*O*-sulfonates Ia and b gave complex mixtures from which, after reduction, the D-*talo* amine IIe (25%) was the only basic product isolated. Likewise, potassium phthalimide (DMF) with sulfonates Ia and c gave the D-*talo*-IIf (20%).

When mesylate Ia was heated at 170° (sealed tube) in dioxane–water (9:1) containing excess sodium bicarbonate or sodium hydroxide, three products, IIa, IIIa, and an unknown V, were formed in about 90% yield (ratios 1:2:6). The unknown V, a liquid, could be isolated (vpc) in 51% yield; $[\alpha]^{27}\text{D}$ −2.5° (*c* 0.48).

The mass spectrum of V indicated a 5-methoxy formulation, and its stereochemistry was shown by synthesis. Mild acid hydrolysis of V followed by phenylhydrazine treatment afforded a new osazone, VI, mp 195–196°. This same osazone was prepared from IId, $[\alpha]^{27}\text{D}$ 64.5° (*c* 2.8), which in turn had been prepared by silver oxide–methyl iodide treatment of IIa. The position of the isopropylidene bridge in V was confirmed when methylation of V produced a two-component mixture (2:1), the major product of which was IId (vpc). Acid hydrolysis of the mixture and phenylhydrazine treatment afforded, again, osazone VI. Had the isopropylidine bridged C-1 and C-2 in V, the above reaction sequence should not have produced osazone VI.

It was considered possible that Ia, under reaction conditions, had rearranged to an intermediate 5-*O*-mesyl-β-L-allofuranoside which then underwent the C-1–C-5 methoxyl migration. As a preliminary test of this consideration the brosylate IIIb was treated at 130° with 9:1 dioxane–water containing sodium hydroxide. Methoxyl migration did indeed occur, producing a reaction mixture (~90% yield) containing 89% V, 9% IIa, and 2% IIIa.

A 1,4 methoxyl migration has been shown to occur in an attempted displacement reaction on an open-chain lyxose derivative.[10,11] To our knowledge the pyranose–furanose ring contraction and accompanying 1,5 methoxyl migration described in this communication are new. Further work on the mechanism and scope of these rearrangements is in progress.

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[11] Previous attempted displacements of the sulfonate ester group of a 4-*O*-tosylate enantiomeric with I (L-rhamnose series) has led to conflicting results: see ref 5b and P. A. Levene and J. Compton, *J. Am. Chem. Soc.*, **57**, 2306 (1935).

Calvin L. Stevens, Ronald P. Glinski, K. Grant Taylor
Peter Blumbergs, Ferenc Sirokman
Department of Chemistry, Wayne State University
Detroit, Michigan 48202

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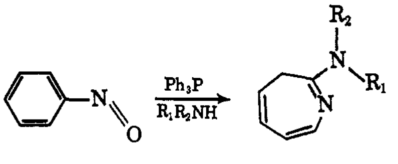
Rearrangement on Deoxygenation of Nitrosobenzene

Sir:

Current interest in deoxygenation of aromatic nitroso and nitro compounds with tervalent organophosphorus compounds stems from a parallelism of these reactions and the pyrolysis or photolysis of corresponding azides.

For example, reduction of *o*-nitrobutylbenzene with triethyl phosphite[1] yields a distribution of products strikingly similar to that obtained on pyrolysis of *o*-azidobutylbenzene,[2] and ring closure on treatment of *o*-nitrosobiphenyl[3] or *o*-nitrobiphenyl[4] with triethyl phosphite or triphenylphosphine is analogous to the thermolytic conversion of *o*-azidobiphenyl into carbazole.[5] These deoxygenation reactions among others[6] are considered by many authors[1,3,4,6] to proceed possibly *via* nitrene intermediates.

We wish to report that deoxygenation of nitrosobenzene with either triphenylphosphine or tributylphosphine in amine solvents results in ring enlargement with the ultimate formation of N-alkyl derivatives of 2-amino-3H-azepines. Similar products have been reported earlier for the photolysis[7] and pyrolysis[8] of phenyl azide in amines.



In a typical experiment, an ethereal solution of nitrosobenzene was added to a refluxing solution of triphenylphosphine in diethylamine. The work-up consisted of distillation of excess solvent and separation of the partially crystalline residue into solid and liquid fractions which were handled separately. The solid, after recrystallization from ethanol, afforded a 70% yield of triphenylphosphine oxide, mp 155.5–156.6°. On distillation the liquid yielded 2-diethylamino-3H-azepine[9] (62%), bp 59.0–61.0° (0.1 mm), $n^{25.5}$ 1.5513.

The yields of alkyl-2-amino-3H-azepine and triphenylphosphine oxide are markedly dependent on the amine. Both decrease with decreasing molecular weight of amine (see Table I). The reaction takes a different course in liquid ammonia, yielding only 18% of triphenylphosphine oxide and trace amounts of aniline[10] as the only basic product. Triphenylphosphine appears to be moderately more effective than tributylphosphine on the basis of comparable experiments in dimethylamine (Table I).

Elemental analysis of the three new alkyl-2-amino-3H-azepines are satisfactory. The infrared spectra of all these azepines are characterized by two strong absorption bands between 1500 and 1600 cm^{-1}: R_1 (C_2H_5), R_2 (C_2H_5) at 1510 and 1560 cm^{-1}; R_1 (n-C_4H_9), R_2 (H) at 1522 and 1599 cm^{-1}; R_1 (CH_3), R_2 (CH_3) at 1510–1560 cm^{-1}; R_1 (CH_3), R_2 (H) at 1522 and 1590 cm^{-1}.

Table I. Yields of Alkyl-3H-azepine and Triphenylphosphine Oxide for Various Amines

Amine		Yield, %	
R_1	R_2	Azepine	Phosphine oxide
C_2H_5	C_2H_5	62	70
n-C_4H_9	H	60	70
CH_3	CH_3	50	65
CH_3	H	4	34

A detailed analysis of the nmr spectrum of 2-diethylamino-3H-azepine and the concomitant basis for structural assignment have been described recently.[7] The portions of the other spectra assigned to the seven ring protons are remarkably similar and, therefore, subject to a similar analysis. A generalized description of all four spectra follows:[11] a quartet (2 H) which appears to be the superpositions of two triplets, in the range τ 7.49–7.39; a quartet in the range τ 4.87–5.00; a quartet in the range τ 4.28–4.38; a quartet in the range τ 3.73–3.80; a doublet in the range τ 2.95–3.04.

Phenyl nitrene and 7-azabicyclo[4.1.0]hepta-2,4,6-triene have been hypothesized as intermediates in the rearrangement of phenyl azide.[7,8] On the basis of this work and that of Sundberg,[1] the same hypothesis is reasonable for the rearrangement of nitrosobenzene.

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(9) The nmr, infrared, and ultraviolet spectra are identical with those reported for the compound prepared by photolysis of phenyl azide in diethylamine.[7]

(10) Analysis of the crude liquid fraction from the amine reactions by gas chromatography always revealed small quantities of aniline. In one case, dimethylamine, N′,N′-dimethyl-N-phenylhydrazine was also present as a minor constituent. This hydrazine along with aniline are products amounting to a few per cent from the photolysis of phenyl azide in dimethylamine.

(11) All nmr spectra were determined with a Varian A-60 spectrometer using tetramethylsilane as an internal standard. Multiplets for all of the five types of ring protons are centered within these ranges.

Robert A. Odum, Martin Brenner
Department of Chemistry
Brooklyn College of the City University of New York
Brooklyn, New York 11210

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Some Novel Features in the Mass Spectra of Polynuclear Metal Carbonyl Derivatives[1]

Sir:

The positive ion mass spectra of numerous metal carbonyl derivatives are presently being studied in this laboratory.[2] Some preliminary results are now being reported in several areas of special significance regarding both metal–metal bonding and the nature of some unusual olefin complexes of iron carbonyl.

I. **"Bare" Metal Cluster Ions.** The tendency for metal carbonyls containing no other ligands to lose carbonyl groups stepwise upon electron bombardment in the mass spectrometer has been demonstrated for the mononuclear derivatives $M(CO)_x$ (x = 6, M = Cr, Mo, or W;[3,4] x = 5, M = Fe;[4,5] x = 4, M = Ni[5]) and the binuclear derivatives $Co_2(CO)_8$ and $Mn_2(CO)_{10}$.[6] Extension of this effect has now resulted in the observa-

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(1) The author is indebted to the National Science Foundation for partial support of this work under Grant GP-3954.

(2) The mass spectra reported in this communication were taken at 70-ev electron energies on an Associated Electrical Industries MS-9 mass spectrometer. The author is indebted to Mr. R. E. Rhodes for taking the mass spectra.

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