The α-isotope effects characteristic of limiting solvolysis reactions of fluorides and iodides have not yet been experimentally established; on the basis that $K_{ex}^{\ddagger}$ is again unity we predict (using $(k_H/k_D)_{Br} = 1.125$) that the values per deuterium are ~ 1.22 and ~ 1.09, respectively. Unfortunately, no appropriate model force field is available for ionization of a C–O bond. However, α-deuterium effects in arenesulfonate solvolyses have been observed to be as large as 1.20,[10] so, if the analogy with halide solvolysis holds, the force constants for the HCO bending motion must be nearly as large as those for the corresponding HCF motion. We believe that α-deuterium effects much different from the values given above must at least in part involve different rate-determining steps.[11]

(10) V. J. Shiner, Jr., and J. G. Jewett, *J. Amer. Chem. Soc.*, **86**, 945 (1964).

(11) Note Added in Proof. A referee has pointed out that a recent note (A. Guinot and G. Lamaty, *Chem. Commun.*, 960 (1967)) reports an unusually large isotope effect in the solvolysis of 1-chloro-1-phenylethane-2,2,2-d_3 in 95% ethanol. He suggests that the α effect may also be abnormally large in this solvent and that the present analysis based on an approximate maximum α effect of 1.15 (25°) for a limiting reaction may not be correct. Dr. Lamaty has informed us that measurements in 95% ethanol on 1-chloro-1-phenylethane-1-*d* give a k_H/k_D ratio of 1.13 ± 0.02 at 50%, consistent with our interpretation; it appears that an artifact, the exact nature of which is under active investigation, caused the β-deuterium effect referred to above to be unusually large.

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Tris(triphenylphosphine)ruthenium Nitrogen Dihydride

Sir:

Preparations of $[(NH_3)_5RuN_2]^{2+}$ [1-3] and of a tris(triphenylphosphine)cobalt nitrogen complex[4-7] by routes involving facile reactions of molecular nitrogen have been reported. More recently a communication revealed that passage of nitrogen through a benzene solution of $[(C_6H_5)_3P]_4RuH_2$ appeared to result in the formation of a triphenylphosphine ruthenium nitrogen complex, although the complex could not be isolated.[8] Working along similar lines we have found that a nitrogen complex can be easily isolated from the reaction of $[(C_6H_5)_3P]_3RuHCl$[9] with triethylaluminum and nitrogen in ether. The complex, $[(C_6H_5)_3P]_3Ru(N_2)H_2$, readily loses nitrogen when treated with additional triphenylphosphine. This observation probably explains the failure to isolate a nitrogen complex from the tetrakis(triphenylphosphine)ruthenium solutions.

$[(C_6H_5)_3P]_3Ru(N_2)H_2$ is an air-sensitive solid which is almost white when pure but frequently is tan or red-brown. It can be recrystallized from benzene–hexane in a nitrogen atmosphere and is stable indefinitely at room temperature. It darkens above 140° and melts at 185°.

Anal. Calcd for $[(C_6H_5)_3P]_3Ru(N_2)H_2$: C, 70.9; H, 5.2; N, 3.1; P, 10.1; Ru, 10.9. Found: C, 70.9; H, 5.3; N, 3.2; P, 10.2; Ru, 10.7.

The infrared spectrum (Nujol mull) has a strong sharp band at 2147 cm^{-1} assigned to the coordinated nitrogen moiety and bands of moderate intensity at 1947 and 1917 cm^{-1} assignable to ruthenium–hydrogen stretching. The assigned composition is further supported by reaction of the complex with hydrogen chloride.

$$[(C_6H_5)_3P]_3Ru(N_2)H_2 \xrightarrow{HCl} [(C_6H_5)_3P]_3RuCl_2 + \underset{81\%}{N_2} + \underset{94\%}{2H_2}$$

The nitrogen in $[(C_6H_5)_3P]_3Ru(N_2)H_2$ is reversibly displaced by ammonia and by hydrogen, forming $[(C_6H_5)_3P]_3Ru(NH_3)H_2$ and $[(C_6H_5)_3P]_3RuH_4$, respectively. Characterization of the latter product as a tetrahydride is supported by sequential reactions with triphenylphosphine and hydrogen chloride.

$$[(C_6H_5)_3P]_3RuH_4 \xrightarrow{(C_6H_5)_3P} \underset{84\%}{H_2} + [(C_6H_5)_3P]_4RuH_2 \xrightarrow{HCl} \underset{83\%}{[(C_6H_5)_3P]_4RuCl_2 + 2H_2}$$

Solutions of the nitrogen complex are stable in a nitrogen atmosphere but slowly lose nitrogen in an argon atmosphere. A tetrahydrofuran solution initially containing both $[(C_6H_5)_3P]_3Ru(N_2)H_2$ and $[(C_6H_5)_3P]_3Ru(NH_3)H_2$ in an argon atmosphere slowly deposits a yellow crystalline solid. Elemental analysis reveals this has the composition $[(C_6H_5)_3P]_5Ru_4(NH_3)_3$. Insolubility has precluded molecular weight measurements; there is no infrared absorption indicative of ruthenium–hydrogen bonds.

Anal. Calcd for $[(C_6H_5)_3P]_5Ru_4(NH_3)_3$: C, 61.2; H, 4.8; N, 2.4; P, 8.8. Found: C, 61.0; H, 5.2; N, 2.3; P, 8.2.

It is postulated that this cluster is a trigonal pyramid consisting of a $[(C_6H_5)_3P]_2Ru$ moiety (from the nitrogen complex *via* loss of triphenylphosphine, nitrogen, and hydrogen) and three $(C_6H_5)_3PRuNH_3$ moieties (from the ammonia complex *via* loss of triphenylphosphine and hydrogen).

It was reported previously that the phenyl groups in $[(C_6H_5)_3P]_3Co(N_2)H$ undergo deuterium–hydrogen exchange at the *ortho* positions.[10] A similar phenomenon is found in the ruthenium system. In an equilibration experiment, 84% of the theoretical amount of hydrogen expected from complete exchange of all *ortho* hy-

(1) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).

(2) A. D. Allen, *et al.*, *J. Amer. Chem. Soc.*, **89**, 5595 (1967).

(3) D. E. Harrison and H. Taube, *ibid.*, **89**, 5706 (1967).

(4) A. Misono, Y. Uchida, and T. Saito, *Bull. Chem. Soc. Japan*, **40**, 700 (1967).

(5) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, 79 (1967); *J. Amer. Chem. Soc.*, **89**, 3071 (1967).

(6) (a) A. Sacco and M. Rossi, *ibid.*, 316 (1967); (b) *Inorg. Chim. Acta*, **2**, 127 (1968).

(7) J. H. Enemark, B. R. Davis, J. A. McGinnety, and J. A. Ibers, *Chem. Comm.*, **2**, 96 (1968).

(8) A. Yamamoto, S. Kitazume, and S. Ikeda, *J. Amer. Chem. Soc.*, **90**, 1089 (1968).

(9) P. S. Hallman, D. Evans, J. A. Osborn, and G. Wilkinson, *Chem. Commun.*, 305 (1967).

(10) G. W. Parshall, *J. Amer. Chem. Soc.*, **90**, 1669 (1968).

drogen atoms was evolved upon treatment of the nitrogen complex with deuterium in benzene for 24 hr at 25°. In a similar experiment at 65° for 2 days, oxidation of the exchange product with hydrogen peroxide gave triphenylphosphine oxide in which proton nmr revealed 82% *ortho* deuteration.[11]

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A New Synthesis of Diazenes. The Preparation and Properties of *trans*-Methyldiazene

Sir:

Diazene, HN=NH, has been proposed as an intermediate in the reaction of hydroxylamine-O-sulfonic acid (I) with hydroxylamine in alkaline solution. Evidence for diazene in this system is the hydrogenation of multiple bonds when olefins and azo compounds are present.[1] We have investigated the kinetics of the reaction of I with hydroxylamine in aqueous solution and have found the rate law to be rate = $k[\mathrm{OH^-}][\mathrm{H_2NOH}][\mathrm{H_2NOSO_3^-}]$. Since similar studies with hydrazine and I revealed no hydroxide ion concentration dependence, we were led to investigate the reaction of I with N- and O-substituted hydroxylamines to clarify the role of the hydroxide ion. We have found that the reaction of I with N-methylhydroxylamine (II) in aqueous sodium hydroxide solution produces *trans*-methyldiazene (III), which is surprisingly stable.

$$\underset{\mathrm{I}}{\mathrm{H_2NOSO_3^-}} + \underset{\mathrm{II}}{\mathrm{CH_3NHOH}} + \mathrm{OH^-} \longrightarrow \underset{\mathrm{III}}{\mathrm{CH_3N{=}NH}} + \mathrm{SO_4^{2-}} + \mathrm{H_2O} \quad (1)$$

To a solution of II in aqueous sodium hydroxide was added a solution of I. Final concentrations of each reactant and the hydroxide ion were about 0.1 *M*. Gas evolution began immediately, and a nitrogen dioxide like odor was detectable. An ultraviolet spectrum of the solution revealed the growth of a peak with $\lambda_{\max}$ at 350 mμ. This peak reached maximum intensity in 2–3 min and then disappeared over a period of hours. The stoichiometry was consistent with eq 1 and with III subsequently decomposing as in eq 2 and 3.

$$\mathrm{CH_3N{=}NH} \longrightarrow \mathrm{CH_4} + \mathrm{N_2} \quad (2)$$

$$\mathrm{CH_3N{=}NH} \longrightarrow \mathrm{CH_2{=}NNH_2} \xrightarrow{\mathrm{H_2O}} \mathrm{H_2CO} + \mathrm{H_2NNH_2} \quad (3)$$

The formation and *trans* configuration of III was confirmed by its ultraviolet spectrum $\lambda_{\max}$ 350 mμ (ϵ 24)[2] and its gas-phase infrared spectrum.

Table I. Observed Infrared Bands of *trans*-Methyldiazene and *trans*-Methyldiazene-N-d_1[a–c]

	trans-Methyldiazene			*trans*-Methyldiazene-N-d_1		
Symmetry	Freq, cm^{-1}	I	Shape	Freq, cm^{-1}	I	Shape
a′	3130	m	A			
	2900–3000[b]	m		2920[b]	m	A
				~2870[b]	m	
				2320	m	A
	1575	w	A	1550	w	A
	1410[b]	m	B	1405[b]	m	B
	1125	m		1060	m	A
				890	m	A
	550	m	B	535	m	A
a′′				2985	m	C
	1470[b]	m	C	1450[b]	m	C
	1140	m	C			
	844	m	C	662	m	C
a′	920	w	A	2110	w	A?

[a] Bands given are believed to be fundamentals except for the last entry for each molecule. Ten a′ and five a′′ fundamentals are expected. [b] Absorption by methane or methane-d_1 in the 2900–3100- and 1150–1450-cm^{-1} regions may have prevented observation of some bands, while those observed in these regions may have been subject to an error of more than ±5 cm^{-1} generally assigned to all bands. [c] The a′′ fundamentals fit the product rule satisfactorily (0.745 calcd, 0.775 found); failure to identify all of the fundamentals that should shift appreciably precludes such a calculation for the a′ modes.

The infrared spectrum of the gas evolved in reaction 1 displayed the bands presented in the left half of Table I. The intensity of these bands decreased with time, and ultimately a spectrum of methane[3] was obtained. When reaction 1 was carried out in deuterium oxide, the infrared spectrum contained the bands presented in the right half of Table I; the spectrum was ultimately that of methane-d_1.[3] In the gas phase III decomposed faster than the N-deuterio isomer IV. Consequently we did not obtain as intense a spectrum of III as of IV, and have placed correspondingly greater confidence in the latter. Confident assignments were made to the N—H stretch at 3130 (2320 in IV), the N=N stretch at 1575 (1550), and the N—H out-of-plane bend at 844 cm^{-1} (662). The N—H stretch agrees with that found for *trans*-diazene.[4]

In addition to survey infrared spectra, high-resolution scans were made of the 844- and 662-cm^{-1} bands on a Perkin-Elmer 621 spectrometer. In analyzing the well-developed rotational structure, the following structural parameters were assumed for methyldiazene: $r_{\mathrm{N-H}} = 1.014$,[5a] $r_{\mathrm{C-H}} = 1.093$,[5a] $r_{\mathrm{C-N}} = 1.470$,[5a,b] and $r_{\mathrm{N=N}} = 1.240$ Å[5b]; $\angle\mathrm{NNH} = 110$,[4] $\angle\mathrm{HCH} = \angle\mathrm{HCN} = 109.5$,[5a] and $\angle\mathrm{CNN} = 110°$.[5b,6]

Moments of inertia and rotational constants were calculated for the *cis* and *trans* configurations of III and IV. The two isomers are near-prolate ($\kappa \sim -0.95$), and calculations for rotamers gave identical results. On the symmetric top approximation the rotational spacings of the near-perpendicular, type-C bands were predicted to be 2.65 (*cis*-III), 2.26 (*cis*-IV), 3.28 (*trans*-III), and 3.32 cm^{-1} (*trans*-IV). Examination of the 844-cm^{-1} band of III and the 662-cm^{-1} band of IV gave average spacings of 3.25 and 3.21 cm^{-1}, respectively. Both the magnitude of the spacing and the small change upon deuteration strongly supported the *trans* configuration. Variation of the NNH angle (±10°) did not appreciably affect these calculations,

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[1] E. Schmitz, R. Ohme, and G. Kozakiewcz, *Z. Anorg. Allgem. Chem.*, **339**, 44 (1965).

[2] For azomethane the *trans* isomer has $\lambda_{\max}$ 343 mμ (ϵ 25), and the *cis* isomer has $\lambda_{\max}$ 353 mμ (ϵ 240): R. F. Hutton and C. Steel, *J. Am. Chem. Soc.*, **86**, 745 (1964).

[3] J. K. Wilmshurst and H. J. Bernstein, *Can. J. Chem.*, **35**, 226 (1957).

[4] A. Trombetti, *Can. J. Phys.*, **46**, 1005 (1968).

[5] "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958: (a) methylamine, p M115; (b) *trans*-azomethane, p M137.

[6] J. H. Bryden, *Acta Cryst.*, **14**, 61 (1961).