

The  $\alpha$ -isotope effects characteristic of limiting solvolysis reactions of fluorides and iodides have not yet been experimentally established; on the basis that  $K_{ex}^{\pm}$  is again unity we predict (using  $(k_H/k_D)_{Br} = 1.125$ ) that the values per deuterium are  $\sim 1.22$  and  $\sim 1.09$ , respectively. Unfortunately, no appropriate model force field is available for ionization of a C-O bond. However,  $\alpha$ -deuterium effects in arenesulfonate solvolyses have been observed to be as large as 1.20,<sup>10</sup> 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  $\alpha$ -deuterium effects much different from the values given above must at least in part involve different rate-determining steps.<sup>11</sup>

(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. Guinet 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*<sub>3</sub> in 95% ethanol. He suggests that the  $\alpha$  effect may also be abnormally large in this solvent and that the present analysis based on an approximate maximum  $\alpha$  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  $1.13 \pm 0.02$  at 50%, consistent with our interpretation; it appears that an artifact, the exact nature of which is under active investigation, caused the  $\beta$ -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<sup>4-7</sup> 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.<sup>8</sup>

(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 M. 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).

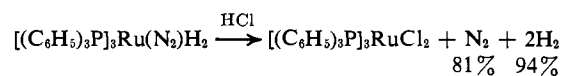
(8) A. Yamamoto, S. Kitazume, and S. Ikeda, *J. Amer. Chem. Soc.*, **90**, 1089 (1968).

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.

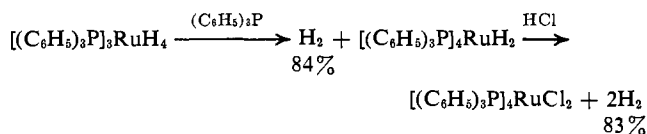
$[(C_6H_5)_3P]_3Ru(N_2)H_2$  is an air-sensitive solid which is almost white when pure but frequently is tan or red-brown. It can be recrystallized from benzene-hexane in a nitrogen atmosphere and is stable indefinitely at room temperature. It darkens above 140° and melts at 185°.

*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.



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.



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.<sup>10</sup> 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-

(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.<sup>11</sup>

(11) Acknowledgment is made to G. W. Parshall for the deuterium-exchange experiments.

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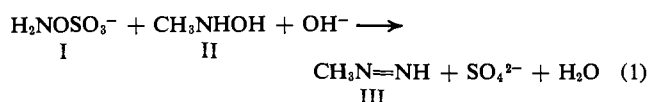
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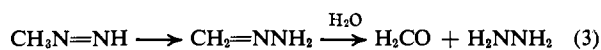
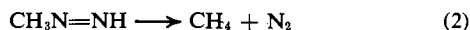
## A New Synthesis of Diazenes. The Preparation and Properties of *trans*-Methyldiazene

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.<sup>1</sup> We have investigated the kinetics of the reaction of I with hydroxylamine in aqueous solution and have found the rate law to be  $\text{rate} = k[\text{OH}^-][\text{H}_2\text{NOH}][\text{H}_2\text{NOSO}_3^-]$ . 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.



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  $\lambda_{\text{max}}$  at 350 m $\mu$ . 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.



The formation and *trans* configuration of III was confirmed by its ultraviolet spectrum  $\lambda_{\text{max}}$  350 m $\mu$  ( $\epsilon$  24)<sup>2</sup> and its gas-phase infrared spectrum.

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<sup>3</sup> was obtained. When reaction 1 was carried out in deuterium oxide,

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

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

Table I. Observed Infrared Bands of *trans*-Methyldiazene and *trans*-Methyldiazene-N-*d*<sub>1</sub><sup>a-c</sup>

Symmetry	<i>trans</i> -Methyldiazene		<i>trans</i> -Methyldiazene-N- <i>d</i> <sub>1</sub>			
	Freq, cm <sup>-1</sup>	I	Shape	Freq, cm <sup>-1</sup>	I	Shape
a'	3130	m	A			
	2900–3000 <sup>b</sup>	m		2920 <sup>b</sup>	m	A
				~2870 <sup>b</sup>	m	
				2320	m	A
				1550	w	A
a''	1575	w	A	1405 <sup>b</sup>	m	B
	1410 <sup>b</sup>	m	B	1060	m	A
	1125	m		890	m	A
				535	m	A
	550	m	B	2985	m	C
				1450 <sup>b</sup>	m	C
	1470 <sup>b</sup>	m	C			
	1140	m	C			
	844	m	C	662	m	C
	920	w	A	2110	w	A?

<sup>a</sup> Bands given are believed to be fundamentals except for the last entry for each molecule. Ten a' and five a'' fundamentals are expected. <sup>b</sup> Absorption by methane or methane-*d*<sub>1</sub> in the 2900–3100- and 1150–1450-cm<sup>-1</sup> regions may have prevented observation of some bands, while those observed in these regions may have been subject to an error of more than  $\pm 5$  cm<sup>-1</sup> generally assigned to all bands. <sup>c</sup> 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 contained the bands presented in the right half of Table I; the spectrum was ultimately that of methane-*d*<sub>1</sub>.<sup>3</sup> 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<sup>-1</sup> (662). The N—H stretch agrees with that found for *trans*-diazene.<sup>4</sup>

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

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<sup>-1</sup> (*trans*-IV). Examination of the 844-cm<sup>-1</sup> band of III and the 662-cm<sup>-1</sup> band of IV gave average spacings of 3.25 and 3.21 cm<sup>-1</sup>, respectively. Both the magnitude of the spacing and the small change upon deuteration strongly supported the *trans* configuration. Variation of the NNH angle ( $\pm 10$ °) did not appreciably affect these calculations,

(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).