TABLE III

TRISPEROXYSILANE

Registry no.	Compd	Yield, % (lit.)	Dec temp, °C	Physical characteristics, lit.	O–O frequency in the ir, cm⁻¹	Characteristic nmr signals, δ
5797-01-3	Tris(*tert*-butylperoxy)silane	55	120	Colorless liquid	940 (s), 940 (s)	1.28 (s, 27, *tert*-butyl), *ca.* 1.35 (s, 1, silane)
10196-45-9	Methyltris(*tert*-butylperoxy)silane[a]	78 (49)[g]	150	Colorless liquid, bp 50° (0.1 mm)[h]	913 (s), 927 (s)	0.45 (s, 3, methyl), 1.28 (s, 27, *tert*-butyl)
31602-50-3	Methyltris(α,α-dimethylbenzylperoxy)silane	57	100	Colorless liquid	923 (s)	0.45 (s, 3, methyl), 1.57 (s, 18, isopropyl), 7.35 (m, 15, phenyl)
31218-59-4	*n*-Hexyltris(*tert*-butylperoxy)silane	76	164	Colorless liquid	912 (s), 927 (m)	0.91 (t, 3, methyl), 1.27 (s, 27, *tert*-butyl)
39810-12-3	*n*-Hexyltris(α,α-dimethylbenzylperoxy)silane	95	154	Colorless liquid	912 (s)	0.91 (t, 3, methyl), 1.57 (s, 18, isopropyl), 7.35 (m, 15, phenyl)
31218-60-7	*n*-Dodecyltris(*tert*-butylperoxy)silane	90	155	Colorless liquid	912 (m), 927 (w)	*Ca.* 0.95 (t, 3, methyl), 1.27 (s, 27, *tert*-butyl)
39810-14-5	*n*-Dodecyltris(α,α-dimethylbenzylperoxy)silane	95	152	Colorless liquid	905 (m), 917 (m)	*Ca.* 0.95 (t, 3, methyl), 1.57 (s, 18, isopropyl), 7.30 (m, 15, phenyl)
15188-09-7	Vinyltris(*tert*-butylperoxy)silane[b]	86 (40)[i]	154	Colorless liquid, bp 78° (1 mm)[j]	913 (s), 930 (m)	1.27 (s, 27, *tert*-butyl), *ca.* 6.22 (m, 3, vinyl)
24685-79-8	Vinyltris(α,α-dimethylbenzylperoxy)silane	93	140	Slightly yellowish liquid	917 (s)	1.57 (s, 18, isopropyl), *ca.* 6.18 (m, 3, vinyl), 7.30 (m, 15, phenyl)
27612-79-9	Allyltris(*tert*-butylperoxy)silane[c]	80	174	Colorless liquid	917 (s), 927 (s)	1.27 (s, 27, *tert*-butyl), 2.05 (m, 2, methylenesilyl)
39810-18-9	Phenyltris(α,α-dimethylbenzylperoxy)silane	61	*f*	Colorless liquid	910–920 (m)	1.57 (s, 18, isopropyl)
39810-19-0	3,3,3-Trifluoropropyltris(*tert*-butylperoxy)silane	80	177	Colorless liquid	913–926 (s)	1.25 (s, 27, *tert*-butyl)
27714-68-7	γ-Methacryloxypropyltris(*tert*-butylperoxy)silane[d]	70	193	Colorless liquid	910 (m), 930 (m)	1.29 (s, 27, *tert*-butyl), 1.95 (s, 3, methyl), 4.17 (t, 2, ether methylene)
27612-88-0	Isocyanatopropyltris(*tert*-butylperoxy)silane[e]	88	140	Colorless liquid	908–920 (s)	

[a] Calcd for $C_{13}H_{30}O_6Si$: C, 50.32; H, 9.68. Found: C, 50.00; H, 9.29. [b] Calcd for $C_{14}H_{30}O_6Si$: C, 52.46; H, 9.43. Found: C, 50.15; H, 9.22. [c] Calcd for $C_{15}H_{32}O_6Si$: C, 53.53; H, 9.58. Found: C, 51.20; H, 9.25. [d] Calcd for $C_{19}H_{38}O_8Si$: C, 54.02; H, 9.00. Found: C, 53.79; H, 8.78. [e] Calcd for $C_{16}H_{33}NO_7Si$: C, 50.66; H, 8.71. Found: C, 50.01; H, 8.41. [f] Decomposed gradually upon standing at room temperature. [g] Reference 11. [h] Reference 9. [i] Reference 10. [j] Reference 8.

TABLE IV

TETRAKISPEROXYSILANE

Registry no.	Compd	Yield, %	Dec temp, °C	Physical characteristics, lit.	O–O frequency in the ir, cm⁻¹	Characteristic nmr signals, δ
10196-46-0	Tetrakis(*tert*-butylperoxy)silane[a]	64	135	White crystal of mp 53°, 35–40°[c]	922 (m), 940 (s)	1.28 (s, 36, *tert*-butyl)
39810-23-6	Tetrakis(α,α-dimethylbenzylperoxy)silane[b]	64	<100	Viscous liquid	920–940 (s)	1.55 (s, 24, isopropyl), 7.35 (m, 20, phenyl)

[a] Calcd for $C_{16}H_{36}O_8Si$: C, 50.00; H, 9.37. Found: C, 49.69; H, 9.06. [b] Calcd for $C_{36}H_{44}O_8Si$: C, 68.35; H, 6.96. Found: C, 67.15; H, 6.59. [c] Reference 9.

tion usually occurred and the reaction temperature was kept below 35°, preferably below 15°, by adjusting the addition rate of halosilane and by using an outside cooling bath. The reaction was practically completed upon finishing addition of halosilane, although an additional 30 min of stirring was normally employed. The insoluble Dabco–HX salt was removed by filtration and used for regenerating the Dabco. The silyl alkyl peroxide was collected from the filtrate by evaporating the solvent under vacuum. The yield was usually greater than 70%. Occasionally, the product may be slightly colored. The color can be removed by a treatment with charcoal.

Silyl Alkyl Peroxides *via* the Hexa–Hydroperoxide Adduct Method. General.—To a slurry of Hexa–hydroperoxide adduct, anhydrous calcium chloride (excess amount) and an inert medium was added, while, under cooling, a stoichiometric amount of halosilane. The reaction was usually rapid and exothermic. Upon completion of reaction, the insoluble Hexa–HX and calcium chloride salts were removed by filtration and discarded. The silyl alkyl peroxide was recovered from the filtrate by evaporating the solvent. The yield and product purity are usually comparable but not quite as good as those of the Dabco–hydroperoxide salt method.

Instrumental.—The Varian Model A-60 and HA-100 instruments were used for the nmr measurements. Tetramethylsilane and $CDCl_3$ were employed as the internal standard and solvent, respectively. For infrared spectra, a Perkin-Elmer Model 221 was used with either KBr pellets or liquid film on NaCl plates. Thermal decomposition temperatures were taken with a Thomas-Hoover capillary apparatus.

Registry No.—Hexa-*tert*-butyl hydroperoxide adduct, 39810-24-7; Dabco–hydroperoxide adduct, 39810-25-8.

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Reactions of *N*-Nitrosamines with Grignard and Lithium Reagents

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In the course of studies on nitrogen-centered radicals we had the occasion to examine the reaction of *N*-nitrosamines with organometallic reagents. It is the purpose of this note to report the results of this study.

The early work in this area was carried out by Wieland and his coworkers. Thus Wieland and Fressel[1] found that the principal product in the reaction of *N*-nitrosodiethylamine and ethylmagnesium iodide was the diethylhydrazone of acetaldehyde, while the products with phenylmagnesium bromide were 1-phenyl-2,2-diethylhydrazine and a small amount of 1-ethyl-1-α-phenylethyl-2-phenylhydrazine. Reactions of *N*-nitrosodiarylamines with arylmagnesium halides were reported to give triarylhydrazines,[2,3] although *N,N,N'*-triphenyl-*o*-phenylenediamine (or an isomer) was reported to be the important product in a study of the reaction carried out by Gilman and Heck.[4]

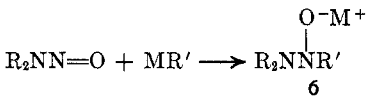
We examined the reactions of diethylnitrosamine (**1**), diisopropylnitrosamine (**2**), diphenylnitrosamine (**3**), and dimethylnitrosamine (**4**) with methylmagnesium bromide, phenylmagnesium bromide, and methyllithium. The results are presented in Table I.

TABLE I

PRODUCTS OF REACTIONS OF *N*-NITROSAMINES WITH ORGANOMETALLIC REAGENTS

Reaction (temp, °C)	Products (yield, %)
$Et_2NNO + 3MeMgBr$	$H_2C{=}NNEt_2$ (4), Et_2NNMe_2 (4), $CH_3CH{=}NNEt_2$ (4), Et_2NNHEt (20)
$Et_2NNO + MeLi$ (35)	Et_2NNHEt (41), $Et_2NN{=}CH\text{-}CH_3$ (<2)
$Et_2NNO + MeLi$ (−40)	$Et_2NN{=}CH_2$ (80)
$Et_2NNO + PhMgBr$	$Et_2NNHC_6H_5$ (50)
$(Me_2CH)_2NNO + MeLi$	$(Me_2CH)_2NN{=}CH_2$ (30)
$(Me_2CH)_2NNO + MeMgBr$ or $PhMgBr$	No reaction
$Ph_2NNO + MeMgBr$	$Ph_2NN{=}CH_2$ (30)
$Ph_2NNO + MeLi$	Tar, trace Ph_2NH
$Ph_2NNO + 2PhMgBr$	Ph_2N-*o*-C_6H_4NHPh (**5**) (5) plus tar
$Ph_2NNO + 5\ PhMgBr$	**5** (9), Ph_2NNHPh (3)
$Me_2NNO + MeLi$ (room temperature or −70)	Complex mixture (at least 8 products)

It is reasonable to assume that the initial reaction of *N*-nitrosamines with organometallic reagents should be the addition to the N=O double bond (eq 1). In



$$R_2NN{=}O + MR' \longrightarrow \underset{\mathbf{6}}{R_2N\overset{O^-M^+}{\overset{|}{N}}R'} \qquad (1)$$

the case of the Grignard reagents this reaction may be preceded by the formation of a loose complex between the organometallic and the substrate. This was dramatically demonstrated in the reaction of diisopropylnitrosamine (**2**) with methylmagnesium bromide in ether solution. When the reactants were mixed the reaction mixture separated into two phases, the upper layer being primarily ether with a little **2** while the lower layer was a brownish, viscous oil which decomposed exothermally when exposed to the atmosphere. When the oil was hydrolyzed with water, better than 90% of the nitrosamine was recovered. The complex was apparently soluble in tetrahydrofuran but again the reaction did not proceed further. The formation of a similar complex was noted in the reaction of nitrosobenzene and phenylmagnesium bromide.[5] In that case, however, the complex dissolved when excess Grignard reagent was added. The complex is probably not compound **6** because attempts to trap it with methyl iodide or benzoyl chloride were unsuccessful.

Compound **6** is apparently very labile. In cases where elimination was possible **6** lost the elements of HO^-M^+. It is interesting to note that initial protonation of **6** does not seem to be necessary for the elimination to proceed. Thus, the formation of formaldehyde *N,N*-diethylhydrazone proceeded rapidly when diethylnitrosamine was mixed with methyllithium at −40° with rigorous exclusion of moisture.

The hydrazones of formaldehyde were easily transformed by addition of a second molecule of the organometallic to the carbon–nitrogen double bond After hydrolysis, the product of this addition was found to be the triethylhydrazine (predominant product) and a smaller amount of the hydrazone derived from acetaldehyde. The latter was formed by the loss of the elements of the metal hydride from the intermediate addition product. The addition of organometallics to C=N bonds has been known for many years and the addition of alkyllithiums to hydrazones is a useful preparative method for substituted hydrazines.[6] Formaldehyde diisopropylhydrazone was hindered enough so that the second addition did not occur under our conditions. The steric effect was also reflected in the relatively low yield of the hydrazone (30%). Diisopropylnitrosamine did not react with Grignard reagents to give stable products (*vide supra*); presumably the greater steric demands of the Grignard reagents, as opposed to the lithium reagents, prevented the addition from occurring.

The reaction of diphenylnitrosamine with phenylmagnesium bromide gives primarily intractable materials except for a small yield of *N,N,N'*-triphenyl-*o*-phenylenediamine and, in the case where a large excess of the Grignard reagent is used, triphenylhydrazine. It is tempting to speculate that the phenylenediamine is a product of the combination of two diphenylamino radicals. Wieland[7] also observed this product along with *N,N'*-diphenyldihydrophenazine in the thermal decomposition of tetraphenylhydrazine. The latter product was not found under our conditions. The triphenylhydrazine was probably formed by the reduction of the initial addition product **6**, probably by another molecule of the Grignard reagent. No isolatable products were obtained when diphenylnitrosamine was treated with methyllithium. The reaction proceeded rapidly but only intractable tars were obtained.

The reaction of dimethylnitrosamine with methyllithium gave a complex mixture of products, even when the reaction was carried out at low temperatures (−70°).

In conclusion, the reaction of dialkylnitrosamines with organometallic reagents, particularly alkyllithium, may provide a relatively simple route for the preparation of trialkylhydrazines, either by a direct reaction or by further reactions of the initially formed alde-

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[1] H. Wieland and H. Fressel, *Chem. Ber.*, **44**, 898 (1911).

[2] H. Wieland and A. Roseeu, *ibid.*, **48**, 1117 (1915).

[3] H. Wieland and A. Reverdy, *ibid.*, **48**, 1112 (1915).

[4] H. Gilman and L. L. Heck, *Recl. Trav. Chim. Pays-Bas*, **50**, 522 (1931).

[5] H. Wieland and S. Gambarjan, *Chem. Ber.*, **39**, 1499 (1906).

[6] A. Marxer and M. Horvath, *Helv. Chim. Acta*, **47**, 1101 (1964).

[7] H. Wieland, *Justus Liebigs Ann. Chem.*, **381**, 206 (1911).

hyde hydrazones. The reaction is sensitive to steric effects, particularly in the case of the Grignard reagents. In general, the lithium reagents gave a cleaner reaction mixture. The yields, as quoted in Table I, probably can be improved by further optimizing the reaction conditions.

Experimental Section

Melting and boiling points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 237 instrument; nmr spectra were recorded on a Varian Model A-60 spectrometer. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6D spectrometer. The glpc separations were carried out on a Varian Aerograph Model 1520 dual column instrument. The columns used for the separations were made of Pyrex (aluminum columns are generally unsatisfactory) and packed with acid-washed Chromosorb W coated with 5% Apiezon N. Microanalyses were performed by A. Bernhardt, Engelskirchen, West Germany.

Materials.—Methylmagnesium bromide was obtained as a 3 *M* ethereal solution and methyllithium as a 2*M* ethereal solution from Alfa Inorganics. Diphenylamine was Aldrich reagent grade and was recrystallized from methanol. Diisopropylamine was Matheson reagent grade. Reagent grade ether (Mallinckrodt) was distilled from sodium or from lithium aluminium hydride and was stored over sodium ribbon.

Preparation of Nitrosamines.—All the nitrosamines were prepared in a similar manner and hence only the preparation of diisopropylnitrosamine will be described. To diisopropylamine hydrochloride [prepared from 50 g (0.5 mol) of diisopropylamine] in acidic aqueous solution was added, dropwise with stirring, 34.5 g (0.5 mol) of sodium nitrite. The reaction was kept at 70° for 2 hr. The reaction mixture separated into two phases and the organic phase was extracted with ether. Evaporation of the ether *in vacuo* yielded the crystalline product, which was recrystallized from methanol, yield 33 g (51%), mp 46–47° (lit.[8] mp 48°).

Reactions with Methyllithium.—All these reactions again were carried out in a similar manner. A detailed procedure will be given for the reaction with diisopropylnitrosamine, followed by a description of the products from the other reactions.

An ethereal solution of methyllithium (0.12 mol) was transferred with a syringe into a flask equipped with a dropping funnel and a condenser and swept with a dry nitrogen stream. The flask was cooled in an ice bath. An ethereal solution of 13 g (0.1 mol) of diisopropylnitrosamine was added dropwise to the methyllithium. After the addition was completed the reaction solution was allowed to warm to room temperature and was then heated at reflux for 2 hr. The flask was cooled in an ice bath and sufficient water was added to dissolve the inorganic precipitates. The ether layer was separated and the aqueous layer was extracted several times with ether. The combined ether extracts were dried and the ether was removed by distillation. The residue was distilled at atmospheric pressure. The product distilled over the range of 138–144°. The residue in the pot contained unreacted nitrosamine and tarry materials. The yield of formaldehyde diisopropylhydrazone was 3.9 g (30%), bp 140–142°. The analytical sample was purified by glpc.

Anal. Calcd for $C_7H_{16}N_2$: C, 65.59; H, 12.57; N, 21.85. Found: C, 65.80; H, 12.32; N, 22.17.

The nmr spectrum (CCl_4) indicated two isopropyl groups (d, 12 H, 1.10 ppm; septet, 2 H, 3.68 ppm, *J* = 6.8 Hz) and an AB quartet (2 H, 5.91 ppm, *J* = 12 Hz).

Reaction of Diethylnitrosamine with Methyllithium.—The reaction carried out at −40° produced exclusively formaldehyde diethylhydrazone in approximately 80% yield.

Anal. Calcd for $C_5H_{12}N_2$: C, 59.93; H, 12.08; N, 27.95. Found: C, 59.87; H, 12.05; N, 27.89.

The nmr spectrum (CCl_4) indicated two ethyl groups (triplet, 6 H, *J* = 7.0 Hz at 1.04 ppm and quartet, 4 H, *J* = 7.0 Hz at 3.11 ppm) and an AB quartet (2 H, *J* = 12 Hz at 5.93 ppm).

The reaction in refluxing ether produced primarily triethylhydrazine. From 10.2 g (0.1 mol) of diethylnitrosamine there was obtained 4.8 g (41%) of triethylhydrazine, bp 115° [lit.[9] bp 43–44° (30 mm)].

Anal. Calcd for $C_6H_{16}N_2$: C, 62.01; H, 13.88; N, 24.10. Found: C, 61.92; H, 14.23; N, 23.83.

The nmr spectrum (CCl_4) indicated two different kinds of ethyl groups. The spectrum consisted of two overlapping methyl triplets at 0.96 and 1.00 ppm in a 1:2 ratio accounting for nine protons and a complex absorption between 2.25 and 3.06 ppm accounting for methylene protons and 1 NH proton.

Reactions with Grignard Reagents.—These reactions were all carried out in a similar manner and so only the reaction of diethylnitrosamine with methylmagnesium bromide will be described. Into a 500-ml flask fitted with a condenser, a dropping funnel, a gas inlet, and a stirrer and cooled in an ice bath was placed 0.6 mol of methylmagnesium bromide. Diethyl-*N*-nitrosamine (20.4 g, 0.2 mol) in 50 ml of dry ether was added dropwise with stirring. A nitrogen atmosphere was maintained throughout. After the addition was complete the mixture was allowed to warm to room temperature and was then heated at reflux for 2 hr. The excess Grignard reagent was decomposed by careful addition of water. After the removal of ether by distillation the reaction mixture was steam distilled. The distillate was saturated with sodium hydroxide and extracted several times with ether. The combined ether extracts were concentrated and the concentrate was subjected to glpc analysis. It was found to contain four products in a 1:5:1:1 ratio. These products were separated by glpc and were found to be 1,1-diethyl-2,2-dimethylhydrazine (4% yield), nmr spectrum (CCl_4) 0.99 (triplet, 6 H, *J* = 7.0 Hz), 2.33 (singlet, 6 H), 2.35 ppm (quartet, 4 H, *J* = 7.0 Hz) (*Anal.* Calcd for $C_6H_{16}N_2$: C, 62.01; H, 13.90; N, 24.10. Found: C, 61.93; H, 14.36; N, 23.94.); triethylhydrazine (20% yield), *vide supra;* formaldehyde diethylhydrazone (4% yield), *vide supra;* and acetaldehyde diethylhydrazone (4% yield), nmr spectrum (CCl_4) 1.00 (triplet, 6 H, *J* = 7.0 Hz), 1.82 (doublet, 3 H, *J* = 5.2 Hz), 2.95 (quartet, 4 H, *J* = 7.0 Hz), 6.65 ppm (quartet, 1 H, *J* = 5.2 Hz).

Anal. Calcd for $C_6H_{14}N_2$: C, 63.10; H, 12.35; N, 24.53. Found: C, 63.05; H, 12.20; N, 24.57.

Reaction of Diethyl-*N*-nitrosamine with Phenylmagnesium Bromide.—From a Grignard reagent generated from 7.2 g (0.3 g-atom) of magnesium turnings and 50 g (0.31 mol) of bromobenzene plus 10.2 g (0.1 mol) of diethyl-*N*-nitrosamine there was collected 8.2 g (50%) of 1-phenyl-2,2-diethylhydrazine: bp 107–108° (14 mm) [lit.[1] bp 107–110° (12 mm)]; nmr spectrum (CCl_4) 1.07 (triplet, 6 H, *J* = 7.0 Hz), 2.62 (quartet, 4 H, *J* = 7.0 Hz), 3.95 (broad singlet, 1 H), 6.36–7.10 ppm (multiplet, 5 H, aromatic); mol wt 164 (mass spectrum).

Anal. Calcd for $C_{10}H_{16}N_2$: C, 73.08; H, 9.82; N, 17.06. Found: C, 72.95; H, 9.92; N, 17.93.

No other product, except some biphenyl, was isolated from this reaction.

Reaction of Diphenyl-*N*-nitrosamine with Methylmagnesium Bromide.—From a reaction of 0.2 mol of methylmagnesium bromide with 19.8 g (0.1 mol) of diphenyl-*N*-nitrosamine at −40° there was obtained a dark, tarry residue. This residue was extracted thoroughly with *n*-hexane. Evaporation of the resulting solution yielded 5.3 g (27%) of formaldehyde diphenylhydrazone, mp 33–34° (lit.[10] mp 34.5°), nmr spectrum (CCl_4) 5.92 (singlet, 2 H), 6.73–7.30 ppm (aromatic multiplet, 10 H).

Anal. Calcd for $C_{13}H_{12}N_2$: C, 79.56; H, 6.17; N, 14.07. Found: C, 79.80; H, 6.14; N, 13.98.

Reaction of Diphenyl-*N*-nitrosamine with Phenylmagnesium Bromide.—The procedure followed was essentially that of Wieland and Roseau[11] except that a nitrogen atmosphere was maintained over the reaction. The resulting tarry product was extracted with cold hexane. The hexane was evaporated to yield 1.7 g (5%) of *N,N,N'*-triphenyl-*o*-phenylenediamine, mp 89–90° (lit.[12] mp 94.5°), nmr spectrum (CCl_4) 5.62 (broad singlet, 1 H), 6.55–7.27 ppm (aromatic multiplet, 19 H).

Anal. Calcd for $C_{24}H_{20}N_2$: C, 85.67; H, 5.99; N, 8.60. Found: C, 85.66; H, 6.10; N, 8.60.

When a fivefold excess of Grignard reagent was used there was obtained a small amount (~3%) of triphenylhydrazine, mp 138–139° (crystals turn brown at 135°) (lit.[13] mp 142°, turned brown at 139°), nmr spectrum (CCl_4) 5.90 (broad singlet, 1 H), 6.65–7.20 (aromatic multiplet, 15 H). The yield of *N,N,N'*-tri-

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[8] J. Bewad, *Chem. Ber.*, **40**, 3068 (1907).

[9] O. Westphal, *Chem. Ber.*, **74**, 759 (1941).

[10] A. D. Maurenbrecher, *Chem. Ber.*, **39**, 3583 (1906).

[11] H. Wieland and A. Roseeu, *ibid.*, **45**, 494 (1912).

[12] E. S. Lane and C. Williams, *J. Chem. Soc.*, 1468 (1955).

[13] M. Busch and R. Hobein, *Chem. Ber.*, **40**, 2099 (1907).

phenyl-*o*-phenylenediamine in this reaction was a somewhat higher 9%.

Reaction of Diisopropyl-*N*-nitrosamine with Phenyl- and Methylmagnesium Bromide.—Many attempts were made to get these reactions to proceed. The following results were typical. A mixture of 0.1 mol of methylmagnesium bromide and 13 g (0.1 mol) of diisopropyl-*N*-nitrosamine was heated at reflux for 6 hr. Upon treatment of the reaction mixture with water and extraction with ether, followed by distillation, there was obtained 11.5 g (90%) of the starting nitrosamine.

Cautionary Note.—While nitrosamines are easy to prepare and to work with, it should be remembered that many of them are potent carcinogens. Proper precautions against inhalation of the vapors and contact with skin should be maintained always. Preparative glpc should be carried out with caution. Unreacted nitrosamines should not be vented into the atmosphere. In our case any unreacted nitrosamine which came through the glpc column was trapped in a collection tube chilled in a Dry Ice-acetone bath.

Registry No.—Methyllithium, 917-54-4; diisopropylnitrosamine, 601-77-4; formaldehyde diisopropylhydrazone, 39837-46-2; diethyl-*N*-nitrosamine, 55-18-5; formaldehyde diethylhydrazone, 28236-89-7; triethylhydrazine, 39837-47-3; methylmagnesium bromide, 75-16-1; 1,1-diethyl-2,2-dimethylhydrazine, 21849-74-1; acetaldehyde diethylhydrazone, 7422-91-5; phenylmagnesium bromide, 100-58-3; 1-phenyl-2,2-diethylhydrazine, 39837-50-8; diphenyl-*N*-nitrosamine, 86-30-6; formaldehyde diphenylhydrazone, 38392-47-1; *N*,*N*,*N*′-triphenyl-*o*-phenylenediamine, 29325-54-0; triphenylhydrazine, 606-88-2.

Deuterium Isotope Effects in the Palladium(II) and Thallium(III) Oxidation of Ethylene[1]

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Palladium(II) salts in aqueous solution oxidize ethylene to acetaldehyde[3] while thallium(III) salts

$$\mathrm{Pd(II)} + C_2H_4 + H_2O \longrightarrow \mathrm{Pd(0)} + CH_3CHO + 2H^+ \quad (1)$$

oxidize ethylene to a mixture of acetaldehyde and ethylene glycol.[4] Kinetic studies[5-7] indicate that in

$$\mathrm{Tl(III)} + C_2H_4 \xrightarrow{H_2O} \mathrm{Tl(I)} + CH_3CHO + HOCH_2CH_2OH \quad (2)$$

chloride containing aqueous solution, the slow step of the Pd(II) oxidation is rearrangement of a hydroxy olefin π complex to a β-hydroxyethylpalladium(II) alkyl, **1** (or hydroxypalladation adduct in analogy with the well-known hydroxymercuration adduct[8]). This intermediate rapidly decomposes to acetaldehyde and Pd(0). Equation 3 was assigned as the slow step on the basis of isotope effects.

$$\mathrm{PdCl_2(OH)}(C_2H_4) \underset{\text{slow}}{\xrightarrow{H_2O}} \underset{\mathbf{1}}{\mathrm{Cl_2(H_2O)Pd{-}CH_2CH_2OH}} \quad (3)$$

$$\mathbf{1} \xrightarrow{\text{fast}} \mathrm{Pd(0)} + HCl + Cl^- + CH_3CHO \quad (4)$$

When the reaction is carried out in D_2O the acetaldehyde is undeuterated.[3] Thus the decomposition of **1** must involve a transfer of proton from one carbon to the other. This transfer of proton would be expected to involve a positive isotope effect if deuterated ethylene is oxidized. However, it was found that the rate of C_2D_4 oxidation was the same as that of C_2H_4 oxidation within experimental error,[7] suggesting that the decomposition of **1** occurs after the slow step of the reaction. This conclusion is subject to some uncertainty, since isotope effects in decomposition of adducts such as **1** have not been studied.

Kinetic studies[9,10] as well as other evidence[11] of the Tl(III) oxidation in aqueous perchloric acid indicate that it proceeds *via* a hydroxythallation adduct, **2**, analogous to **1**. The formation of the adduct was

$$Tl^{3+} + C_2H_4 + H_2O \xrightarrow{\text{slow}} \underset{\mathbf{2}}{HOCH_2CH_2Tl^{2+}} + H^+ \quad (5)$$

$$\mathbf{2} \xrightarrow{\text{fast}} \text{products} \quad (6)$$

again assigned as the slow step on the basis of the kinetics. Thus the reaction displayed no proton inhibition, which would have been expected if eq 5 were an equilibrium.

This note will describe further studies of the isotope effects in these two oxidations for the purpose of testing earlier conclusions concerning the rate-determining steps. First, C_2D_4 was oxidized by both reagents and the acetaldehyde product was analyzed for deuterium content. In both cases the product was over 95% CD_3CDO, indicating that both **1** and **2** decompose by hydride shifts. In the case of Pd(II), this result confirms the earlier work using C_2H_4 in D_2O.[3]

Next the kinetic isotope effect for C_2D_4 as compared with C_2H_4 was measured for Tl(III) in aqueous $HClO_4$. The value of k_H/k_D was found to be 0.8. The isotope effect of less than one must result from the fact that hydrogen is a better electron withdrawer than deuterium,[15] and the Tl(III) oxidation is very sensitive to electronic effects. In any case the isotope effect is about one, the value expected if eq 5 is the rate-determining step.

In order to substantiate this conclusion concerning the rate-determining steps of these oxidations, it is necessary to have some knowledge of the actual deuterium isotope effects in the decomposition of **1** and **2**. Since they cannot be measured by kinetic measurements, they were determined by a competitive method using *cis*- and *trans*-1,2 dideuterioethylene.

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