which benzophenone abstracts hydrogen from the *N*-methyl groups of Michler's ketone.[17] The present results are also explicable in terms of a triplet exciplex which leads to type I cleavage of the benzoin ether; *i.e., in this case the photochemistry is independent of the sensitizer.* Triplet energy transfer is clearly excluded by kinetic arguments. Thus, utilizing the 12 kcal/mol endothermicity, the specific rate for energy transfer may be calculated[18] to be more than 8 powers of 10 lower than the diffusional rate, *i.e.*, on the order of 10^2 M^{-1} $\sec^{-1}$. Furthermore, taking into account the initial concentration of **1a** (0.078 *M*), the initial rate of energy transfer is predicted to be 3 orders of magnitude lower than the rate of radiationless decay of triplet Michler's ketone, taken as 10^4 $\sec^{-1}$.[17] While the nature of the exciplex is a matter for speculation at present, the finding that 61 kcal/mol shared by Michler's ketone and **1a** may be utilized specifically for C–C bond cleavage of the ether in as high efficiency as observed (25% of the direct yield) is considered noteworthy. Indeed, the bond dissociation energy in question may be estimated as 63 ± 2 kcal/mol.[19] The potential importance of the concept of low energy sensitization for efficient energy utilization is particularly exemplified by dye sensitized photoimaging processes.[20]

Acknowledgment. We wish to express our appreciation to the Alcoa Foundation for financial assistance and to Dr. Fred D. Lewis for helpful discussions.

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Diethyl Ether Soluble Aluminum Hydride[1]

Sir:

We would like to report the preparation of diethyl ether soluble aluminum hydride prepared by three different reactions: (1) the reaction of lithium aluminum hydride and beryllium chloride, (2) the reaction of 100% H_2SO_4 with lithium aluminum hydride, and (3) the reaction of lithium aluminum hydride and zinc chloride. The yield in all three cases is quantitative.

$$2LiAlH_4 + BeCl_2 \xrightarrow{Et_2O} Li_2BeH_2Cl_2\downarrow + 2AlH_3 \tag{1}$$

$$2LiAlH_4 + H_2SO_4 \xrightarrow{Et_2O} H_2\uparrow + Li_2SO_4\downarrow + 2AlH_3 \tag{2}$$

$$2LiAlH_4 + ZnCl_2 \xrightarrow{Et_2O} 2\,LiCl\downarrow + ZnH_2\downarrow + 2AlH_3 \tag{3}$$

Previous to this report soluble aluminum hydride could only be prepared in tetrahydrofuran. All attempts to prepare aluminum hydride in diethyl ether according to the method of Schlesinger (eq 4) resulted

$$3LiAlH_4 + AlCl_3 \xrightarrow{Et_2O} LiCl\downarrow + 4AlH_3\downarrow \tag{4}$$

in significant precipitation of the aluminum hydride within 20 min after the rapid addition of reactants.[2,3]

To 20 mmol of $LiAlH_4$ in 150 ml of ether was added 10 mmol of $BeCl_2$ The solution was stirred for 2 hr and filtered. Analysis of the filtrate gave an Al:H:Li ratio of 1.0:2.97:0.002. No beryllium or chlorine was detected in the solution. Reversing the order of addition of the reactants yielded the same results. No precipitate of AlH_3 from solution was observed after 24 hr. The concentration of the solution dropped 4% in 1 week and 20% in 2 weeks. The infrared spectrum of the resulting solution[3] of AlH_3 (before precipitation) prepared by the Schlesinger method showed an Al–H stretching vibration at 1801 cm^{-1}. The AlH_3 which we have prepared has absorption bands at 1788 cm^{-1} owing to the Al–H stretching vibration and at 765 cm^{-1} owing to the Al–H deformation vibration.

Removal of the solvent under vacuum yields a white solid which was shown by elemental analysis to have the empirical formula of $AlH_3 \cdot 0.24(C_2H_5)_2O$. The X-ray powder diffraction pattern of this solid shows five main lines: 11.5 Å (s); 4.55 Å (m); 3.85 Å (m); 2.85 Å (m); and 2.32 Å (m). Bousquet, Choury, and Claudy,[4] have reported a powder pattern for $AlH_3 \cdot 0.25(C_2H_5)_2O$. Their lines match ours with the exception of the line at 3.85 Å.

DTA–TGA analysis of the solid AlH_3 etherate prepared from $LiAlH_4$ and $BeCl_2$ shows that evolution of ether begins at 50°. Evolution of hydrogen begins at 90° and is centered at 110°. Molecular association studies on a freshly prepared sample of AlH_3 in ether indicate that AlH_3 prepared from $LiAlH_4$ and $BeCl_2$ is monomeric at a concentration of 0.13–0.16 *m*.

The reduction of ketones was investigated in order to evaluate ether soluble AlH_3 as a stereoselective reducing agent. With 4-*tert*-butylcyclohexanone, AlH_3 in diethyl ether gave 46% axial alcohol, compared with 13% axial alcohol using AlH_3 in THF and 12% axial alcohol using $LiAlH_4$ in ether.

The preparation of soluble AlH_3 in diethyl ether provides an opportunity to prepare compounds that normally disproportionate in THF solvent. For example, we have prepared HBeCl by reaction of AlH_3 with $BeCl_2$ (eq 5). HBeCl was prepared unequivocally from

$$AlH_3 + BeCl_2 \longrightarrow HBeCl + H_2AlCl \tag{5}$$

BeH_2 and $BeCl_2$ in diethyl ether establishing the infrared bands for HBeCl at 1330, 1050, 970, 908, 840 (sh), 790, and 700 cm^{-1}. The infrared spectrum of DBeCl showed the band at 1330 cm^{-1} shifted to 985 cm^{-1} and the band at 970 cm^{-1} in HBeCl had disappeared in DBeCl. Molecular weight determination of HBeCl in ether shows the compound to be dimeric indicating that the BeH frequency at 1330 cm^{-1} is a bridge stretching mode.[5]

Exactly why stable ether solutions of AlH_3 are so

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[1] We are indebted to the Office of Naval Research (Contract No. N00014-67A-0159-0005 and Contract Authority No. NR-93-050/12-5-67-429) for support of this work.

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[4] J. Bousquet, J. J. Choury, and P. Claudy, *Bull. Soc. Chim. Fr.*, 3848 (1967).

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easily prepared by the presently reported methods (eq 1–3), whereas all reports in the past claimed AlH_3 precipitates from ether, is not understood. We are, however, investigating this aspect further.[6]

Since MH_2 compounds of group II metals are insoluble in all organic solvents, it has been impossible to assign exact vibrational frequencies for the M–H band. It appears now that stable HMX compounds can be prepared from MX_2 and AlH_3 in ether, thus providing a means of obtaining stretching and deformation frequencies for M–H compounds. In this connection we are continuing our studies concerning reactions of AlH_3 in ether with groups I, II, and III metal halides.

(6) Note Added in Proof. We have just found that preparation of AlH_3 by the Schlesinger method also results in ether-soluble AlH_3 under comparable reaction conditions. We are presently investigating the effect of $LiAlH_4$ purity and lithium content in the product AlH_3 as sources of this unique behavior.

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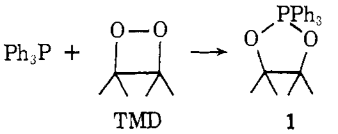
An Insertion Reaction of Triphenylphosphine with Tetramethyl-1,2-dioxetane. Deoxygenation of a Dioxetane to an Epoxide

Sir:

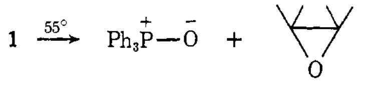
The reaction of phosphines and phosphites with dialkyl peroxides to give phosphoranes has been investigated recently.[1] We here report the quantitative formation of phosphorane **1** *via* the reaction (eq 1) of



TMD 1

(1)

3,3,4,4-tetramethyl-1,2-dioxetane, TMD, with triphenylphosphine. Decomposition of phosphorane **1** at 55° smoothly yields quantitative amounts of triphenylphosphine oxide and tetramethylethylene oxide **2** (reaction 2).



2

(2)

Triphenylphosphine (23.0 mg, 0.088 mmol) was added to 10.1 mg (0.087 mmol) of TMD[2] (methyls, singlet at δ 1.2 in benzene[3]) in cool (∼6°), dry benzene. The dioxetane was completely consumed within minutes to yield phosphorane **1** in 94% yield. In its ^1H nmr spectrum the methyl region displayed a singlet at δ 1.0 in benzene. Careful removal of the solvent at reduced pressure, from an ice bath, afforded a white solid, unstable above room temperature: ^1H nmr (in CCl_4) δ 1.02 (singlet, 12 H), 7.0–7.6 (multiplet, 15 H); ir (salt plate) 3050 w, 2980 w, 1480 m, 1430 m, 1385 w, 1360 w, 1160 s, 1145 s, 1100 m, 1090 m, 1085 m, 1002 w, 975 s, 955 w, 915 s, 800 s, 750 s, 712 s, 695 s, 680 w. The ^{31}P nmr spectrum[4] of a 0.1 *M* solution of **1** in benzene:deuteriobenzene (1:1) gave a sharp singlet at δ +73.2 from triphenylphosphine oxide (used as external standard). Triphenylphosphine oxide in benzene:deuteriobenzene (1:1) absorbs at δ −24.8 from external phosphoric acid standard. Hence the corrected chemical shift for phosphorane **1** relative to external phosphoric acid is δ 48.4. This is clearly indicative of the phosphorane structure.

A sample of 5 mg of **1** was dissolved in 0.2 cm^3 of CCl_4 and heated in a tightly capped nmr tube at 55° for 30 min. The resulting ^1H nmr spectrum showed quantitative appearance of a new singlet at δ 1.22 and a new multiplet at δ 7.4–7.9. The new singlet at δ 1.22 was characteristic of tetramethylethylene oxide[5] (in CCl_4) and the multiplet at δ 7.4–7.9 was characteristic of triphenylphosphine oxide (in CCl_4). Removal of volatile materials at reduced pressure afforded a white solid (mp 153.5–155°), the ir spectrum of which was identical with that of authentic triphenylphosphine oxide[6] (mp 155–156°).

A larger sample of **1** (∼15 mg) was heated in 0.5 cm^3 of benzene at 55° for 60 min. Vpc analysis[7] showed only one volatile component with the same retention time as authentic tetramethylethylene oxide. While **1** was found to be stable in benzene at room temperature (no detectable decomposition after 12 hr), it was found that **1** decomposed readily at room temperature in $CDCl_3$. A 0.1 *M* solution of **1** (0.12 g in 3 cm^3) in $CDCl_3$ was prepared in a 7 in. × 12 mm nmr tube. The ^1H nmr spectrum minutes after dissolution showed complete decomposition to triphenylphosphine oxide and tetramethylethylene oxide. The ^{31}P nmr spectrum showed only one sharp peak at the same chemical shift as external triphenylphosphine oxide (standard). Vpc analysis as before showed only one other product. An ir spectrum of the collected volatile component in CCl_4 (0.1-mm cell) proved identical with that of authentic tetramethylethylene oxide.[5]

The conversion of a phosphorane with a five-membered ring into an epoxide is a known reaction.[1a,8] Denney and Jones[1a] have observed that the epoxide is formed stereospecifically with configurative inversion at one of the carbon atoms and retention at the other.

An unusual structural feature of **1** is that its preferred configuration places the two ring oxygen atoms apical–equatorial in the trigonal bipyramid[9] around the P atom. The remaining apical site must then be occupied by a phenyl substituent. Such a violation of the normal preferences of substituents of different

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(3) All ^1H nmr spectra taken on a Varian T-60 spectrometer.

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