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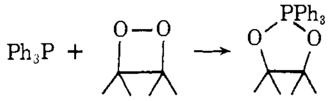
An Insertion Reaction of Triphenylphosphine with Tetramethyl-1,2-dioxetane. Deoxygenation of a Dioxetane to an Epoxide

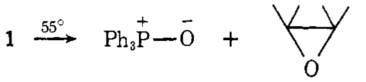
Sir:

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 cm³ 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 cm³ 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 cm³) 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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[1] Some relevant papers: (a) D. B. Denney and D. H. Jones, *J. Amer. Chem. Soc.*, **91**, 5821 (1969); (b) B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelman, R. L. Powell, and D. W. White, *ibid.*, **93**, 4004 (1971); (c) D. B. Denney, D. Z. Denney, C. D. Hall, and K. L. Marsi, *ibid.*, **94**, 245 (1972), and references therein.

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

[4] All ^{31}P nmr spectra taken on a Varian XL-100 spectrometer at 40.5 MHz and proton decoupled (deuterium lock).

[5] Spectral data were identical with those of F. D. Greene and W. Adam, *J. Org. Chem.*, **29**, 136 (1964), and also with that of tetramethylethylene oxide prepared by the reaction of *m*-chloroperbenzoic acid and tetramethylethylene.

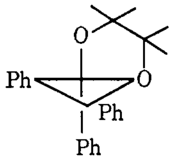
[6] Authentic triphenylphosphine oxide obtained from A. Frimer.

[7] Vpc analyses performed on Aerograph A-700 using a 4 m × 0.25 in. 20% Carbowax 20M on Chromosorb W column.

[8] F. Ramirez, A. S. Gulati, and C. P. Smith, *J. Org. Chem.*, **33**, 13 (1968).

[9] (a) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966); (b) D. Gorenstein and F. H. Westheimer, *J. Amer. Chem. Soc.*, **92**, 634 (1970); (c) D. Gorenstein, *ibid.*, **92**, 644 (1970).

electronegativities on phosphorus would never occur without the constraint of the small ring.



1

The preparation of an epoxide has been reported by the use of singlet oxygen on an olefin in pinacolone as a solvent,[10] in analogy to the isolation of dioxetanes from the action of ozone on olefins in the same solvent.[11] In each of these cases it has been postulated that the monodeoxygenation involves the removal of coordinate oxygen from a perepoxide[10] or perdioxetane (Staudinger molozonide) intermediate[12a] through Baeyer–Villiger attack on pinacolone. The present report represents the first instance of reduction of a dioxetane to an epoxide through initial insertion of the oxygen acceptor into the ring. We shall report shortly on some metal insertions into the dioxetane ring followed by reductive fragmentation, which provide models for the extremely rapid catalytic dioxetane decompositions recently observed.[13]

Acknowledgments. This work was supported by grants from the National Science Foundation and the National Institutes of Health. We thank Charles L. Lerman for arousing our interest in the reactions of dioxetanes with trivalent phosphorus compounds.

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Rearrangement and Decomposition of Trialkylgold(III) Complexes

Sir:

Trialkylgold(III) species are the key intermediates in the catalytic coupling of alkyl groups from organogold(I) complexes and alkyl halides.[1] They are also rather unique among transition metal alkyls in undergoing reductive elimination by alkyl coupling rather than by disproportionation.[2] Thus, ethyl groups are coupled in high yields during the decomposition of diethyl(methyl)(triphenylphosphine)gold,[1,3] *e.g.*

$$(CH_3CH_2)_2CH_3Au^{III}PPh_3 \longrightarrow CH_3CH_2CH_2CH_3 + CH_3Au^{I}PPh_3 \quad (1)$$

Various isomeric trialkyltriphenylphosphinegold complexes can now be obtained, which have square-planar configurations characteristic of four-coordinate gold(III).[4] The known stereochemical structures of these complexes[4,5] allowed us to examine the stereochemistry and the manner in which alkyl groups are reductively eliminated from alkylgold(III) species, and they have provided mechanistic insight into the coupling process.

trans-Ethyldimethyl(triphenylphosphine)gold was synthesized by oxidative addition of ethyl iodide to lithium dimethyl(triphenylphosphine)aurate(I).[6] The corresponding cis isomer was prepared by stereospecific alkyl exchange between *cis*-dimethyliodotriphenylphosphinegold and ethyl Grignard.[4c] Other analogs in Table I were synthesized by similar procedures. The stereoisomeric pairs are readily distinguished by their proton nmr spectra.[4,6] Molecular weight measurements by vapor pressure osmometry indicated that these alkyldimethyltriphenylphosphine gold complexes are monomeric in solutions of benzene as well as *n*-heptane.

Table I. Decomposition of Stereoisomeric Alkyldimethyl(triphenylphosphine)gold[a]

$R(CH_3)_2AuPPh_3$	(10^3 mmol)	PPh_3 (10^3 mmol)	T, °C	Time,[b] min	Alkane (mol %)[c,d]		
					RCH_3	CH_3CH_3	RR
trans-Ethyl	70	0	70	75	83	3	2
	51	0	90	45	93	3	2
	49	57	90	180	96	2	2
cis-Ethyl	44	0	70	100	58	28	4
	51	0	90	80	54	29	8
	56	55	90	150	86	3	2
trans-*n*-Propyl	50	0	70	60	65[e]	6	
	50	51	90	170	80[e]	3	
cis-*n*-Propyl	50	0	70	200	60[e]	45	
	51	51	90	300	60[e]	4	
trans-Isopropyl	50	0	70	13	95[f]	10	
	50	50	90	25	75[g]	1	
cis-Isopropyl	51	0	70	75	70[h]	45	
	50	51	90	60	85[i]	1	

[a] Decalin solution. [b] Time required for major decomposition (arbitrary). [c] Yields relative to $R(CH_3)_2AuPPh_3$ charged. [d] Yields in excess of 100% due to additional ethane formed by decomposition of CH_3AuPPh_3 in the absence of added PPh_3 (see text). [e] Including isobutane 5%. [f] *n*-Butane, 40%. [g] *n*-Butane, 20%. [h] *n*-Butane, 25%. [i] *n*-Butane, 20%, yields formed relative to $R(CH_3)_2AuPPh_3$.

The decomposition of *trans*-$CH_3CH_2(CH_3)_2AuPPh_3$ afforded high yields of only propane. On the other hand, the decomposition of *cis*-$CH_3CH_2(CH_3)_2AuPPh_3$, which proceeded at significantly slower rates under the same conditions, produced a mixture of pro-

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