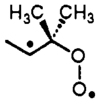
or 1.0 kcal/mol, respectively, in good agreement with the 1.1 kcal/mol difference between carbinol and radical stabilities.

In conclusion, the regioselectivity observed in the oxirane reductive ring opening is consistent with a mechanism involving cleavage of a radical anion to give the more substituted *carbinol* or *carbinolate*, rather than the more substituted radical. Such control necessarily leads to intermediacy of the less substituted radical. We are assuming that the rate of ring opening is related to the stability of the acyclic product.

These results are reminiscent of calculations by Goddard and co-workers on the anti-Markovnikov addition of singlet oxygen to unsymmetric olefins,[23] which predict that diradicals of type **10** are more stable than their regioisomers **11** by about 0.6 kcal/mol.



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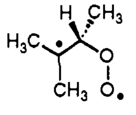

11

The larger stability of branched over linear species is quite general; for example, 2,2-dimethylpropane is more stable than 2-methylbutane by 3.4 kcal/mol.[20] Here the preference for the branched molecule is not as large as in the case of the alcohols, and the derived radicals, neopentyl and 1,1-dimethylpropyl, are in the traditional relative stability order, although the tertiary radical is only 1.9 kcal/mol more stable than the primary. In general, the magnitude of this preference depends on how the C–X bond strength varies with substitution at carbon. Thus, while the tertiary C–H bond in isobutane is about 6 kcal/mol weaker than the primary C–H bond,[14] the heats of homolysis of *tert*-butyl and isobutyl halides differ by only 0.5–1.5 kcal/mol,[24] and the heat of dissociation of *tert*-butyl alcohol is actually higher than that of isobutyl alcohol by about 1 kcal/mol.

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Matrix Isolation Studies of Chemical Vapor Deposition: Isolation and Characterization of the Trimethylgallium–Arsine Adduct

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Chemical vapor deposition (CVD) is a widely used technique for the production of thin semiconductor films such as gallium arsenide (GaAs) and related III–V compounds.[1,2] These films have applications in such diverse areas as solar energy conversion and microelectronics. In CVD, gaseous precursors are passed over a heated substrate, initiating a complex series of homogeneous (gas phase) and heterogenous chemical reactions. Despite the commercial importance of these semiconductors, relatively little is known about the mechanism of thin-film formation. The most common precursors[3] for GaAs CVD are trimethylgallium and arsine, with an overall reaction $(CH_3)_3Ga(g) + AsH_3(g) \rightarrow GaAs(s) + 3CH_4(g)$. On the basis of the Lewis acid/base tenets,[4] initial formation of an adduct is reasonable, yet this adduct has never been conclusively identified or characterized, and its existence and role in CVD have been debated. One group reported[5] formation of this adduct, but the primary evidence was a slight decrease in intensity of the parent absorptions upon mixing; no spectral features attributable to the adduct were reported. Likewise, one patent[6] invokes formation of GaAs(s) from the adduct; here, too, scientific data that conclusively identified the adduct were not presented. GaAs CVD has also been initiated[7] photochemically through excimer laser irradiation at 193 nm; again, little is known about the initial photochemical steps.

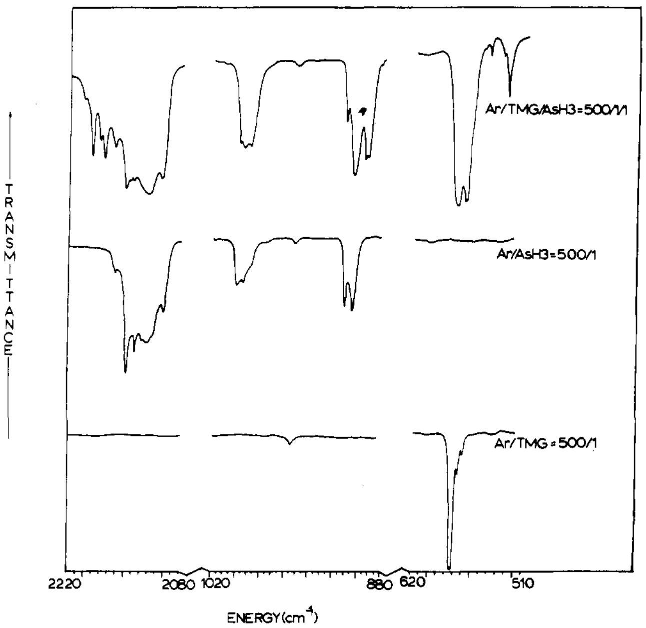

Figure 1. Infrared spectrum, over selected spectral regions, of a sample of $Ar/(CH_3)_3Ga/AsH_3 = 500/1/1$ (top trace) compared to blank spectra of each reagent alone in argon (middle and bottom spectra).

In this communication, the first definitive identification and infrared spectroscopic characterization of the 1:1 molecular complex of $(CH_3)_3Ga$ with AsH_3 is reported. Matrix isolation[8,9] is well suited to the study of transient intermediates, particularly weakly bound or reactive molecular complexes.[10] Preliminary photochemical studies of the dissociation/rearrangement of this complex by an excimer laser operating at 193 nm are also reported.

The experiments in this study were carried out on a conventional matrix isolation apparatus.[11,12] $(CH_3)_3Ga$ (Alfa Products) and AsH_3 (Alphagaz) were introduced into the vacuum system and purified by freeze–thaw cycles at 77 K. Samples of $(CH_3)_3Ga$ contained residual amounts of CH_4. Argon was used as the matrix gas in all experiments. Samples were deposited in both the twin-jet and the single-jet mode; in the former, separate samples were prepared of each reagent and codeposited simultaneously onto the cold window. In the latter, the reagents were premized in a single vacuum manifold with argon, and the mixture was deposited. Spectra were recorded after 20–24 h of deposition at 2 mmol/h

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Table I. Band Positions (cm^{-1}) and Assignments for the 1:1 $(CH_3)_3Ga\cdot AsH_3$ Molecular Complex in Argon Matrices

product	parent[a]	assignment
520	526	ν_3, GaC_3 sym st
565	576	ν_{16}, GaC_3 antisym st
892, 895	912	ν_2, AsH_3 sym def
989	1003	ν_4, AsH_3 antisym def
2175, 2181	2140	ν_1, AsH_3 sym st
2191, 2201	2150	ν_3, AsH_3 antisym st

[a] From ref 13–15.

on a Mattson Cygnus FTIR spectrometer at 1-cm^{-1} resolution. A number of the matrices were irradiated by the 193-nm output of a Lambda Physik EMG 103 MSC laser. In some cases, samples were irradiated after deposition (in situ), while in other experiments, irradiation was concurrent with deposition. The laser repetition rate was 5 Hz, with a pulse duration of approximately 10 ns and a pulse energy of up to 200 mJ.

$(CH_3)_3Ga$ and AsH_3 were codeposited in a number of experiments, over a wide range of concentrations. When a sample of $Ar/(CH_3)_3Ga = 500$ was codeposited with a sample of $Ar/AsH_3 = 500$, several new absorptions were observed that were not present in the blank experiments of either reagent, as shown in Figure 1. These include sharp, intense bands at 520 and 565 cm^{-1}, a doublet at 892 and 895 cm^{-1}, a band of medium intensity at 989 cm^{-1}, and a multiplet of bands near 2190 cm^{-1}. When the concentration of either reagent was increased, the intensity of the product bands increased as well. When the reagents were premixed and codeposited in the single-jet mode, the same product absorptions were observed.

Each of the product absorptions falls near a fundamental of either[13] $(CH_3)_3Ga$ or[14] AsH_3, indicating that both reagents have maintained their structural integrity, yet are perturbed in the product species. Two fundamentals of $(CH_3)_3Ga$ were perturbed, the GaC_3 symmetric and antisymmetric stretching modes, which would be expected for an interaction at the gallium center. All four fundamentals of AsH_3 were perturbed, in the same direction as and of similar magnitude to their shifts in the $HF\cdot AsH_3$ complex.[15] These observations strongly support the formation of a complex between $(CH_3)_3Ga$ and AsH_3. Consideration of the dilutions employed here and the fact that only a single product species was observed argues that the stoichiometry of the complex is 1:1. *This, then, represents the first positive identification of the $(CH_3)_3Ga\cdot AsH_3$ adduct.*

Band assignments for the complex may be made by comparison to the spectra of the parent species[13,14] and are presented in Table I. It is interesting to note that the symmetric GaC_3 stretch is dramatically activated in the complex compared to the parent, where it is nominally forbidden. This indicates a significant distortion of the GaC_3 skeleton from planarity in the complex. Also, the antisymmetric GaC_3 stretch and the antisymmetric AsH_3 deformation, both of which are doubly degenerate in the parent species, did not split upon complex formation. This indicates that they remain degenerate and that the effective symmetry of the complex is C_{3v}.

In situ irradiation of matrices containing the adduct led to no changes in the spectrum. However, when samples were irradiated with the laser at 193 nm during deposition, several new features were observed, including bands at 493 and 1139 cm^{-1}. These bands were not present when either precursor was irradiated alone during deposition. While analysis and assignment of these product bands is in progress, these results suggest that the adduct undergoes photochemical rearrangements after excitation at 193 nm. Lack of photochemistry with in situ irradiation is likely due to recombination induced by the matrix cage.

The observation of a stable 1:1 adduct here suggests that this species should also be observable in the gas phase, and the spectral data reported here may guide researchers studying the gas-phase chemistry of this system. While the environment of a CVD reactor is quite different from the conditions in the present study, this adduct *may* also be present during the CVD process.

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Synthesis of Completely Fixed Porphyrin–Quinone Compounds and the Mutual Orientation Effect on Electron Transfer

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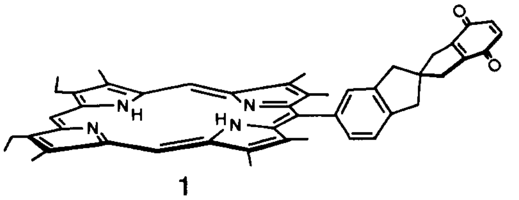
The requirements of structural factors (the separation distance and the mutual orientation of a redox pair) for electron transfer have been the subject of lively investigations in recent years in connection with the primary process of photosynthesis, and a number of model compounds have so far been prepared.[1] The distance dependence[2] on electron-transfer rates is well-recognized by the synthesis of systematic donor–acceptor linked molecules with rigid organic spacers at fixed distances,[3–5] while little is known about the orientation effect[6] because of the lacking of suitable compounds with fixed orientation of different kinds. We report here the synthesis of compounds **1**[7] and **2**, where a porphyrin and a quinone ring are connected with a rigid spacer of spiro[4.4]-



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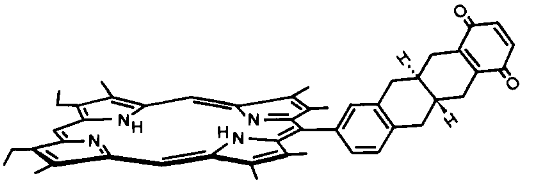

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