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Intrinsic Acidity of Dimethylhalonium Ions: Evidence for Hyperconjugation in Dimethylhalonium Ylides in the Gas Phase

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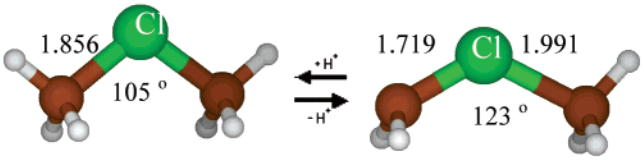

The intrinsic acidity of dimethylhalonium ions has been determined, both by theoretical methods and by gas-phase reactions of the isolated ions with pyridine bases. The calculated geometry of the dimethylhalonium ions shows a bent structure with the C−X−C angle decreasing in the order Cl > Br > I. Thermochemical calculations for the reaction of the dimethylhalonium ions with pyridine, 2,6-dimethylpyridine, and 2,6-di-*tert*-butylpyridine indicate that proton transfer, with the formation of the dimethylhalonium ylide is endothermic, whereas methyl transfer, with formation of methylhalide, is exothermic. The endothermicities for proton transfer are, nevertheless, dependent on the steric hindrance of the base. The bulkier the bases, the less endothermic the proton-transfer reaction is. Experimental gas-phase reactions support the calculations, showing that methyl transfer is the major reaction of dimethylchloronium and dimethyliodonium with pyridine, whereas proton transfer, as well as single electron transfer, is observed for the bulkier bases. The calculations also indicate that acidity increases in the order chloronium > bromonium > iodonium. NBO calculations predict that hyperconjugation with the σ^* carbon−halogen orbital plays a role in stabilizing the halonium ylide species in the gas phase.

Introduction

Halonium ions[1] are very popular in organic reaction mechanisms. These stable onium ions were first proposed[2] by Roberts and Kimball to account for the stereospecificity of the addition of bromine to olefins. Olah and co-workers were the first to prepare[3] bridged-halonium ions in superacid solutions and to characterize them by spectroscopic methods. They also reported[4] that open-chain dialkylhalonium ions are formed under the same conditions. For instance, dimethylchloronium, dimethylbromonium, and dimethyliodonium were prepared by reacting the respective methylhalide with a $SbF_5−SO_2$ solution. The formation of the dimethylhalonium ions was characterized by deshielded singlet peaks in the NMR spectra at 4.1, 3.8, and 3.4 δ, assigned to the methyl protons in the chloronium, bromonium, and iodonium ions, respectively. Dimethylbromonium and dimethyliodonium are presently commercialized as stable fluoroantimonate salts, showing their good stability at room temperature. They are good alkylating agents[5] for aromatics, olefins, and n-donor bases.

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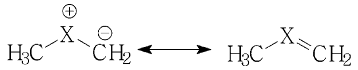
Although bridged-halonium ions have been studied thoughtfully by theoretical methods,[6] the open-chain analogues have received much less attention. Olah and co-workers carried out[7] DFT studies of the dimethylhalonium ions and found, at the B3LYP/6-31G+(d,p) level, that their structures are bent, with the C−X−C angle decreasing in the series Cl > Br > I. Charge distribution calculations have indicated that the positive charge on the halogen atom increases in the same order, as a function of the eletronegativity of the halogen atom.

Dimethylhalonium ions are widely used[8] in chemical ionization mass spectroscopy. They are good methylating agents for a variety of compounds, such as amines, alcohols, and ethers. The reaction seems to occur through an S_N2 mechanism, with methylhalide as the leaving group, but shows dependence with the thermochemistry of the formed products. For instance, the methylethylchloronium cation ($CH_3Cl^+CH_2CH_3$) reacts[8a] with amines, transferring a methyl group, whereas with ethers there is preference for transferring an ethyl group. Protonated methyl halides[9] are also important species in chemical ionization mass spectroscopy. The proton affinity of methylhalides[10] decreases with the increasing electronegativity of the halogen atom, being 155.3 kcal/mol for chloromethane, 158.1 kcal/mol for bromomethane, and 163 kcal/mol for iodomethane.

On the other hand, conversion of chloromethane to light olefins, such as ethene and propene, over zeolite catalysts has[11] gained increased importance. This might be an alternative process for converting natural gas into light olefins, avoiding the production of synthesis gas, as in the traditional[12] methanol to hydrocarbon process. Although the mechanism of this reaction is not completely understood, there are proposals[13] for the intermediacy of an oxonium-ylide intermediate. In a similar way, there could be involvement[14] of a halonium-ylide species, formed upon deprotonation of the dimethylhalonium ion on a basic site, during the catalyzed transformation of halomethanes to olefins. Because the chlorine atom has available d orbitals, there could be stabilization of the ylide through p−d π bonding (Scheme 1).

SCHEME 1. Possible Resonance Structures of the Dimethylhalonium Ylides, Showing p−d π Bonding



Halonium ylides have been proposed as intermediates in carbene reactions for a long time.[15] The isolation of halonium ylides was reported[16] in the reaction of diazodicyanoimidazole with aryl halides. The photochemical and metal-catalyzed reactions of α-diazoketones with alkyl and aryl halides also involves[17] the formation of halonium ylides as intermediates. In this contribution, we report on the gas-phase formation and structure of dimethylhalonium ylides.

Experimental Section

Computational Details. Structures were optimized within the DFT approach at the B3LYP/6-31+(d,p) B3LYP/aug-cc-pVTZ levels.[18] For iodine compounds, LANL2DZ pseudo-potential, available in the Gaussian code, was used to describe its inner shells and so was done to bromine compounds for comparison purposes. Vibrational frequencies were also computed at the same level, to include zero-point vibrational energies in thermodynamic parameters and to characterize all structures as minima in the potential energy surface. A natural bond orbital analysis[19] was performed at the same level, especially for dimethylhalonium-ylide ions, to verify electronic interactions that might be relevant to stabilization. This was done in terms of second-order perturbation interaction energy ($E^{(2)}$). In this work our interest is in the interactions between the ylide-carbon lone-pair orbitals as donors and the ylide-carbon antibonding orbitals as receptors. All calculations were carried out with the Gaussian 98 package of molecular orbital programs.[20]

Gas-Phase MS Experiments. The $MS^{(2)}$ experiments[21] were performed using a pentaquadrupole (QqQqQ) mass spectrometer.[22] The QqQqQ consists of three mass-analyzing quadrupoles (Q1, Q3, and Q5), in which ion mass selection and mass analysis are performed, and two radio frequency-only reaction quadrupoles (q2, q4). Reactions were then performed in q2 with selected neutral reactants. For the $MS^{(2)}$ experiments, the ion of interest was generated by the dissociative 70 eV electron ionization of appropriate precursors (chloromethane and iodomethane) and mass-selected by Q1. After its ion−molecule reactions in q2 with the neutral reagents, Q5 was used to record the product ion mass spectrum, while operating Q3 and q4 in the "full" ion-transmission rf-only mode.

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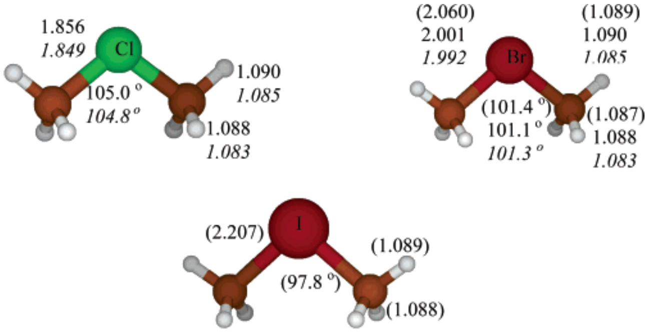

FIGURE 1. Optimized structures of the dimethylhalonium ions at B3LYP/6-31G+(d,p). Distances are in angstroms and angles are in degrees. In parentheses, the optimized values at B3LYP/LANL12DZ for the halogen atoms. In italic, the optimized values at the B3LYP/aug-cc-pVTZ level.

TABLE 1. Selected Geometric Parameters for the Dimethylhalonium and Dimethylhalonium Ylides at B3LYP/6-31G+(d,p)[a,b]

species	*d* CH_3-X (Å)	*d* CH_2-X (Å)	∠C−X−C (°)
	dimethylhaloniums		
dimethylchloronium	1.856		105.0°
	1.849		*104.8°*
dimethylbromonium	(2.060)		(101.4°)
	2.001		101.1°
	1.992		*101.3°*
dimethyliodonium	(2.207)		(97.8°)
	dimethylhalonium ylides		
dimethylchloronium ylide	1.991	1.719	123.0°
	1.964	*1.707*	*120.9°*
dimethylbromonium ylide	(1.998)	(1.998)	(123.3°)
	1.883	1.883	122.1°
	1.870	*1.870*	*120.9°*
dimethyliodonium ylide	(2.294)	(2.121)	(123.6°)

[a] In parentheses, the optimized values at B3LYP/LANL12DZ for the halogen atoms. [b] In italic, the optimized values at the B3LYP/aug-cc-pVTZ level.

Nominal sample and neutral gas pressures were typically 5 × 10^{-6} and 5 × 10^{-5} Torr, respectively, as monitored by a single ionization gauge located centrally in the vacuum chamber. The target gas pressure corresponds to a typical beam attenuation of 50−70% and to multiple collision conditions.[23] However, lower reaction yields, but similar sets of products, were always observed at lower pressure, mainly single collision conditions in q2. Instrument parameters, such as quadrupole offset potentials and lens voltages, were adjusted to maximize the abundance of the ionic products. The collision energy for ion−molecule reactions was typically 1 eV, calculated by the voltage difference between the ion source and the collision quadrupole.

Results and Discussion

Structure of the Dimethylhalonium and Dimethylhalonium Ylides. Figure 1 and Table 1 show the optimized structures of the dimethylhalonium cations at the B3LYP/6-31G+(d,p) level. The ions have a bent structure with the C−X−C angle increasing in the order I < Br < Cl. The calculated geometry is in good agreement with previous calculations[7] at the same level of theory. Figure 2 shows the calculated structures of the dimethylhalonium ylides. Compared with the respective halonium ions, the C−X−C angle for the halonium ylides increases considerably with substantial changes in the C−X bond lengths. The $^-CH_2-X$ bond (carbon atom bearing the negative charge) shrinks, whereas the CH_3-X bond elongates, compared with those for the dimethylhalonium ions. For instance, the CH_3-Cl bond length in the dimethylchloronium is 1.856 Å, whereas in the dimethylchloronium ylide the $^-CH_2-Cl$ and CH_3-Cl bond lengths are 1.719 and 1.991 Å, respectively. The C−X−C angle varies quite extensively for the halonium ions (105.0° in the dimethylchloronium, 101.1° in the dimethylbromonium, and 97.8° in the dimethyliodonium) but remains near constant for the halonium ylides (123.0°, 122.1°, and 123.6° in the respective chloronium, bromonium, and iodonium ylides). The angles in the dimethylhalonium ions reflect the steric repulsion of the methyl groups. As the halogen atom changes from chlorine to iodine, the angle decreases and the C−X bond increases. This suggests that in the dimethyliodonium ion the steric repulsion is less pronounced, and the angle approaches the geometry of a p orbital bonding, near 90°. In fact, NBO analysis shows over 75% of p orbital character for the halogen atoms. The basis set has little influence in the geometry. For instance, the CH_3-Cl bond in the dimethylchloronium ion is only 0.007 Å shorter, and the C−Cl−C bond angle is just 0.2° lower at the B3LYP/aug-cc-pVTZ level. Upon forming the dimethylchloronium ylide, the situation does not change much, with the CH_3-Cl bond being 0.27 Å and the CH_2-Cl being just 0.01 Å shorter than the values calculated at B3LYP/6-31G+(d,p). The C−Cl−C angle is 120.9° at B3LYP/aug-cc-pVTZ level, only 2.9° lower than the value calculated at B3LYP/6-31G+(d,p).

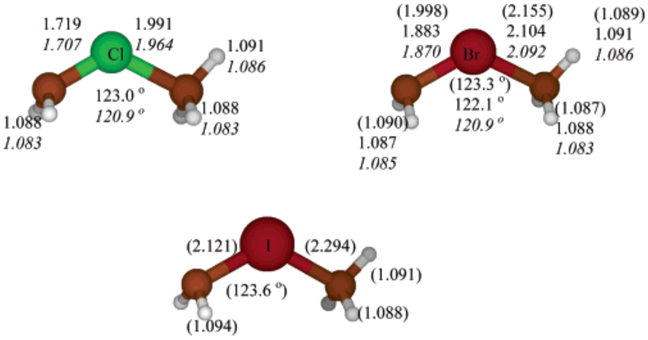

FIGURE 2. Optimized structures of the dimethylhalonium ylides at B3LYP/6-31G+(d,p). Distances are in angstroms and angles are in degrees. In parentheses, the optimized values at B3LYP/LANL12DZ for the halogens atoms. In italic, the optimized values at the B3LYP/aug-cc-pVTZ level.

NBO analysis showed that hyperconjugation between the ylide carbon lone-pair orbital and the methyl carbon−halogen antibonding orbital plays an important role in stabilizing the dimethylhalonium ylides. This hyperconjugation can be traced by the highest $E^{(2)}$ value found (between all interactions in each ion) for each ylide, as shown in Table 2. The increase in the $X-CH_3$ bond length and the C−X−C bond angle reflect this interaction. The same trend has been reported for other systems, especially when electronegative groups are attached. The crystal structure of the CF_3O^- anion shows[24] that the C−O bond length is significantly shorter compared to that of other alkoxides. Calculations[24,25] indicated that hyperconjugation is the main factor affecting the structural properties of fluorinated alcohols

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TABLE 2. Second-Order Perturbation Interaction Energy ($E^{(2)}$, kcal/mol) between the Carbon Ylide Lone Pair Orbital as the Donor and the Carbon(methyl)−Halogen Antibonding Orbital as the Receptor

halogen (X)	$E^{(2)}$, $(CH_2^-) \rightarrow (Cl-CH_3)^*$ (kcal/mol)
Cl[a]	39.2 (36.3)
Br[a]	32.6 (32.1)
Br[b]	23.3
I[b]	26.0

[a] Calculated at the B3LYP/6-31G+(d,p) level. In parentheses are shown $E^{(2)}$ values at the B3LYP/aug-cc-pVTZ level. [b] Calculated at the B3LYP/LANL2DZ level. In parentheses are shown $E^{(2)}$ values at B3LYP/aug-cc-pVTZ level.

and alkoxides. Yet, hyperconjugation has been described[26] to account for the high stability of CF_4. It also seems to play an important role in conformational analysis of alkanes[27] and half-cage alcohols.[28] The present results point out a significant stabilization of the dimethylhalonium ylides through hyperconjugation. On the other hand, the halogen d orbitals do not seem to account for any significant stabilization of the ylides, appearing in the orbital analysis with no more than 0.2% in its composition.

A recent DFT study on the structure and stabilization of the ethyl anion has appeared in the literature.[29] The preferred staggered conformation is due to hyperconjugative stabilization of the anion, which is most efficient in that conformation. The calculated second-order pertubation interaction energy ($E^{(2)}$) for the ethyl anion was about 12 kcal/mol, for the lone pair/σ^* C−H (anti) interaction. Table 2 shows that the $E^{(2)}$ pertubation energies are in the range of 23−39 kcal/mol for the dimethylhalonium ylides, indicating a much stronger stabilization of these species by hyperconjugation. The stabilization of anions through hyperconjugation has long been proposed[30] in the literature, especially to explain the acidity of alcohols, thiols, and amines in the gas phase.

Bond lengths and angles seem to be overestimated for the dimethylbromonium ylide and dimethylbromonium ions when calculated at the LANL2DZ level, as shown in Figures 1 and 2. It can also be seen that $E^{(2)}$ is smaller, using the pseudopotential method. This reduction may arise from the failure of this pseudopotential to correctly reproduce the bonding in the hypercoordinated bromine atom.

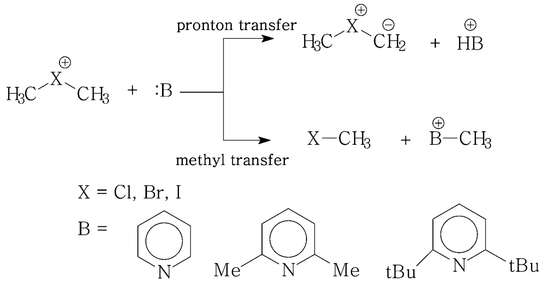
Acidity of the Dimethylhalonium Ions. Table 3 shows the thermochemical results for the acidity of the dimethylhalonium ions. Two reactions were considered, as shown in Scheme 2: (1) proton transfer, with the formation of the respective dimethylhalonium ylide, and (2) methyl transfer, with the formation of the respective methylhalide. One can see that for all calculated halonium ions, methyl transfer is exothermic, but proton transfer is otherwise endothermic. Nevertheless, for bulkier bases, the exothermicity of the methyl transfer and the endothermicity of the proton transfer decreases, making the energy difference for proton transfer less pronounced. These results indicated that dimethylhalonium ions are better Lewis acids than Bronsted acids, in agreement with results in solution, in which they are extensively used as methylating reagents.[5]

TABLE 3. Thermochemistry of the Acidity of the Dimethylhalonium Ions at the B3LYP/6-31+G (d,p) Level[a]

system	Δ*H* proton transfer (kcal/mol)	Δ*H* methyl transfer (kcal/mol)
	deprotonation energy	
dimethylchloronium	+255	
dimethylbromonium	+258	
dimethyliodonium[b]	+260	
	pyridine	
dimethylchloronium	+32 (+30)	−60 (−57.8)
dimethylbromonium	+35 (+31)	−60 (−53.2)
dimethyliodonium[b]	+36	−53
	2,6-dimethylpyridine	
dimethylchloronium	+24	−58
dimethylbromonium	+27	−58
dimethyliodonium[b]	+28	−51
	2,6-di-*tert*-butylpyridine	
dimethylchloronium	+18	−45
dimethylbromonium	+21	−45
dimethyliodonium[b]	+23	−38

[a] In parentheses, thermochemistry calculated at the B3LYP/aug-cc-pVTZ level. [b] Calculated at the B3LYP/LANL2DZ level for the halogen atom.

SCHEME 2. Gas-Phase Reactions of the Dimethylhalonium Ions with Pyridine Derivative Bases



The acidity of the dimethylhalonium ions follows the order Cl > Br > I, in terms of Lewis acidity (methyl transfer) and Bronsted acidity (proton transfer). This might be understood in terms of the polar (electrostatic) effect of the halogen atom and through the stabilization by hyperconjugation. The interaction energy $E^{(2)}$ in the halonium ylides increases in the same order as the acidity (Cl > Br > I). It is well-recognized[25] that negative hyperconjugation is more effective as the electronegativity of the atoms involved increases. Thus, the σ^* C−Cl antibonding orbital is a better electron pair receptor than the σ^* C−Br and C−I antibonding orbitals. However, the fact that methyl transfer is preferred over proton transfer indicates the poor coordinating ability of the halogen atoms in the dimethylhalonium ions. Moreover, C−X bond breaking, probably through an S_N2 reaction mechanism, prevails over C−H bond breaking to form the ylide. It is worth mentioning that a chloromethane iridium phosphine complex has been recently isolated.[31] Although the X-ray crystallographic analysis showed a bent Ir−Cl−CH_3 connection, with an angle of 109.3°, the C−Cl bond length is 1.77 Å, considerably shorter than the calculated C−Cl bond (1.849 Å) in the dimethylchloronium.

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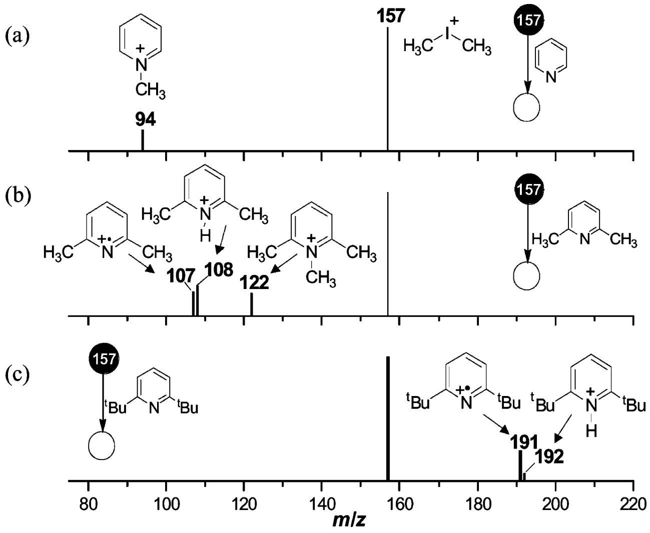

FIGURE 3. Mass spectra for the reaction of dimethyliodonium with (a) pyridine, (b) 2,6-dimethylpyridine, and (c) 2,6-di-*tert*-butylpyridine.

To evaluate the effect of the basis set, we performed calculations for dimethylchloronium and dimethylbromonium with pyridine at the B3LYP/aug-cc-pVTZ level. One can see in Table 2 that improving the basis set permitted a better discrimination of the thermochemistry for methyl transfer. At the B3LYP/6-31+G(d,p) level, the calculated ΔH for methyl transfer was virtually the same for both halonium ions (-60 kcal/mol), whereas at B3LYP/aug-cc-pVTZ, the reaction with the dimethylchloronium is 4.6 kcal/mol more exothermic than with dimethylbromonium. For proton transfer, the results were not much affected.

Compared with CH_3X^+H ions, the dimethylhalonium ions are much less acidic. For instance, the experimental[10] deprotonation energy of CH_3Cl^+H is 155 kcal/mol to form CH_3Cl. This is 100 kcal/mol lower than the calculated deprotonation energy of the dimethylchloronium ion, showing that the acidity of the proton bonded to the halogen atom is significantly higher than the acidity of the proton bonded to the methyl group, as would be expected. The trend is similar for the other halonium ions.

Comparison with the Experimental Gas-Phase Results. To verify whether the reactivity trends predicted by calculations would indeed be experimentally observed, we investigated the gas-phase intrinsic reactivity of the dimethylchloronium and dimethyliodonium ions with pyridine derivatives. As Figure 3 shows, methyl transfer is the preferred reaction, as predicted by calculations. With pyridine, the dimethylchloronium and dimethyliodonium ions react exclusively by methyl transfer to form methylated pyridine, with $m/z = 94$. For reactions with bulkier bases, like 2,6-dimethylpyridine and 2,6-di-*tert*-butylpyridine, proton transfer ($m/z = 108$ and 191, respectively) as well as single electron transfer (formation of a dimethylhalonium radical) are also observed (Figure 3). The gas-phase results are in good agreement with calculations, which predicted that methyl transfer is the preferred thermodynamic pathway. Notwithstanding, for bulkier bases, proton transfer and single electron transfer become competitive, likely because the transition state for methyl transfer is sterically demanding.

The results of the acidity of the dimethylhalonium ions indicated that these species are better Lewis acids than Bronsted acids. A possible explanation is related with the stabilization of the dimethylhalonium ylide. As shown in the NBO calculations, the negative charge is not significantly delocalized in the d orbitals of the halogen atom, and hyperconjugation with the antibonding C−X orbital is the main factor responsible for the stabilization of the species in the gas phase. On the other hand, the transfer of a methyl group and the formation of a methylhalide molecule, which releases the positive charge on the halogen atom and decreases its coordination state, is the preferred thermodynamic pathway.

Conclusions

The structure and acidity of the dimethylhalonium ions were studied at the DFT level of calculations. Results indicated that upon proton transfer to form the dimethylhalonium ylide, the C−X−C bond angle increases and there are modifications in the C−X bond lengths, indicative of hyperconjugation between the electron pair with the C−X antibonding orbital.

Calculations predict that methyl transfer to pyridine derivatives is preferred over proton transfer, but the predominance of methyl transfer becomes less pronounced for bulkier bases. The theoretical results have been fully corroborated by the gas-phase reactions, which showed that methyl transfer occurs exclusively with pyridine, but proton transfer, as well as single electron transfer, also occurs competitively for 2,6-dimethylpyridine and 2,6-di-*tert*-butylpyridine.

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Supporting Information Available: Atom coordinates and the **Z** matrix of the methylhalides, the dimethyhalonium ions, and the dimethylhalonium ylides. This material is available free of charge via the Internet at http://pubs.acs.org.

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