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ARTICLES

Density Functional Studies on the Thermal Aryl Migration in *β*-Dicarbonyl Ylides and Related Compounds[†]

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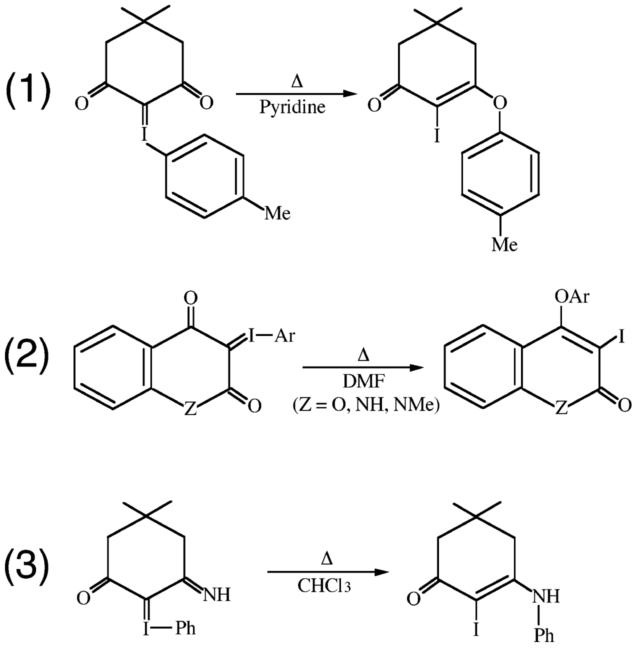
The potential energy surfaces for the unimolecular rearrangement reactions of *β*-dicarbonyl ylides and *β*-carbonylimidoyl ylides have been studied using the density functional method. All of the stationary points were determined at the B3LYP/LANL2DZdp level of theory. Four kinds of *β*-dicarbonyl ylide species containing fluorine, chlorine, bromine, and iodine have been chosen in this work as model reactants. Also, five *β*-carbonylimidoyl ylide molecules bearing nitrogen, phosphorus, arsenic, stibium, and bismuth have been used in the present study. In the latter reactions, two different reaction pathways have been proposed: (1) a 1,2-aryl shift to the pnicogen element and (2) A 1,2-aryl shift to the oxygen atom. That is, path 1 is reactant → TS-1 → Pro-1 and path 2 is reactant → TS-2 → Pro-2. Our theoretical findings strongly suggest that all intramolecular aryl migration reactions proceed via a one-step (concerted) reaction path. For the *β*-dicarbonyl ylide species, the smaller the atomic number of the halogen atom, the lower the barrier height, the larger the reaction enthalpy, and, in turn, the easier it is to undergo the intramolecular aryl migration under thermal conditions. Alternatively, the heavier the pnicogen element in the *β*-carbonylimidoyl ylides, the smaller the barrier height, and the larger the migration reaction enthalpy, even under thermal conditions. The results obtained allow a number of predictions to be made.

I. Introduction

Very recently, Moriarty published an elegant review paper in the *Journal of Organic Chemistry*.[1,2] In this fascinating paper, he found that the aryl group in *β*-dicarbonyl ylides can migrate from iodine to oxygen under thermal conditions.[1,2] In fact, three kinds of similar reactions reported in the literature can be found in Scheme 1. Of these, Nozaki et al.[2a] observed that reaction A → C should occur by way of B, which would result in C as shown in Scheme 2. They thus concluded that, "the rearrangement must proceed through a five-membered intermediate B rather than D".

These fascinating synthetical results inspired this study. If a *β*-dicarbonyl ylide containing the iodine atom (A) can undergo an aryl migration through five-membered B resulting in the final product (C), then would it be possible to extend this to other halogen atoms containing *β*-dicarbonyl ylide species? If this is possible, then which halogen atom containing *β*-dicarbonyl ylide species has the lowest activation energy and therefore can undergo the aryl migration fastest? In addition to these questions, it is interesting to know whether or not a similar reaction occurs when the halogen atom is replaced by a pnicogen element (such as eq 3 in Scheme 1). As far as we know, until now neither experimental nor theoretical studies have been performed on these systems. In this theoretical work, four typical *β*-dicarbonyl ylides with halogen atoms and five with pnicogen elements were selected as model systems for investigation of the geometry and energetics of aryl migration. The reason for choosing these compounds is that they are isoelectronic species and might therefore be expected to show similar chemical behavior. Moreover, because most of these molecules have not yet been synthesized and characterized, it is reasonable to infer that they

SCHEME 1



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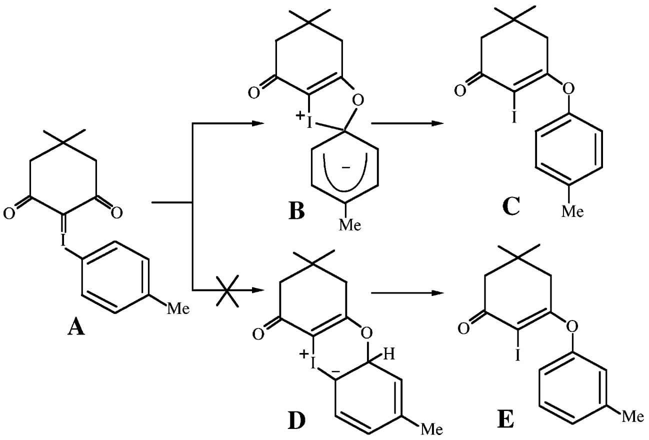
SCHEME 2



may serve as potential molecules for making further development in the chemistry of thermal aryl migrations.

II. Methology

All geometries were fully optimized without imposing any symmetry constraints, although in some instances the resulting structure showed various elements of symmetry. For our density functional (DFT) calculations, we used the hybrid gradient-corrected exchange functional proposed by Becke[3] combined with the gradient-corrected correlation functional of Lee, Yang, and Parr.[4] This functional is commonly known as B3LYP and has been shown to be quite reliable for both geometries and energies.[5] These B3LYP calculations were carried out with relativistic effective core potentials on group-15 elements modeled using the double-ζ (DZ) basis sets[6] augmented by a set of d-type polarization functions.[6e] The DZ basis set for the hydrogen element was augmented by a set of p-type polarization functions (p exponents 0.356). The d exponents used for N, P, As, Sb, and Bi are 0.736, 0.364, 0.286, 0.207, and 0.192, respectively. Accordingly, we denote our B3LYP calculations by B3LYP/LANL2DZdp. Vibrational frequency calculations at the B3LYP/LANL2DZdp level were used to characterize all stationary points as either minima (the number of imaginary frequencies (NIMAG) = 0) or transition states (NIMAG = 1). The relative energies were thus corrected for vibrational zero-point energies (ZPE, not scaled). Thermodynamic corrections to 298 K, ZPE corrections, heat capacity corrections, and entropy corrections (ΔS) obtained were applied at the B3LYP/LANL2DZdp level. Thus, the relative free energy (ΔG) at 298 K was also calculated at the same level of theory. All of the DFT calculations were performed using the GAUSSIAN 03 package of programs.[7]

III. Results and Discussion

(1) Geometries and Energetics of Intramolecular Aryl Migration in β-Dicarbonyl Ylides Containing the Halogen Atom. The four sets of β-dicarbonyl ylides incorporating a halogen atom used in this work are represented as follows: Rea-F (fluorine), Rea-Cl (chlorine), Rea-Br (bromine), and Rea-I (iodine). To the best of our knowledge, none of these molecules have been isolated and characterized.[2a] The following reaction mechanism has been used to explore the intramolecular aryl migration reaction of a halogen containing β-dicarbonyl ylide: Rea → TS → Pro. For the systems Rea-F, Rea-Cl, Rea-Br, and Rea-I, their geometries and energetics have been calculated using the B3LYP/LANL2DZdp level of theory. The relative energies of the stationary points for the above mechanism are collected in Table 1 and Figure 1. Their Cartesian coordinates are given in the Supporting Information. The major conclusions drawn from the current study can be summarized as follows.

First, the theoretical results depicted in Figure 1 reveal that all of the β-dicarbonyl ylide reactants adopt a bent structure around the halogen X center. It is intriguing to find that the $\angle$CXC angle decreases in the order Rea-F (118.4°) > Rea-Cl (109.4°) > Rea-Br (107.3°) > Rea-I (104.7°). The reason that the species containing the heavier halogen element favors a smaller bond angle may be attributed to the "orbital nonhybridization effect", also known as the "inert s-pair effect".[8] As X changes from fluorine to iodine, the valence s orbital becomes more strongly contracted than the corresponding p orbitals.[8] Namely, the size difference between the valence s and p orbitals increases from F to I. Consequently, the valence s and p orbitals of the heavier members of the group overlap less to form strong hybrid orbitals.[8] It is therefore expected that a β-dicarbonyl ylide compound with a heavier X center favors a smaller bond angle $\angle$CXC.

Second, the optimized transition state structures (TS-F, TS-Cl, TS-Br, and TS-I) together with arrows indicating the main atomic motion in the transition state eigenvector are shown in Figure 1, respectively. All four transition state structures show the same five-center pattern involving halogen (X), carbon, and oxygen atoms. The transition state vectors represented by the heavy arrows in TS-F, TS-Cl, TS-Br, and TS-I are all in accordance with the aryl migration process, primarily the aryl group migrating from the X element to the oxygen center. The B3LYP frequency calculations for transition states TS-F, TS-Cl, TS-Br, and TS-I predict the unique imaginary frequency values of 368i, 356i, 346i, and 345i, respectively. It should be mentioned here that our calculated transition state structures for the aryl migration in the β-dicarbonyl ylides are quite similar to those proposed by Nozaki et al.[2a] as stated in the Introduction. That is to say, our B3LYP computation results demonstrate that it is the five-membered transition state, rather than the six-membered one, that occurs in the intramolecular aryl migration reaction of β-dicarbonyl ylide as shown in Scheme 2.

Third, our theoretical findings suggest that, from a kinetic viewpoint, the aryl migration reactions of the less-bent β-dicarbonyl ylide systems (larger $\angle$CXC angle) are more facile. For instance, the trend in activation energy increases in the following order: TS-F (15.43 kcal/mol) < TS-Cl (18.10 kcal/mol) < TS-Br (21.14 kcal/mol) < TS-I (22.61 kcal/mol). Also, we have calculated the free energy differences ($\Delta G^{\ddagger}$) for such rearrangements at 298 K, which are also given in Table 1. As shown there, the values of $\Delta G^{\ddagger}$, the free energy difference between transition state and its corresponding reactant, are +16.42, +19.63, +22.21, and +23.89 kcal/mol for TS-F, TS-Cl, TS-Br, and TS-I, respectively. It is therefore predicted that the smaller the atomic number of halogen, the larger the $\angle$CXC bond angle in the reactant and the easier the intramolecular aryl migration of β-dicarbonyl ylide under thermal conditions (vide infra).

Fourth, it is obvious that all of the intramolecular aryl migration reactions (left to right in Figure 1) are thermodynamically exothermic; the trend in reaction enthalpy follows the same trend as the activation energy: Pro-F (−58.24 kcal/mol) < Pro-Cl (−43.98 kcal/mol) < Pro-Br (−36.66 kcal/mol) < Pro-I (−32.35 kcal/mol). Besides these, we have calculated the free energy differences (ΔG) for these aryl migrations at 298 K. As one can see in Table 1, the values of ΔG increase in the same order: Pro-F (−57.28 kcal/mol) < Pro-Cl (−42.94 kcal/mol) < Pro-Br (−36.00 kcal/mol) < Pro-I (−31.90 kcal/mol). It

TABLE 1: Relative Energies for the Aryl Migration in β-Dicarbonyl Ylides: Reactant → Transition State → Product[a,b]

system	reactant (kcal mol^{-1})	$\Delta E^{\ddagger c}$ (kcal mol^{-1})	ΔH^{c} (kcal mol^{-1})	$\Delta G^{\ddagger d}$ (kcal mol^{-1})	ΔG^{d} (kcal mol^{-1})
X = F	0.0	15.43	−58.24	16.42	−57.28
X = Cl	0.0	18.10	−43.98	19.63	−42.94
X = Br	0.0	21.14	−36.66	22.21	−36.00
X = I	0.0	22.61	−32.35	23.89	−31.90

[a] All were calculated at the B3LYP/LANL2DZdp level of theory. The B3LYPdp optimized structures of the stationary points are provided in the Supporting Information. [b] Energy differences have been zero-point corrected. See the text. [c] The energy relative to the corresponding reactant. [d] The Gibbs free energy (298 K) relative to the corresponding reactant.

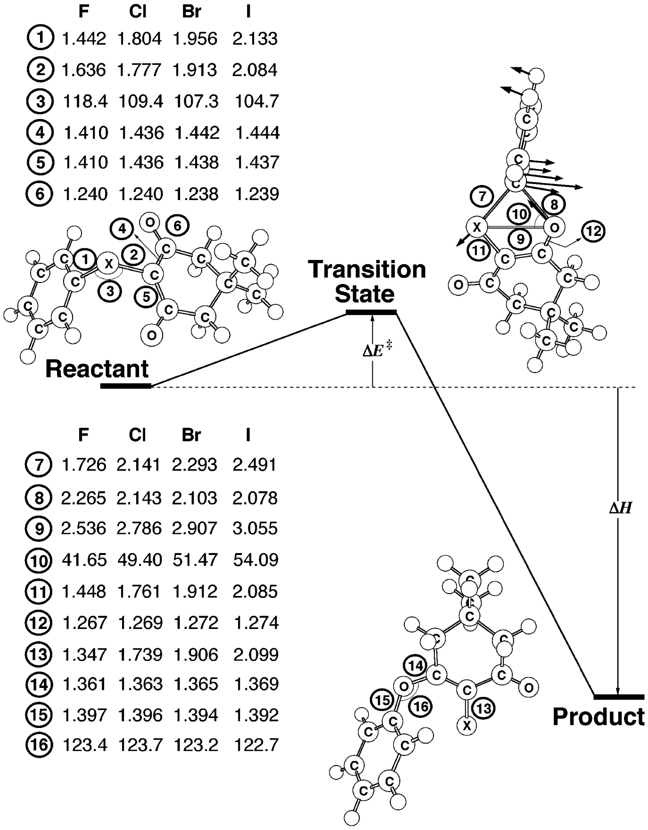


Figure 1. B3LYP/LANL2DZ optimized geometries (in angstroms and degrees) of the reactants (singlet), transition states, and migration products of Rea-X (X = F, Cl, Br, and I). The relative energies for each species are listed in Table 1. The heavy arrows in the transition structure indicate the main components of the transition vector. Hydrogens are omitted for clarity.

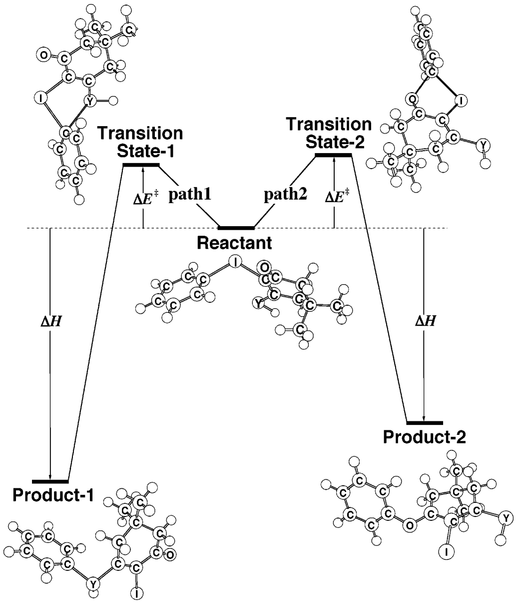


Figure 2. Potential energy surfaces of the reactants, transition states, and different migration products of Rea-Y (Y = N, P, As, Sb, and Bi). The relative energies for each species are listed in Table 2. Hydrogens are omitted for clarity.

should be noted that the calculated values of both activation energy and reaction enthalpy at low temperature (0 K) are slightly larger than those at room temperature (298 K). Again, our DFT results demonstrate that the smaller the atomic number of the halogen atom (X), the lower the barrier height, the more exothermic the reaction enthalpy, and, in turn, the easier the intramolecular aryl migration.[1,2] Because there are no relevant experimental and theoretical data on other halogen-containing systems, the above result is a prediction.

In short, the present calculations suggest the following about the intramolecular aryl migration mechanism for the β-dicarbonyl ylide reaction: (1) It may proceed via a one-step reaction path (formation of one transition state, then in a subsequent step to the final product). (2) In principle, all of the β-dicarbonyl ylide species containing one halogen atom should undergo intramolecular aryl migration under thermal conditions. (3) Nevertheless, the unimolecular aryl migration in the β-dicarbonyl ylide bearing a fluorine atom is predicted to be faster than that in species containing the other halogen elements.

(2) Geometries and Energetics of Intramolecular Aryl Migration in β-Carbonylimidoyl Ylides Containing the Pnicogen Atom. The five sets of β-carbonylimidoyl ylides containing a pnicogen atom used in this work are shown in Figure 2: Rea-N, Rea-P, Rea-As, Rea-Sb, and Rea-Bi. To our knowledge, to date only Rea-N has been reported in the literature (also see eq 3 in Scheme 1).[2d] For consistency with our previous work, the following reaction mechanisms have been used to explore the unimolecular aryl migration reaction of β-carbonylimidoyl ylides: (path 1) Rea → TS-1 → Pro-1 (the aryl migrating to the pnicogen center) or (path 2) Rea → TS-2 → Pro-2 (the aryl migrating to the oxygen center). For the systems Rea-N, Rea-P, Rea-As, Rea-Sb, and Rea-Bi, their geometries and energetics have been calculated using the B3LYP/LANL2DZdp level of theory. The relative energies of the stationary points for the above mechanisms are collected in Table 2. Their Cartesian coordinates are given in the Supporting Information. There are several important conclusions from these results to which attention should be drawn.

First, according to the discussion in the previous section, it is expected that the heavier the atomic number of pnicogen Y (Y = N, P, As, Sb, and Bi), the smaller its bond angle ∠CYH. Our B3LYP results are in agreement with this prediction. Namely, the theoretical investigations suggest that the bond angle ∠CYH decreases in the order Rea-N (110.2°) > Rea-P

TABLE 2: Relative Energies (in kcal/mol) for Two Reaction Paths: Reactant → Transition State-1 → Product-1 (Path 1; the Aryl Migrating to the Pnicogen Center) and Reactant → Transition State-2 → Product-2 (Path 2; the Aryl Migrating to the Oxygen Center)[a,b]

system	$\Delta E^{\ddagger}$ [c] (path 1)	ΔH [d] (path 1)	$\Delta E^{\ddagger}$ [c] (path 2)	ΔH [d] (path 2)	$\Delta G^{\ddagger}$ [e] (path 1)	ΔG [f] (path 1)	$\Delta G^{\ddagger}$ [e] (path 2)	ΔG [f] (path 2)
Y = N	+15.65	−58.81	+17.09	−56.67	+17.34	−57.48	+18.88	−57.96
Y = P	+10.93	−58.12	+16.37	−51.64	+12.30	−57.79	+17.73	−52.13
Y = As	+7.319	−56.26	+14.55	−47.68	+9.349	−55.38	+16.89	−48.19
Y = Sb	+4.178	−56.54	+13.52	−43.89	+5.605	−56.41	+14.80	−44.26
Y = Bi	+5.009	−52.20	+15.77	−42.17	+6.637	−51.98	+17.22	−42.46

[a] At the B3LYP/LANL2DZdp level of theory. The B3LYP optimized structures of the stationary points can be found in the Supporting Information. [b] Energy differences have been zero-point corrected. See the text. [c] The activation energy of the transition state, relative to the corresponding reactants. [d] The reaction enthalpy of the product, relative to the corresponding reactants. [e] The Gibbs free activation energy (298 K) relative to the corresponding reactant. [f] The Gibbs free enthalpy energy (298 K) relative to the corresponding reactant.

(96.41°) > Rea-As (96.00°) > Rea-Sb (94.73°) > Rea-Bi (91.91°). Again, the ∠CYH angles in Rea-Sb and Rea-Bi are closed to 90° and provide evidence for the core-like nature of the 5s and 6s electrons, that is, for the so-called "inert s-pair effect"[8] discussed earlier. Apparently, the heavier group-15 elements are pivotal atoms in this regard. These results are consistent with those reported in the previous studies cited above and will not be discussed further.

Second, as one can see in Figure 2, the unimolecular aryl migration to both the pnicogen atom and to the oxygen atom were investigated in the Rea-N, Rea-P, Rea-As, Rea-Sb, and Rea-Bi systems, and are denoted by path 1 and path 2, respectively. Of the two reaction paths, the more favorable is path 1 at the B3LYP/LANL2DZdp level of theory as shown in Table 2 and Figure 2. Our B3LYP results indicate that the activation energy (kcal/mol) decreases in the order TS-N-Path1 (15.65) > TS-P-Path1 (10.93) > TS-As-Path1 (7.319) > TS-Bi-Path1 (5.009) > TS-Sb-Path1 (4.178); a similar trend can also be found in path 2, that is, TS-N-Path2 (17.09) > TS-P-Path2 (16.37) > TS-Bi-Path2 (15.77) > TS-As-Path2 (14.55) > TS-Sb-Path2 (13.52). Besides this, the computational results show that the transition state for path 2 is 1.4−11 kcal/mol less stable than that for path 1. One may thus conclude that the heavier the atomic number of the pnicogen atom, the more facile the intramolecular aryl migration of the corresponding β-carbonylimidoyl ylide. To consider the thermal conditions, we calculated the free energy differences ($\Delta G^{\ddagger}$) for the two reaction paths at room temperature (298 K). As seen in Table 2, the order of $\Delta G^{\ddagger}$ at 298 K for path 1 is quite similar to that of $\Delta H^{\ddagger}$ at 0 K, that is, TS-N-Path1 (17.34) > TS-P-Path1 (12.30) > TS-As-Path1 (9.349) > TS-Bi-Path1 (6.637) > TS-Sb-Path1 (5.605). The analogous effect for path 2 can also be seen in Table 2; that is, TS-N-Path2 (18.88) > TS-P-Path2 (17.73) > TS-Bi-Path2 (17.22) > TS-As-Path2 (16.89) > TS-Sb-Path2 (14.80). In other words, even considering thermal effects, the barrier for path 1 is still lower than that for path 2 for the corresponding reactant. In consequence, all of these results demonstrate that the heavier the atomic number of the pnicogen atom (Y), the lower the barrier height and, in turn, the easier it is to undergo the intramolecular aryl migration to the pnicogen atom. For β-carbonylimidoyl ylides bearing antimony or bismuth elements, these species would readily undergo unimolecular aryl migration from the iodine atom to the pnicogen element (vide infra).

Third, although these two reaction pathways can produce two kinds of migration products (i.e., the phenyl group attached to either the pnicogen atom or to the oxygen atom), their reaction enthalpies are similar to each other. For instance, as can be seen in Table 2, at 0 K the reaction enthalpy (ΔH) for these two reaction paths are all exothermic, ranging from −59.0 to −52.0 and −57.0 to −42.0 kcal/mol for paths 1 and 2, respectively. Again, the reaction enthalpy for the former reaction is more exothermic than that for the latter by 2.1−10 kcal/mol. We also calculated ΔG (kcal/mol) at room temperature (298 K) for these two reaction paths. As demonstrated in Table 2, the free energy difference ΔG (kcal/mol) between reactant and final migration product ranges from −58.0 to −52.0 and −58.0 to −43.0 kcal/mol for paths 1 and 2, respectively. Taking all of the above computational results together, our theoretical findings therefore strongly suggest that intramolecular aryl migration from the iodine atom to the pnicogen element is both kinetically and thermodynamically more favorable than migration from the iodine atom to the oxygen atom.

In summary, the intramolecular aryl migration reaction in the β-carbonylimidoyl ylide species is not only concerted (proceeding without formation of an intermediate) but also synchronous (with bond forming and breaking occurring simultaneously in the transition states of lower energy). Additionally, in the case of Rea-N, Rea-P, Rea-As, Rea-Sb, and Rea-Bi, it appears that the intramolecular aryl group should migrate to the pnicogen element rather than to the oxygen atom. Moreover, we also predict that the heavier the pnicogen element contained in the β-carbonylimidoyl ylide, the smaller the barrier height, and the more exothermic the migration reaction enthalpy, even under thermal conditions.

IV. Conclusions

In this paper, possible mechanisms for the thermal intramolecular aryl migration reactions in β-dicarbonyl ylides and β-carbonylimidoyl ylides have been studied systematically. The present study predicts that the barrier height for the unimolecular aryl migration in the β-dicarbonyl ylide bearing a halogen atom decreases in the order F > Cl > Br > I, whereas the activation energy for a similar reaction in the β-carbonylimidoyl ylide with a pnicogen element increases in the order N < P < As < Sb ≈ Bi. In the latter reactions, our theoretical study anticipates that intramolecular aryl migration from the iodine atom to the pnicogen element are both kinetically and thermodynamically more favorable than migration from the iodine atom to the oxygen under thermal conditions.

It should be pointed out that the present calculations provide the first theoretical estimation of the activation energy for these processes and qualitative evidence for the feasibility of such elementary reactions. Although generalization of the results presented here might be questioned by the limitations of the applied methodology, we think that the level of interest in this subject and the important implications suggested by these results make further research in this area a priority.

We encourage experimentalists to carry out further experiments to confirm our predictions.

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Supporting Information Available: The Cartesian coordinates and the B3LYPdp optimized structures of the stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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