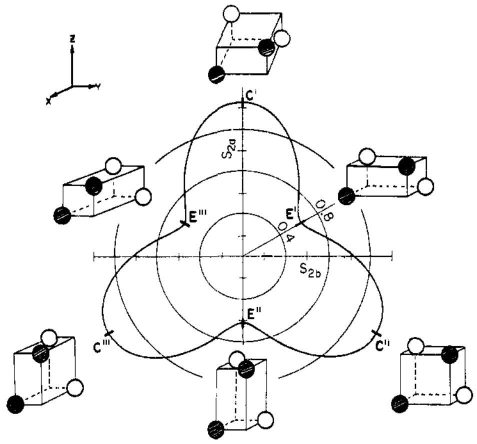

Figure 2. Plot of $\rho(\alpha)$ representing the shape of the minimum energy pathway in S_{2a}, S_{2b} (rad Å) vibrational space. T_d is at (0,0). C′, C″, C‴ are the compressed and E′, E″, E‴ are the elongated tetrahedra (D_{2d}). The space has a minimum symmetry of D_2. Square planes would be $\rho = 3.62$; $\alpha = 0, 2\pi/3, 4\pi/3$. The structures shown along the pathway contain an aribitrarily selected shaded pair of atoms in order to show the dynamical averaging.

represent two different electronic states. Relative sizes of the different electronic states of the cluster are shown in Figure 1b. Here we observe the participation of the totally symmetric stretch. For T_d Sn_4^{2-} the electron occupancy can be summarized as (inner valence)^{16} e^2. Distortion to D_{2d} symmetry breaks the e orbital symmetry down to a_1 and b_1, so that the energies plotted are for the states a_1^2 and b_1^2. These single-determinant spin singlets are degenerate for T_d symmetry but without "essential" configuration interaction (CI) do not represent either of the expected singlet terms (^1E and $^1A_1$) for this symmetry. Thus our method is incomplete for T_d symmetry itself. If the equilibrium geometry were tetrahedral, a paramagnetic $^3A_2$ ground term would be expected. However, there is no evidence of paramagnetism in solution,[7] suggesting a nontetrahedral species. Far from T_d symmetry the CI becomes less important and our single-determinantal description becomes valid.

Distortions of two other types were tried: (1) for a given θ, the azimuthal angle ϕ was increased for the two atoms above the x–y plane and decreased a like amount for those below it, reducing the symmetry to D_2 and (2) for a given θ the "radial" coordinates of an opposite pair of atoms were increased while those of the second opposite pair were decreased keeping the "edge lengths" constant (diamond-type bend for the square), reducing the symmetry to C_{2v}. The energy of the compressed tetrahedron specified above proved to be minimum with respect to these distortions, while the energy of the elongated tetrahedron was at a maximum with respect to the variation of ϕ.

In Figure 2 a fluxional pathway is represented by the trefoil $\rho(\alpha) = \rho_0 + \rho_1 \cos(3\alpha)$, where $\rho = (S_{2a}^2 + S_{2b}^2)^{1/2}$, $\alpha = \tan^{-1}(S_{2b}/S_{2a})$, and S_{2a} and S_{2b} are e-bending coordinates for a tetrahedron.[20] Constants ρ_0 and ρ_1 are obtained from the minimum energy compressed and elongated tetrahedra and are, respectively, 1.037 rad Å and 0.405 rad Å. Threefold symmetry in the S_{2a}, S_{2b} space (e-bend in T_d) requires the periodicity of the functional form of $\rho(\alpha)$. Further, the wave function changes smoothly from b_1^2 to a_1^2 as the metal cluster follows the motion through D_2 symmetry (as the phase angle α increases by π). Our calculated value of 40 kJ mol^{-1} for the barriers encountered along the pseudorotational pathway (Figure 2) falls below the minimum barrier height detectable by room-temperature NMR. Thus, per our calculations, there should be "effective" T_d symmetry, i.e., only one type of ^{119}Sn–^{117}Sn interaction.

We emphasize that while NMR evidence[7] is compatible with either statically or dynamically equivalent Sn–Sn pairs for Sn_4^{2-} in solution, the former explanation implying T_d symmetry, our ab initio study clearly supports the latter interpretation. The structural data[8] for the ion in the solid are characterized by substantial thermal parameters and thus may be compatible with, but do not confirm, our result that this 4-atom 18-valence electron cluster is more stable as a flattened tetrahedron of D_{2d} symmetry than as a regular tetrahedron or a square.

Acknowledgment. We thank Professor R. W. Rudolph, M. W. L. Wilson, and Professor J. D. Corbett for informing us of the results of their experiments, Dr. C. S. Ewig for his pseudopotential program (POLYATOM-EP), and the University of Michigan Computing Center for a generous allocation of computing time.

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(20) S. J. Cyvin, "Molecular Vibrations and Mean Square Amplitudes", Elsevier, Amsterdam, 1968, pp 122–123.

Azidomethyl Phenyl Sulfide. A Synthon for NH_2^+

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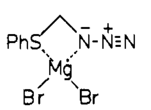
Received December 12, 1980

The growth in the importance of direct metalation methods[1] creates a requirement for conjunctive reagents capable of directly combining with such organometallics. The importance of primary amines, both as synthetic intermediates and as entries into nitrogen heterocycles, led us to search for a source of NH_2^+ which could be introduced by a conjunctive reagent requiring nothing more than a hydrolytic workup.[2-4] Our work on α-sulfenylated alkyl azides[5] turned our attention to azidomethylphenyl sulfide (**1**). While azides bearing electron-withdrawing groups are facilely attacked by Grignard reagents at the terminal nitrogen to give triazenes, very few reports exist for alkyl azides in which the

$PhSCH_2N_3$

1



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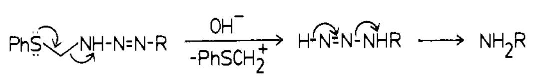

(1)

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(1) Gilman, H.; Morton, J. W., Jr. *Org. React.* **1954**, *6*, 258. Stowell, J. C. "Carbanions in Organic Synthesis"; Wiley: New York, 1979. Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *29*, 1.

(2) Hydroxylamine and chloramine derivatives are not satisfactory due to the presence of acidic hydrogens. For a review, see: Tamura, Y.; Minamikawa, J.; Ikeda, M. *Synthesis* **1977**, 1. For representative references, see: Sheradsky, T.; Nir, Z. *Tetrahedron Lett.* **1969**, 77. Sheradsky, T.; Salemnick, G.; Nir, Z. *Tetrahedron* **1972**, *28*, 3833. Radhakrishna, A.; Loudon, G. V.; Miller, M. J. *J. Org. Chem.* **1979**, *44*, 4837. Scopes, D. I. C.; Kluge, A. F.; Edwards, J. A. *Ibid.* **1977**, *42*, 376. Wallace, R. G. *Aldrichim. Acta* **1980**, *13*, 3. Schmitz, E.; Jahnisch, K. *Z. Chem.* **1971**, 458. Tamura, Y.; Kato, S.; Ikeda, M. *Chem. Ind.* (*London*) **1971**, 767. Yamada, S.; Oguri, T.; Shioiri, T. *Chem. Commun.* **1972**, 623. Oguri, T.; Shioiri, T.; Yamada, S. *Chem. Pharm. Bull. Jpn.* **1975**, *23*, 167. Coleman, G. H.; Hauser, C. R. *J. Am. Chem. Soc.* **1928**, *50*, 1193. Coleman, G. H.; Forrester, R. A. *Ibid.* **1936**, *58*, 27. Coleman, G. H.; Hermanson, J. L.; Johnson, H. L. *J. Am. Chem. Soc.* **1937**, *59*, 1896. Horiike, M.; Oda, J.; Inouye, Y.; Ohno, M. *Agric. Biol. Chem.* **1969**, *33*, 292.

(3) Disubstituted hydroxylamine derivatives have served as a way to introduce disubstituted amino groups. Boche, G.; Mayer, N.; Bernheim, M.; Wagner, K. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 687. Barton, D. H. R.; Bould, L.; Clive, D. L. J.; Magnus, P. D.; Hase, T. *J. Chem. Soc. C.* **1971**, 2204.

(4) Previous use of azides have required reductive conditions to create the amino group. Smith, P. A. S.; Rowe, C. D.; Brunner, L. B. *J. Org. Chem.* **1969**, *34*, 3430. For reviews, see: "The Chemistry of the Azido Group"; Patai, S., Ed.; Wiley: New York, 1971. Boyer, J. H.; Canter, F. C. *Chem. Rev.* **1954**, *54*, 1. Azidotriphenylsilane has been used to aminate two Grignard reagents in low yield: Wiberg, N.; Joo, W. C. *J. Organomet. Chem.* **1970**, *22*, 333.

(5) Trost, B. M.; Vaultier, M.; Santiago, M. *J. Am. Chem. Soc.* **1980**, *102*, 7929.

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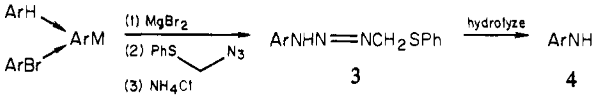
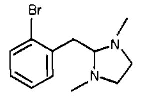
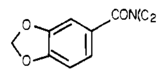
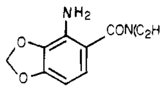
Table I. Amination of Organometallics



entry	ArX	3, yield, % (mp, °C)[d]	product	yield,[h] %	hydrolysis[v] method
1	C_6H_5Br[a]	75[e] (73.0-73.5)	$C_6H_5NH_2$	88[i,o]	A
			$C_6H_5NH_2$	90[i,o]	B
2	$4\text{-}CH_3OC_6H_4Br$[a]	40[e] (87)	$4\text{-}CH_3OC_6H_4NH_2$ (**5**)	72[i,o]	B
		70[e,f]	$4\text{-}CH_3OC_6H_4NH_2$ (**5**)	50[i,o]	A
3	$C_6H_5OCH_3$[b]	79[e] (55.5-56.5)	$2\text{-}CH_3OC_6H_4NH_2$ (**6**)	98[i,o]	A
4	$C_6H_5CH_2N(CH_3)_2$[b]	---	$2\text{-}NH_2C_6H_4CH_2N(CH_3)_2$ (**7**)	71-85[k,p]	A
5	 [c]	---	indole	60[j,m,o]	A
6	$1,3\text{-}(CH_3O)_2C_6H_4$[b]	---	$2,6\text{-}(CH_3O)_2C_6H_3NH_2$ (**8**)	50-67[k,l,q]	A
7	$4\text{-}C_6H_5C_6H_4OCH_3$[b]	90[g] (90.0)	$2\text{-}CH_3O\text{-}5\text{-}C_6H_5C_6H_3NH_2$ (**9**)	91[i,r]	A
8	$4\text{-}ClC_6H_4NHCO\text{-}t\text{-}C_4H_9$[b]	75[g] (111-112)	$2\text{-}NH_2\text{-}4\text{-}ClC_6H_3NHCO\text{-}t\text{-}C_4H_9$ (**10**)	88[i,s,t]	A
9	 [b]	---	 **11**[k,n,t,u]	71[k,n,t,u]	A

[a] Grignard reagent prepared directly in normal fashion with Mg.

[b] Lithiation performed with *n*-butyllithium, except for entry 9, in which case *sec*-butyllithium was employed. Anhydrous magnesium bromide added.

[c] Metal-halogen exchange performed with *n*-butyllithium. Anhydrous magnesium bromide added.

[d] Yield of recrystallized triazenes. The triazenes have been fully characterized spectrally and by combustion analysis and/or high-resolution mass spectroscopy; - - - indicates triazene not isolated but directly converted to amine.

[e] Yield based upon the titer of the solution of the organometallic intermediate.

[f] Yield of crude product as determined by NMR analysis.

[g] Yield based upon starting hydrocarbon.

[h] Yield of isolated, purified product.

[i] Yield from triazene.

[j] Overall yield from aryl bromide.

[k] Overall yield from starting hydrocarbon.

[l] In addition, a 23–14% yield of 2,6-dimethoxy-4-[phenyl(thiomethyl)]aniline, bp 150 °C (0.05 mm), mp 62–63 °C, was isolated.[10] It was fully characterized by spectral analysis and elemental composition. In this case, yield of **8** was a function of concentration in the hydrolysis with higher dilution enhancing the yield.

[m] Product isolated after acidification.

[n] Yield becomes 77% based upon recovered starting material.

[o] Product has been characterized by comparison to authentic sample.

[p] Bp 57–60 °C (0.2 mm), mp 36.5–37 °C (lit.[11] bp 107 °C (14 mm), mp 36–7 °C).

[q] Mp 75–76 °C (lit.[12] 75.5–77 °C).

[r] Mp 79.5–81.0 °C (lit.[13] 80–81 °C).

[s] Mp 153.0–153.5 °C.

[t] Compound fully characterized spectrally and elemental composition determined by high-resolution mass spectroscopy.

[u] Mp 63.8–64.0 °C.

[v] Method A = KOH, H_2O, CH_3OH, THF; method B = HCO_2H, H_2O.

reactions are claimed to be very slow or proceed in low yield.[6] The sulfur substitutent could facilitate attack on an alkyl azide by coordination as shown in **2** and provide a pathway for base-catalyzed decomposition to the desired amines as shown in eq 1.

Azidomethyl phenyl sulfide [IR 2090 cm^{-1}; ^{1}H NMR δ 7.2–7.6 (m, 5 H) and 4.42 (s, 2 H); ^{13}C NMR δ 134.5, 131.2, 129.8, 128.0, 55.9] was prepared in 93% overall yield from thioanisole by chlorination (SO_2Cl_2, CH_2Cl_2, reflux) and azide displacement [NaN_3, NaI (catalytic), CH_3CN, reflux].[7] Azide **1** is a colorless, stable[8] liquid, bp 55–58 °C (0.23 mm), which has been stored in a freezer for prolonged periods of time. Direct utilization of organolithium reagents failed presumably because of the lower Lewis acidity of lithium salts. Addition of 1 equiv of anhydrous magnesium bromide[9] to the organolithium and then addition of the resultant solution to **1** between −78 and 0 °C gave the triazenes **3** as summarized in Table I, entries 3–9. Obviously, direct utilization of Grignard reagents (Table I, entries 1 and 2) precluded the need to add magnesium bromide. The triazenes could easily be isolated as was done in entries 1–3,7, and 8, but for the purpose of amination, it was unnecessary. Direct treatment with aqueous potassium hydroxide at room temperature caused gas evolution and isolation of the aromatic primary amines **4** in good to high yields (Table I). Alternatively, aqueous formic acid also accomplishes the same reaction (Table I, entries 1 and 2).

In a typical procedure, to 1.1–1.2 equiv of azide **1** in dry THF (~0.5 M) at −78 °C was added 1.0 equiv of the ether, hexane, or THF solution of the organometallic reagent, to which, in the case of organolithium reagents, 1.0 equiv of anhydrous magnesium bromide in ether had already been added. After 1–2 h, the mixture was warmed to −20 or 0 °C and then quenched with saturated aqueous ammonium chloride. The resulting triazene was dissolved in degassed THF and methanol (1 mL of each per mmol) and 50% aqueous potassium hydroxide solution (1 mL per mmol) was added slowly. After stirring for 2–24 h, aqueous workup followed by purification (distillation and/or recrystallization) gave the pure amines.

This amination approach offers several advantages. Steric factors are minimal as shown by introduction of the amino group at the extremely sterically hindered positions in Table I, entries 6 and 9, to give amines **8** and **11**. The general ortho regioselectivity also shown by formation of amines **6**,**7**,**9**, and **10** (Table I, entries 3,4,7, and 8) complements an approach via standard electrophilic substitution reactions. Selective formation of the anthranilic acid derivative **11**[14] illustrates the utility for generation of substituted arynes derived from anthranilic acids. Chemoselective monoacylation of ortho diamines, a virtually impossible task, is avoided by the selective ortho amination as illustrated by the synthesis

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(6) Dimroth, O. Chem. Ber. **1905**, *38*, 670; **1906**, *39*, 3905. Pochirok, V. Y.; Mitarbb, U. *Ukr. Khim. Zh.* (*Russ. Ed.*) **1959**, *25*, 774; *Chem. Abstr.* **1960**, *54*, 1303i. Labbe, B. *Ind. Chim. Belge.* **1969**, *34*, 519. For an exception, see: Sieh, D. H.; Wilbur, D. J.; Michejda, C. J., *J. Am. Chem. Soc.* **1980**, *102*, 3883.

(7) (a) Trost, B. M.; Kunz, R. A. *J. Org. Chem.* **1974**, *39*, 2648. (b) Bohme, H.; Morf, D. *Chem. Ber.* **1957**, *90*, 446.

(8) Although low molecular weight azides may be explosive, **1** was stable to temperatures of at least 105 °C and could not be detonated by shock. Preparation on a 1-mol scale presented no problems.

(9) Prepared by reacting magnesium with 1,2-dibromoethane in ether and used as an ~2 M solution in ether-benzene.

(10) This product presumably arises by the trapping of $PhSCH_2^+$ or its equivalent (such as the initial triazene) by the very electron-rich ring of **8**.

(11) Stedman, E. *J. Chem. Soc.* **1927**, 1902. Barnish, I. T.; Hauser, C. R. *J. Org. Chem.* **1968**, *34*, 1372.

(12) Lofgren, N. M.; Takman, B. *Acta Chem. Scand.* **1952**, *6*, 1006. Kauffmann, H.; Franck, W. *Chem. Ber.* **1907**, *40*, 4006.

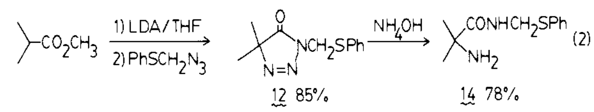
(13) Tarbell, D. S.; Hirschler, H. P.; Hall, T. J. *J. Am. Chem. Soc.* **1953**, *75*, 1985. Bell, F.; Kenyon, J. *J. Chem. Soc.* **1926**, 3047.

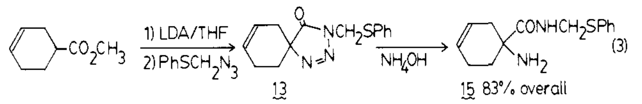
(14) For lithiation of amides, see: Osmund de Silva, S.; Reed, J. N.; Snieckus, V. *Tetrahedron Lett.* **1978**, 5099. Beak P.; Brown, R. A. *J. Org. Chem.* **1979**, *44*, 4463. Meyers, A. I.; Lutomiski, K. *Ibid.* **1979**, *44*, 4464.

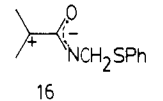
of **10**.[15] Formation of heterocycles is demonstrated by the indole synthesis (Table I, entry 5).

Initial efforts to extend this amination reaction to aliphatic and heteroaromatic (furan, thiophene, indole) organometallic reagents have not been fruitful. Formation of the triazenes occurred smoothly with aliphatic Grignard reagents, but satisfactory yields of amines upon hydrolysis have not been obtained.

On the other hand, enolates derived from α,α-disubstituted esters reacted smoothly to give a new heterocycle, a 5*H*-1,2,3-triazol-4-one (eq 2 and 3).[16] While in the case of **12**,[17] this heterocycle was isolated as a crystalline solid, mp 78.5–79.5° (dec), their general instability (thermally decompose well below 100 °C) led us to react the crude triazolones immediately. For α-amination, a THF solution of the triazolones **12** and **13** was treated with aqueous ammonium hydroxide which gave the α-amino amides **14**[18] and **15**[18] in excellent overall yields.[19] In fact, these heterocycles behave as if they are a functional equivalent of a zwitterion such as **16**. For example, dissolution of **12** in methanol containing magnesium methoxide led to a quantitative yield of **17**.[20] The thermal lability of the triazolones is further highlighted by the exceptional stability of the carbon and nitrogen analogues **18**[21] and **19**.[22]







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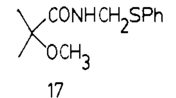

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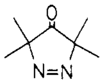

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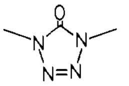

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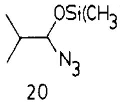

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Previous work has demonstrated the utility of substituted α-azido sulfides in molecular rearrangements to lactams and imino thioethers.[5] The present work demonstrates the utility of the parent system as a NH_2^+ equivalent. The uniqueness of this sulfur substituted reagent is further indicated by the recovery of the oxygen analogue[21] **20** unchanged after treatment with phenylmagnesium bromide. Further synthetic applications of this class of compounds is under investigation.

Acknowledgment. We thank the National Science Foundation for their generous support of our programs.

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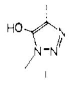
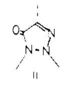
(15) For lithiation of anilides, see: Fuhrer, W.; Gschwend, H. W. *J. Org. Chem.* **1979**, *44*, 1133.

(16) (a) The marked difference in physical and chemical properties between the heterocycles **12** and **13** and a related tautomer i[16b] and isomer ii[16b] emphasize the uniqueness of this heterocyclic system.





(b) Begtrup, M.; Pedersen, C. *Acta Chem. Scand.* **1969**, *23*, 633.

(17) IR ($CDCl_3$) 1730, 1667, 1575 cm^{-1}; NMR ($CDCl_3$) δ 7.40–7.65 (6 H, m), 5.30 (2 H, s), 1.31 (6 H, s). Mass spectrum, *m/z* (relative intensity) 151 (23), 123 (27), 110 (35), 109 (21), 98 (19), 84 (16), 70 (100). Anal. Calcd for $C_{11}H_{13}N_3OS$: 235.0777. Found: 235.0782.

(18) This compound has been characteirzed by IR and NMR spectroscopy. For complete characterization, the α-amino substituent was acetylated to give the crystalline acetamide derivatives, mp 127.5–128.0 and 136.5–137.0 °C from **14** and **15**, respectively. The amides were fully characterized spectrally and elemental composition established by high-resolution mass spectroscopy.

(19) For example, the triazolone **12** (3.2 mmol) was dissolved in THF (3.5 mL) and aqueous ammonium hydroxide (4.5 mL of 30% solution) was added. After stirring vigorously at room temperature overnight, aqueous workup and Florisil chromatography gave 0.56 g (78%) of **14**.

(20) The triazalone **12** (1.06 mmol) in THF (1 mL) was added to magnesium methoxide (1.17 mmol) in methanol (4 mL). After stirring 24 h at room temperature, ether was added, the mixture was filtered, and the filtrate was washed with 5% HCl. Workup followed by Florisil chromatography gave 235 mg (100%) of **17**.

(21) Engel, P. S.; Shen, L. *Can. J. Chem.* **1974**, *52*, 4040. Crawford, R. J.; Tokunaga, H. *Ibid.* **1974**, *52*, 4033. Pirkle, W. H.; Hoover, D. J. *J. Org. Chem.* **1980**, *45*, 3407.

(22) Wadsworth, W. S. *J. Org. Chem.* **1969**, *34*, 2994.

(23) Vorbrüggen, H.; Krolikiewicz, K. *Synthesis* **1979**, 35.

On the Stereo- and Regiochemistry of a Palladium-Catalyzed O to C Migration

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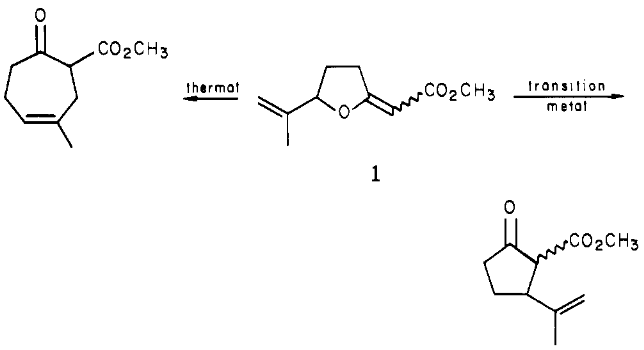
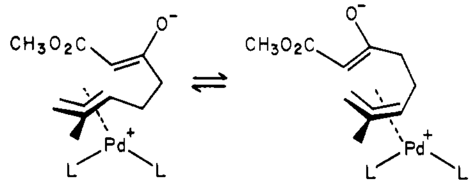
Received December 11, 1980

The ability to isomerize allyl vinyl ethers such as **1** to cyclopentanones under the influence of a transition-metal catalyst represents a reordering of the normal chemical reactivity of such compounds which, under thermolysis conditions, rearrange to cycloheptenones.[1-3] Such a reaction also can resolve a classic problem of O vs. C alkylation of β-keto esters.[1] Mechanistic insight into this novel isomerization, especially its stereochemistry and regiochemistry, is required in order to apply it. In particular, if a π-allylpalladium complex such as **2** is an intermediate, the





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