X-ray Structural Determination of 5 and 8. Single crystals were obtained by slowly cooling the DMF solution of 5 from 120 to 70 °C in the oven and evaporating a DMF solution of 8. The crystal of 5 was sealed in a capillary under nitrogen. Suitable crystals of 5 and 8 were selected, and crystal data and single crystal data were obtained by use of a Nicolet R3 automated diffractometer that utilized graphite-monochromated Mo Kα radiation (λ = 710 69 Å). The lattice parameters and orientation matrix were obtained with a least-squares procedure utilizing several carefully centered reflections. Single-crystal data were obtained with use of a θ–2θ variable scan rate technique. Crystal data and experimental conditions are listed in Table IVS of the supplementary material. The space group for the 5 was $P\bar{1}$, which was obtained from the lattice parameters, single crystal data statistics, and by the successful solution and refinement of the crystal structure. The space group for 8, $Pna2_1$, was determined by examination of systematic extraction and single-crystal statistics.

Both structures were solved by use of direct methods. The refinement for 5 proceeded in normal fashion. The ligand was located about a center of symmetry. ^{1}H NMR data established that these were two DMF solvent molecules for each ligand, and this was substantiated by the structural study. Positions for all hydrogen atoms were obtained from the difference map. The hydrogen atoms were added to the refinement and allowed to ride on the heavy atoms to which they were bonded. Only the thermal parameters of the hydrogen atoms were refined. All heavy atoms were refined anisotropically. The resulting R values were R = 0.048, and R_W = 0.060. Weights were based on counting statistics.

The trial model for 8 was obtained by use of direct methods. The entire molecule was evident in the resulting E map, and the conformation was reasonable. However, it was not possible to refine the structure below 0.18. Several peaks in the difference map that were larger than 1 eÅ^{-3} indicated that the problem in refinement was due to disorder. The difference map contained groupings of peaks with geometry consistent with atomic geometry in organic structures containing carbons, nitrogens, and oxygens that were located near the molecule. These fragments were added to the atom list with occupancy factors of 0.3, but only their isotropic thermal parameters were refined. The R value dropped to 0.14. The two fragments consisting of 9 and 5 atoms were in the neighborhood of the amine six-membered rings, and while neither contained six-membered rings it was possible to visualize at least four atoms of such rings in each fragment. The structure of 8 at this point was consistent with an acceptable conformation, and so refinement was terminated. Scattering factors for both studies were obtained for Vol. 4 of the *International Tables of X-Ray Crystallography*.[56] All computer programs used in this study are contained in the program package SHELXTL.[57]

Determination of the Protonation Constants for 2. The protonation of 2 in aqueous solution was studied by potentiomeric titration of the solution containing the ligand in a 0.1 M KCl solution at 25.0 °C. The titrant was a standard KOH solution. The computer program SUPERQUAD was used to process the potentiomeric data and calculate the protonation constants. The ionic strength was adjusted to 0.10 mol/dm^3 by addition of the appropriate amount of KCl. The emf of these solutions was measured by using a Corning semimicro glass electrode coupled with an Orion 701A digital potentiometer. The pK_a values are given in Table II.

Acknowledgment. We are grateful to the State of Utah Centers of Excellence Program for financial support of this work.

Supplementary Material Available: Tables of atomic parameters for the atoms of 5 and 8, the bond lengths and angles of 5, and crystal and experimental data for 5 and 8 (7 pages). Ordering information is given on any current masthead page.

(56) *International Tables for X-Ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. 4 p 99.

(57) Sheldrick, G. M. *SHELXTL. An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*; University of Göttingen: Federal Republic of Germany, 1983; 4th Revision.

1,2,3-Triazoles from (*Z*)-β-(Formyloxy)vinyl Azides and Triethyl Phosphite

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(*Z*)-Sodium enolates of two α-azido ketones are O-formylated with Me_3CCO_2CHO in high yield to give isolable (*Z*)-β-(formyloxy)vinyl azides, which are converted to 1,2,3-triazoles under the influence of triethyl phosphite. A mechanism is proposed for triazole formation involving 1,5-electrocyclization of a vinyl phosphazide intermediate.

1,5-Electrocyclizations are a class of concerted reactions that are of paramount importance in the preparation of five-membered heterocyclic ring systems.[1] The generality of this reaction type has resulted in the exceptions to the rule being more interesting than the confirmations. Vinyl azides[2] represent one such exception. In general, thermolysis of vinyl azides results in the formation of 2*H*-azirines and N_2 without the intermediacy of 1,2,3-triazoles.[3] The inability of these systems to undergo 1,5-cyclization prior to loss of N_2 is due in part to the energy required to bend the linear azido group into a suitable geometry for such a cyclization. Conversion of vinyl azides to 1,2,3-triazoles[4] occurs only in special cases. α-Azido enamines cyclize to 2*H*-1,2,3-triazoles.[5] This unusual behavior has been attributed to the nucleophilic character of the enamine carbon and the lower rotation barrier of the carbon–carbon double bond.[5a] β-Metalated (Na) vinyl azides also cyclize readily, again likely due to enhanced nucleo-

(1) For a review, see: Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 947.

(2) For a review of azides, see: (a) Scriven, E. F. V.; Turnbull, K. *Chem. Rev.* **1988**, *88*, 298. (b) *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic Press: New York, 1984.

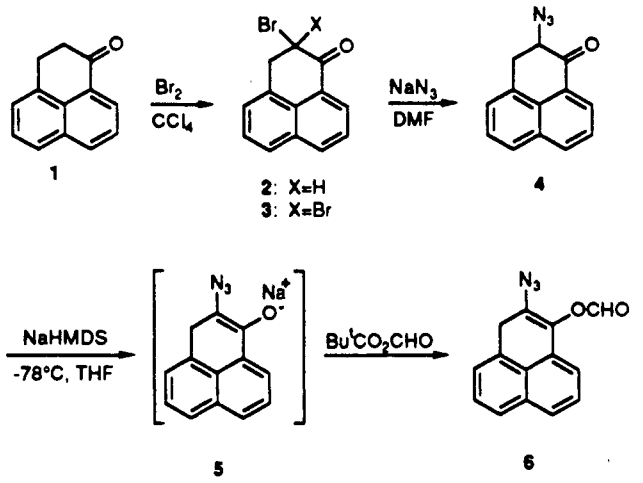
(3) (a) Burke, L. A.; Leroy, G.; Nguyen, M. T.; Sana, M. *J. Am. Chem. Soc.* **1978**, *100*, 3668. (b) Hassner, A.; Wiegand, N. H.; Gottlieb, H. E. *J. Org. Chem.* **1986**, *51*, 3176.

(4) For a review of 1,2,3-triazoles, see: Wamhoff, H. *Comprehensive Heterocyclic Chemistry*; Potts, K. T., Ed.; Pergamon Press: New York, 1984; p 669.

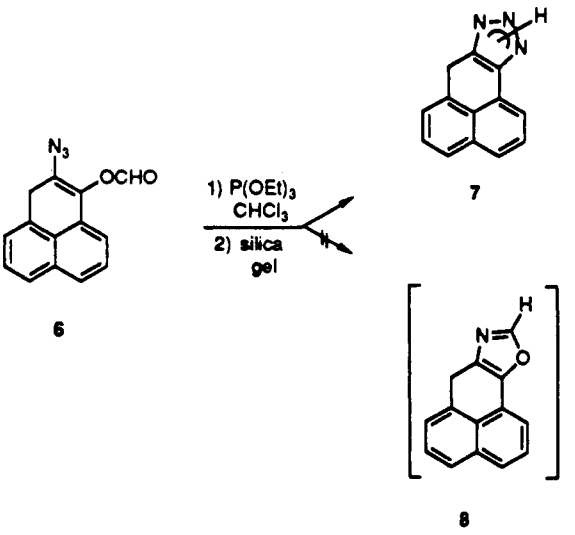
(5) (a) Saalfrank, R. W.; Wirth, U.; Lurz, C.-J. *J. Org. Chem.* **1989**, *54*, 4356. (b) Carrie, R.; Danion, D.; Ackermann, E.; Saalfrank, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 288. (c) Henriet, M.; Houtekie, B.; Techy, R.; Touillaux, R.; Ghosez, L. *Tetrahedron Lett.* **1980**, *21*, 223. (d) Bernard, C.; Ghosez, L. *J. Chem. Soc., Chem. Commun.* **1980**, 940.

0022-3263/91/1956-2680$02.50/0

Scheme I



Scheme II



philicity at the β-carbon.[6] Allenyl azides formed in situ undergo a 1,5-electrocyclization to ultimately give 1,2,3-triazoles. Banert suggests that the advantageous geometry of the additional p orbitals of the central allenyl carbon may explain this fast cyclization.[7]

One of the major synthetic applications of azides involves their conversion to phosphazenes by reaction with phosphines and phosphites.[8] In contrast to phosphazenes ($R_3P{=}NR$), their elusive precursors, phosphazides ($R_3P^+N{=}N^-NR$), have not yet found a niche in synthetic organic chemistry. In fact, we are aware of only one application of phosphazides in synthesis.[9] This is due primarily to their rapid conversion to phosphazenes by loss of N_2. However, some special phosphazides are isolable and a few have been analyzed by single-crystal X-ray crystallography.[10] The solid-state structures reveal that these stable phospazides have zwitterionic character and adopt a trans stereochemistry about the N=N bond.[10b] This paper describes a case where a vinyl phosphazide intermediate may participate in an unprecedented 1,5-electrocyclization, thus bypassing the usual Staudinger pathway (N_2 elimination to give the phosphazene).

Results and Discussion

A field of azide chemistry of current interest is the Staudinger reaction and its application to inter- and intramolecular aza-Wittig reactions. Eguchi has reported an oxazole synthesis that relies on intramolecular aza-Wittig reactions of (Z)-β-(acyloxy)vinyl azides.[11] We were interested in extending this chemistry to include the corresponding formyl derivatives,[12] thereby providing access to the 2-unsubstituted oxazoles,[13] particularly in the case of the 2,3-dihydrophenalene template, which is currently of interest to us.[14]

The synthesis of the intramolecular aza-Wittig precursor, (Z)-β-(formyloxy)vinyl azide **6**, is outlined in Scheme I.[15] Bromination of 2,3-dihydrophenalenone (**1**) produced α-bromo ketone **2** slightly contaminated with the dibromide **3**. One recrystallization produced sufficiently pure **2** for further use. α-Bromo ketone **2** was converted to α-azido ketone **4** by reaction with sodium azide in DMF. Careful control of the temperature and reaction time was required to ensure a high yield of reasonably pure material. Both substituted 2,3-dihydrophenalenones **2** and **4** were prone to elimination or oxidation as reported previously for this class of compounds.[16]

With azido ketone **4** in hand, our attention turned to *O*-formylating this compound. Being unaware of any reports describing this transformation on simple enolates, we concentrated on using the mixed anhydride Me_3CCO_2CHO. As reported by Vlietstra et al.,[17] this mixed anhydride is easily prepared, can be distilled to a high purity, and is a potent and selective formylating agent. Enolate formation as described by Eguchi[11] (LDA, THF, −78 °C) followed by quenching with Me_3CCO_2CHO produced some of the desired formate **6**; however, analysis of the crude material (^1H NMR) showed a low conversion of **4** to **6**. Separation of the small amounts of **6** from other byproducts (diisopropyl amine, diisopropylformamide) proved difficult. Formate **6** did not survive standard chromatography and was not easily separated by crystallization.

Substitution of sodium hexamethyldisilazane (NaHMDS) overcame these difficulties. Analysis of the crude reaction product using this new base indicated that the O-alkylation proceeded efficiently to give **6**. The crude product in ether was easily purified by washing with 1% aqueous $NaHCO_3$ to remove the residual sodium trimethylacetate and HMDS. Removal of the solvent gave **6** in 76% yield (90% purity). Analytically pure material was obtained by repeated recrystallizations from ether. The identity of **6** was clearly established by analysis of the

(6) (a) Meek, J. S.; Fowler, J. S. *J. Am. Chem. Soc.* **1967**, *89*, 1967; (b) *J. Org. Chem.* **1968**, *33*, 985. (c) Woerner, F. P.; Reimlinger, H. *Chem. Ber.* **1970**, *103*, 1908.

(7) Banert, K. *Chem. Ber.* **1989**, *122*, 911.

(8) For a review of the Staudinger reaction, see: Gololobov, Yu. G.; Zhmurova, I. N.; Kasukhin, L. F. *Tetrahedron* **1981**, *37*, 437.

(9) For an example of an intramolecular trapping of a phosphazide by an imine, see: Molina, P.; Arques, A.; Vinader, M. V. *J. Org. Chem.* **1990**, *55*, 4724.

(10) (a) Chidester, C. G.; Szmuszkovicz, J.; Duchamp, D. J.; Laurian, L. G.; Freeman, J. P. *Acta Crystallogr.* **1988**, *C44*, 1080. (b) Kukhar, V. P.; Kasukhin, L. F.; Ponomarchuk, M. P.; Chernega, A. N.; Antipin, M. Yu.; Struchkov, Yu. T. *Phosphorus, Sulfur, Silicon* **1989**, *44*, 149.

(11) Takeuchi, H.; Yanagida, S.; Ozaki, T.; Hagiwara, S.; Eguchi, S. *J. Org. Chem.* **1989**, *54*, 431.

(12) An aryl formate has undergone an intramolecular aza-Wittig reaction to give a 1,3-benzoxazepine: Lee, K.-J.; Choi, D. O.; Kim, S.; Jeong, J. U.; Park, H. *Synthesis* **1990**, 455.

(13) Turchi, I. J. *Chemistry of Heterocyclic Compounds*: Turchi, I. J., Ed.; Wiley: New York, 1986; Vol. 45.

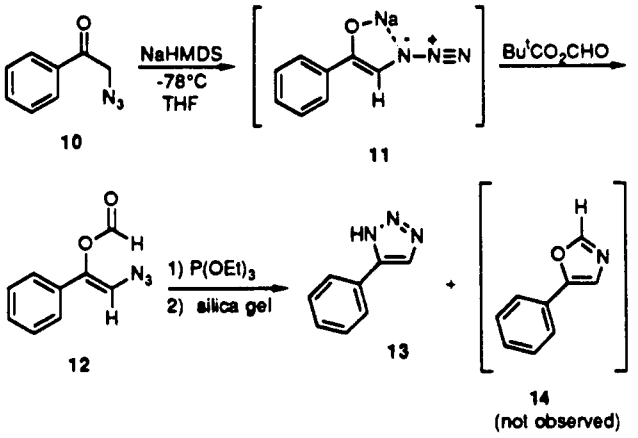
(14) Darlington, W. H.; Szmuszkovicz, J. *Tetrahedron Lett.* **1988**, 1883.

(15) The inherent instability of the phenalene and 2,3-dihydrophenalenone nuclei toward air and light added to the difficulty of this synthetic sequence.

(16) Reid, D. H. *Q. Rev. Chem. Soc.* **1965**, *19*, 274.

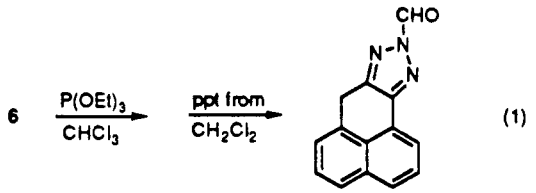
(17) Vlietstra, E. J.; Zwikker, J. W.; Nolte, R. J. M.; Drenth, W. *Rec. Trav. Chim. Pays-Bas* **1982**, *101*, 460.

Scheme III



^{1}H and ^{13}C NMR, HRMS, and IR spectra. To our knowledge, this β-(formyloxy)vinyl azide functionally has not been reported previously.[18]

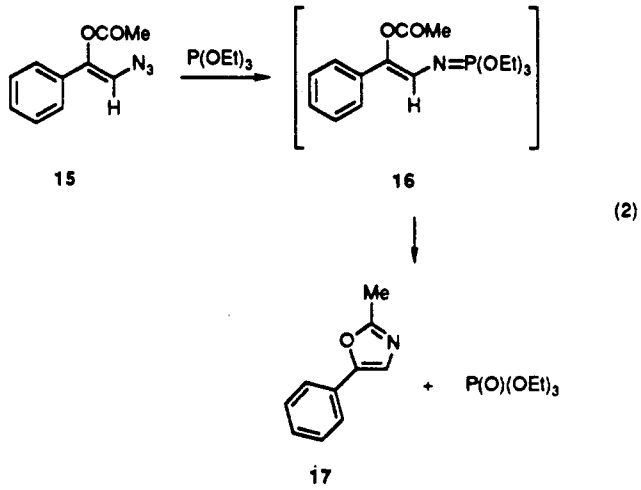
Treatment of **6** in $CHCl_3$ with triethyl phosphite produced a deep orange solution. Removal of the solvent provided an orange residue, which after silica gel chromatography gave 1*H*-1,2,3-triazole **7** (46%) rather than the expected oxazole **8** (Scheme II). The assignment of **7** as the product was determined initially by HRMS[19] and later supported by elemental analysis. Monitoring the reaction by ^{1}H NMR (300 MHz, $CDCl_3$) revealed a number of details: (1) **6** was converted almost instantaneously (<10 min) upon addition of triethyl phosphite to an intermediate (not **7**), (2) triethyl phosphite (δ 3.88 CH_2) was oxidized in a stoichiometric fashion to triethyl phosphate (δ 4.12 CH_2). The intermediate visible by ^{1}H NMR, could be isolated in 83% yield by precipitation from CH_2Cl_2 (eq 1). This orange solid contained absorptions in its NMR



(1)

(^{1}H, δ 9.24; ^{13}C, δ 156.55) and IR (1730 cm^{-1}) spectra indicative of an *N*- or *O*-formyl group. The spectral data including HRMS are consistent with structure **9** shown in eq 1. Hydrolysis of the *N*-formyl group in **9** during chromatography would be expected to give 1*H*-1,2,3-triazole **7**.

Formate **12** was synthesized as described above for formate **6** to probe the generality of this unexpected transformation. The sodium enolate **11** was assumed to be in a *Z* conformation by analogy to the reported lithium derivative.[11] Formylation of **11** similarly provided only one isomer, presumably **12**. Formate **12** was somewhat more stable than **6** and could be subjected to flash chromatography, but the best yields (86%) were obtained when **6** was purified by crystallization. As before, **12** was treated with triethyl phosphite in $CHCl_3$. Again, purification of the crude product by silica gel chromatography gave the triazole **13** (62%) rather than the oxazole **14**[20] (Scheme III).[21] In contrast to this result, it has been reported[11] (eq 2) that acetate **15** is converted to oxazole **17** via phosphazene **16** when treated with triethyl phosphite.



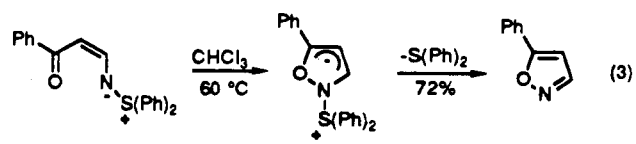
(2)

Mechanistic Considerations

Before developing a mechanistic rationale for the formation of 1,2,3-triazoles from (*Z*)-β-(formyloxy)vinyl azides and triethyl phosphite, it was important to establish the necessity of both reagents. Since formates are known to hydrolyze much faster than acetates,[22] we considered that ketone **4** could be the actual species undergoing triazole formation. This possibility was ruled out by treating **4** with triethyl phosphite under the usual conditions (23 °C, $CHCl_3$) and monitoring the reaction by ^{1}H NMR. In the time frame required for conversion of **6** to **9**, no significant change was observed in the spectra of **4** or triethyl phosphite. After 24 h, the ketone **4** had been consumed but no sign of **9** was detected. Apparently, the Staudinger reaction is slow compared to the reaction taking place in Scheme II. It was also established that triethyl phosphite is required for the conversion of **6** to **9**. In the absence of triethyl phosphite, formate **6** does not convert to **9** even after an extended reaction time (24 h).

Any mechanism proposed for the conversion of these azido formates should answer the following questions. (1) What is the role of triethylphosphite? (2) Why do the formates lead to triazoles while the analogous acetates give oxazoles? The mechanism we propose for this unprecedented transformation is shown in Scheme IV. The initially formed trans phosphazide **18** undergoes a reversible pseudo-1,5-electrocyclization to give mesoionic intermediate **20**, which then undergoes an O-to-N formyl transfer to **21**. The new zwitterion **21**, being analogous to a standard aza-Wittig intermediate, then eliminates triethyl phoshate to give 1,2,3-triazole **9**.

This type of pseudo-1,5-electrocyclization belongs to a small class of cyclizations that involve the loss of a leaving group concurrent with or subsequent to ring formation.[1] Typically N_2 serves as the departing group; however, one cyclization involves the loss of a sulfide (eq 3).[23]



(3)

(18) A CAS ONLINE search (1962 to 1990) for this substructure provided no matches.

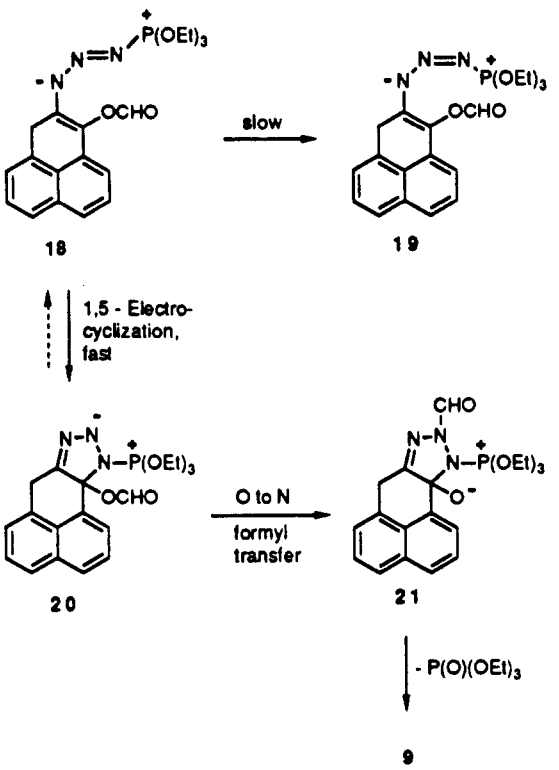
(19) The calculated molecular weights for triazole **7** and oxazole **8** are 207.0796 and 207.0684, respectively. The observed molecular weight of the product from Scheme II is 207.0791 as determined by HRMS.

(20) LaMattina, J. L. *J. Org. Chem.* **1980**, *45*, 2261.

(21) Monitoring the reaction by ^{1}H NMR provided evidence for an *N*-formyl intermediate; however, this compound was not isolated.

(22) Dilute NH_3 cleaves formate esters 100 times faster than acetates: Reese, C. B.; Stewart, J. C. M. *Tetrahedron Lett.* **1968**, 4273.

Scheme IV



A number of factors are key to the reaction cascade shown in Scheme IV. The cis phosphazide **19** required for elimination of N_2 and phosphazene formation is essentially never formed, because the electrocyclization must be faster than the trans–cis isomerization. The bent phosphazide provides an enhanced geometry for the 1,5-electrocyclization in comparison to the parent azide. Also, the formyl transfer sets the stage for the real thermodynamic driving force of the reaction—the formation of triethyl phosphate. The corresponding acetate apparently does not undergo the O-to-N transfer as readily, thereby allowing the reaction to follow the alternate course. The mechanism shown in Scheme II remains highly speculative; however, we feel it best explains the available experimental results.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Melting points were taken in a Thomas Hoover apparatus and are uncorrected. Chloroform (Fisher, certified A.C.S.) was predried over $CaCl_2$ and then distilled from P_2O_5. Dimethylformamide (Fisher, certified A.C.S.) was dried over 4-Å molecular sieves and then distilled under reduced pressure. THF (Fisher, certified) was refluxed over sodium benzophenone ketyl under N_2 and distilled just prior to use. Product purities were routinely checked by TLC. Silica gel 60 HF_{254} (E. Merck) was used for preparative layer chromatography (PLC). During extractive isolations, the organic layer was dried with sodium sulfate. Trimethylacetic formic anhydride (99% pure by ^1H NMR) was prepared according to the literature procedure[17] except that it was distilled at 10 °C/1 Torr rather than 0 °C/0.01 Torr. Sodium bis(trimethylsilyl)amide was used as its 1.0 M solution in THF available from Aldrich. α-Azidoacetophenone[11] and 2,3-dihydrophenalenone (**1**)[24] were prepared according to literature procedures.

^1H NMR spectra (200 MHz) were recorded on a Magnachem instrument, and 300-MHz ^1H NMR and 75.6-MHz ^{13}C NMR spectra were obtained on a GN 300 spectrometer in $CDCl_3$ solution. NMR peak positions are indicated in ppm (δ units) relative to an internal standard (TMS = 0 ppm for ^1H; $CDCl_3$ = 77.0 ppm for ^{13}C). ^1H coupling constants (J) are given in Hz. IR spectra were recorded on a Perkin-Elmer 1420 ratio recording spectrophotometer. Mass spectra were obtained on MAT CH-5-DF (FAB) and Finnigan 8230 B (EI) mass spectrometers. Elemental analyses were performed by The Upjohn Company. The NMR experiments were carried out on a 0.05-mmol scale in $CDCl_3$ solution. All 2,3-dihydrophenalenone and phenalene derivatives were handled with the least possible exposure to light and air.

2-Bromo-2,3-dihydrophenalenone (2). To a stirred solution of the 2,3-dihydrophenalenone (**1**)[24] (1.8 g, 10 mmol) in CCl_4 (15 mL) was added dropwise over the course of 10 min a solution of bromine (1.6 g, 10 mmol) in CCl_4 (5 mL). The resulting yellow solution was left stirring for 1 h at room temperature. The reaction mixture was filtered, and the filtrate was concentrated to afford **2** slightly contaminated with some of the dibromide **3** (presence indicated by ^1H NMR). However, crystallization from Et_2O/hexane furnished an analytically pure sample of **2** (2.1 g, 79%): mp 122–4 °C; ^1H NMR (300 MHz) δ 3.67 (dd, J = 5, 17, 1 H), 3.95 (dd, J = 4, 17, 1 H), 4.94 (t, J = 5, 1 H), 7.45 (m, 2 H), 7.57 (t, J = 8, 1 H), 7.80 (d, J = 8, 1 H), 8.08 (dd, J = 1, 8, 1 H), 8.25 (dd, J = 1, 7, 1 H); ^{13}C NMR[25] δ 37.82, 48.68, 125.92, 126.45, 126.57, 126.84, 126.93, 127.28, 129.21, 130.18, 132.87, 134.76, 190.52; HRMS (EI) calcd for $C_{13}H_9BrO$ 259.9837, found 259.9852. Anal. Calcd for $C_{13}H_9BrO$: C, 59.80; H, 3.47; Br, 30.60. Found: C, 59.41; H, 3.30; Br, 30.86.

2-Azido-2,3-dihydrophenalenone (4). To a cold (10 °C) solution of **2** (1.5 g, 5.9 mmol) in DMF (20 mL) and acetic acid (7.5 mL) was added a solution of NaN_3 (2.9 g, 40 mmol) in H_2O (14.5 mL) dropwise over the course of 10 min. The reaction mixture was stirred at 10 °C for 1 h and poured into crushed ice–water (20 mL). The brownish precipitate was collected by filtration and washed repeatedly with ice-cold water. The resulting solid was redissolved in Et_2O and washed once each with H_2O and brine. The organic layer was dried and concentrated (*caution: use 40 °C bath to avoid overheating*) to furnish **4** as a reddish brown solid. Crystallization of this solid from Et_2O/hexane furnished **4** (1.0 g, 81%) as sharp melting orange crystals: mp 69–71 °C; IR (KBr) 2100 (N_3), 1685 (CO) cm^{-1}; ^1H NMR (300 MHz) δ 3.38 (dd, J = 12, 16, 1 H), 3.56 (dd, J = 6, 16, 1 H), 4.55 (dd, J = 6, 12, 1 H), 7.49 (m, 2 H), 7.61 (m, 1 H), 7.82 (d, J = 8, 1 H), 8.11 (dd, J = 1, 8, 1 H), 8.21 (dd, J = 1, 7, 1 H); ^{13}C NMR δ 34.47, 63.46, 126.03, 126.40, 126.61, 126.95, 128.35, 130.03, 130.89, 133.07, 134.67, 193.77; HRMS (EI) calcd for $C_{13}H_9N_3O$ 223.0740, found 223.0732.

Synthesis of α-(Formyloxy)vinyl Azide 6. To a stirred and cooled (−78 °C) solution of sodium bis(trimethylsilyl)amide (1.0 M solution in THF, 0.89 mL, 0.89 mmol) in THF (10 mL) was added dropwise via syringe a solution of the azido ketone **4** (200 mg, 0.89 mmol) in THF (5 mL). The enolate formation was almost instantaneous as was evidenced from the color change of the solution from orange to dark brown. After being stirred for 25 min at −78 °C, the reaction mixture was quenched with trimethylacetic formic anhydride (117 mg, 0.9 mmol) and stirred for another 10 min. During this time the dark color of the solution faded to a light yellow color. The solution was concentrated in vacuo to one-third of its volume, diluted with H_2O (5 mL), and extracted with CH_2Cl_2 (3 × 20 mL). The combined CH_2Cl_2 extracts were washed with 1% aqueous $NaHCO_3$ solution and H_2O and then dried. The residue obtained after evaporation (*caution: avoid overheating*) of the solvent was crystallized from CH_2Cl_2/hexane to provide pale yellow crystals of **6** (170 mg, 76%): mp 115 °C dec; IR (KBr) 2100 (N_3), 1730 (CO) cm^{-1}; ^1H NMR (300 MHz) δ 4.38 (s, 2 H), 7.09 (dd, J = 1, 7, 1 H), 7.32 (m, 2 H), 7.43 (t, J = 8, 1 H), 7.58 (d, J = 8, 1 H), 7.64 (dd, J = 1, 8, 1 H), 8.28 (s, 1 H); ^{13}C NMR δ 31.40, 117.53, 123.23, 125.54, 126.14, 126.19, 126.37, 127.41, 127.46, 127.67, 129.69, 131.49, 133.44, 158.33; HRMS (EI) calcd for $C_{14}H_9N_3O_2$ 251.0695, found 251.0698.

Synthesis of Triazole 7. To the formate **6** (158 mg, 0.63 mmol) dissolved in dry $CHCl_3$ (20 mL) was added $P(OEt)_3$ (106 mg, 0.63 mmol) with stirring. As soon as the $P(OEt)_3$ was added, an exothermic reaction was initiated. The reaction mixture was left stirring for another 24 h at room temperature. The residue

(23) Tamura, Y.; Sumoto, K.; Matsuchima, H.; Taniguchi, H.; Ikeda, J. *J. Org. Chem.* **1973**, *38*, 4324.

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(25) One carbon remains unassigned, because it could not be distinguished unequivocally from base-line absorptions.

obtained after removal of solvent (*caution: avoid overheating*) was chromatographed (silica gel column, EtOAc–hexane, 1:4) to give triazole **7** (60 mg, 46%) in 90% purity. This was further purified by PLC (EtOAc/hexane, 1:4) to give **7** as a colorless solid: mp 220 °C; IR (KBr) 3000–2200 (br, NH), 1250, 1030, 810 cm^{-1}; ^1H NMR (DMSO-d_6, 200 MHz) δ 4.57 (s, 2 H), 7.20–7.85 (m, 7 H); ^1H NMR ($CDCl_3$, 200 MHz) δ 4.68 (s, 2 H), 7.50–8.00 (m, 7 H); HRMS (EI) calcd for $C_{13}H_9N_3$ 207.0796, found 207.0791. Due to the unstable nature of this compound, a satisfactory elemental analysis was not obtained. Anal. Calcd for $C_{13}H_9N_3 \cdot 1.3H_2O$: C, 67.70; H, 5.07; N, 18.22. Found: C, 68.11; H, 4.57; N, 17.73. (For oxazole **8**: Anal. Calcd for $C_{14}H_9NO$: C, 81.14; H, 4.38; N, 6.76).

Triazole 9. Formate **6** was treated with $P(OEt)_3$ as described above (0.63 mmol scale). After 20 min the solvent was removed to give a red residue. Analysis of this product by ^1H NMR indicated that complete conversion of the starting materials to compound **9** and $P(O)(OEt)_3$ had occured. The crude mixture was triturated with hexane and the solid was crystallized from CH_2Cl_2/hexane to afford crystals of **9** (123 mg, 83%): mp 143–5 °C; IR (KBr) 1730 (CO) cm^{-1}; ^1H NMR δ 4.54 (s, 2 H), 7.45 (m, 3 H), 7.20 (d, J = 7, 1 H), 7.85 (d, J = 8, 1 H), 8.13 (d, J = 7, 1 H), 9.24 (s, 1 H); ^{13}C NMR δ 27.22, 121.80, 121.89, 126.16, 126.34, 126.95, 127.15, 128.95, 129.43, 130.80, 133.94, 148.00, 149.10, 156.55; HRMS (EI) calcd for $C_{14}H_9N_3O$ 235.0747, found 235.0747.

2-Azido-1-phenylvinyl Formate (12). To a stirred and cooled (−78 °C) solution of sodium bis(trimethylsilyl)amide (1.0 M solution in THF, 0.93 mL, 0.93 mmol) in THF (10 mL) was added dropwise a solution of α-azidoacetophenone **10**[11] (150 mg, 0.93 mmol) in THF (5 mL). The stirring was continued at −78 °C for 25 min, and the dark brown enolate was quenched by the addition of trimethylacetic formic anhydride (121 mg, 0.93 mmol). After another 10 min of stirring at −78 °C, the yellow solution was concentrated to one-third of its volume, diluted with H_2O (5 mL), and extracted with Et_2O (3 × 10 mL). The combined extracts were dried and evaporated to afford pale yellow crystals. This compound was further purified by crystallization from Et_2O/hexane to give **12** as a yellow crystalline solid (150 mg, 86%): mp 63–65 °C; IR (KBr) 2110, 1725 cm^{-1}; ^1H NMR (300 MHz) δ 6.70 (s, 1 H), 7.35 (m, 5 H), 8.21 (s, 1 H); ^{13}C NMR δ 115.82, 123.97, 128.82, 128.87, 132.08, 137.13, 158.03; HRMS (EI) calcd for $C_9H_7N_3O_2$ 189.0538, found 189.0546.

5-Phenyl-1*H*-1,2,3-triazole (13). To a solution of formate **12** (100 mg, 0.53 mmol) in $CHCl_3$ (10 mL) was added $P(OEt)_3$ (88 mg, 0.53 mmol). The exothermic reaction was complete within 10 min. The solvent was removed by rotary evaporation, and the residue was chromatographed (silica gel column, EtOAc–hexane, 1:4) to furnish **13** (48 mg, 62%) as a fluffy white solid: mp 145–7 °C (lit.[6c] mp 147–8 °C): ^1H NMR (300 MHz) δ 7.45 (m, 3 H), 7.84 (m, 2 H), 8.00 (s, 1 H). An authentic sample of **13** was prepared according to a literature procedure[6c] and was found to have an identical ^1H NMR spectrum: HRMS (EI) calcd for $C_8H_7N_3$ 145.0640, found 145.0634.

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Supplementary Material Available: ^1H NMR for compounds **4**, **6**, **7**, **9**, and **12** and ^{13}C NMR for compounds **4**, **6**, **9**, and **12** (13 pages). Ordering information is given on any current masthead page.

Stereocontrolled Oxazolidinone Formation by the Addition of 4,5-Disubstituted Iminodioxolane to Oxirane via a Spiro Compound

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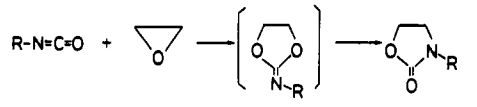
4,5-Disubstituted 2-imino-1,3-dioxolanes readily add to oxiranes in the presence of $AlCl_3$, furnishing 1,3-oxazolidin-2-ones in a stereospecific manner, where the configurations of oxiranes and iminodioxolanes are responsible for the configuration of products and the feasibility of the addition, respectively. A preliminary adduct, a spiro compound intermediate, is isolated, and its decomposition to oxazolidinone is demonstrated.

Introduction

The cycloaddition of heterocumulenes with oxiranes seems to be a versatile tool for stereocontrolled introduction of heteroatoms because of facile availability of various types of heterocumulenes and sterically pure oxiranes.[1] In particular, 1,3-oxazolidin-2-ones, adducts of isocyanates and oxiranes, have attracted attention[2,3] because they are important biologically active compounds[4] and precursors of β-amino alcohols.[5] Unfortunately, many formations of 4,5-disubstituted oxazolidinones have used β-amino alcohols as precursors,[6] and so other synthetic pathways have been ardently investigated.[7] Their stereocontrolled synthesis by the cycloaddition, however, has been limited to some extent perhaps due to the lower reactivity of 2,3-disubstituted oxiranes[8] and due to the occurrence of other types of products such as isocyanurates[9] and iminodioxolanes.[3] The iminodioxolanes are generally considered to be the preliminary adduct, being readily arranged to

Scheme I



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