was filtered and washed with 1 L of 20% NaOH, 2 L of water, and 1 L of ether to afford 196 g (95%) of a white solid: mp 173–4 °C (lit.[8] mp 176–80 °C).

5-Methyl-1-(phenylmethyl)-1*H*-imidazole-4-carboxaldehyde (6). To a solution of 70 g (0.35 mol) of **5** in 1 L of CH_2Cl_2 was added 210 g (2.42 mol) of activated manganese dioxide, and the mixture was stirred at room temperture for 18 h. The reaction mixture was filtered over Celite and the filter cake washed with 2 L of CH_2Cl_2. The filtrate was concentrated under vacuum, and the residue was crystallized from hexanes to provide 63 g (91%) of a white solid: mp 110–1 °C (lit.[8] mp 107–10 °C).

2-[5-Methyl-1-(phenylmethyl)-1*H*-imidazol-4-yl]-1-nitroethene (7). A mixture of 70 g (0.35 mol) of **6** and 30 g (0.39 mol) of ammonium acetate in 400 mL of nitromethane was heated at 40–5 °C under nitrogen for 5 h. The reaction mixture was concentrated under vacuum, slurried in 500 mL of CH_2Cl_2, and filtered over 300 g of silica gel. The filtrate was concentrated under vacuum, and the residue was crystallized from ether to provide 70 g (82%) of a yellow solid (light sensitive): mp 129–30 °C; IR (CH_2Cl_2) 1630, 1500, 1325 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.18 (s, 3), 5.11 (s, 2), 7.07 (d, 2), 7.34 (m, 3), 7.57 (s, 1), 7.75 (d, 1), 7.89 (d, 1). Anal. Calcd for $C_{13}H_{13}N_3O_2$: C, 64.19; H, 5.39; N, 17.27. Found: C, 63.94; H, 5.37; N, 17.23.

2-[5-Methyl-1-(phenylmethyl)-1*H*-imidazol-4-yl]ethanone Oxime (8). To a mixture of 50 g (0.21 mol) of **7** and 5 g of 10% palladium on carbon in 1 L of THF under nitrogen was added a solution of 200 g (2.27 mol) of sodium hypophosphite hydrate in 500 mL of water over 1.5 h. Occasional cooling was required to maintain temperature at 20–5 °C. After the mixture was stirred for 1 h at room temperature, the catalyst was removed, and 500 mL of ethyl acetate was added. The reaction mixture was washed with 1 L of saturated K_2CO_3, dried over $MgSO_4$, and concentrated under vacuum. The residue was crystallized from CH_3CN to afford 35 g (74%) of a white solid: mp 145–6 °C; IR (CH_2Cl_2) 1690, 1500, 1445, 1420 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.04 (s, 3), 3.46 (d, 1), 3.67 (d, 1), 5.02 (s, 2), and 6.94–7.53 (m, 7). Anal. Calcd for $C_{13}H_{15}N_3O$: C, 68.10; H, 6.59; N, 18.33. Found: C, 67.81; H, 6.40; N, 18.39.

2-[5-Methyl-1-(phenylmethyl)-1*H*-imidazol-4-yl]ethanamine (9). To a slurry of 10 g (0.26 mol) of LAH in 350 mL of THF under nitrogen was added in portions 30 g (0.13 mol) of **8**, and the mixture was stirred for 3 h at room temperature. Following standard workup, the solvent was removed under vacuum to provide 28 g of a crude oil, which was used without further purification.

2-(5-Methyl-1*H*-imidazol-4-yl)ethanamine Dihydrochloride (1). A mixture of 28 g of crude **9** and 3 g of 10% palladium on carbon in 500 mL of ethanol was hydrogenated at 50 °C and 50 psi for 20 h. After removal of the catalyst, 25 mL of 12 N HCl was added, and the mixture was concentrated under vacuum. Crystallization of the residue from 1-propanol afforded 22 g (85% overall) of an off-white solid: mp 233–5 °C (lit.[4] mp 236–8 °C).

1-[5-Methyl-1-(phenylmethyl)-1*H*-imidazol-4-yl]-2-nitropropene (10). A mixture of 40 g (0.20 mol) of **6** and 17 g (0.22 mol) of ammonium acetate in 250 mL of nitroethane was heated at 70–80 °C for 4 h. The excess nitroethane was removed under vacuum, and the residue was slurried in 700 mL of CH_2Cl_2, dried over $MgSO_4$, charcoal treated, and concentrated under vacuum. Crystallization of the residue from ether gave 48 g (93%) of a yellow solid: mp 158–9 °C; IR (CH_2Cl_2) 1655, 1500, 1305 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.25 (s, 3), 2.79 (s, 3), 5.12 (s, 2), 7.05 (d, 2), 7.35 (m, 3), 7.61 (s, 1), and 7.94 (s, 1). Anal. Calcd for $C_{14}H_{15}N_3O_2$: C, 65.36; H, 5.88; N, 16.33. Found: C, 64.98; H, 5.80; N, 16.18.

1-[5-Methyl-1-(phenylmethyl)-1*H*-imidazol-4-yl]propan-2-one Oxime (11). To a mixture of 60 g (0.23 mol) of **10** and 5 g of 10% palladium on carbon in 1.5 L of THF under nitrogen was added a solution of 200 g (2.27 mol) of sodium hypophosphite hydrate in 500 mL of water over 1 h. After the mixture was stirred for 0.5 h, the catalyst was removed, and the reaction mixture was washed with 1 L of saturated K_2CO_3. The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was crystallized from ether to provide 47 g (83%) of a white solid: mp 137–8 °C; IR (CH_2Cl_2) 1690, 1500, 1445, 1425 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.82 (s, 0.4), 1.86 (s, 2.6), 2.03 (s, 3), 3.44 (s, 1.8), 3.70 (s, 0.2), 5.01 (s, 2), 7.02 (m, 2), 7.30 (m, 3), and 7.45 (s, 1). Anal. Calcd for $C_{14}H_{17}N_3O$: C, 69.11; H, 7.04; N, 17.27. Found: C, 68.97; H, 6.89; N, 17.11.

1-(5-Methyl-1*H*-imidazol-4-yl)propan-2-amine Dihydrochloride (2). A mixture of 10 g (41 mmol) of **11** and 5 g of 10% palladium on carbon in 300 mL of 1 M HCl(g)/EtOH was hydrogenated at 50 °C and 50 psi for 20 h. After the mixture was cooled to room temperature, 100 mL of water was added, and the catalyst was removed by filtration. The filtrate was concentrated under vacuum, and the residue was crystallized from THF/AcOH (1:1) to provide 6.2 g (70%) of a tan solid: mp 228–30 °C (lit.[1] mp 223–4 °C).

1-[5-Methyl-1-(phenylmethyl)-1*H*-imidazol-4-yl]propan-2-one Hydrochloride (12). To a solution of 30 g (0.12 mol) of **11** in 300 mL of 20% (v/v) sulfuric acid at 0 °C was added a solution of 18 g (0.26 mol) of sodium nitrite in 50 mL of water, the temperature being maintained at <5 °C. After stirring for 0.5 h at 0 °C, the reaction mixture was made basic with 20% K_2CO_3 and extracted with two 700-mL portions of CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and charcoal treated, and the solvent was removed under vacuum to give 28 g (99%) of the free base as an oil. Conversion to the hydrochloride with HCl(g) in acetone afforded 27 g (83% recovery) of a white solid: mp 159–61 °C; IR (CH_2Cl_2) 1870, 1730, 1420 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.10 (s, 3), 2.31 (s, 3), 3.98 (s, 2), 5.43 (s, 2), 7.22–7.38 (m, 5), and 9.32 (s, 1). Anal. Calcd for $C_{14}H_{16}N_2O$·HCl: C, 63.51; H, 6.47; N, 10.58. Found: C, 63.49; H, 6.34; N, 10.46.

α-Amino-α,5-dimethyl-1-(phenylmethyl)-1*H*-imidazole-4-propanoic Acid (13). A mixture of 20 g (76 mmol) of **12**, 15 g of NH_4Cl, 20 g of KCN, 10 mL of 2-propanol, and 200 mL of concentrated NH_4OH was stirred for 5 h at room temperature. The reaction mixture was poured into 400 mL of 10% K_2CO_3 and extracted with two 400-mL portions of CH_2Cl_2. The combined extracts were charcoal treated and concentrated under vacuum. The residue was dissolved in 500 mL of 6 N HCl and heated at reflux for 6 h. The mixture was concentrated to 100 mL and the pH adjusted to 7 with NaOH. The resulting precipitate was filtered and washed with water and ether to provide 10.5 g (51%) of a white, hygroscopic solid: mp 218–22 °C; IR (Nujol) 3180, 1600, 1490 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.45 (s, 3), 2.06 (s, 3), 2.80 (d, 1), 3.04 (d, 1), 5.15 (s, 2), 7.09 (d, 2), 7.30 (m, 3), 7.63 (s, 1). Anal. Calcd for $C_{15}H_{19}N_3O_2$·0.1H_2O: C, 65.48; H, 7.03; N, 15.27. Found: C, 65.42; H, 6.90; N, 15.26.

α-Amino-α,5-dimethyl-1*H*-imidazole-4-propanoic Acid Dihydrochloride (3). A mixture of 11.8 g (43 mmol) of **13** and 5 g of 10% palladium on carbon in 300 mL of 1 M HCl was hydrogenated at 50 °C and 50 psi for 24 h. The catalyst was removed by filtration, and the filtrate was concentrated to dryness under vacuum. Crystallization of the residue from AcOH afforded 8.5 g (77%) of a white solid: mp 236–8 °C; IR (Nujol) 3150, 1730, 1625, 1585 cm^{-1}; ^1H NMR (D_2O) δ 1.64 (s, 3), 2.32 (s, 3), 3.35 (s, 2), 8.60 (s, 1). Anal. Calcd for $C_9H_{13}N_3O_2$·2HCl: C, 37.52; H, 5.90; N, 16.41. Found: C, 37.69; H, 6.03; N, 16.22.

Registry No. **1**·2HCl, 36376-47-3; **2**·2HCl, 120231-05-2; **3**·2HCl, 120262-58-0; **4**, 75815-53-1; **5**, 75815-55-3; **6**, 75815-57-5; **7**, 120231-06-3; **8**, 120231-07-4; **9**, 120231-08-5; **10**, 120231-09-6; (*E*)-**11**, 120231-12-1; (*Z*)-**11**, 120262-59-1; **12**·HCl, 120231-10-9; **12** (free base), 120231-11-0; **13**, 120231-13-2.

A Convenient Route to Adenine N^1-Oxide Mono- and Polynucleotides by Oxidation with Potassium Monopersulfate

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Direct oxidation to *N*-oxides of purines and related derivatives has been previously described, but syntheses are not straightforward: the oxidizing reagent is not always readily and easily available (case of monopermaleic acid[1]),

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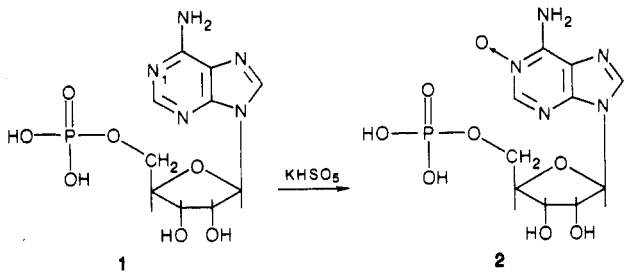
Scheme I



reactions have to be performed in a heterogeneous medium (*m*-chloroperoxybenzoic acid in a biphasic mixture aqueous acetic acid–sodium acetate/ethyl acetate[2,3]) or under drastic conditions (acetic acid/aqueous 30% hydrogen peroxide[4]). Furthermore, reaction times vary from 1 to 16 days. We show here that potassium monopersulfate is a promising reagent for N^1-oxidation in the adenine series. This compound is known for its oxidizing properties[5a] and for example it is able to *N*-oxidize diazines.[5b] In a previous paper, we have recorded the oxidation of adenosine 5′-monophosphate (**1**) (AMP) to its N^1-oxide derivative as a minor side reaction during its catalytic oxidation by the Mn–porphyrin–$KHSO_5$ system.[6] Recently, $KHSO_5$ has also been reported to hydroxylate thymine.[7] Optimization of our initial observation allows us to propose a convenient synthesis of adenosine N^1-oxide 5′-monophosphate (**2**) (Scheme I); reaction conditions are sufficiently mild to be directly applied to polyadenylic acid (Poly A) and to give polynucleotides containing various percentages of adenine N^1-oxide sites.

Experimental Section

Adenosine 5′-monophosphoric acid, adenosine N^1-oxide 5′-monophosphoric acid, polyadenylic acid (potassium salt), and nuclease P_1 were obtained from Sigma, and potassium monopersulfate (Oxone) from Alfa-Ventron.

HPLC analysis was performed using a Waters chromatograph equipped with a M440 detector (detection at 254 nm) and either a Waters Protein Pak 125 protein analysis column or a μ-Bondapak C_{18} column. NMR spectra were recorded on a Bruker 250-MHz spectrometer operated in the Fourier transform mode. Ultraviolet–visible spectra were run on a Varian Cary 219 spectrophotometer.

Synthesis of Adenosine N^1-Oxide 5′-Monophosphate. Adenosine 5′-monophosphoric acid, 0.15 mmol (53.2 mg), and 0.3 mmol of $KHSO_5$ (92.1 mg of the triple salt $2KHSO_5$, $KHSO_4$, K_2SO_4, Oxone) were dissolved in 1 mL of water adjusted to pH 8 with aqueous 1 M NaOH and maintained at this value throughout the reaction by the subsequent addition of 1 M NaOH. After 1 h at room temperature, the reaction gave **2** as the main product (90% **2**, 8% **1**, 2% minor oxidative products, analysis by HPLC according to conditions described in the caption of Figure 1; for unknown reasons, complete conversion was not reached). Separation of **1** by semipreparative HPLC was carried out on a μ-Bondapak C_{18} column (0.78 × 30 cm) Waters. An isocratic elution was performed with methanol/5 mM ammonium acetate/acetic acid (8/91.9/0.1, v/v/v) at a flow rate of 2.5 mL/min. After alkalinization of the collected samples with ammonium hydroxide, two freeze-drying sequences followed by precipitation from an aqueous solution with methanol gave 31.5 mg (yield 53%) of pure **2** (diammonium salt, purity >98%): ^1H NMR (200 MHz, D_2O) δ 8.52 (1 H, s, H_2 or H_8), 8.40 (1 H, s, H_2 or H_8), 5.97 (1 H, d, J = 5.0 Hz, H'_1), 4.62 (1 H, dd, J = 5.0 and 5.5 Hz, H'_2), 4.33 (1 H, dd, J = 5.5 and 4.0 Hz, H'_3), 4.20 (1 H, m, H'_4), 3.84 (2 H, m, H'_5 and H''_5); UV (H_2O) λ_{max} 233 (ε = 40), 261 (ε = 8.3), 295 nm (ε = 2 mM^{-1} cm^{-1}). These values, as well as the HPLC data, are identical with those of an authentical sample of adenosine N^1-oxide 5′-monophosphoric acid. Attempts at higher temperature (60 °C) have shown an increase of the percentage of other oxidized products. The optimum reaction pH was 8 as shown in the figure.

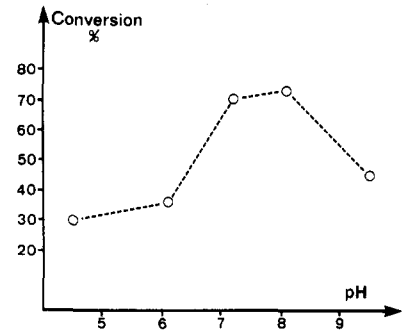


Figure 1. Effect of pH on the conversion of **1** to **2** in the presence of $KHSO_5$; 50 mM of **1** and 150 mM of $KHSO_5$ were mixed in 500 mM phosphate buffer pH 4.5, 6.1, 7.2, 8.1, or 9.3. The reaction mixture was analyzed by HPLC after 30 min at room temperature. HPLC conditions were as follows: analytical μ-Bondapak C_{18} column; isocratic elution with methanol/5 mM ammonium acetate/acetic acid, 8/91.9/0.1, v/v/v; flow rate 1.5 mL/min; detection at 254 nm; calibration curves were used for calculating the concentration of **1** and **2** during the reaction.

Synthesis of Modified Poly A. Poly A (potassium salt), 24 mg (0.048 mmol in nucleotides), and 36.8 mg (0.12 mmol) of $KHSO_5$ were mixed in 2 mL of a 250 mM phosphate buffer pH 8.3 and incubated at 25 °C. Aliquots of 30 μL were withdrawn at various periods of time and diluted in 60 μL of 200 mM HEPES buffer pH 7 (HEPES completely decomposes $KHSO_5$ within a few seconds) and 200 μL of 60 mM CH_3COONH_4, 2 mM $ZnSO_4$ solution. Enzymatic hydrolysis then was performed by addition of 6 μL of nuclease P_1 (200 units per mg, 1 mg/mL) and incubation at 37 °C. Analysis of the digestion products was performed by HPLC (see conditions in the caption of Figure 1). Complete degradation was ascertained by additional HPLC analysis on a Waters Protein Pak 125 protein analysis column eluted isocratically with 15 mM phosphate buffer (pH 6.8)–0.1 M NaCl at a flow rate of 1.0 mL/min. After reacting Poly A and $KHSO_5$ under the conditions described above for 5, 30, and 180 min and 18 h, the percentage of **2** after complete hydrolysis was 5, 25, 75, and 80, respectively. For example, 24 mg of Poly A treated as described above gave, after stopping the reaction at t = 3 h and acidifying to pH 3 with 1 M HCl, 19 mg (yield 79%) of poly A (acid form) containing 75% of adenine N^1-oxide instead of adenine. The HPLC profile of this polymer observed in the above conditions on Waters Proteins Pak 125 column was similar to the starting material but for a reduced absorption at 254 nm due to conversion of adenine to adenine N^1-oxide. No degradation products were observed.

It is noteworthy that enzymatic hydrolysis by nuclease P_1 of a 60% modified polymer was about 20 times slower than the starting Poly A.

Such a simple and straightforward preparation of modified polynucleotides with sequences rich in A bases might be potentially very useful at a time when various chemical tricks are being tried to slow down the digestion of synthetic anti-RNA's by nucleases.[8]

(1) Mantsch, H. H.; Goia, I.; Kezdi, M.; Bârzu, O.; Dânsoreanu, M.; Jebeleanu, G.; Ty, N. G. *Biochemistry* **1975**, *14*, 5593.
(2) Meyer, R. B.; Shuman, D. A.; Robins, R. K.; Miller J. P.; Simon, L. N. *J. Med. Chem.* **1973**, *16*, 1319.
(3) Kapetanovic, E.; Bailey J. M.; Colman, R. F. *Biochemistry* **1985**, *24*, 7586.
(4) Stevens, M. A.; Smith, H. W.; Brown, G. B. *J. Am. Chem. Soc.* **1959**, *81*, 1734.
(5) (a) Trost, B. M.; Braslau, R. *J. Org. Chem.* **1988**, *53*, 532 and references therein. (b) Fieser, M. *Reagents for Organic Synthesis*; John Wiley and Sons: New York, 1980; Vol. 8, p 79.
(6) Bernadou, J.; Gelas, P.; Meunier, B. *Tetrahedron Lett.* **1988**, *29*, 6615.
(7) Itahara, T.; Fujii, Y.; Tada, M. *J. Org. Chem.* **1988**, *53*, 3421.
(8) (a) Blake, K. R.; Murakami, A.; Spitz, S. A.; Glave, S. A.; Roddy, M. P.; Ts'o, P. O. P.; Miller, P. S. *Biochemistry* **1985**, *24*, 6139. (b) Thuong, N. T.; Asseline, U.; Roig, V.; Takasugi, M.; Helene, C. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 5129.

Registry No. 1, 61-19-8; 2·2NH$_3$, 120311-44-6; KHSO$_5$, 10058-23-8; Poly A (potassium salt), 26763-19-9.

Comparison of the Relative Rates of Radical Addition versus Diradical Intermediate Formation in [2 + 2] Cycloaddition Reactions of Similarly Substituted Alkenes and Alkynes

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Numerous studies have focused on the determination of the relative reactivities of substituted alkenes and alkynes toward free-radical addition. The available data indicates that free-radical additions occur more rapidly to the substituted alkenes than to the similarly substituted alkynes. The relative reactivities for trapping R (R = *n*-butyl or *tert*-butyl generated by the reduction of RHgCl with NaBH$_4$) are $H_2C{=}CHCO_2Et$ (1.0) and $HC{\equiv}CCO_2Et$ (0.19), and $H_2C{=}CHC_6H_5$ (0.15) and $HC{\equiv}CC_6H_5$ (0.02).[1] In a similar type of study the relative reactivities for the trapping of the cyclohexyl radical were found to be $H_2C{=}CHCO_2Et$ (6.7) and $HC{\equiv}CCO_2Et$ (2.1), and $H_2C{=}CHC_6H_5$ (1.0) and $HC{\equiv}CC_6H_5$ (0.25).[2] The addition of substituted benzenethiyl radicals to $H_2C{=}CHCO_2Et$ and $HC{\equiv}CCO_2Et$ favored the alkene by factors of 24–47.[3] And finally, the rates have been measured for the gas-phase addition of the methylthiyl radical to ethylene and acetylene (2.8 and $<2 \times 10^{15}$ cm^3/s) and propene and propyne (10 and $<6 \times 10^{15}$ cm^3/s).[4] In all of these comparative cases the addition of the free radical to the alkene occurred faster than to the alkyne by factors that range from 1.4 to 47.

Recent studies in our laboratories have shown that the [2 + 2] cycloaddition reactions of 1,1-dimethylallene (DMA) with substituted alkynes occur very cleanly to produce substituted methylenecyclobutenes.[5] Qualitatively, these reactions appeared to proceed considerably more rapidly than did the [2 + 2] cycloaddition reactions with substituted alkenes,[6] which prompted us to carry out relative rate comparisons of similarly substituted alkenes and alkynes toward cycloaddition with DMA. The two pairs of substituted alkenes and alkynes used in this study are $H_2C{=}CHCO_2Et$ and $HC{\equiv}CCO_2Et$, and $H_2C{=}CHC_6H_5$ and $HC{\equiv}CC_6H_5$.[7] *In both cases the substituted alkyne was essentially completely reacted; there was no indication of any reaction having occurred with the substituted alkene. In these [2 + 2] cycloaddition reactions the substituted alkynes are more reactive than the corresponding alkene by a factor of >100!*

What accounts for this dramatic change in relative reactivities in radical addition reactions versus the cyclo-

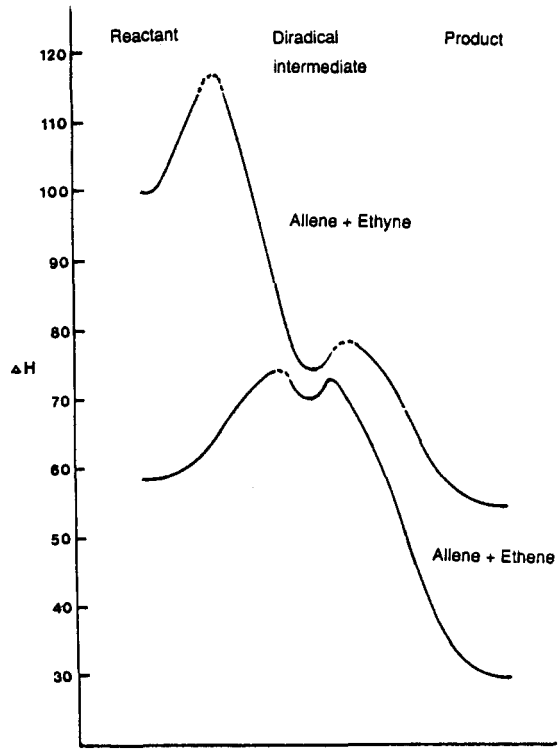

Figure 1. Heats of formation of reactants diradical intermediates and products.

addition reactions with DMA? In the addition of an alkyl radical to a C=C or C≡C, a C—C bond is formed, a C=C π-bond is cleaved, and one radical center disappears while another radical center is formed. Overall, this reaction will be quite exothermic, and, thus, the transition state for the addition should occur early along the reaction coordinate. In this case the relative reactivities will be controlled by FMO properties. The calculated energies (4-31G fully geometry optimized structures)[8] for the HOMO's and LUMO's of ethylene and acetylene are −10.21 and −11.04 eV, and +5.07 and +6.16 eV, respectively; with c_i's of 0.564 and 0.911, and 0.558 and 0.986, respectively. In radical addition reactions there is an interaction between the SOMO of the radical (whose energy lies between the HOMO and the LUMO of the π-system) with both the HOMO and the LUMO of the π-system of the alkene or alkyne. According to PMO theory the alkene is thus expected to react more rapidly than the alkyne in reactions involving very early transition states.

In the [2 + 2] cycloaddition reactions of substituted allenes all of the data collected in the author's laboratories indicate that these cycloaddition reactions occur via diradical intermediates that are formed via transition states that occur late along the reaction coordinate.[6] This is fully consistent with the nature of the process: two C=C bonds being cleaved, one C—C bond being formed along with two radical centers, which will result in a rather endothermic process. At first glance, the greater reactivity of the substituted alkynes in the cycloaddition process would appear to suggest that the vinyl radical portion of intermediate **1** is lower in energy than the alkyl radical portion in **2**. However, this is not consistent with the well-recognized relative stabilities of the ethyl and vinyl radicals as indicated by C–H bond dissociation energies and heats of formation, which indicate that the ethyl radical is lower in energy than the vinyl radical. An understanding of the

(1) Russell, G. A.; Jiang, W.; Hu, S. S.; Khanna, R. K. *J. Org. Chem.* **1986**, *51*, 5498.
(2) Giese, B.; Lachhein, S.; Meixner, J. *Tetrahedron Lett.* **1980**, *21*, 2505.
(3) Ito, O.; Omori, R.; Matsuda, M. *J. Am. Chem. Soc.* **1982**, *104*, 3934.
(4) Balla, R. J.; Weiner, B. R.; Nelson, H. H. *J. Am. Chem. Soc.* **1987**, *109*, 4804.
(5) Pasto, D. J.; Kong, W. *J. Org. Chem.* **1988**, *53*, 4807.
(6) Pasto, D. J.; Yang, S.-H. *J. Am. Chem. Soc.* **1984**, *106*, 152.
(7) All of the cycloadducts except that of styrene with DMA have been previously characterized (ref 5 and 6).
(8) Carnegie-Mellon Quantum Chemistry Archive, Carnegie-Mellon University, Pittsburgh, PA.

0022-3263/89/1954-3215$01.50/0