

INTERMOLECULAR CYCLOADDITION REACTIONS OF EXOCYCLIC NITRONES
FACILE SYNTHESIS OF 1-AZASPIROCYCLES

Raymond L. Funk*† and Joy Umstead Daggett

Department of Chemistry
University of Nebraska-Lincoln
Lincoln, Nebraska 68588, U.S.A.

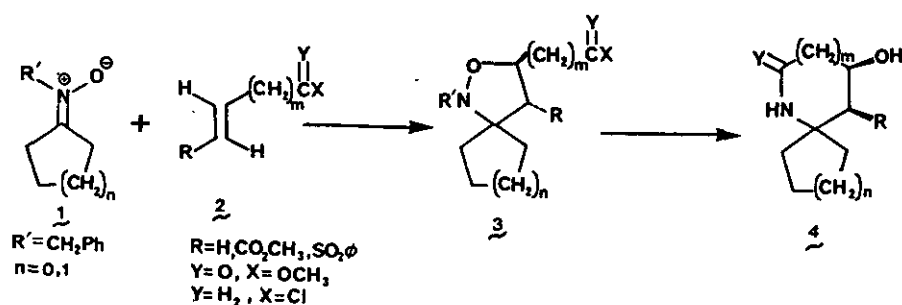
Abstract - A two step procedure for transforming cycloalkanones via intermediate exocyclic nitrones to 1-azaspirocycles is described.

The 1-azaspirocyclic ring system is common to a variety of natural products including the histrionicotoxin alkaloids¹, erythrina alkaloids², cephalotaxus alkaloids³ and spirobenzylisoquinolines⁴ and is responsible for interesting biological activity⁵. Consequently, considerable attention has been directed toward the development of new methodology for the introduction of this ring system. Three distinct strategies have been employed: 1) Beckmann rearrangement of a spiro-1-alkanone to a spirocyclic lactam⁶; 2) Ring closure of the carbocyclic ring onto a pre-existing azacycle⁷; or 3) Ring closure of the azacyclic ring onto a preformed carbocycle⁸. We now describe a new variant of the latter strategy which features rapid construction of 1-azaspirocycles from cycloalkanones mediated by nitron-olefin cycloaddition reactions⁹.

The general approach is illustrated in Scheme I. It was hoped that the exocyclic nitron 1 would undergo intermolecular cycloaddition reactions with various functionalized olefins. In contrast to the well documented cycloaddition reactions of endocyclic or acyclic nitrones, the similar cyclizations employing exocyclic nitrones have not been investigated¹⁰ despite the initial preparation of exocyclic nitrones by Exner over 30 years ago.¹¹ If successful, the resulting cycloadducts 3 could then be easily elaborated to the 1-azaspirocycles 4 by N-O bond cleavage and concomitant intramolecular acylation or alkylation of the liberated amine with the corresponding functionality which originated in the dipolarophile.

*Fellow of the Alfred P. Sloan Foundation, 1985-1987

SCHEME I

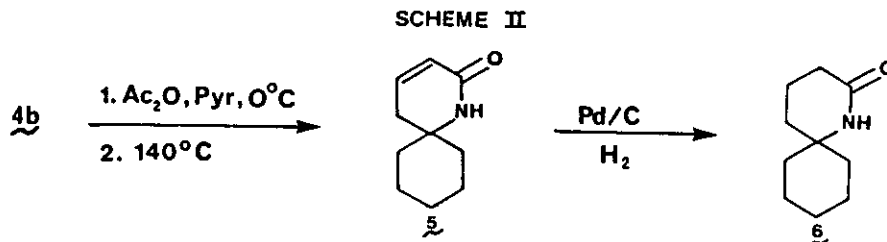


The various 1-azaspirocycles that have been synthesized using this methodology are shown in Table I. Typically the nitrones **1** were prepared from the corresponding cycloalkanone (1 equiv) and N-benzylhydroxylamine (1 equiv) by refluxing in dry ethanol (4h). The ethanol was removed in vacuo, replaced with toluene, and the requisite dipolarophile was added (1-1.5 equiv). The mixture was heated for the indicated time period (Table I) and the products were purified by flash chromatography on silica gel (ethyl acetate/hexanes 1:5). Regioisomeric 4-substituted isoxazolidines were obtained when methyl acrylate was used as the dipolarophile (entry a, 10%; entry c, 12%). Hydrogenolysis was accomplished using 20% Pd(OH)₂¹² (0.2 equiv) in 95% EtOH under 1 atmosphere of hydrogen. The yields indicated are after recrystallization.

TABLE I

ENTRY	1	2	TEMP (Hrs.)	3 (% yield)	4 (% yield)	MP 4 (°C)
a	n=1		0 (0.25)			208-209
b	n=1		111 (5)			202-204
c	n=0		25 (0.25)			182-183
d	n=1		111 (10)			179-181

The 1-azaspirocycles **4** possess functionality useful for further synthetic manipulation. For example, dehydration of **4b** (1. Ac_2O , Pyr, 0°C ; 2. 140°C) gave the unsaturated lactam **5** which was hydrogenated to afford the known lactam **6** (mp $117-118^\circ\text{C}$)¹³ which serves to confirm the structural integrity of these compounds (Scheme II).



This work demonstrates that exocyclic nitrones smoothly participate in intermolecular cycloaddition reactions and also serve as viable intermediates for the preparation of functionalized 1-azaspirocycles. The application of this methodology in the total synthesis of the histrionicotoxin alkaloids is underway.

EXPERIMENTAL

^1H nmr spectra were recorded on a Varian EM-390 (90 MHz), a Varian XL-200 (200 MHz), or a Nicolet 1180 WB (360 MHz) spectrometer. Data are reported as follows: chemical shift in parts per million downfield of internal tetramethylsilane (Me_4Si), or relative to chloroform (7.26 ppm), (number of protons, multiplicity, coupling constant[s]). The ^{13}C nmr spectra were recorded on a Nicolet 1180 WB (90.5 MHz) spectrometer or a Varian XL200 (50.4 MHz) spectrometer. Chemical shifts are reported in parts per million downfield from Me_4Si referenced to the central peak of the deuterochloroform triplet (77.0 ppm downfield from Me_4Si). Infrared absorption spectra were obtained on a Perkin-Elmer Model 283 or model 1430 ratio recording spectrometer and are referenced to polystyrene (1601 cm^{-1}). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

General Procedure for Cycloaddition. To a dry flask equipped with a stirring bar and a condenser was placed the desired cycloalkanone and dry ethanol was added (1M solution). N-Benzylhydroxylamine (1 equivalent) was added and the solution was refluxed for 2-4 h to afford the corresponding nitrone. (^1H nmr revealed a singlet at approximately 5 ppm indicative of the nitrone benzyl proton resonance.) The ethanol was evaporated in vacuo and the appropriate solvent for the subsequent cycloaddition reaction was added (Table 1). After addition of the dipolarophile (1-1.5 equivalent) and heating to the required temperature for

the time indicated, the solvent was removed in vacuo and the product purified via flash chromatography (1:5 ethyl acetate/hexanes).

Cycloadduct 3a: The cycloaddition was effected by first cooling the flask containing the neat nitrone followed by addition of enough methyl acrylate to make a 0.1 molar solution. 77% yield. Ir (film) 3030, 2930, 2865, 1735, 1455, 1365, 1205, 785, 695 cm^{-1} ; ^1H nmr (200 MHz, CDCl_3) δ 7.53-7.28 (5H, m), 4.54 (1H, dd, $J=8, 10$ Hz), 3.94 (1H, d, $J=14$ Hz), 3.82 (1H, d, $J=14$ Hz), 3.70 (3H, s), 2.51 (1H, dd, $J=10, 13$ Hz), 2.36 (1H, dd, $J=8, 13$ Hz), 1.82-1.20 (10H, m); Mass spectrum m/z (relative intensity) 289(5) [M^+], 246(9), 230(6), 187(7), 117(15), 103(11), 98(8), 91(100), 77(13), 69(5), 65(11), 55(16). Exact mass calc. for $\text{C}_{17}\text{H}_{23}\text{NO}_3$: 289.1678. Found: 289.1681. Anal. calc. for $\text{C}_{17}\text{H}_{23}\text{O}_3\text{N}$: C, 70.56; H, 8.01. Found: C, 70.29; H, 8.20. The regioisomeric cycloadduct was also isolated (10%). ^1H nmr (200 MHz, CDCl_3) δ 7.5-7.2 (5H, m), 4.33 (1H, t, 6 Hz), 4.16 (1H, t, 6 Hz), 4.10 (1H, d, $J=16$ Hz), 3.96 (1H, d, $J=16$ Hz), 3.74 (3H, s), 3.19 (1H, t, $J=6$ Hz), 1.9-1.2 (10H, m).

Cycloadduct 3b: 55% yield. Ir (film) 3025, 2940, 2860, 1740, 1495, 1457, 1449, 1203, 732, 695 cm^{-1} ; ^1H nmr (90MHz, CDCl_3) δ 7.60-7.10 (5H, m), 4.47 (1H, dddd, $J=15, 9, 6, 4$ Hz), 3.83 (2H, s), 3.64 (3H, s), 2.82 (1H, dd, $J=15, 6$ Hz), 2.65 (1H, dd, $J=9$ and 6 Hz), 2.39 (1H, dd, $J=6, 4$ Hz), 1.87 (1H, dd, $J=15, 6$ Hz), 1.8-1.2 (10H, m); Mass spectrum m/z (relative intensity) 303(7) [M^+], 260(15), 230(9), 186(6), 103(8), 91(100), 77(1), 70(8), 65(10), 55(8). Exact mass calc. for $\text{C}_{18}\text{H}_{25}\text{NO}_3$: 303.1834. Found: 303.1825.

Cycloadduct 3c: 75% yield. Ir (film) 3020, 2940, 2860, 1750, 1490, 1450, 1200, 1025, 725, 690 cm^{-1} ; ^1H nmr (200MHz, CDCl_3) δ 7.50-7.20 (5H, m), 4.49 (1H, dd, $J=8$ and 8 Hz), 3.97 (1H, d, $J=13$ Hz), 3.83 (1H, d, $J=13$ Hz), 3.73 (3H, s), 2.51 (2H, m), 1.95-1.50 (8H, m); Mass spectrum m/z (relative intensity) 275(4) [M^+], 246(4), 216(10), 173(8), 91(100), 77(6), 65(11), 55(11). Exact mass calc. for $\text{C}_{16}\text{H}_{21}\text{NO}_3$: 275.1521. Found: 275.1523. The regioisomeric cycloadduct was also isolated (12%). ^1H nmr (90 MHz, CDCl_3) δ 7.5-7.2 (5H, m), 4.28 (1H, t, $J=7$ Hz), 4.19 (1H, t, $J=7$ Hz), 3.96 (1H, d, $J=12$ Hz), 3.65 (1H, d, $J=12$ Hz), 3.70 (3H, s), 3.40 (1H, t, $J=7$ Hz), 2.1-1.4 (8H, m).

Cycloadduct 3d: 54% yield. Ir (film) 2930, 2845, 1533, 1435, 1355, 1260, 1200, 1155, 735, 690 cm^{-1} ; ^1H nmr (90MHz, CDCl_3) δ 7.40-7.10 (5H, m), 4.85 (1H, br q, $J=7$ Hz), 4.18 (1H, d, $J=14$ Hz), 3.80 (1H, d, $J=14$ Hz), 3.72 (3H, s), 3.57 (3H, s), 2.85 (1H, d, $J=8$ Hz), 2.77 (1H, dd, 15 and 6 Hz), 2.45 (1H, dd, $J=15$ and 9 Hz), 2.00-1.20 (10H, m); Mass spectrum m/z (relative intensity) 361(13) [M^+], 318(9), 173(10), 160(24), 143(59), 135(41), 131(60), 127(93), 91(100), 89(69), 71(100), 59(56), 43(52). Exact mass calc. for $\text{C}_{20}\text{H}_{27}\text{NO}_5$: 361.1889. Found: 361.1909.

General Procedure for Hydrogenolysis. To a 0.1 molar solution of the cycloadduct in 95%

ethanol was added 0.2-0.3 equivalents of 20% palladium hydroxide on carbon (Pearlman's catalyst)¹². The solution was then subjected to 1 atmosphere of hydrogen until the calculated volume of hydrogen had been consumed. Filtration followed by evaporation of the solvent yielded the desired product which was recrystallized from chloroform.

1-Azaspirolactam 4a: 82% yield. mp 208-209°C. Ir (KBr pellet) 3320(br), 3200(br), 2930, 2850, 1680, 1445, 1310, 1280, 1255, 1130, 855, 805, 610 cm^{-1} ; ^1H nmr (200 MHz, 5% D_2O in acetone, d_6) δ 7.36 (1H, br s), 4.30 (1H, t, $J=8$ Hz), 3.56 (1H, br s), 2.37 (1H, dd, $J=8$ and 12 Hz), 1.70-1.20 (11H, m); Mass spectrum m/z (relative intensity) 169(31) [M^+], 140(9), 126(100), 113(28), 98(46), 91(16), 81(14), 70(10), 67(24), 55(15). Exact mass calc. for $\text{C}_9\text{H}_{15}\text{NO}_2$: 169.1103. Found: 169.1102. Anal. calc. for $\text{C}_9\text{H}_{15}\text{NO}_2$: C, 61.91; H, 8.44. Found: C, 62.09; H, 8.62.

1-Azaspirolactam 4b: 81% yield. mp 202-204°C. Ir (KBr pellet) 3340, 3170, 3030, 2916, 2852, 1665, 1450, 1365, 1275, 1055, 855 cm^{-1} ; ^1H nmr (90 MHz, CDCl_3) δ 6.25 (1H, br s), 4.10 (1H, br s), 2.60-1.00 (15H, m); Mass spectrum m/e (relative intensity) 183(14) [M^+], 166(3), 154(4), 140(100), 127(40), 122(29), 112(6), 98(8), 94(9), 81(6), 70(42), 67(4), 57(8). Exact mass calc. for $\text{C}_{10}\text{H}_{17}\text{NO}_2$: 183.1259. Found: 183.1262.

1-Azaspirolactam 4c: 56% yield. mp 182-183°C. Ir (KBr pellet) 3155 (br), 2950, 2870, 1670, 1435, 1305, 1095, 815, 725, 653 cm^{-1} ; ^1H nmr (200 MHz, 5% D_2O in acetone, d_6) δ 4.32 (1H, t, $J=9$ Hz), 2.35 (1H, dd, $J=9$ and 13 Hz), 1.80 (1H, dd, $J=9$ and 13 Hz), 1.80-1.40 (10H, m); Mass spectrum m/e (relative intensity) 155(38) [M^+], 126(100), 113(56), 98(48), 94(9), 85(16), 83(19), 79(26), 77(9), 70(25), 67(46), 57(17), 54(24). Exact mass calc. for $\text{C}_8\text{H}_{13}\text{NO}_2$: 155.0946. Found: 155.0944.

1-Azaspirolactam 4d: 51% yield. mp 179-181°C. Ir (KBr pellet) 3300(br), 3180, 3020, 2922, 2858, 1730, 1630, 1455, 1400, 1312, 1212, 1192, 1163, 987, 725 cm^{-1} ; ^1H nmr (90 MHz, CD_3OD) δ 5.20 (1H, br s), 4.35 (1H, m), 3.63 (3H, s), 3.22 (1H, m), 2.60 (2H, d, $J=9$ Hz), 1.80-1.30 (11H, m); Mass spectrum m/z (relative intensity) 242(22) [M^+], 241(55) [M^+], 198(53), 185(31), 164(40), 128(100), 96(98), 83(11), 71(17). Exact mass calc. for $\text{C}_{12}\text{H}_{19}\text{NO}_4$: 241.1314. Found: 241.1303.

Unsaturated 1-Azaspirolactam 5: Azaspirolactam **4b** (0.14 mmol, 25 mg) was dissolved in 1 ml of pyridine followed by addition of a catalytic amount of *N,N*-dimethyl-4-aminopyridine. To this solution was added 1 ml of freshly distilled acetic anhydride and the reaction was stirred at room temperature for 6 h. Upon reaction completion, the solution was poured onto ether/water and the layers were separated. The ether extracts were washed twice more with water, saturated bicarbonate, then water again followed by drying over sodium sulfate. Evaporation of the

solvent in vacuo yielded 23 mg (72%) of product which was taken on immediately to the next step.

The crude acetate was dissolved in xylenes and a catalytic amount of acetic acid was added. This solution was refluxed for 8 h at which time the solvent was removed. After purification by flash chromatography on silica gel (1.4:1 ethyl acetate/hexanes), a colorless oil was obtained (10 mg, 60%). ^1H nmr (90 CDCl_3) δ 6.41 (1H, dt, $J=9$ and 4 Hz), 6.00 (1H, br s), 5.82 (1H, dd, $J=9$ and 2 Hz), 2.40-2.20 (2H, m), 1.75-1.10 (10H, m); Mass spectrum m/z (relative intensity) 165(51) [M^+], 122(100), 109(80), 94(13), 81(16), 68(12), 54(8). Exact mass calc. for $\text{C}_{10}\text{H}_{15}\text{NO}$: 165.1154. Found: 165.1147.

1-Azaspinolactam 6: The unsaturated lactam 5 (0.06 mmol, 10 mg) was dissolved in 1 mL of 95% ethanol followed by addition of a catalytic amount of palladium on carbon. The reaction mixture was subjected to 1 atmosphere of hydrogen until 1 equivalent had been consumed. The solution was then filtered and the solvent removed in vacuo to yield the desired product. This material was filtered through a plug of silica gel (1.4:1 ethyl acetate/hexanes) to yield a white solid (10 mg, 100%) whose melting point (117-118°C) corresponded to that reported in the literature (116.5-118°C).¹³ ^1H nmr (90 MHz, CDCl_3) δ 6.75 (1H, br s), 2.45-2.20 (2H, m), 1.90-1.30 (14H, m); Mass spectrum m/z (relative intensity) 167(25) [M^+], 138(4), 124(100), 111(38), 96(40), 82(18), 55(15). Exact mass calc. for $\text{C}_{10}\text{H}_{17}\text{NO}$: 167.1310. Found: 167.1304.

ACKNOWLEDGEMENT

We thank the National Science Foundation (CHE-8205144) and the Alfred P. Sloan Foundation for financial and material support. High-field (360 MHz) ^1H and ^{13}C nmr spectra were obtained on a spectrometer purchased with funds provided, in part, by the National Science Foundation (CHE80-24328). Mass spectra were obtained through the National Science Regional Mass Spectroscopy Center at the University of Nebraska (CHE-82-11164).

REFERENCES

- (a) J.W. Daly, I.L. Karle, C.W. Meyers, T. Tokuyama, J.A. Walters and B. Witkop, Proc. Nat. Acad. Sci. U. S., **1971**, 68, 1870. (b) T. Tokuyama, K. Uenoyama, G. Brown, J.W. Daly and B. Witkop, Helv. Chim. Acta, **1974**, 57, 2597. (c) B. Witkop, Experientia, **1971**, 27, 1121. (d) I. Karle, J. Am. Chem. Soc., **1973**, 95 4036. (e) I. Karle, J. Am. Chem. Soc., **1980**, 102, 830. (f) Y. Inubushi and T. Ibuka, Heterocycles, **1982**, 17, 507. (g) C. Myers and J. Daly, Scientific American, **1983**, 248, 120. (h) J.W. Daly, "Progress in the Chemistry of Natural Products"; W. Herz, H. Grisebach and G.W. Kirby, Eds.; Springer Verlag; Wien, New York, **1982**, 41, 206.

2. (a) S.F. Dyke and S.N. Quessy, in "The Alkaloids"; R.G.A. Rodrigo and R.H.F. Manske, Eds.; Academic Press: New York, 1981, **18**; pp 1-98. (b) R.K. Hill; *ibid*; R.H.F. Manske, Ed.; 1967, **9**, pp 483-515.
3. M.F. Semmelhack and W.M. Weinreb, Accts. Chem. Res., **1975**, **8**, 158.
4. (a) M. Shamma, in "The Isoquinoline Alkaloids"; Academic Press: New York, 1972; pp 380-398. (b) M. Shamma, in "The Alkaloids"; R.H.F. Manske, Ed; Academic Press: New York, 1971, **13**, pp 165-188.
5. Anticholinergic and antispasmodic activity: (a) R.B. Moffett, J. Am. Chem. Soc., **1957**, **79**, 3186. (b) J. Elliott and M.A. Raftery, Biochem. Biophys. Res. Comm., **1977**, **77**, 1347. (c) I.L. Karle, J. Am. Chem. Soc., **1973**, **95**, 4036. (d) K. Takahashi, B. Witkop, A. Brossi, M. Maleque, and E.X. Albuquerque, Helv. Chim. Acta, **1982**, **65**, 252. (e) I. McCance, J.W. Phillis, Experientia, **1964**, **20**, 217. (f) K. Takahashi, A.E. Jacobson, C-P. Mak, B. Witkop, A. Brossi, E.X. Albuquerque, J.E. Warnick, M.A. Maleque, A. Bavoso, and J.V. Silverton, J. Med. Chem., **1982**, **25**, 919. Analgesic, antipyretic, antiphlogistic properties: (g) Swiss Patent 417.591, **1968**. (h) Chem. Abstr., **1968**, 39482n. Antileukemic activity: (i) R.G. Powell, D. Weisleder, and C.R. Smith, J. Pharm. Sci., **1972**, **61** 1227. (j) M.T. Huang, Mol. Pharmacol., **1975**, **11**, 511.
6. (a) R.K. Hill and R.T. Conley, J. Am. Chem. Soc., **1960**, **82**, 645, (b) R.K. Hill, *Ibid.*, **1957**, **22**, 830. (c) T. Ibuka, Y. Mitsui, K. Hayashi, H. Minakawa, and Y. Inubushi, Tetrahedron Lett., **1981**, 4425. (d) T. Ibuka, H. Minakata, Y. Mitsui, E. Tabushi, T. Taga, and Y. Inubushi, Chem. Lett., **1981**, 1409. (e) E.J. Corey, M. Petrziłka, and Y. Ueda, Helv. Chim. Acta, **1977**, **60**, 2294. (f) E.J. Corey, J.F. Arnett, G.N. Widiger, J. Am. Chem. Soc., **1975**, **97**, 430. (g) F.T. Bond, J.E. Stemke, D.W. Powell, Syn. Comm., **1975**, **5**, 427.
7. (a) D.A. Evans and E.W. Thomas, Tetrahedron Lett., **1979**, 411. (b) D.A. Evans, E.W. Thomas, and R.E. Cherpeck, J. Am. Chem. Soc., **1982**, **104**, 3695. (c) H.E. Schoemaker and W.N. Speckamp, Tetrahedron, **1980**, **36**, 951. (d) E.J. Corey and R.D. Balanson, Heterocycles, **1976**, **5**, 445. (e) J.T. Tufariello, and E.J. Trybulski, J. Org. Chem., **1974**, **39**, 3378.
8. (a) M. Pfau and R. Dulou, Bull. Chim. Soc. Fr., **1967**, 336. (b) L.E. Overman, Tetrahedron Lett., **1975**, 1149. (c) W. Kissing and B. Witkop, Chem. Ber., **1975**, **108**, 1623. (d) M. Aratani, L.V. Dunkerton, T. Fukuyama, Y. Kishi, H. Kakoi, S. Sugiura, and S. Inoue, J. Org. Chem., **1975**, **40**, 2009. (e) P. Magnus and J.J. Venit, Tetrahedron Lett., **1980**, 4815. (f) A.J. Pearson, P. Ham, and D.C. Rees, *Ibid*, **1980**, 4637. (g) S.A. Godleski, J.D. Meinhardt, and D.J. Miller, *Ibid*, **1981**, 2247. (h) S.A. Godleski and D.J. Heacock, J. Org. Chem., **1982**, **47**, 4822. (i) T. Fukuyama, L.V. Dunkerton, M. Aratani, and Y. Kishi, J. Org. Chem., **1975**, **40**, 2011. (j) G.E.

- Keck, and J.B. Yates, J. Org. Chem., **1982**, 47, 3590. (k) F-T. Chiu, J.W. Ullrich, and P.S. Mariano, J. Org. Chem., **1984**, 49, 228 and references therein. (l) A.J. Pearson, Science, **1984**, 223, 895. (m) A.B. Holmes, K. Russell, E.S. Stern, M.E. Stubbs, and N.K. Wellard, Tetrahedron Letters, **1984**, 25, 4163. (n) T. Ibuka, H. Minakata, M. Hashimoto, L. Overman, and R. Freerks Heterocycles, **1984**, 22, 485. (o) D. Tanner and P. Somfai, Tetrahedron Letters, **1985**, 26, 3883. (p) J.D. Winkler, P.M. Hershberger, and J.P. Springer, ibid, **1986**, 27, 5177. (q) C.-K. Sham, S.-L. Ouyang, D.-Y. Hsieh, R.-C. Chang, and S.-C. Chang, J. Org. Chem., **1986**, 51, 1490.
9. (a) D. Black St. C., R.F. Crozier, and V.C. Davis, Synthesis, **1975**, 205. (b) G.R. Delpierre, and M. Lamchen, Quarterly Rev., **1965**, 19, 329. (c) J. Hamer, and A. Macaluso, Chem. Rev., **1964**, 64, 473. (d) R. Huisgen, Angew. Chem., Int. Ed. Eng., **1963**, 2, 565, 633.
10. However, the intramolecular cycloaddition reactions of the exocyclic nitrones have been investigated, see: (a) R.L. Funk, L.H.M. Horcher, J.U. Daggett, and M.M. Hansen, J. Org. Chem., **1983**, 48, 2632. (b) R.L. Funk and G.L. Bolton, ibid, **1984**, 49, 5021. (c) R.L. Funk, G.L. Bolton, J.U. Daggett, M.M. Hansen, and L.H.M. Horcher, Tetrahedron, **1985**, 41, 3479. (d) S. Takahashi, T. Kusumi, Y. Sato, Y. Inouy¹, and H. Kakisawa, Bull. Chem. Soc. Jpn., **1981**, 54, 177.
11. O. Exner, Coll. Czech. Chem. Comm., **1951**, 16, 258.
12. W.M. Pearlman, Tetrahedron Letters, **1967**, 17, 1663.
13. Richard K. Hill, J. Am. Chem. Soc., **1957**, 22, 830.

Received, 8th April, 1987