

REACTION OF CYCLOHEXA-1,2,3-TRIENE WITH *N*, α -DIPHENYL-NITRONE: FORMATION OF SEVEN-MEMBERED CYCLIC AMINES VIA PIRADONE DERIVATIVES

Michihito Sakura, Shinichi Ando, Atsushi Hattori, and Katsuhiko Saito*

Department of Applied Chemistry, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

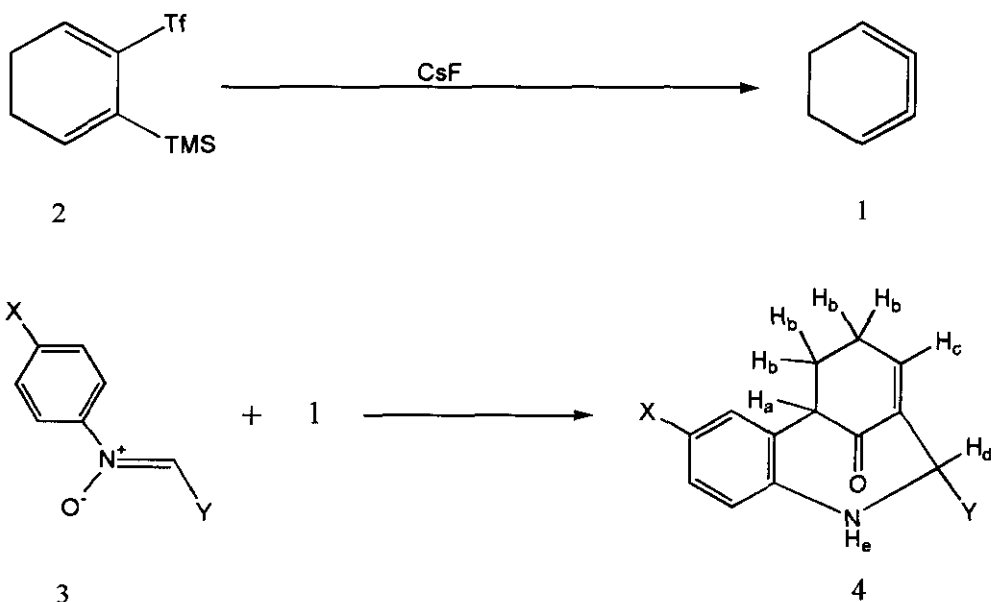
Abstract——Cyclohexa-1,2,3-triene was generated in the presence of *N*, α -diphenylnitrones to form seven-membered cyclic amines *via* piradone derivatives, which were formed through [4+2] type cycloaddition of the central double bond of cyclohexa-1,2,3-triene with nitrones.

Generally, cumulenes are recognized to have linear structures because of the sp -hybridization of the carbon atoms. Cyclic cumulenes usually have high reactivity owing to the high strain energy of the bent cumulene structures. The smallest cyclic allene isolated is cyclonona-1,2-diene, although it dimerizes with a half life time of *ca.* 10 min at 0 °C. Cyclohexa-1,2-diene is known only as a reactive intermediate.¹ A conjugated seven-membered cyclic allene, cyclohepta-1,2,4,6-tetraene, was reported to be a tautomeric mixture of a conjugated seven-membered cyclic carbene, cycloheptatrienyliene.²

Cyclic cumulenes, which have three double bonds in continued positions, have been targets of syntheses and investigations. Cyclonona-1,2,3-triene has been isolated as a stable compound.³ However, cyclohepta-1,2,3-triene has been too unstable to be isolated and known to exist as only a reactive intermediate.⁴

Recently, it has been reported that cyclohexa-1,2,3-triene (1) can be generated as a reactive intermediate by treatment of a triflate (2) with cesium fluoride.⁵ As a part of our research on the reactivity of strained double bonds,⁶ we have now examined the reaction of the triene (1) with *N*, α -diphenylnitrone and have found a formation of seven-membered cyclic amines *via* piradone derivatives.

The typical experiment is as follows. To a solution of 2 and four molar equivalents of *N*, α -diphenylnitrone (3a) in dry DMSO were added seven molar equivalents of cesium fluoride. After stirring at room temperature for 3 h, the reaction mixture was purified by column and

Table 1. Cycloaddition of Cyclohexa-1,2,3-triene(**1**) with Nitron(**3**).

entry	Nitron	X	Y	Product	Yield (%)
1	3a	H	Ph	4a	54
2	3b	H	<i>p</i> -Me-C ₆ H ₄	4b	24
3	3c	H	1-Naph	4c	19
4	3d	H	2-Naph	4d	33
5	3e	H	<i>p</i> -Cl-C ₆ H ₄	4e	28
6	3f	H	<i>p</i> -Br-C ₆ H ₄	4f	41
7	3g	H	<i>p</i> -CN-C ₆ H ₄	4g	14
8	3h	H	<i>p</i> -NO ₂ -C ₆ H ₄	4h	6
9	3i	Me	Ph	4i	57
10	3j	Cl	Ph	4j	21

thin-layer chromatography on silica gel to give **4a** in 54 % yield. The results of the analogous reactions with various nitrones are summarized in Table 1.

The structures of these products were deduced on the basis of their spectral properties as follows. The molecular ion peaks in MS spectra showed these products to be 1:1 adducts between **1** and **3**. The IR spectra indicated the existence of a carbonyl group. The broad singlet peak at *ca.* 3.6 ppm in ¹H NMR spectra, which was exchangeable with deuterium in deuterium oxide, was assigned to a proton attached to a nitrogen atom. The detailed analysis of the signals of the aromatic protons clearly showed existence of an *o*-disubstituted benzene moiety. These analyses lead to the structures illustrated in the Figure, which were supported by good resemblance of the spectral properties with those of an analogous compound.⁴ Furthermore, the complete and unequivocal structural characterization of **4** was accomplished by single crystal X-Ray analysis.

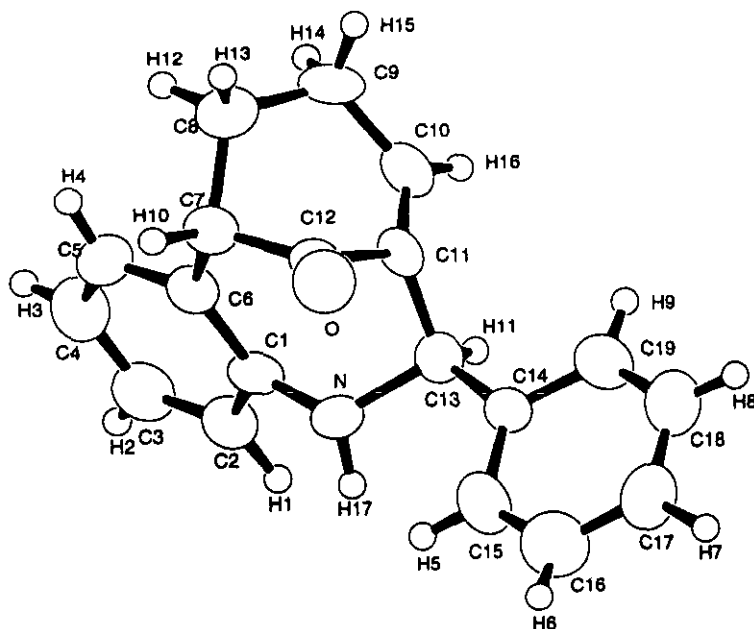


Figure 1. ORTEP drawing the X-Ray structure of 4a.

Table 2. Atomic coordinates for 4a.

atom	x	y	z	atom	x	y	z
O	0.7042(3)	0.1403(3)	-0.2955(7)	C(18)	0.9108(5)	0.0749(7)	-0.150(1)
N	0.7159(3)	0.1669(4)	0.1023(7)	C(19)	0.8540(5)	0.0588(6)	-0.077(1)
C(1)	0.6536(4)	0.1553(5)	0.1604(9)	H(1)	0.674(3)	0.180(3)	0.405(7)
C(2)	0.6404(5)	0.1722(5)	0.324(1)	H(2)	0.567(5)	0.183(6)	0.49(1)
C(3)	0.5807(5)	0.1703(5)	0.386(1)	H(3)	0.491(4)	0.144(5)	0.322(9)
C(4)	0.5320(5)	0.1499(6)	0.282(1)	H(4)	0.514(3)	0.114(3)	0.043(6)
C(5)	0.5446(4)	0.1323(5)	0.118(1)	H(5)	0.808(3)	0.239(6)	0.000(10)
C(6)	0.6046(4)	0.1340(4)	0.0546(9)	H(6)	0.903(6)	0.263(7)	-0.13(2)
C(7)	0.6126(4)	0.1145(5)	-0.1296(9)	H(7)	0.975(4)	0.165(5)	-0.22(1)
C(8)	0.5861(5)	0.0288(5)	-0.182(1)	H(8)	0.938(4)	0.038(6)	-0.18(1)
C(9)	0.6226(5)	-0.0442(6)	-0.108(1)	H(9)	0.844(4)	0.004(5)	-0.063(10)
C(10)	0.6824(4)	-0.0208(6)	-0.027(1)	H(10)	0.593(2)	0.155(3)	-0.192(6)
C(11)	0.7105(4)	0.0500(5)	-0.0612(9)	H(11)	0.760(4)	0.059(3)	0.149(6)
C(12)	0.6800(4)	0.1072(5)	-0.179(1)	H(12)	0.540(4)	0.025(5)	-0.143(10)
C(13)	0.7536(4)	0.0947(5)	0.054(1)	H(13)	0.585(4)	0.025(5)	-0.31(1)
C(14)	0.8148(3)	0.1200(5)	-0.0246(9)	H(14)	0.591(4)	-0.071(5)	-0.02(1)
C(15)	0.8342(4)	0.1995(6)	-0.046(1)	H(15)	0.623(4)	-0.083(5)	-0.20(1)
C(16)	0.8913(6)	0.2156(8)	-0.116(2)	H(16)	0.700(3)	-0.056(4)	0.051(8)
C(17)	0.9303(5)	0.1547(7)	-0.169(1)	H(17)	0.738(4)	0.198(4)	0.171(9)

Table 3. Bond lengths for 4a.

bond distant		bond distant		bond distant	
O-C(12)	1.204(8)	C(5)-C(6)	1.39(1)	C(11)-C(13)	1.50(1)
N-C(1)	1.431(9)	C(6)-C(7)	1.53(1)	C(13)-C(14)	1.52(1)
N-C(13)	1.482(10)	C(7)-C(8)	1.57(1)	C(14)-C(15)	1.37(1)
C(1)-C(2)	1.379(10)	C(7)-C(12)	1.51(1)	C(14)-C(19)	1.37(1)
C(1)-C(6)	1.399(10)	C(8)-C(9)	1.55(1)	C(15)-C(16)	1.38(1)
C(2)-C(3)	1.38(1)	C(9)-C(10)	1.49(1)	C(16)-C(17)	1.37(1)
C(3)-C(4)	1.38(1)	C(10)-C(11)	1.330(10)	C(17)-C(18)	1.37(1)
C(4)-C(5)	1.39(1)	C(11)-C(12)	1.49(1)	C(18)-C(19)	1.38(1)

Table 4. Bond angles for 4a.

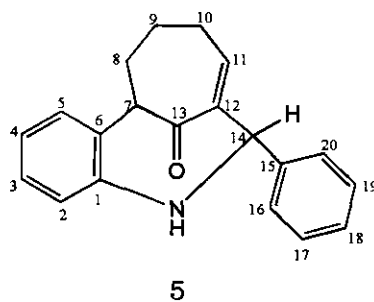
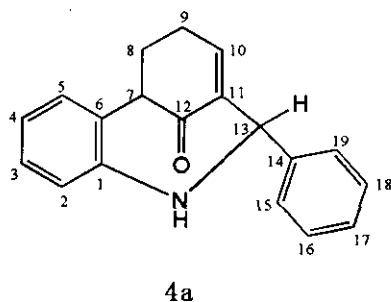
angle		angle		angle	
C(1)-N-C(13)	119.6(7)	C(8)-C(7)-C(12)	101.8(7)	N-C(13)-C(11)	102.3(6)
C(1)-N-H(17)	111(4)	C(8)-C(7)-H(10)	108(3)	N-C(13)-C(14)	111.7(7)
C(13)-N-H(17)	109(4)	C(12)-C(7)-H(10)	109(3)	N-C(13)-H(11)	110(3)
N-C(1)-C(2)	118.7(7)	C(7)-C(8)-C(9)	113.3(8)	C(11)-C(13)-C(14)	113.9(7)
N-C(1)-C(6)	122.3(6)	C(7)-C(8)-H(12)	108(4)	C(11)-C(13)-H(11)	106(2)
C(2)-C(1)-C(6)	118.8(8)	C(7)-C(8)-H(13)	109(4)	C(14)-C(13)-H(11)	111(2)
C(1)-C(2)-C(3)	122.5(9)	C(9)-C(8)-H(12)	108(4)	C(13)-C(14)-C(15)	124.9(8)
C(1)-C(2)-H(1)	120(3)	C(9)-C(8)-H(13)	111(4)	C(13)-C(14)-C(19)	117.6(8)
C(3)-C(2)-H(1)	116(3)	H(12)-C(8)-H(13)	106(6)	C(15)-C(14)-C(19)	117.4(8)
C(2)-C(3)-C(4)	119.2(10)	C(8)-C(9)-C(10)	114.2(8)	C(14)-C(15)-C(16)	120.2(10)
C(2)-C(3)-H(2)	129(6)	C(8)-C(9)-H(14)	104(4)	C(14)-C(15)-H(5)	114(5)
C(4)-C(3)-H(2)	111(6)	C(8)-C(9)-H(15)	102(5)	C(16)-C(15)-H(5)	124(5)
C(3)-C(4)-C(5)	118.9(10)	C(10)-C(9)-H(14)	110(4)	C(15)-C(16)-C(17)	122(1)
C(3)-C(4)-H(3)	121(4)	C(10)-C(9)-H(15)	119(5)	C(15)-C(16)-H(6)	120(9)
C(5)-C(4)-H(3)	119(4)	H(14)-C(9)-H(15)	104(6)	C(17)-C(16)-H(6)	116(9)
C(4)-C(5)-C(6)	122.1(9)	C(9)-C(10)-C(11)	121.6(9)	C(16)-C(17)-C(18)	117(1)
C(4)-C(5)-H(4)	123(3)	C(9)-C(10)-H(16)	119(3)	C(16)-C(17)-H(7)	124(4)
C(6)-C(5)-H(4)	114(3)	C(11)-C(10)-H(16)	118(4)	C(18)-C(17)-H(7)	117(4)
C(1)-C(6)-C(5)	118.4(7)	C(10)-C(11)-C(12)	118.4(8)	C(17)-C(18)-C(19)	119(1)
C(1)-C(6)-C(7)	124.2(7)	C(10)-C(11)-C(13)	124.9(7)	C(17)-C(18)-H(8)	114(6)
C(5)-C(6)-C(7)	117.4(8)	C(12)-C(11)-C(13)	111.4(7)	C(19)-C(18)-H(8)	125(6)
C(6)-C(7)-C(8)	114.1(7)	O-C(12)-C(7)	125.9(8)	C(14)-C(19)-C(18)	122.5(9)
C(6)-C(7)-C(12)	112.5(7)	O-C(12)-C(11)	126.4(7)	C(14)-C(19)-H(9)	121(5)
C(6)-C(7)-H(10)	109(3)	C(7)-C(12)-C(11)	107.6(8)	C(18)-C(19)-H(9)	116(5)

Table 5. Torsion angles for 4a.

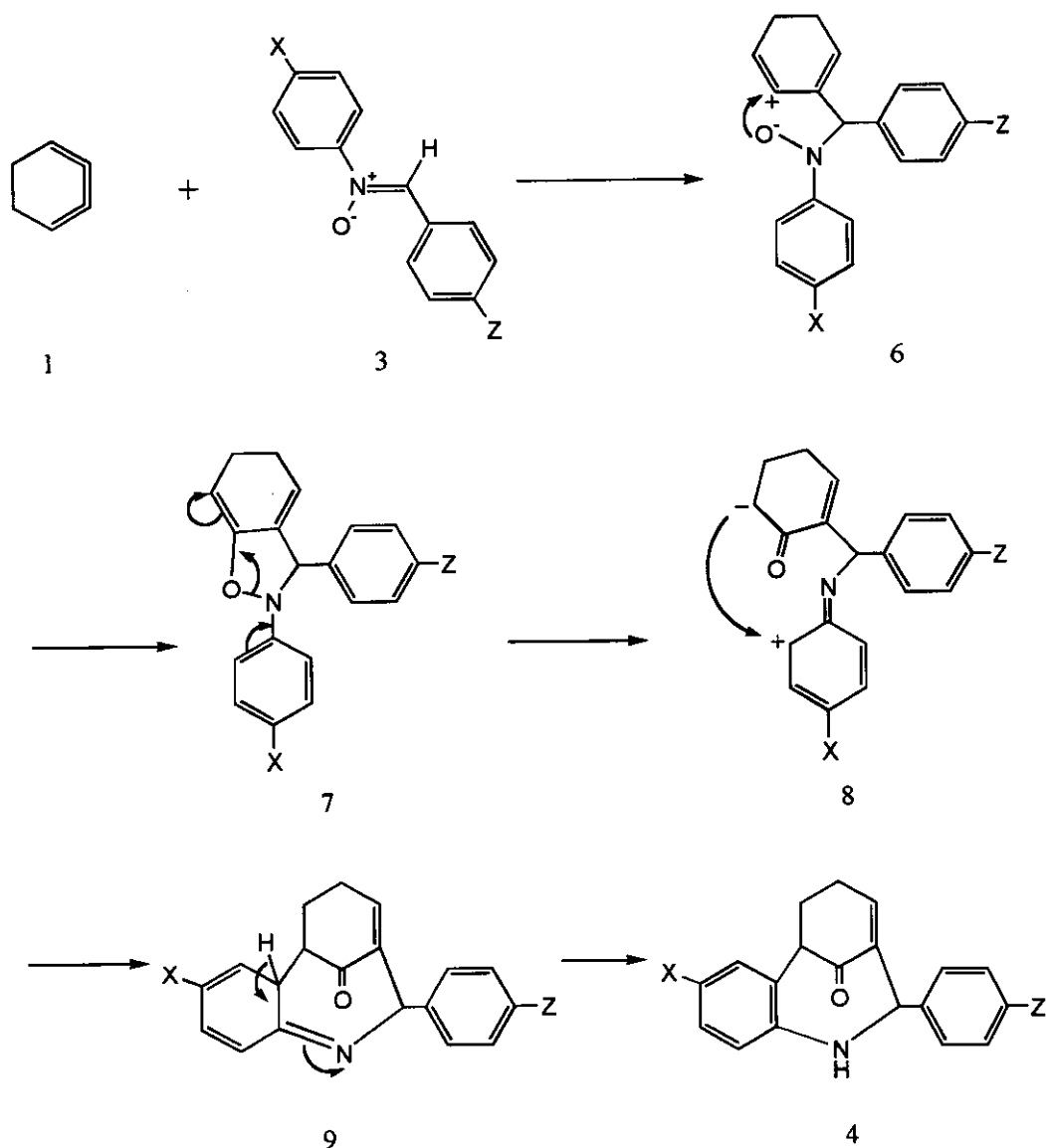
angle		angle	
C(9)-C(10)-C(11)-C(12)	1(1)	O-C(12)-C(11)-C(10)	-130.9(8)
C(9)-C(10)-C(11)-C(13)	153.8(9)	O-C(12)-C(11)-C(13)	73.4(10)
C(10)-C(11)-C(13)-C(14)	130.2(8)	O-C(12)-C(7)-C(6)	-131.0(8)
C(10)-C(11)-C(13)-N	-109.2(8)	O-C(10)-C(7)-C(8)	106.4(9)

Atomic positional parameters, bond lengths, and bond angles are given in Tables 2, 3, 4, and 5, respectively.

The torsion angles depicted in Table 5 show that the plane formed by the α,β -unsaturated carbonyl group (O-C₁₂-C₁₁-C₁₀) of 4a is -130.9°, suggesting that the conjugation between the C-C double bond and the C-O double bond is incomplete. The high wave number of the absorption of the carbonyl group of 4a in the IR spectrum (1722 cm⁻¹) can be explained by this weak conjugation. However, the rather low field resonance of the signal at H(C₁₀) proton (6.05 ppm) tells that the conjugation still exists albeit weak.



Zoch *et al.* have investigated the analogous compound (5) by a single crystal X-Ray analysis⁴ and reported that 5 have the corresponding torsion angle but the magnitude is smaller than that of 4a, showing the better planarity of 5 (4a: O-C₁₂-C₁₁-C₁₀; -130.9 °, 5: O-C₁₃-C₁₂-C₁₁; -88.5 °). The low wave number of the carbonyl absorption in the IR spectrum (1708 cm⁻¹; CHCl₃) of 5 compared to that of 4a (1726 cm⁻¹; CHCl₃) may be explained in terms of less strain energy in 5. A discrepancy observed is the chemical shift of the signal of the proton attached to the conjugation system. The chemical shift of the proton in 5 is apparently higher (H(C₁₁), 5.68 ppm) compared to that of 4a (H(C₁₀), 6.05 ppm). The better planarity in 5 should result in the better conjugation, and as a result, in the low field resonance of the proton. This is attributed to an anisotropic effect of the phenyl group, which wraps up the proton more closely in 5.



According to an investigation based on molecular orbital calculations⁷ and measurements of relative rate ratios,^{8,9} the reaction is considered to proceed as follows.⁴ A nucleophilic⁷ stepwise [4+2] type cycloaddition reaction of the central double bond of **1** with **3** leads to formation of a piradone derivative (**6**), which generates an ionic intermediate (**8**) by cleavage of the N-O bond. A C-C bond formation between the ionic center in **8** followed by an appropriate hydrogen shift can afford the final product (**4**).

A failure of the reaction of α -phenyl-*N*-methylnitrone with **1** to form the corresponding adduct seems to suggest the importance of the stability of **8** through delocalization of the ionic center.

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EXPERIMENTAL

IR spectra were taken with a JASCO FT/IR 5300 spectrophotometer. MS spectra were measured with a Hitachi M-2000 spectrometer. NMR spectra were measured with Hitachi R-90, Varian XL-200, or Varian GEMINI 2000 spectrometers with tetramethylsilane as an internal standard. Melting points were recorded on a Yanagimoto Micro Melting Point Apparatus and are uncorrected. X-Ray measurements were made on a Rigaku AFC7R diffractometer with graphic monochromated Mo-K α radiation and a rotating anode generator. Wakogel C-200 and Wakogel B5-F were used for column and thin-layer chromatographies, respectively. The solvents were purified according to the standard procedures. 2-Trifluoromethylsulfonyl-3-trimethylsilyl-1,3-cyclohexadiene (**2**) and several nitron derivatives (**3**) were prepared by a method described in the literatures.⁵

Only typical reactions are mentioned below.

Reaction of Cyclohexa-1,2,3-triene (1) with N, α -Diphenylnitrone (3a). A solution of *N, α* -diphenylnitrone (**3a**) (790 mg, 4.1 mmol) and CsF (920 mg, 6.0 mmol) in dry DMSO (13 mL) was stirred at 25 °C during a dropwise addition of 2-trifluoromethylsulfonyl-3-trimethylsilyl-1,3-cyclohexadiene (**2**) (240 mg, 0.8 mmol) in dry DMSO (4 mL). After stirring for 2 h, the mixture was poured into cold water, and extracted with ethyl acetate. The extract was washed with brine and water. After evaporation of the solvent on a rotary evaporator, the residual oil was separated with column chromatography on silica gel (hexane: ethyl acetate = 85: 15 elution) to give brown crystals (**4a**) (120 mg, 54 %).

4a: brown crystals. mp 161–162 °C (ethyl acetate–ethanol). HRMS *m/z*: 275.1330. Calcd for C₁₉H₁₇NO *m/z*: 275.1319. MS *m/z* (rel intensity): 275 (M⁺, 77), 257 (24), 219 (26), 206 (30), 185 (100). IR (KBr): 3350, 1722, 1599, 756 cm⁻¹. ¹H NMR (CDCl₃) δ ppm: 2.15–2.27 (m, 2H, H_b),

2.48–2.60 (m, 2H, H_b), 3.61 (br s, H_e), 3.76 (t, H_a), 5.00 (s, H_d), 6.05 (t, H_c), 6.80–7.64 (m, 9H, aromatic protons). Coupling constants in Hz: J_{ab} = 4.3, J_{bc} = 5.2. ^{13}C NMR (CDCl_3) δ ppm: 20.7, 30.8, 53.1, 67.7, 123.0, 123.4, 126.8, 127.1, 127.8, 128.3, 128.8, 133.0, 135.7, 139.7, 142.2, 144.6, 209.0. Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{NO}$: C, 82.88; H, 6.22; N, 5.09. Found: C, 83.18; H, 6.12; N, 5.08.

4b: brown oil. HRMS m/z : 289.1476. Calcd for $\text{C}_{20}\text{H}_{19}\text{NO}$ m/z : 289.1467. MS m/z (rel intensity): 289 (M^+ , 15), 271 (7), 210 (8), 195 (100), 121 (25). IR (KBr): 3433, 1726, 1599, 756 cm^{-1} . ^1H NMR (CDCl_3) δ ppm: 2.15–2.27 (m, 2H, H_b), 2.48–2.60 (m, 2H, H_b), 2.37 (s, 3H, Me), 3.61 (br s, H_e), 3.75 (t, H_a), 4.90 (s, H_d), 6.02 (t, H_c), 6.60–7.50 (m, 8H, aromatic protons). Coupling constants in Hz: J_{ab} = 4.5, J_{bc} = 5.0. ^{13}C NMR (CDCl_3) δ ppm: 22.5, 22.8, 32.7, 54.9, 69.3, 124.8, 125.2, 128.5, 128.8, 130.6, 130.9, 134.4, 137.6, 138.6, 139.3, 144.5, 146.5, 210.7.

4c: brown oil. MS m/z (rel intensity): 401 (M^+ , 1), 396 (37), 307 (100), 305 (60). IR (KBr): 3339, 1728, 1597, 783 cm^{-1} . ^1H NMR (CDCl_3) δ ppm: 2.20–2.35 (m, 2H, H_b), 2.48–2.70 (m, 2H, H_b), 3.67 (br s, H_e), 3.78 (dd, H_a), 5.80 (s, H_d), 6.27 (t, H_c), 6.85–8.14 (m, 11H, aromatic protons). Coupling constants in Hz: J_{ab} = 5.9, 2.8, J_{bc} = 5.2. ^{13}C NMR (CDCl_3) δ ppm: 20.9, 30.6, 53.2, 63.7, 121.9, 123.3, 123.7, 124.3, 125.3, 125.4, 125.5, 126.1, 127.3, 128.3, 128.7, 129.0, 129.1, 133.8, 134.3, 136.1, 141.6, 144.9, 208.5.

4d: brown oil. MS m/z (rel intensity): 401 (M^+ , 1), 396 (20), 325 (100), 307 (71). IR (KBr): 3439, 1726, 1599, 754 cm^{-1} . ^1H NMR (CDCl_3) δ ppm: 2.15–2.29 (m, 2H, H_b), 2.50–2.61 (m, 2H, H_b), 3.71 (br s, H_e), 3.78 (t, H_a), 5.14 (s, H_d), 6.10 (t, H_c), 6.83–8.05 (m, 11H, aromatic protons). Coupling constants in Hz: J_{ab} = 4.6, J_{bc} = 5.2. ^{13}C NMR (CDCl_3) δ ppm: 20.9, 31.0, 53.3, 67.8, 123.2, 123.6, 125.2, 125.5, 125.8, 126.0, 127.2, 127.6, 128.1, 128.2, 128.9, 133.2, 133.9, 135.8, 137.3, 142.2, 144.7, 209.0.

4e: brown crystals. mp 202–203 $^{\circ}\text{C}$ (ethyl acetate–ethanol). HRMS m/z : 309.0908. Calcd for $\text{C}_{19}\text{H}_{16}\text{NOCl}$ m/z : 309.0919. MS m/z (rel intensity): 309 (M^+ , 62), 290 (24), 253 (20), 228 (13), 178 (100). IR (KBr): 3354, 1722, 760 cm^{-1} . ^1H NMR (CDCl_3) δ ppm: 2.14–2.27 (m, 2H, H_b), 2.46–2.60 (m, 2H, H_b), 3.47 (br s, H_e), 3.67 (dd, H_a), 4.95 (s, H_d), 6.02 (t, H_c), 6.80–7.55 (m, 8H, aromatic protons). Coupling constants in Hz: J_{ab} = 5.0, 4.0, J_{bc} = 5.5. ^{13}C NMR (CDCl_3) δ ppm: 20.8, 30.8, 53.2, 67.0, 123.2, 123.5, 127.2, 128.3, 128.5, 128.8, 132.1, 133.5, 135.6, 138.3, 141.7, 144.4, 209.0.

4f: brown oil. HRMS m/z : 353.0402. Calcd for $\text{C}_{19}\text{H}_{16}\text{NOBr}$ m/z : 353.0414. MS m/z (rel intensity): 353 (M^+ , 100), 336 (26), 297 (34), 261 (28). IR (KBr): 3356, 1726, 1599, 760 cm^{-1} . ^1H NMR (CDCl_3) δ ppm: 2.16–2.30 (m, 2H, H_b), 2.47–2.60 (m, 2H, H_b), 3.54 (br s, H_e), 3.74 (dd, H_a), 4.92 (s, H_d), 6.03 (t, H_c), 6.80–7.57 (m, 8H, aromatic protons). Coupling constants in Hz: J_{ab} = 4.7, 3.8, J_{bc} = 5.3. ^{13}C NMR (CDCl_3) δ ppm: 20.8, 30.8, 53.2, 67.1, 121.8, 123.3, 123.5, 127.2, 128.6, 129.1, 131.5, 133.6, 135.6, 138.8, 141.6, 144.4, 209.0.

4g: brown oil. HRMS m/z : 300.1243. Calcd for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}$ m/z : 300.1261. MS m/z (rel intensity): 300 (M^+ , 53), 244 (21), 222 (29), 209 (77), 185 (100). IR (KBr): 3327, 2228, 1724, 1601, 768 cm^{-1} .

^1H NMR (CDCl_3) δ ppm: 2.15–2.29 (m, 2H, H_b), 2.49–2.60 (m, 2H, H_b), 3.74 (dd, H_a), 5.02 (s, H_d), 6.07 (t, H_c), 6.70–7.30 (m, 8H, aromatic protons). Coupling constants in Hz: J_{ab} = 5.8, 2.8, J_{bc} = 5.2. ^{13}C NMR (CDCl_3) δ ppm: 21.4, 30.9, 53.4, 67.3, 115.6, 116.2, 123.6, 123.8, 127.8, 127.9, 129.4, 132.4, 134.7, 135.5, 140.9, 144.3, 145.3, 208.9.

4h: brown oil. HRMS m/z : 320.1182. Calcd for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_3$ m/z : 320.1160. MS m/z (rel intensity): 320 (M^+ , 19), 250 (16), 242 (55), 226 (27), 185 (100). IR (KBr): 3447, 1720, 1601, 1346, 754 cm^{-1} .

^1H NMR (CDCl_3) δ ppm: 2.16–2.29 (m, 2H, H_b), 2.43–2.60 (m, 2H, H_b), 3.73 (dd, H_a), 5.09 (s, H_d), 6.09 (t, H_c), 6.70–7.55 (m, 8H, aromatic protons). Coupling constants in Hz: J_{ab} = 5.7, 3.1, J_{bc} = 5.2. ^{13}C NMR (CDCl_3) δ ppm: 21.1, 30.8, 53.3, 67.1, 123.5, 123.7, 123.8, 127.5, 127.7, 128.0, 129.5, 129.6, 129.9, 130.3, 134.9, 137.5, 209.0.

4i: brown oil. HRMS m/z : 289.1472. Calcd for $\text{C}_{20}\text{H}_{19}\text{NO}$ m/z : 289.1467. MS m/z (rel intensity): 289 (M^+ , 100), 233 (19), 194 (11), 144 (5), 131 (7). IR (KBr): 3018, 1728, 1215, 756 cm^{-1} . ^1H NMR (CDCl_3) δ ppm: 2.10–2.24 (m, 2H, H_b), 2.27 (s, 3H, Me), 2.43–2.56 (m, 2H, H_b), 3.47 (br s, H_e), 3.68 (t, H_a), 4.92 (s, H_d), 6.00 (t, H_c), 6.67–7.62 (m, 8H, aromatic protons). Coupling constants in Hz: J_{ab} = 4.5, J_{bc} = 5.1. ^{13}C NMR (CDCl_3) δ ppm: 20.6, 20.7, 30.9, 53.1, 67.9, 123.3, 126.9, 127.6, 127.8, 128.4, 129.4, 132.5, 132.8, 135.6, 140.0, 142.0, 142.5, 209.1.

4j: brown oil. HRMS m/z : 309.0892. Calcd for $\text{C}_{19}\text{H}_{16}\text{NOCl}$ m/z : 309.0919. MS m/z (rel intensity): 309 (M^+ , 100), 253 (20), 214 (13), 183 (8), 140 (6). IR (KBr): 3018, 1728, 1215, 756 cm^{-1} . ^1H NMR (CDCl_3) δ ppm: 2.17–2.27 (m, 2H, H_b), 2.43–2.52 (m, 2H, H_b), 3.54 (br s, H_e), 3.68 (t, H_a), 4.98 (s, H_d), 6.03 (t, H_c), 6.53–7.61 (m, 8H, aromatic protons). Coupling constants in Hz: J_{ab} = 4.1, J_{bc} = 5.1. ^{13}C NMR (CDCl_3) δ ppm: 20.7, 30.8, 53.1, 67.8, 116.1, 122.1, 124.7, 126.8, 127.1, 128.0, 128.5, 128.8, 128.9, 133.5, 141.9, 143.3, 208.0.

Single Crystal X-Ray Analysis of 4a.

A colorless prismatic crystal of $\text{C}_{19}\text{H}_{16}\text{NO}$ having approximate dimensions of 0.20 $\times$ 0.20 $\times$ 0.20 mm was mounted in a glass capillary. All measurements were made on a Rigaku AFC7R diffractometer with graphic monochromated Mo- $\text{K}\alpha$ radiation and a rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $22.36 < 2\theta < 24.28^\circ$ corresponded to a primitive orthorhombic cell with dimensions: $a = 21.479(8)$, $b = 16.300(5)$, $c = 8.093(4)$ Å; $V = 2833(3)$ Å³. For $Z = 8$ and F.W. = 274.34, the calculated density is 1.29 g/cm³. The space group was established from systematic absences as $\text{Pbca}(\#61)$. The data were collected at a temperature of $23 \pm 1^\circ\text{C}$ using the ω - 2θ scan technique to a maximum 2θ value of 55.0° . Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.31° with a take-off angle of 6.0° . The linear absorption coefficient, μ , for Mo- $\text{K}\alpha$ radiation is 0.8 cm^{-1} . An empirical absorption correction using the program DIFABS¹⁰ was applied which resulted in transmission factors ranging from 0.75 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = $1.72830\text{e}-7$).

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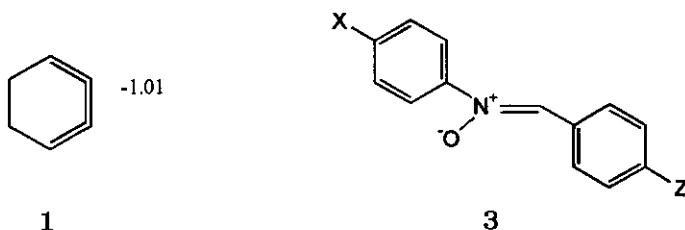


Table 6. Net atomic charge of 3 (Calcd by the PM3 method).

Nitrone	X= H	X= H	X= H	X= Me	X= Cl
	Z= H	Z= Me	Z= Cl	Z= H	Z= H
C	-0.523	-0.519	-0.531	-0.527	-0.519
N	+1.059	+1.057	+1.064	+1.063	+1.058
O	-0.638	-0.639	-0.632	-0.639	-0.638

The net atomic charge of 1 and several nitron derivatives were calculated as shown in Table 6. The sp -carbon atoms of 1 are negatively charged and the nitrogen atom of 3 is positively charged, suggesting the Michael type nucleophilic attack of the sp -carbon atom of 1 to the sp^2 -carbon atom of 3.

The MO calculations were carried out using an NEC PC-9801 RA 32-bit personal computer with "PASOCON MOPAC/386" program which is based on the MOPAC (Ver. 5.0, QCPA No.455) by Toray System Center.

8. The relative rate ratios (k_z/k_H) between several types of nitrones (3) for the reactions of 1 with 3 were measured by a similar method to our previous way.⁹ The relationship between the logarithms of the relative rate ratios ($\log(k_z/k_H)$) against Hammett's sigma values (σ_p) is shown in the following figures.

A rate promotion tendency of chlorine atom in the case of substituents X is thought to reflect a stabilization of the cationic center on the ionic intermediate (8) by the electron donating effect of the n-orbital of the chlorine atom.

Comparing the rate ratios between Z= H, Me, Br, a tendency of accelerative effect of Z= Br can be seen. This is recognized to be a result of promotion of the initial nucleophilic attack of nitron by the electron withdrawing effect of Br.

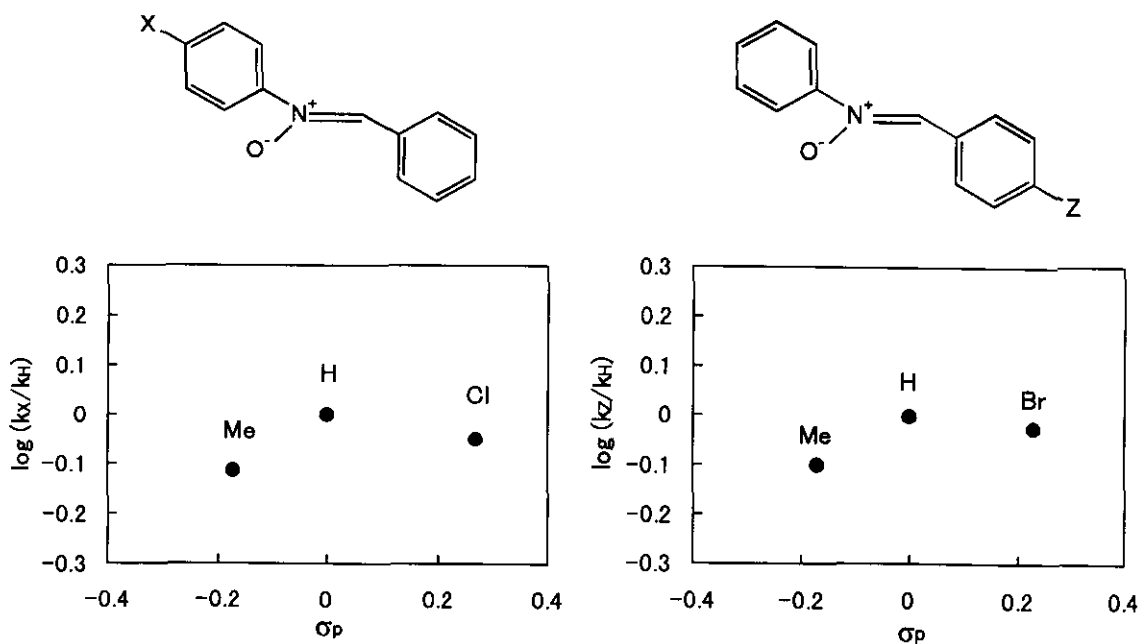


Figure 2. Plot of Hammett's sigma values (σ) versus logarithms of relative rate ratios ($\log(k_x/k_H)$ or $\log(k_z/k_H)$).

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