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1,3-Dipolar cycloadditions: Part III[1]—Cycloaddition of C,N-diarylnitrones to N-cinnamoylpiperidines

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The cycloaddition reactions of three *C,N*-diarylnitrones **1-3** to *N*-cinnamoylpiperidines have been investigated. The all-*trans*-5-aryl-4-piperidinyloxoisoxazolidines are obtained regio- and stereoselectively as the major products with the corresponding 3,4-*cis* isomers as minor cycloadducts. Structures and stereochemistry of the products have been determined by detailed N M R studies and X-ray crystallographic analyses.

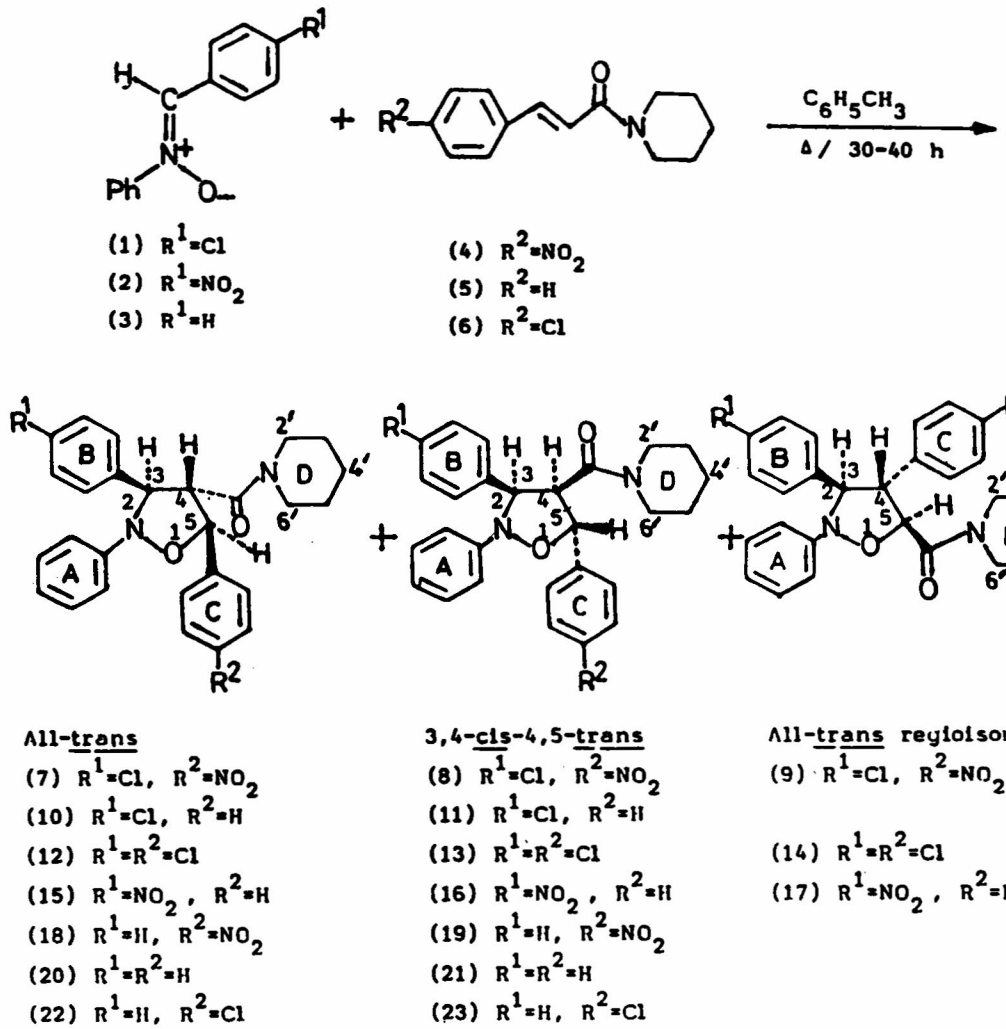
Introduction

1,3-Dipolar cycloaddition of nitrones to olefins has been extensively studied[2-4]. Certain areas, however, remain relatively unexplored, such as the nitrone cycloadditions to unsaturated carbonyl derivatives[1,5] involving detailed investigations of their regio- and stereochemical courses. We report here our studies involving cinnamoylpiperidines as the dipolarophiles, with three different aldonitrones **1-3.**

Results and Discussion

The three *C*-aryl-*N*-phenylnitrones **1-3** with different *para*-substituents on the *C*-aryl group were reacted with *N*-cinnamoyl-piperidines **4-6**. The reactions were carried out with equimolar amounts of the reactants in refluxing toluene (110°) under nitrogen atmosphere. Monitoring of the reactions showed that periods of about 30-40 hr were necessary to obtain products in good yields. At the end of this period, only small amounts of the dipolarophile survived. The solvent was stripped off under reduced pressure and the crude post-reaction mixture chromatographed over neutral alumina. Two products, the all-*trans* series and the diastereoisomeric 3,4-*cis* series of 5-aryl-4-piperidinyloxo-isoxazolidines could be isolated in all cases (cf. Scheme I). However, the regioisomeric 4-aryl-5-piperidinyloxoisoxazolidines were also obtained in certain reactions. The product ratios of the cycloadducts were determined by ^{1}H NMR analysis of the crude reaction mixture in some cases. The structure and stereochemistry of the products were established on the basis of spectroscopic data, particularly NMR analysis (including two-dimensional experiments) (cf. Figures 1-4) and X-ray crystallographic data. The ^{1}H and ^{13}C NMR data of the representative compounds are collected in Tables I and II.

The IR spectra of all the compounds in the all-*trans* series exhibited tertiary amide bands at 1630-1660 cm^{-1}. The appearance of both the benzylic protons as doublets without any coupling between them indicated that none of them could be the C-4 proton. The benzylic protons could be identified as those at C-3 and C-5 in both series of products by COSY-LR experiments which showed long-range couplings between the *ortho*-protons of the relevant aromatic rings and these protons. In the all-*trans* series of the products, H-3 appeared as a doublet at ~ δ 5.2-5.4 (J = ~ 9.0-9.5 Hz) while H-5 also resonated as a doublet at δ 5.3-5.6 (J = ~ 8.0-9.5 Hz), the low-field values of these protons testifying to their presence adjacent to a hetero-atom. The H-4 appeared as a double-doublet in the region δ 3.73-3.79 ($J_{3,4} \approx 9.5$ Hz, $J_{4,5} \approx 8.0$ Hz).



Scheme I

These observations decided in favour of the 2-phenyl-3-aryl-4-piperidinyloxo-5-arylisoxazolidine structure.

The non-aromatic protons H-3 and H-5 in compound **9** in the regioisomeric all-*trans* series appeared as doublets at δ 4.60 ($J_{3,4}$ = 8.0 Hz) and 4.94 ($J_{4,5}$ = 7.1 Hz) respectively while H-4 resonated as a broad triplet at 4.71 ($J \approx 7.5$ Hz). From the COSY-LR-90° experiment of this compound (Figure 4), it was apparent that H-3 and H-4 but not H-5 showed long-range benzylic coupling with the aromatic protons H-2 and H-6 of rings 'B' and 'C'. This established unambiguously the structure **9** for 2-phenyl-3,4-diaryl-5-piperidinyloxoisoxazolidine regioisomer. The mass spectral fragmentations of the cycloadducts were also informative regarding the regiochemistry of the cycloadducts. There were some characteristic differences for the two diastereoisomeric series of the 2-phenyl-3-aryl-4-piperidinyloxo-5-arylisoxazolidine cycloadducts. For example, both compounds **7** and **8** gave a strong M^+ at m/z 491. Common and significant fragments in both the cases included those at m/z 379 ($M^+ - C_6H_{10}NO$), 340 [M^+ (↷) $-C_7H_6NO_3+H^\bullet$], 276 [M^+ (↷) – $C_{13}H_9NCl$], 256 (379 $-C_6H_5NO_2$), 193 (276 – $C_6H_{10}NO+H^\bullet$], 150 [M^+ (↷) $-C_{18}H_{20}N_2OCl-2H^\bullet$], 120 (165 $-NO_2+H^\bullet$), 104 (150 $-NO_2$) and 77 (C_6H_5+) [The rearranged molecular ion has been designated as M^+ (↷)]. In both the compounds **7** and **8**, the mass spectral fragmentation resulted in two peaks at m/z 340 and 150 by 4,5-bond

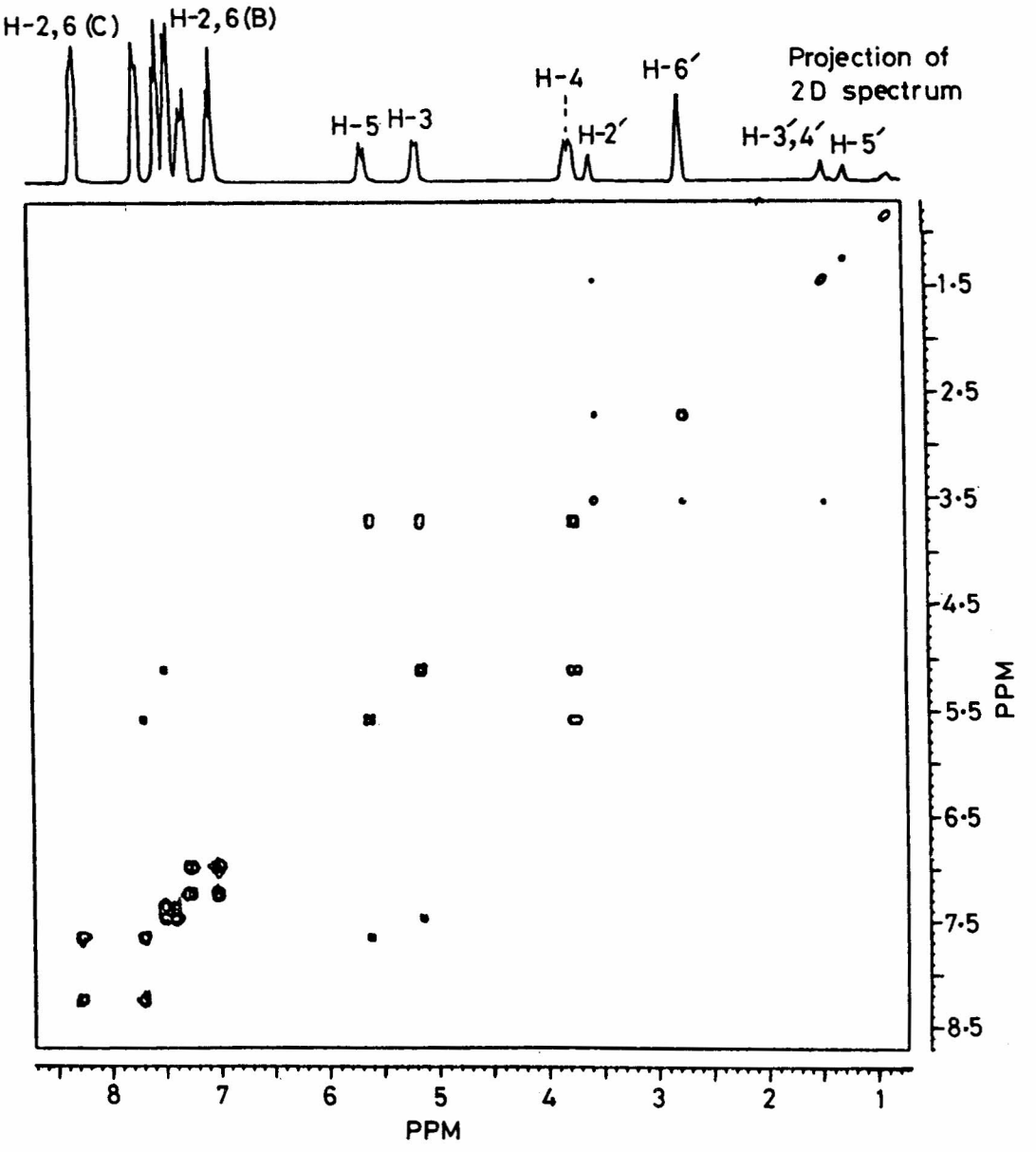


Figure 1—300 MHz ^{1}H-^{1}H COSY-LR-90° spectrum of **7** in $CDCl_3$.

cleavage while in compound **9**, a similar fragmentation pattern resulted in two peaks at m/z 350 [M^+ (⌒) $-C_7H_{12}NO_2$], and m/z 141 [M^+ (⌒) – $C_{18}H_{14}N_2O_2Cl$] respectively. These observations established unambiguously **7** and **8** as diastereoisomers possessing structures with a 4-piperidinyloxo-5-aryl system, whereas **9** was identified as the regioisomer having a 4-aryl-5-piperidinyloxo system.

Since the magnitude of the coupling constants in 5-membered rings do not always lend themselves to stereochemical assignments, recourse was taken to X-ray crystallographic analysis. The X-ray analysis of **22** showed that the compound had the all-*trans* stereochemistry, including the lone pair of ring-nitrogen (N2) *trans* to C3-H (Figure 5). Compound **22** crystallised in the triclinic system in the space-group P_1. Table III lists the positional parameters, bond lengths and bond angles, while the refined positional parameters ($\times 10^3$) for hydrogen atoms are given in Table IV. Compounds **7**, **10**, **12**, **15**, **18**, **20** and **22** showed similar chemical shifts (^{1}H and ^{13}C) and coupling constants (^{1}H) for the isoxazolidine ring system—thus these compounds could be assigned the structure and stereochemistry of the all-*trans* series.

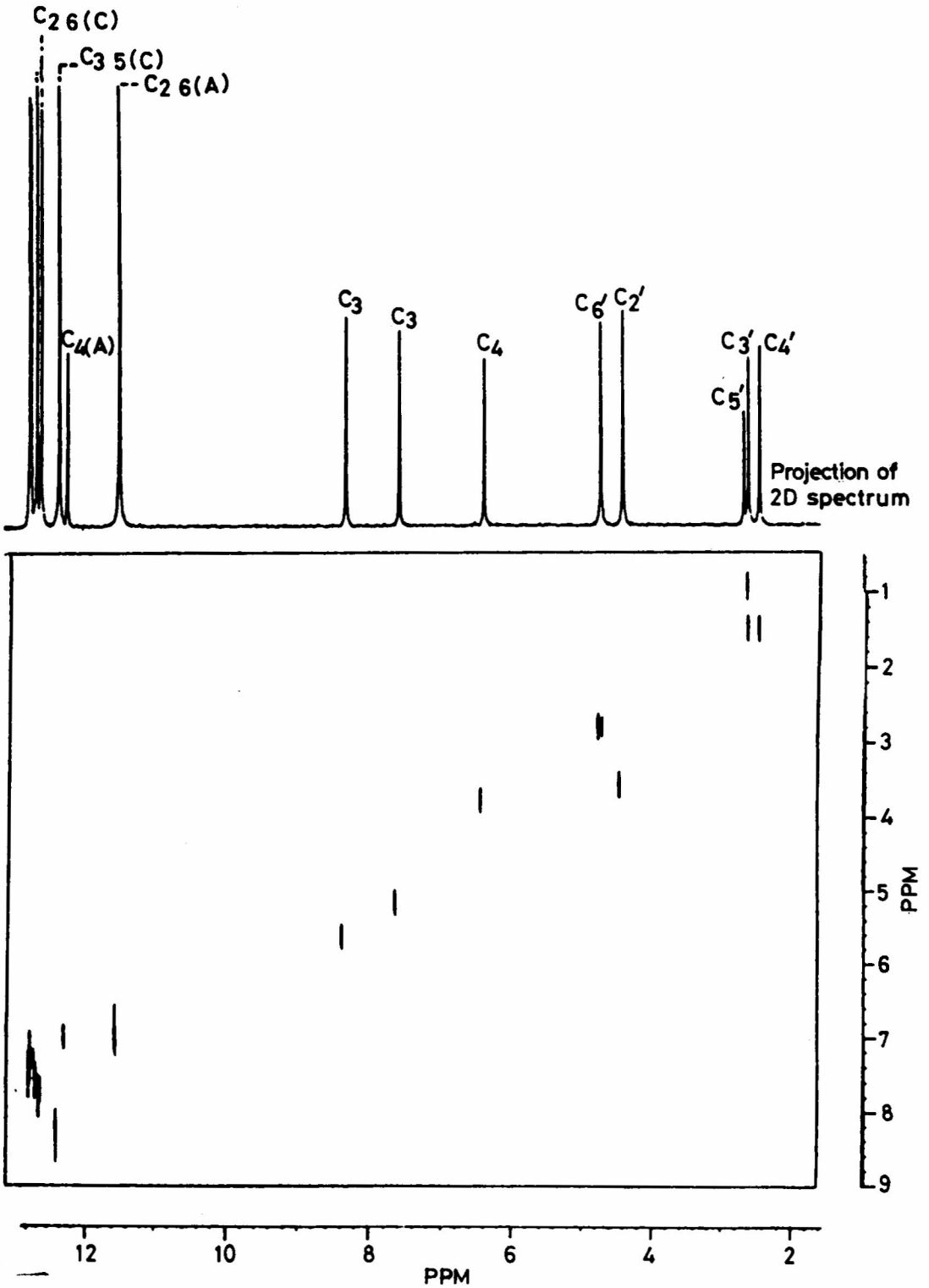


Figure 2—300 MHz ^{1}H/75.5 MHz ^{13}C NMR heteronuclear shift correlation spectrum (one-bond) of **7** in $CDCl_3$ using the XHCORR sequence.

Hence, the other series of products (**8, 11, 13, 16, 19, 21** and **23**) the minor cycloadducts, could be assigned the stereoisomeric formulation (3,4-*cis*). These assignments are in agreement with spectroscopic data. The assignments of the benzylic protons followed similarly from decoupling experiments and COSY-LR correlations with *ortho*-protons. There was a

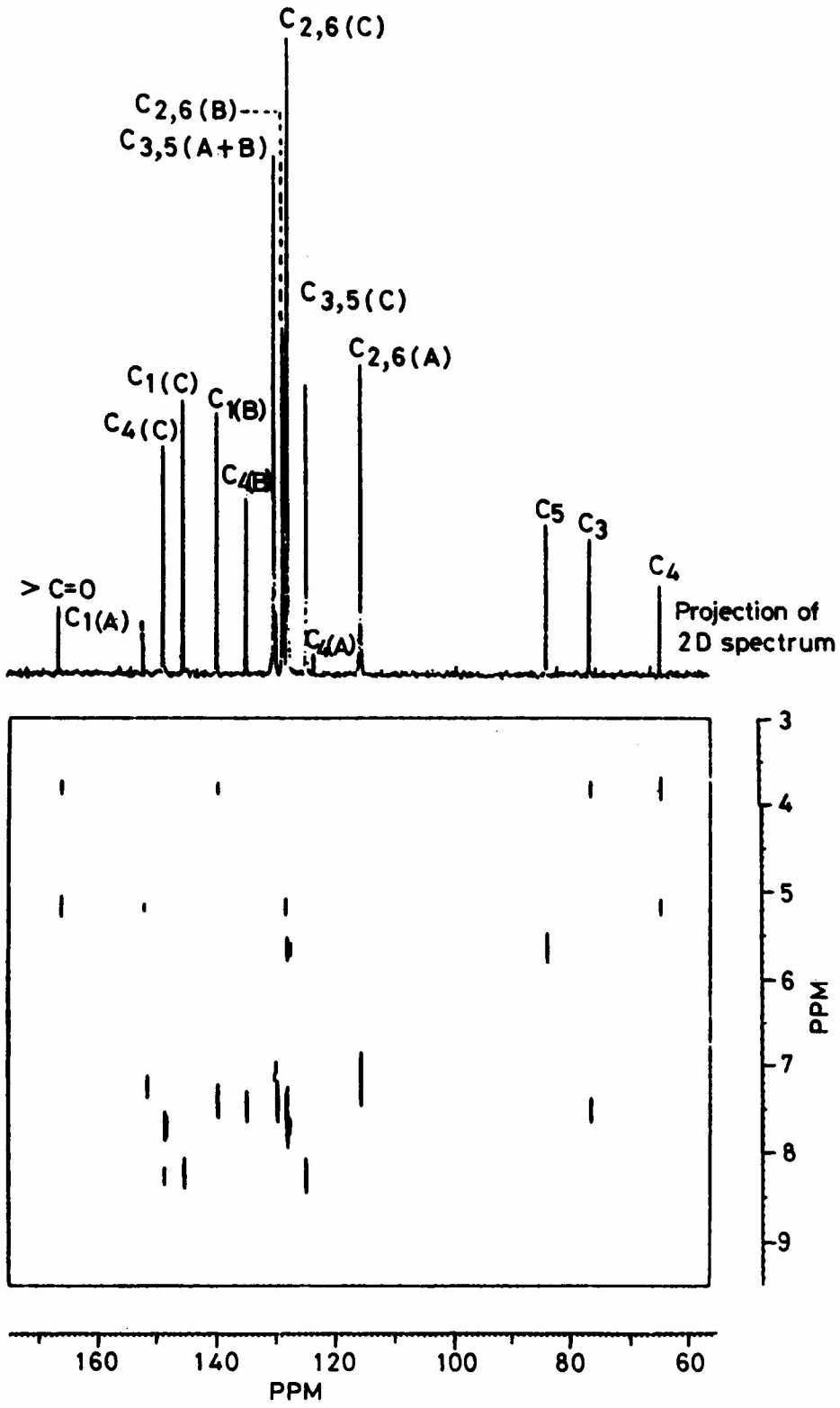


Figure 3—300 MHz ^{1}H/75.5 MHz ^{13}C NMR heteronuclear shift correlation spectrum (long range) of **7** in $CDCl_3$ using the XHCORR sequence.

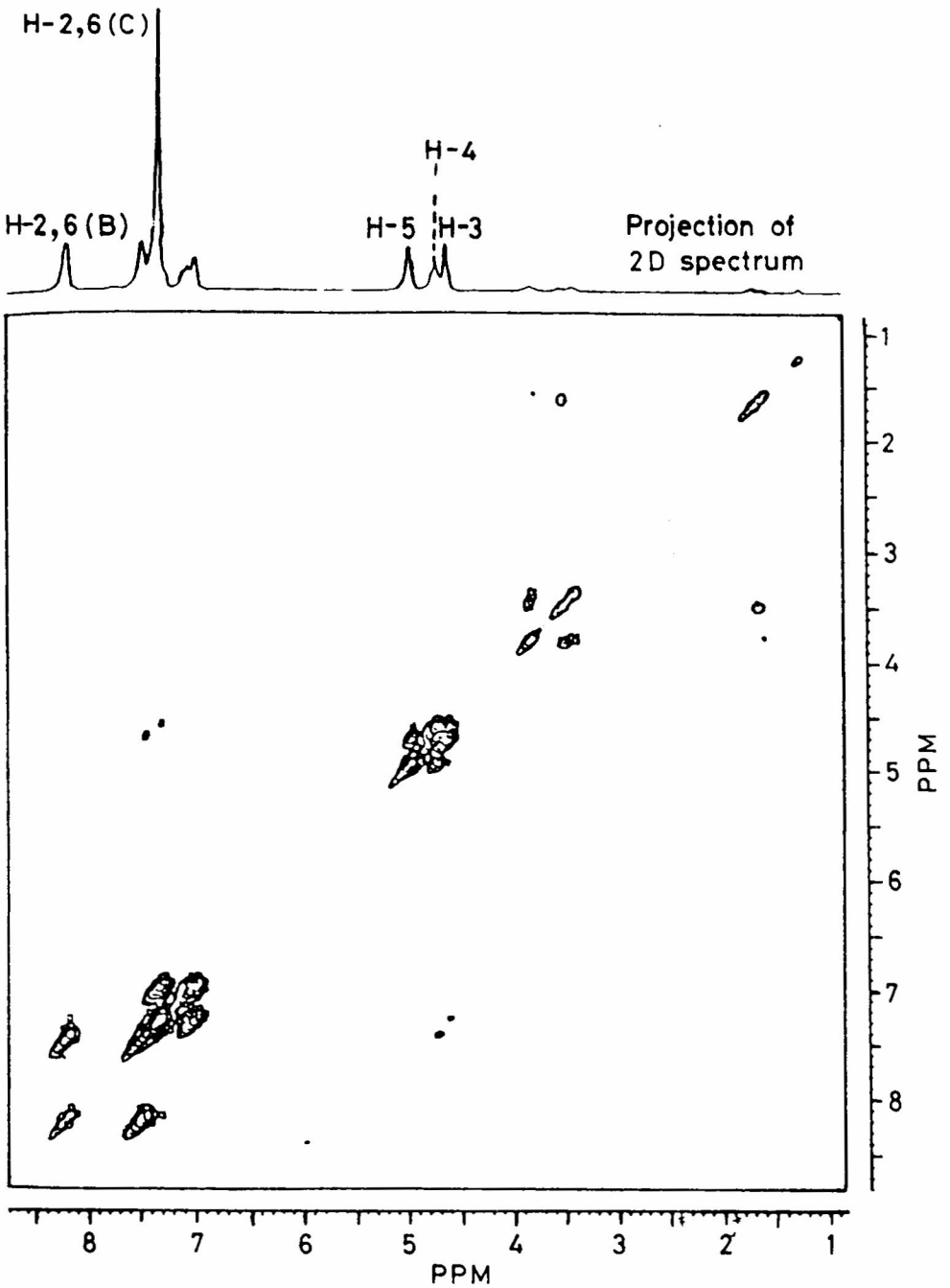


Figure 4—300 MHz ^{1}H-^{1}H COSY-LR-90° spectrum of **9** in $CDCl_3$.

significant difference in the coupling constants $J_{3,4}$ (10-11 Hz) and $J_{4,5}$ (8-9 Hz). The larger value of $J_{3,4}$ was compatible with the *cis*-orientation of H-3 and H-4.

The proportion of the all-*trans*: 3,4-*cis* isomers was determined to be 100: 12-15 of the crude product mixture by ^{1}H NMR and HPLC analyses. The diastereoisomeric excess (de) was thus ~ 76-84% (Table V).

The regio- and stereo-chemical courses of cycloadditions could be explained on the basis of FMO theory. Mention may be made in this connection of the earlier work of Joucla *et al.* (calculation of HOMO and LUMO energies and coefficients of *C,N*-diarylnitrone and methyl cinnamate using the INDO method)[6] (Table VI).

It seems that the relative importance of the two pairs of FMO. interactions, the dipole HOMO-

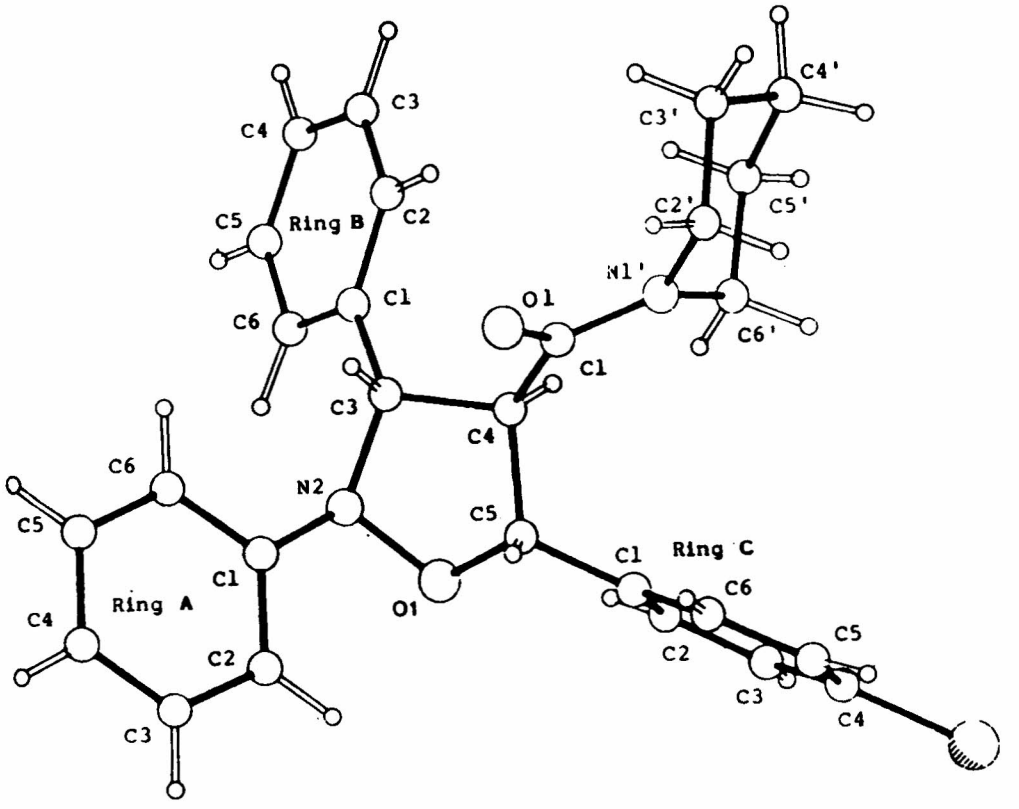


Figure 5—X-Ray crystallographic structure of **22** (ORTEP Projection).

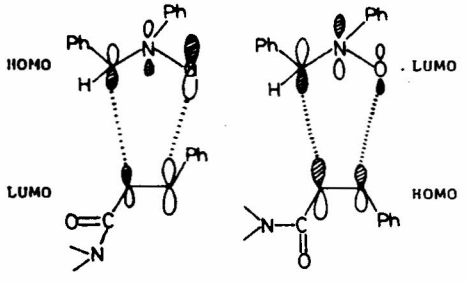


Figure 6

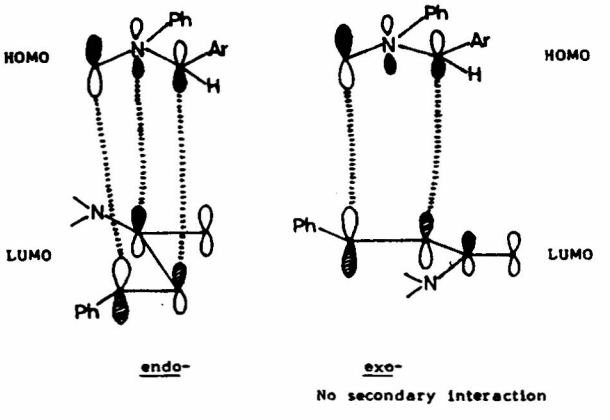


Figure 7

dipolarophile LUMO and dipole LUMO-dipolarophile HOMO, would depend on the aryl substituents of the dipole and dipolarophile. Thus, the reactions of C,N-diphenylnitrone **3** will be dipole-HOMO controlled (Sustmann Type-I)[7], while those of the other two nitrones (**1** and **2**) will be increasingly of Sustmann Type-II (both pairs of FMO interactions are important). The formation of that regio-isomer would be favoured in which the larger terminal coefficients interact. For these aldonitrones, both the interactions, dipole-HOMO controlled, and dipole-LUMO controlled would favour the formation of the same regioisomeric transition state which would lead to 2,3,5-triaryl-4-piperidinyloxoisoxazolidine. Qualitatively, the HOMOs and LUMOs of all the diarylnitrones have similar shapes with $C_{O\text{-}3} > C_{C\text{-}1}$ in the HOMO and $C_{O\text{-}3} < C_{C\text{-}1}$ in the LUMO. However, the differentiation in the coeffiicients is less than in the LUMO of the N-phenyl-C-(*p*-nitrophenyl)nitrone **2** and this would lead to a loss of regioselectivity for this nitrone —the degree of loss depending on the relative importance of different FMO interactions.

The presence of an electron-withdrawing group

Table I—300 MHz ^{1}H-NMR Assignments of **7, 8, 9, 22** and **23** in $CDCl_3$ (chemicl shifts in δ, ppm, *J* values in Hz)

Proton	7	8	9	22	23
H-3	5.15 (d, 9.0)	4.82 (d, 11.0)	4.60 (d, 8.0)	5.18 (d, 8.3)	4.76 (d, 10.4)
H-4	3.75 (t, 9.0)	3.74 (dd, 11.0, 9.0)	4.71 (br.t., 7.5)	3.77 (t, 8.8)	3.72 (dist.t. ~ 9.5)
H-5	5.60 (d, 9.0)	6.18 (d, 9.0)	4.94 (d, 7.1)	5.40 (d, 9.4)	6.04 (d, 9.1)
H_A, H_B-2' (D)	3.55 (m)	2.91 (m) 3.34 (m)	3.43 (m) 3.77 (m)	3.50 (m)	2.82 (m) 3.36 (m)
H_A,H_B-6' (D)	2.74 (m)	3.08 (m) 3.48 (m)	3.52 (m) 3.82 (m)	2.73 (m)	3.06 (m) 3.48 (m)
H-3',4' (D)	1.42 (m)			1.39 (br.m)	
H_A-5' (D)	0.91 (m)	1.25-1.60 (m)	1.60-1.70 (m)	0.80-0.48 (m)	1.23-1.40 (m)
H_B-5' (D)	0.83 (m)				
H-2,6 (A)	6.99 (d, 7.9)	7.01 (d, 7.8)	6.95 (d)	7.00 (d, 7.8)	6.98 (d, 7.7)
H-3,5 (A)	7.25 (t, 8.5)	7.20 (t ~ 8.0)	7.23†	7.21 (dist.t. ~ 7.5)	7.28 (dist.t, 7.5)
H-4 (A)	δ 6.99*	δ 7.00	7.02‡	6.92 (t, 7.2)	6.92 (obscured)
H-2,6 (B)	7.48 (d, 8.7)	7.48 (d, 8.5)	7.27 (s)	7.54 (d, 7.1)	7.50 (d, 7.1)
H-3,5 (B)	7.38 (d, 8.5)	7.41 (d, 8.5)		7.29-7.44 (m)	7.31-7.45 (m)
H-4 (B)	—	—	—	—	—
H-2,6 (C)	7.67 (d, 8.7)	7.71 (d, 8.8)	7.45 (d, 8.0)	7.29-7.44 (m)	7.31-7.45 (m)
H-3,5 (C)	8.26 (d, 8.7)	8.22 (d, 8.8)	8.15 (d, 8.7)		

* Obscured by overlap with H-2,6 (A)

‡ Obscured by overlap with H-2,6 (A)

† Overlapped signals

(i) Numberings of aromatic ring protons are distinguished by referring to the aromatic rings A, B and C in parantheses or as superscripts.

(ii) Multiplicity and coupling constant in parentheses.

(iii) COSY-LR-90° correlations (in addition to the 1-bond correlations) :

(a) **7** and **8** : H-2,6 (B) with H-3; H-2,6(C) with H-5,

(b) **9** : H-2,6(B) with H-3; H-2,6(C) with H-4.

such as *p*-nitro in the dipolarophile would lower HOMO and LUMO energies and reduce the difference in magnitude between the orbital coefficients on C-2 and C-3. Hence, reactions involving **4** as the dipolarophile are expected to be less regioselective. The *p*-chloro compound **6** would also be expected to show a loss of regioselectivity, albeit to a lesser extent.

The cycloadduct ratios of some of the reactions has been determined by ^{1}H NMR analysis of the crude reaction mixture (Table VI). The general trends expected from the reasoning given above is borne out by the results. Significant amounts of the regio-isomers **9, 14, 17** were detected only when electron-withdrawing groups were present on either the dipolarophile or the dipole.

A high degree of stereoselectivity was observed in these reactions. *C,N*-Diaryl nitrones exist and react almost exclusively in the *E*-form. The *endo*-mode of approach is expected to predominate due to favourable secondary orbital interactions.

In the case of the regioisomeric transition state, the *endo*-approach would again be favoured, due to similar bonding secondary MO interactions.

The product arising from the *endo*- approach also greatly predominates to the extent of 1:10 to 1:12 (diastereoisomeric excess of ~ 76-74%) for the regioselective course of cycloaddition. For the minor regio-unfavoured pathway, only the *endo*-product could be detected as a similar stereoselectivity to the above would mean that the *exo*-regioisomer would be present to the extent of <1% of the cycloadduct compositions, these would be difficult to detect by ^{1}H NMR analysis of the crude mixture.

Experimental Section

General. M.ps were recorded on a Köfler block

Table II—75.5 MHz ^{13}C NMR data of the cycloadducts

Carbon No	7		8	9		22	23
	Chemical shift (δ, ppm)	LR—XHCORR*	Chemical shift (δ, ppm)	Chemical shift (δ, ppm)	LR—XHCORR+	Chemical shift (δ, ppm)	Chemical shift (δ, ppm)
C-3	75.52	4, 2^B, 6^B	72.22	77.99	2^B, 6^B	76.00	73.46
C-4	63.60	3	58.76	61.06	2^C, 6^C	63.84	59.09
C-5	82.95	4, 2^C, 6^C	80.19	81.98	—	83.55	80.91
C-2'	43.74	—	42.62	43.89	—	43.55	44.72
C-3'	25.72	—	25.16	25.53	—	25.78	24.61
C-4'	24.10	—	24.09	24.45	—	24.10	24.22
C-5'	26.36	—	26.09	26.70	—	26.11	26.14
C-6'	46.66	—	46.48	47.02	—	46.69	45.72
>C=0	165.97	—	165.20	164.74	—	166.66	165.18
C-1 (A)	151.29	2^A,6^A,3^A,5^A,3	149.32	149.76	—	151.93	151.05
C-2 (A)					4^A, 6^A		
	115.05	2, 6, 2^A, 6^A	116.38	115.83		114.78	116.77
C-6 (A)					2^A, 4^A		
C-3 (A)	129.35	3,5,4^A,5^A,3^A	130.03	129.02	—	128.90	128.97
C-5 (A)							
C-4 (A)	122.65	4, 2^A, 6^A	123.14	123.10	—	121.66	122.70
C-1 (B)	138.71	3^B, 5^B	138.27	137.71	3^B,5^B	140.93	140.39
C-2 (B)	127.86	3	128.61	128.35	3	126.40	128.13
C-6 (B)					3		
C-3 (B)	128.97	—	128.75	129.15	—	128.90	128.97*
C-5 (B)							
C-4 (B)	134.06	2^B, 6^B	136.37	134.03	2^B, 6^B	127.72	127.70
C-1 (C)	144.68	3^C, 5^C	144.84	145.96	3^C, 5^C	135.87	135.23
C-2 (C)	127.00	5	127.38	129.32	—	128.72	128.73
C-6 (C)							
C-3 (C)	123.92	—	123.80	124.14	—	128.90	128.73
C-5 (C)							
C-4	148.11	2^C, 6^C	148 14	147.43	2^C, 6^C	134.40	134.43

*Superscripts A, B, C refer to protons of the three designated aromatic rings.
XHCORR-LR correlations refer only to the additional long-range correlations. C-H 1-bond correlations were in agreement with assignments in Tables I and II, and are not mentioned in the Table.

and are uncorrected. IR spectra were recorded on a Perkin-Elmer 782 spectrophotometer. Mass spectra were recorded on Joel JMS-D 300 and Jeol-AX500 mass spectrometers. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions at 300 MHz and 75.5 MHz respectively on a Bruker AM 300L spectrometer (δ scale, TMS = 0 ppm). XHCORR spectra were recorded using the following sequence as developed by Bax and Morris[8].

^1H = Dec. off -90° -D_ϕ. -D_ϕ - D3-90°-D4-CPD Dec.

^{13}C = Dl -180°- 90°-D4-FID

with Dl = 2.00, sec D3 = 0.0036 μ sec and D4 = 0.0018 μ sec for 1-bond CH couplings; D3 = 0.07 μ sec and D4 = 0.035 μ sec for long-range couplings optimised for $J \approx 7$ Hz.

Analytical samples were routinely dried over calcium chloride *in vacuo* at room temperature. Column and thin layer chromatography were

Table III—Positional parameters ($x10^4$) and mean recalculated isotropic factors ($x10^3$) for non-hydrogen atoms (*) in compound **22**

ATOM	X	Y	Z	<U>
O1	11198 (2)	-4843 (3)	-2167 (3)	42 (3)
C5	11703 (3)	-3534 (5)	-1043 (5)	42 (5)
C4	12504 (2)	-4372 (4)	-366 (5)	36 (4)
C3	12685 (2)	-5843 (5)	-1892 (5)	37 (5)
N2	11831 (2)	-6055 (4)	-3016 (4)	39 (4)
		Ring C		
C1	11138 (3)	-2384 (5)	166 (5)	36 (5)
C2	10515 (3)	-2875 (5)	743 (5)	48 (5)
C3	10002 (3)	-1823 (5)	1866 (6)	53 (6)
C4	10100 (3)	-237 (5)	2454 (5)	48 (5)
C5	10719 (3)	275 (5)	1906 (6)	58 (6)
C6	11218 (3)	-803 (5)	758 (6)	52 (6)
Cl	9443 (1)	1131 (2)	3853 (2)	76 (1)
		Ring D		
C1	13295 (3)	-3381 (5)	402 (6)	49 (6)
O1	13760 (2)	-3273 (4)	-491 (4)	74 (4)
N1'	13457 (2)	-2602 (5)	2036 (5)	60 (5)
C2'	14238 (3)	-1685 (7)	2769 (7)	77 (7)
C3'	14888 (4)	-2441 (8)	3702 (8)	94 (9)
C4'	14461 (5)	-2603 (9)	5011 (8)	115 (11)
C5'	13603 (5)	-3422 (8)	4253 (7)	103 (10)
C6'	12997 (4)	-2665 (7)	3258 (6)	77 (7)
		Ring B		
C1	13003 (3)	-7266 (5)	-1542 (5)	41 (5)
C2	13783 (3)	-7222 (5)	-488 (6)	57 (6)
C3	14078 (3)	-8489 (7)	-102 (7)	75 (7)
C4	13621 (4)	-9808 (7)	-789 (7)	81 (8)
C5	12862 (4)	-9859 (6)	-1836 (7)	79 (8)
C6	12547 (3)	-8597 (5)	-2241 (6)	56 (6)
		Ring A		
C1	11869 (3)	-6130 (5)	-4583 (5)	40 (5)
C2	11223 (3)	-5332 (5)	-5294 (6)	52 (6)
C3	11255 (4)	-5560 (6)	-6875 (7)	77 (8)
C4	11901 (5)	-6554 (8)	-7753 (6)	91 (9)
C5	12533 (4)	-7331 (7)	-7038 (7)	78 (8)
C6	12511 (3)	-7121 (6)	-5466 (6)	57 (6)

(*) Given in $Å^2$ and calculated as $<U> = {}^1/_3 \sum_i \sum_j U_{ij}.a_i^*.a_j^*.a_i.a_j$

carried out using neutral alumina (Qualigens), silica gel (Qualigens 60-120 mesh, and 100-200 mesh) and silica gel G (Qualigens) respectively. Nitrones **1-3** were prepared from appropriate aldehydes and phenyl hydroxylamine according to the standard procedure[9,10].

General method of cycloaddition. To a hot solution of the nitrone (0.0066 mole **4-6**) in anhydrous toluene (20 mL), a solution of piperidide (0.0066 mole **4-6**) in anhydrous toluene (50 mL) was added at a time and the reaction mixture was refluxed under nitrogen atmosphere for 30-40 hr. The reaction was monitored by TLC. The solvent was stripped off from the crude reaction mixture under reduced pressure and the crude post-reaction mixture chromatographed over neutral alumina to separate the products.

3*RS*-(3*R,4*S**,5*R**) and 3*RS*-(3*R**,4*R**,5*S**)-2-phenyl-3-(*p*-chlorophenyl)-5- (*p*-nitrophenyl)-4-piperidinyloxoisoxazolidine 7 and 8 and 3*RS* (3R*, 4*S**, 5*S**)-2-phenyl-4-(*p*-nitrophenyl)-3-(*p*-chlo-**

Table IV—Refined positional parameters ($\times 10^3$) for hydrogen atoms (*) in compound **22**.

ATOM	X	Y	Z
H2	1318	-572	-238
H3	1238	-459	55
H4	1191	-287	-149
		Ring A	
H2	1075	-461	-466
H3	1080	-500	-742
H4	1190	-668	-888
H5	1300	-805	-770
H6	1297	-770	-495
		Ring B	
H2	1414	-628	0
H3	1463	-843	69
H4	1384	-1071	-52
H5	1252	-1082	-233
H6	1200	-867	-304
H2'	1452	-166	189
H2'	1406	-59	353
H3'	1510	-351	292
H3'	1541	-179	425
H4'	1433	-154	588
H4'	1489	-324	550
H5'	1329	-337	514
H5'	1375	-455	353
H6'	1280	-157	400
H6'	1246	-329	269
		Ring C	
H2	1045	-402	33
H3	956	-220	226
H5	1081	141	235
H6	1165	-43	34

*Calculated average e.s.d.'s are : x = (2); y = (3) and z = (2) on the last digit.

rophenyl)-5-piperidinyloxoisoxazolidine 9 from 1 and 4: Column-chromatography yielded **7** [(758 mg, 35%) m.p. 165°, R_f 0.68 (silica gel., benzene-ethyl acetate, 4:1)], **8** [(325 mg, 15%) m.p. 171-172°, R_f = 0.71 (silica gel, benzene-ethyl acetate 4:1)] and **9** [(650 mg, 30%), m.p. 135°] from the benzene eluates.

7. IR (KBr): 2940-2860 (m, $-CH_2-$), 1645 (s, amide >C=0), 1535, 1355 (s, aromatic NO_2), 850 (1,4-disubstituted benzene ring), 755, 705 cm^{-1} (mono-substituted benzene ring); Anal. (Found: C, 66.02, H, 5.15; N, 8.48. Calcd for $C_{27}H_{26}N_3O_4Cl$: C, 66.04; H, 5.35; N, 8.56%); MS: see MS of **8**.

8. IR (KBr): 2940-2840 (m, $-CH_2-$), 1630 (s, amide >C=0), 1510, 1340 (s, aromatic $-NO_2$), 850 (m, 1,4-disubstituted benzene ring), 750, 740, 890 cm^{-1} (monosubstituted benzene ring); Anal. (Found: C, 66.01; H, 5.12; N, 8.54. Calcd for $C_{27}H_{26}N_3O_4Cl$: C, 66.04; H, 5.35; N, 8.56%). MS of both **7** and **8**: m/z 491 (M^+); 379 ($M^+ - C_6H_{10}NO$), 340 [M^+ (↷) $-C_7H_6NO_3+H^\bullet$], 276 [M^+ (↷) $-C_{13}H_9NCl$], 256 (379 $-C_6H_5NO_2$), 193 (276 $-C_5H_{10}N+H^\bullet$), 165 (276 $-C_6H_{10}NO+H^\bullet$), 150 [M^+ (↷) $-C_{18}H_{20}N_2OCl-2H^\bullet$], 120 (165 $-NO_2+H^\bullet$), 104 (150 $-NO_2$), 77 ($C_6H_5^+$).

9. IR (KBr): 2960-2880 (m, $-CH_2-$), 1660 (s, amide >C=O), 1540, 1360 (s, aromatic $-NO_2$ group), 860, 840 (m, 1,4-disubstituted benzene), 770, 710 cm^{-1} (m, monosubstituted benzene ring), MS: m/z 491 (M^+), 350 [M^+ (↷) $-C_7H_{12}NO_2$], 276 [M^+ (↷) $-C_{13}H_9NCl$], 231 (276 $-NO_2+H^\bullet$), 215 [M^+ (↷) $-C_{14}H_{12}N_2O_4$], 141 [M^+ (↷) $-C_{18}H_{14}N_2O_2Cl$], 112 ($C_6H_{10}NO^+$), 91 ($C_6H_5N^+$), 77 ($C_6H_5^+$). [The rearranged molecular ion has been designated as M^+ (↷)]; Anal. (Found: C, 66.03; H, 5.30; N, 8.53. Calcd for $C_{27}H_{26}N_3O_4Cl$: C, 66.04; H, 5.35; N, 8.56%).

3RS-(3R*,4S*,5R*) and 3RS-(3R*,4R*,5S*)-3-(p-chlorophenyl)-2,5-diphenyl-4-piperidinyloxo-isoxazolidines 10, 11, from 1 and 5: Column-chromatography yielded **10** [(945 mg, 35%), m.p. 170°, R_f 0.50 (silica gel, benzene-ethyl acetate 9:1)] from 25% petrol in benzene eluates and **11** [(460 mg, 17%), m.p. 150°, R_f 0.54 (silica gel, benzene-ethyl acetate ,9:1)] from the same eluates.

10. IR (KBr): 2960-2840 (m, $-CH_2-$), 1640 (s, amide >C=0), 840 (m, 1,4-disubstituted benzene ring), 755, 710 cm^{-1} (m, monosubstituted benzene nuclues); δ_H ^1H NMR (300 MHz; $CDCl_3$): δ 5.32 (1H, d, J=7.7 Hz, H-3), 3.79 (1H, dd, J=9.6 Hz, 7.7, H-4), 5.33 (1H, d, J=9.6 Hz, H-5), 2.76 (1H, m, H_A-2'), 3.39 (1H, m, H_B-2'), 1.36 (4H, m, H-3',4'), 0.92 (1H, m, H_A-5'), 0.66 (1H, m, H_B-5'), 2.76 (1H, dist.t, H_A-6'), 3.62 (1H, dist.t, H_B-6'), 7.01-7.38 (aromatic); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 75.15 (C-3), 64.04 (C-4), 84.77 (C-5), 43.67 (C-2'), 25.70 (C-3'), 24.21 (C-4'), 26.12 (C-5'), 46.82 (C-6'), 166.46 (>C=0); Anal. Found: C, 72.50; H, 6.09; N, 6.21. Calcd for $C_{27}H_{27}N_2O_2Cl$: C, 72.56; H, 6.10; N, 6.27%.

11. IR (KBr): 2940-2840 (m, $-CH_2-$), 1630 (s, amide >C=O), 850 (m, 1,4-disubstituted benzene ring), 760, 705 cm^{-1} (m, monosubstituted benzene ring), ^1H NMR (300 MHz, $CDCl_3$): δ 4.75 (1H, d, J= 10.3 Hz, H-3), 3.79 (1H, dist.t, H-4), 6.03 (1H, d, J=9.1 Hz, H-5), 2.85 (1H, m, H_A-2'), 3.43 (1H, m, H_B-2'), 1.35 (4H, m, H-3',4'), 0.98 (2H, m, H-5'),

Table V—Product Ratios of Regio- and Stereo- isomers obtained by Integration of ^{1}H-NMR Peaks

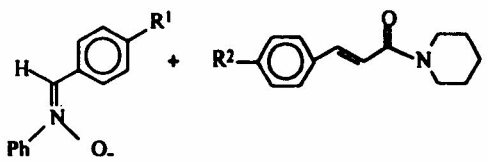
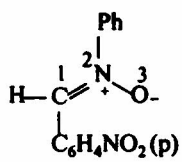
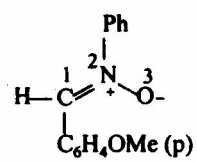
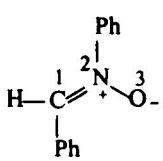
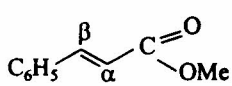
Sl. No.	Reaction	Product Ratios		
		Series A (3,4; 4,5-*trans* stereoisomer)	Series B (3,4-cis, 4,5-*trans* stereoisomer)	Series C (3,4; 4,5-*trans* regioisomer)
				
1.	R^1=Cl, R^2=H	100	11	—
2.	R^1=R^2=Cl	100	13	14
3.	R^1=NO_2, R^2=H	100	9	—
4.	R^1=R^2=H	100	9	—

Table VI —HOMO and LUMO Energies and Coefficients of C,N-diaryl nitrone and Methyl Cinnamate

Compound	FMO	Energy (eV)	Coefficients at		
			C_1	N_2	O_3
	HOMO	−10.25	−0.47	−0.24	0.66
	LUMO	1.07	0.34	−0.40	0.25
	HOMO	-9.2	−0.40	−0.27	0.61
	LUMO	2.19	0.44	−0.41	0.25
	HOMO	−9.6	−0.46	−0.25	0.66
	LUMO	2.06	0.44	−0.42	0.25

			Coefficients at			
			Cβ	Cα	>C(=0)	O
	HOMO	−11.52	−0.34	0.44	0.13	0.49
	LUMO	2.04	−0.50	0.42	0.33	−0.33

3.03 (1H, m, H_A-6'), 3.43 (1H, m, H_B-6'), 6.99-7.35 (aromatic): ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 72.72 (C-3), 58.35 (C-4), 81.60 (C-5), 42.71 (C-2'), 25.27 (C-3'), 24.31 (C-4'), 26.26 (C-5'), 46.53 (C-6'), 166.50 (>C=0); Found: C, 72.49; H, 6.08; N, 6.24.Calcd for $C_{27}H_{27}N_2O_2Cl$: C, 72.56; H, 6.10; N, 6.27%).

3*RS*-(3*R,4*S**,5*R**) and 3*RS*-(3*R**,4*R**,5*S**)-2-phenyl-3-(*p*-chlorophenyl)-5- (*p*-chlorophenyl)-4-piperidinyloxoisoxazolidines 12 and 13 from 1 and 6**: Column chromatography yielded **12** [(1.2 g, 37%), m.p. 125° R_f 0.58 (silica gel, benzene-ethylacetate 4:1)] from the benzene eluates and **13** [(750 mg, 23%), m.p. 130°, R_f 0.72 (silica gel, benzene-ethylacetate 4:1)] from 2% ethylacetate in benzene eluates.

12. IR (KBr): 2930-2850 (m, -CH_2-), 1640 (s, amide >C=O), 1015 (s, aryl-Cl), 845, 825 (m, 1,4-disubstituted benzene ring), 770, 700 cm^{-1} (m, monosubstituted benzene ring); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.22 (1H, d, *J*=7.0 Hz, H-3), 3.72 (1H, dist.t *J*=8.8 Hz, H-4), 5.35 (1H, d, *J*=9.4 Hz, H-5), 3.54 (1H, m, H_A-2'), 3.47 (1H, m; H_B-2'), 2.76 (2H, m H-6'), 1.35 (4H, m, H-3', H-4'), 0.94 (1H, m, H_A-5'), 0.77 (1H, m; H_B-5'), 6.96-7.34 (aromatic); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 75.20 (C-3), 63.73 (C-4), 83.86 (C-5), 43.64 (C-2'), 25.70 (C-3'), 24.15 (C-4'), 26.22 (C-5'), 46.64 (C-6'), 166.07 (>*C*=O); Anal. Found: C, 78.95; H, 6.28; N, 6.79. Calcd for $C_{27}H_{26}N_2O_2Cl_2$: C, 79.00; H, 6.38; N, 6.82%).

13. IR (KBr): 2920-2850 (m, –CH_2–), 1640 (s, amide >C=0), 1010 (m, aryl-Cl), 820 (m, 1,4-disubstituted benzene), 750, 690 cm^{-1} (s, m, monosubstituted benzene ring); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.99 (1H, d, *J*=9.1 Hz, H-3), 4.75 (1H, dist.t, *J*=10.4 Hz, H-4), 3.73 (1H, d, *J*=9.7 Hz, H-5), 3.48 (1H, m, H_A-2'), 3.38 (1H, m, H_B-2'), 3.03 (1H, m, H_A-6'), 2.82 (1H, m, H_B-6'), 1.44 (4H, m, H-3', H-4'), 1.31 (2H, m, H-5'), 7.00-7.34 (aromatic); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 72.32 (C-3), 58.38 (C-4), 80.72 (C-5), 42.53 (C-2'), 25.16 (C-3'), 24.17 (C-4'), 26.10 (C-5'), 46.44 (C-6'), 165.48 (>*C*=O); Anal. Found: C, 78.94; H, 6.29; N, 6.78. Calcd for $C_{27}H_{26}N_2O_2Cl_2$: C, 79.00; H, 6.38; N, 6.82%.

The regioisomeric cycloadduct **14** was detected in the crude mixture by ^{1}H NMR analysis—^{1}H NMR (300 MHz, $CDCl_3$): δ 4.58 (1H, d, *J*=8.2 Hz, H-3), 4.47 (1H, t *J*=8.0 Hz, H-4), 4.88 (1H, d, *J*=7.6 Hz, H-5).

3*RS*-(3*R,4*S**,5*R**) and 3*RS*-(3*R**,4*R**,5*S**)-2, 5-diphenyl-3-(*p*-nitrophenyl)-4-piperidinyloxoisoxazolidines 15 and 16 from 2 and 5:** Column chromatography yielded **15** [(721 mg 36%) m.p. 158° R_f, 0.61 (silica gel, benzene-ethyl acetate 4:1)] from benzene eluates and **16** [(280 mg, 14%) m.p. 175°, R_f 0.67 (silica gel, benzene-ethylacetate, 4:1)] from the same eluates.

15. IR (KBr): 2940-2860 (s, m, –CH_2–), 1650 (s, amide >C=0), 1520, 1350 (s, aromatic –NO_2), 860, 830 (m, 1,4-disubstituted benzene ring), 750, 700 cm^{-1} (s, mono-substituted benzene ring); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.28 (1H, d, *J*=9.5 Hz, 7.8, H-4), 5.54 (1H, d, 7.7 Hz, H-5), 2.73 (1H, m; H_A-2'), 3.39 (1H, m H_B-2'), 2.73 (1H, m H_A-6'), 3.66 (1H, m, H_B-6'), 1.40 (4H, m, H-3', H-4'), 0.92 (1H, m, H_A-5'), 0.63 (1H, m, H_B-5'), 6.97-7.39 (aromatic); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 74.78 (C-3), 63.99 (C-4), 85.11 (C-5), 43.76 (C-2'), 25.66 (C-3'), 24.08 (C-4'), 26.11 (C-5'), 46.64 (C-6'), 165.69 (>C=0); Anal. Found: C, 70.66; H, 5.75; N, 9.05. Calcd for $C_{27}H_{27}N_3O_4$: C, 70.88; H, 5.95; N, 9.18%.

16. IR (KBr): 2940-2860 (m, –CH_2–), 1635 (s, amide >C=O), 1520, 1350 (s, aromatic–NO_2), 860 (m, 1,4-disubstituted benzene ring), 750, 700 cm^{-1} (m, monosubstituted benzene ring); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.90 (1H, d, *J*=10.2 Hz, H-3), 3.88 (1H, t, *J*=9.7 Hz, H-4), 6.00 (1H, d, *J*=9.1 Hz, H-5), 2.83 (1H, m, H_A-2'), 3.46 (1H, m, H_B-2'), 3.11 (1H, m, H_A-6'), 3.46 (1H, m, H_B-6'), 1.43 (4H, m, H-3', H-4'), 1.35 (2H, m, H-5'), 6.99-7.36 (aromatic); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 72.28 (C-3), 58.09 (C-4), 81.83 (C-5), 43.60 (C-2'), 25.50 (C-3'), 24.27 (C-4'), 26.41 (C-5'), 46.71 (C-6'), 166.42 (>C=0); Anal. Found: C, 70.79; H, 5.91; N, 9.08. Calcd. For $C_{27}H_{27}N_3O_4$; C, 70.88; H, 5.95; N, 9.18%.

The regioisomeric cycloadduct **17** was detected in the crude mixture by ^{1}H NMR analysis. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.81 (1H, d, *J*=7.6 Hz, H-3), 4.50 (1H, t *J*=7.5 Hz, H-4), 4.97 (1H, d, *J*=7.4 Hz, H-5).

3*RS*-(3*R,4*S**,5*R**) and 3*RS*-(3*R**,4*R**,5*S**)-2,3-diphenyl-5-(*p*-nitrophenyl)-4- piperidinyloxoisoxa-zolidine 18 and 19 from 2 and 1:** Column chromatography yielded **18** [(767 mg,

38%) m.p. 150°, R_f 0.63 (silica gel, benzene-ethyl acetate, 4:1)] from 2% ethyl acetate in benzene eluates and **19** (464 mg, 23%) m.p. 137°, R_f 0.68 (silica gel, benzene-ethyl acetate, 4:1)] from the same eluates.

18, IR (KBr): 2940-2860 (m, $-CH_2-$), 1640 (s, amide >C=0), 1530, 1355 (s, aromatic $-NO_2$), 860, 830 (m, 1,4-disubstituted benzene ring), 760, 750, 700 cm^{-1}(m, monosubstituted benzene ring), MS: (m/z) 459 (M+2), 346 ($M^+ - C_6H_{10}NO+H^+$), 308 ($M+2-C_7H_5NO_3$), 307 ($M^+-C_7H_5NO_3+H^+$), 260 ($M^+-C_{13}H_{11}NO$), 223 ($308-C_5H_{10}N+H^+$), 198 ($M+2-C_{14}H_{16}N_2O_3+H^+$), 197 ($M^+-C_{14}H_{16}N_2O_3$), 181 ($C_{13}H_{11}N^+$), 131 ($223-C_6H_5N$), 105 ($181-C_6H_5^+ +H^+$); ^1H NMR (300 MHz, $CDCl_3$): δ 5.07 (1H, d, *J*=8.6 Hz, H-3), 3.77 (1H, t, *J*=8.8 Hz, H-4), 5.60 (1H, d, *J*=9.1 Hz, H-5), 2.71 (1H, m, H_A-2′), 3.47 (1H, m, H_B-2′), 2.71 (1H, m, H_A-6′), 3.58 (1H, m, H_B-6′), 1.42 (4H, br, m, H-3′, H-4′), 0.82 (2H, br.m, H-5′), 7.02-8.25 (aromatic); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 76.34 (C-3), 63.77 (C-4), 82.81 (C-5), 43.69 (C-2′), 25.72 (C-3′), 24.14 (C-4′), 26.25 (C-5′), 46.81 (C-6′), 166.27 (>C=0); Anal. Found: C, 70.60; H, 5.92; N, 9.12. Calcd. for $C_{27}H_{27}N_3O_4$: C, 70.88; H, 5.95; N, 9.18%.

19. IR (KBr): 2940-2860 (m, $-CH_2-$), 1640 (s, amide >C=0), 1530, 1355 (s, aromatic $-NO_2$), 860 (m, 1,4-disubstituted benzene ring), 760, 710 cm^{-1} (m, mono-substituted benzene ring); ^1H NMR (300 MHz, $CDCl_3$): δ 4.79 (1H, d *J*=10.3 Hz, H-3), 3.69 (1H, dist.t, *J*=9.8 Hz, H-4), 6.19 (1H, d, *J*=9.1 Hz, H-5), 2.79 (1H, m, H_A-2′), 3.34 (1H, m, H_B-2′), 3.00 (1H, m, H_A-6′), 3.46 (1H, m, H_B-6′), 1.28-1.52 (6H, m, H-3′, H-4′, H-5′), 6.99-8.22 (aromatic); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 74.03 (C-3), 59.12 (C-4), 81.05 (C-5), 43.05 (C-2′), 25.25 (C-3′), 24.20 (C-4′), 26.25 (C-5′), 46.80 (C-6′); Anal. Found: C, 70.75; H, 5.93; N, 9.15. Calcd for $C_{27}H_{27}N_3O_4$: C, 70.88; N, 5.95; N, 9.18%.

3RS-(3R*,4S*,5R*)-2, 3, 5-triphenyl-4-piperidinyloxoisoxazolidine 20 from 3 and 5: Column chromatography yielded **20** [(1.05 g, 42%), m.p. 135°, R_f 0.60 (silica gel, benzene-ethyl acetate, 4:1)] from the benzene eluates; IR (KBr): 2940-2860 (m, $-CH_2-$), 1640 (s, amide >C=0), 760, 710 cm^{-1} (s, mono-substituted benzene ring); MS: m/z 412 (M^+), 306 ($M^+-C_7H_6O$), 300 ($M^+-C_6H_{10}NO$), 222 ($306-C_5H_{10}N$), 195 ($300-C_7H_5O$), 194 ($306-C_6H_{10}NO$), 180 ($C_{13}H_{10}N^{\bullet+}$), 112 ($C_6H_{10}NO^{\bullet+}$), 105 ($C_7H_5O^+$), 91 ($C_6H_5N^+$), 84 ($C_5H_{10}N^{\bullet+}$), 77 ($C_6H_5^+$); ^1H NMR (300 MHz, $CDCl_3$): δ 5.27 (1H, d, *J*=8.2 Hz, H-3), 3.83 (1H, dist.t, *J*=8.8 Hz, H-4), 5.37 (1H, d, *J*=9.5 Hz, H-5), 3.44 (1H, m, H_A-2′), 3.57 (1H, m, H_B-2′), 2.74 (2H, m, H-6′), 1.36 (4H, m, H-3′, H-4′), 0.86 (1H, m, H_A-5′), 0.68 (1H, m, H_B-5′); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 75.92 (C-3), 63.99 (C-4), 84.68 (C-5), 43.58 (C-2′), 25.70 (C-3′), 24.20 (C-4′), 26.01 (C-5′), 46.78 (C-6′), 166.63 (>C=0); Anal. Found : C, 78.58; H, 6.79; N, 6.68. Calcd for $C_{27}H_{28}N_2O_2$: C, 78.61; H, 6.84; N, 6.79%.

The stereoisomeric cycloadduct **21** was detected in the crude mixture by ^1H NMR analysis. ^1H NMR (300 MHz, $CDCl_3$): δ 4.64 (1H, d, *J*=10.5 Hz, H-3), 5.98 (1H, d, *J*=8.9 Hz, H-5).

3*RS*-(3*R,4*S**,5*R**) and 3*RS*-(3*R**,4*R**,5*S**)-2,3-diphenyl-5-(*p*-chlorophenyl)-4- piperidinyloxoisoxazolidine 22 and 23 from 3 and 6:** Column chromatography yielded **22** [(884 mg, 30%) m.p. 149° R_f 0.65 (silica gel, benzene-ethyl acetate 4:1)] from benzene eluates and **23** [(471 mg, 16%) m.p. 134° R_f 0.67 (silica gel, benzene-ethyl acetate 4:1)] from the benzene-ethylacetate (10:1) eluates.

22. IR (KBr): 2940-2860 (m, $-CH_2-$), 1645 (s, amide >C=O), 1100 (m, aryl-Cl), 840 (m, 1,4-disubstituted benzene ring), 770, 720, 710 cm^{-1} (s, m, monosubstituted benzene ring) ^1H NMR (300 MHz, $CDCl_3$): δ 5.18 (1H, d, *J* = 8.3 Hz, H-3), 3.77 (1H, t. *J*=8.8 Hz, H-4), 5.40 (1H, d, *J*=9.4 Hz, H-5), 3.50 (2H, m, H-2′), 2.73 (2H, m, H-6′), 1.39 (4H, m, H-3′, H-4′), 0.80-0.84 (2H, m, H-5′); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 76.00 (C-3), 63.84 (C-4), 83.55 (C-5), 43.55 (C-2′), 25.78 (C-3′), 24.10 (C-4′), 26.11 (C-5′), 46.69 (C-6′), 166.66 (>*C*=0); Anal. Found: C, 72.50; H, 5.98; N, 6.23. Calcd for $C_{27}H_{27}N_2O_2Cl$: C, 72.56; H, 6.10; N, 6.27%.

23. IR (KBr): 2940-2860 (m,$-CH_2-$), 1650 (s, amide >C=0), 1100 (m, aryl-Cl), 840 (m, 1,4-disubstituted benzene ring), 760, 690 cm^{-1} (m, mono-substituted benzene ring); ^1H NMR (300 MHz, $CDCl_3$): δ 4.76 (1H, d, *J*=10.4 Hz, H-3), 3.72 (1H, dist.t, *J*=9.5 Hz, H-4), 6.04 (1H, d, *J*=9.1 Hz, H-5), 2.82 (1H m, H_A-2′), 3.36 (1H, m, H_B-2′), 3.06 (1H, m, H_A-6′), 3.48 (1H, m, H_B-6′), 1.23-1.40 (6H, m, H-3′, H-4′, H-5′); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 73.46 (C-3), 59.09 (C-4), 80.91 (C-5), 44.72 (C-2′), 24.61 (C-3′), 24.22 (C-4′), 26.14 (C-5′), 45.72 (C-6′), 165.18 (>*C*=0); Anal. Found: C,

72.52; H, 5.96; N, 6.35. Calcd for $C_{27}H_{27}N_2O_2Cl$: C, 72.56; H, 6.10; N, 6.27%.

X-ray diffraction studies were carried out using PHILIPS PW 11 automatic four-circle diffractometer operating with Cu-Kα radiation (λ = 1.5418Å) monochromated by graphite.

Crystallographic data of 22: Mol. formula $C_{27}H_{27}N_2O_2Cl$, Mol wt 446.5, triclinic, space group PI, parameters: Z = 2, a = 15.336(4)Å, b = 9.492(4)Å, C = 9.181(3)Å, α = 115.8° (1), β = 100.90(1), γ = 81.6° (1). The structure was solved by direct methods and refined with isotropic, then anisotropic thermal factors, by full matrix least squares procedure. All hydrogen atoms were calculated at their theoretical places and their positional parameters were refined. The final agreement factor $R = \sum | F_o | - | F_c | / \sum |F_o|$ converged to 0.079/0.074 for the weighted R_w factor $= \sum | W_i (| F_o | - | F_c |) \sum W_i | F_o |$. The positional parameters ($\times 10^4$) and mean recalculated isotropic factors ($\times 10^3$) for non-hydrogen atoms are given in Table III while the refined positional parameters ($\times 10^3$) for hydrogen atoms are given in Table IV.

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