Synthesis of 1,3,4-Oxadiazaspiro[4.4]nona-2,6,8-trienes *via* 1,3-Dipolar Cycloadditions of Diphenylnitrilimine with Cyclopentadienones. Crystal and Molecular Structure of a Cycloadduct

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The cycloaddition of diphenylnitrilimine with substituted cyclopentadienones leads to the formation of the title spirooxadiazoline derivatives **2**, in good yields. The reaction is examined on the basis of the frontier molecular orbitals of the reacting reagents. An X-ray crystallographic analysis of the product **2b** is made.

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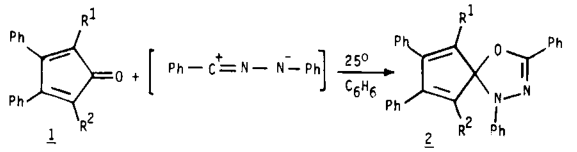
In connection with our previous work [2] on the cycloaddition between nitrile oxides and cyclopentadienones, we have undertaken the present study on the cycloaddition of diphenylnitrilimine with the same dipolarophiles **1**. We have found quite unexpectedly that although the nitrile oxides attack the ethylene double bond the nitrilimine prefferentially attacks the carbonyl double bond of **1** with the formation of 1,3,4-oxadiazaspiro[4.4]nona-2,6,8-triene derivatives and the reaction in this respect resembles with the cycloaddition of nitrile oxides with cyclobutenediones [3]. It is mentioned that several cycloaddition reactions of nitrilimines have been studied recently by Tewari *et al.* [4,5]. On the other hand the cycloadduct **2a** was also prepared by an unusual photochemical decomposition [6] of *N,C*-diphenyl sydnone in the presence of cyclopentadienone **1a**.

The cycloaddition between cyclopentadienones **1**, appropriately substituted to exist as monomers and diphenylnitrilimine in excess (3:1), generated *in situ* by the action of triethylamine on *N*-phenylbenzhydrazidoyl chloride were carried out at room temperature whereas the reaction time was 30-40 hours. The only reaction product isolated was the mono-adduct sprio-Δ^2-1,3,4-oxadiazoline **2** in a 20-70% yield.



a: $R^1 = R^2 = -C_6H_5$; b: $R^1 = -C_6H_5$, $R^2 = -CH_3$; c: $R^1 = -C_6H_5$, $R^2 = -C_2H_5$;
d: $R^1 = R^2 = -C_2H_5$

The spirooxadiazolines **2** show in ir no carbonyl absorption but instead a C=N stretching vibration at 1630-1640 cm^{-1}. The nmr spectra of **2b, 2c**, and **2d** gave signals for methyl and ethyl protons at almost the same chemical

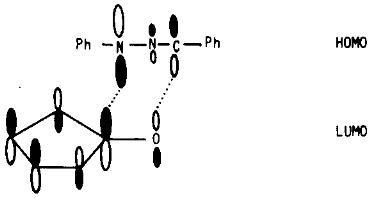


Figure 1. HOMO-LUMO interaction between diphenylnitrilimine and cyclopentadienone **1a**.

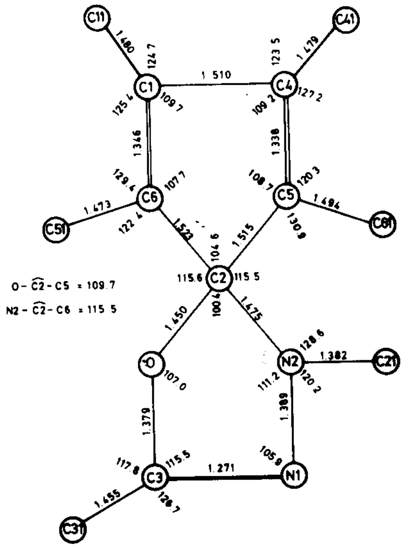


Figure 2. Bond distances and angles for the cycloadduct **2b**. (Average C-C bond length for phenyls 1.380 Å and average internal angles for phenyl groups 120.0°. Standard deviations for bond lengths 0.002-0.003 Å and for angles 0.3°).

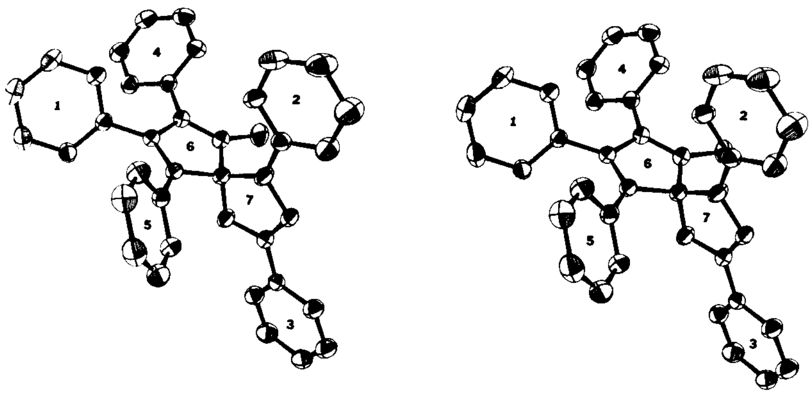


Figure 3. ORTEP drawing for **2b**.

Table I

Summary of Crystal and Intensity Collection Data for Compound **2b**

formula	$C_{37}H_{28}N_2O$
M.W.	516.64
a,b,c, Å	11.006(2), 12.681(2), 11.238(2)
α,β,γ, deg	94.51(2), 104.10(2), 112.03(2)
V, Å^3	1384.6(5)
Z	2
D_{calcd}, g/cm^3	1.239
D_{measd}, g/cm^3	1.23
space group	$P\bar{1}$
cryst. dimens., mm	0.2 × 0.3 × 0.5
radiation	MoKα (0.71069) Zr- filtered
μ, cm^{-1}	0.40
scan speed	Variable between 1 and 10 deg in 2θ/min
scan range	0.9° below Kα_1 to 0.9° above Kα_2
bkgd counting, s	0.5 of scan time
2θ limit, deg	45.5
data collected / unique	3959/3754
data used	3148 with $F_o \geq 4.0\sigma(F_o)$
R	0.0375, 0.0457 (All data)
Rw	0.0332, 0.0347 (All data)

shifts of the same protons in parent cyclopentadienones. Thus the signals for methyl protons were upfield shifted by δ 0.12, 0.20 and 0.08 for the compounds **2b, 2c, 2d** respectively, whereas the signals for methylene protons of **2c** and **2d** were again shifted by δ 0.13 and 0.02. These data are found to be quite different to those observed in cycloadducts [2] obtained from an addition to the ethylene double bond of **1**. The observed shifts could be attributed to a diamagnetic ring current caused by the *N*-phenyl group. The products **2** show in the mass spectra very strong molecular ion peaks, followed by those corresponding to the retro-1,3-dipolar cycloaddition and to other decomposition fragments of the spiro ring.

The formation of these cycloadducts **2** can be explained after consideration of FMO of the reacting species [7,8]. From examination of these orbitals it is concluded that the present cycloaddition is HOMO dipole controlled, in contrast to analogous reactions with nitrile oxides [2,7,8]. Thus the energy levels of frontier orbitals of the dipolarophile **1a** were estimated to be $E_{HOMO} = -8.1$ eV and $E_{LUMO} = -2.1$ eV [2], whereas the corresponding values for diphenylnitrilimine [7,8] are $E_{HOMO} = -7.5$ eV and $E_{LUMO} = -0.5$ eV. Therefore for the energy difference ΔE we have $\Delta E\ (\mathrm{HOMO}_{dipole} - \mathrm{LUMO}_{dipolarophile}) = 5.4$ eV and this value is smaller than the energy difference $(\mathrm{HOMO}_{dipolarophile} - \mathrm{LUMO}_{dipole})$ by 2.2 eV.

The regioselectivity of the reaction and the position of attack by the dipole are also explained by considering an orbital interaction like that in Figure 1.

Cycloadducts of the dipole on ethylene double bond have not been isolated, although their formation should be expected as another possible orbital interaction and this fact might be attributed to steric interactions. On the other hand no other peri-isomers of the type $[{}_{\pi}6_S + {}_{\pi}4_S]$ have been formed.

The structure of the cycloadducts was fully characterised from the X-ray crystallographic analysis carried out on the 6-methyl-2,4,7,8,9-pentaphenyl-1,3,4-oxadiazaspiro[4.4]nona-2,6,8-triene **2b**. Bond distances and angles as well as an ORTEP drawing for **2b** are given in Figures 2 and 3 respectively. On the other hand crystal and other related experimental data as well as positional parameters are given in Tables I and II respectively.

The X-ray study shows that both rings of the spiro system are almost planar and perpendicular to each other, the angle between their planes being 89.47°. On the other hand both phenyls and the oxadiazoline ring are almost co-planar, the dihedral angles between planes 3 - 7 (see Figure 3) and 2 - 7 being equal to 11.59° and 0.47° respectively. The phenyls and the cyclopentadiene ring are completely out of co-planarity and their planes are as follows: 5 - 6, 44.98°; 1 - 6, 55.58°; 4 - 6, 50.02°.

EXPERIMENTAL

All melting points are uncorrected and they were obtained with a hot stage apparatus. The ir spectra were obtained with a Perkin-Elmer 297

Table II

Positional Parameters (× 10^4) for Carbon Nitrogen and Oxygen Atoms

Atoms	x	y	z	Atoms	x	y	z
C(1)	1592(2)	1760(1)	1569(2)	C(33)	2765(2)	−3601(2)	1029(2)
C(2)	3229(2)	994(1)	1919(2)	C(34)	3706(2)	−3860(2)	1857(2)
N(2)	4575(1)	1357(1)	2862(1)	C(35)	4676(2)	−3032(2)	2845(2)
N(1)	4916(1)	420(1)	3043(1)	C(36)	4726(2)	−1927(1)	3010(2)
C(3)	3922(2)	−458(1)	2310(2)	C(4)	2303(2)	1972(1)	565(2)
O(1)	2868(1)	−237(1)	1588(1)	C(5)	3249(2)	1532(2)	762(2)
C(11)	515(2)	2160(1)	1683(2)	C(6)	2146(2)	1222(1)	2383(2)
C(12)	−728(2)	1394(2)	1788(2)	C(61)	4186(2)	1463(2)	25(2)
C(13)	−1681(2)	1796(2)	2011(2)	C(41)	2010(2)	2622(1)	−424(2)
C(14)	−1408(2)	2951(2)	2115(2)	C(42)	673(2)	2368(2)	−1135(2)
C(15)	−202(2)	3714(2)	1975(2)	C(43)	419(2)	3014(2)	−2030(2)
C(16)	750(2)	3320(1)	1751(2)	C(44)	1486(2)	3917(2)	−2219(2)
C(21)	5442(2)	2448(1)	3554(2)	C(45)	2808(2)	4173(2)	−1527(2)
C(22)	5129(2)	3404(2)	3396(2)	C(46)	3073(2)	3533(2)	−639(2)
C(23)	6022(2)	4482(2)	4096(2)	C(51)	1955(2)	1011(1)	3608(1)
C(24)	7228(2)	4643(2)	4937(2)	C(52)	1889(2)	1864(1)	4412(2)
C(25)	7541(2)	3698(2)	5091(2)	C(53)	1747(2)	1696(2)	5584(2)
C(26)	6656(2)	2606(2)	4421(2)	C(54)	1675(2)	676(2)	5971(2)
C(31)	3798(2)	−1647(1)	2160(2)	C(55)	1750(2)	−170(2)	5192(2)
C(32)	2808(2)	−2489(2)	1181(2)	C(56)	1897(2)	−7(2)	4024(2)

Table III

Analytical and Spectral Data of **2**

Compound	Mp, °C	Yield %	Molecular Formula	Analysis % Calcd./Found C	H	N	Spectral Data
2a	256-259	50	$C_{42}H_{30}N_2O$	87.17	5.23	4.84	ir (nujol): 1640 cm^{-1} (C=N); nmr (deuteriochloroform): 6.7-7.9 δ (m); $M^{+\cdot}$ at m/e 578 (100), 384 (66), 194 (57)
			M.W. 578	87.22	5.45	4.86	
2b	191-193	70	$C_{37}H_{28}N_2O$	86.20	5.46	5.42	ir (nujol): 1640 cm^{-1} (C=N); nmr (deuteriochloroform): 6.85-8.0 (m, 25H), 1.8 (s, 3H); $M^{+\cdot}$ at m/e 516 (100), 322 (40), 194 (57)
			M.W. 516	86.10	5.59	5.22	
2c	168-170	20	$C_{38}H_{30}N_2O$	86.01	5.70	5.28	ir (nujol): 1635 cm^{-1} (C=N); nmr (deuteriochloroform): 6.7-7.98 (m, 25H), 2.2 (q, 2H), 1.0 (t, 3H); $M^{+\cdot}$ at m/e 530 (100), 336 (10), 194 (87)
			M.W. 530	85.99	5.76	4.94	
2d	102-104	50	$C_{34}H_{30}N_2O$	84.61	6.27	5.81	ir (nujol): 1630 cm^{-1} (C=N); nmr (deuteriochloroform): 6.68-8.1 (m, 20H), 2.23 (q, 4H), 0.93 (t, 6H); $M^{+\cdot}$ at m/e 482 (10), 288 (10), 194 (100)
			M.W. 482	84.58	6.15	5.70	

spectrophotometer. The nmr spectra, reported in δ units (TMS), were recorded with a Varian A60A spectrometer, whereas mass spectra were measured with a Hitachi-Perkin-Elmer Model RMU-6L spectrometer with an ionization energy of 70 eV.

The cyclopentadienones used in this work were prepared as reported [9], while diphenylnitrilimine was liberated *in situ* from *N*-phenylbenzhydrazidoyl chloride [10] with triethylamine.

General Procedure for the Cycloaddition Reactions of Cyclopentadienones **1** with Diphenylnitrilimine.

Triethylamine (10 mmoles) was added to a benzene solution (10 ml) of cyclopentadienones **1** (2 mmoles) and *N*-phenylbenzhydrazidoyl chloride (6 mmoles). The reaction mixture was kept at room temperature until the colour of cyclopentadienones disappeared (30-40 hours). Then the triethylamine hydrochloride was removed by filtration and after evaporation of the solvent the oily residue was chromatographed on Silica and eluted with a chloroform/hexane (3:1) mixture. The reaction products were further purified by recrystallization with dichloromethane/hexane mixtures. Analytical and spectral data are summarized in Table III.

Crystallographic Analysis.

Yellow orange single crystals suitable for X-ray work, were obtained by a slow evaporation of a methylene chloride solution. Photographic investigation and statistics indicate the space group (Table I). All data were collected on a Synthex $P2_1$ diffractometer. Lattice parameters (Table I) were refined by a least squares procedure using 15 automatically centered reflections. Periodically monitored reference reflections showed no significant changes in intensity. Lorenz and polarization but no absorption corrections were made. The direct-methods program of SHELX [11] was used to solve the structure. All nonhydrogen atoms were located from the E-map. All chemically anticipated hydrogen atoms were located from a difference Fourier synthesis calculated from the full-matrix least squares [11] refined structural model (R = 0.065) [12] which included unit weights and anisotropic thermal parameters. The final full-matrix least squares cycle used weights calculated by the formula $1/\omega = \sigma^2(F_o) + 0.006\ F_o^2$, and refined the positional parameters of all atoms, isotropic thermal parameters for the hydrogen atoms and anisotropic for the rest and converged to R = 0.0375, Rω = 0.0322 and GOF = 2.41 [12]. A difference map calculated at this point showed no unusual features. Lists of positional parameters for the hydrogen atoms, thermal parameters for all atoms, bond distances and angles for the phenyl rings and structure factor amplitudes may be obtained from the author (AT).

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[11] The following computer programs were used: SHELX by G. Sheldrick (for direct methods); CRYSTAN by H. Burzlaff, R. Böhme, M. Gomm (for refinement, Fourier maps and bond distances and angles); ORTEP by C. K. Johnson (for drawings).

[12] $R = \| F_o| - |F_c\| / \Sigma |F_o|$, $R\omega = [\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega |F_o|^2]^{1/2}$ and $GOF = [\Sigma\omega(|F_o| - |F_c|)^2 / (N_{ref} - N_{var})^2]^{1/2}$.