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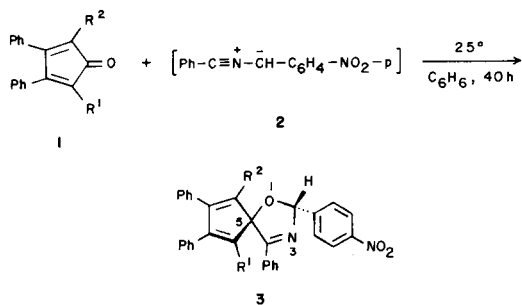
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1,3-Dipolar cycloaddition of benzonitrile-4-nitrobenzylide with four substituted cyclopentadienones **1** afforded the title compounds **3** in good yields (20-50%), by addition of the 1,3-dipole to the carbonyl double bond. The cycloaddition is examined on the basis of frontier molecular orbitals of the reacting species and an X-ray crystallographic analysis of the cycloadduct **3c** is made.

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Cyclopentadienone ring has been proved to be an interesting and peculiar dipolarophile. Thus, in the cycloaddition with nitrile oxides the 1,3-dipole attacks the ring ethylene double bond [3], whereas with diphenylnitrilimine the dipole attacks the carbonyl double bond [1] of **1**. It was of interest, therefore, to study the cycloaddition of the same dipolarophile **1** with benzonitrile-4-nitrobenzylid [4] and to examine the position of attack by this dipole and the regioselectivity of the cycloadducts.

The cycloadditions between **1** and **2** in a mole ratio 1:3 were carried out in benzene solution at 25° and we have found that the dipole **2** reacts again with the carbonyl double bond of **1** with the formation of spiro-oxazoline derivatives **3** in 20-50% yield, according to the following reaction scheme.

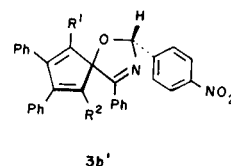


a, R¹ = R² = Ph; b, R¹ = CH₃, R² = Ph; c, R¹ = C₂H₅, R² = Ph, d, R¹ = R² = C₂H₅

In the cycloaddition reaction between **1** and **2** and for a certain regioselectivity we have formation of two chiral centers at C-2 and C-5 and in addition to this problem the possibility of a [6 + 4] cycloaddition make the whole system very complicated.

For these reasons and for an unambiguous structural assignment an X-ray crystallographic analysis was carried out (see below) on compound **3c**, which found to possess the structure as given in **3**.

It is of interest to note that from the reaction of **1b** with **2** besides **3b** another product **3b'** was also isolated in 2% yield, which could be considered as a stereoisomer of **3b**.



Products **3** lack carbonyl absorption in ir, but they show a C=N stretching vibration at 1610-1620 cm⁻¹ (Table I).

In the nmr spectra, in deuteriochloroform, the aromatic protons resonate at δ 6.70-8.30, whereas the methyl protons in **3b** and **3b'** resonate at δ 1.91 and 1.55 respectively. The ethyl protons in **3c** give signals for methyl and methylene protons at δ 1.10 and 2.25, whereas in **3d** the same protons give one triplet at δ 0.58, one triplet at δ 1.05 and two masked quartets centered at δ 2.15 respectively. On the other hand the C-2 proton resonates in the area of aromatic protons at a value δ 6.70. If this proton was located at C-4 it should resonate at higher field [5].

The cycloadducts **3** in the mass spectra show prominent peaks for molecular ion M⁺, in addition to other peaks corresponding to a retro-1,3-dipolar cycloaddition and to decomposition fragments of the two spiro-rings.

The regioselectivity of the cycloadducts **3** is the same to that observed in the addition of **2** to acetaldehyde and benzaldehyde [4,6] where the terminal "anionic" carbon atom became attached to the carbonyl oxygen atom [4,5,6].

The observed regioselectivity can be explained from FMO considerations of the reacting species. Thus, from the frontier orbital energies of 1,3-dipole and dipolarophile it is concluded that the present cycloadditions are HOMO-dipole controlled, as in the reactions of **1** with diphenylnitrilimine [1]. The energies of the frontier orbitals of dipolarophile **1a**, as they were approximated [3] by

Table I
Analytical and Spectral Data of **3**

Compound	Mp °C	Yield %	Molecular Formula MW	Analysis % Calcd/Found			Spectral Data
				C	H	N	
3a	178-179	50	C ₄₃ H ₃₀ N ₂ O ₃ 622.69	82.90	4.80	4.50	ir: (nujol) 1620 cm ⁻¹ (C=N); nmr (δ, CDCl ₃): 6.7-8.25 (m); ms: m/z 622 (3), M ⁺ , 383 (98), 238 (95), 178 (100)
				82.86	5.09	4.26	
3b	189-191	46	C ₃₈ H ₂₈ N ₂ O ₃ 560.62	81.41	5.03	5.00	ir (nujol): 1620 cm ⁻¹ (C=N); nmr (δ, CDCl ₃): 1.91 (s, 3H), 6.7-8.83 (m, 25H); ms: m/z 560 (100) M ⁺ , 457 (100), 322 (96), 238 (90), 178 (90)
				81.61	4.79	4.77	
3b'	175-183	2	C ₃₈ H ₂₈ N ₂ O ₃ 560.62	81.41	5.03	5.00	ir (nujol): 1620 cm ⁻¹ (C=N); nmr (δ, CDCl ₃): 1.55 (s, 3H), 6.7 (s, 1H), 6.83-8.20 (m, 24H); ms: m/z 560 (100) M ⁺ , 457 (68), 322 (19), 238 (51), 178 (63)
				81.71	4.95	5.29	
3c	178-180	20	C ₃₅ H ₃₀ N ₂ O ₃ 574.65	81.51	5.26	4.88	ir (nujol): 1610 cm ⁻¹ (C=N); nmr (δ CDCl ₃): 1.10 (t, 3H), 2.25 (q, 2H), 6.60-8.33 (m, 25H); ms: m/z 574 (15) M ⁺ , 336 (100), 238 (50), 178 (15)
				81.27	5.38	5.04	
3d	155-158	36	C ₃₅ H ₃₀ N ₂ O ₃ 526.61	79.82	5.74	5.32	ir (nujol): 1620 cm ⁻¹ (C=N); nmr (δ, CDCl ₃): 0.58 (t, 3H), 1.05 (t, 3H), 2.15 (two masked quartets, 4H), 6.88-8.33 (m, 20H); ms: m/z 526 (22) M ⁺ , 288 (55), 238 (100)
				79.65	5.73	5.19	

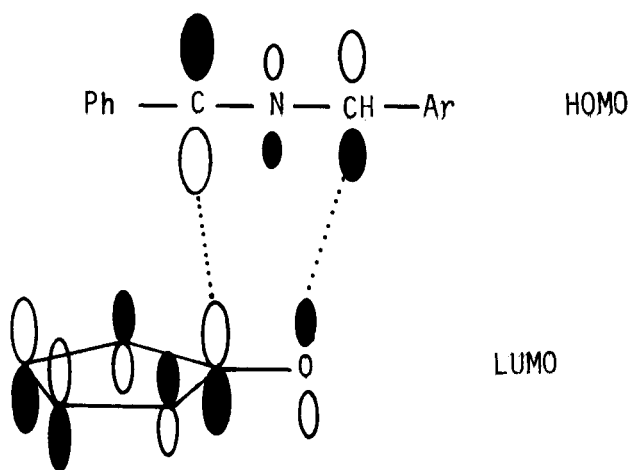


Figure 1. HOMO-LUMO interaction between benzonitrile-4-nitrobenzylide and cyclopentadienone **1a**.

Houk's method [7,8], are $E_{HOMO} = -8.1$ eV and $E_{LUMO} = -2.1$ eV, whereas the corresponding values [8] for benzonitrile-methylide (C₆H₅CNCH₂) are $E_{HOMO} = -6.4$ eV and $E_{LUMO} = 0.6$ eV. Thus, the energy difference for HOMO_{dipole}-LUMO_{dipolarophile} interaction is equal to 4.3 eV and smaller than the opposite interaction by 4.4 eV. The difference is large enough to compensate any influence caused by nitrophenyl group on the energy levels of benzonitrile-methylide, although it should be expected that this energy difference will be larger [8], since the destabilization of substituted HOMO dipole is larger than the stabilization of LUMO-dipole.

In respect to the orientation of cycloaddition an interaction like that in Figure 1 is found to be in agreement with the observed regioselectivity. In this orbital interaction a larger orbital coefficient on the sp carbon atom ("neu-

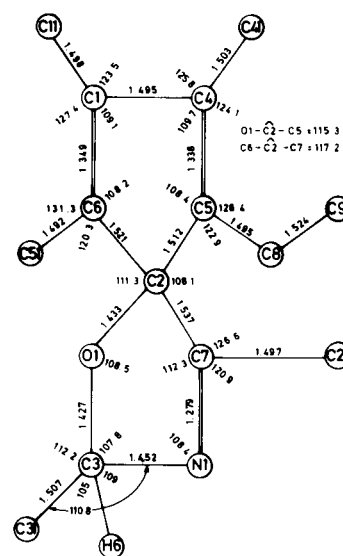


Figure 2. Angles and bond distances for the cycloadduct **3c**. (Estimated standard deviations are 2-4 in last significant figure. Average C-C and C-H bond length for phenyls is equal to 1.385 Å and 1.00 Å respectively and average internal angles for phenyls 120.0°).

tral" carbon) of HOMO_{dipole} is presumed [9].

The structure of the cycloadducts was completely confirmed from the X-ray crystallographic analysis carried out on the 4,7,8,9-tetraphenyl-2-(4-nitrophenyl)-6-ethyl-1,3-oxazaspiro[4.4]nona-3,6,8-triene (**3c**). Angles and bond distances and an ORTEP drawing for **3c** 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 II and III respectively.

The rings are almost perpendicular to each other, the angles between the planes 6-7 (see Figure 3) being 85.5°.

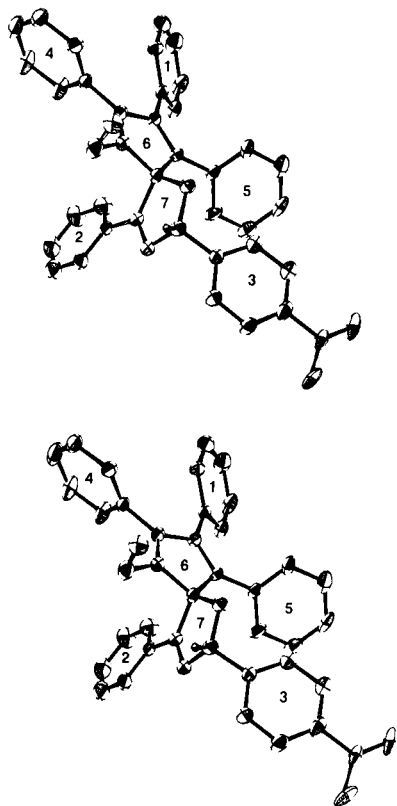


Figure 3. ORTEP drawing for **3c** at 40% probability ellipsoids.

Table II

Summary of Crystal and Intensity Collection Data for Compound **3c**

formula	C ₃₉ H ₃₀ N ₂ O ₃
MW	574.65
a,b,c, Å	15.438(2), 10.097(1), 10.621(1)
α,β,γ, deg	109.64(1), 87.19(1), 101.70(1)
V, Å ³	1526.5(4)
Z	2
D _{calcd} , g/cm ³	1.254
D _{measd} , g/cm ³	1.24
space group	P ₁
cryst. dimens., mm	0.3 × 0.4 × 0.5
radiation	MoKα (0.71069) Zr-filtered
μ, cm ⁻¹	0.44
scan speed	variable between 1 and 12 deg in 2θ/min
scan range	1.0° below Kα ₁ to 1.0° above Kα ₂
bkgd counting, s	0.5 of scan time
2θ limit, deg	44.6
data collected/unique	4219/3933
data used	3018 with F _o ≥ 6.2 σ(F _o)
R	0.0452, 0.0584 (all data)
Rw	0.0636, 0.0696 (all data)

The plane of phenyl 2 is almost co-planar to oxazoline ring 7, in contrast to the nitrophenyl which is out of co-planarity the corresponding dihedral angles between the planes 2-7 and 3-7 being equal to 22.5° and 59.3° respec-

Table III

Positional Parameters (× 10⁴) for all Non-hydrogen Atoms

Atoms	x	y	z	Atoms	x	y	z
O1	3594(1)	3407(2)	392(1)	C23	-236(1)	3121(1)	445(2)
O31	5568(2)	2333(3)	3883(2)	C24	-694(1)	1822(1)	9607(2)
O32	5911(1)	4591(3)	5020(2)	C25	-238(1)	794(1)	8837(2)
N1	2538(1)	1847(2)	8811(2)	C26	677(1)	1065(1)	8903(2)
N2	5523(2)	3368(4)	4875(3)	C31	4017(1)	2585(1)	8061(1)
C1	2352(1)	5371(2)	2783(2)	C32	4458(1)	3962(1)	8189(1)
C2	2743(1)	3557(2)	961(2)	C33	4946(1)	4224(1)	7141(1)
C3	3474(1)	2232(2)	9166(2)	C34	4994(1)	3110(1)	5965(1)
C4	2235(1)	4025(2)	3123(2)	C35	4554(1)	1732(1)	5837(1)
C5	2523(1)	3007(2)	2122(2)	C36	4065(1)	1470(1)	6885(1)
C6	2666(1)	5125(2)	1534(2)	C41	1765(1)	3774(2)	4320(1)
C7	2123(1)	2588(2)	9778(2)	C42	2188(1)	3452(2)	5267(1)
C8	2585(2)	1525(2)	2052(2)	C43	1714(1)	3136(2)	6305(1)
C9	3493(2)	1457(3)	2498(3)	C44	818(1)	3142(2)	6396(1)
C11	2139(1)	6745(2)	3718(1)	C45	396(1)	3464(2)	5449(1)
C12	2306(1)	7130(2)	5075(1)	C46	869(1)	3780(2)	4411(1)
C13	2120(1)	8403(2)	5942(1)	C51	2972(1)	6112(2)	756(1)
C14	1766(1)	9291(2)	5453(1)	C52	3656(1)	7277(2)	1257(1)
C15	1598(1)	8906(2)	4096(1)	C53	3998(1)	8119(2)	487(1)
C16	1785(1)	7633(2)	3229(1)	C54	3656(1)	7795(2)	9215(1)
C21	1135(1)	2364(1)	9741(2)	C55	2972(1)	6629(2)	8713(1)
C22	678(1)	3392(1)	512(2)	C56	2630(1)	5788(2)	9484(1)

tively. Out of co-planarity are also the phenyls 1,4,5 in respect to the plane of cyclopentadiene ring 6, the corresponding dihedral angles 1-6, 4-6, 5-6 being 34.87°, 68.36° and 60.81° respectively. On the other hand rings 6 and 7 are almost planar, with a maximum distance deviation from the mean plane defined by the corresponding ring atoms equal to ±0.04 and ±0.09 Å respectively.

EXPERIMENTAL

Melting points are uncorrected and they were obtained with a Kofler hot stage apparatus. The ir spectra were obtained with a Perkin-Elmer Model 297 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 **1** used in this work, were prepared as reported [10], while benzonitrile-4-nitrobenzylid liberated *in situ* from *N*-(*p*-nitrobenzyl)benzimidoyl chloride [6].

General Procedure for the Cycloaddition of Cyclopentadienones with Benzonitrile-4-nitrobenzylid.

Triethylamine (~10 mmoles) was added to a benzene solution (~10 ml) of cyclopentadienones **1** (2 mmoles) and imidoyl halide (6 mmoles). The reaction mixture was kept at room temperature until the colour of cyclopentadienones disappeared (~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. Products **3** were further purified by recrystallization with dichloromethane:hexane mixtures. Analytical and spectral data of all cycloadducts are summarized in Table I.

Crystallographic Analysis.

Pale yellow single crystals suitable for X-ray work, were obtained by slow evaporation of a dichloromethane solution. Photographic investiga-

tion and intensity statistics indicate the space group (Table II). The data were collected on a Syntex P2, diffractometer. Lattice parameters were refined by a least-square procedure using 15 automatically centered reflections. Periodically monitored reference reflections showed no significant changes in intensity. Lorenz and polarization but no absorption corrections were applied. The direct-methods program of SHELX [11] was used to solve the structure. All non-hydrogen atoms were located from the E-map. All chemically anticipated hydrogen atoms were located from a difference Fourier synthesis. However, all phenyl groups were refined as hexagonal rigid groups with C-C 1.385 Å and C-H 1.00 Å and only their atomic temperature factors were free to refine. The final full-matrix least-squares cycle used weights calculated by the formula $1/\omega = \sigma^2(F_o) + 0.00115 F_o^2$, and refined the positional parameters of all non-hydrogen atoms except for the rigid phenyl group, isotropic thermal parameters for the hydrogen atoms and anisotropic for the rest. A difference map calculated at this time showed no unusual features. Lists of positional parameters for the hydrogen atoms, thermal parameters for all atoms and structure factor amplitudes may be obtained by the author (A. T.).

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