# 1,3-Dipolar Cycloadditions of Cyclopentadienones with Nitrile *N*-Oxides (1)



*N. G. Argyropoulos (2) and N. E. Alexandrou*

Laboratory of Organic Chemistry, University of Thessaloniki, Greece

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The cycloaddition reactions of nitrile oxides with several substituted cyclopentadienones leads to the formation of condensed mono-isoxazolines (3α,5-bis-substituted-6,6α-diphenyl-3α*H*,4*H*,6α*H*-cyclopenta[2,3-*d*]isoxazol-4-ones) and in some cases to bis-isoxazoline derivatives as minor products. The cycloaddition to mono-adducts is regioselective and only one regioisomer is formed, which can be predicted after consideration of the frontier molecular orbitals of the reacting species. The spectral data of the isoxazolines **3-7** are examined, whereas their structure was fully characterized by X-ray analysis.

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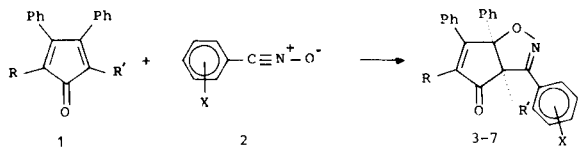
It has been shown (3) previously that in the cycloaddition between nitrile oxides and cyclobutenediones the 1,3-dipole prefferentially attacks the carbonyl rather than the ethylene double bond. As another interesting dipolarophile the cyclopentadienone ring was chosen to examine both the position of attack by the 1,3- dipole and the regioselectivity of the adducts.

The cyclopentadienones, as nonaromatic annulenones, are very reactive dienes and they have been used in several Diels-Alder reactions (4). On the other hand, very little is known concerning their behaviour as dipolarophiles. Thus, the reaction of dipolarophiles with diazoalkanes was described (5) and an unusual reaction (6), (7) of tetracyclone (tetraphenyl-cyclopentadienone) with nitrile imines, where the 1,3-dipole was added on the carbonyl double bond to produce stable spirooxadiazoline compounds was also described.

The cycloaddition between cyclopentadienones **1**, appropriately substituted to exist as monomers and several nitrile oxides **2** took place in ether solution, at room temperature. The nitrile oxide was always in excess (3:1). The reaction time was about 12 hours.



1 2 3-7

1a : R = R'= Ph ; 1b : R = R'=$COOCH_3$ ; 1c : R = R'= Et ;
1d : R = Ph , R'= Me ; 1e : R = Ph , R'=Et .

| | 2 | 3 | | 4 | | 5 | | 6 | | 7 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | X | R | R' | R | R' | R | R' | R | R' | R | R' |
| a | H | Ph | Ph | $COOCH_3$ | $COOCH_3$ | Et | Et | Ph | Me | Ph | Et |
| b | 2,4,6-$(CH_3)_3$ | " | " | " | " | " | " | " | " | " | " |
| c | 4-$CH_3$ | " | " | " | " | " | " | " | " | " | " |
| d | 4-Cl | " | " | " | " | " | " | " | " | " | " |
| e | 4-$NO_2$ | " | " | " | " | " | " | " | " | " | " |

The main reaction product was the mono-adduct usually isolated in a 50-70% yield, with certain and unique regioselectivity, (**3-7**) by adding the nitrile oxide to one of the ethylene double bonds.

The isoxazolines **3-7** absorb in the ir carbonyl region in the range of 1700-1710 $cm^{-1}$. The nmr spectra of **4a-e** show two peaks for the methyl protons of the carbomethoxy-group at δ 3.1-3.2 and 3.9-4.1. The low field peak is found in the same range as in the cyclopentadienone **1b** and consequently in the reaction product this peak must be attributed to carbomethoxy protons of the 5-position. The bis-ethyl derivatives **5a-e** also show two different signals for ethyl protons in the nmr (Table I).

It is of interest to mention that the high field shift of the methyl protons (peaks at δ 0.23-0.40) could arise from a diamagnetic shielding effect of the 3-aryl group and probably, in part, from the carbonyl group. Another interesting point in this respect is that the methylene protons of the 3α-ethyl group show two multiplets instead of a quartet (Fig. 1) and this suggests that the methylene protons are non-equivalent, since they are attached to an asymmetric carbon atom (Table I).

It has shown from the nmr spectra, that in the cycloadducts **6** and **7** derived from the asymmetrically substituted cyclopentadienones **1d** and **1e**, the alkyl group is located in the 3α-position (see Table II), since the methyl and ethyl protons were shifted to high field with respect to the starting compounds **1d** and **1e** as in the cycloadducts **5a-e**.

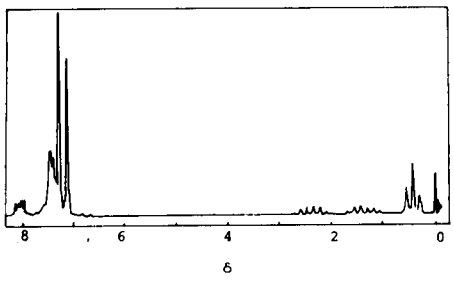



Figure 1. Nmr spectrum of isoxazoline **7a** in deuteriochloroform.

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Table I

Chemical Shifts of Ethyl Protons of Isoxazolines **5** and **7**
(δ-values, deuteriochloroform)

| Compound | $3\alpha$-$CH_AH_B$-$CH_3$ | | | 5-$CH_2$-$CH_3$ | |
|---|---|---|---|---|---|
| | $H_A$ (a) | $H_B$ (b) | $CH_3$ (c) | -$CH_2$- (d) | -$CH_3$ (e) |
| **5a** | 1.33 | 2.37 | 0.23 | 2.37 | 1.05 |
| **5b** | 1.50 | 2.37 | 0.23 | 2.33 | 1.02 |
| **5c** | 1.20 | 2.45 | 0.38 | 2.45 | 1.05 |
| **5d** | 1.32 | 2.32 | 0.37 | 2.32 | 1.10 |
| **5e** | 1.37 | 2.37 | 0.37 | 2.37 | 1.07 |
| **7a** | 1.33 | 2.35 | 0.47 | | |
| **7b** | | 1.92 (f) | 0.27 | | |
| **7d** | 1.33 | 2.38 | 0.43 | | |

(a) Multiplet. (b) Multiplet masked by a quartet of 5-methylene protons. (c) Unresolved triplet. (d) Quartet. (e) Triplet. (f) Broad multiplet.

The cyclopentaisoxazolines **3-7** show in the mass spectra peaks corresponding to fragments from a retro-1,3-dipolar cycloaddition, besides the molecular ion, which in some cases is the most abundant one. The other fragments arise from decomposition either of the isoxazoline or the cyclopentenone ring.

The structure of the cycloadducts **3-7** was determined from the X-ray crystallographic analysis carried out on compounds **3a** and **4e** by Rentzeperis, Kokkou, *et al.*, (8).

Compound **3d** crystallizes in space group $P2_{1/n}$ (monoclinic plates) with Z = 4 and cell constants $\alpha$ = 14.373, b = 21.084, c = 9.261 Å, $\beta$ = 99.27°. The structure was refined to a final R = 0.060 value.

Compound **4e** crystallizes in space group $P\bar{1}$ (tricyclic prisms) with Z = 2 and cell constants $\alpha$ = 12.576, b = 10.014, c = 10.492 Å, $\alpha$ = 91.66, $\beta$ = 95.52, $\gamma$ = 88.46° (R = 0.082). Their clinographic projections are given in Figures 2 and 3, respectively.

The regioselectivity observed in these cycloaddition reactions can be explained on the basis of the model proposed by Houk and co-workers (9) for HOMO-LUMO interactions between the reacting species. Using the values for energy levels of HO and LU orbitals for 1,3-dipole (benzonitrile oxide) and some dipolarophiles, as their energies can be approximated by Houk's method (10), it is concluded that the cycloaddition is LUMO-dipole controlled. Thus, the HO-LU energy for the dipolarophile **1a** was estimated to be $\epsilon_{HO}$ = -8.1 eV, and $\epsilon_{LU}$ = -2.1 eV, whereas the values (10) for benzonitrile oxide are $\epsilon_{HO}$ = -10 and $\epsilon_{LU}$ = -1 eV. Therefore, since the energy difference $LU_{(dipole)} - HO_{(dipolarophile)}$ is smaller than that of $LU_{(dipolarophile)} - HO_{(dipole)}$ by ~ 1 eV the previous interaction should be more favorable. On the other hand, it is estimated that the $a_2$ symmetry of HO of the dipolarophile should have a larger orbital coefficient on carbon -2

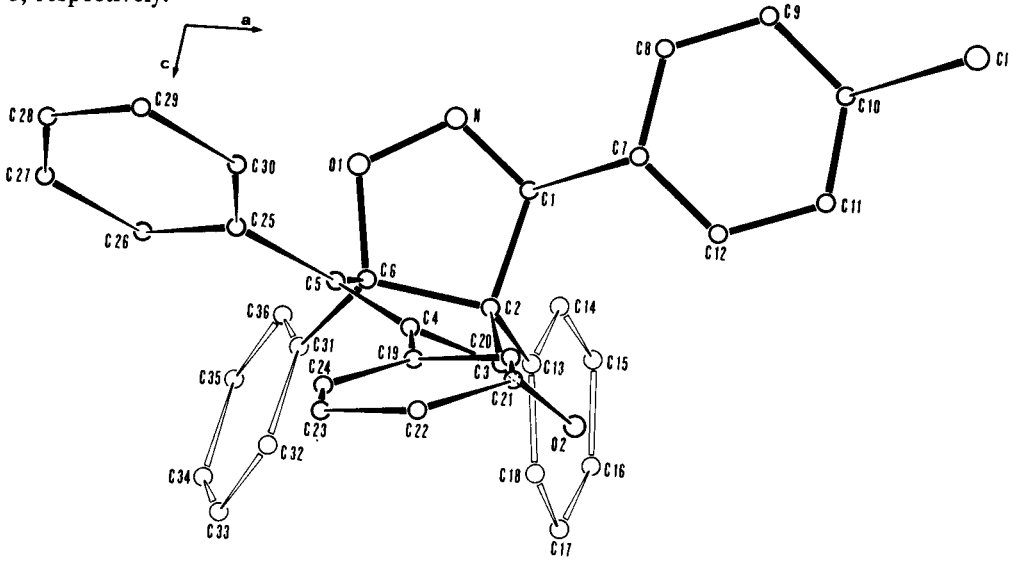



Figure 2. Clinographic projection of isoxazoline **3d**.

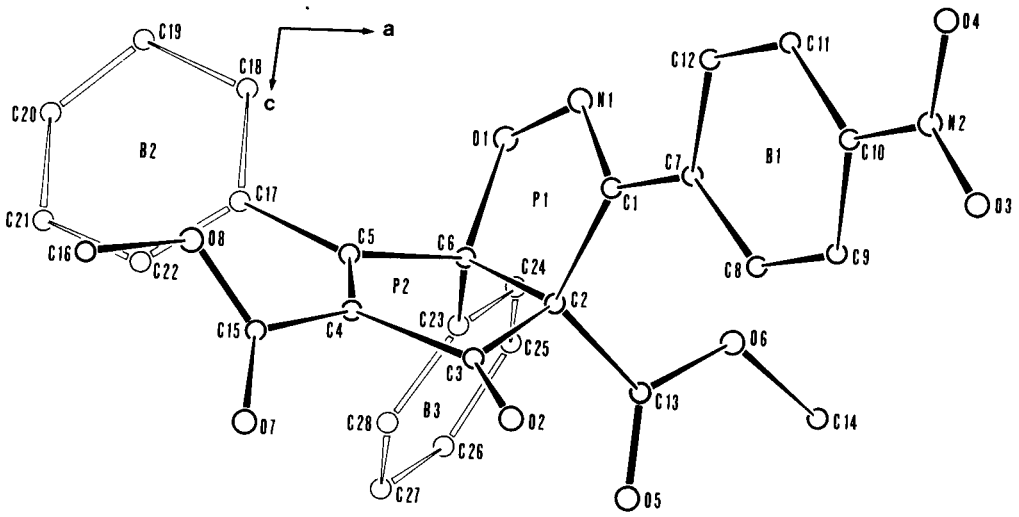



Figure 3. Clinographic projection of isoxazoline **4e**.

and this atom should be combined to the carbon atom of the nitrile oxide leading to products **3-7** as shown in Figure 4.

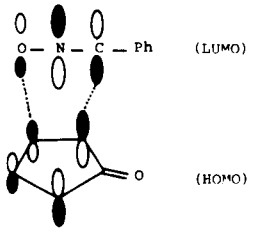


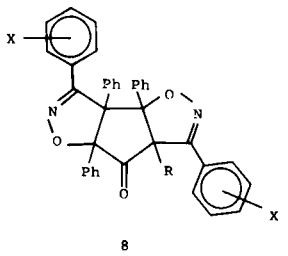

Figure 4. Favourable HOMO-LUMO interaction between cyclopentadienone **1a** and benzonitrile oxide.

It is of interest to note that products with analogous regioselectivity are obtained from the reaction of tropone with nitrile oxides (11) and the reaction of furan with nitrile oxides (12).

Another factor which might affect the observed regioselectivity could be the dipole-dipole interaction (11) of the reacting species, which also favors the formation of regioisomers **3-7**.

From this cycloaddition reactions other *peri*-isomers, especially of the type $[\pi^{6s} + \pi^{4s}]$ have not been isolated. However, in some cases bis-adducts were isolated in low yields (~ 10%) by reacting both ethylene double bonds with two nitrile oxide molecules **8**.

These bis-adducts show ir carbonyl absorptions at 1700-1720 $cm^{-1}$ and their nmr spectra are in general similar to those of the mono-adducts (Table II).




8

| 8 | R | X |
|---|---|---|
| a | $-CH_3$ | -H |
| b | $-CH_3$ | -4-$CH_3$ |
| d | $-C_2H_5$ | -H |
| e | $-C_2H_5$ | -4-$CH_3$ |

Table II

Chemical Shifts of 3α-Methyl or Ethyl Protons for the Isoxazolines **8** (δ-values, deuteriochloroform)

| Compound | 3α-$CH_3$ (a) | 3α-$CH_2$-$CH_3$ $-CH_2-$ (b) | $-CH_3$ (c) |
|---|---|---|---|
| **8a** | 0.47 | | |
| **8b** | 0.48 | | |
| **8d** | | 1.19 | 0.05 |
| **8e** | | 1.22 | 0.05 |

(a) Singlet. (b) Very broad multiplet. (c) Unresolved triplet.

Table III

Chemical Shifts for *p*-Tolyl Methyl Protons (δ-values, deuteriochloroform)

| Compound | $-CH_3$ (a) |
|---|---|
| **3c** | 2.30 |
| **4c** | 2.38 |
| **5c** | 2.40 |
| **6c** | 2.47 |
| **8d** | 2.45 |
| | 2.28 |

(a) Singlet.

Table IV

Analytical Data for the Mono-isoxazolines **3-7**

| Compound | M.p. °C | Yield % | Formula | Mol. Weight | Analyses Calcd. % C | H | N | Found % C | H | N | Ir ($cm^{-1}$) (Nujol) C=O | C=N | MS m/e (R.I. %) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **3a** | 203-205 (a) | 75 | $C_{36}H_{25}NO_2$ | 503.57 | 85.86 | 5.00 | 2.78 | 86.34 | 5.16 | 2.71 | 1710 | 1620 | $M^{+\cdot}$ 503 (80), 400 (13), 398 (9), 384 (16), 311 (55), 178 (45), 119 (2). |
| **3b** | 178-180 (b) | 74 | $C_{39}H_{31}NO_2$ | 545.65 | 85.86 | 5.73 | 2.57 | 84.45 | 5.69 | 2.69 | 1700 | 1625 | $M^{+\cdot}$ 545 (50), 440 (9), 400 (14), 384 (100), 311 (40), 178 (85), 161 (35). |
| **3c** | 194-195 (c) | 73 | $C_{37}H_{27}NO_2$ | 517.59 | 85.85 | 5.26 | 2.71 | 85.65 | 5.36 | 2.70 | 1705 | 1610 | $M^{+\cdot}$ 517 (100), 412 (9), 400 (21), 384 (31), 311 (100), 178 (65), 133 (4). |
| **3d** | 213-214 (c) | 79 | $C_{37}H_{24}ClNO_2$ | 538.02 | 80.37 | 4.48 | 2.61 | 79.89 | 4.55 | 2.90 | 1700 | 1605 | $M^{+\cdot}$ 537 (82), 432 (7), 400 (20), 384 (21), 311 (100), 178 (67), 153 (4). |
| **3e** | 159-161 (c) | 69 | $C_{36}H_{24}N_2O_4$ | 548.57 | 78.82 | 4.41 | 5.11 | 78.91 | 4.42 | 5.08 | 1700 | 1605 | $M^{+\cdot}$ 548 (100), 443 (8), 400 (50), 384 (22), 311 (44), 178 (100), 164 (4). |
| **4a** | 158-159 (c) | 52 | $C_{28}H_{21}NO_6$ | 467.46 | 71.94 | 4.53 | 3.00 | 71.57 | 4.60 | 3.08 | 1705 | 1605 | $M^{+\cdot}$ 467 (90), 408 (40), 364 (13), 362 (90), 348 (10), 160 (33), 119 (10). |
| **4b** | 181-183 (c) | 77 | $C_{31}H_{27}NO_6$ | 509.53 | 73.07 | 5.34 | 2.75 | 72.58 | 5.41 | 3.04 | 1710 | 1620 | $M^{+\cdot}$ 509 (n), 450 (10), 478 (5), 404 (20), 348 (20), 161 (41), 160 (12). |
| **4c** | 167-169 (c) | 42 | $C_{29}H_{23}NO_6$ | 481.48 | 72.34 | 4.82 | 2.91 | 72.30 | 4.81 | 2.45 | 1710 | 1605 | $M^{+\cdot}$ 481 (100), 422 (30), 376 (90), 364 (4), 348 (3), 160 (23), 133 (4). |
| **4d** | 160-161 (c) | 46 | $C_{28}H_{20}ClNO_6$ | 501.90 | 66.87 | 3.95 | 2.79 | 67.16 | 4.03 | 2.49 | 1705 | 1620 | $M^{+\cdot}$ 501 (70), 442 (28), 364 (9), 348 (17), 160 (60), 153 (28). |
| **4e** | 166-169 (c) | 23 | $C_{28}H_{20}N_2O_8$ | 512.46 | 65.62 | 3.93 | 5.47 | 65.60 | 3.93 | 5.63 | 1710 | 1600 | $M^{+\cdot}$ 512 (32), 453 (37), 407 (85), 364 (11), 348 (5), 160 (52), 164 (6). |
| **5a** | 85-87 (c) | 24 | $C_{28}H_{25}NO_2$ | 407.49 | 82.52 | 6.18 | 3.44 | 82.94 | 6.26 | 3.33 | 1700 | 1610 | $M^{+\cdot}$ 407 (100), 379 (16), 378 (41), 304 (37), 288 (21), 130 (24), 119 (1). |
| **5b** | 195-196 (c) | 74 | $C_{31}H_{31}NO_2$ | 449.57 | 82.81 | 6.95 | 3.12 | 82.85 | 7.05 | 3.06 | 1700 | 1620 | $M^{+\cdot}$ 449 (100), 421 (12), 420 (25), 304 (18), 288 (55), 161 (3), 130 (19). |
| **5c** | 89-91 (c) | 60 | $C_{29}H_{27}NO_2$ | 421.51 | 82.61 | 6.46 | 3.32 | 82.36 | 6.42 | 3.01 | 1710 | 1630 | $M^{+\cdot}$ 421 (20), 392 (10), 304 (3), 288 (8), 133 (10), 130 (5). |
| **5d** | 116-118 (d) | 55 | $C_{28}H_{24}ClNO_2$ | 441.94 | 75.82 | 5.47 | 2.87 | 76.09 | 5.43 | 3.17 | 1695 | 1620 | $M^{+\cdot}$ 441 (100), 412 (34), 336 (7), 288 (23), 153 (6), 130 (5). |
| **5e** | 128-129 (c) | 47 | $C_{28}H_{24}N_2O_4$ | 452.49 | 74.32 | 5.35 | 6.19 | 74.49 | 5.40 | 6.41 | 1700 | 1630 | $M^{+\cdot}$ 452 (100), 423 (100). 304 (100), 288 (45), 164 (4), 130 (90). |
| **6a** | 154-155 (a) | 64 | $C_{31}H_{23}NO_2$ | 441.50 | 84.33 | 5.25 | 3.17 | 84.03 | 5.38 | 3.11 | 1710 | 1610 | $M^{+\cdot}$ 441 (100), 413 (12), 338 (18), 336 (10), 322 (45), 178 (86), 119 (n). |
| **6b** | 209-210 (c) | 82 | $C_{34}H_{29}NO_2$ | 483.58 | 84.44 | 6.04 | 2.90 | 84.66 | 6.08 | 2.87 | 1710 | 1610 | $M^{+\cdot}$ 483 (80), 455 (4), 378 (9), 338 (17), 322 (100), 178 (50), 161 (7). |
| **6c** | 173-174 (c) | 57 | $C_{32}H_{25}NO_2$ | 455.53 | 84.37 | 5.53 | 3.08 | 84.64 | 5.67 | 3.29 | 1700 | 1615 | $M^{+\cdot}$ 455 (100), 427 (7), 350 (8), 338 (9), 322 (62), 178 (73), 133 (12). |
| **6d** | 134-137 (e) | 46 | $C_{31}H_{22}ClNO_2$ | 475.95 | 78.63 | 4.63 | 2.94 | 78.48 | 4.71 | 2.90 | 1710 | 1610 | $M^{+\cdot}$ 475 (100), 447 (8), 370 (6), 338 (10), 322 (60), 178 (70), 153 (9). |
| **7a** | 148-150 (c) | 48 | $C_{32}H_{25}NO_2$ | 455.53 | 84.37 | 5.53 | 3.08 | 84.43 | 5.66 | 2.98 | 1710 | 1610 | $M^{+\cdot}$ 455 (100), 427 (13), 426 (11), 352 (11), 350 (14), 336 (40), 178 (65), 119 (4). |
| **7b** | 229-230 (c) | 88 | $C_{33}H_{31}NO_2$ | 497.61 | 84.47 | 6.28 | 2.82 | 84.92 | 5.83 | 2.73 | 1700 | 1610 | $M^{+\cdot}$ 497 (67), 468 (6), 392 (6), 352 (4), 336 (100), 178 (20), 161 (32). |
| **7d** | 151-152 (c) | 52 | $C_{32}H_{24}ClNO_2$ | 489.98 | 78.44 | 4.90 | 2.86 | 78.29 | 4.93 | 2.69 | 1720 | 1630 | $M^{+\cdot}$ 489 (100), 461 (11), 460 (9), 384 (10), 352 (15), 336 (55), 178 (85) 153 (5). |

(a) Recrystallized from chloroform-ether. (b) Recrystallized from cyclohexane. (c) Recrystallized from dichloromethane-cyclohexane. (d) Recrystallized from benzene. (e) Recrystallized from methanol. (n) Negligible intensity.

In the mass spectra some do not show any peak for the molecular ion, but only for the ion $(M)^{+\cdot}$ - ArCNO.

An interesting feature appears in the nmr spectra of compounds **8b** and **8e**, where the methyl protons of the *p*-tolyl groups have different chemical shifts (**8b**: $\delta$ 2.25 and 2.45; **8e**: $\delta$ 2.28 and 2.45.

The peak at $\delta$ 2.45 is found to be almost at the same position as in the mono-adducts (see Table III) and this

Table V

Analytical Data for the Bis-isoxazolines **8**

| Compound | M.p. °C | Yield % | Formula | Mol. Weight | Analyses Calcd. % C | H | N | Found % C | H | N | Ir ($cm^{-1}$) (Nujol) C=O | C=N | MS m/e (R.I. %) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **8a** | 134-136 dec. | 10 | $C_{38}H_{28}N_2O_3$ | 560.62 | 81.41 | 5.03 | 5.00 | 81.00 | 5.18 | 5.45 | 1725 | 1625 | 441 (3), 413 (n), 338 (2), 322 (37), 178 (20), 119 (24) (b) |
| **8b** | 178-180 dec. | 11 | $C_{40}H_{32}N_2O_3$ | 588.67 | 81.61 | 5.48 | 4.76 | 81.91 | 5.54 | 4.86 | 1710 | 1610 | $M^{+\cdot}$ 588 (n), 455 (13), 378 (n), 322 (90), 178 (56), 133 (36), 117 (100). |
| **8d** | 111 dec. | 11 | $C_{39}H_{30}N_2O_3$ | 574.65 | 81.50 | 5.26 | 4.88 | 81.60 | 5.48 | 4.49 | 1710 | 1620 | 455 (n), 336 (17), 178 (4), 119 (26), (b). |
| **8e** | 138 dec. | 4 | $C_{41}H_{34}N_2O_3$ | 602.70 | 81.70 | 5.69 | 4.65 | 81.71 | 5.89 | 4.62 | 1710 | 1615 | 469 (9), 364 (n), 336 (85), 178 (10), 133 (26), 117 (100), (b). |

(a) Recrystallized from dichloromethane -cyclohexane. (b) No peak for the molecular ion. (n) Negligible intensity.

can be taken as an indication that one of the isoxazoline rings has the same regio-form as the mono-adducts.

The peak at $\delta$ 2.25 or at 2.28 is attributed to the isoxazoline ring with the opposite regioselectivity. This assumption is also supported by analogous structures found in bis-adducts of nitrile oxides with cyclopentadiene (13), furan (12) and thiophene (14).

However, the structural problem of these bis-adducts remains open for further investigation, since there are 4 possible isomers and 8 *cis-trans* stereo-forms.

## EXPERIMENTAL

All melting points are uncorrected and they were obtained with a Kofler hot stage apparatus. Ir spectra were obtained with a Perkin-Elmer Model 257 spectrophotometer, whereas nmr spectra, reported in $\delta$ units, were obtained with a Varian A-60A spectrometer, with TMS as the internal reference. The mass spectra were measured with a Hittachi-Perkin-Elmer Model RMU-6L spectrometer, with an ionization energy of 70 eV. Elemental analyses were performed with a Perkin-Elmer Analyser Model 240.

General Procedure for the Cycloadditions of Cyclopentadienones **1** with Nitrile *N*-Oxides **2**.

An ether solution of cyclopentadienones **1** (3 mmoles), prepared according to a standard procedure (15), was added to an ether solution of the nitrile oxides **2** (9 mmoles), prepared by a known method (16). The reaction mixture remained at room temperature, until the colour of the solution had disappeared (about 12 hours). The solution was evaporated and the oily residue chromatographed on silica gel and eluted with a mixture of chloroform-cyclohexane 3:1. The bis-adducts were eluted after the corresponding mono-adducts. In some cases (**3a-e, 4b, 5b, 6b, 7b**) the mono-adducts were separated by adding to the reaction mixture a small amount of petroleum ether. In cases where the nitrile oxide used was unstable, furoxans were also isolated from the reaction mixture.

The analytical data of mono-adducts **3-7** are summarized in Table IV, whereas those of bis-adducts **8** are recorded in Table V.

Acknowledgement.

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