

in the Cycloaddition of Mesitronitrile Oxide to
Isopropylidenemalononitrile

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Mesitronitrile oxide reacts with isopropylidenemalononitrile to give mono- and bis-1,2,4-oxadiazole derivatives **2** and **3** and Δ^2 -isoxazolines **4** and **5** in moderate yields. The dipolarophilic character of the ethylene and nitrile functions in these cycloadditions is examined.

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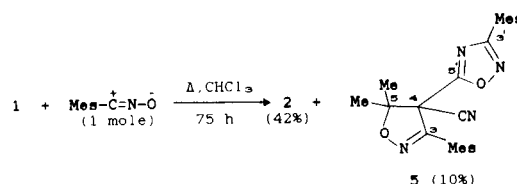
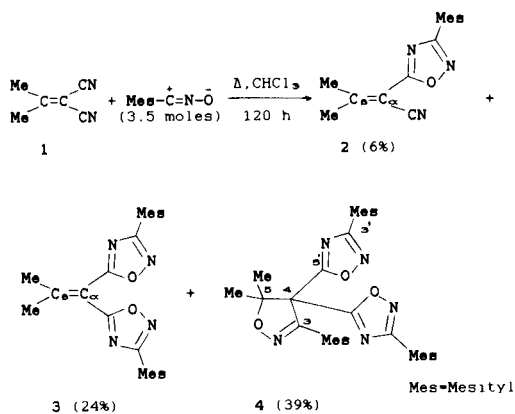
The dipolarophilic character of the C=C double bond is, in general, much stronger than the C≡N bond and several 1,3-dipoles like nitrile oxide and nitrilimines react with acrylonitrile to give the corresponding cyano-heterocyclic systems [1]. On the contrary to this finding it has been shown [2,3] that some nitrones react with isopropylidenemalononitrile forming 1,2,4-oxadiazolines and in this case the C≡N bond becomes more reactive than the C=C double bond. However, it has been reported recently [4] that nitrilimines give with arylidenemalononitriles and with other α,β -disubstituted acrylonitriles the corresponding pyrazolines by exclusive addition of the dipole on the ethylene double bond and not on the nitrile function. On the other hand we have found previously [5] that the cycloaddition of mesitronitrile oxide to 9-fluorenylidene-malononitrile proceeds exclusively on both *gem*-nitrile groups with the formation of bis-1,2,4-oxadiazole derivatives.

These contradictory results prompted us to examine the cycloaddition of mesitronitrile oxide with a simpler dipolarophile like isopropylidenemalononitrile to determine the site selectivity and the relative reactivity as dipolarophiles of the geminal dinitrile function in respect to the C=C bond. However, from the above discussion it is evident that generalizations and successful predictions on the site selectivity can not be made, because of the peculiarities of the reacting species. The variation of the

site selectivity in these cycloadditions is mainly due to the multiple substitutions and to the existence of cross substituent effects in the dipolarophiles as well as to steric effects.

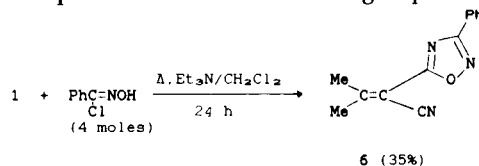
The reaction of isopropylidenemalononitrile **1** with mesitronitrile oxide takes place in refluxing chloroform solution for about 120 hours to give after column chromatography the mono- **2** and bis-adduct **3** by addition of the dipole on nitrile groups and the tris-adduct **4** by further addition of the dipole to the ethylene double bond.

It is mentioned that the same reaction products **2-4** were also obtained when the mole ratio dipolarophile/dipole was 1:2.5, the only difference being in the reaction yields, which for the products **2**, **3** and **4** were 43, 17 and 29% respectively. However, when the mole ratio dipolarophile/dipole was 1:1 and the reaction time 75 hours, the reaction afforded the mono-1,2,4-oxadiazole derivative **2** and the bis-adduct **5**, by addition of one dipole on nitrile function and another one on ethylene double bond.

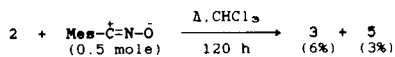


The above experimental data show that the cycloaddition of the dipole initially takes place on one nitrile group to give 1,2,4-oxadiazole derivative **2**, in agreement with our previous results [5] and the compound **2** further reacts with the dipole to form the other reaction products **3-5**.

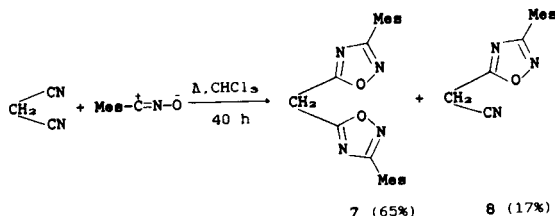
The higher reactivity of the C≡N group over the C=C bond in **1** was confirmed by the reaction of **1** with the more reactive and unstable benzonitrile oxide, which mainly gave the mono-adduct **6** in moderate yield, by reaction of the dipole with one of the nitrile groups.



In order to evaluate the relative reactivity of the $C \equiv N$ group in respect to $C=C$ bond in the cycloadduct **2** a test experiment was carried out using a limited amount of the dipole (mole ratio dipolarophile/dipole 1:0.5). From this reaction the starting compound **2** was recovered in 78% yield and the bis-adducts **3** and **5** were isolated in small yields by addition of the dipole on the second nitrile group and on the ethylene double bond, indicating a comparable reactivity of these functions.



It is also mentioned that the cycloaddition of mesitronitrile oxide with malononitrile proceeds more faster than that with **2** and gives the bis- and mono-adducts **7** and **8** in yields 65 and 17% respectively.



The conclusion from these reactions is that in isopropylidene malononitrile both the $C \equiv N$ and the $C=C$ bonds are deactivated in cycloaddition reactions with nitrile oxides. Furthermore, the geminal dinitrile function deactivates the ethylene double bond in comparison to acrylonitrile and the cycloaddition with the dipole takes place on the nitrile group in agreement with previous findings [1,5]. After the formation of the cycloadduct **2** the reactivity of the remaining $C \equiv N$ group is similar to that of the $C=C$ bond and this leads to the formation of the cycloadducts **3**, **4** and **5**.

The structures of the compounds **2-8** were elucidated on the basis of their analytical and spectral data. Thus, the compounds **2**, **6** and **8** show in the ir spectra a strong $C \equiv N$ absorption at $2220-2240 \text{ cm}^{-1}$, whereas compound **5** gives a very weak $C \equiv N$ band at 2220 cm^{-1} .

In the ^1H nmr spectra of compound **2** the methyl protons of the isopropylidene function appear at $\delta = 2.45$ and 2.54 ppm and that of compound **6** at $\delta = 2.71$ and 2.82 ppm. In the symmetrical compound **3** the two methyls give one singlet peak at $\delta = 2.30$ ppm. In compound **5** the two methyls attached at the C-5 of the isoxazoline ring, give peaks at $\delta = 1.54$ and 1.95 ppm, whereas in compound **4** the two methyls give a singlet peak at $\delta = 1.69$ ppm. These low field shifts of the methyl protons in the compounds **4** and **5** could be considered as an indication for the proposed regio-forms, where the two methyls are attached to the carbon bearing the oxygen of the isoxazoline

ring. For the other regio-forms these methyl protons are expected to resonate at higher field at *ca* 1 ppm.

In the ^{13}C nmr spectra of the compounds **2-8** the oxadiazole gives two peaks for C-3' and C-5' carbons at $\delta = 168.5$ and $170-172$ ppm respectively in agreement to our previous finding [5], whereas the mesityl group shows the expected peaks for the aromatic and the methyl-carbons.

In the compounds **4** and **5** there are two peaks at 64.6 and 93.0 ppm and at 61.4 and 92.7 ppm respectively corresponding to C-4 and C-5 atoms of the isoxazoline ring. The peak at about 93 ppm which remains almost unchanged in going from compound **4** to **5** is attributed to C-5 carbon atom of the isoxazoline ring in agreement to the proposed regio-form. This peak in the coupled spectra is splitted to a multiplet with a $^2J = 4.5$ Hz. In these compounds (**4** and **5**) the isoxazoline C-3 carbons atom resonates at the expected for the $C=N$ bond values of $\delta = 155.4$ and 152.5 ppm respectively.

In the spectra of the compounds **2** and **6** the C- α and C- β carbons of the ethylene double bond resonate at about 99 and 170 ppm respectively. In compound **3**, where the cyano-group is replaced by the 1,2,4-oxadiazole ring, these carbons appear at 109.4 and 160.9 ppm respectively. The low field signal of the ethylene C- β carbon in these compounds could be explained considering the shift additivities of methyl- and cyano-groups and assuming that the oxadiazol-5-yl-group causes a down field shift of about 10 ppm to the C- β carbon. This behaviour of the 1,2,4-oxadiazole ring is in contrast to that of the phenyl-group, which causes an upfield shift of about 10 ppm to C- β carbon in styrene [6]. In the coupled spectra of compounds **2** and **3** the signals of the C- β carbons at $\delta = 170.5$ and 160.9 ppm respectively become multiplets, with a 2J value equal to about 7 Hz [7].

In the mass spectra all the cycloadducts give the molecular ion M^+ with a moderate relative intensity and their fragmentation pattern is in agreement with their structure and with the pattern expected for the 1,2,4-oxadiazole ring system [8,9]. Thus, all the compounds give peaks corresponding to retro-1,3-cycloaddition with the cleavage of mesitronitrile oxide, or benzonitrile oxide for the compound **6**, from the molecular ion. Other prominent ion peaks are those corresponding to mesitronitrile oxide, at m/z 161, 160 and to MesCN_2^+ ion at m/z 159, as well as the ion at m/z 187 attributed to the mesityl-1,2,4-oxadiazolyl fragment. The compounds **4** and **5** also give the ion fragment $[M-58]^+$ with a very low intensity, which corresponds to acetone cleavage from the molecular ion and this peak provides evidence for the proposed regio-forms.

EXPERIMENTAL

Melting points were determined on a Kofler hot stage appara-

tus and are uncorrected. The ir spectra were recorded on a Perkin-Elmer 1430 spectrometer in potassium bromide disk. The ^1H nmr spectra were obtained with a Bruker AW-80 and a Varian VXR-300 spectrometers and the ^{13}C nmr spectra were obtained with a Varian CFT-20 and a Varian VXR-300 spectrometers. All spectra were recorded using tetramethylsilane (TMS) as internal standard in deuteriochloroform solutions. The mass spectra were obtained at 70 eV with a Hitachi-Perkin-Elmer RMU-6L and high resolution mass measurements were obtained with an AEI MS 30 mass spectrometers. Elemental analyses were performed with a Perkin-Elmer 240B CHN analyser. Silica gel (Merck 60 70-230 mesh) was used for the column chromatography.

Isopropylidenemalononitrile **1**, bp 80-82°, 6 torr, [10]; ^1H nmr: δ 2.30 (s), ^{13}C nmr: δ (ppm) 24.54 (CH_3), 86.2 (C- α), 111.9 (CN), 178.9 (C- β), and mesitronitrile oxide, mp 110-114° [11], were prepared according to the literature [10,11]. Benzonitrile oxide was prepared *in situ* by the reaction of benzohydroxymoyl chloride [12] and triethylamine.

General Procedure for the Cycloadditions of Isopropylidenemalononitrile **1** with Mesitronitrile Oxide.

Isopropylidenemalononitrile **1** (1 mmoles) and mesitronitrile oxide (1-3.5 mmoles) were refluxed in dry and ethanol free chloroform (3 ml) for 75-140 hours, until tlc control experiments did not show the presence of free mesitronitrile oxide. Evaporation of the solvent gave a yellowish residue, which was chromatographed on a silica gel column to afford the cycloadducts **2-5**. In some cases it was necessary the various fractions to be further chromatographed for one or more times. Mixtures of *n*-hexane-methylene chloride 50:50 to 20:80 as well as *n*-hexane-ethyl acetate 90:10 were used as eluants. Compounds **2-6** were recrystallized from a 9:1 *n*-hexane-methylene chloride mixture. The cycloaddition products are given in the way they appear from the column.

Reaction of Isopropylidenemalononitrile **1** with Mesitronitrile Oxide.

A solution of **1** (0.106 g, 1 mmoles) and mesitronitrile oxide (0.563 g, 3.5 mmoles) in dry and ethanol free chloroform (3 ml) was refluxed for 140 hours. After evaporation of the solvent the gummy residue was chromatographed (*n*-hexane-methylene chloride in varying proportions) to give compounds **4**, **3** and **2**.

3-Mesityl-5,5-dimethyl-4,4-bis-(3-mesityl-1,2,4-oxadiazol-5-yl)- Δ^2 -isoxazoline (**4**).

This compound was obtained as colorless crystals, (0.231 g, 39%), mp 132-135°; ir: 1610, 1565, 1550 cm^{-1} ; pmr: (300 MHz) δ 1.69 (s, 6H, CH_3 -5), 2.06 (s, 6H), 2.12 (s, 12H), 2.25 (s, 3H), 2.29 (s, 6H), 6.85 (s, 2H), 6.91 (s, 4H); cmr: (75 MHz) δ (ppm) 23.0 (CH_3 -5), 64.64 (C-4), 92.97 (C-5), 155.36 (C-3), 168.40 (C-3' oxd), 172.2 (C-5' oxd, where oxd refers to oxadiazole-ring); mesityl carbons: 20.17, 20.70, 20.74, 21.16, 122.75 and 124.90 (C-1), 128.72 and 129.34 (C-3, C-5), 137.89 and 138.23 (C-2, C-6), 139.60 and 140.18 (C-4); ms: m/z 589 (M^+ , 22), 574 (5), 531 (M^+ -58, 0.8) 430 (1), 429 (4), 428 (8), 270 (36), 269 (20), 268 (9), 267 (14), 225 (20), 187 (89), 161 (100), 160 (93), 159 (33), 145 (80), 130 (67), 103 (29), 91 (50), 77 (40).

Anal. Calcd. for $\text{C}_{36}\text{H}_{39}\text{N}_5\text{O}_3$: C, 73.32; H, 6.67; N, 11.88. Found: C, 72.97; H, 6.70; N, 11.74.

2-Methyl-1,1-bis-(3-mesityl-1,2,4-oxadiazol-5-yl)propene (**3**).

This compound was obtained as colorless crystals, (0.101 g, 24%), mp 122-123°; ir: 1610, 1580 cm^{-1} ; pmr: (80 MHz) δ 2.19 (s, 12H), 2.30 (s, 6H,

CH_3 - β), 2.32 (s, 6H), 6.95 (s, 4H); cmr: (20 MHz) δ (ppm) 24.65 ($^1\text{J} = 129.0$ Hz, $^3\text{J} = 4.0$ Hz, CH_3 - β), 109.37 (C- α), 160.88 ($^1\text{J} = 7$ Hz, C- β), 168.40 (C-3' oxd), 172.76 (C-5' oxd); mesityl carbons: 20.24, 21.21, 123.54 (C-1), 128.62 (C-3, C-5), 137.93 (C-2, C-6), 139.79 (C-4); ms: m/z 428 (M^+ , 62), 413 (75), 385 (22), 372 (2), 269 (50), 268 (21), 267 (17), 253 (42), 241 (15), 240 (15), 223 (16), 187 (83), 186 (50), 161 (33), 160 (92), 159 (58), 145 (100), 144 (58), 130 (83), 119 (42), 118 (17), 108 (17), 107 (17), 106 (17), 105 (50), 103 (50), 91 (83), 77 (67); exact mass. Calcd. for $\text{C}_{26}\text{H}_{28}\text{N}_4\text{O}_2$: 428.2212. Found: 428.2233.

Anal. Calcd. for $\text{C}_{26}\text{H}_{28}\text{N}_4\text{O}_2$: C, 72.87; H, 6.59; N, 13.08. Found: C, 72.96; H, 6.60; N, 13.12.

β,β -Dimethyl- α -(3-mesityl-1,2,4-oxadiazol-5-yl)acrylonitrile (**2**).

This compound was obtained as colorless crystals, (0.016 g, 6%), mp 74-76°; ir: 2220 (s) (CN), 1610, 1560 cm^{-1} ; pmr: (80 MHz) δ 2.19 (s, 6H), 2.32 (3H, s), 2.45 (3H, s, CH_3 - β), 2.54 (s, 3H, CH_3 - β), 6.95 (2H, s); cmr: (20 MHz) δ (ppm) 23.77 ($^1\text{J} = 129.5$ Hz, $^3\text{J} = 4.3$ Hz, CH_3 - β), 27.11 ($^1\text{J} = 128.9$ Hz, $^3\text{J} = 4.5$ Hz, CH_3 - β), 98.77 (C- α), 114.40 (CN), 168.54 (C-3' oxd), 170.54 (C-5' oxd and C- β , $^1\text{J} = 7.5$ Hz); mesityl carbons: 20.23, 21.20, 123.19 (C-1), 128.69 (C-3, C-5), 137.88 (C-2, C-6), 140.12 (C-4); ms: m/z 267 (M^+ , 55), 266 (10), 252 (38), 224 (27), 187 (6), 161 (7), 160 (49), 159 (100), 145 (15), 130 (21), 119 (3), 108 (16), 104 (4), 103 (7), 91 (12), 77 (13).

Anal. Calcd. for $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}$: C, 71.88; H, 6.41; N, 15.72. Found: C, 71.75; H, 6.30; N, 15.80.

Reaction of **1** (0.106 g, 1 mmoles) with mesitronitrile oxide (0.402 g, 2.5 mmoles), in dry chloroform, after refluxing for 120 hours and working up as above and after column chromatography, gave **4** (0.173 g, 29%), mp 128-131°, **3**, (0.075 g, 17%), mp 122-125°, and **2**, (0.116 g, 43%), mp 72-75°. All these compounds were identical (ir nmr, ms) with those isolated from the previous reaction.

Reaction of **1** (0.159 g, 1.5 mmoles) with mesitronitrile oxide (0.241 g, 1.5 mmoles), in dry chloroform (3 ml), after refluxing for 75 hours and working up as above and after column chromatography, gave compound **5** and compound **2** (0.17 g, 42%), mp 74-76°.

4-Cyano-3-mesityl-5,5-dimethyl-4-(3-mesityl-1,2,4-oxadiazol-5-yl)- Δ^2 -isoxazoline (**5**).

This compound was isolated as colorless crystals, (0.064 g, 10%), mp 122-125°; ir: 2240 (vw) (CN), 1610, 1555 cm^{-1} ; pmr: (300 MHz) δ 1.54 (s, 3H, CH_3 -5), 1.95 (s, 3H, CH_3 -5), 2.13 (s, 6H), 2.26 (s, 6H), 2.28 (s, 3H), 2.31 (s, 3H), 6.90 (s, 2H), 6.93 (s, 2H); cmr: (75 MHz) δ (ppm) 21.41 (CH_3 -5), 25.85 (CH_3 -5), 61.37 (C-4), 92.72 ($^1\text{J} = 4.5$ Hz, C-5), 112.63 (CN), 152.53 (C-3), 169.13 and 169.98 (C-3' oxd and C-5 oxd); mesityl carbons: 20.19, 20.70, 21.05, 21.23, 122.25 and 122.5 (C-1), 128.79 and 129.50 (C-3, C-5), 137.79 and 138.46 (C-2, C-6), 140.53 (C-4); ms: m/z 428 (M^+ , 8.5), 413 (2), 370 (M^+ -58, 0.5), 270 (3), 269 (16), 268 (12), 267 (9) 253 (49), 225 (30), 211 (36), 187 (14), 161 (50), 160 (100), 159 (38), 145 (22), 144 (27), 130 (22), 119 (16), 117 (19), 116 (14), 115 (22), 108 (20), 106 (8), 105 (13), 104 (10), 103 (14), 91 (42), 77 (25).

Anal. Calcd. for $\text{C}_{26}\text{H}_{28}\text{N}_4\text{O}_2$: C, 72.87; H, 6.58; N, 13.08. Found: C, 73.01; H, 6.62; N, 13.18.

Reaction of **2** with Mesitronitrile Oxide.

A solution of **2** (0.09 g, 0.34 mmole) and mesitronitrile oxide (0.027 g, 0.17 mmole) in dry chloroform (3 ml) was refluxed for 120 hours. After evaporation of the solvent the gummy residue was chromatographed on a silica gel column (eluted with *n*-hexane-ethyl acetate 90:10) to give:

a: A mixture of compounds **3** and **5** (0.02 g) which after a further chromatography column on silica gel (eluted with *n*-hexane-methylene chloride 50:50) gave **3**, (0.009 g, 6%), mp 122-125°, and **5** (0.005 g, 3%), mp 122-125°, both **3** and **5** being identical with those obtained from the previous reactions.

b: Starting compound **2** (0.07 g, 78%), had mp 74-76°.

β,β -Dimethyl- α -(3-phenyl-1,2,4-oxadiazol-5-yl)acrylonitrile (**6**).

To a stirred and refluxing solution of **1** (0.106 g, 1 mmole) and benzohydroxymoyl chloride (0.622 g, 4 mmole) in dry methylene chloride (2 ml) a solution of triethylamine (0.505 g, 5 mmole) in methylene chloride (3 ml) was slowly added (3 hours). The reaction mixture was refluxed for one hour more and after standing for 24 hours at 25°, washed twice with water and dried. After evaporation of the solvent the gummy residue was chromatographed on a silica gel column with a mixture of *n*-hexane-methylene chloride as eluant. From the various fractions eluted from the column the last one (0.1 g) was further chromatographed with the same eluant to give **6** (0.078 g, 35%), mp 114-116°; ir: 2220 (s) (CN), 1610, 1530 cm^{-1} ; pmr: (80 MHz) δ 2.71 (s, 3H), 2.82 (s, 3H), 7.64-7.84 (m, 3H), 8.24-8.44 (m, 2H); cmr: δ (ppm) 23.71 (CH_3), 27.15 (CH_3), 98.73 (C- α), 113.90 (CN), 168.65 (C-3' oxd), 170.61 (C-5' oxd and C- β); phenyl carbons: 126.27 (C-1), 127.59, 128.91, 131.53 (C-4); ms: m/z 225 ($M + \cdot$, 22), 119 (27), 118 (100), 108 (2), 107 (6), 106 (2), 105 (8), 104 (7), 103 (13), 91 (15), 77 (18).

Anal. Calcd. for $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}$: C, 69.32; H, 4.92; N, 18.66. Found: C, 69.36; H, 4.72; N, 18.73.

Bis-(3-mesityl-1,2,4-oxadiazol-5-yl)methane (**7**).

A solution of malononitrile (0.066 g, 1 mmole) and mesitonitrile oxide (0.322 g, 2 mmole) in dry chloroform (3 ml) was refluxed for 40 hours. After evaporation of the solvent the residue was treated with *n*-hexane to give **7**, (0.25 g, 65%), mp 152-154° (*n*-hexane-ether); ir (Nujol): 1610, 1590, 1570 cm^{-1} ; pmr: (80 MHz) δ 2.07 (s, 12H), 2.13 (s, 6H), 4.85 (s, 2H), 6.95 (s, 4H); cmr: (20 MHz) δ (ppm) 25.22 ($J = 134.7$ Hz, CH_2), 168.87 (C-3' oxd), 171.70 (C-5' oxd); mesityl carbons: 20.15, 21.19, 123.12 (C-1), 128.65 (C-3, C-5), 137.85 (C-2, C-6), 140.06 (C-4); ms: m/z 388 ($M + \cdot$, 31), 373 (1), 229 (41), 228 (11), 227 (4), 187 (95), 161 (62), 160 (100), 159 (50), 145 (52), 130 (21), 119 (13), 104 (9), 103 (13), 91 (29), 77 (19).

Anal. Calcd. for $\text{C}_{23}\text{H}_{24}\text{N}_4\text{O}_2$: C, 71.11; H, 6.23; N, 14.42. Found: C, 71.07; H, 6.20; N, 14.42.

(3-Mesityl-1,2,4-oxadiazol-5-yl)acetonitrile (**8**).

The mother liquor and filtrates of the previous reaction were combined and the solvent was evaporated *in vacuo* giving a yellowish oil. This was chromatographed on a silica gel column (eluted with a mixture of *n*-hexane-methylene chloride 20:80) to give **8**, (0.04 17%), mp 54-56°; ir (Nujol): 2260 (w) (CN), 1620, 1570 cm^{-1} ; pmr: δ 2.16 (s, 6H), 2.30 (s, 3H), 4.11 (s, 2H), 6.93 (s, 2H); ms: m/z 227 ($M + \cdot$, 37), 226 (16), 212 (4), 187 (43), 161 (13), 160 (70), 159 (100), 145 (34), 130 (16), 119 (6), 118 (6), 117 (13), 116 (10), 115 (14), 105 (8), 104 (7), 103 (4), 91 (20), 77 (22).

Anal. Calcd. for $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}$: C, 68.70; H, 5.77; N, 18.49. Found: C, 68.47; H, 5.86; N, 18.21.

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