

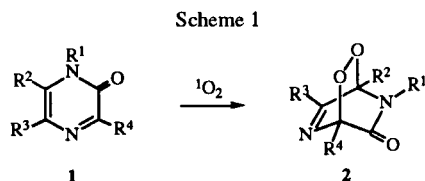
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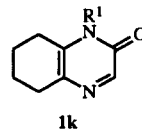
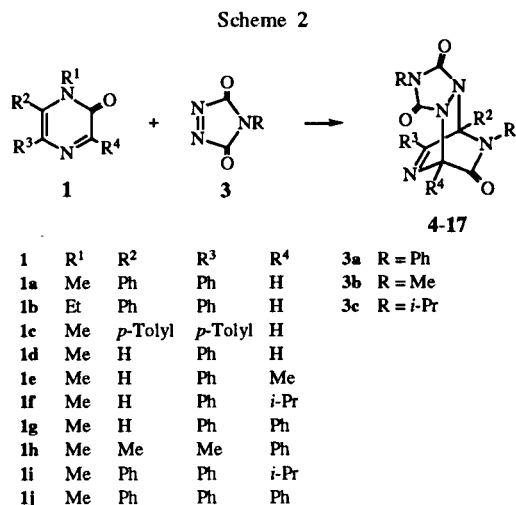
The reaction of 2(1*H*)-pyrazinones **1** and 1,2,4-triazoline-3,5-diones **3** was investigated by comparing that of **1** with singlet oxygen. 2(1*H*)-Pyrazinones **1** reacted in Diels-Alder fashion with 1,2,4-triazoline-3,5-diones **3** to afford [4+2]-adducts **4-17** in high yields.

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It is well known that triazolinediones undergo the same classes of reactions as singlet oxygen: these species react with conjugated dienes to afford Diels-Alder adducts, with various mono-alkenes in an ene fashion to afford *N*-allylurazoles, and with some alkenes to afford products corresponding to [2+2] cycloaddition, diazetidene derivatives [1]. A set of these three types of reactions also have been reported by singlet oxygen [2]. In the course of our studies on the photochemical reactivities of cyclic conjugated nitrogen-carbonyl systems such as 2(1*H*)-pyrimidiones [3] and 2(1*H*)-pyrazinones **1** [3a,4], we found that 2-(1*H*)-pyrazinones **1** reacted with singlet oxygen in a Diels-Alder fashion to give the corresponding pyrazinone 3,6-endoperoxides **2** [4a-c] (Scheme 1). We have been attracted to the reaction of 2(1*H*)-pyrazinones **1** with 1,2,4-triazoline-3,5-diones **3** by comparing the reactivity of **1** and singlet oxygen. In the present paper, we report the results of these reactions.



When 1-methyl-5,6-diphenyl-2(1*H*)-pyrazinone **1a** was treated with an equivalent of 4-phenyl-1,2,4-triazoline-3,5-dione **3a** in dichloromethane under argon at room temperature, the typical red color of **3a** disappeared within several minutes and chromatographic purification of the product afforded the [4+2]-adduct **4** of **1a** and **3a** in 98% yield. The ir spectrum of **4** shows absorptions at 1785, 1725 (sh) and 1715 cm^{-1} due to three amide carbonyl groups. The ^1H nmr spectrum of **4** displays two singlets at δ 2.37 (3H) and 6.19 (1H), which are assigned to *N*-methyl and bridgehead protons, respectively, in addition to aromatic protons. The ^{13}C nmr spectrum of **4** shows the *N*-methyl carbon at δ 28.8 (q), two bridgehead carbons at δ 72.6 (d) and 81.9 (s), imino carbon at δ 165.8 (s) and three amide carbonyl carbons at δ 154.8 (s), 155.0 (s) and 174.5 (s), respectively, in addition to aromatic carbons. A [4+2]-adduct **4** was also



obtained in 98 and 55% yields, respectively when the reaction of **1a** and **3a** was carried out in benzene and methanol. The [4+2]-adduct **4** thus obtained was converted back to the starting 2(1*H*)-pyrazinone **1a** when a solution of **4** in acetonitrile was irradiated in a Pyrex tube with a high-pressure mercury lamp under argon for 5 hours. In a similar manner, 2(1*H*)-pyrazinones **1** reacted in a Diels-Alder fashion with 1,2,4-triazoline-3,5-diones **3** to give [4+2]-adducts **5-17** in good yields (Table). It was observed that substituents at the 3, 5, and 6 positions of 2(1*H*)-pyrazinones **1** affected the yields and formation of the [4+2]-adducts. 3-Phenyl-2(1*H*)-pyrazinone **1g** gave a better yield than 3-isopropyl-2(1*H*)-pyrazinone **1f**, probably due to the steric effect. More than 80% of the starting pyrazinones were recovered even when 3,5,6-trisubstituted-2(1*H*)-pyrazinones **1i-j** were heated to reflux with 4-phenyl-**3a** or 4-methyl-1,2,4-triazoline-3,5-dione **3b** in dichloromethane. The corresponding [4+2]-adduct was not isolated by treatment of the fused ring compound, 1-methyl-

Table
Yield of [4+2]-Adducts 4-17 [a]

Product	R	R ¹	R ²	R ³	R ⁴	Yield (%) [b]
4	Ph	Me	Ph	Ph	H	98
4						98 [c]
4						55[d]
5	Me	Me	Ph	Ph	H	100
6	<i>i</i> -Pr	Me	Ph	Ph	H	100
7	Ph	Et	Ph	Ph	H	100
8	Ph	Me	<i>p</i> -Tolyl	<i>p</i> -Tolyl	H	93
9	Me	Me	<i>p</i> -Tolyl	<i>p</i> -Tolyl	H	100
10	Ph	Me	H	Ph	H	88
11	Me	Me	H	Ph	H	84 [e]
12	Ph	Me	H	Ph	Me	75
13	Me	Me	H	Ph	Me	100
14	Ph	Me	H	Ph	<i>i</i> -Pr	41
15	Ph	Me	H	Ph	Ph	94
16	Me	Me	H	Ph	Ph	96
17	Me	Me	Me	Me	Ph	73 [f]

[a] Reaction conditions: Room Temperature in dichloromethane for 10-30 minutes. [b] Isolated yield. [c] Room Temperature in benzene. [d] Room Temperature in methanol for 1 hour. [e] Reaction time: 1 hour. [f] Reaction time: 2 hours.

5,6,7,8-tetrahydroquinoxalin-2(1*H*)-one **1k** with 4-phenyl-1,2,4-triazoline-3,5-dione **3a**, although the starting materials disappeared. Furthermore, 1-methyl-5,6-diphenyl-2(1*H*)-pyrazinone **1a** did not undergo a [4+2] cycloaddition reaction to the acyclic diazene, diethyl azodicarboxylate and any cycloaddition reactions [5] to alkenes such as methacrylonitrile, methyl methacrylate, *N*-phenylmaleimide, and styrene.

In summary, the similarity of 1,2,4-triazoline-3,5-dione and singlet oxygen in dienophilic reactivity, *i.e.* [4+2] cycloaddition [6] was shown in the reaction of 2(1*H*)-pyrazinones **1** with 1,2,4-triazoline-3,5-diones **3**.

EXPERIMENTAL

Melting points were measured with Yanako micro melting point apparatus (MP-3J) and are uncorrected. The ir spectra were recorded on a Hitach 260-30 spectrophotometer (in potassium bromide and are in cm⁻¹). The ¹H and ¹³C nmr spectra were run on a JEOL FX 100 spectrometer (100 MHz) in deuteriumchloroform using TMS as an internal standard (δ in ppm, *J* in Hz). Chromatographic purifications were carried out on a silica gel column (flash chromatography: Wakogel C-300 or Merck kieselgel 60).

Starting Materials 1.

2(1*H*)-Pyranzinones **1a-d**, **1i-k** were prepared according to methods previously described in the literatures [4a,5a] and 2(1*H*)-pyrazinones **1e-h** were prepared by a modification of this method.

1,3-Dimethyl-5-phenyl-2(1*H*)-pyrazinone (1e).

This compound had mp 100-101°; ir: ν 1635 (CO); ¹H nmr: δ 2.53 (s, 3H), 3.55 (s, 3H), 7.23-7.50 (m, 4H), 7.60-7.78 (m, 2H);

¹³C nmr: δ 21.0 (q), 37.5 (q), 123.9 (d), 124.9 (d), 127.7 (d), 132.1 (d), 132.1 (s), 135.8 (s), 155.8 (s), 156.8 (s).

Anal. Calcd. for C₁₂H₁₂N₂O (200.23): C, 71.98; H, 6.04; N, 13.99. Found: C, 72.32; H, 6.01; N, 13.74.

1-Methyl-5-phenyl-3-isopropyl-2(1*H*)-pyrazinone (1f).

This compound had mp 107-108°; ir: ν 1630 (CO); ¹H nmr: δ 1.35 (d, 6H, *J* = 6.8), 3.55 (sept, 1H, *J* = 6.8), 3.57 (s, 3H), 7.21-7.50 (m, 4H), 7.64-7.84 (m, 2H); ¹³C nmr: δ 20.1 (q), 30.1 (d), 37.5 (q), 123.4 (d), 124.7 (d), 127.6 (d), 128.7 (d), 131.7 (s), 136.1 (s), 155.2 (s), 163.4 (s).

Anal. Calcd. for C₁₄H₁₆N₂O (228.28): C, 73.66; H, 7.06; N, 12.27. Found: C, 73.57; H, 7.08; N, 12.31.

3,5-Diphenyl-1-methyl-2(1*H*)-pyrazinone (1g).

This compound had mp 183-184°; ir: ν 1635 (CO); ¹H nmr: δ 3.62 (s, 3H), 7.24-7.55 (m, 7H), 7.77-7.88 (m, 2H), 8.42-8.53 (m, 2H); ¹³C nmr: δ 38.1 (q), 124.9 (d), 127.8 (d), 127.9 (d), 128.7 (d), 129.1 (d), 129.9 (d), 132.5 (s), 135.8 (s), 136.0 (s), 151.0 (s), 155.1 (s).

Anal. Calcd. for C₁₇H₁₄N₂O (262.30): C, 77.84; H, 5.38; N, 10.68. Found: C, 77.58; H, 5.33; N, 10.59.

3-Phenyl-1,5,6-trimethyl-2(1*H*)-pyrazinone (1h).

This compound had mp 123-125°; ir: ν 1640 (CO); ¹H nmr: δ 2.31 (s, 3H), 2.39 (s, 3H), 3.57 (s, 3H), 7.33-7.53 (m, 3H), 8.21-8.36 (m, 2H); ¹³C nmr: δ 16.3 (q), 28.6 (q), 31.5 (q), 127.8 (d), 128.7 (d), 129.0 (d), 129.2 (s), 133.5 (s), 136.5 (s), 147.7 (s), 155.5 (s).

Anal. Calcd. for C₁₃H₁₄N₂O (214.26): C, 72.85; H, 6.58; N, 13.05. Found: C, 72.90; H, 6.54; N, 12.85.

Reaction of 2(1*H*)-Pyrazinones **1** and 1,2,4-Triazoline-3,5-diones **3**.

Typical Procedure.

A mixture of the 2(1*H*)-pyrazinone **1** (1 mmole) and 1,2,4-triazoline-3,5-dione **3** (1.1 mmoles) in dichloromethane (or benzene, methanol) (30 ml) was stirred for 10 minutes to 2 hours at room temperature until the typical red color of the 1,2,4-triazoline-3,5-dione **3** disappeared. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene-ethyl acetate (4-1) to yield [4+2]-adducts **4-17**.

[4+2]-Adduct 4.

This compound had mp 145-146°; ir: ν 1785, 1725 (sh), 1715 (CO); ¹H nmr: δ 2.37 (s, 3H), 6.19 (s, 1H), 7.19-7.55 (m, 15H); ¹³C nmr: δ 28.8 (q), 72.6 (d), 81.9 (s), 125.6 (d), 127.5 (d), 127.8 (s), 128.1 (d), 128.3 (d), 128.8 (d), 128.9 (d), 129.1 (s), 130.5 (s), 130.6 (d), 131.2 (d), 132.8 (s), 154.8 (s), 155.0 (s), 165.8 (s) and 174.5 (s).

Anal. Calcd. for C₂₅H₁₉N₅O₃ (437.44): C, 68.64; H, 4.38; N, 16.01. Found: C, 68.66; H, 4.43; N, 15.80.

[4+2]-Adduct 5.

This compound had mp 107-109°; ir: ν 1780, 1715 (CO); ¹H nmr: δ 2.34 (s, 3H), 2.97 (s, 3H), 6.74 (s, 1H), 7.18-7.55 (m, 10H); ¹³C nmr: δ 26.1 (q), 28.6 (q), 72.3 (d), 81.4 (s), 127.5 (d), 127.8 (s), 128.0 (d), 128.2 (d), 128.8 (d), 130.6 (d), 131.1 (d), 132.8 (s), 156.0 (s), 156.4 (s), 165.8 (s), 174.1 (s).

Anal. Calcd. for C₂₀H₁₇N₅O₃ (375.38): C, 63.99; H, 4.56; N, 18.66. Found: C, 63.69; H, 4.55; N, 18.59.

[4+2]-Adduct 6.

This compound had mp 130-131°; ir: ν 1780, 1715 (CO); ^1H nmr: δ 1.24 (d, 3H, $J = 6.8$), 1.27 (d, 3H, $J = 6.8$), 2.33 (s, 3H), 4.16 (sept, 1H, $J = 6.8$), 6.46 (s, 1H), 7.26-7.53 (m, 10H); ^{13}C nmr: δ 19.1 (q), 19.3 (q), 28.6 (q), 45.8 (d), 72.5 (d), 81.6 (s), 127.4 (d), 128.0 (d), 128.5 (d), 130.5 (d), 131.0 (d), 131.2 (d), 132.9 (s), 156.0 (s), 156.3 (s), 165.9 (s), 173.9 (s).

Anal. Calcd. for $\text{C}_{22}\text{H}_{21}\text{N}_5\text{O}_3$ (403.43): C, 65.50; H, 5.25; N, 17.36. Found: C, 65.21; H, 5.28; N, 17.26.

[4+2]-Adduct 7.

This compound had mp 152-153°; ir: ν 1780, 1730 (sh), 1715 (CO); ^1H nmr: δ 0.87 (t, 3H, $J = 7.3$), 2.59 (dq, A of ABX₃, 1H, $J = 7.3$, 14.3), 3.20 (dq, B of ABX₃, 1H, $J = 7.3$, 14.3), 6.56 (s, 1H), 7.18-7.58 (m, 15H); ^{13}C nmr: δ 3.8 (q), 36.6 (t), 72.8 (d), 82.1 (s), 125.6 (d), 127.1 (s), 127.3 (d), 128.1 (d), 128.7 (d), 128.9 (d), 129.1 (d), 130.5 (s), 130.7 (d), 131.1 (d), 131.4 (d), 133.0 (s), 154.8 (s), 155.1 (s), 165.5 (s), 174.8 (s).

Anal. Calcd. for $\text{C}_{26}\text{H}_{21}\text{N}_5\text{O}_3$ (451.47): C, 69.17; H, 4.69; N, 15.51. Found: C, 68.91; H, 4.68; N, 15.50.

[4+2]-Adduct 8.

This compound had mp 162-163°; ir: ν 1780, 1730 (sh), 1720 (CO); ^1H nmr: δ 2.35 (s, 3H), 2.37 (s, 3H), 2.39 (s, 3H), 6.55 (s, 1H), 7.04-7.40 (m, 13H); ^{13}C nmr: δ 21.3 (q), 21.4 (q), 28.6 (q), 72.4 (d), 81.7 (s), 124.8 (s), 125.4 (d), 128.1 (d), 128.8 (d), 129.0 (d), 130.0 (s), 130.5 (s), 131.1 (d), 140.8 (s), 141.6 (s), 154.6 (s), 155.0 (s), 165.8 (s), 174.4 (s).

Anal. Calcd. for $\text{C}_{27}\text{H}_{23}\text{N}_5\text{O}_3$ (465.49): C, 69.66; H, 4.98; N, 15.04. Found: C, 69.77; H, 4.92; N, 14.85.

[4+2]-Adduct 9.

This compound had mp 164-165°; ir: ν 1785, 1720 (CO); ^1H nmr: δ 2.33 (s, 3H), 2.35 (s, 3H), 2.41 (s, 3H), 2.96 (s, 3H), 6.43 (s, 1H), 7.03-7.34 (m, 8H); ^{13}C nmr: δ 21.3 (q), 21.4 (q), 26.0 (q), 28.5 (q), 72.3 (d), 81.3 (s), 124.9 (s), 128.1 (d), 128.7 (d), 128.8 (d), 130.0 (s), 131.0 (d), 140.8 (s), 141.6 (s), 156.0 (s), 156.4 (s), 165.9 (s), 174.0 (s).

Anal. Calcd. for $\text{C}_{22}\text{H}_{21}\text{N}_5\text{O}_3$ (403.43): C, 65.50; H, 5.25; N, 17.36. Found: C, 65.67; H, 5.30; N, 17.06.

[4+2]-Adduct 10.

This compound had mp 194-196°; ir: ν 1785, 1720, 1705 (CO); ^1H nmr: δ 3.15 (s, 3H), 6.38 (s, 1H), 6.40 (s, 1H), 7.19-7.69 (m, 8H), 7.88-7.99 (m, 2H); ^{13}C nmr: δ 31.8 (q), 62.7 (d), 72.5 (d), 125.3 (d), 127.2 (d), 129.0 (d), 129.2 (d), 129.4 (d), 130.5 (s), 130.9 (s), 133.5 (d), 154.9 (s), 165.5 (s), 170.5 (s).

Anal. Calcd. for $\text{C}_{19}\text{H}_{15}\text{N}_5\text{O}_3$ (361.35): C, 63.15; H, 4.18; N, 19.38. Found: C, 62.83; H, 4.21; N, 19.14.

[4+2]-Adduct 11.

This compound had mp 202-204°; ir: ν 1785, 1710 (CO); ^1H nmr: δ 2.96 (s, 3H), 3.13 (s, 3H), 6.29 (s, 1H), 6.31 (s, 1H), 7.41-7.63 (m, 3H), 7.85-7.92 (m, 2H); ^{13}C nmr: δ 26.0 (q), 31.6 (q), 66.9 (d), 72.3 (d), 127.1 (d), 129.3 (d), 130.9 (s), 133.3 (d), 156.1 (s), 165.6 (s), 170.3 (s).

Anal. Calcd. for $\text{C}_{14}\text{H}_{13}\text{N}_5\text{O}_3$ (299.28): C, 56.18; H, 4.38; N, 23.40. Found: C, 55.91; H, 4.45; N, 23.30.

[4+2]-Adduct 12.

This compound had mp 125-127°; ir: ν 1785, 1705 (CO); ^1H nmr: δ 2.39 (s, 3H), 3.16 (s, 3H), 6.38 (s, 1H), 7.23-7.68 (m,

8H), 7.87-7.98 (m, 2H); ^{13}C nmr: δ 18.1 (q), 32.3 (q), 62.6 (d), 79.3 (s), 125.5 (d), 127.1 (d), 128.8 (d), 129.2 (d), 129.4 (d), 130.5 (s), 131.1 (s), 133.3 (d), 154.2 (s), 167.5 (s), 169.4 (s).

Anal. Calcd. for $\text{C}_{20}\text{H}_{17}\text{N}_5\text{O}_3$ (375.38): C, 63.90; H, 4.38; N, 18.66. Found: C, 63.85; H, 4.21; N, 18.84.

[4+2]-Adduct 13.

This compound had mp 202-204°; ir: ν 1775, 1705 (CO); ^1H nmr: δ 2.33 (s, 3H), 2.95 (s, 3H), 3.13 (s, 3H), 6.30 (s, 1H), 7.40-7.68 (m, 3H), 7.85-7.95 (m, 2H); ^{13}C nmr: δ 17.9 (q), 25.8 (q), 32.0 (q), 65.8 (d), 78.9 (s), 127.0 (d), 129.2 (d), 131.0 (s), 133.1 (d), 155.0 (s), 155.5 (s), 167.5 (s), 169.2 (s).

Anal. Calcd. for $\text{C}_{15}\text{H}_{15}\text{N}_5\text{O}_3$ (313.31): C, 57.50; H, 4.83; N, 22.35. Found: C, 57.21; H, 4.82; N, 22.39.

[4+2]-Adduct 14.

This compound had mp 176-177°; ir: ν 1775, 1705, 1695 (CO); ^1H nmr: δ 1.42 (d, 3H, $J = 6.8$), 1.43 (d, 3H, $J = 6.8$), 3.13 (s, 3H), 3.38 (sept, 1H, $J = 6.8$), 6.47 (s, 1H), 7.25-7.65 (m, 8H), 7.90-8.04 (m, 2H); ^{13}C nmr: δ 17.0 (q), 17.3 (q), 29.4 (d), 32.4 (q), 65.6 (d), 83.8 (s), 125.5 (d), 127.1 (d), 128.8 (d), 129.2 (d), 129.3 (d), 130.7 (s), 131.2 (s), 133.2 (d), 152.6 (s), 155.0 (s), 165.9 (s), 171.2 (s).

Anal. Calcd. for $\text{C}_{22}\text{H}_{21}\text{N}_5\text{O}_3$ (403.43): C, 65.50; H, 5.25; N, 17.36. Found: C, 65.89; H, 5.50; N, 17.08.

[4+2]-Adduct 15.

This compound had mp 185-187°; ir: ν 1790, 1735, 1700 (CO); ^1H nmr: δ 3.23 (s, 3H), 6.46 (s, 1H), 7.11-7.35 (m, 6H), 7.45-7.66 (m, 5H), 8.01-8.15 (m, 4H); ^{13}C nmr: δ 32.4 (q), 66.8 (d), 82.0 (s), 125.3 (d), 127.3 (d), 127.8 (d), 129.0 (d), 129.3 (d), 129.5 (d), 130.4 (s), 130.6 (s), 131.3 (s), 133.4 (d), 153.8 (s), 154.5 (s), 166.8 (s), 168.2 (s).

Anal. Calcd. for $\text{C}_{25}\text{H}_{19}\text{N}_5\text{O}_3$ (437.44): C, 68.64; H, 4.38; N, 16.01. Found: C, 68.95; H, 4.26; N, 15.88.

[4+2]-Adduct 16.

This compound had mp 175-177°; ir: ν 1785, 1720, 1700 (CO); ^1H nmr: δ 2.81 (s, 3H), 3.16 (s, 3H), 6.35 (s, 1H), 7.35-7.66 (m, 6H), 7.96-8.11 (m, 4H); ^{13}C nmr: δ 25.8 (q), 32.3 (q), 66.5 (d), 81.6 (s), 124.9 (d), 127.2 (d), 127.7 (d), 129.2 (d), 129.3 (d), 129.5 (d), 130.7 (s), 131.3 (s), 133.3 (d), 155.2 (s), 155.7 (s), 166.9 (s), 168.0 (s).

Anal. Calcd. for $\text{C}_{20}\text{H}_{17}\text{N}_5\text{O}_3$ (375.38): C, 63.99; H, 4.56; N, 18.66. Found: C, 63.63; H, 4.49; N, 18.31.

[4+2]-Adduct 17.

This compound had mp 189° (dec); ir: ν 1770, 1720, 1700 (CO); ^1H nmr: δ 2.25 (s, 3H), 2.29 (s, 3H), 2.87 (s, 3H), 3.02 (s, 3H), 7.40-7.51 (m, 3H), 7.85-7.99 (m, 2H); ^{13}C nmr: δ 15.8 (q), 20.8 (q), 25.7 (q), 26.9 (q), 73.9 (s), 79.7 (s), 127.5 (d), 129.2 (d), 129.4 (d), 130.8 (s), 154.2 (s), 154.9 (s), 167.2 (s), 173.4 (s).

Anal. Calcd. for $\text{C}_{16}\text{H}_{17}\text{N}_5\text{O}_3$ (327.34): C, 58.71; H, 5.23; N, 21.39. Found: C, 59.00; H, 5.21; N, 21.10.

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