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PHOTOCHEMISTRY OF AN α,β-UNSATURATED γ,δ-EPOXY NITRILE

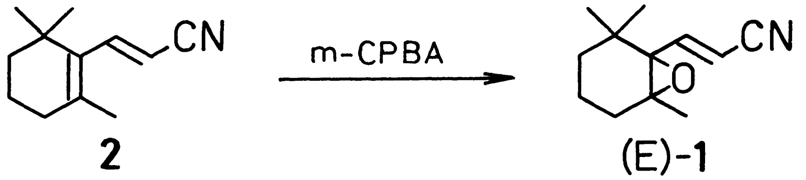
Keitaro ISHII and Masanori SAKAMOTO*
Meiji College of Pharmacy,
1-35-23 Nozawa, Setagaya-ku, Tokyo 154

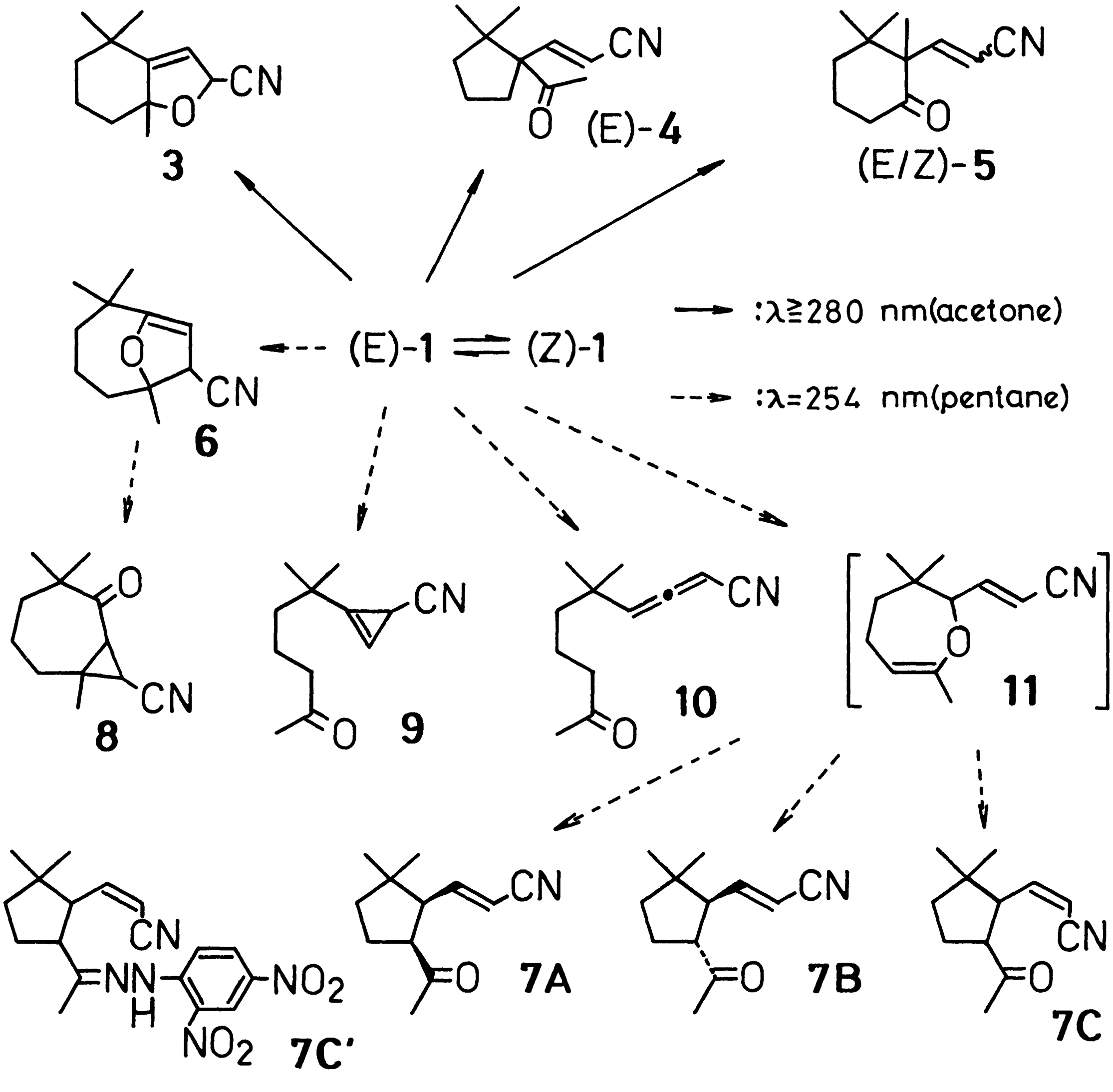
On $^1\pi,\pi^*$-excitation (λ=254 nm, pentane), α,β-unsaturated γ,δ-epoxy nitrile showed selective product formation via carbonyl ylide and carbene intermediates; (E/Z)-isomerization and C(γ),O-cleavage of the oxirane, which are triplet processes, did not occur.

Photochemical reactions of γ,δ-epoxy enones have been studied in great detail.[1) From these studies, it has been known that, on $^1n,\pi^*$-excitation ($\lambda \geq 347$ nm), epoxy enones undergo (E/Z)-isomerization and/or product formation via selective C(γ),O-cleavage of the oxirane. However, $^1\pi,\pi^*$-excitation (λ=254 nm) of epoxy enones gives a complex mixture of photoproducts. Since the n,π^*-state of the carbonyl group lies lower than the π,π^*-state, the products are formed not only via C(γ),C(δ)-cleavage and the carbene intermediate but also via C(γ),O-cleavage and (E/Z)-isomerization. We now report photochemical reactions of 3-(2,6,6-trimethyl-1,2-epoxycyclohexyl)acrylonitrile (1) which, because of the symmetry of the cyano group, does not have a low lying n,π^*-state.[2)

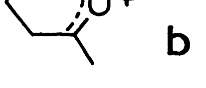
Compound 1 was prepared from dienenitrile 2[3) in 81% yield by epoxidation with m-chloroperbenzoic acid. Irradiation of an acetone solution of (E)-1 with a high pressure mercury lamp through a Pyrex filter ($\lambda \geq 280$ nm; 88% conversion) under argon at room temperature gave the following products:[4) (Z)-1(10%), 3(21%),[5) (E)-4(8%), (E)-5(21%), and (Z)-5(15%). On the other hand, irradiation of a solution of (E)-1 in pentane with a low pressure mercury lamp (λ=254 nm; 86% conversion) under argon at room temperature gave the following products:[4) 6(6%),[5) 7A(23%), 7B(8%), 7C(5%),[5) 8(10%),[5) 9(18%), and 10(2%).

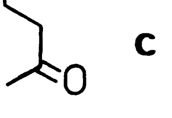
On triplet sensitization ($\lambda \geq 280$ nm, acetone) of nitrile (E)-1, the similar types of photoproducts are formed as on triplet sensitization of the corresponding α,β-unsaturated γ,δ-epoxy ester,[6) undergoing (E/Z)-isomerization of the side chain ((Z)-1) and C(γ),O-cleavage ((E)-1 → a) leading to 3, (E)-4, and (E/Z)-5. Meanwhile, on $^1\pi,\pi^*$-excitation (λ=254 nm, pentane), (E)-1 undergoes C(γ),C(δ)-cleavage of the oxirane leading to carbonyl ylide b and carbene c. The carbonyl ylide b reacts to enolethers 6 and 11 followed by a 1,3-sigmatropic rearrangement leading to 8 and 7A-C, respectively.[6) The carbene intermediate c, showing typical behavior of vinyl carbenes,[1,7) undergoes addition to the adjacent double bond furnishing cycolopropene 9 and a 1,2-H-shift to allene 10. On $^1\pi,\pi^*$-excitation of (E)-1, however, (E/Z)-isomerization of the side chain and transformation via


CN
m-CPBA
2
O
CN
(E)-1


CN
O
3
CN
O
(E)-4
CN
O
(E/Z)-5
O
CN
6
(E)-1
(Z)-1
:λ≧280 nm(acetone)
:λ=254 nm(pentane)
O
CN
8
CN
O
9
CN
O
10
CN
O
11
CN
NH
H
NO2
NO2
7C'
CN
O
7A
CN
O
7B
CN
CN
O
7C


CN
O
a


CN
O+
b


CN
O
c

C(γ),O-bond cleavage of the oxirane ((E)-1 ➞ a) do not occur as observed on $^1\pi,\pi^*$-excitation of γ,δ-epoxy enones1) and corresponding ester.6) These results suggest clearly that the formations of the carbonyl ylide and carbene intermediates occur from singlet state and (E/Z)-isomerization and cleavage of C(γ),O-bond from triplet state.

Characterization of 1 and 3-10 is as follows;

(E)-1: IR (neat) 2220 and 1630 cm^{-1}; ^{1}H-NMR8) 0.91, 1.11, and 1.14 (9H, 3s), 5.53 (1H, d, J=16 Hz), and 6.94 (1H, d, J=16 Hz); ^{13}C-NMR 20.4, 25.7 (3q, 2q at 25.7), 16.8, 29.8, 35.6 (3t), 102.8, 150.9 (2d), and 33.5, 66.5, 70.9, 117.2 (4s).

(Z)-1: IR (neat) 2220 and 1625 cm^{-1}; ^{1}H-NMR 1.05, 1.10, 1.25 (9H, 3s), 5.53 (1H, d, J=12 Hz), and 6,59 (1H, d, J=12 Hz); ^{13}C-NMR 21.4, 25.5, 25.8 (3q), 16.8, 29.5, 35.2 (3t), 102.3, 149.6 (2d), and 34.2, 64.9, 70.6, 116.1 (4s).

3: IR (neat) 1645 cm^{-1}; ^{1}H-NMR 1.11, 1.17, 1.52 (9H, 3s), 5.17 (1H, d, J=2 Hz), and 5.30 (1H, d, J=2 Hz); ^{13}C-NMR 25.5, 25.8, 30.3 (3q), 20.1, 40.9 (3t, 2t at 40.9), 69.2, 112.1 (2d), and 35.1, 90.4, 118.7, 158.8 (4s).

(E)-4: IR (neat) 2225, 1700, and 1625 cm^{-1}; ^{1}H-NMR 0.99, 1.02, 2.12 (9H, 3s), 5.30 (1H, d, J=17 Hz), and 7.03 (1H, d, J=17 Hz); ^{13}C-NMR 24.9, 30.5 (3q, 2q at 24.9), 19.9, 29.7, 39.3 (3t), 100.4, 156.2 (2d), and 47.1, 67.8, 117.1, 207.5 (4s).

(E)-5: IR (CHCl$_3$) 2225, 1705, and 1615 cm^{-1}; ^{1}H-NMR 0.91, 0.97, 1.21 (9H, 3s), 2.32-2.50 (2H, m), 5.29 (1H, d, J=17 Hz), and 7.16 (1H, d, J=17 Hz).

(Z)-5: IR (neat) 2215 and 1705 cm^{-1}; ^{1}H-NMR 1.00, 1.54 (9H, 3s, 2s at 1.00), 2.40-2.60 (2H, m), 5.55 (1H, d, J=12 Hz), and 6.82 (1H, d, J=12 Hz); ^{13}C-NMR 16.6, 24.1, 24.5 (3q), 22.1, 35.4, 37.0 (3t), 100.3, 154.1 (2d), and 42.0, 59.7, 115.9, 210.8 (4s).

6: IR (neat) 2240 and 1635 cm^{-1}; ^{1}H-NMR 1.04, 1.16, 1.55 (9H, 3s), 3.90 (1H, d, J=2 Hz), and 4.95 (1H, d, J=2 Hz); ^{13}C-NMR 23.1, 24.5, 24.6 (3q), 23.4, 37.9, 40.0 (3t), 41.5, 101.0 (2d), and 39.5, 94.3, 118.3, 168.8 (4s).

7A9): IR (neat) 2230, 1715, and 1635 cm^{-1}; ^{1}H-NMR 0.89, 1.03, 2.15 (9H, 3s), 2.55 (1H, t, J=9 Hz), 2.83-3.13 (1H, m), 5.35 (1H, d, J=16 Hz), and 6.55 (1H, dd, J_1=16 Hz, J_2=9 Hz); ^{13}C-NMR 22.6, 27.4, 29.6 (3q), 26.5, 40.6 (2t), 55.6, 101.6, 154.8 (4d, 2d at 55.6), and 44.4, 117.1, 208.4 (3s).

7B10): IR (neat) 2225, 1710, and 1630 cm^{-1}; ^{1}H-NMR 0.93, 1.06, 2.09 (9H, 3s), 2.17-2.27 (1H, m), 2.54 (1H, dd, J_1=11.2 Hz, J_2=8 Hz), 5.33 (1H, d, J=16.6 Hz), and 6.53 (1H, dd, J_1=16.6 Hz, J_2=11.2 Hz).

7C'11): IR (CHCl$_3$) 3330, 2230, and 1625 cm^{-1}; ^{1}H-NMR 0.97, 1.16, 2.08 (9H, 3s), 2.80-3.25 (2H, m), 5.39 (1H, d, J=11 Hz), and 6.32 (1H, t, J=11 Hz); ^{13}C-NMR 15.0, 22.9, 28.1 (3q), 28.2, 40.7 (2t), 52.5, 55.1, 101.4, 154.9 (4d), and 45.3, 116.4, 157.7 (3s).

8: IR (CHCl$_3$) 2240 and 1710 cm^{-1}; ^{1}H-NMR 0.99, 1.11, 1.17 (9H, 3s), 2.18 (1H, d, J=8 Hz), and 2.58 (1H, d, J=8 Hz); ^{13}C-NMR 19.2, 22.5, 28.7 (3q), 23.4, 33.7, 40.4 (3t), 20.3, 41.0 (2d), and 28.7, 48.4, 117.4, 203.4 (4s).

9: IR (neat) 2230, 1785, and 1720 cm^{-1}; ^{1}H-NMR 1.26, 2.14 (9H, 3s, 2s at 1.26), 1.85 (1H, d, J=2 Hz), and 6.42 (1H, d, J=2 Hz); ^{13}C-NMR 25.4, 29.9 (3q, 2q at 25.4), 18.9, 39.7, 43.6 (3t), 2.3, 92.5 (2d), 34.5, 122.0, 123.3, 208.2 (4s).

1010): IR (neat) 2225, 1960, and 1710 cm^{-1}; ^{1}H-NMR 1.09, 1.10, 2.13 (9H, 3s), 2.44

(2H, t, J=7.3 Hz), 5.28 (1H, d, J=6.4 Hz), and 5.66 (1H, d, J=6.4 Hz).

In conclusion, the present investigation shows that the photochemical reactions of γ,δ-epoxy enones and ester are applicable to the corresponding nitrile (E)-1. Particularly, on $^1\pi,\pi^*$- excitation of (E)-1, the isomerization via C(γ),O-cleavage is avoided and the products via the carbonyl ylide b and the carbene intermediate c are selectively obtained.

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4) Yields are based on converted starting material and were determined by ^{1}H-NMR analysis of the fractions obtained after chromatography on SiO_2.
5) Only one stereoisomer was detected.
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8) NMR-spectra were measured in $CDCl_3$ solution with tetramethylsilane as an internal standard and chemical shifts given in δ-values.
9) The configuration of 7A was proven by methanolysis of 7A leading to the corresponding methyl ester.[6)]
10) The mixture 7B and 10 (8:2) could not be separated. They were identified by means of the IR and ^{1}H-NMR spectra.
11) Compound 7C could be isolated as the 2,4-dinitrophenyl hydrazone derivative 7C'.

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