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Azadi-π-methane Rearrangement Involving an Oxime Group

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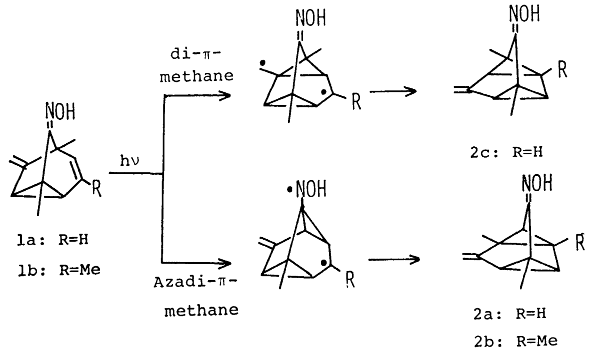
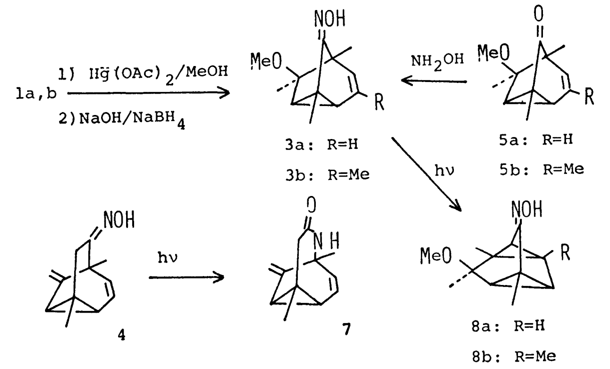
Synopsis. Photoreaction of *exo*-6-methoxy-1,5,6-trimethyl or *exo*-6-methoxy-1,3,5,6-tetramethyltricyclo[3.2.1.0^{2,7}]oct-3-en-8-one oxime underwent azadi-π-methane rearrangement leading to endo-7-methoxy-2,6,7-trimethyl or endo-7-methoxy-1,2,6,7-tetramethyltetracyclo[3.3.0.0.^{2,8}0^{4,6}]octan-3-one oxime. However, the one-carbon ring enlarged 5,8-dimethyl-9-methylenetricyclo[3.3.1.0^{2,8}]nona-3-en-6-one oxime underwent photo-Beckmann rearrangement to afford 5-aza-2,6-dimethyl-10-methylenetricyclo[4.3.1.0^{2,9}]deca-7-en-4-one.

Oximes undergo photoreactions leading to nitriles1) or oxaziridine which rearranges to amides and/or lactams (photo-Beckmann rearrangement).2) In a previous paper, we reported the photochemical reaction of 1,5-dimethyl- and 1,3,5-trimethyl-6-methylenetricyclo[3.2.1.0^{2,7}]oct-3-en-8-one oximes (**1a** and **1b**). These compounds underwent two types of di-π-methane rearrangement to afford **2a**, **2b**, and **2c**. The former two photoproducts are considered to be derived from the azadi-π-methane rearrangement involving the oxime moiety.3) To examine the complementary effect of the ring size and chromophore on the azadi-π-methane rearrangement, we investigated the photochemistry of *exo*-6-methoxy-1,5,6-trimethyl and *exo*-6-methoxy-1,3,5,-6-tetramethyltricyclo[3.2.1.0^{2,7}]oct-3-en-8-one oximes (**3a** and **3b**) and 5,8-dimethyl-9-methylenetricyclo-[3.3.1.0^{2,8}]nona-3-en-6-one oxime (**4**), which is an one-carbon ring enlarged oxime of **1a**.



Scheme 1.

The required oximes **3a**, **3b**, and **4** were synthesized from the known ketones by the standard method (see Experimental). Direct preparative irradiation of **3a** and **3b** in anhydrous acetonitrile with 254 nm lamps afforded **8a** and **8b** in 20% and 57% yields, respectively. The NMR spectrum of **8a** exhibited four protons of cyclopropane ring at δ 1.90 (d, *J*=6.0 Hz), 1.92 (d, *J*=6.0 Hz), 2.25 (d, *J*=6.0 Hz), 2.29 (d, *J*=6.0 Hz) and hydroxyl proton at δ 8.90 (broad s) in addition to the protons of three methyl groups and methoxyl group at δ 1.09, 1.17, 1.35, and 3.26. The NMR spectrum of **8b** exhibited three protons of cyclopropane ring at δ 1.44 (d, *J*=6.0 Hz), 1.82 (d, *J*=6.0 Hz), 2.04 (s) and hydroxyl proton at δ 8.20 (broad s), in addition to the protons of four methyl groups and methoxyl group at δ 1.06, 1.20, 1.29, 1.35, and 3.29. These chemical shifts, the coupling patterns of these photoproducts, and the comparison of these data with those of **2a**, **b**, **c**3) and their related compounds7) are in good agreement with the proposed structures. The formations of **8a**, **b** are ascribed to be an azadi-π-methane rearrangement involving the oxime group. Since the photorearrangement did not proceed in the presence of acetophenone or acetone as the sensitizer, the singlet excited state might be involved in the photorearrangement of **3a**, **b**.



Scheme 2.

On the other hand, the direct irradiation of **4** in anhydrous acetonitrile with 254 nm lamps afforded 5-aza-2,6-dimethyl-10-methylenetricyclo[4.3.1.0^{2,9}]deca-7-en-4-one (**7**) in 60% yield. The absorption due to a carbonyl group at 1695 cm^{-1} suggests the existence of an amide function. The NMR spectrum of **7** exhibited the existence of a divinylcyclopropane moiety (see Experimental) similar to **4**. Each signal and coupling constant could be assigned with the help of a decoupling technique. The relatively high chemical shift at δ 2.44 (2H, s) for hydrogens of methylene group is suggestive of α-methylene of carbonyl group;2d,e) thus the structure of **7** was deduced. This photoproduct **7** might be derived from the intermediate of oxaziridine and subsequent photoinduced migration of an alkyl group.2)

The oximes **3a**, **b** which have azadi-π-methane systems in similar skeletons to the oxime **1a**, **b** underwent azadi-π-methane rearrangement. An attempted photoreaction of bicyclo[2.2.1]hept-2-en-5-isopropylimine did not undergo azadi-π-methane rearrangement.8) As is shown in the present study, the oxime **4** which has two di-π-methane systems in the one-carbon ring enlarged skeleton, underwent photo-Beckmann rearrangement. The present results provide a complementary support for the first example of azadi-π-methane rearrangement of **1a**, **b**3) as well as suggesting that the azadi-π-methane rearrangement might be controlled by the effect of suitable chromophoric interaction and/or the rigidity of the molecular framework.

Experimental

Preparation of exo*-6-Methoxy-1,5,6-trimethyltricyclo*$[3.2.1.0^{2,7}]$*-oct-3-en-8-one Oxime (***3a***).* *Method A*: To the stirred solution of mercury (II) acetate (6.4 g, 20 mmol) in anhydrous methanol (40 cm^3) was added **1a** (3.5 g, 20 mmol). After 30 min, 20 cm^3 of 3 mol dm^{-3} aqueous sodium hydroxide, then 380 mg (10 mmol) of sodium borohydride in 20 cm^3 of 3 mol dm^{-3} aqueous sodium hydroxide were added to the reaction mixture. This reaction mixture was stirred an additional 15 min and extracted with ether. The dried (Na_2SO_4) organic portion was evaporated *in vacuo*, and the residue was separated by preparative TLC on alumina with chloroform as the eluent. The first band from the TLC plates gave a colorless crystalline solid of **3a**: mp 161—163 °C (from EtOH); IR ($CHCl_3$): 3580, 1680, 1115 cm^{-1}; NMR ($CDCl_3$): δ 1.00 (3H, s), 1.06 (3H, s), 1.8—2.0 (2H, m), 1.68 (3H, s), 3.32 (3H, s), 5.45 (1H, d×d, J=9.0, 3.5 Hz), 5.96 (1H, d×d, J=9.0, 5.0 Hz), 8.54 (1H, broad s); UV (EtOH): 240 nm (end absorption, ε 4000); MS *m/e* (rel intensity): 207 (38, M$^+$), 43 (100). Found: C, 69.43; H, 8.00; N, 6.74%. Calcd for $C_{12}H_{17}O_2N$: C, 69.54; H, 8.27; N, 6.76%.

Method B: The mixture of **5a**4,5) (1.78 g, 9.3 mmol), hydroxylamine hydrochloride (1.3 g, 18.6 mmol), and 5 cm^3 of pyridine was heated for 4 h at 100 °C. The reaction mixture was then poured into 50 cm^3 of water, followed by ether extraction. The dried (Na_2SO_4) ethereal portion was filtered and evaporated *in vacuo* to give 1.35 g (70%) of **3a**.

Preparation of exo*-6-Methoxy-1,3,5,6-tetramethyltricyclo*$[3.2.1.0^{2,7}]$*oct-3-en-8-one Oxime (***3b***).* *Method A*: Exactly the same procedure as *Method A* in the case of **3a** was applied to **1b**. The colorless crystalline solid of **3b** (47%) was obtained: mp 162—163 °C (from EtOH); IR (KBr): 3226, 1686, 1111 cm^{-1}; NMR ($CDCl_3$): δ 1.00 (3H, s), 1.03 (3H, s), 1.29 (1H, d, J=6.0 Hz), 1.68 (3H, s), 1.70 (overlapped with methyl signal, 1H), 1.80 (3H, s), 3.31 (3H, s), 5.13 (1H, m), 8.35 (1H, broad s); UV (EtOH): 230 nm (end absorption, ε, 3900); MS *m/e* (rel intensity): 221 (10, M$^+$), 188 (100). Found: C, 70.21; H, 8.51; N, 6.14%. Calcd for $C_{13}H_{19}O_2N$: C, 70.55; H, 8.65; N, 6.33%.

Method B: Exactly the same procedure as *Method B* in the case of **3a** was applied to **5b**,5) and **3b** was obtained in 65% yield.

Irradiation of **3a**. A solution of **3a** (240 mg, 0.76 mmol) in a quartz vessel with 254 nm lamps (Rayonet Photoreactor, MGR-100) in a nitrogen atmosphere. After removal of the solvent, the residue was separated by preparative TLC on alumina with chloroform–ethyl acetate (5/2) as the eluent to give 11 mg of **3a** and colorless crystals of **8a** (146 mg, 20%): mp 119—120 °C (from EtOH); IR ($CHCl_3$): 1580, 1115 cm^{-1}; NMR ($CDCl_3$): δ 1.09 (3H, s), 1.17 (3H, s), 1.35 (3H, s), 1.90 (1H, d, J=6.0 Hz), 1.92 (1H, d, J=6.0 Hz), 2.25 (1H, d, J=6.0 Hz), 2.29 (1H, d, J=6.0 Hz), 3.26 (3H, s), 8.90 (1H, broad s); MS *m/e* (rel intensity): 207 (6, M$^+$), 160 (100). Found: C, 69.46; H, 8.63; N, 6.95%. Calcd for $C_{12}H_{17}O_2N$: C, 69.54; H, 8.27; N, 6.76%.

Irradiation of **3b**. A solution of **3b** (150 mg, 0.68 mmol) in anhydrous acetonitrile (50 cm^3) was irradiated for 3.6 h in a quartz vessel with 254 nm lamps in a nitrogen atmosphere. After removal of the solvent, the residue was separated by preparative TLC on silica gel with chloroform–ethyl acetate (5/2) as the eluent to give 85 mg (57%) of **8b**: mp 118—120 °C (from EtOH); IR ($CHCl_3$): 1580, 1115 cm^{-1}; NMR ($CDCl_3$): δ 1.06 (3H, s), 1.20 (3H, s), 1.29 (3H, s), 1.35 (3H, s), 1.44 (1H, d, J=6.0 Hz), 1.82 (1H, d, J=6.0 Hz), 2.04 (1H, s), 3.29 (1H, s), 8.20 (1H, broad s); MS *m/e* (rel intensity): 221 (3, M$^+$), 190 (100). Found: C, 70.94; H, 8.27; N, 6.36%. Calcd for $C_{13}H_{19}O_2N$: C, 70.55; H, 8.65; N, 6.33%.

Irradiation of **4**. A solution of **4**6) (150 mg, 0.8 mmol) in anhydrous acetonitrile (50 cm^3) was irradiated for 3 h in a quartz vessel with 254 nm lamps in a nitrogen atmosphere. After removal of the solvent, the residue was separated by preparative TLC on silica gel with chloroform as the eluent. The first band from the TLC plates contained **7** (68 mg, 60% based on consumed **4**): mp 139—140 °C (from EtOH); IR ($CHCl_3$): 3290, 1695 cm^{-1}; NMR ($CDCl_3$): δ 1.06 (6H, s), 2.25 (1H, t, J=6.0 Hz), 2.41 (1H, d, J=6.0 Hz), 2.44 (2H, s), 4.77 (1H, s), 4.90 (1H, s), 5.88 (1H, d×d, J=8.0, 6.0 Hz), 6.26 (1H, broad d, J=8.0 Hz), 8.95 (1H, broad s); MS *m/e* (rel intensity): 189 (5, M$^+$), 131 (100). Found: C, 76.45; H, 7.92; N, 7.02%. Calcd for $C_{12}H_{15}ON$: C, 76.15; H, 7.99; N, 7.40%.

Sensitized Irradiation of **3a**. Three Pyrex vessels, which contained **3a** (30 mg, 0.14 mmol) in (a) acetonitrile (10 cm^3), (b) acetone (10 cm^3), and (c) acetonitrile contained acetophenone (35 mg, 0.29 mmol) were irradiated with 300 nm lamps (Rayonet photoreactor, MGR-100) for 10 h in a nitrogen atmosphere. The reactions were monitored by GC (5% SE-30 on Rhromosorb W, 130 °C), but no new peak was observed. After removal of the solvents, each of the residues was purified by preparative TLC on alumina with chloroform as the eluent to give the starting oxime **3a** in 80% (a), 80% (b), and 90% (c) yield.

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References

1) a) T. Sato and H. Obase, *Tetrahedron Lett.*, **1967**, 1633; b) A. Stijilikovic and R. Tasovac, *Tetrahedron Lett.*, **1970**, 1405.

2) a) J. H. Amin and P. de Mayo, *Tetrahedron Lett.*, **1963**, 1585; b) I. Izawa and P. de Mayo, *Can. J. Chem.*, **47**, 51 (1969); c) T. Oine and T. Mukai, *Tetrahedron Lett.*, **1969**, 157; d) H. Suginome and H. Takahashi, *Bull. Chem. Soc. Jpn.*, **48**, 576 (1975); e) H. Suginome and F. Yagihashi, *J. Chem. Soc., Perkin Trans.* **1**, **1977** 2488 and references cited therein.

3) M. Nitta, O. Inoue, and M. Tada, *Chem. Lett.*, **1977**, 1065.

4) J. P-Katalinic, J. Zindely, and H. Schmid, *Helv. Chim. Acta*, **57**, 223 (1974).

5) M. Nitta, A. Omata, and H. Sugiyama, unpublished results.

6) M. Nitta, A. Omata, and H. Sugiyama, submitted to *Bull. Sci. Eng. Res. Rab.* (Waseda Univ).

7) M. Nitta, O. Inoue, and M. Tada, *Chem. Lett.*, **1977**, 59.

8) R. G. Weiss and G. S. Hammond, *J. Am. Chem. Soc.*, **100**, 1172 (1978).