

PHOTOLYSIS OF DIMETHYL 2-DIAZO-6-OXO-2,6-DIHYDROAZULENE-1,3-DICARBOXYLATE AND METHYL 3-CYANO-2-DIAZO-6-OXO-2,6-DIHYDROAZULENE-1-CARBOXYLATE IN TETRAHYDROFURAN

Shih-Jue Lin, Shuan-Ya Jiang, Tian-Chyuan Huang,^a Ping Kao, Pai-Feng Tsai,^b Hitoshi Takeshita,^c Yun-Shan- Lin,^{*} and (the late) Tetsuo Nozoe^d

Department of Chemistry, Tamkang University, Tamsui, Taiwan, 251 R.O.C.

^aNational Taipei College of Nursing, Shih-Pai, Taiwan, 112 R.O.C.

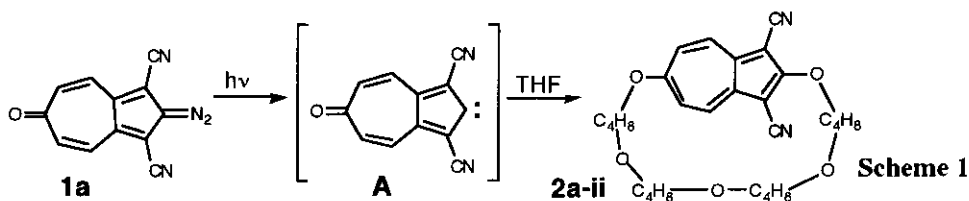
^bChia Nan College of Pharmacy and Science, Tainan, Taiwan, 717 R.O.C.

^cTohwa Institute for Orient Studies, Tohwa University, Chikushi-ga-oka, Minami-ku, Fukuoka 815 Japan

^dTokyo Laboratories, Kao Corporation, Bunka, Sumida-ku, Tokyo 113 Japan

Abstract—Upon photolysis in tetrahydrofuran, dimethyl 2-diazo-6-oxo-2,6-dihydroazulene-1,3-dicarboxylate afforded a crown-type oligomerized cyclic ether in very low yield, but the major products were the C-H insertion products such as 2,6-disubstituted azulenedicarboxylate, whereas methyl 3-cyano-2-diazo-6-oxo-2,6-dihydroazulene-1-carboxylate gave, similar to 1,3-dicyano-2-diazo-2,6-dihydroazulene-6-one, oligomeric crown ethers predominantly, suggesting that a steric factor played a crucial role in their formations.

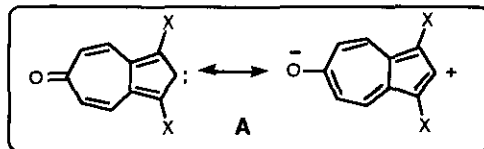
When 1,3-dicyano-2-diazo-2,6-dihydroazulene-6-one (**1a**)¹ was photolyzed in tetrahydrofuran (THF), we have found a formation of crown-type ether (**2a-ii**) by incorporation of four units of solvent residue into the azulene nucleus in good yield,^{2,3} together with a small amount of 1,3-dicyanoazulene-6-ol (**3a**) (Scheme 1).



This was also the case for methyl 3-cyano-2-diazo-4-oxo-2,4-dihydroazulene-1-carboxylate to form dimeric and trimeric crown-type ethers.⁴ In a comparative view point we have now extended the study to that of

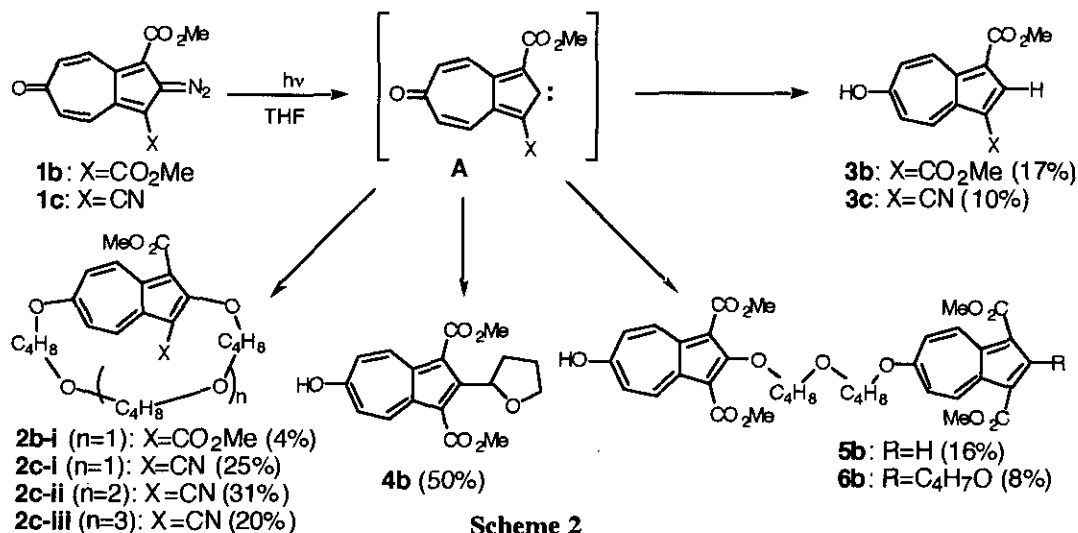
dimethyl 2-diazo-6-oxo-2,6-dihydroazulene-1,3-dicarboxylate (**1b**) and methyl 3-cyano-2-diazo-6-oxo-2,6-dihydroazulene-1-carboxylate (**1c**) with tetrahydrofuran (THF).

As has been stated, the carbene species (**A**) generated from these diazo compounds are expressed as a hybrid of the dipolar form, and the positive charge delocalized in five-membered ring of azulene system could be stabilized by mesomeric form.



When a solution of **1b** in THF was irradiated by means of 400-W Rayonet lamp for 2 h, five photoproducts, dimethyl 6-hydroxyazulene-1,3-dioate (**3b**), a trimeric crown ether (**2b-i**), dimethyl 6-hydroxy-2-(2-oxacyclopentyl)azulene-1,3-dioate (**4b**), and bisethers of dibutyleneglycol of two azulene units (**5b** and **6b**), were formed in 17, 4, 50, 16, and 8% yields, respectively.⁵ Their structures were deduced as depicted in Scheme 2 from ¹H and ¹³C NMR spectra as well as high-resolution mass spectral (MS) determination.

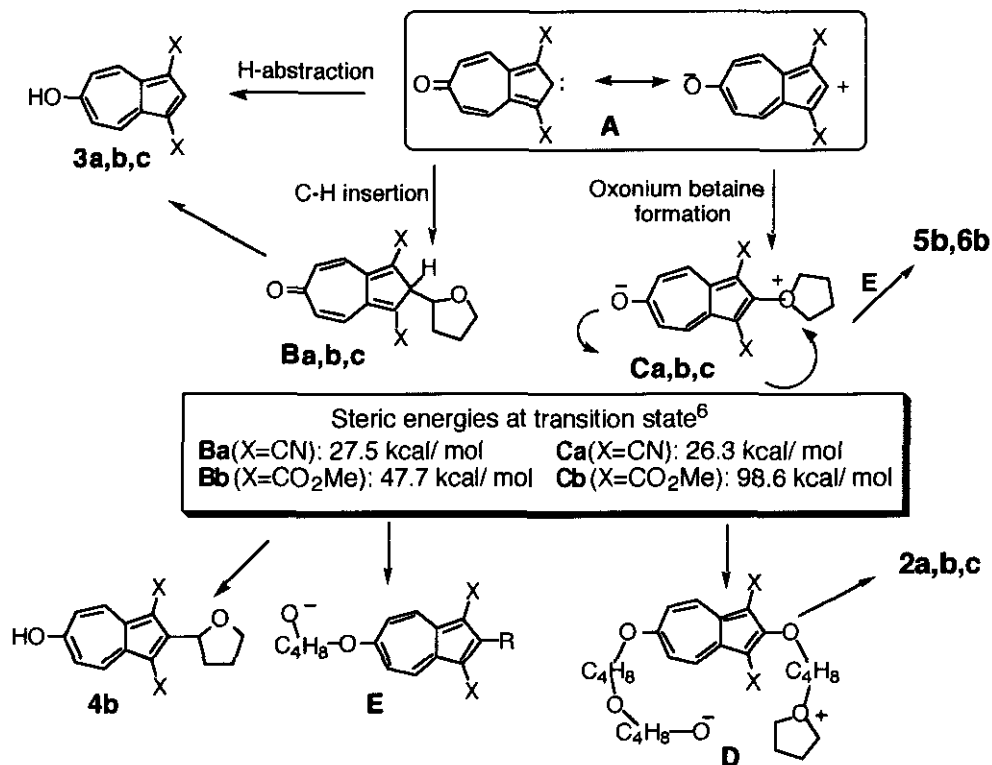
Thus, the product distribution was markedly different from that of **1a**, and this prompted us to carry out the experiments with methyl 3-cyano-2-diazo-6-oxo-2,6-dihydroazulene-1-carboxylate (**1c**); an irradiation under similar conditions, it afforded **3c**, a trimeric crown ether (**2c-i**), a tetrameric crown ether (**2c-ii**), and a pentameric crown ether (**2c-iii**) in 10, 25, 31, and 20% yields, respectively. No C-H insertion product was detected. Consequently, **1c** behaves similarly to **1a**, but not to **1b**.



Thus, the carbene **A** with C-H insertion of THF led to a formation of, *via proto*-product (**B**), **3** or **4**, although the former of which might be simply derived from the hydrogen abstraction, since THF is highly reactive toward abstraction of α -hydrogens. On the other hand, an attack of the n-electrons should give the oxonium betaine intermediates (**C**). Predominant formation of crown ethers from **1a** and **1c** can be explained in terms of a steric hindrance; the generated carbene center of **1b** is sterically hindered, and an attack of the ethereal oxygen is disfavored, but sterically unhindered carbenes from **1a** and **1c** gave **C** which then suffers an nucleophilic and/or electrophilic attack of the solvent molecules to form oligomers (**D**). According to Chem3D calculations of steric energies for *proto*-products **B** and **C** supported this.⁶ Intramolecular

cyclization at the appropriate sizes of oligomers neutralizes the formal charges to result in the crown ethers (2). It is interesting that the formation of dimers, **5b** and **6b**, should be derived from nucleophilic attack of **E** to **C**, suggesting these intermediates are long-lived to enable the intermolecular reaction.

This general feature, formations of oligomeric products from **1** and THF in good material balance, is shown in Scheme 3.



Scheme 3

One-step formation of the macrocyclic crown-type compounds from highly electrophilic carbene precursors are of particular interest in views of host-guest chemistry, which will be reported in future.

The authors cordially thank National Science Council of Republic of China for financial support. Also, S. J. L. is grateful to National Youth Commission, Taipei, Taiwan, R.O.C., for the award of a post-doctoral fellowship, 1996-1997.

REFERENCES AND NOTES

1. T. Nozoe, T. Asao, H. Susumago, and M. Ando, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 1471; T. Nozoe, T. Asao, M. Yasunami, H. Wakui, T. Suzuki, and M. Ando, *J. Org. Chem.*, 1995, **60**, 5919; W.-C. Wun, T.-C. Huang, S.-J. Lin, B.-B. Lin, T. Morita, and Y.-S. Lin, *J. Chin. Chem. Soc.*, 1993, **40**, 593.
2. T. Nozoe, T.-C. Huang, M.-H. Shyr, Y.-S. Lin, and H. Takeshita, *Synlett.*, 1995, 952.

3. As accompanied products, trimeric (**2a-i**), and pentameric (**2a-iii**) analogous ethers have been isolated. The results will be a subject of forthcoming full paper.
4. The results preliminarily disclosed in ref. 2 are in press. (Y.-S. Lin, S.-Y. Jiang, T.-C. Huang, S.-J. Lin, and Y. L. Chow, *J. Org. Chem.*, **62**).
5. The new compounds are fully characterized. The ^1H NMR spectra in acetone- d_6 are compiled as follows: **2b-i**: yellow needles, mp 82-84 °C. $\delta(\text{H})=1.25(2\text{H}, \text{m}), 1.41-1.47(4\text{H}, \text{m}), 1.69-1.72(4\text{H}, \text{m}), 1.90-1.94(2\text{H}, \text{m}), 2.64(2\text{H}, \text{t}, J=6.6 \text{ Hz}), 2.78(2\text{H}, \text{t}, J=6.8 \text{ Hz}), 3.15(2\text{H}, \text{t}, J=6.4 \text{ Hz}), 3.37(2\text{H}, \text{t}, J=4.7 \text{ Hz}), 3.89(6\text{H}, \text{s}), 4.45-4.49(4\text{H}, \text{m}), 7.34(2\text{H}, \text{d}, J=9.9 \text{ Hz}),$ and $9.38(2\text{H}, \text{d}, J=11.6)$. **4b**: orange yellow needles, mp 188-190 °C. $\delta(\text{H})=1.99-2.13(3\text{H}, \text{m}), 2.50-2.54(1\text{H}, \text{m}), 3.85(1\text{H}, \text{m}), 3.95(1\text{H}, \text{m}), 3.88(6\text{H}, \text{m}), 5.65(1\text{H}, \text{t}, J=6.9 \text{ Hz}), 7.22(2\text{H}, \text{d}, J=10.2),$ and $8.86(2\text{H}, \text{d}, J=10.2 \text{ Hz})$. **5b**: yellow needles, mp 90-91 °C. $\delta(\text{H})=1.75(4\text{H}, \text{m}), 1.87-1.92(4\text{H}, \text{m}), 3.46-3.48(4\text{H}, \text{m}), 3.90(6\text{H}, \text{s}), 3.94(6\text{H}, \text{s}), 4.06-4.10(2\text{H}, \text{m}), 4.19-4.23(2\text{H}, \text{m}), 8.52(1\text{H}, \text{s}), 9.15(2\text{H}, \text{m}), 9.21(2\text{H}, \text{d}, J=11.4 \text{ Hz}),$ and $9.56(4\text{H}, \text{d}, J=11.4 \text{ Hz})$. **6b**: orange yellow needles, mp 90-91 °C. $\delta(\text{H})=1.75(4\text{H}, \text{m}), 1.80-1.92(4\text{H}, \text{m}), 3.46-3.48(4\text{H}, \text{m}), 3.90(6\text{H}, \text{s}), 3.94(6\text{H}, \text{s}), 4.06-4.10(2\text{H}, \text{m}), 4.19-4.23(2\text{H}, \text{m}), 9.21(2\text{H}, \text{d}, J=11.7 \text{ Hz}), 8.52(1\text{H}, \text{s}), 9.15(2\text{H}, \text{m}),$ and $9.56(2\text{H}, \text{d}, J=11.4 \text{ Hz})$. **3c**: orange needles, mp >300 °C. $\delta(\text{H})=3.38(3\text{H}, \text{s}), 7.15-7.21(2\text{H}, \text{m}), 8.28(1\text{H}, \text{d}, J=11.3 \text{ Hz}), 9.27(1\text{H}, \text{d}, J=11.3 \text{ Hz})$. **2c-i**: yellow needles, mp 88-91 °C. $\delta(\text{H})=1.25-1.27(2\text{H}, \text{m}), 1.56-1.68(6\text{H}, \text{m}), 1.86-2.08(2\text{H}, \text{m}), 2.61-2.81(4\text{H}, \text{m}), 3.30-3.36(4\text{H}, \text{m}), 3.95(3\text{H}, \text{s}), 5.19-5.24(2\text{H}, \text{m}), 8.37(1\text{H}, \text{d}, J=11.3 \text{ Hz}),$ and $9.37(1\text{H}, \text{d}, J=11.7 \text{ Hz})$. **2c-ii**: yellow needles, mp 57-58 °C. $\delta(\text{H})=1.24-1.28(12\text{H}, \text{m}), 1.77-1.83(4\text{H}, \text{m}), 1.97-2.04(4\text{H}, \text{m}), 2.94-2.98(4\text{H}, \text{m}), 3.21-3.28(4\text{H}, \text{m}), 3.46-3.51(4\text{H}, \text{m}), 3.94(3\text{H}, \text{s}), 3.99(2\text{H}, \text{t}, J=6.4 \text{ Hz}), 4.88(2\text{H}, \text{t}, J=6.3 \text{ Hz}), 7.36-7.41(2\text{H}, \text{m}), 8.36(1\text{H}, \text{d}, J=10.9 \text{ Hz}),$ and $9.35(1\text{H}, \text{d}, J=11.6 \text{ Hz})$. **2c-iii**: yellow needles, mp 176-178 °C. $\delta(\text{H})=1.22-1.35(10\text{H}, \text{m}), 1.49-1.54(10\text{H}, \text{m}), 1.55-1.69(4\text{H}, \text{m}), 1.85-1.88(4\text{H}, \text{m}), 1.98-2.04(2\text{H}, \text{m}), 3.48-3.59(6\text{H}, \text{m}), 3.91(3\text{H}, \text{s}), 3.96(2\text{H}, \text{t}, J=6.7 \text{ Hz}), 4.75(2\text{H}, \text{t}, J=6.5 \text{ Hz}), 6.92(1\text{H}, \text{d}, J=13.9 \text{ Hz}), 7.10(1\text{H}, \text{d}, J=14.7 \text{ Hz}), 8.02(1\text{H}, \text{d}, J=11.1 \text{ Hz}),$ and $9.12(1\text{H}, \text{d}, J=11.6 \text{ Hz})$.
6. For a simple approximation, steric energies of **B** and **C** were taken as the transition energies of the reactions. In the transition geometries to form **C**, the line set by connection of two α -carbons of THF residue was assumed to be parallel with the azulene ring; according to Chem3D Pro calculations (licensed from Cambridge Scientific Computing), we obtained **Ba**(X=CN)=27.5, **Bb**(X=CO₂Me)= 47.7, **Ca**(X=CN)=26.3, and **Cb**(X=CO₂Me)=98.6 kcal/ mol, respectively. The energy-minimized conformations of **C** became two ring systems perpendicular being **Ca**(X=CN)=15.8 and **Cb**(X=CO₂Me)=37.6 kcal/ mol, respectively. Thus, while **Ba** and **Ca** are comparable in transition energies, **Bb** is much favorable than **Cb**. Indeed, the most severe close-contacts of non-bonding atoms were observed in **Cb**.

Received, 23rd June, 1997