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

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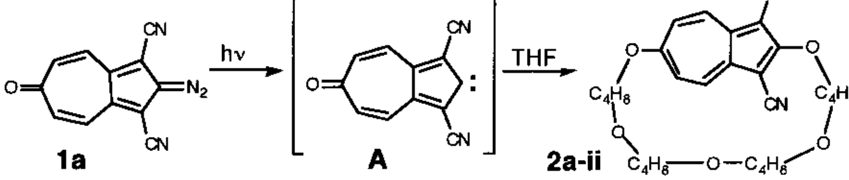
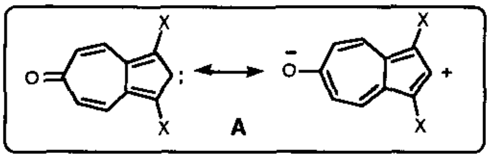
Abstract—Upon photolysis in tetrahydrofuran, dimethyl 2-diazo-6-oxo-2,6-dihydroazulene-1,3-dicarboxylate afforded a crown-type origomerized cyclic ether in very low yield, but the major products were the C-H insertion products such as 2,6-disubstituted azulenedicarboxylate, whereas methyl 3-cyano-2-diazo-6-oxo-2,6-dihydroazulene-1-carboxylate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

When 1,3-dicycano-2-diazo-2,6-dihydroazulen-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 nucleusin good yield,[2,3] together with a small amount of 1,3-dicyanoazulen-6-ol (**3a**) (Scheme 1).



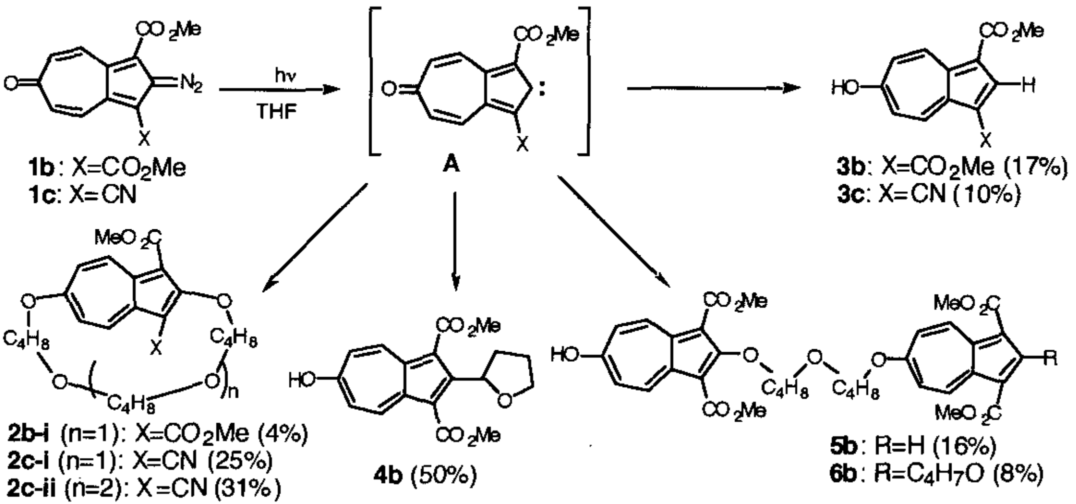
Scheme 1

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.

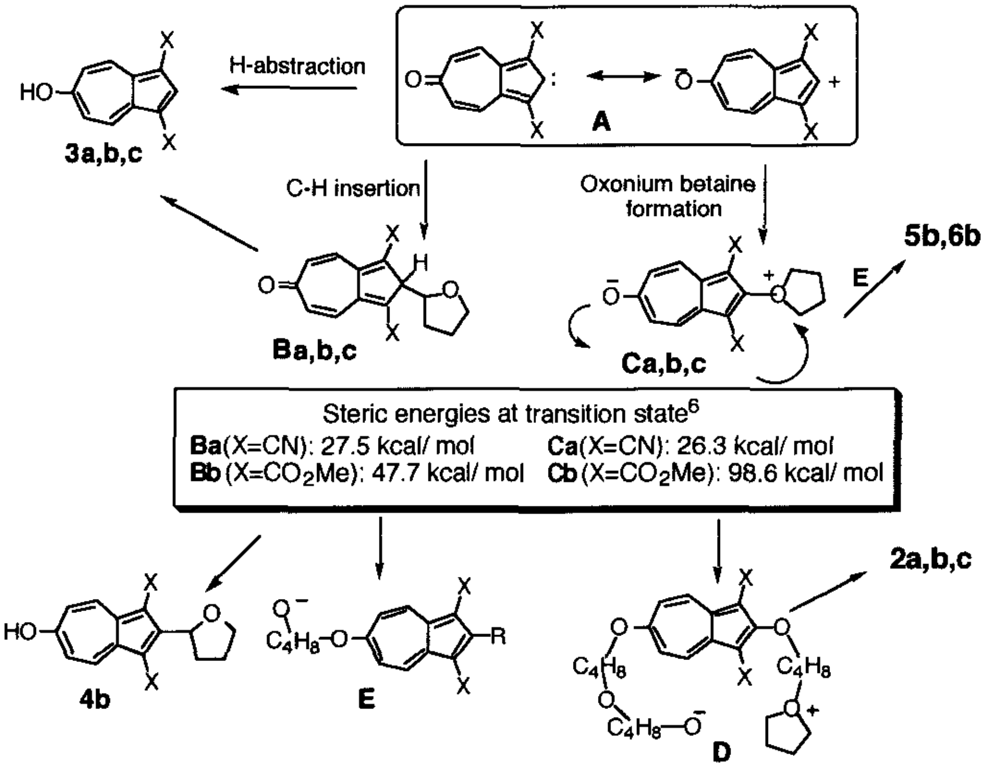
When a solution of **1b** in THF was irradiated by means of 400-W Rayonet lamp for 2 h, five photoproducts, dimethyl 6-hydroxyazulene-1,3-dioate (**3b**), a trimeric crown ether (**2b-i**), dimethyl 6-hydroxy-2-(2-oxacyclopentyl)azulene-1,3-dioate (**4b**), and bisethers of dibutyleneglycol of two azulene 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 ^{1}H and ^{13}C 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**.



Scheme 2

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.

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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 ^{1}H NMR spectra in acetone-d_6 are compiled as follows: **2b-i**: yellow needles, mp 82-84 °C. δ(H)=1.25(2H, m), 1.41-1.47(4H, m), 1.69-1.72(4H, m), 1.90-194(2H, m), 2.64(2H, t, *J*=6.6 Hz), 2.78(2H, t, *J*=6.8 Hz), 3.15(2H, t, *J*=6.4 Hz), 3.37 (2H, t, *J*=4.7 Hz), 3.89(6H, s), 4.45-4.49(4H, m), 7.34(2H, d, *J*=9.9 Hz), and 9.38(2H, d, *J*=11.6). **4b**: orange yellow needles, mp 188-190 °C. δ(H)=1.99-2.13(3H, m), 2.50-2.54(1H. m), 3.85(1H, m), 3.95(1H, m), 3.88(6H, m), 5.65(1H, t, *J*=6.9 Hz), 7.22(2H, d, *J*=10.2), and 8.86(2H, d, *J*=10.2 Hz. **5b**: yellow needles, mp 90-91 °C. δ(H)=1.75(4H, m), 1.87-1.92(4H, m), 3.46-3.48(4H, m), 3.90(6H, s), 3.94(6H, s), 4.06-4.10(2H, m), 4.19-4.23(2H, m), 8.52(1H, s), 9.15(2H, m), 9.21(2H, d, *J*= 11.4 Hz), and 9.56(4H, d, *J*=11.4 Hz). **6b**: orange yellow needles, mp 90-91 °C. δ (H)=1.75(4H, m), 1.80-1.92(4H, m), 3.46-3.48(4H, m), 3.90(6H, s), 3.94(6H, s), 4.06-4.10(2H, m), 4.19-4.23 (2H, m), 9.21(2H, d, *J*=11.7 Hz), 8.52(1H, s), 9.15(2H, m), and 9.56(2H, d, *J*=11.4 Hz). **3c**: orange needles, mp >300 °C. δ(H)=3.38 (3H, s), 7.15-7.21(2H, m), 8.28(1H, d, *J*=11.3 Hz), 9.27(1H, d, *J*= 11.3 Hz). **2c-i**: yellow needles, mp 88-91°C. δ(H)=1.25-1.27(2H, m), 1.56-1.68(6H, m), 1.86-2.08 (2H, m), 2.61-2.81(4H, m), 3.30-3.36(4H, m), 3.95(3H, s), 5.19-5.24(2H, m), 8.37(1H, d, *J*=11.3 Hz), and 9.37(1H, d, *J*=11.7 Hz). **2c-ii**: yellow needles, mp 57-58 °C. δ(H)=1.24-1.28(12H, m), 1.77-1.83(4H, m), 1.97-2.04(4H, m), 2.94-2.98(4H, m), 3.21-3.28(4H, m), 3.46-3.51(4H, m), 3.94 (3H, s), 3.99(2H, t, *J*=6.4 Hz), 4.88(2H, t, *J*=6.3 Hz), 7.36-7.41(2H, m), 8.36(1H, d, *J*=10.9 Hz), and 9.35(1H, d, *J*=11.6 Hz). **2c-iii**: yellow needles, mp 176-178 °C. δ(H)=1.22-1.35(10H, m), 1.49-1.54(10H, m), 1.55-1.69(4H, m), 1.85-1.88(4H, m), 1.98-2.04(2H, m), 3.48-3.59(6H, m), 3.91(3H, s), 3.96(2H, t, *J*=6.7 Hz), 4.75(2H, t, *J*=6.5 Hz), 6.92(1H, d, *J*=13.9 Hz), 7.10(1H, d, *J*=14.7 Hz), 8.02(1H, d, *J*=11.1 Hz), and 9.12(1H, d, *J*=11.6 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=CO_2Me)= 47.7, **Ca**(X= CN)=26.3, and **Cb**(X=CO_2Me)=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=CO_2Me)=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**.

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