Cycloadditions of 2,8,11-Triphenyl-7,9,10,11b-tetraazanaphth[1,2,3-*cd*]azulene and 2,8,10-Triphenyl-9-oxa-7,10b-diazaindeno[4,5,6-*cd*]azulene with Dimethyl Acetylenedicarboxylate

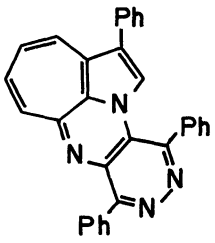
Noritaka Abe,* Yoshimasa Hirai,† and Yoshimasa Fukazawa†
Department of Chemistry, Faculty of Science, Yamaguchi University, Yamaguchi 753
† Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima 730
(Received January 21, 1991)

Synopsis. Cycloadditions of the title compounds with dimethyl acetylenedicarboxylate gave 1:2-cycloadducts. The structural assignments of the products were deduced by spectral inspections; the structure for one compound was established by X-ray crystallography.

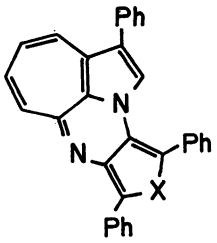
Many investigations have been carried out concerning the reactions of heterocycles with dimethyl acetylenedicarboxylate (DMAD) due to interesting surprises regarding their reactions and usefulness for building heterocyclic rings.[1-3] The reaction of poly-fuzed heterocyclies having multi reaction sites with DMAD is very interesting. One of the authors (NA) has been investigating the syntheses and cycloadditions of azaazulenes, and recently reported the syntheses of pyridazine-, furan-, and thiophene-fused 2a,5-diazabenz[*cd*]azulenes (**1**, **2a**, and **2b**).[4] The cycloaddition of these compounds is attractive, since they comprise different aromatic heterocyclic moieties. The authors have therefore advanced the reaction.

The treatment of **1** with DMAD in refluxing acetonitrile for 70 h gave a 1:2-adduct (**3**) in 78.7% yield. Its structure was elucidated using spectroscopic data as well as elemental analysis. Its ^{1}H NMR spectrum displays four ester-methyl singlets at δ=3.38, 3.64, 3.80, and 3.95; four seven-membered protons at δ=5.47, 5.95, 6.07, and 6.38; 15H phenyl protons at δ=7.0-8.0; and one singlet at δ=6.69. Information concerning chemical shifts of the seven-membered ring protons have suggested that compound **3** retains the 2a,5-diazabenz[*cd*]azulene nuclei.[4] Since the chemical shift of the singlet is comparable to that of **1**, the environments of both singlet protons would be similar. It is therefore considered that the reaction occured at both the N-9 and C-8 positions. In the ^{13}C NMR spectrum of **2**, one sp^3 carbon (s) was observed at δ=63.51; the other signals are in accord with the structure. This reaction is comparable to that of 4-methylphthalazine with DMAD.[5]

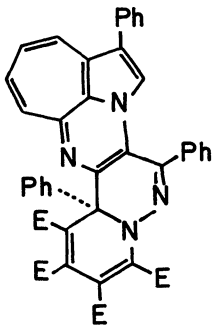
Treatment of **2a** with DMAD in refluxing acetonitrile for 50 h gave the 1:2-adduct (**4**) in 45.8% yield. The structure was assumed by spectroscopic data and established by an X-ray analysis. In its ^{1}H NMR spectrum, four ester-methyl singlets at δ=3.21, 3.48, 3.49, and 3.63; four seven-menbered protons at δ=6.67, 7.11, 7.64, and 7.73; 15H phenyl protons at δ=7.2—7.9; and one singlet at δ=6.41 were observed. The chemical shifts and signal patterns of seven-membered ring protons resemble those of **5**.[6] In the ^{13}C NMR spectrum of **4**, two sp^3 carbons were observed at δ=58.05 (d) and 94.52 (s); these are comparable to dihydrofuran derivatives. The mass spectrum of **4** displays intense peaks at *m*/*z* 384 and 336, which would be attributed to ions of the cyclazine and furan moieties, respectively, produced by fragmentation of the molecular ion; this strongly suggests the structure (the structure of **4** is shown in Fig. 1).



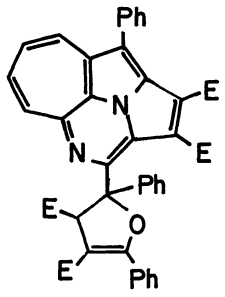
1



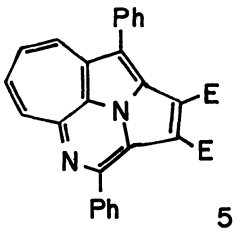
2a: X = O
2b: X = S



3: E = CO_2Me

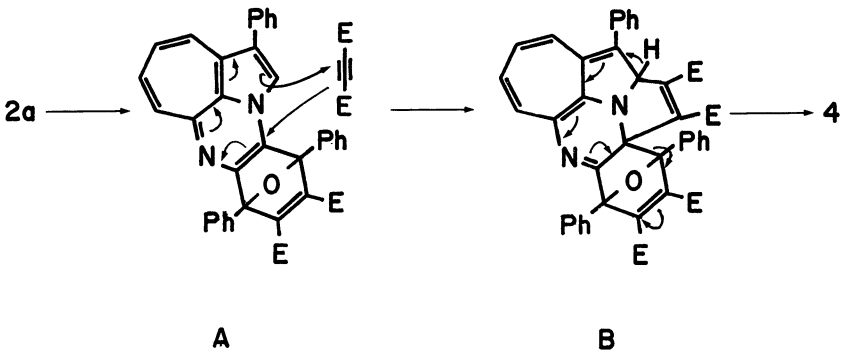


4: E = CO_2Me



5: E = CO_2Me

A plausible mechanism for the formation of **4** is shown in Scheme 1. DMAD initially attacks the furan moiety of **2a** to give intermidiate **A**; a successive attack of a second molar of DMAD on **A** gives **B**. Bond scission attended by aromatization of **B** leads to **4**. The second step followed by aromatization is similar to a reaction in which 1,4-diphenyl-2a,5-diazabenz[*cd*]azulene reacts



Scheme 1.

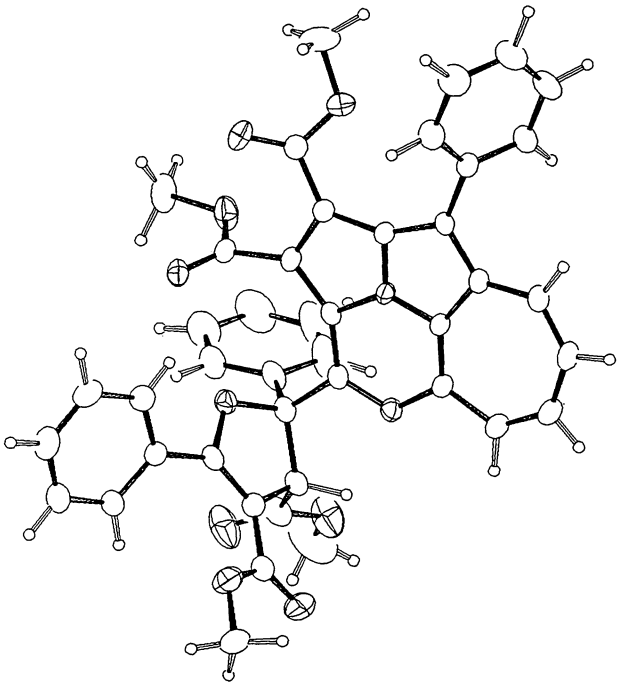


Fig. 1. Molecular structure of **4**.

with DMAD to give **5**.[6]

Compound **2b** did not react with DMAD under the conditions used.

Experimental

All melting points are uncorrected. ^{1}H NMR spectra (250 MHz) and ^{13}C NMR spectra (62.87 MHz) were taken on a Hitachi R-250H spectrometer using $CDCl_3$ as a solvent (TMS as an internal standard). IR spectra were recorded for Nujol mulls with a Hitachi 270-50 infrared spectrophotometer. Mass spectra were determined with a JEOL-01SG-2 spectrometer an ionization energy of 70 eV. Column chromatography was performed on a Kieselgel 60.

Reaction of 1 with DMAD. A mixture of **1** (0.070 g) and DMAD (0.150 g) in dry acetonitrile (50 ml) was refluxed for 70 h and evaporated. Elution with benzene–chloroform (1:1) gave **3** (0.090 g, 78.7%), which was recrystallized from cyclohexane to give reddish-brown needles; mp 283—284 °C; ^{1}H NMR δ=3.38, 3.64, 3.80, 3.95 (each 3H, s, OMe), 5.47 (1H, dd, J=11.6 and 7.9 Hz, H-5), 5.95 (1H, dd, J=12.2 and 7.9 Hz, H-4), 6.07 (1H, d, J=12.2 Hz, H-3), 6.38 (1H, d, J=11.6 Hz, H-6), 6.69 (1H, s, H-2), 7.05 (2H, dd, J=7.9 and 1.8 Hz, H-*o*-phenyl), 7.27—7.45 (9H, m, H-*m*,*p*-phenyl), 7.61 (2H, dd, J=7.9 and 1.8 Hz, H-*o*-phenyl), and 7.90 (2H, dd, J=7.9 and 1.8 Hz, H-*o*-phenyl); ^{13}C NMR δ=52.01 (q), 52.24 (q), 52.83 (q×2), 63.51 (s), 103.23 (s), 103.74 (s), 114.61 (d), 119.10 (s), 123.89 (s+d), 125.44 (s), 127.29 (d×2), 127.34 (d×2), 127.49 (s), 127.52 (d×2), 128.57 (d×2), 128.62 (d×3), 129.33 (d), 129.63 (d), 130.11 (d×2), 130.83 (d), 132.11 (s), 133.28 (s), 135.10 (d), 135.29 (d), 136.06 (s), 136.19 (s), 137.29 (s), 142.73 (s), 147.64 (s), 157.01 (s), 162.40 (s), 163.23 (s), 164.84 (s), and 166.79 (s); IR 1746, 1740, and 1710 (C=O), 780, 764, 736, 707, and 696 cm^{-1} (phenyl). Found: C, 70.44; H, 4.65; N, 7.48%. Calcd for $C_{43}H_{32}N_4O_8$: C, 70.48; H, 4.36; N, 7.64%.

Reaction of 2a with DMAD. A mixture of **2a** (0.140 g) and DMAD (0.30 g) in dry acetonitrile (80 ml) was refluxed for 50 h and then evaporated. The residue was chromatographed. Elution with benzene gave recoverded **2a** (0.038 g, 27.1%). Elution with benzene–chloroform (1:1) gave **4** (0.106 g, 45.8%), which was recrystallized from cyclohexane to give red needles; mp 274—275 °C; ^{1}H NMR δ=3.21, 3.48, 3.49, 3.63 (each 3H, s, OMe), 6.41 (1H, s, H-3'), 6.67 (1H, dd, J=11.0 and 8.6 Hz, H-7), 7.11 (1H, dd, J=11.6 and 8.6 Hz, H-8), 7.25—7.60 (13H, m, H-phenyl), 7.64 (1H, d, J=11.0 Hz, H-6), 7.73 (1H, d, J=11.6 Hz, H-9), and 7.77 (2H, dd, J=7.9 and 1.8 Hz, H-*o*-phenyl); ^{13}C NMR δ=51.15 (q), 51.34 (q), 51.54 (q), 52.46 (q), 58.05 (d), 94.52 (s), 104.05 (s), 115.21 (s), 115.64 (s), 122.43 (s), 124.80 (d), 126.46 (d×2), 126.78 (s), 127.30 (d×4), 127.70 (d), 127.73 (d×2), 127.96 (s), 128.06 (d), 128.79 (s), 129.34 (s), 129.68 (d×2), 130.35 (d), 130.48 (d×2), 131.72 (d), 131.93 (d), 132.72 (s), 132.91 (d), 137.75 (s), 141.71 (s), 151.02 (s), 163.31 (s), 164.28 (s), 166.34 (s), and 171.06 (s); IR 1742, 1724, and 1705 (C=O), 774, 754, and 696 cm^{-1} (phenyl). MS m/z (rel intensity) 721 (0.8, M$^+$+1), 720 (0.6, M$^+$), 719 (6), 384 (6), 336 (14), 105 (30), 81 (42), 69 (70), 32 (100). Found: C, 71.82; H, 4.73; N, 3.78%. Calcd for $C_{43}H_{32}N_2O_9$: C, 71.66; H, 4.48; N, 3.89%.

Single Crystal X-Ray Structure Determination of 4. The crystals of **4** belong to a monoclinic system with cell dimensions of a= 16.513 (3) Å, b= 21.153 (7) Å, c= 10.714 (4) Å, β=107.14 (2)°, and V= 3621.8 (17) Å^3. The space group is $P2_1/n$, and Z= 4. The empirical formula is $C_{43}H_{32}N_2O_9$, the molecular weight is 720.47, and the caluculated density is 1.29 g cm^{-3}. Three-dimensional X-ray data were collected by the use of graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å) on a Syntex R3 automatic four-circle diffractometer up to a maximum 2θ of 50°. The intensity data from 5762 independent reflections were collected and 3513 with $|F_o|>3\sigma|F_o|$ were used in the present X-ray analysis. The structure was solved by a direct method (MULTAN78). All non-hydrogen atoms were located by an initial E synthesis. The remaining hydrogens were located by a difference Fourier map, and were included in additional calculations. Block-diagonal least

squares refinements with anisotropic 54 non-hydrogen atoms and 32 isotropic hydrogens converged to a conventional R factor of 0.066. All of the calculations were carried out on a HITAC M-680H computer of Hiroshima University using a structure analysis program system (UNICS3).[7,8]

We thank Dr. Akira Mori (Kyushu University) for performing mass spectra and elemental analyses.

References

1) R. M. Acheson and N. F. Elmore, *Adv. Heterocycl. Chem.*, **23**, 263 (1978).
2) R. M. Acheson, *Lect. Heterocycl. Chem.*, **6**, 59 (1982).
3) M. V. George, S. K. Khetan, and R. K. Gupta, *Adv. Heterocycl. Chem.*, **19**, 279 (1976).
4) N. Abe and T. Ueno, *Bull. Chem. Soc. Jpn.*, **63**, 2121 (1990).
5) R. M. Acheson and M. W. Foxton, *J. Chem. Soc. C*, **1966**, 2218.
6) N. Abe, *Heterocycles*, **26**, 59 (1987).
7) T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem. Res. (Jpn.)*, **55**, 69 (1979).
8) Tables of the bond lengths, bond angles, fractional atomic coordinates, and anisotropic thermal parameters are deposited as Document No. 9111 at the Office of the Editor of Bull. Chem. Soc. Jpn.