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CYCLOADDITION OF 2-PHENYL-3-ETHOXYCARBONYL-Δ^2-PYRROLINE-4,5-DIONE TO CYCLOPENTADIENE[1]

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Cycloaddition of 2-phenyl-3-ethoxycarbonyl-Δ^2-pyrroline-4,5-dione to cyclopentadiene in either photochemical or thermal condition gave three products: the dihydropyridone (A), the cyclobutane (B), and the bicycloheptane (C), the structures of which were established by spectroscopic means and by X-ray analyses of their bromo-derivatives. A possible mechanitic rationalization would involve [2a+2s]cycloaddition governed by donor-acceptor interaction followed by cleavage and recombination of a trans-fused cyclobutane.

Previously we showed that the cycloaddition of butadiene to 2-phenyl-3-ehtoxycarbonyl-Δ^2-pyrroline-4,5-dione (1) proceeded in highly regio- and stereoselective manners with an exclusive formation of the cyclobutane derivative (2) under either thermal or photolytic condition[2], and suggested that the product would be the result of [2s+2a] step governed by donor-acceptor interaction between the electron-rich olefin and the electron-deficient dioxo-pyrroline[3]. We now demonstrate that the reaction of cyclopentadiene with the pyrrolinedione proceeds essentially in the same manner.

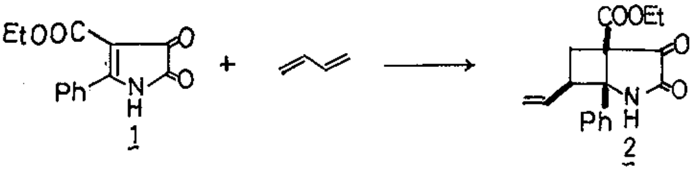


Fig.1

Irradiation of 1 with cyclopentadiene in dimethoxyethane with high pressure mercury lamp (100 W, quartz) at -30° for 1.5 hr yielded three products; [(3), m.p. 119-120°, $C_{17}H_{17}NO_3$ (type A) (4), m.p. 174-176°,$C_{18}H_{17}NO_4$ (type B) and (5), m.p. 180-183°, $C_{18}H_{17}NO_4$ (type C)], in the ratio of 2:1:1 (total yield 60%). The 4'-bromo-derivative (6)[4] similarly gave the adducts; [(7), m.p. 168-170°, $C_{17}H_{16}NO_3Br$ (type A) (8), m.p. 216-218°, $C_{18}H_{16}NO_4Br$ (type B) and (9), m.p. 200-202°, $C_{18}H_{16}NO_4Br$ (type C)]; in the yields of 11, 5, and 22%, respectively. They were easily characterized by their spectral properties (Table I).

Table I. *Spectral Data of Cycloadducts*

Type	Comp.	UV nm (ε)[a]	IR cm^{-1}[b]	NMR[c]	
				-CH$_2$-	H^1 and H^2
A	3	285(9,000)	1670, 1640	2.37, 3.07	3.67 (2H)
	7	285(11,000)	1695, 1635	2.33, 3.07	3.68 (2H)
	11	286(10,000)	1670, 1630	2.33, 3.07	3.63 (2H)
	12	288(9,800)	1680, 1640	2.30, 3.07	3.63 (2H)
B	4	252(4,000)	1760, 1742, 1725	2.60 (2H)	3.88, 4.12
	8	230(21,700) 260 sh (7,800)	1760, 1735, 1700	2.60 (2H)	3.87, 4.04
C	5	end abs.	1775, 1742, 1720	1.75 (2H)	3.16, 3.35
	9	228(22,000)	1775, 1730, 1720	1.75 (2H)	3.12, 3.35

a : in 95% EtOH
b : on Nujol mull
c : 100 MHz in $CDCl_3$, ppm from TMS

Under non-irradiated condition (2 weeks, room temp.) 1 gave the same adducts (3, 4 and 5) in the similar ratios (total yield, 15%) with recovery of a considerable amount of the pyrrolinedione (1).

1-Methyl-Δ^2-pyrroline-4,5-dione (10) gave, however, only the type A adduct (11), m.p. 89-91°, under either photolytic (yield 11%) or thermal condition (yield 17%), which was derivable from 3 on methylation with dimethyl sulfate in CH_3CN. Methylation of 7 similarly gave the corresponding N-methyl derivative (12), m.p. 103-104°.

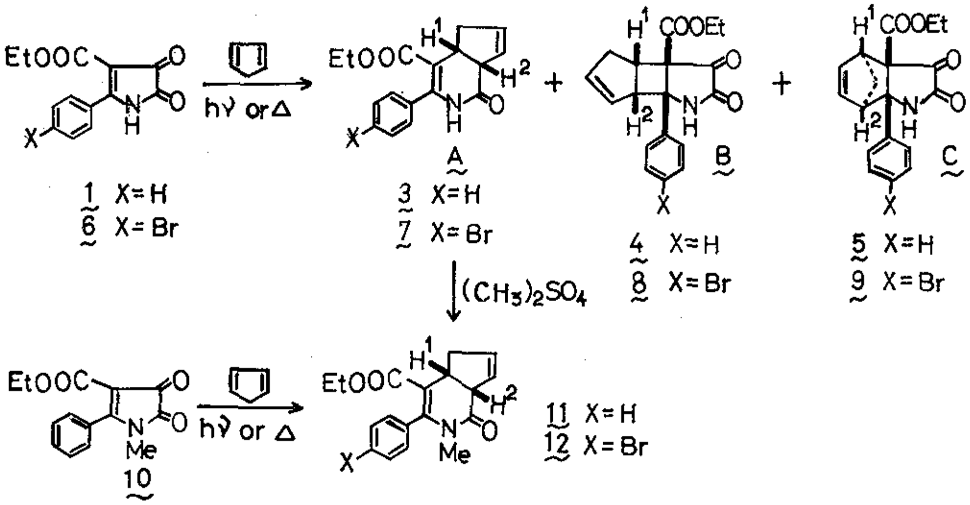


Fig. 2

The structures and stereochemistries of the adducts, (A) and (C), were established by single crystal *X*-ray crystalographic analyses of the 4′-bromo derivatives, (12) and (9).

The compound (12): monoclinic, space group $P2_1/n$ with *a*=22.466, *b*=11.598, *c*=6.464Å, β=95.18°, *Z*=4.

The compound (9): monoclinic, space group $P2_1/c$ with *a*=9.365, *b*=15.311, *c*=11.832Å, β=98.48°, *Z*=4

Three dimensional intensity data were collected on a Philips PW-1100 automatic diffractometer using graphite-monochromated Cu-*K*α radiation. The structures were solved by the heavy atom method. Block-diagonal least-squares refinements based on 2107 and 1980 observed reflections reduced R factors to 0.067 and 0.089 for 12 and 9, respectively. The resulting molecular structures are shown in Fig. 3 and 4, respectively

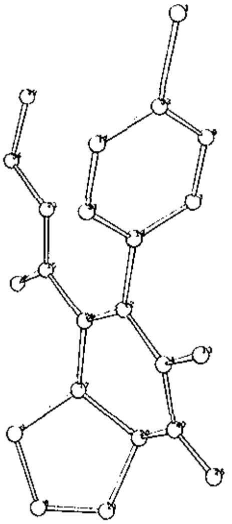


Fig. 3

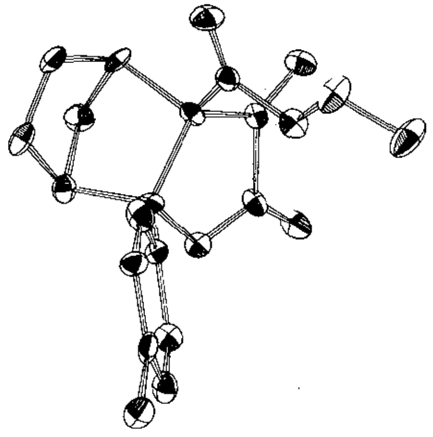
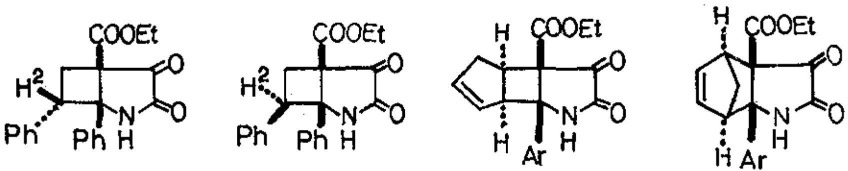


Fig. 4

The adduct B (8) did not give a suitable crystal for X-ray analysis. Its structure and stereochemistry were elucidated as follows. The multiplet PMR signals centered at δ 3.87 and 4.04 ppm for the H^1 and H^2 respectively collapsed into two doublets of $J_{H^1-H^2}=7Hz$ upon simultaneous irradiation at the frequencies of the methylene protons and one of the olefinic protons, thus indicating the presence of $-\overset{H^1}{\underset{|}{C}}-\overset{H^2}{\underset{|}{C}}-$ (cis) grouping[5]. The unusually low chemical shift (4.04 ppm) of H^2 indicated that the ethoxycarbonyl and H^2 are also in cis arrangement as discussed in the cases of 13 and 14[6]; the corresponding signal of 2 appeared at δ 3.30 ppm which would shift to lower field by about 0.7 ppm when the stereochemistry of the vinyl group is inverted[2]. Thus the compound B is the endo[2s+2s]cycloadduct (8). This elucidation was supported by the observation that B changed into C, though in minute amount, on heating it in toluene at 160° for 2 hr (TLC detection)[7].



13 14 B′ C′

Fig. 5

It should be noted that neither the stereoisomer (B′) of B nor the isomer (C′) of C was isolated from this cycloaddition reaction, and that neither B nor C is the intermediate to A, since they were not interconvertible each other nor convertible to A under the reaction conditions where they have been formed (either photolytic or thermal). They should be the independent products.

The above evidence will be reasonably explained by Epiotis' theory[8] which predicted that in semipolar cycloadditions the both [2s+2s] and [2a+2s] steps are allowed for either thermal or photolytic process. If we assume that the reaction is governed by donor-acceptor interaction (DA-complex 15) and [2a+2s] step is preferable as we have already suggested[3], the initial cycloadducts should be 16 and 17. Concomitant [2s+2s] step will also give B though to a lesser extent, and its stereoisomer (B′) should not be produced. The adducts (16 and 17) will be cleaved, due to severe strain of trans-fused cyclobutane, to the biradical intermediates (18 and 19) which on rotating around the central bond as depicted in Fig. 6 and by recombining at the carbons with asterisk each other (principle of least motion)[9] will yield

C and 20. The latter will easily lose a CO function to furnish the dihydropyridone A.

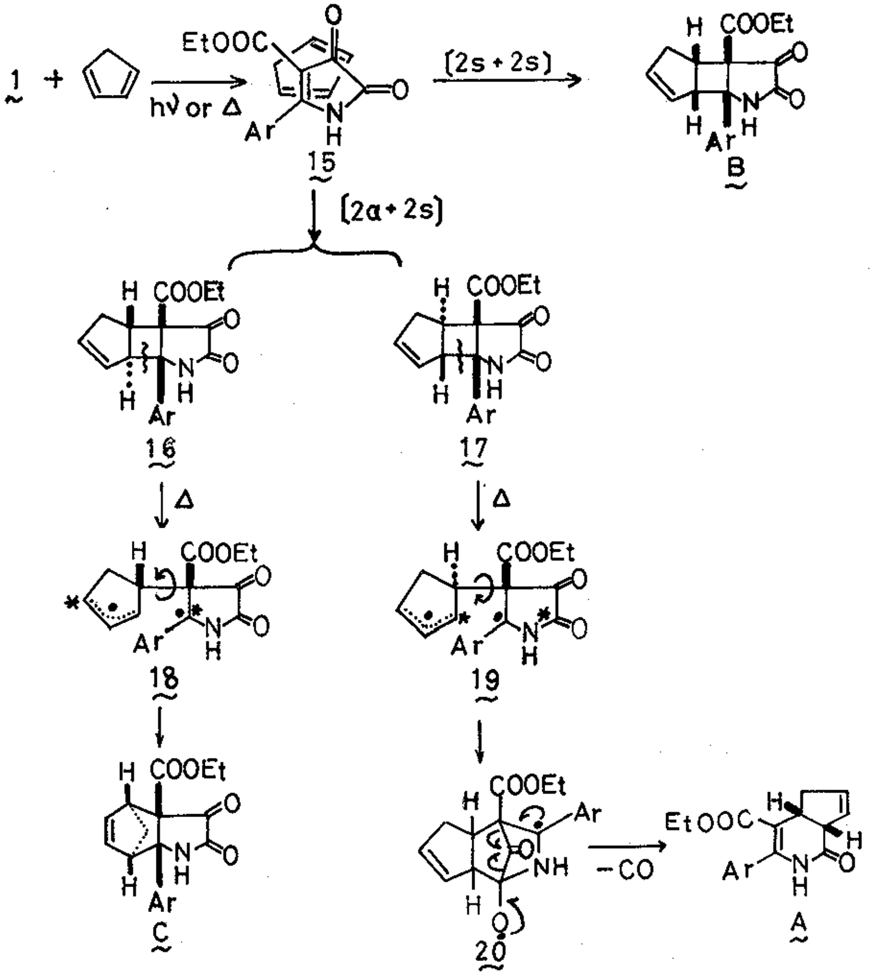


Fig.6

The compound C should not be the direct 1,4-addition product, for [4s+2s] step from the transition state 15 would give the stereoisomer C′.

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3. T. Sano and Y. Tsuda, H. Ogura. K. Furuhata, and Y. Iitaka, *Heterocycles*, **4**, 1233 (1976).
4. **6** was prepared by condensation of ethyl β-amino-β-(p-bromophenyl)acrylate with oxalyl chloride as orange prisms, m.p. 204-207°, IR: 3300-3200, 1785, 1730, 1710 cm^{-1}.
5. The coupling constant between H^1 and H^2 in **9** (C) was proved to be nearly zero by the similar experiment.
6. H^2 in **13** and its epimer **14** appeared at δ4.83 and 4.17 ppm respectively, $\Delta\delta$=0.66 ppm [T. Sano and Y. Tsuda, *Heterocycles*, **4**, 1229 (1976)].
7. Prolonged heating caused profound pyrolysis to give a complex mixture with concomitant disappearance of C.
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