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CYCLOADDITION OF 2-PHENYL-3-ETHOXYCARBONYL-Δ^2-PYRROLINE-4,5-DIONE WITH BUTADIENE. EVIDENCE OF [1,3]SIGMATROPY FOR FORMATION OF THE DIELS-ALDER PRODUCT[1]

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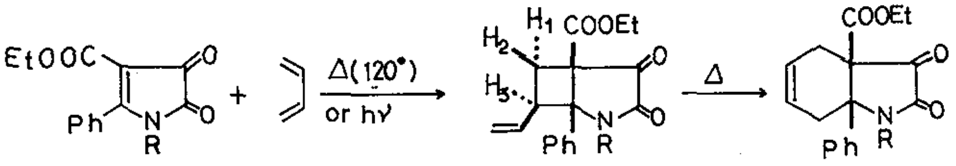
Thermal and photochemical cycloaddition of 2-phenyl-3-ethoxycarbonyl-Δ^2-pyrroline-4,5-dione (1) with butadiene afforded the same 1,2-adduct (2) in regio- and stereoselective manner. At elevated temperature the 1,2-adduct (2) changed by an 1,3-sigmatropic shift into the normal Diels-Alder adduct (3). The easiness of sigmatropy was greatly influenced by the nature of N-substituents and decreased by the following order : H > Me > Ph. In case of N-phenyl derivative, the rearrangement was not observed.

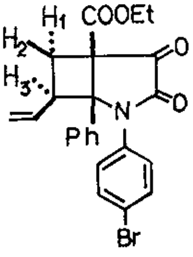
Previously Tsuda and Isobe[2] reported that 3-phenyl-Δ^2-pyrroline-4,5-dione possessed a dienophile character and gave the nomal Diels-Alder product in thermal reaction with butadiene. We present here cycloaddition reaction of 2-phenyl derivative with butadiene, which behaves quite differently.

Heating of 2-phenyl-3-ethoxycarbonyl-Δ^2-pyrroline-4,5-dione (1a) with butadiene in CH_2Cl_2 or in DMF at 120° for 40 hr gave an 1:1 adduct in about 10% yield, which was unexpectedly the [2+2] cycloadduct (1,2-adduct) and identical with the photocycloadduct[3] (2a) obtained (47%) by irradiation of 1a and butadiene in dimethoxyethane (-10°, 40 min.) with high pressure mercury lamp. The formation of 2a in the both photolytic and thermal reaction was highly regio- and stereoselective, no 1,4-adduct being found in the mixture. While heating of 1a and butadiene at 180° for 28 hr in CH_2Cl_2, the [4+2] cycloadduct (3a) was produced in 10% yield, the 1,2-adduct being not detected in this case. The 1,2- and 1,4-cycloadduct were easily characterized respectively by their spectral data as seen in Table I.



(1) (2) (3)

R: a=H, b=$COCH_3$, c=Me, d=Ph



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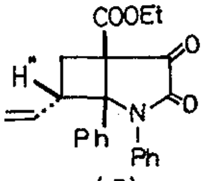

(5)

Table I. Physical and Spectral Data of the Cycloadducts

1,2-adduct	m.p.	IR(Nujol)cm^{-1}	NMR(δ,ppm) olefinic protons (3H)*
2a	146-149°	1765, 1740, 1700	4.9 6.0
2b	146-148°	1775, 1760, 1740, 1717	5.0 6.0
2c	164-166°	1765, 1740	5.1 6.3
2d	199-201°	1765, 1741, 1725	5.2 6.5
4	193-195°	1772, 1741, 1720	5.2 6.5
5	180-183°	1762, 1742, 1725	4.9 5.5
1,4-adduct			olefinic protons
3a	228-230°	1780, 1755, 1730	6.03¶
3b	164-166°	1780, 1740, 1720, 1700	5.97†
3c	158-160°	1765, 1740, 1720	6.02†

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* Signal showed a typical splitting pattern of vinyl protons.

¶ Signal appeared as diffused multiplets.

† Signal appeared as a broad singlet.

The regio- and stereochemistry of the vinyl group in 1,2-adduct (2) was elucidated from the analogy of the photocycloadduct (4) of N-4′-bromophenyl derivative with butadiene, whose structure has been determined by X-ray analysis[4]. The chemical shifts and the splitting patterns due to the protons on the cyclobutane ring of 2a～2d were similar to those of 4 as shown in Table II.

Table II. NMR Spectra of 1,2-Adduct (δ, ppm)

compound	H_1	H_2	H_3
2a	2.50	3.07	3.30
2c	2.45	∼[π]	3.20
2d	2.60	3.26	3.45
4	2.55	3.17	3.48

H_1 : Signals appeared as a pair of two quartets.

H_2 : The signal appeared as a quartet. The chemical shift given here indicates a half (doublet) of it, which appeared at upper field. The other half at lower field is overlapped with signals of other protons.

H_3 : Signal appeared as a multiplet.

[π] : Signal is overlapped with N-Me signal.

On heating the compound (**2a**) at 180° for 6 hr in toluene it furnished quantitatively the 1,4-adduct (**3a**). This indicates that [4+2] adduct (**3a**) formed by the reaction of **1a** with butadiene is not the initial product but was formed from the [2+2] adduct (**2a**) by [1,3] sigmatropic rearrangement with retention of the configuration at migrating carbon.

The yield of **2a** and hence that of **3a** were markedly improved by changing the solvent to acetic anhydride. Thus, by the reaction at 100° for 80 hr N-acetyl-1,2-adduct (**2b**) and at 160° for 8 hr N-acetyl-1,4-adduct (**3b**) were produced in 20% and 60% yields, respectivly. Again **2b** rearranged to **3b** on heating at

160° for 10 hr in acetic anhydride. This marked improvement of the yield by using acetic anhydride is not merely attributable to the solvent effect of changing the polarity but is understood by assuming the formation of an intermediate N-acetyl-Δ^2-pyrroline-4,5-dione (1b) whose electrophilicity at C_2 is apparantly increasing compared to 1a. In fact, acetic anhydride was not effective for N-methyl derivative (1c) which gave 1,2-adduct (2c) (~10%) at 160° for 8 hr and 1,4-adduct (3c) (~10%) at 180° for 24 hr by reaction with butadiene in either CH_2Cl_2 or acetic anhydride. The same 1,2-adduct (2c) was obtained in 30% yield by photo-cycloaddition and rearranged into 1,4-adduct (3c) on heating at 180°. Photo-cycloaddition of N-phenyl derivative (1d) with butadiene gave two 1,2-cycloadducts (2d) (major) and (5) (minor). The minor product (5) was elucidated as a stereoisomer of 2d since its spectral data were very close to those of 2d except that the NMR signal (δ, 4.31m.) of the proton with asterisk in 5 appeared at lower field by 0.86 ppm than that of 2d. This indicated that the ethoxycarbonyl in 5 are in cis-arrangement. Even heating above 200°, 2d did not rearranged to the N-phenyl-1,4-cycloadduct (3d), but thermal decomposition took place to give a complex mixture. The above evidence indicates that the thermal [1,3]sigmatropy of (2)→(3) is greatly influenced by the nature of N-substituent.

Ionic rearrangement (2)→(3) in the case of N-hydrogen derivative was also observed. Treatment of 2a with 5% hydrochloric acid in methanol for 30 min. gave 3a in good yield. Neither

N-methyl nor N-phenyl derivatives rearranged into the corresponding 1,4-adduct.

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