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PHOTOCHEMICAL CYCLOADDITION OF 2-PHENYL-3-ETHOXYCARBONYL-Δ^2-PYRROLINE-4,5-DIONE WITH OLEFINS[1]

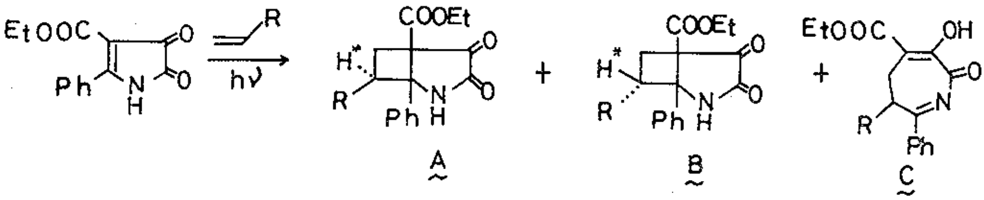
Takehiro Sano and Yoshisuke Tsuda*
Showa College of Pharmaceutical Sciences, Setagaya-ku,
Tokyo-154, Japan

Photocycloaddition of 2-phenyl-3-ethoxycarbonyl-Δ^2-pyrroline-4,5-dione with olefins carrying electron rich group proceeds in highly regio- and stereoselective manner to give [2+2] cycloadducts, while olefins substituted by electron withdrawing group gave no cycloadduct, suggesting that donor-acceptor interaction between two reactants may play an important role in this reaction.

Very little is hitherto known about the reactivity of the double bond in Δ^2-pyrroline-4,5-diones (dioxopyrrolines)[2]. We describe here the photochemical cycloaddition reaction of olefins with 2-phenyl-3-ethoxycarbonyl-Δ^2-pyrroline-4,5-dione (1), deep yellow crystals, m.p. 185-186° which was prepared by reaction of oxalyl chloride with ethyl β-amino-cinammate.

Irradiation of a mixture of 1 and styrene in dimethoxyethane with high pressure mercury lamp at 0° for 30 min gave three products: A, m.p. 202-204°, $C_{21}H_{19}O_4N$; B, m.p. 180-183°, $C_{21}H_{19}O_4N$, (spectral data see Table II); and C, m.p. 134-135°, $C_{21}H_{19}O_4N$, IR (Nujol): 3200, 3100, 1690, 1670, 1640 cm^{-1}, UV λmax: 285 nm (ε 10,000).

The formula and spectral data of the major product (A) revealed that it is the [2+2] cycloadduct (2) of the two reactants. The regio- and stereochemistry of the substituent was elucidated by analogy with the structure of photo-cycloadduct (7) of 1-[4'-bromophenyl]-2-phenyl-3-ethoxycarbonyl-Δ^2-pyrroline-4,5-dione with styrene, whose structure has been determined by X-ray analysis[3]. The spectral data of 2 were similar to those of 7.



A

(2) R=Ph

(3) R=OEt

(4) R=OAc

(5) R=CH=CH$_2$

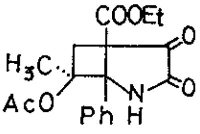
B

(8) R=Ph

C

(9) R=Ph

(10) R=OEt



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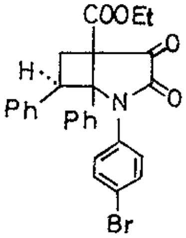

(7)

The analogous [2+2] photo-cycloadducts (3)-(6) were similary obtained, in moderate yield by reaction of 1 with ethyl vinyl ether, vinyl acetate, butadiene, and isopropenyl acetate, respectively, the results and the properties of the products being

Table I Photo-cycloaddition of 1 with Olefins

Olefin	Reaction Conditions		Product (Yield, %)		
	temp. (°c)	time(min)	A	B	C
$CH_2=CH-Ph$	0	30	(2) 37	(8) 1	(9) 1
$CH_2=CH-OEt$	0	60	(3) 55	—	(10) 4
$CH_2=CH-OAc$	0	45	(4) 21	—	—
$CH_2=CH-CH=CH_2$	-10	60	(5) 47	—	—
$CH_2=C(Me)-OAc$	0	45	(6) 54†	—	—

† Assignment of the stereochemistry is tentative.

Table II Spectral Data of Photocycloadducts

Compound	m.p.	UV(dioxane)	IR(Nujol)	NMR(H^*)
		λ nm (ε)	cm^{-1}	δ (ppm)
(2)	202-204°	227 (7,600) 260sh (3,900)	1780, 1745, 1732	4.17t. J=10 Hz
(3)	149-152°	225 (5,100) 255sh (3,300)	1760, 1720	4.77q. $J_1=8$ $J_2=7$ Hz
(4)	oil	255	1780, 1740¶	5.88q. $J_1=9$ $J_2=6$ Hz
(5)	146-149°	258 (3,800)	1765, 1740, 1700	overlapped
(6)	164-166°	258 (3,400)	1775, 1730	
(7)	181-183°	223 (19,000) 260sh (4,800) 310 (6,200)	1762, 1740, 1718	3.87t. J=10 Hz
(8)	180-183°	227 (7,600) 255sh (3,600)	1781, 1745, 1720	4.83t. J=9 Hz

¶ measured in CH_2Cl_2 solution.

summarized in Table I and II. The structures of these cycloadducts were elucidated by comparisons of their spectral data with those of **2**. In most cases the compounds of type **B** and **C** were not isolated.

Contrary to the above olefins, olefins carrying electron withdrawing group (e.q. methyl acrylate, acrylonitrile) gave no cycloadduct, the starting material being recovered. This evidence suggests that donor-acceptor interaction between electron deficient double bond of **1** and electron rich olefins may play an important role in the above photo-cycloaddition[4].

One of the minor by-product (**B**) was elucidated as a stereoisomer (**8**) of compound **A** since its spectral data were very similar to those of **2** except that the NMR signal of the proton with asterisk in compound **B** (see compound **8** in Table II) appeared at lower field by 0.66 ppm than that of **2**. This marked shift indicated that the proton and the ethoxycarbonyl group in compound (**8**) are in cis-arrangement.

The spectral data of compound **C** were profoundly different from those of compounds **A** and **B**. To this compound we tentatively assigned the dihydroazatropolone structure (**9**) which will be discussed in a separate communication.

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