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THERMAL REACTION OF 1-PHENYL-2-ETHOXYCARBONYL-3-BENZOYL-Δ^2-PYRROLINE-4,5-DIONE WITH OLEFINS[1]

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Olefins carrying electron rich substituents thermally cycloadded to 1-phenyl-2-ethoxycarbonyl-3-benzoyl-Δ^2-pyrroline-4,5-dione in regio- and stereospecific manner to give [4+2] cycloadducts, while olefins with electron deficient substituents did not react at all. These facts indicated that the donor-acceptor interaction played an important role in this reaction.

Here we present a new example of cycloaddition of olefins with 3-acyl-dioxopyrroline by choosing 1-phenyl-2-ethoxycarbonyl-3-benzoyl-Δ^2-pyrroline-4,5-dione (1) as a model, which was prepared from ethyl benzoylpyruvate by the route shown in chart 1.

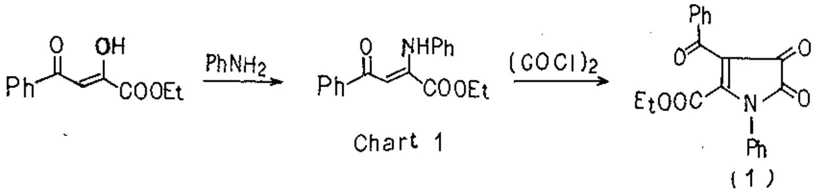
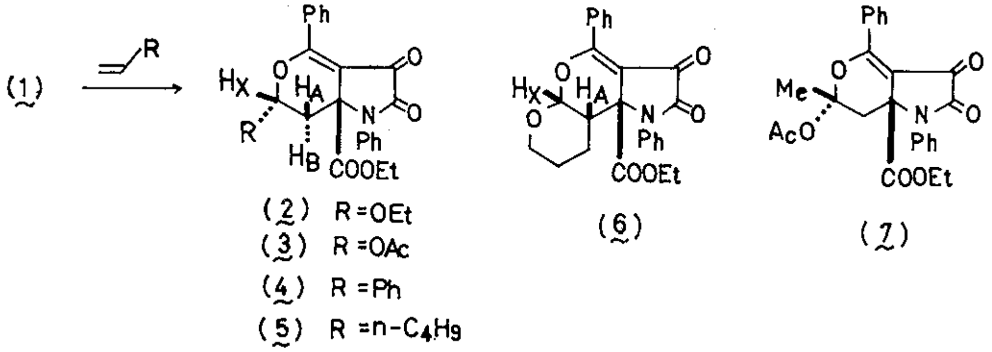


Chart 1

The compound (1) was obtained as deep orange crystals, m.p. 165-168°, IR: 1780, 1740, 1730, 1640, 1600 cm^{-1}, UV (in dioxane): peaks at 230-275 (ε 12,600-14,000), broad peak centred at 410 nm (ε 3,000).

On heating 1 with ethyl vinyl ether in toluene at 80-100°, rapid reaction took place to afford 1:1 cycloadduct (2) in a quantitative yield. Dihydropyran, vinyl acetate, isopropenyl acetate, and styrene also gave the similar cycloadducts, (3), (4), (6), (7), respectively in satisfactory yields, the results being summarized in Table I.



(2) R =OEt
(3) R =OAc
(4) R =Ph
(5) R =n-C_4H_9
(6)
(7)

Chart 2

The structure and stereochemistry of the cycloadducts were established as illustrated in chart 2 from their spectral data. For example, the adduct (2) from ethyl vinyl ether exhibited λ max 235 (ε 12,700) and 323 nm (ε1,500) in the UV spectrum (in dioxane), and carbonyl absorptions at 1730 and 1720 cm^{-1} in the IR spectrum (Nujol). In NMR spectrum, besides two phenyl and two OEt groups, signals due to H_A, H_B, and H_X were observed at δ 3.33 (q.), 1.98(q.), and at δ 5.83(q.). Appreciable difference in chem-

Table I. Cycloaddition of 1 with Olefins and Physical Data of Cycloadducts

	temp.	time (hr)	yield (%)	cycloadduct	
				comp*.	m.p.
CH_2=CH-OEt	80-100°	2	100	(2)	188-190°
	"	0.5	100	(6)	232-235°
CH_2=CH-OAc	120°	15	76	(3)	209-213°
CH_2=CH-Ph	120°	3	77	(4)	240-243°
CH_2=C(CH_3)-OAc	120°	5	42	(7)†	180-182°
CH_2=CH-C_4H_9	120°	6	12	(5)	195-196°

* All compounds gave satisfactory elementary analyses.

† Assignment of the stereochemistry is tentative.

Table II. NMR Spectra of Cycloadducts (δ ppm, 60 MHz, $CDCl_3$)

adducts	H_X	H_A	H_B
2	5.83q. J_1=4, J_2=10 Hz	3.33q. J_1=4, J_2=13 Hz	1.98q. J_1=10, J_2=13 Hz
6	6.10d. J=5 Hz	3.00m.	—
3	6.93q. J_1=5, J_2=10 Hz	3.10q. J_1=5, J_2=13 Hz	2.08q. J_1=10, J_2=13 Hz
4	5.80q. J_1=4, J_2=13 Hz	3.07q. J_1=4, J_2=13 Hz	2.01t. J_1=13, J_2=13 Hz
7	—	3.53d. J=15 Hz	2.67d. J=15 Hz
5	4.85m.	2.87q. J_1=4, J_2=13 Hz	overlapped

ical shift of H_A and H_B indicated that stereochemical situation of these two protons to the ethoxycarbonyl and to the N-phenyl group are markedly different. Coupling constants between H_A and H_X (J=4 Hz) and between H_B and H_X (J=10 Hz) indicated that H_X and H_B were diaxially oriented while H_X and H_A were in cis-relationship.

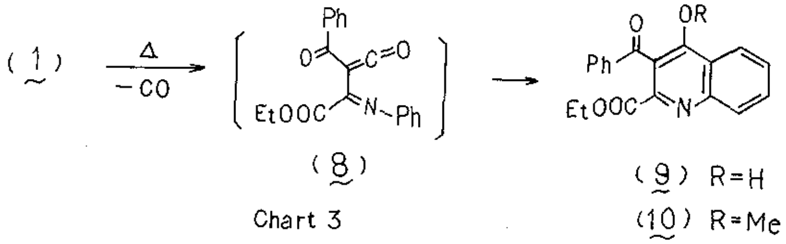
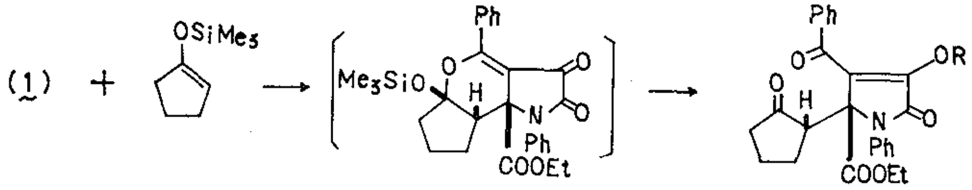


Chart 3

The structure thus elucidated revealed that the products are [4+2] cycloadducts in which the 3-acyl-dioxopyrroline played as a diene (electron deficient) and the olefins as dienophiles (electron rich). Alkyl substituted olefins such as 1-hexene also gave the cycloadduct (5) but in lower yield. Contrary to the above results, olefins with electron withdrawing group (methyl acrylate, cis- and trans-1,2-dichloroethylene) did not give cycloadduct at all, but on heating at 160° thermolysis of 1 took place to afford the quinoline derivative (9), m.p. 233-236°, (methyl ether 10, m.p. 131-135°), which probably proceeded by initial loss of CO followed by cyclization of the resulting acylketene to N-phenyl group as shown in chart 3. Similar thermolysis of 1,2-diphenyl-3-benzoyl-Δ^2-pyrroline-4,5-dione was reported by Ziegler et al[2], but higher temperature (250°) was required in their case.

The cycloaddition here we presented is formally equivalent to Michael type condensation of active methylene group to the positive centre (C_2) of dioxopyrroline, although the mechanisms are entirely different each other. Our reaction was slightly affected by acids (e.g. TsOH, $SnCl_4$). However, in the cases of enolacetates the yield of the cycloadducts decreased by addition of TsOH probably due to decomposition of the reactants. Base (NEt_3) did not show catalytic action at all. The main factor controlling the reaction was temperature. For example, the reaction of vinyl acetate at 120° afforded 3 in 70% yield which decreased to 8% at 80°, and only trace amount of 3 was found in the reaction at 40°.

We therefore concluded that the reaction was a concerted thermal cycloaddition accelerated by polar charactors of the two reactants[3].



(11)

(12) R=H
(13) R=CH_3

Chart 4

Interestingly the reaction of trimethylsilyloxycyclopent-1-ene[4] with 1 in toluene at 100° gave the compound (12) [$C_{25}H_{23}O_6N$, m.p. 203-205°, IR: 3200, 1741, 1697, 1680, and 1648 cm^{-1} ; UV: λ max 258 (ε 11,300), 306 (shoulder, ε 6,000) and 354 nm (ε 3,000);

NMR: no $SiMe_3$ group; methyl ether (13), m.p. 140-141°], whose cyclopentanone moiety would be directly inserted. This may be due to instability of the intermediate trimethylsilyl ether of hemiacetal (11).

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