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DIELS-ALDER REACTION IN A POLAR SYSTEM. THERMAL CYCLOADDITION OF 1-PHENYL-2-ETHOXYCARBONYL-3-BENZOYL-Δ^2-PYRROLINE-4,5-DIONE WITH BUTADIENES[1]

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In thermal reactions of 1-phenyl-2-ethoxycarbonyl-3-benzoyl-Δ^2-pyrroline-4,5-dione (1) with butadienes, two types of [4+2] cycloaddition were observed. One was a formation of pyrano-pyrrole deivative (type A), where butadiene behaved as a dienophile and pyrroline-4,5-dione as a diene. The other was an usual Diels-Alder product (type B). The type A adduct thermally rearranged in a [3,3]sigmatropic manner into the type B adduct. 1-Acetoxy-, 1-sulphenyl-, and 1-trimethylsilyloxy butadienes also cycloadded to 1 and afforded only type B adducts, which were suggested to be formed from the initially generated type A adducts. The similar phenomenon was observed in the cycloaddition reaction of 1 with norbornadiene.

In a preceding paper[1] we showed that 1-phenyl-2-ethoxycarbonyl-3-benzoyl-Δ^2-pyrroline-4,5-dione (1) thermally reacts with olefins to afford the [4+2] cycloadduct (2). Reaction of 1 with butadiene is of theoretical interest since there are two possible [4+2] ways; whether 1 behaves as an electron deficient diene giving the product (A) or it behaves as an electron deficient dienophile to give the usual Diels-Alder product (B).

Heating of 1 with butadiene in toluene at 100° afforded two cycloadducts of the same molecular folmula, $C_{24}H_{21}O_5N$ (3) and (4), which have the following properties. (3), m.p.247°, IR: 1740, 1730, 1500 cm^{-1}, UV: λmax 320nm (ε=15,800); (4), m.p.150-152°, IR: 1780, 1740, 1715, 1640 cm^{-1}, UV: λmax 245 (ε=19,300), 349 nm (ε=1,900).

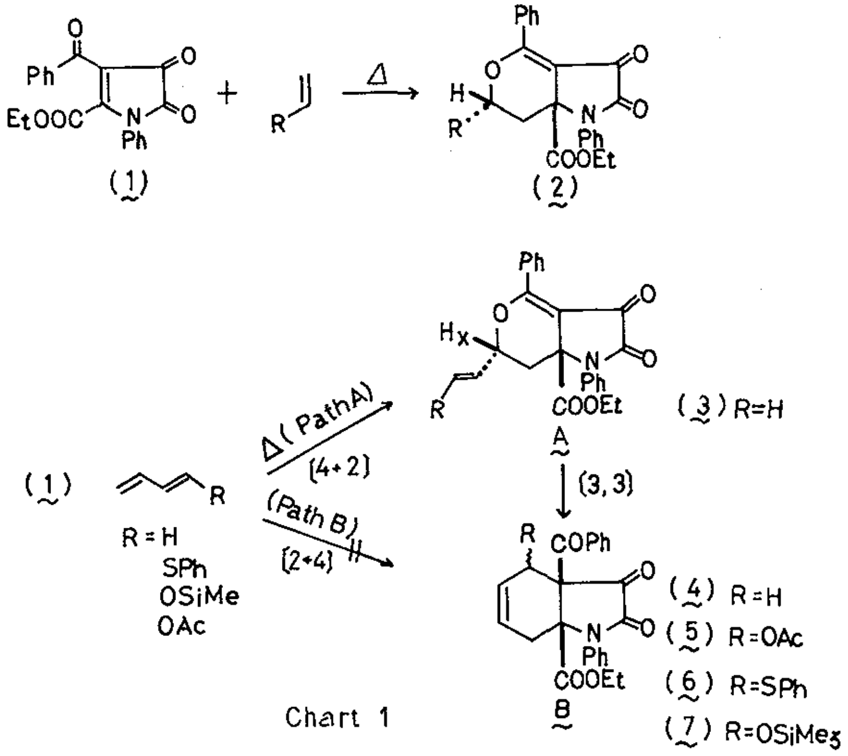


Chart 1

3 was the compound of type A since its spectral data were similar with those of 2 obtained in a previous paper except that it showed complex peaks at δ5.0∿6.2 corresponding to four protons indicative of presence of $-CH=CH_2$ grouping which was overlapped with Hx signal.

The structure of 4 was elucidated as follows. Its carbonyl absorption (1780 cm^{-1}) was characteristic of that of dioxopyrrolidines and the olefinic proton signal at δ5.67 appearing as a broad singlet of 2H was characteristic of cis-fused tetrahydroindan system. In accordance with these evidence the UV absorption of 4 showed that PhCO group was not conjugated with the dioxo-system.

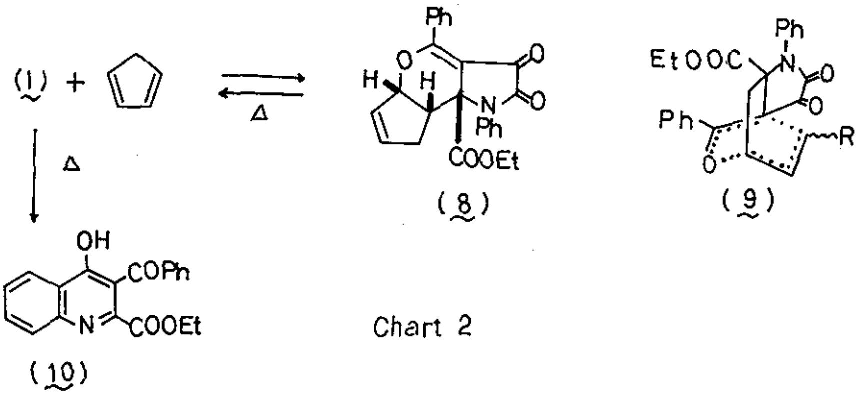
Interestingly the ratio of 3 and 4 was dependent on the reaction temperature: the reaction at 160° afforded 4 as a major product and, on the contrary, 3 was obtained as an only isolable product from the reaction at 90°, although the total yield decreased by lowering temperature. These facts suggested that the type A adduct (3) rearranged thermally in a [3,3]sigmatropic manner to the type B adduct (4). In fact, on heating 3 at 160° for 8 hr it quantitatively changed into 4, this rearrangement being not observed below 90°.

1-Acetoxy-, 1-sulphenyl-, and 1-trimethylsilyloxy-butadiene smoothly cycloadded to 1 at lower temperature to give, contrary to butadiene, only one product of type B, (5)∿(7)[2] in moderate yield, respectively (for reaction conditions and results, see Table I).

Table I. Reaction of 1 with Butadienes

Dienes	Temp. (°C)	Time (hr)	Product and Yield (%) A	B	m.p.
$\mathrm{CH_2=CH-CH=CH_2}$	160°	6	(3) 7	(4) 66	(3) 247°
	100°	9	40	10	(4) 150-152°
	90°	48	18	trace	
$\mathrm{AcO-CH=CH-CH=CH_2}$	80°	3.5	—	(5) 46	(5) 257-259°
$\mathrm{PhS-CH=CH-CH=CH_2}$	80°	5	—	(6) 70	(6) 185-187°
$\mathrm{Me_3SiO-CH=CH-CH=CH_2}$	20°	48	—	(7) 27	(7) 148-151°
	-60°	12	(8) 60	—	(8) 193-194°

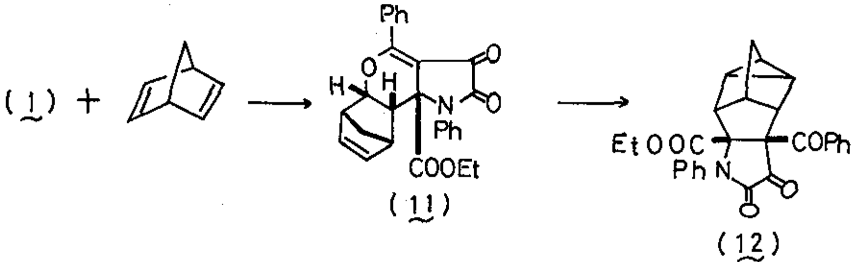
At first sight these products seemed to be directly produced by path B, since the type A product could not be found even in the reaction mixture obtained at the lower temperature conditions. We, however, claim that they are again produced by [3,3]sigmatropic rearrangement of the intermediate type A compounds during the reaction or on work-up, since electron releasing substituents (-OAc, -SPh, $\mathrm{-OSiMe_3}$, etc) on the double bond are known to decrease the activation energy of sigmatropy[3]. If we anticipate the activation energy from (3) to (4) is ca. 20 Kcal/mol[4], whose decrease of 5 Kcal/mol[5] will lower the reaction temperature about 100°. The above consideration may be supported by the following evidence. Cyclopentadiene cycloadded to 1 at -60° only in type A fashion to give 8 in excellent yield, which however did not rearrange to type B compound on heating at above 180° (24 hr), instead retro-cycloaddition took place to furnish the pyro-compund (10)[6]. Apparrently the formation of transition state (9) of [3,3]sigmatropic rearrangement (A)→(B) is sterically prohibited by introduction of the additional methylene group into 9.



(8) (9) (10)

Chart 2

We therefore conclude that in the Diels-Alder reaction of 1 butadienes always behaved as the electron rich dienophiles to give type A compounds which, if they have suitable stereochemical requirement, rearranged thermally in a [3,3] fashion to the usual Diels-Alder products.



(11) (12)

Chart 3

The similar phenomenon was observed in reaction of norbornadiene with 1. When the two reactants were heated in toluene at 120°, two products, (11), m.p. 222-225° and (12), m.p. 178-180°, were produced in 27% and 7% yield, respectively. The former rearranged to the latter, the usully expected [2+2+2] product, on heating at 180°, the structures of both products being elucidated from this observation and from their spectral data.

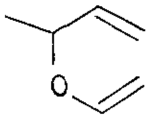
REFERENCES AND FOOTNOTES

1 Dioxopyrrolines V. Part IV: Y. Tsuda, Y. Horiguchi, and T. Sano, Heterocycles, 1976, 4, 1237.

2 Position of the substituents (R) were tentatively assigned as depicted in the Chart 1.

3 N. D. Epiotis, Angew. Chem., Internat. Edn., 1974, 13, 751

4 The activation energy of Cope and oxo-Cope rearrangement decreases by mutual increase of opposite polarity of two migrating residues. In our system the sigmatropy may be more favored by structural and electronic reasons than that in the simple system (13), for which 27.9 Kcal/mole of activation energy was suggested[3].



(13)

5 In a extreme case, 9 Kcal/mole decrease of the activation energy by substitution with trimethylsilyloxy group was reported. (G. M. Trost and M. J. Bogdanowicz, J. Amer. Chem. Soc., 1973, 95, 5311.)

6 See Part IV.

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