Tetrahedron Letters No. 49, pp 4517 - 4520, 1976. Pergamon Press. Printed in Great Britain.

THE INTRAMOLECULAR DIELS-ALDER ADDITION OF ALLYL- AND PROPARGYLAMIDES OF 2,4-DIENECARBOXYLIC ACIDS; SYNTHESIS OF POLYCYCLIC γ-LACTAMS.

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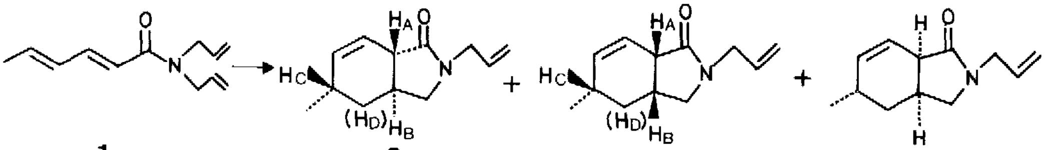
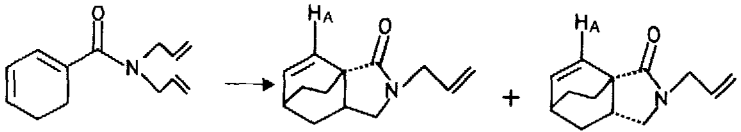
(Received in UK 4 October 1976; accepted for publication 18 October 1976)

The interesting possibility of creating two rings in one step has lately made the intramolecular Diels-Alder addition an increasingly utilized tool in organic synthesis [1] (for some newer examples see ref. 2). In connection with our interest [3,4] for the scope of this reaction we investigated, among others, the pyrolysis of the αβγδ-unsaturated N-allyl and N-propargylamides 1, 5, 8, 11 and 14 [5].



1 2 3 4

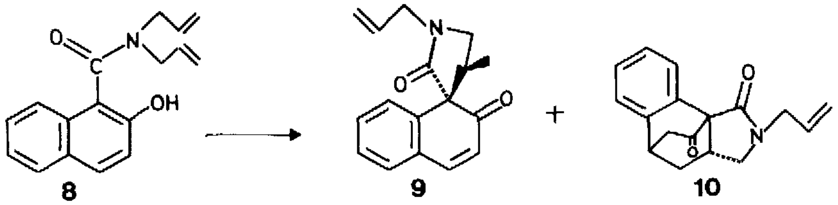
Pyrolysis of 1 gave rise to three products (Table 1), the exo-addition product 2, the endo-product 3 and 4, which is derived from 2 [6] (see ref. 7). In the cis-fused derivative 2:J_{AB} = 12 Hz, J_{CD} = 7 Hz, $J_{CD'}$ = 3 Hz; in 3:J_{AB} = 10.5 Hz, J_{CD} = 11 Hz and $J_{CD'}$ = 4-5 Hz. 2 can be quantitatively converted into 4 by heating in boiling DMF or by potassium t-butylate at room temperature.



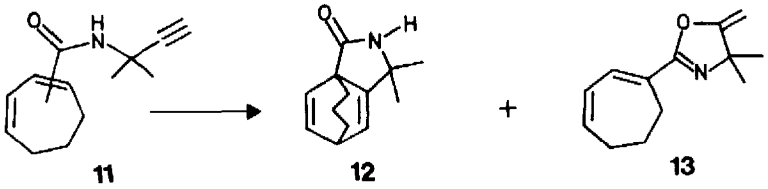
5 6 7

Similarly, amide 5, prepared from cyclohexa-1,3-dienecarboxylic acid [8], gave a mixture of the endo- and exo-addition products 6 and 7, respectively. Models show, that H_A (6.62 ppm) in 6 should be more deshielded by the carbonyl group than H_A (5.96 ppm) in 7.

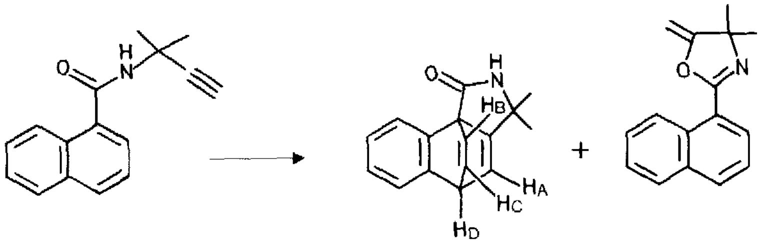
In the thermal reaction (218°) of 8, the main product 9 was formed by an intramolecular ene reaction. In contrast to the above results of the pyrolysis of 5, 8 gave rise only to the one Diels-Alder product 10 [9,10].



Amide 11, prepared from a mixture of isomeric cycloheptadiene carboxylic acids [11], was a mixture of three isomers, which under the pyrolytic conditions (218°) underwent a series of rapid [1,5] H-shifts [11]. The only intramolecular 4+2-adduct was the lactam-bridged bicyclo [3,2,2] -derivative 12, which was accompanied by small amounts of the oxazoline derivative 13.



Finally, the naphthalenecarboxamide 14 gave rise to the benzobarrelene derivative 15 [NMR (100 MHz, CDCl$_3$): 8.0-7.8 ppm, NH; 7.5-6.77 ppm, 4 aromatic protons and H_C; 7.04 ppm, dxd, J_{BC} = 6.5 Hz, J_{BD} = 1.5 Hz, H_B; 6.54 ppm, d, J_{AD} = 5.8 Hz, H_A; 4.97 ppm, dxdxd, J_{DA} = 5.8 Hz, J_{DC} = 5.2 Hz, J_{DB} = 1.5 Hz, H_D; 1.42 and 1.27 ppm, s of the CH$_3$-groups. IR. (CHCl$_3$): 3420 cm^{-1}, 1700 cm^{-1}]. This high yield (Table 1) reaction represents a surprisingly facile 4+2-addition of the naphthalene nucleus [10] (for intermolecular examples see ref. 12) and an easy access to a substituted benzobarrelene [13].



14 15 16

TABLE 1

Products and conditions of pyrolysis of carboxamides 1, 5, 8, 11 and 14

Educts	Conditions	Yield	Products
1	3 hours, [a]	80%	40% 2, 55% 3, 5% 4
5	1.5 hours, [a]	80%	70% 6, 30% 7 [c]
8	3.5 hours, [b]	70%	48% 9, 22% 10
11	3 hours, [b]	78%	71% 12, 7% 13
14	3.5 hours, [b]	76%	72% 15, 4% 16

[a] 156°, DMF

[b] 218°, N,N-Diethylaniline

[c] not separated.

Acknowledgement:

I thank Dr. W. Arnold (F. HOFFMANN-LA ROCHE & CO. AG, Basle) for his help in the discussion of the NMR spectra.

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