Thermolysis of Allene-1,1-dicarboxamides: Acceleration of the Intramolecular Diels–Alder Reaction by Intramolecular Hydrogen Bonding and a Novel Bicyclo[2.2.2]- to Bicyclo[3.2.1]-alkadiene Rearrangement

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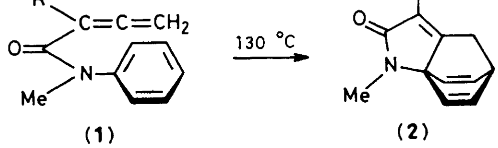
Allene carboxanilides (**5**) with an additional geminal secondary carbamoyl group undergo intramolecular Diels–Alder reactions at rather low temperature (80 °C) to furnish the tricyclic lactams (**6**), which, in turn, isomerize to give the tricyclic lactams (**8**) at about 130 °C.

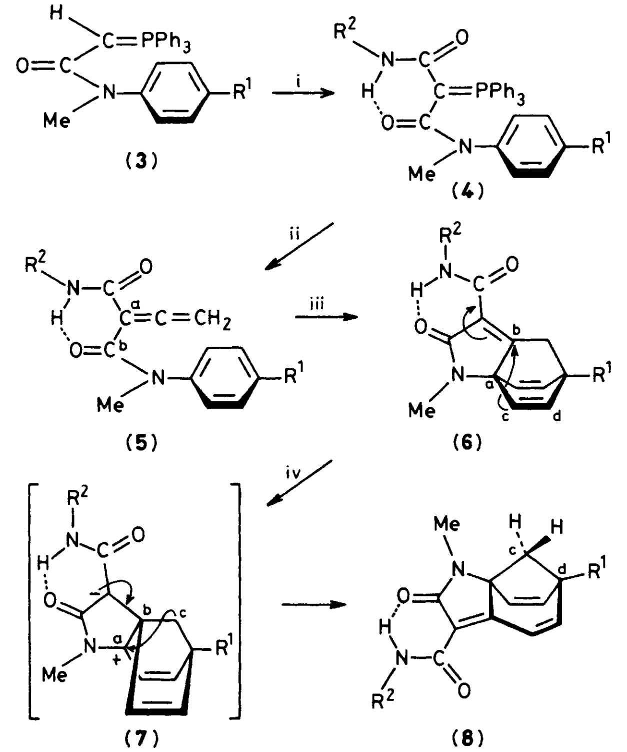
Recently we reported that allene carboxanilides of type (**1**) isomerize in boiling xylene to give the tricyclic compounds (**2**) (Scheme 1).[1] This was the first clear-cut example of a monocyclic aromatic nucleus playing the role of a diene in an intramolecular Diels–Alder reaction.[†] In an effort to delineate the scope of this reaction we have synthesized the allene carboxanilides (**5**) bearing an additional secondary carbamoyl group (Scheme 2) and investigated their thermoly-



(**1**) (**2**)

Scheme 1. R = H, Me, or SiR'_3

[†] There is only one report in the literature (R. F. C. Brown, F. W. Eastwood, N. Chaichit, B. M. Gatehouse, I. M. Pfeiffer, and D. Woodroffe, *Aust. J. Chem.*, 1981, **34**, 1467) in which the formation of a product obtained in very low yield is explained by an intramolecular Diels–Alder reaction of a monocyclic aromatic nucleus.



a; R^1 = H, R^2 = Ph
b; R^1 = H, R^2 = Pr^i
c; R^1 = Br, R^2 = Ph

Scheme 2. *Reagents:* i, $R^2N{=}C{=}O$, CH_2Cl_2, room temp.; ii, $CH_2{=}C{=}O$, $CHCl_3$; iii, 80 °C, benzene; iv, 130 °C, xylene.

tic behaviour. The allenes (**5**) isomerize quantitatively in boiling benzene (80 °C) to give the intramolecular Diels–Alder reaction products (**6**). Under these conditions the half-life for the isomerization is *ca.* 1 h, while allenes of type (**1**) have half-lives of *ca.* 3—5 h in boiling xylene (135 °C). It seems unlikely that the lower temperature for the intramolecular Diels–Alder reactions of (**5**) is a result of the electron-withdrawing effect of the additional carbonyl group, as this substituent and the reacting C=C double bond of the allene moiety are perpendicular to each other. Rather, we believe that the formation of an intramolecular hydrogen bond (Scheme 2) fixes the conformation around C^a and C^b and thus provides a favourable geometry for the intramolecular [4 + 2] cycloaddition.[2]

On heating in xylene, compounds (**6**) isomerize quantitatively to give the new tricyclic compounds (**8**), corresponding to a bicyclo[2.2.2] → bicyclo[3.2.1] transformation. Similar rearrangements of other bicyclo[2.2.2] compounds often take place when a positive charge is generated in the course of a reaction (*e.g.* solvolysis, deamination, or protonation of a double bond).[3,4] To our knowledge, the rearrangement (**6**) → (**8**) represents the first example of a purely thermolytic reaction of this type. The conversion probably proceeds *via* the well stabilized zwitterion (**7**), which results from an anionotropic migration of the $C^c{=}C^d$ vinyl group in (**6**) from position a to position b. For intermediate (**7**) the electron-attracting ability of the additional carbamoyl group is obviously important, as the tricyclic compounds of type (**2**) do not show any tendency to rearrange in the same sense. The Wagner–Meerwein shift of the C^cH_2 group from C^b to C^a finally completes the rearrangement to give the lactams (**8**).

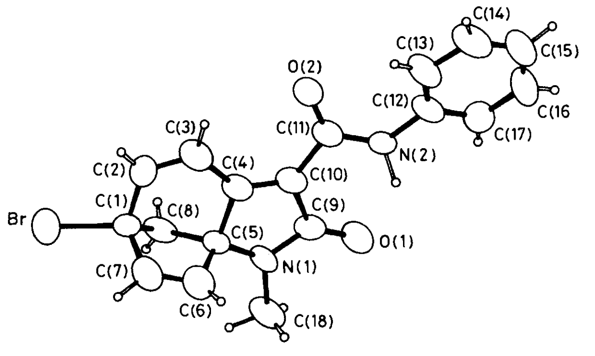


Figure 1. ORTEP plot of the structure of (**8c**). Thermal ellipsoids are on the 50% probability level.

The structures of the tricyclic compounds (**6**) and (**8**) were assigned on the basis of their ^1H and ^{13}C n.m.r. data. Especially characteristic is the loss of symmetry present in (**6**). All proton and carbon resonances are different in the bicyclo[3.2.1] moiety of (**8**); the geminal hydrogen atoms at C^c become diastereotopic ($|^2J|$ = *ca.* 9 Hz) and only the proton *syn* with respect to the smaller ring couples with the hydrogen in position d [(**8a**) and (**8b**); $|^3J|$ = *ca.* 4.5 Hz]. Furthermore, the structure of (**8c**) has been established by *X*-ray analysis (Figure 1).‡ Some marked deviations of bond angles from ideal values point to the considerable strain in the tricyclic skeleton: ∠ C(3)–C(4)–C(10) 134.4(7), C(6)–C(5)–C(8) 99.5(6), N(1)–C(5)–C(6) 116.2(6), N(1)–C(5)–C(8) 122.0(7), and C(1)–C(8)–C(5) 97.6(6)°. An intramolecular hydrogen bond N(2)–H · · · O(1) [N(2)–H 1.00, H · · · O(1) 2.17 Å; ∠ N(2)–H–O(1) 118.8°] forms another six-membered ring in the crystalline state.

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References

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2 The facilitation of the intramolecular Diels–Alder reaction by intramolecular hydrogen bonding is known; see for example T. Takebayashi, N. Iwasawa, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1107.

3 Review: C. D. Gutsche and D. Redmore in 'Carbocyclic Ring Expansion Reactions,' Academic Press, New York, 1968, p. 54.

4 Review: J. A. Berson, in 'Molecular Rearrangements,' ed. P. de Mayo, Interscience, New York, 1967, vol. 1, p. 111.

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‡ *Crystal data* for (**8c**): $C_{18}H_{15}BrN_2O_2$, M = 371.2, triclinic, space group $P\bar{1}$, a = 9.309(2), b = 9.565(2), c = 10.603(1) Å, α = 71.20(1), β = 91.29(1), γ = 114.43(2)°, Z = 2, D_c = 1.528 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 25.3 cm^{-1}. Data collection on an Enraf-Nonius CAD4 diffractometer (monochromatised Mo-K_α radiation, 2.00 ≤ θ ≤ 24.00°, $\omega/2\theta$ scan, scan speed 1.67—5.0 deg min^{-1}), no absorption correction. Full-matrix refinement with 1545 reflections having $I > 2.5\sigma(I)$ gave R = 0.0758, R_w = 0.0757 (w = 1, heavy atoms were treated anisotropically, hydrogen atoms isotropically).

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.