The Thiophene Nucleus as a Diene or a Dienophile in the Intramolecular Diels–Alder Reaction of *N*-(2-Thienyl)allene Carboxamides

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N-(2-Thienyl)allene carboxamides undergo an intramolecular Diels–Alder reaction, whereby, as a function of the substituents in the allenic ω-position, the thiophene nucleus acts as a diene (two H atoms or two methyl groups) or as a dienophile (two phenyl groups in the allenic ω-position).

In intermolecular Diels–Alder reactions, the thiophene nucleus functions rarely as a diene or as a dienophile. The few known examples include rigorous conditions or very reactive partners (*e.g.*, dehydroarene or 1,2,4,5-tetrazine derivatives).[1] As far as the intramolecular version[2] is concerned, only its diene activity in *N*-allyl [or *N*-(prop-2-ynl)]-*N*-(2-thenyl)-ammonium salts[3] has been reported.

In this paper, we wish to report on the intramolecular cycloaddition behaviour of *N*-(2-thienyl)allene carboxamides. Since we have shown before that in the related *N*-arylallene carboxamides the structural conditions are so favourable, that even the benzene nucleus can act as diene in an intramolecular Diels–Alder reaction,[5] it was hoped that the thiophene ring would behave analogously.

In fact, heating (**1a**) at 130 °C for 4 h in a sealed tube furnishes the 2-indoline derivative (**3**) in 73% yield. The formation of (**3**) is explicable *via* the intermediates shown in Scheme 1. First, the intramolecular Diels–Alder reaction between the thiophene as the diene and the allenic double bond as the dienophile produces the tricyclic compound (**2a**).

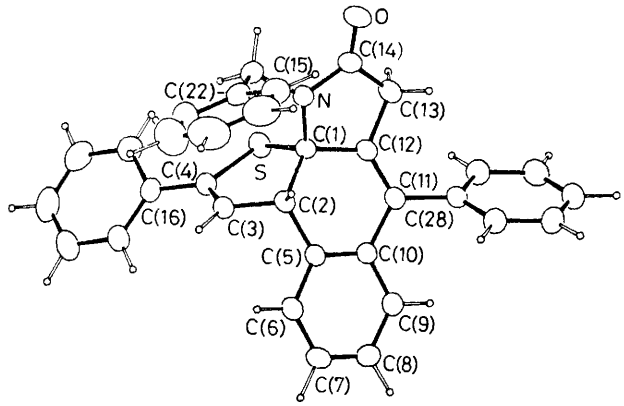
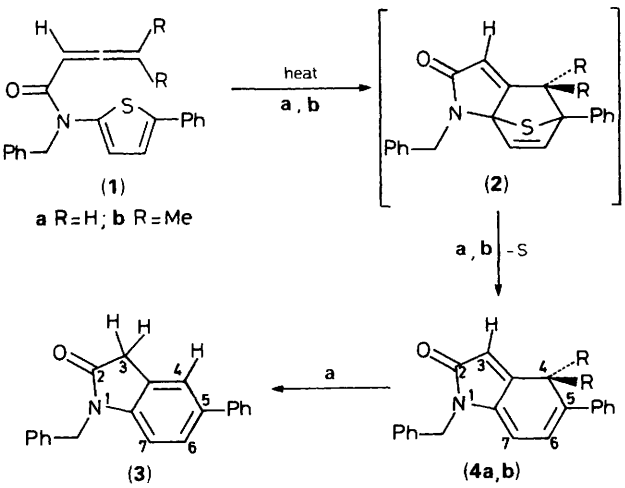
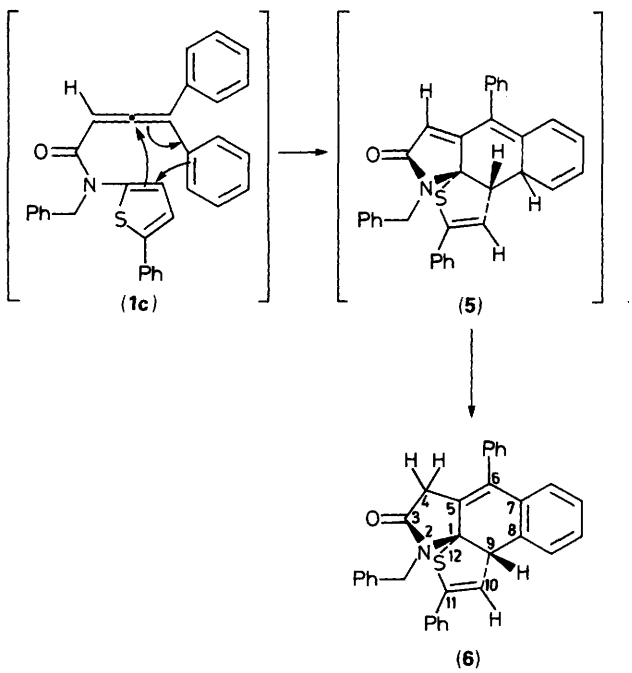


Figure 1. Molecular structure of (**6**). Selected distances (Å) and angles (°): S–C(1) 1.859(2), S–C(4) 1.771(2), C(1)–C(2) 1.544(3), C(2)–C(3) 1.500(3), C(3)–C(4) 1.319(3), C(1)–C(12) 1.501(3), C(11)–C(12) 1.323(3), C(10)–C(11) 1.475(3), C(2)–C(5) 1.519(3), C(5)–C(10) 1.393(3); C(4)–S–C(1) 91.5(1), S–C(1)–C(2) 104.3(1), C(1)–C(2)–C(3) 106.6(2), C(2)–C(3)–C(4) 116.3(2), C(3)–C(4)–S 113.0(2), C(1)–N–C(14) 113.5(2), N–C(1)–C(12) 101.9(2).



Scheme 1



Scheme 2

Spontaneous loss of sulphur leads to bicyclic product (**4a**), which then aromatizes by a hydrogen shift.†

In an analogous reaction sequence, the (4*H*)-indolinone (**4b**) is isolated from (**1b**); obviously the two methyl groups at C(4) of (**4b**) prevent the aromatization step observed for (**4a**).†

In the light of the behaviour and relative thermal stability of (**1a, b**), the intramolecular reactivity of the diphenyl-substituted allene derivative (**1c**) came as a surprise. This compound is not isolable at room temperature, since it rearranges to the polycycle (**6**) (31% yield) already under the conditions of its synthesis. The constitution of (**6**) was established beyond doubt by an *X*-ray crystal structure analysis.‡ Certainly, this transformation includes the Diels–Alder reaction (**1c**) → (**5**), whereby the thiophene nucleus has functioned as a dienophile, while a formal styrene moiety has taken the role of the diene.[6]§ A [1,5] hydrogen shift in the cycloadduct (**5**) furnishes the stable polycycle (**6**).†

These results show that the thiophene nucleus may react both as a diene or as a dienophile in intramolecular cycloaddition reactions. The latter reaction mode has been observed for the first time; obviously the structural conditions in *N*-(2-thienyl)allene carboxamides provide an energetically favourable situation for this exceptional behaviour of the thiophene nucleus.

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References

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3 K. Ts. Tagmazyan, R. S. Mkrtchyan, and A. T. Babayan, *Arm. Khim. Zh.*, 1974, **27**, 587; *Chem. Abstr.*, 1974, **81**, 169451f.
4 For the synthesis of (**1a—c**) the normal ylide methodology is applied: reaction of the corresponding 2-triphenylphosphoranylidene-acetamide with ketene, dimethyl and diphenyl ketene, respectively.
5 G. Himbert, K. Diehl, and H.-J. Schlindwein, *Chem. Ber.*, 1989, **122**, 1691, and papers cited therein.
6 The diene reactivity of phenyl-substituted allenes has been found in a number of examples; see ref. 2.

† *Selected data*: (**3**) m.p. 108—110 °C; IR (KBr) ν_{CO} 1701vs cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$), δ 3.64 (2 H, s, 3,3-H_2), 4.92 (2 H, s, NCH_2), 6.75 [d, $^3J_{AB}$ 8.1 Hz, 1 H, H(7)]; ^{13}C NMR (100.61 MHz, $CDCl_3$) δ 35.80 [t, *J* 133.9 Hz, C(3)], 43.87 (t, *J* 138.8 Hz, NCH_2), 109.19 [d, *J* 161.6 Hz, C(7)], 175.02 [s, C(2)]. (**4b**) M.p. 117—118 °C; IR (KBr) $\nu_{CO/C=C}$ 1672vs, 1644m cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.34 (6 H, s, 2Me), 4.88 (2 H, s, NCH_2), 5.87 [ν_Bd, $^3J_{AB}$ 6.0 Hz, $^5J_{H,H}$ 1.8 Hz, 1 H, H(7)], 5.98 [ν_A, $^3J_{AB}$ 6.0 Hz, 1 H, H(6)], 6.06 [d, $^5J_{H,H}$ 1.8 Hz, 1 H, 3(H)]; ^{13}C NMR (100.61 MHz, $CDCl_3$) δ 29.16 (q, Me), 39.58 [s, C(4)], 42.96 (t, *J* 138.4 Hz, NCH_2), 104.87, 114.52, 121.06 [3d, *J* 163.1, 175.5, 161.8 Hz, respectively, C(7), C(3), C(6)], 158.69, 169.96 [2s, C(3a), C(2)]. (**6**) M.p. 203—204 °C; IR (KBr) ν_{CO} 1689vs cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.06, 3.45 (AB signal, $^2J_{AB}$ 21.0 Hz, 2 H, 4,4-H_2], 3.93 [d, $^3J_{H,H}$ 4.0 Hz, 1 H, H(9)], 4.06, 5.18 (AB signal, $^2J_{AB}$ 15.6 Hz, 2 H, NCH_2), 6.22 [d, $^3J_{H,H}$ 4.0 Hz, 1 H, H(10)]; ^{13}C NMR (101.61 MHz, $CDCl_3$) δ 35.94 [t, *J* 131.3 Hz, C(4)], 43.51 (t, *J* 138.3 Hz, NCH_2), 53.89 [d, *J* 133.85 Hz, C(9)], 86.70 [s, C(1)], 116.89 [d, *J* 169.25 Hz, C(10)], 173.21 [s, C(3)].

‡ *Crystal data* for (**6**): $C_{33}H_{25}NOS$, *M* = 483.64, monoclinic, $P2_1/c$, *a* = 9.017(12), *b* = 16.870(5), *c* = 16.822(3) Å, β = 103.83(3)°, *U* = 2485(5) Å^3, *F*(000) = 1016, *Z* = 4, D_c = 1.29 g cm^{-3}, Enraf-Nonius CAD4 diffractometer, monochromatized Mo-K_α radiation, 2835 independent reflections, 2.0 ≤ θ ≤ 21.5°, full-matrix least-squares refinement with 2543 reflections [$I > 2\sigma(I)$], R = 0.030, R_w = $(\Sigma\Delta^2 F/\Sigma F_o^2)^{1/2}$ = 0.031. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ A referee has pointed out that the formation of (**6**) can also be explained by a process (**1c**) → (**2c**) → (**5**) → (**6**). The Diels–Alder product (**2c**) is transformed to (**5**) by a [3.3] sigmatropic process between the double bond of the bicyclic moiety and the 'first double bond' of the *endo* phenyl group.