29. Intramolecular Cyclizations of Allenic Acylureas and -amides

by **Latchezar S. Trifonov** and **Alexander S. Orahovats***

Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria

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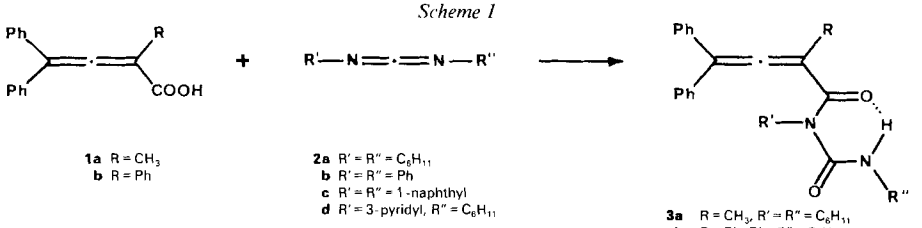
Allenic acids are found to add to dicyclohexylcarbodiimide affording, in the presence of Et_2NH, the 4*H*-1,3-oxazin-4-ones **5** *via* **4**. Under neutral conditions, they add to diaryl- or pyridyl(cyclohexyl)carbodiimides and triphenylketene imine to give the corresponding tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-ones **7, 8, 9,** and **12**. The allenic phenyl ester **13a** dimerises, on heating in a [2+2] head-to-head fashion, to **14** but fails to undergo intramolecular *Diels-Alder* cyclization to **15**.

In [1], we reported on the cyclizations of some allenic acylureas and -amides and also on some chemical transformations conducted with them. We now wish to provide the experimental details, some new transformations, and also the thermally induced reactions of two allenic phenyl esters.

The allenic acylureas **3a** and **3b** were obtained in high yields from the corresponding allenic acids **1a** [2] and **1b** by treatment with dicyclohexylcarbodiimide (**2a**) in dry THF at r.t. (*Scheme 1*). The starting acid **1b** was prepared according to the method of *Bestmann*

Scheme 1



1a R = CH_3
b R = Ph

2a R' = R'' = C_6H_{11}
b R' = R'' = Ph
c R' = R'' = 1-naphthyl
d R' = 3-pyridyl, R'' = C_6H_{11}

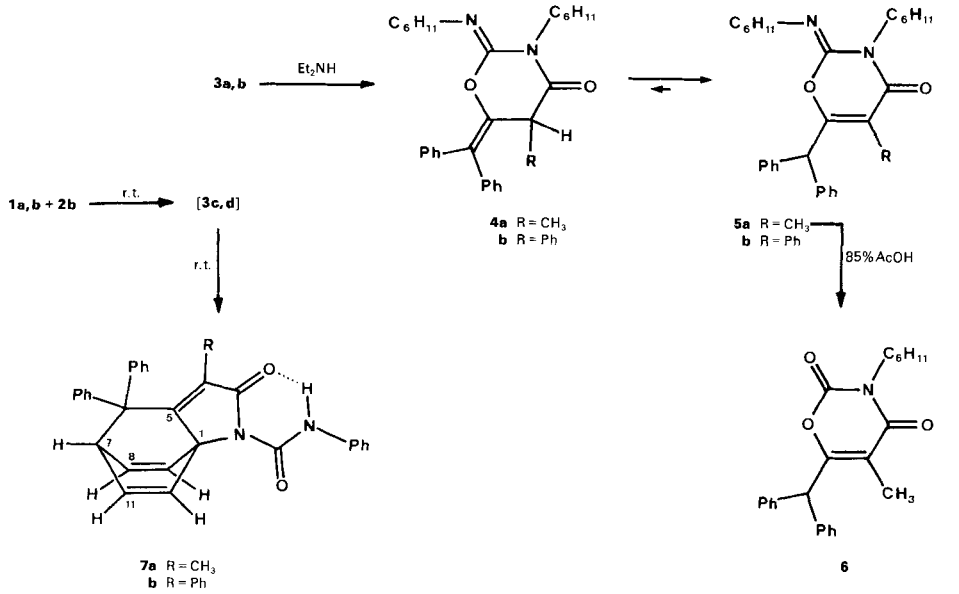
3a R = CH_3, R' = R'' = C_6H_{11}
b R = Ph, R' = R'' = C_6H_{11}
c[1]) R = CH_3, R' = R'' = Ph
d[1]) R = R' = R'' = Ph
e[1]) R = CH_3, R' = R'' = 1-naphthyl
f[1]) R = CH_3, R' = 3-pyridyl, R'' = C_6H_{11}

and *Hartung* [2]. Diagnostically useful for the determination of the structures of **3a** and **3b** were the absorptions in the IR spectra (see *Exper. Part*) and also the ^{13}C-NMR chemical shift for C(3), which appears at 203.5 and at 203.2 ppm. Compounds **3a** and **3b** cyclize under basic conditions to the corresponding 2-cyclohexylimino-4*H*-1,3-oxazin-4-ones **4a, b**[2]) and **5a, b** (*Scheme 2*). Product **4** was found to be an intermediate, the exocyclic

[1]) Intermediate compound.

[2]) Compound **4b** supposed to be an intermediate was detected by TLC but not isolated.

Scheme 2



double bond first formed migrating to give the more stable 4*H*-1,3-oxazin-4-one **5** with an endocyclic double bond. The transformation of **4** to **5** is an equilibrium reaction, indeed under the same basic conditions, **4a** was obtained starting from pure **5a** the latter strongly predominating.

The oxazinones **4a** and **5a** could also be obtained, albeit in low yields, under neutral conditions by heating **3a**. In this case, however, **4a** was the major product. 1,3-Oxazinone **5a** was also prepared by treating the allenic acid **1a** with dicyclohexylcarbodiimide (**2a**) in THF in the presence of Et_2NH.

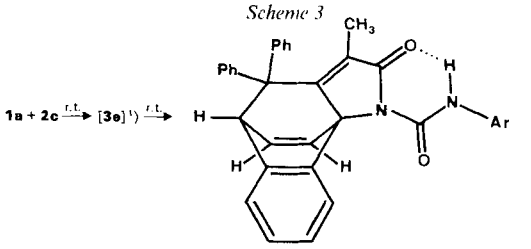
Structure **4a** is supported by the ^{1}H-NMR spectrum which shows a *d* at 1.39 ppm for the CH_3 group and a *q* at 3.45 ppm for the H–C(5). Structures **5a** and **5b** were assigned on the basis of the following data. The Ph_2CH signal appears in the ^{1}H-NMR spectra as a *s* at 5.36 and 5.11 ppm, the signal for the CH_3 group in **5a** appearing as a *s* at 1.92 ppm. The structure **5a** is also supported by the mild hydrolysis in aq. AcOH to the 2*H*-1,3-oxazine-2,4(3*H*)-dione **6** *(Scheme 2)*.

Quite unexpectedly, the allenic acid **1a**, on treatment with diphenylcarbodiimide (**2b**) under neutral conditions at r.t., afforded the 4-methyl-6,6-diphenyl-2-(*N*-phenylcarbamoyl)-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one (**7a**) in excellent yield *(Scheme 2)*. In this case, neither the allene **3c** nor the *N*-phenyl analogues of **4a** or **5a** were detected in the reaction mixture. The 2,4,4-triphenylallenic acid **1b** gave, under the same conditions, a mixture containing the tricyclic compound **7b** (25%) and the allenic acylurea **3d** (65%).

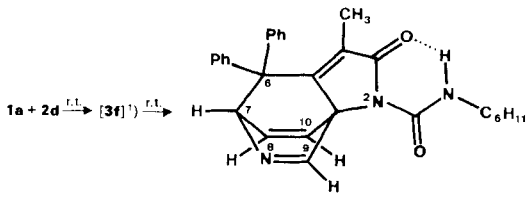
Aiming at the preparation of the *N*-phenyl analogue of **5a**, the allenic acid **1a** and **2b** were reacted in THF in the presence of Et_2NH. In this case, however, a precipitate formed which was shown to be the salt derived from the allenic acid **1a** and N^1,N^1-diethyl-N^2,N^3-diphenylguanidine, the latter compound being the product of a very rapid addition of Et_2NH to **2b**.

The formation of the tricyclic compounds **7a** and **7b** is surprising and is the second observed case of a non-catalysed intramolecular *Diels-Alder* reaction of a non-strained benzene ring [3]. In contrast to the already known formation of very similar tricyclic compounds containing a carbamoyl moiety at C(4) in boiling benzene, in our case the reaction proceeds simply on standing at r.t. We believe that the loss of aromaticity can be ascribed to the inherent strain of the allenic system, but is unlikely to be associated with conformational restrictions due to internal H-bonding as invoked by *Himbert* and co-workers [3b]. This, indeed, is supported by the smooth formation of compounds **7a** and **7b** observed under mild conditions, H-bonding in this case is irrelevant. It is worth noting that this reaction was also observed when the allenic acid **1a** was treated with *N,N'*-bis (1-naphthyl)carbodiimide (**2c**) [4] or with N-cyclohexyl-*N'*-(3-pyridyl)carbodiimide (**2d**) giving smoothly the tetracyclic compound **8** and the tricyclic 2,8-diaza compound **9**, respectively *(Scheme 3)*. The latter case represents the first example of an intramolecular cycloaddition with the participation of a pyridine ring as a heterodiene [5].

Scheme 3



8 (Ar = 1-naphthyl)



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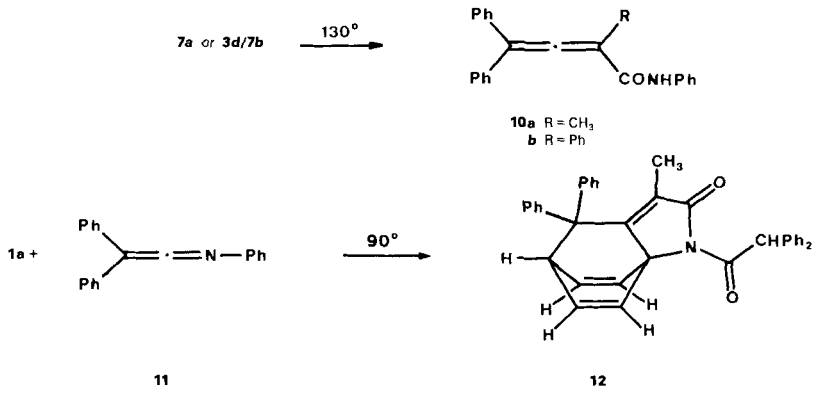
Characteristic for compounds **7a, 7b, 8**, and **9** were the ^{1}H-NMR signals ascribed to H–C(7) at 4.52–4.80 ppm for **7a, 7b**, and **8**, and at 6.08 ppm for **9**. Compounds **7a, 8**, and **9** exhibited ^{13}C-NMR signals at 72.9–74.5 ppm ascribed to C(1) and at 58.9–59.8 ppm ascribed to C(6); for **7a, 8**, and **9**: C(7): 52.6, 55.7, and 72.1 ppm, respectively.

Not unexpectedly, the tricyclic compound **7a** did not rearrange into the tricyclo [6.2.1.$0^{1,5}$]undecatriene on heating in boiling xylene [3b]. As already pointed out, carbanion stabilization seems to play a determining role in this rearrangement [3b]. In the presently studied case, we observed a loss of PhNCO [6] and a *retro-Diels-Alder* reaction leading to the allenic carboxanilide **10a**.

The attempt to facilitate this rearrangement (see [3b]) by BF_3 and heating at 80° failed, **10a** was islated as the sole product. The mixture containing the allenic acylurea **3d** and the tricyclic compound **7b** which was difficult to separate afforded, on refluxing in xylene, the allenic carboxanilide **10b**. In this manner, it was demonstrated that under these conditions, both **3d** and **7b** undergo conversion to **10b**.

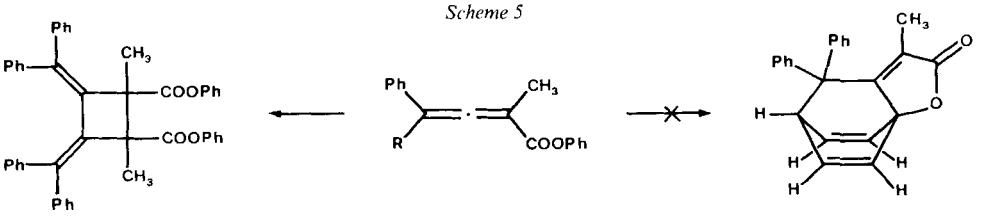
Scheme 4



The allenic acid **1a** reacted analogously with triphenylketene imine (**11**), heating was required, however, giving 4-methyl-6,6-diphenyl-2-(diphenylacetyl)-2-azatricyclo [5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one (**12**; *Scheme 4*). The formation of this lactam once more illustrates that intramolecular H-bonding has no essential place in this reaction sequence.

Quite recently, *Kanematsu* and coworkers [7] and *Himbert* and *Fink* [8] reported on the intramolecular cyclizations of allenic esters leading to bi- and tricyclic lactones. In our case, however, heating the allenic phenyl ester **13a** in refluxing xylene afforded the yellow [2+2] dimer **14**, but not the expected tricyclic lactone **15** [8] *(Scheme 5)*.

Scheme 5



14 **13a** R = Ph, **b** R = H **15**

The structure of the dimer **14** was substantiated by its MS ($M^{+\cdot}$ 652) and also by the UV spectrum 260 (53400) and 356 nm (30900), in agreement well with the absorption of similar dimers described in [9] and [10]. The structure of the head-to-head dimer is corroborated by the ^{1}H- and especially by the ^{13}C-NMR spectra. Thus, the chemical shifts for the CH_3 groups (*s* at 1.21 ppm) and for the Ph groups (7.55–7.00 (20 H) and 7.00–6.75 ppm (10 H) in the ^{1}H-NMR spectrum support structure **14** and not alternative ones having olefinic CH_3 group(s) or Ph groups attached directly to the cyclobutane ring (see [11]). The high molecular symmetry of the dimer **14** is reflected in the ^{13}C-NMR spectrum (two signals for the ipso-C(arom.), two signals for the olefinic C-atoms, and one signal at 60.6 ppm for C(1) and C(2)).

The allenic phenyl ester **13b**, on heating in refluxing xylene, gave a complex mixture of products. The UV spectrum of this mixture showed absence of a [2+2] dimer analogous to **14** (no absorption in the region 350–380 nm).

Experimental Part

General. Prep. TLC: *Merck* silica gel *60* PF_{254} (Art. *7749*) on 20×20 cm plates (10 g per plate). Column chromatography: *Merck* silica gel *60* (Art. *7734*). M. p.: *Kofler* apparatus; not corrected. UV spectra: *Specord M40* (*Carl Zeiss*, Jena) spectrophotometer. IR spectra: *UR-20* (*Zeiss*, Jena) for $CHCl_3$ solns., *Bruker IFS 113v* spectrophotometer for KBr pellets. ^{1}H-NMR spectra: *Bruker WM-250* spectrometer at 250 MHz and *Tesla* spectrometer at 80 MHz. ^{13}C-NMR spectra: *Bruker WM-250* spectrometer at 62.9 MHz; chemical shifts (δ) in ppm downfield from internal TMS. MS: *JEOL JMS D300* apparatus.

1. *2,4,4-Triphenyl-2,3-butadienoic Acid* (**1b**). The ethyl ester of **1b** was obtained following the procedure given in [2]. A soln. of [α-(ethoxycarbonyl)benzylidene]-triphenylphosphorane [12] (12.72 g, 30 mmol) and diphenylacetyl chloride (3.75 g, 15 mmol) in dry THF (50 ml) was refluxed for 31 h. The solvent was evaporated and the residue filtered through a short column with silica gel using petroleum ether/Et_2O 8:1. The combined fraction preceding the triphenylphosphine oxide was evaporated and the residue recrystallised from EtOH to give the ethyl ester of **1b** (3.52 g, 70%) as colourless prisms, m.p. 98.0–99.0°. UV (cyclohexane): 235 (sh, 24000), 266 (23800). IR ($CHCl_3$): 3050*m*, 2975*m*, 2920*m*, 2870*m*, 1945*w*, 1925*w*, 1910*w*, 1710*s*, 1595*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.61 (*dd*, J = 8.2, 1.4, 2 H); 7.45–7.25 (*m*, 13 H); 4.32 (*q*, J = 7.2, CH_3CH_2O); 1.34 (*t*, J = 7.2, CH_3CH_2O). ^{13}C-NMR ($CDCl_3$): 214.6 (*s*, C(3)); 165.8 (*s*, C(1)); 135.0 (*s*, *C*(arom.)–C(4)); 132.5 (*s*, *C*(arom.)–C(2)); 128.7, 128.5, 128.2, 127.9 (4 *d*, CH(arom.)); 114.7 (*s*, C(4)); 105.6 (*s*, C(2)); 61.3 (*t*, CH_3CH_2O); 14.3 (*q*, CH_3CH_2O). MS (70 eV): 341 (20), 340 (60, $M^{+\cdot}$), 312 (25), 311 (80), 294 (25), 268 (25), 267 (100, $Ph_2C_3Ph^+$), 265 (40), 189 (25), 165 (40), 105 (85). Anal. calc. for $C_{24}H_{20}O_2$ (340.42): C 84.68, H 5.92; found: C 84.68, H 6.06.

The ethyl ester of **1b** (1.84 g, 5.44 mmol) was refluxed for 2 h in EtOH/H_2O 1:1 (15 ml) containing NaOH (0.24 g, 6 mmol). The solvent was removed under reduced pressure, the residue dissolved in H_2O and extracted with Et_2O (3 × 20 ml). The aq. layer was acidified with dil. H_2SO_4 and the precipitate filtered off, washed with H_2O, dried in an exsiccator over P_2O_5 and recrystallised from MeCN to give **1b** (1.36 g, 81%), m.p. 175.0–180°. IR ($CHCl_3$): 3450*m*, 3300–2300*m* (br.), 1870*w*, 1720*s*, 1680*s*, 1585*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.64 (*d*, J = 7.5, 2 H); 7.50–7.20 (*m*, 13 H). ^{13}C-NMR ($CDCl_3$): 215.9 (*s*, C(3)); 171.0 (*s*, C(1)); 134.3 (*s*, *C*(arom.)–C(4)); 131.9 (*s*, *C*(arom.)–C(2)); 128.8, 128.5, 128.1 (3 *d*, CH(arom.)); 115.0 (*s*, C(4)); 104.7 (*s*, C(2)). MS (70 eV): 313 (7), 312 (100, $M^{+\cdot}$), 294 (28), 268 (38), 267 (69), 265 (34), 252 (14), 207 (10), 206 (10), 189 (14), 179 (14), 178 (10), 165 (24), 105 (14). Anal. calc. for $C_{22}H_{16}O_2$ (312.37): C 84.59, H 5.16; found: C 83.98, H 4.95.

2. N,N'-*Dicyclohexyl*-N-*(4,4-diphenyl-2-methyl-2,3-butadienoyl)urea* (**3a**) *and* N,N'-*Dicyclohexyl*-N-*(2,4,4-triphenyl-2,3-butadienoyl)urea* (**3b**). 2.1. To a soln. of DCC (**2a**; 228 mg, 1.17 mmol) in dry THF (10 ml) was added **1a** (250 mg, 1 mmol) in 3 equal portions, the time interval between each of them being 24 h. After the last portion, the mixture was stirred at r.t. for 24 h. The solvent was evaporated and the residue subjected to prep. TLC on 6 plates with petroleum ether/Et_2O 10:3. The product from an UV(254 nm)-active zone at R_f 0.3 was eluted with $CHCl_3$ and the obtained colourless oil recrystallised from hexane to give pure **3a** (334 mg, 73%), m.p. 125.0–127.0° (partial melting at 75–80°). IR ($CHCl_3$): 3420*w*, 3280*m*, 2980*m*, 2920*s*, 2895*m*, 1935*w*, 1685*s*, 1620*s*, 1590*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.49 (*d*, J = 5.9, NH); 7.45–7.25 (*m*, $2C_6H_5$); 3.97 (*tt*, J = 11.9, 3.3, CH–N); 3.36 (*m*, CH–N); 2.14 (*s*, CH_3); 2.10–2.00 (*m*, 2 H); 1.81 (*d*, J = 11.8, 2 H); 1.70–0.80 (*m*, 16 H). ^{13}C-NMR ($CDCl_3$): 203.5 (*s*, C(3)); 170.7 (*s*, C(1)); 153.7 (*s*, N–CO–N); 135.6 (*s*, C(arom.)); 128.8, 128.6, 128.0 (3 *d*, CH(arom.)); 113.3 (*s*, C(4)); 100.9 (*s*, C(2)); 59.4 (*d*, *C*H–N–C(1)); 49.6 (*d*, *C*H–N–CO–N); 32.7, 30.9, 26.1, 25.6, 25.1, 24.7 (6 *t*, CH_2); 17.3 (*q*, CH_3). MS (70 eV): 457 (10), 456 (25, $M^{+\cdot}$), 375 (17), 374 (22), 332 (16), 331 (65, $M^{+\cdot} - C_6H_{11}NCO$), 292 (25), 234 (80), 206 (100), 205 (81, $Ph_2C_3CH_3^+$), 191 (33), 165 (20), 97 (20), 83 (40, $C_6H_{11}^+$), 77 (23), 55 (70). Anal. calc. for $C_{30}H_{37}N_2O_2$ (456.63): C 78.91, H 7.95, N 6.14; found: C 79.20, H 7.97, N 6.13.

2.2. In a similar way, **3b** was obtained from **1b** and **2a**. The reaction mixture was evaporated and the residue subjected to column chromatography on silica gel with petroleum ether/Et_2O 9:1. The oily product was recrystallised from hexane to afford **3b** (87%), m.p. 138.0–141.0°. IR ($CHCl_3$): 3285*m* (br.), 2920*s*, 2850*m*, 1960*vw*, 1940*vw*, 1925*vw*, 1690*s*, 1635*m*, 1590*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.35 (*d*, J = 5.7, NH); 7.50–7.20 (*m*, 15 arom. H); 3.95 (*t*, J = 11.5, CH–N); 3.60–3.50 (*m*, CH–N); 2.25–2.05 (*m*, 2 H); 1.91 (*d*, J = 4.9, 2 H); 1.80–0.70 (*m*, 16 H). ^{13}C-NMR ($CDCl_3$): 203.2 (*s*, C(3)); 169.4 (*s*, C(1)); 153.5 (*s*, N–CO–N); 145.4, 135.2 (2 *s*, *C*(arom.)–C(2), 2*C*(arom.)–C(4)); 129.2, 128.7, 128.3, 126.2 (4 *d*, CH(arom.)); 117.5 (*s*, C(4)); 109.2 (*s*, C(2)); 60.9, 49.5 (2 *d*, CH–N); 32.7, 30.6, 26.3, 25.6, 25.0, 24.8 (6 *t*, CH_2). MS (70 eV): 519 (1), 518 (2, $M^{+\cdot}$), 394 (15), 393 (52, $M^{+\cdot} - C_6H_{11}NCO$), 269 (20), 268 (100), 267 (60, $Ph_2C_3Ph^+$), 165 (18), 125 (18), 97 (71), 83 (22, $C_6H_{11}^+$), 82 (57), 69 (30), 67 (93). Anal. calc. for $C_{35}H_{38}N_2O_2$ (518.70): C 81.05, H 7.38, N 5.40; found: C 80.58, H 7.15, N 5.39.

3. *3-Cyclohexyl-2-cyclohexylimino-6-(diphenylmethylidene)-2,3,5,6-tetrahydro-5-methyl-4*H-*1,3-oxazin-4-one* (**4a**), *3-Cyclohexyl-2-cyclohexylimino-6-(diphenylmethyl)-2,3-dihydro-5-methyl-4*H-*1,3-oxazin-4-one* (**5a**), *and 3-*

*Cyclohexyl-2-cyclohexylimino-6-(diphenylmethyl)-2,3-dihydro-5-phenyl-4*H*-1,3-oxazin-4-one* (**5b**). 3.1. **4a** *and* **5a**. To a soln. of DCC (**2a**; 228 mg, 1.17 mmol) in dry THF (10 ml) were added Et_2NH (73 mg, 1 mmol) and **1a** (250 mg, 1 mmol). The mixture was kept at r.t. for 4 days, the solvent evaporated, and the residue subjected to column chromatography on silica gel with petroleum ether/Et_2O 6:1. The combined fraction containing **4a/5a** preceding trace amounts of **3a** was evaporated and recrystallised from hexane to afford **5a** (270 mg), m.p. 122.5–124.0°. From the mother liquor, an additional amount of **5a** (40 mg) was obtained. The new mother liquor was chromatographed on 5 prep. TLC plates with petroleum ether/Et_2O 7:1. From the zone at R_f 0.5, after elution with $CHCl_3$ and recrystallisation from hexane, was obtained **5a** (40 mg, total 76%). From the zone at R_f 0.6, after elution with $CHCl_3$ and recrystallisation from hexane, was obtained **4a** (25 mg, 5%) as colourless prisms, m.p. 110.0–116.0°. IR ($CHCl_3$): 2920*m*, 2850*m*, 1700*m*, 1650*s*, 1590*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.45–7.15 (*m*, 10 arom. H); 4.47 (*tt*, J = 12.0, 3.5, CH–N(3)); 3.55–3.40 (*m*, CH–N=C); 3.45 (*q*, J = 7.3, H–C(5)); 2.38 (*td*, J = 18.0, 12.0, 3.4, 2 H); 1.85–1.50 (*m*, 8 H); 1.39 (*d*, J = 7.3, CH_3); 1.40–1.00 (*m*, 10 H). MS (70 eV): 456 (7, $M^{+\cdot}$), 376 (22), 375 (100, $M^{+\cdot}-C_6H_{10}$), 293 (10), 250 (7), 206 (85, $Ph_2C_2CHCH_3^+$), 194 (82), 166 (30), 125 (21, $C_6H_{11}NCO^+$), 83 (17, $C_6H_{11}^+$), 81 (9), 55 (26).

5a: IR ($CHCl_3$): 2920*s*, 2845*m*, 1685*s*, 1670*s*, 1630*s*, 1595*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.40–7.15 (*m*, 10 arom. H); 5.36 (*s*, HC–C(6)); 4.66 (*tt*, J = 12.0, 3.5, CH–N(3)); 3.12 (*m*, CH–N=C); 2.45 (*qd*, J = 12.3, 3.5, 2 H); 1.92 (*s*, CH_3); 1.80–1.00 (*m*, 18 H). ^{13}C-NMR ($CDCl_3$): 162.8, 158.9 (2 *s*, C(2), C(6)); 139.0 (*s*, C(4)); 138.9 (*s*, C(arom.)); 129.0, 128.6, 127.3 (3 *d*, CH(arom.)); 106.8 (*s*, C(5)); 55.0, 53.1, 51.7 (3 *d*, 2CH–N, *C*H–C(6)); 33.9, 28.1, 26.4, 25.9, 25.5, 24.5 (6 *t*, CH_2); 10.0 (*q*, CH_3). MS (70 eV): 456 (7, $M^{+\cdot}$), 376 (30), 375 (100), 293 (10), 251 (3), 250 (3), 207 (7), 167 (20, Ph_2CH^+); 125 (10, $C_6H_{11}NCO$); 83 (20, $C_6H_{11}^+$); 81 (9); 55 (22). Anal. calc. for $C_{30}H_{37}N_2O_2$ (456.63): C 78.91, H 7.95, N 6.14; found: C 78.90, H 7.92, N 6.06.

3.2. **5b** *from* **3b**. To a soln. of **3b** (259 mg, 0.5 mmol) in dry THF (10 ml) was added Et_2NH (37 mg, 0.5 mmol), and the mixture was kept for 24 h at r.t. The solvent was evaporated and the residue recrystallised from hexane to give **5b** (140 mg, 54%), m.p. 89.0–94.0° (anal. sample, m.p. 100.0–105.0°). IR ($CHCl_3$): 2925*m*, 2900*m*, 1695*m*, 1660*s*, 1635*s*, 1595*w*. ^{1}H-NMR (80 MHz, $CDCl_3$): 7.50–7.00 (*m*, 15 arom. H); 5.11 (*s*, CH–C(6)); 4.70 (*m*, CH–NCO); 3.35 (*m*, CH–N=C); 2.70–2.30 (*m*, 2 H); 1.90–1.00 (*m*, 18 H). ^{13}C-NMR ($CDCl_3$): 161.7, 160.4 (2 *s*, C(2), C(6)); 139.3, 138.8, 131.8 (3 *s*, C(4), *C*(arom.)–CH, *C*(arom.)–C(5)); 130.5, 128.9, 128.6, 128.4, 128.2, 127.3 (6 *d*, CH(arom.); 114.1 (*s*, C(5)); 55.5, 53.4, 51.9 (3 *d*, 2 CH–N, *C*H–C(6)); 33.9, 28.1, 26.4, 25.9, 25.5, 24.5 (6 *t*, CH_2). MS (70 eV): 519 (1), 518 (2, $M^{+\cdot}$), 438 (28), 437 (76, $M^{+\cdot}-C_6H_{11}$), 351 (7), 312 (5), 268 (12), 167 (100, Ph_2CH^+), 145 (30), 129 (39), 55 (50). Anal. calc. for $C_{35}H_{38}N_2O_2$ (518.70): N 5.40; found: N 5.45.

3.3. **5b** *from* **1b** *and* **2a** *in the Presence of* Et_2NH. A soln. of **1b** (312 mg, 1 mmol), DCC (**2a**; 228 mg, 1.17 mmol), and Et_2NH (73 mg, 1 mmol) in dry THF (10 ml) was heated at 65° for 72 h. The solvent was evaporated and the residue filtered through a short silica-gel column with petroleum ether/Et_2O 5:1. The combined fraction containing **5b** was evaporated and the residue recrystallised from hexane to give **5b** (340 mg, 66%).

4. *3-Cyclohexyl-6-(diphenylmethyl)-5-methyl-2*H*-1,3-oxazine-2,4(3*H*)-dione* (**6**). A soln. of **5a** (260 mg, 0.57 mmol) in 85% aq. AcOH (5 ml) was kept at r.t. for 4 days. The solvent was evaporated and the residue recrystallised from Et_2O/hexane. The solid was filtered of the mother liquor evaporated, and the residue recrystallised twice from hexane to give **6** (168 mg, 78%), m.p. 119.0–123.0°. IR ($CHCl_3$): 3030*w*, 2930*m*, 2855*m*, 1750*s*, 1670*s*, 1595*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.40–7.20 (*m*, 10 arom. H); 5.39 (*s*, CH–C(6)); 4.70–4.55 (*m*, CH–N); 2.40–2.20 (*m*, 2 H); 2.03 (*s*, CH_3); 1.85 (br. *d*, J = 10.4, 2 H); 1.70–1.15 (*m*, 6 H). ^{13}C-NMR ($CDCl_3$): 163.3, 161.1, 147.8 (3 *s*, C(2), C(4), C(6)); 138.1 (*s*, C(arom.)); 128.93, 128.88, 127.7 (3 *d*, CH(arom.)); 108.9 (*s*, C(5)); 54.9, 51.6 (2 *d*, CH–N, *C*H–C(6)); 28.4, 26.1, 25.1 (3 *t*, CH_2); 10.3 (*q*, CH_3). MS (70 eV): 376 (2), 275 (3, $M^{+\cdot}$), 295 (12), 294 (68), 168 (15), 167 (100, Ph_2CH^+), 165 (25), 83 (30, $C_6H_{11}^+$). Anal. calc. for $C_{24}H_{25}NO_3$ (375.47): C 76.77, H 6.71; found: C 76.77, H 6.63.

5. *4-Methyl-6,6-diphenyl-2-(*N*-phenylcarbamoyl)-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* (**7a**). A soln. of **1a** (267 mg, 1.07 mmol) and **2b** (207 mg, 1.07 mmol) in dry THF (1.5 ml) was kept at r.t. for 5 days. The mixture was filtered to give, after washing with Et_2O/hexane 1:1, **7a** (345 mg, 81%) as large colourless prisms, m.p. 153.0–156.0° (anal. sample from CH_2Cl_2/hexane, m.p. 156.5–158.0°). UV (cyclohexane): 220 (33700), 267 (13200). IR ($CHCl_3$): 3260*m*, 3220*m*, 3130*w*, 3030*m*, 2980*m*, 1710*s*, 1670*s*, 1595*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 10.75 (*s*, NH); 7.64 (*d*, J = 8.0, 2 *o*–H in C_6H_5N); 7.35 (*t*, J = 8.0, 2 *m*–H in C_6H_5N); 7.30–7.15 (*m*, 10 arom. H); 7.10 (*t*, J = 8.0, *p*–H in C_6H_5N); 6.52 (*dd*, J = 6.9, 1.3, H–C(9), H–C(10)); 6.31 (*t*, J = 6.9, H–C(8), H–C(11)); 4.57 (*t*, J = 7.0, H–C(7)); 1.67 (*s*, CH_3). ^{13}C-NMR ($CDCl_3$): 174.4 (*s*, C(3)); 161.2 (*s*, NCON); 149.3 (*s*, C(5)); 143.5 (*s*, *C*(arom.)–C(6)); 137.7 (*s*, C(arom.)–N); 134.3, 132.2 (2 *d*, C(8), C(9), C(10), C(11)); 129.1, 128.7, 128.2, 126.9, 124.0, 120.0 (6 *d*, CH(arom.)); 126.1 (*s*, C(4)); 72.9 (*s*, C(1)); 58.9 (*s*, C(6)); 52.6 (*d*, C(7)); 11.6 (*q*, CH_3). MS (70 eV): 444 (3, $M^{+\cdot}$), 326 (24), 325 (100, $M^{+\cdot}$–PhNCO), 324 (39), 311 (21), 310 (90), 248 (9), 246 (10), 234 (6), 205 (59,

$Ph_2C_3CH_3^+$), 203 (28), 202 (24), 191 (31), 189 (17), 178 (14), 165 (24), 119 (86, $PhNCO^+$), 91 (52), 77 (28), 64 (28). Anal. calc. for $C_{30}H_{24}N_2O_2$ (444.54): N 6.30; found: N 6.34.

6. *N,N'-Diphenyl-N-(2,4,4-triphenyl-2,3-butadienoyl)urea* (**3d**) *and 4,6,6-Triphenyl-2-(N-phenylcarbamoyl)-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* (**7b**). A soln. of diphenylcarbodiimide (**2b** [13]; 343 mg, 1.77 mmol) in dry THF (2.5 ml) was kept at r.t. for 7 days. The mixture was chromatographed on silica gel with petroleum ether/Et_2O/$CHCl_3$ 10:2:1. The 1st fraction was evaporated and the crude oily product (almost pure **3d**, 316 mg) was recrystallised from CH_2Cl_2/hexane to afford pure **3d** (202 mg, 22%), m.p. 132.0–134.0°. The 2nd fraction gave an oily product (600 mg) which soon crystallised. The ^{1}H-NMR showed this to be a mixture **3d**/**7b** (1.8:1). The 3rd fraction afforded, after similar workup, pure **7b** (12 mg, 2%), m.p. 137.0–137.5°. **3d**: IR (KBr): 3220*m* (br.), 3170*m*, 3050*m* (br.), 1935*w*, 1860 *vw*, 1715*s*, 1645*m*, 1590*m*, 1585*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.58 (*d*, *J* = 7.0, 2 H); 7.45–7.25 (*m*, 17 H); 7.20–7.00 (*m*, 4 H); 6.93 (*t*, *J* = 7.0, 2 H). ^{13}C-NMR ($CDCl_3$): 205.4 (*s*, C(3)); 170.4 (*s*, C(1)); 151.7 (*s*, N–CO–N); 137.7, 137.2 (2 *s*, C(arom.)–N); 134.5, 132.4 (2 *s*, *C*(arom.)–C(4), *C*(arom.)–C(2)); 129.3, 129.0, 128.9, 128.7, 128.4, 128.2, 126.8, 126.3, 124.3, 120.3 (10 *d*, CH(arom.)); 117.4 (*s*, C(4)); 109.5 (*s*, C(2)). MS (70 eV): 506 (0.2, $M^{+\cdot}$), 477 (1), 388 (56), 387 (100, $M^{+\cdot}$ – PhNCO), 268 (63), 267 (98, $Ph_2C_3Ph^+$), 265 (32), 252 (16), 191 (12), 189 (17), 165 (40), 77 (12).

7b: IR (KBr): 3420*m*, 3220*m*, 3065*m*, 1718*s*, 1682*m*, 1625*m* (sh), 1600*m*, 1557*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 10.88 (*s*, NH); 7.70 (*d*, *J* = 8.2, 2 *o*-H in C_6H_5–N); 7.40 (*t*, *J* = 8.2, 2 *m*-H in C_5H_5–N); 7.30–7.05 (*m*, 15 arom. H); 6.91 (*d*, *J* = 8.0, 4 *o*-H in 2 C_6H_5–C(6)); 6.74 (*dd*, *J* = 8.0, 2.0, H–C(9), H–C(10)); 6.42 (*t*, *J* = 8.0, H–C(8), H–C(11)); 4.80 (*t*, *J* = 8.0, H–C(7)). MS (70 eV): 388 (18), 387 (55, $M^{+\cdot}$ – PhNCO), 296 (10), 268 (20), 267 (30, $Ph_2C_3Ph^+$), 265 (12), 252 (6), 191 (7), 189 (5), 165 (10), 119 (100, $PhNCO^+$), 91 (30), 64 (17).

7. *(1R*,7R*)-4-Methyl-2-[N-(1-naphthyl)carbamoyl]-6,6-diphenyl-2-azabenzo[8,9]tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* (**8**). A soln. of **1a** (500 mg, 2 mmol) and **2c** (590 mg, 2 mmol) in dry THF (2 ml) was kept at r.t. for 7 days. The crystals formed were filtered off and washed with hexane/Et_2O 1:1 yielding **8** (632 mg, 63%), m.p. 221.0–227.0° (anal. sample, m.p. 226.5–229.0°). IR ($CHCl_3$): 3200*m* (br.), 3000*m* (br.), 1715*s*, 1670*m*, 1625*m*, 1590*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 11.68 (*s*, NH); 8.43 (*d*, *J* = 7.6, 1 H); 8.29 (*d*, *J* = 8.5, 1 H); 7.92 (*d*, *J* = 7.8, 1 H); 7.7–7.0 (*m*, 15 H); 7.83 (*d*, *J* = 7.2, 1 H); 6.75 (*dd*, *J* = 11.3, 7.7, 1 H); 6.55 (*dd*, *J* = 7.8, 6.1, 1 H); 6.36 (*d*, *J* = 7.2, 2 H); 4.76 (*d*, *J* = 6.0, H–C(7)); 1.58 (*s*, CH_3). ^{13}C-NMR ($CDCl_3$): 174.9 (*s*, C(3)); 163.4 (*s*, N–CO–N); 149.7 (*s*, C(5)); 142.4, 141.9 (2 *s*, *C*(arom.)–C(6)); 139.2, 138.6, 135.4 (3 *s*, C(arom.)); 134.2, 132.9 (2 *d*, C(10), C(11)); 130.4, 129.1, 128.8, 128.5, 128.1, 127.7, 127.1, 127.0, 126.8, 126.7, 126.5, 126.0, 125.9, 125.8, 120.7, 119.9, 117.9 (C(arom.)); 124.5 (*s*, C(4)); 73.2 (*s*, C(1)); 59.1 (*s*, C(6)); 55.7 (*d*, C(7)); 11.5 (*q*, CH_3). MS (70 eV): 544 (6, $M^{+\cdot}$), 376 (28), 375 (100, $M^{+\cdot}$ – $C_{10}H_7NCO$), 374 (24), 360 (10), 205 (40, $Ph_2C_3CH_3^+$), 169 (93, $C_{10}H_7NCO^+$), 141 (24), 140 (20). Anal. calc. for $C_{38}H_{28}N_2O_2$ (544.66): N 5.14; found: N 5.02.

8. *N-Cyclohexyl-N'-(3-pyridyl)carbodiimide* (**2d**). This carbodiimide was prepared following the procedure given in [14]: A soln. of pyridine-3-carbonyl azide [15] (4.44 g, 30 mmol) in dry benzene (10 ml) was refluxed under N_2 untill the N_2 evolution ceased (2 h). To the cooled soln. of 3-pyridyl isocyanate thus obtained was added (cyclohexylimino)triphenylphosphorane [16] (10.77 g, 30 mmol) dissolved in dry benzene (5 ml). The mixture was stirred at r.t. for 5 h, and then hexane (30 ml) was added. The solid formed (Ph_3PO) was filtered off and washed with hexane. The filtrate was evaporated at r.t. to afford **2d** as colourless oil (5.0 g, 83%) which was used directly for the preparation of **9**. **2d**: IR ($CHCl_3$): 2930*m*, 2850*m*, 2125*s*, 1580*m*, 1480*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 8.50–8.25 (*m*, 2 H); 7.65–7.10 (*m*, 2 H); 3.57 (*m*, CH–N); 2.50–1.00 (*m*, 10 H). MS (70 eV): 202 (4), 201 (16, $M^{+\cdot}$), 120 (34), 119 (100, $M^{+\cdot}$ – C_6H_{10}), 92 (6), 83 (6, $C_6H_{11}^+$), 78 (10, $C_5H_4N^+$), 67 (10), 55 (36).

9. *(1R*,7R*)-2-(N-Cyclohexylcarbamoyl)-4-methyl-6,6-diphenyl-2,8-diazatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* (**9**). A soln. of **1a** (750 mg, 3 mmol) and **2d** (603 mg, 3 mmol) in dry THF (4 ml) was kept at r.t. for 2 days. The mixture was chromatographed on neutral alumina using petroleum ether/$CHCl_3$/acetone 2:1:1. The combined fraction containing **9** was evaporated, and the residue was recrystallised from benzene/CH_2Cl_2 to give **9** (1.61 g, 72%), m.p. 199.0–204.5° (anal. sample, m.p. 204.0–208.5°). IR ($CHCl_3$): 3305*m*, 2930*m*, 2850*m*, 1700*s*, 1665*m*, 1590*w*, 1520*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 8.56 (*d*, *J* = 8.0, NH); 8.40 (*s*, H–C(9)); 7.55–7.00 (*m*, 10 arom. H); 6.35 (br. *t*, *J* = 5.0, H–C(11)); 6.08 (*d*, *J* = 5.0, H–C(7), H–C(10)); 3.88 (*m*, *CH*–NH); 2.15–1.15 (*m*, 5 CH_2); 1.70 (*s*, CH_3). ^{13}C-NMR ($CDCl_3$): 173.5 (*s*, C(3)); 164.5 (*d*, C(9)); 153.0 (*s*, N–CO–N); 150.8 (*s*, C(5)); 143.3, 141.6 (2 *s*, 2 *C*(arom.)–C(6)); 132.1, 129.8, 128.4, 128.2, 128.0, 127.1 (6 *d*, CH (arom.), C(10), C(11)); 127.7 (*s*, C(4)); 74.5 (*s*, C(1)); 72.1 (*d*, C(7)); 59.8 (*s*, C(6)); 48.7 (*d*, CH–NH); 33.1, 25.5, 24.6 (3 *t*, CH_2). MS (70 eV): 452 (6), 451 (18, $M^{+\cdot}$), 424 (4, $M^{+\cdot}$ – HCN), 369 (8), 327 (24), 326 (100, $M^{+\cdot}$ – $C_6H_{11}NCO$), 325 (35), 299 (40), 205 (55, $Ph_2C_3CH_3^+$), 97 (18), 78 (41). Anal. calc. for $C_{29}H_{29}N_3O_2$ (451.58): C 77.13, H 6.47, N 9.31; found: C 77.15, H 6.74, N 9.26.

10. *2-Methyl-4,4-diphenyl-2,3-butadienanilide* (**10a**). A soln. of **7a** (1.40 g) in xylene (5 ml) was refluxed for 20 min. The solvent was evaporated and the residue recrystallised from $CHCl_3$/heptane to afford **10a** (732 mg, 73%), m.p. 154.0–155.0°. UV (cyclohexane): 259 (22700). IR ($CHCl_3$): 3390*m*, 3000*m* (br.), 2920*w*, 1927*m*, 1670*s*, 1595*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.80 (*s*, NH); 7.50–7.20 (*m*, 14 arom. H); 7.08 (*t*, J = 7.5, *p*-H in C_6H_5–N); 2.16 (*s*, CH_3). ^{13}C-NMR ($CDCl_3$): 206.9 (*s*, C(3)); 163.8 (*s*, C(1)); 138.6 (*s*, C(arom.)–N); 134.9 (*s*, 2 *C*(arom.)–C(4)); 129.0, 128.9, 128.6, 128.4, 124.1, 119.5 (6 *d*, CH(arom.)); 115.0 (*s*, C(4)); 102.1 (*s*, C(2)); 14.5 (*q*, CH_3). MS (70 eV): 326 (20), 325 (97, $M^{+\cdot}$), 324 (48), 311 (22), 310 (100, $M^{+\cdot} - CH_3$), 282 (7), 248 (13), 246 (16), 206 (24), 205 (90, $Ph_2C_3CH_3^+$), 203 (38), 202 (34), 191 (44), 165 (30), 77 (26). Anal. calc. for $C_{23}H_{19}NO$ (325.41): C 84.89, H 5.89, N 4.30; found: C 84.18, H 5.28, N 4.58.

11. *2,4,4-Triphenyl-2,3-butadienanilide* (**10b**). This product was obtained as described above for **10a**, starting from **3d**/**7b** (1.8:1). Yield 87%, m.p. 129.0–130.0°. IR ($CHCl_3$): 3390*m*, 3020*m* (br.), 1940*vw*, 1910*w*, 1870*vw*, 1670*s*, 1585*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 7.80–6.95 (*m*). ^{13}C-NMR ($CDCl_3$): 208.9 (*s*, C(3)); 162.9 (*s*, C(1)); 137.8 (*s*, C(arom.)–N); 134.5 (*s*, *C*(arom.)–C(4)); 132.2 (*s*, *C*(arom.)–C(2)); 129.1, 129.0, 128.6, 128.5, 128.3, 124.5 (6 *d*, CH(arom.)); 119.7 (*s*, C(4)); 116.6 (*s*, C(2)). MS (70 eV): 388 (28), 387 (100, $M^{+\cdot}$), 386 (20), 268 (34), 267 (58, $M^{+\cdot}$ – PhNHCO), 265 (22), 191 (7), 189 (11), 165 (24). Anal. calc. for $C_{28}H_{21}NO$ (387.48): N 3.62; found: N 3.71.

12. *2-(Diphenylacetyl)-4-methyl-6,6-diphenyl-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* (**12**). A soln. of **1a** (250 mg, 1 mmol) and triphenylketene imine [17] (269 mg, 1 mmol) in dry THF (2 ml) was heated in a sealed tube at 90° for 18 h. After cooling, the mixture was filtered and the solid washed with Et_2O to give **12** (236 mg) as colourless prisms, m.p. 182.5–184.5°. From the mother liquor, an additional amount of **12** (51 mg, total 55%) was obtained. IR ($CHCl_3$): 3045*m*, 3000*m*, 1720*s*, 1690*s*, 1670*m* (sh), 1595*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.47 (*d*, J = 8.0, 4H); 7.40–7.10 (*m*, 16 H); 6.78 (*s*, CH–CO); 6.33 (*dd*, J = 7.0, 1.5, H–C(9), H–C(10)); 6.24 (*t*, J = 6.0, H–C(8), H–C(11)); 4.51 (*tt*, J = 5.9, 1.5, H–C(7)); 1.59 (*s*, CH_3). ^{13}C-NMR ($CDCl_3$): 171.8, 171.2 (2 *s*, C(3), N–*C*O–CH); 160.7 (*s*, C(5)); 143.5 (*s*, *C*(arom.)–C(6)); 138.9 (*s*, 2*C*(arom.)–CH); 133.8, 129.3, 128.7, 128.6, 128.1, 126.8 (6 *d*, CH(arom.), C(8), C(9), C(10), C(11)); 127.2 (*s*, C(4)); 72.4 (*s*, C(1)); 59.0 (*s*,C(6)); 55.7 (*d*, *C*H–CO); 52.2 (*d*, C(7)); 11.9 (*q*, CH_3). MS (70 eV): 520 (7), 510 (18, $M^{+\cdot}$–Ph_2C=C=O), 310 (19), 270 (8), 269 (8), 246 (5), 205 (18), 194 (15, Ph_2C=C=O^+), 167 (100, Ph_2CH^+), 165 (50), 152 (12), 77 (10). Anal. calc. for $C_{37}H_{29}NO_2$ (518.64): C 85.69, H 5.44, N 2.70; found: C 84.99, H 5.64, N 2.62.

13. *Phenyl 2-Methyl-4,4-diphenyl-2,3-butadienoate* (**13a**). To a stirred soln. of [(phenoxycarbonyl)ethylidene]-triphenylphosphorane [18] (8.20 g, 20 mmol) and Et_3N (2.02 g, 20 mmol) in dry CH_2Cl_2 (30 ml) cooled at 0° was added dropwise under N_2 a soln. of diphenylacetyl chloride (4.60 g, 20 mmol) in dry CH_2Cl_2 (5 ml). After stirring for 6 h at r.t., the solvent was evaporated and the residue was filtered through a short column with silica gel using petroleum ether/Et_2O 4:1. The pale-yellow fraction preceding the triphenylphosphine oxide gave **13a** as a pale-yellow viscous oil which soon crystallised. The recrystallisation from Et_2O/hexane afforded pure **13a** (3.6 g, 74%), m.p. 101.0–102.0°. UV (cyclohexane): 238 (sh, 5300), 255 (4100). IR ($CHCl_3$): 3050*m*, 2955*m*, 2925*m*, 2860*w*, 1935*m*, 1720*s*, 1595*m*, 1490*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.45–7.10 (*m*, 15 H); 2.16 (*s*,CH_3). ^{13}C-NMR ($CDCl_3$): 213.2 (*s*, C(3)); 165.8 (*s*, C(1)); 151.3 (*s*, C(arom.)–O); 135.3 (*s*, *C*(arom.)–C(4)); 129.4, 128.9, 128.7, 128.1, 125.7, 121.6 (6 *d*, CH(arom.)); 113.0 (*s*, C(4)); 97.9 (*s*, C(2)); 15.3 (*q*, CH_3). MS (70 eV): 327 (5), 326 (40, $M^{+\cdot}$), 311 (4), 240 (3), 205 (100, $M^{+\cdot}$–COOPh), 167 (50), 165 (20), 77 (15), 65 (12), 51 (6). Anal. calc. for $C_{23}H_{18}O_2$ (326.38): C 84.64, H 5.56; found: C 84.76, H 5.80.

14. *Diphenyl 3,4-Bis(diphenylmethylidene)-1,2-dimethylcyclobutane-1,2-dicarboxylate* (**14**). A soln. of **13a** (1.84 g) in dry xylene (10 ml) was refluxed for 15 h. The solvent was evaporated and the residue recrystallised from hexane to give **14** (0.82 g, 45%) as yellow prisms, m.p. 182.5–186.5° (anal. sample m.p. 185.0–187.0°, from benzene/hexane). UV ($CHCl_3$): 260 (53400), 356 (30900). IR ($CHCl_3$): 3050*m* (br.), 1735*s*, 1590*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 7.55–7.00 (*m*, C_6H_5O, 2 C_6H_5); 7.00–6.75 (*m*, 2 C_6H_5); 1.21 (*s*, 2 CH_3). ^{13}C-NMR ($CDCl_3$): 172.8 (*s*, CO); 150.9 (*s*, C(arom.)–O); 141.8, 141.4, 138.7, 135.9 (4 *s*, C(arom.), C(olef.)); 129.7, 128.2, 127.8, 127.5, 126.9, 126.1, 121.5 (7 *d*, CH(arom.)); 60.6 (*s*, C(1), C(2)); 17.6 (*q*, CH_3). MS (70 eV): 653 (37), 652 (73, $M^{+\cdot}$), 559 (30), 558 (53), 531 (20, $M^{+\cdot}$–COOPh), 530 (13), 437 (70), 409 (70), 359 (27), 331 (30), 233 (28), 205 (100, $Ph_2C_3CH_3^+$), 165 (30), 105 (23), 77 (17). Anal. calc. for $C_{46}H_{36}O_4$ (652.76): C 84.64, H 5.56; found: C 84.67, H 5.66.

15. *Phenyl 2-Methyl-4-phenyl-2,3-butadienoate* (**13b**). Was obtained following the procedure of *Lang* and *Hansen* [19] as a colourless oil which was used without further purification. IR ($CHCl_3$): 3050*w*, 3000*w*, 2920*w*, 1940*m*, 1720*s*, 1590*m*, 1485*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 7.50–6.70 (*m*, 10 arom. H); 6.52 (*q*, J = 2.5, H–C(4)); 2.09 (*d*, J = 2.5, CH_3).

REFERENCES

[1] L.S. Trifonov, A.S. Orahovats, *Helv. Chim. Acta* **1986,** *69,* 1585.
[2] H.J. Bestmann, H. Hartung, *Ber. Dtsch. Chem. Ges.* **1966,** *99,* 1198.
[3] a) G. Himbert, L. Henn, *Angew. Chem. Suppl.* **1982,** 1473; b) G. Himbert, K. Diehl, G. Maas, *J. Chem. Soc., Chem. Commun.* **1984,** 900; c) L. Henn, G. Himbert, K. Diehl, M. Kaftory, *Ber. Dtsch. Chem. Ges.* **1986,** *119,* 1953.
[4] K.C. Smeltz, U.S. Patent No. 3426025 (*CA:* **1969,** *70,* 69007v).
[5] D.L. Boger, *Tetrahedron* **1983,** *39,* 2869.
[6] J.R. Michael, *Dissertation Abstr.* **1957,** *7,* 2820 (*CA:* **1958,** *52,* 4650b).
[7] M. Yoshida, M. Hiromatsu, K. Kanematsu, *Heterocycles* **1986,** *24,* 881.
[8] G. Himbert, D. Fink, *Tetrahedron Lett.* **1985,** *26,* 4363.
[9] P.D. Landor, S.R. Landor, *J. Chem. Soc.* **1963,** 2707.
[10] K.B. Alberman, F.B. Kipping, *J. Chem. Soc.* **1951,** 779.
[11] R. Kuhn, D. Rewicki, *Ber. Dtsch. Chem. Ges.* **1965,** *98,* 2611.
[12] P. Ykman, G. L'abbe, G. Smets, *Tetrahedron* **1973,** 195.
[13] C.L. Stevens, G.H. Singhal, A.B. Ash, *J. Org. Chem.* **1967,** *32,* 2895.
[14] H. Staudinger, J. Meyer, *Helv. Chim. Acta* **1919,** *2,* 619; *ibid.* **1921,** *5,* 75; O. Tsuge, S. Kanemasa, M. Matsuda, *J. Org. Chem.* **1984,** *49,* 2688.
[15] T. Curtius, E. Mohr, *Ber. Dtsch. Chem. Ges.* **1898,** *31,* 2493.
[16] A.S. Yim, M.H. Auhtar, A.M. Unrau, A.C. Oehlschlager, *Can. J. Chem.* **1978,** *56,* 289.
[17] C.L. Stevens, G.H. Singhal, *J. Org. Chem.* **1964,** 34.
[18] M. Le Corre, *C.R. Hebd. Séances Acad. Sci., Ser. C* **1973,** *276,* 963.
[19] R.W. Lang, H.-J. Hansen, *Helv. Chim. Acta* **1980,** *63,* 438.