Pericyclic Transformations at the Periphery of Chromen-4-one (=4*H*-1-Benzopyran-4-one): An Unusual Preference for a 1,5-Shift of Allylic Moieties over the Ene Reaction

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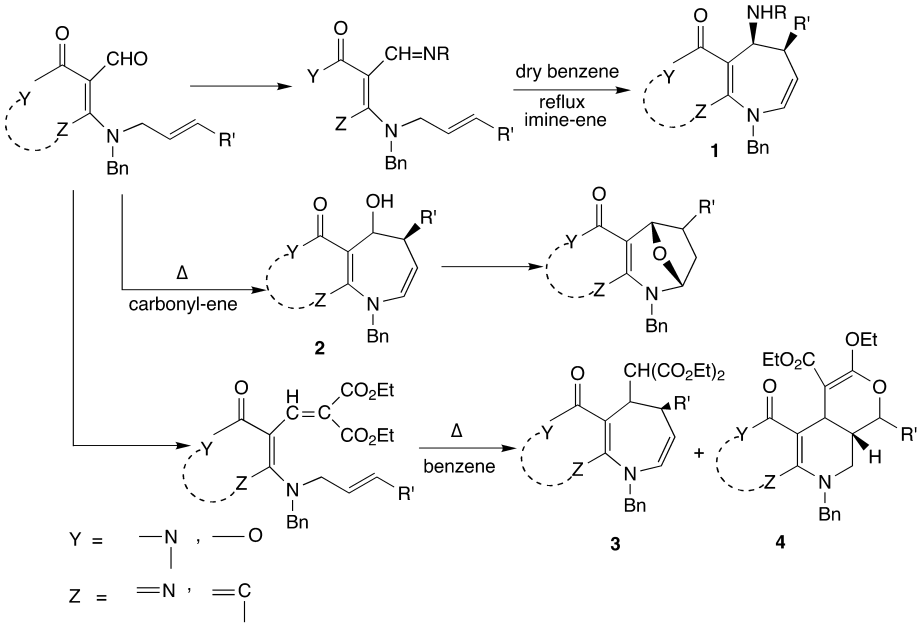
Quite unlike the reported facile ene reactions on the periphery of many related heterocyclic systems, similarly disposed moieties on the periphery of the chromen-4-one (=4*H*-1-benzopyran-4-one) system fail to undergo an ene reaction and display a rather unusual preference for an overall [1,5] shift of the allylic C-atom. Thus, heating xylene solutions of 2-(*N*-allylanilino)-, 2-(*N*-crotylanilino)-, and 2-(*N*-cinnamylamino)-substituted (*E*)-(oxochromenyl)propenoates **9a**–**c** and 2-[allyl(benzyl)amino]-, 2-[benzyl(crotyl)amino]-, and 2-[benzyl(cinnamyl)amino]-substituted (*E*)-(oxochromenyl)propenoates **16a**–**c** in a sealed tube at 220–230° leads to a [1,5] shift of the allylic moieties (allyl, crotyl, cinnamyl), which is followed by intramolecular cyclization involving the N-atom and the ester function, to give the 3-allyl-3-crotyl-, and 3-cinnamyl-substituted-1-phenyl- or 1-benzyl-2*H*-[1]benzopyrano[2,3-*b*]pyridine-2,5(1*H*)-diones **10a**–**c** and **17a**–**c**. The anticipated carbonyl–ene reaction in the 2-(*N*-allylanilino)-, 2-(*N*-crotylanilino)-, 2-(*N*-cinnamylanilino)-, 2-[allyl(benzyl)-amino]-, 2-[benzyl(crotyl)amino]-, and 2-[benzyl(cinnamyl)amino]-substituted 4-oxochromene-3-carboxaldehydes **8a**–**c** and **15a**–**c** is also not observed, and these molecules remain untransformed under identical conditions. No [1,5] shifts of benzyl, phenyl, or methyl groups are observed, even in the absence of allylic moieties, though facile [1,5]-H shift occurs in 2-(benzylamino)- and 2-(phenylamino)-substituted (*E*)-(oxochromenyl)propenoates **23a**,**b**, which is followed by a similar intramolecular cyclization leading to the 2*H*-[1]benzopyrano[2,3-*b*]pyridine-2,5(1*H*)-diones **24a**,**b**.

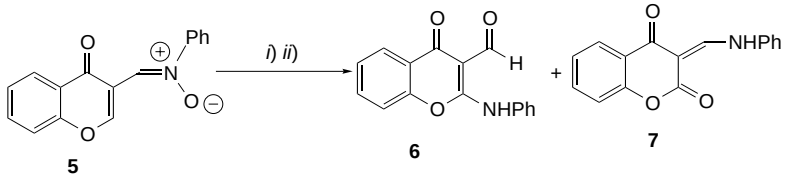
Introduction. – Recently, ene reactions on the periphery of a number of heterocyclic systems such as pyridinones, pyrimidinones, pyrido[1,2-*a*]pyrimidinones, and coumarin (=2*H*-1-benzopyran-2-one) have been utilized [1] to obtain heteroannulated azepines **1**–**3** (*Scheme 1*), which are anticipated to display useful biological activities; an intramolecular hetero-*Diels–Alder* reaction has been reported to intervene only in one case leading to a minor product **4** (*Scheme 1*). Subsequent kinetic and theoretical investigations on these reactions have also been reported [2], which support a concerted mechanism for these transformations.

We have recently reported [3] that *C*-(4-oxo-4 H-1-benzopyran-3-yl)-*N*-phenyl-nitrone **5** undergoes intramolecular rearrangement to 2-anilino-4-oxochromene-3-carboxaldehyde (**6**) in 70–90% yield and 3-(anilinomethylene)chromene-2,4-diones (**7**) in 10–25% yield (*Scheme 2*), and that the yield of **6** could be improved to >95% by refluxing **5** in benzene under acidic conditions [3b]. It was, therefore, decided to utilize **6** to investigate similar reactions at the periphery of the chromen-4-one (=4*H*-1-benzopyran-4-one) system. The investigations were of considerable interest as the targeted azepino-chromenones were potentially biologically active molecules.

Scheme 1



Scheme 2

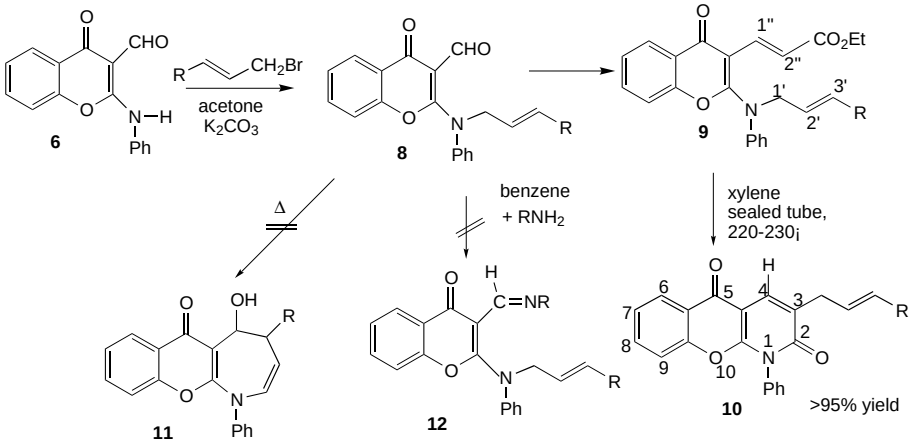


i) $ChCl_3$, r.t., 20 days; 70% of **6**, 25% of **7**. *ii*) H^+/Benzene, reflux, 8 h; 96% of **6**, **7** negligible.

Results and Discussion. – Initially, 2-anilino-4-oxochromen-3-carboxaldehyde (**6**) was reacted with allyl, crotyl (=(2*E*)-but-2-enyl), and cinnamyl (=(2*E*)-3-phenylprop-2-enyl) bromides in presence of fused potassium carbonate to give the *N*-allylated products **8a**–**c** in high yield (*Scheme 3*). However, refluxing **8** in benzene under conditions as employed in [1] and even heating a xylene solution in a sealed tube up to 220° (furnace temperature) did not lead to any carbonyl–ene reaction (↛**11**), and starting materials were recovered unchanged. Attempts to obtain the corresponding *Schiff* bases **12** for investigating an imine–ene reaction did not succeed because reacting **8a**–**c** with amines led to substitution at C(2), and a number of products were formed, which could not be separated. Subsequently, the 2-(*N*-allylanilino)-, 2-(*N*-crotylanilino)-, and 2-(*N*-cinnamylanilino)-substituted (*E*)-(oxochromenyl)propenoates **9a**–**c** were obtained from **8a**–**c** in more than 90% yield by *Wittig* reaction of the 3-carboxaldehyde function with ethyl (triphenylphosphoranylidene)acetate by

refluxing in dry benzene. Compounds **9a–c** were purified by flash column chromatography (silica gel) and characterized spectroscopically. When a benzene solution of **9a–c** was refluxed under N_2 for extended periods, no transformation occurred, and these compounds were recovered unchanged. However, when solutions of **9a–c** in xylene were sealed in *Pyrex*-glass tubes and heated at 220–230° for 6 h, these were transformed to **10a–c** in high yields (>95%); the latter were isolated by column chromatography (silica gel) and characterized spectroscopically (*Scheme 3*). The structures **10a–c** were established by rigorous spectroscopic analyses and microanalytical data.

Scheme 3

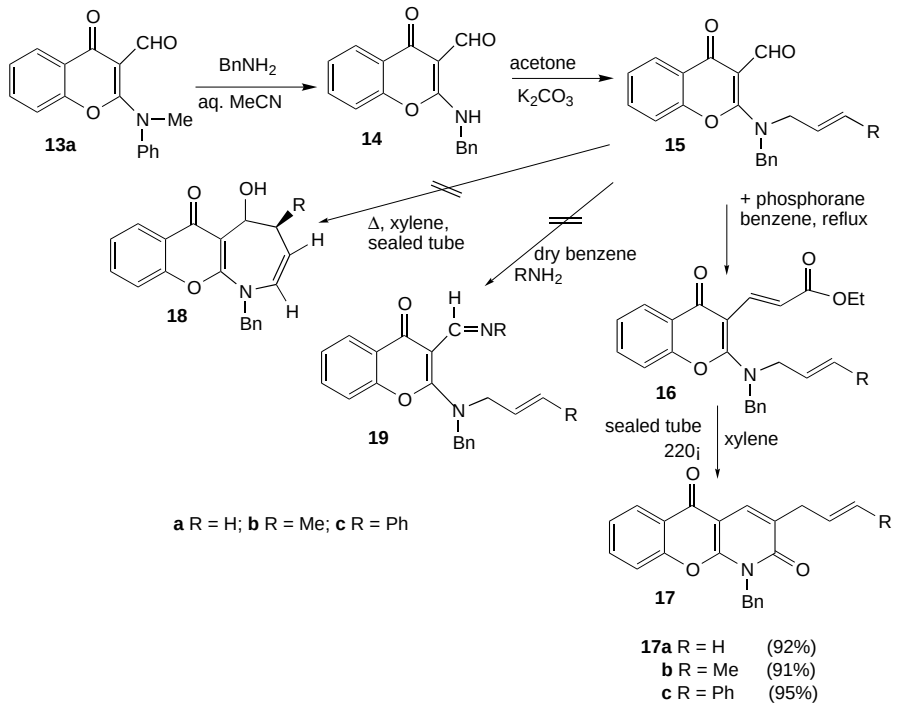


The initial evidence for the assigned structures was provided by the ^{1}H-NMR spectra of **10a–c**, which indicated the loss of the EtO moiety of the ester function. A δ(H) 8.20–8.27 for H–C(6), along with δ(C) 173.8 for C(5), and UV spectral data indicated that not only the chromenone moiety is intact but that the erstwhile C(2)=C(3) bond of chromenone is also present [4]. The NMR spectral data also clearly indicated that the allyl, crotyl, and cinnamyl moieties of **10a–c**, respectively, are intact. However, an upfield shift was observed for the resonances of 2 H–C(1′) in going from **9a–c** (δ 4.65 in **9a**, 4.61 in **9b**, and 4.75 in **9c**) to **10a–c** (δ 3.35 in **10a**, 3.27 in **10b**, and 3.44 in **10c**), an observation that is interpreted as migration of these moieties from an N- to a C-atom. This was also supported by comparison of the ^{13}C-NMR chemical shifts of C(1′) in **9c** (δ 55.30) and **10c** (δ 33.89). Assigned structures are also supported by the presence of a 1-H *s* at δ *ca.* 8.12–8.13 attributed to H–C(4). The presence of a pyridin-2-one moiety was established, *inter alia*, by a band [5] in the IR spectra around 1665–1675 cm^{-1} and a δ(C) *ca.* 162 for C(2) [6]; overall ^{13}C-NMR assignments, mass spectra, and microanalytical data are consistent with the assigned structures.

The investigations were extended to *N*-benzyl analogues **16a–c** because it was thought that the nonobservance of the ene reaction in the case of **9a–c** may be a consequence of working with *N*-phenyl compounds, whereas *N*-benzyl derivatives have been investigated in case of other heterocyclic systems (see *Scheme 1*) [1][2]. The *N*-benzyl derivatives **16a–c** were obtained starting from 2-(*N*-methylanilino)-4-oxochromene-3-carboxaldehyde (**13a**) [3b] *via* **14** and **15** as described in *Scheme 4*. However, there was no change in the general behavior, and only a [1,5] shift of the allylic C-atom

followed by cyclization was observed as the only mode of transformation of **16a–c** leading to **17a–c**, and no ene-reaction product was observed (*Scheme 4*). Here, again, no carbonyl–ene reaction to **18** was observed starting from the 3-carboxaldehyde derivative **15**, and imine–ene reactions could not be investigated due to similar difficulties in obtaining **19**.

Scheme 4

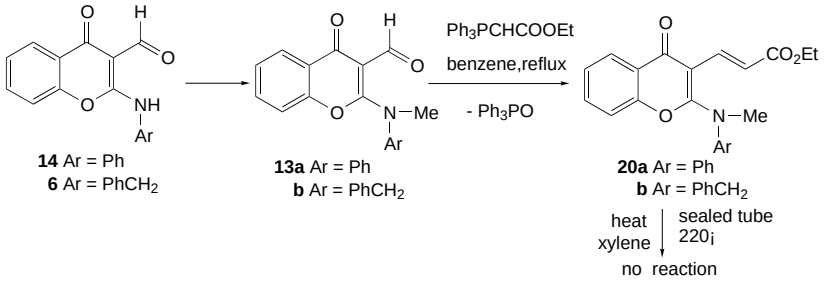


Since in all these reactions, a [1,5] shift of only an allylic C-atom was observed and not even a trace of product derived from phenyl or benzyl migration was detected, it was decided to exclude the allylic moiety and than have a look at possible migration of other groups. Towards this 2-(*N*-methylanilino)- and 2-[benzyl(methyl)amino]-4-oxochromene-3-carboxaldehydes **13a**,**b** were reacted with ethyl (triphenyl phosphoranylidene)acetate to give esters **20a**,**b** (*Scheme 5*), which were characterized spectroscopically. However, heating the xylene solutions of **20a**,**b** in a sealed tube at 220° for 30 h did not lead to any reaction.

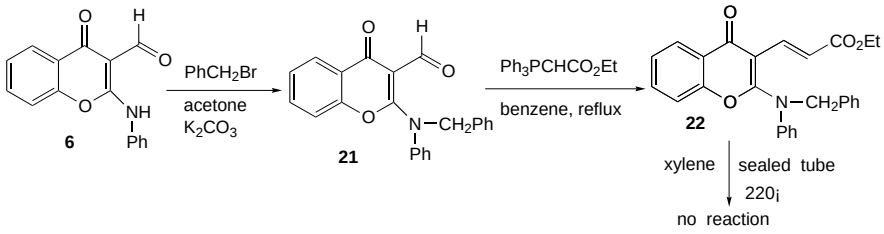
Thinking that the benzyl group may be amenable to such shifts and the presence of a phenyl group may be necessary to force certain conformational requirements, compound **22** was prepared from **6** *via* **21** as described in *Scheme 6*; however, heating a xylene solution of **22** at 220° for 30 h did not lead to any transformation.

However, when the corresponding 2-anilino-and 2-(benzylamino)-4-oxochromene-3-carboxaldehydes **6** and **14**, respectively, were reacted with ethyl (triphenylphosphoranylidene)acetate in refluxing benzene, these were transformed to chromeno-

Scheme 5

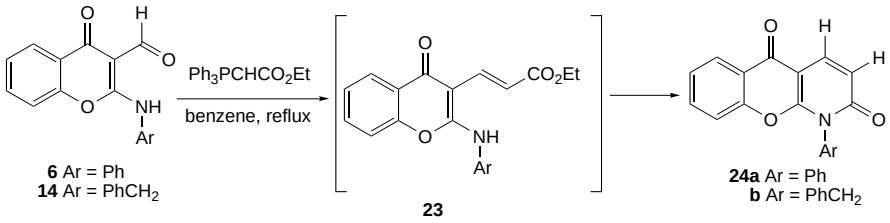


Scheme 6



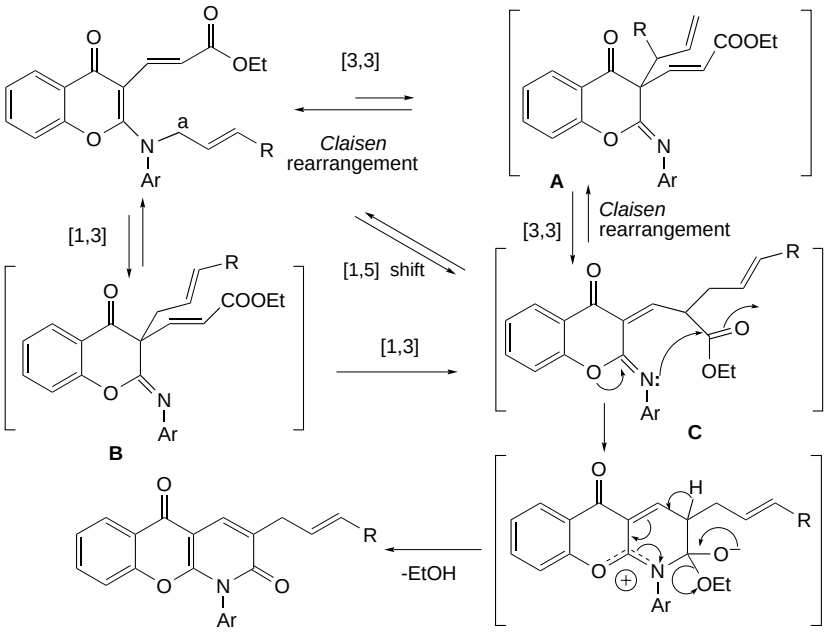
pyridinediones **24** (*Scheme 7*). That the compounds **24a**,**b** are derived from an initially formed **23** was established by carrying out the reaction of **6** (Ar = Ph) with ethyl (triphenylphosphoranylidene)acetate in CH_2Cl_2 at room temperature, when **23a** was isolated, characterized, and subsequently converted to **24a** by refluxing in benzene, thereby confirming the facile [1,5]-H shift in **23**.

Scheme 7



Mechanistically, the observed overall [1,5] shift of various allylic moieties (allyl, crotyl, cinnamyl) can be envisaged as either involving two successive [3,3] shifts (*Claisen* rearrangement) or two [1,3] shifts or a single [1,5] shift, which is followed by cyclization in intermediate **C** (*Scheme 8*). That benzyl, phenyl, or methyl groups fail to undergo [1,5] shifts under identical conditions points towards involvement of two successive *Claisen* rearrangements. However, stopping the reaction after shorter reaction times, *i.e.*, after 1 h, 3 h, and 5 h, afforded either unreacted starting or final product. No other product or one of the postulated intermediates **A**, **B**, or **C** could be

Scheme 8



detected even in the ^{1}H-NMR spectrum of the crude products, and these observations suggest either a fast second [3,3]/[1,3] shift or a single [1,5] suprafacial shift.

Molecular modeling of the starting materials **9a**–**c** and **16a**–**c** by means of DTMM (version 2.0) did not reveal any conformational preference favoring [1,5] shifts of allylic moieties. Rather, the conformational preference in the molecule appears to favor a *Claisen* rearrangement. At this level of modeling, the starting compounds appeared to be more stable than the intermediates, including **C**, indicating that the overall process becomes unidirectional due to the last cyclization step.

It may be mentioned here that the delocalization of the lone pair of the N-atom up to C(4)=O and to the ester moiety is likely to create electron deficiency in the N–C(1′) linkage of **9** and **16**, and this electron deficiency at the migratory center may be better stabilized by allylic systems, moreso even than by phenyl or benzyl moieties. The observed facile [1,5]-H migration in **23** under refluxing in benzene, leading to **24**, may involve a simple proton shift. Literature reveals that in general, [3,3]-sigmatropic shifts are favored in the case of allylic systems and occur, generally, at relatively lower temperatures as compared to the temperatures employed in the present case [7]. The [1,3] shifts of the allylic moiety from an N- to a C-atom are precedented [8], and an example of a [1,5] shift of an allylic moiety from an N- to a C-atom is reported in the case of five-membered heterocycles [9]. Though the exact sequence of events in the cyclization step are not delineated, the loss of the H-atom has to be either concomitant with or following the interaction between the N-atom and the ester carbonyl group, and may not precede the cyclization.

Conclusions. – Though the exact nature of the involved sigmatropic shift, *i.e.*, two [3,3], two [1,3], or a single [1,5] shift, could not be ascertained, the ene reactions at the periphery of the chromen-4-one moiety is certainly suppressed, which is contrary to the reported facile ene reactions at the periphery of many related heterocyclic systems. The reaction offers an interesting example of an overall [1,5] shift of an allylic moiety over a noncyclic diene wherein the allylic C-atom shows a higher migratory aptitude than a benzyl or phenyl group. The reaction provides an easy access to potentially biologically active chromeno-pyridinones; the involvement of the chromenone moiety in pharmacophores of a variety of biologically active molecules and medicinal compounds is well-documented [10], and valuable medicinal properties are ascribed to heteroannulated pyridinones [11].

Experimental Part

General. Starting materials and reagents were purchased from commercial suppliers and used after further purification (crystallization or distillation). The 4-oxo-4*H*-1-benzopyran-3-carboxaldehyde (= 3-formylchromone) was purchased from *Aldrich* and used as such. CC = Column chromatography, FC = flash chromatography. M.p.: precision (make) *MP-D* digital melting point apparatus; in open glass capillaries; uncorrected. UV/VIS Spectra: *Shimadzu 160A* spectrophotometer; in nm. IR Spectra: *Shimadzu DR-2001* FT-IR spectrophotometer; $CHCl_3$ soln. or KBr pellets; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker AC-200 FT* (200 MHz) and *Bruker-F* (300 MHz); at 200 or 300 MHz (^1H) and 50 or 75 MHz (^{13}C); chemical shifts δ in ppm downfield from $SiMe_4$ as internal standard and J values in Hz. Mass spectra: electron ionization (EI); *Shimadzu GCMS-QP-2000A* spectrometer; in m/z (rel. %). Elemental analyses were performed at RSIC, Chandigarh, and are reported in percent atomic abundance.

*4-Oxo-2-[phenyl(prop-2-enyl)amino]-4*H*-1-benzopyran-3-carboxaldehyde* (**8a**). To a soln. of **6** [3] (1.0 g, 3.8 mmol) in dry acetone (75 ml) was added allyl bromide (0.73 g, 6.0 mmol) and anh. K_2CO_3 (2.0 g). The mixture was refluxed with stirring to completion of the reaction (9 h, TLC monitoring). The hot mixture was filtered, the residue washed with a little acetone, and the solvent from filtrate distilled off. The obtained product was purified by FC (silica gel (200–400 mesh, 20 g); hexane/AcOEt 9:1): **8a** (1.11 g, 96%). Cream-colored solid. M.p. 110–111° ($CHCl_3$/hexane 1:2). UV (MeOH): 240, 285, 327. IR ($CHCl_3$): 1676 (HC=O), 1654 (C=O), 1610, 1597, 1518, 1495, 1466, 1425, 1385, 1350, 1325, 1213. ^1H-NMR ($CDCl_3$, 300 MHz): 10.02 (*s*, H–C=O); 8.20 (*dd*, J = 7.74, 1.59, H–C(5)); 7.70–7.52 (*m*, 3 arom. H); 7.49–7.21 (*m*, 5 arom. H); 6.04–5.92 (*m*, H–C(2′)); 5.32–5.21 (*m*, 2 H–C(3′)); 4.61 (*d*, J = 5.46, 2 H–C(1′)). EI-MS: 305 (4, M^+), 304 (20, $[M-1]^+$), 276 (6), 235 (5), 158 (5), 144 (5).

*2-{[(2*E*)-But-2-enyl]phenylamino}-4-oxo-4*H*-1-benzopyran-3-carboxaldehyde* (**8b**). As described for **8a**, with **6** (1.0 g, 3.8 mmol), crotyl bromide (0.81 g, 6.0 mnmol), anh. K_2CO_3 (2.0 g), and acetone (75 ml): **8b** (1.14 g, 95%). Cream-colored solid. M.p. 113–114° ($CHCl_3$/hexane 1:2). UV (MeOH): 236, 276, 318. IR ($CHCl_3$): 1678 (H–C=O), 1650 (C=O), 1604, 1572.2, 1518.2, 1493.1, 1466.1, 1423.6, 1219.2. ^1H-NMR ($CDCl_3$, 300 MHz): 9.98 (*s*, H–C=O); 8.20 (*dd*, J = 7.78, 1.6, H–C(5)); 7.61 (*dt*, J = 7.93, 1.6, H–C(7)); 7.41–7.39 (*m*, 3 arom. H); 7.36–7.33 (*m*, 4 arom. H); 5.73–5.56 (*m*, H–C(2′), H–C(3′)); 4.52 (*d*, J = 5.34, CH_2N); 1.63 (*d*, J = 5.73, Me). EI-MS: 319 (21, M^+), 318 (78, $[M-1]^+$), 304 (19), 171 (37).

*4-Oxo-2-{phenyl[(2*E*)-3-phenylprop-2-enyl]amino}-4*H*-1-benzopyran-3-carboxaldehyde* (**8c**). As described for **8a**, with **6** (1.00 g, 3.8 mmol), dry acetone (75 ml), cinnamyl bromide (1.18 g, 6.0 mmol), and anh. K_2CO_3 (2.0 g): **8c** (1.37 g, 97%). Cream-colored solid. M.p. 117–118° (Et_2O). UV (MeOH): 247, 280, 290, 305, 355. IR ($CHCl_3$): 1682 (H–C=O), 1640 (C=O), 1620, 1570, 1560, 1550, 1530, 1475, 1466, 1423, 1360, 1346, 1217. ^1H-NMR ($CDCl_3$, 300 MHz): 10.02 (*s*, H–C=O); 8.27 (*d*, J = 8.36, H–C(5)); 7.60 (*t*, J = 8.15, H–C(7)); 7.43–7.22 (*m*, 12 arom. H); 6.58 (*d*, J = 15.72, H–C(3′)); 6.35–6.25 (*m*, H–C(2′)); 4.76 (*d*, J = 6.12, CH_2N). EI-MS: 381 (0.2, M^+), 380 (1.0, $[M-1]^+$), 352 (0.15), 275 (5), 198 (3), 158 (5), 144 (5).

*Ethyl (2*E*)-3-{4-Oxo-2-[phenyl(prop-2-enyl)amino]-4*H*-1-benzopyran-3-yl}prop-2-enoate* (**9a**). To a soln. of **8a** (0.61 g, 2.0 mmol) in dry benzene (100 ml) was added ethyl (triphenylphosphoranylidene)acetate (0.70 g, 2.0 mmol), and the mixture was refluxed with stirring, under a moisture-free setup, to completion of reaction (7 h). After evaporation, the residue was purified by FC (silica gel (200–400 mesh, 20 g); hexane/Et_2O 9:1): **9a** (0.71 g, 95%). Cream-colored solid. M.p. 81–82° ($CHCl_3$/hexane 1:2). UV (MeOH): 218, 240.6, 295, 335. IR

($CHCl_3$): 1701 (CO_2Et), 1645.5 (C=O), 1625, 1520, 1493, 1470, 1414, 1380, 1294, 1270, 1230, 1210, 1197. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.17 (*d*, *J* = 7.68, H–C(5)); 7.68–7.06 (*m*, 10 arom. and olef. H); 6.02–5.90 (*m*, H–C(2′)); 5.30 (*d*, *J* = 18.62, 1 H–C(3′)); 5.23 (*d*, *J* = 11.08, 1 H–C(3′)); 4.56 (*d*, *J* = 5.28, 2 H–C(1′)); 4.04 (*q*, *J* = 7.12, MeCH_2O); 1.19 (*t*, *J* = 7.12, *Me*CH_2O). EI-MS: 376 (1.3, $[M+1]^+$), 375 (4.3, M^+), 374 (0.5, $[M-1]^+$), 305 (5), 279 (5), 238 (3), 147 (8). Anal. calc. for $C_{23}H_{21}NO_4$: C 73.58, H 5.64, N 3.73; found: C 73.82, H 5.92, N 3.94.

*Ethyl (*2E*)-3-{2-{[(*2E*)-But-2-enyl]phenylamino}-4-oxo-4*H*-1-benzopyran-3-yl}prop-2-enoate* (**9b**). As described for **9a**, with **8b** (0.64 g, 2.0 mmol), dry benzene (100 ml), and ethyl (triphenylphosphoranylidene)acetate (0.70 g, 2.0 mmol): **9b** (0.733 g, 94%). Cream-colored solid. M.p. 92° ($CHCl_3$/hexane 1:2). UV (MeOH): 301, 283, 258, 221.2. IR ($CHCl_3$): 1705.3 (CO_2Et), 1643.6 (C=O), 1616.5, 1526, 1493.1, 1468, 1417.9, 1363.8, 1290.5, 1207.6. ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.31 (*dd*, *J* = 7.84, 1.66, H–C(5)); 7.67 (*dt*, *J* = 7.51, 1.70, H–C(7)); 7.49–7.37 (*m*, 4 arom. and olef. H), 7.27–7.17 (*m*, 5 arom. and olef. H); 5.84–5.78 (*m*, H–C(2′), H–C(3′)); 4.61 (*d*, *J* = 3.69, 2 H–C(1′)); 4.17 (*q*, *J* = 7.07, MeCH_2O); 1.81 (*d*, *J* = 4.32, Me); 1.33 (*t*, *J* = 7.07, *Me*CH_2O). EI-MS: 390 (17, $[M+1]^+$), 389 (38, M^+), 316 (24), 262 (29), 169 (100). Anal. calc. for $C_{24}H_{23}NO_4$: C 74.02, H 5.95, N 3.60; found: C 73.79, H 5.62, N 3.48.

*Ethyl (*2E*)-3-{4-Oxo-2-{phenyl[(*2E*)-3-phenylprop-2-enyl]amino}-4*H*-1-benzopyran-3-yl}prop-2-enoate* (**9c**). As described for **9a**, with **8c** (0.76 g, 2.0 mmol), ethyl (triphenylphosphoranylidene)acetate (0.70 g, 2.0 mmol), and dry benzene (100 ml): **9c** (0.87 g, 97%). Cream-colored solid. M.p. 128–130° ($CHCl_3$/hexane 1:2). UV (MeOH): 215, 245.6, 285, 290.5, 320, 355. IR ($CHCl_3$): 1695 (CO_2Et), 1650 (C=O), 1624, 1580, 1550, 1518, 1495, 1468, 1444, 1421, 1400, 1344, 1320, 1250, 1230. ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.20 (*dd*, *J* = 7.16, 1.59, H–C(5)); 7.61 (*t*, *J* = 8.47, H–C(7)); 7.41–7.10 (*m*, 14 arom. H); 6.62 (*d*, *J* = 15.80, H–C(3′)); 6.41–6.32 (*m*, H–C(2′)); 4.75 (*d*, *J* = 6.12, 2 H–C(1′)); 4.05 (*q*, *J* = 7.11, MeCH_2O); 1.16 (*t*, *J* = 7.11, *Me*CH_2O). ^{13}C-NMR ($CDCl_3$, 75 MHz): 176.94 (C(4)); 167.80 (ester C=O); 162.73 (C(2)); 153.12 (C(8a)); 144.78 (quat. arom. C); 136.11 (quat. arom. C); 135.72 (olef. CH); 133.90 (C(7)); 133.04 (CH); 129.68 (CH); 128.64 (CH); 128.08 (CH); 126.53 (CH); 126.29 (CH); 125.63 (CH); 125.36 (CH); 123.97 (CH); 123.83 (CH); 123.24 (C(4a)); 118.71 (C(8)); 116.73 (olef. CH); 102.35 (C(3)); 59.78 (Me*C*H_2O); 55.30 (CH_2N); 14.32 (*Me*CH_2O). EI-MS: 355 (0.62, $[M-96]^+$), 341 (0.55), 327 (0.30), 311 (0.40), 305 (0.55), 301 (5), 284 (20). Anal. calc. for $C_{29}H_{25}NO_4$: C 77.14, H 5.58, N 3.10; found: C 77.37, H 5.37, N 3.34.

*1-Phenyl-3-(prop-2-enyl)-*2H*-[1]benzopyrano[2,3-*b*]pyridine-2,5(1*H*)-dione* (**10a**). A soln. of **9a** (0.38 g, 1.00 mmol) in xylene (10 ml) was sealed in a glass tube, which was heated at 220–230° (6 h). The tube was chilled and cut, and the soln. was concentrated to 1/4 of the original volume. The crystals, which appeared after chilling for 2 h, were recrystallized from benzene: **10a** (0.32 g, 96%). Light brown crystalline solid. M.p. 180–182° (benzene). UV (MeOH): 338, 325, 310, 287, 235. IR ($CHCl_3$): 1674.4 (N–C=O), 1649.3 (C=O), 1614.6, 1583.7, 1552.9, 1481.5, 1468, 1450, 1427.5, 1410, 1390, 1344, 1290, 1267, 1190. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.27 (*dd*, *J* = 7.88, 1.69, H–C(6)); 8.13 (*s*, H–C(4)); 7.65–7.52 (*m*, 4 arom. H); 7.45–7.25 (*m*, 3 arom. H); 7.10 (*d*, *J* = 8.38, H–C(9)); 6.07–5.91 (*m*, H–C(2′)); 5.26 (*d*, *J* = 10.90, 1 H–C(3′)); 5.17 (*d*, *J* = 8.64, 1 H–C(3′)); 3.35 (*dd*, *J* = 5.29, 1.1, 2 H–C(1′)). ^{13}C-NMR ($CDCl_3$, 50 MHz): 173.69 (C(5)); 161.67 (C(2)); 154.74 (C(10a)); 153.43 (C(9a)); 134.36 (CH); 134.00 (N–C); 133.76 (CH); 132.06 (CH); 129.58 (CH); 129.42 (C(3)); 128.37 (CH); 128.22 (CH); 126.48 (CH); 125.68 (CH); 122.13 (C(5a)); 117.70 (C(9)); 117.48 (C(3′)); 101.96 (C(4a)); 34.41 (C(1′)). EI-MS: 329 (0.4, M^+), 285 (25), 288 (1.0), 211 (2). Anal. calc. for $C_{21}H_{15}NO_3$: C 76.58, H 4.59, N 4.25; found: C 76.82, H 4.71, N 4.41.

*3-[(*2E*)-But-2-enyl]-1-phenyl-*2H*-[1]benzopyrano[2,3-*b*]pyridine-2,5(1*H*)-dione* (**10b**). As described for **10a**, with **9b** (0.39 g, 1.00 mmol) and xylene (10 ml): **10b** (0.33 g, 97%). Light brown solid. M.p. 222–223°. UV (MeOH): 325.6, 289.8, 235.2. IR ($CHCl_3$): 1674.4, 1649.3, 1608.8, 1545.2, 1493.1, 1464.1, 1444.9, 1313.7, 1261.6. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.28 (*dd*, *J* = 7.80, 1.66, H–C(6)); 8.08 (*s*, H–C(4)); 7.64–7.54 (*m*, 4 arom. H); 7.46–7.26 (*m*, 3 arom. H); 7.11 (*d*, *J* = 8.16, H–C(9)); 5.68–5.62 (*m*, H–C(2′), H–C(3′)); 3.27 (br., 2 H–C(1′)); 1.75 (*s*, Me). ^{13}C-NMR ($CDCl_3$, 50 MHz): 173.81 (C(5)); 162.02 (C(2)); 154.70 (C(10a)); 153.43 (C(9a)); 134.08 (C_{ipso}–N); 133.81 (C(8)); 131.67 (CH); 129.62 (CH); 129.43 (CH); 128.45 (CH); 128.26 (CH); 127.16 (C(3)); 126.80 (CH); 126.41 (CH); 125.68 (CH); 122.14 (C(5a)); 117.53 (C(9)); 102.01 (C(4a)); 33.21 (C(1′)); 18.03 (Me). EI-MS: 344 (7, $[M+1]^+$), 343 (23, M^+), 314 (22), 169 (100). Anal. calc. for $C_{22}H_{17}NO_3$: C 76.95, H 4.99, N 4.08; found: C 77.21, H 4.84, N 4.33.

*1-Phenyl-3-[(*2E*)-3-phenylprop-2-enyl]-2*H*-[1]benzopyrano[2,3-*b*]pyridine-2,5(1*H*)-dione* (**10c**). As described for **10a**, with **9c** (0.45 g, 1.00 mmol) and xylene (10 ml): **10c** (0.38 g, 95%). Yellowish solid. M.p. 240–242° (benzene). UV (MeOH): 236.6, 250, 290, 326.6, 340. IR ($CHCl_3$): 1665 (N–C=O), 1657 (C=O), 1610, 1549, 1493.1, 1464.1, 1442.9, 1415, 1390, 1361.9, 1300, 1270. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.25 (*dd*, *J* = 7.64, 1.89, H–C(6)); 8.12 (*s*, H–C(4)); 7.59–7.55 (*m*, 3 arom. H); 7.32–7.06 (*m*, 10 arom. H); 6.59 (*d*, *J* = 15.78,

H–C(3′)); 6.32–6.20 (*dt*, *J* = 15.78, 6.76, H–C(2′)); 3.44 (*d*, *J* = 6.76, 2 H–C(1′)). ^{13}C-NMR ($CDCl_3$, 50 MHz): 173.83 (C(5)); 162.19 (C(2)); 154.2 (C(10a)); 153.51 (C(9a)); 137.25 (quat. arom. C); 133.91 (C(8)); 132.67 (quat. arom. C); 132.24 (CH); 129.69 (CH); 129.52 (CH); 128.88 (C(3)); 128.54 (CH); 128.47 (CH); 128.27 (CH); 127.26 (CH); 126.48 (CH); 126.26 (CH); 126.11 (C(3)); 125.78 (CH); 122.13 (C(5a)); 117.58 (C(9)); 102.08 (C(4a)); 33.89 (C(1′)). EI-MS: 405 (0.8, M^+), 315 (10), 285 (20), 269 (4), 255 (4), 219 (6). Anal. calc. for $C_{27}H_{19}NO_3$: C 79.98, H 4.72, N 3.45; found: C 80.23, H 4.66, N 3.62.

*2-[Benzyl(prop-2-enyl)amino]-4-oxo-4*H-*1-benzopyran-3-carboxaldehyde* (**15a**). To a soln. of **14** [3b] (0.84 g, 3.0 mmol) in dry acetone (100 ml) was added allyl bromide (0.61 g, 5.0 mmol) and anh. K_2CO_3 (2.0 g), and the mixture was refluxed for 9 h. The hot mixture was filtered, the solid washed with little acetone, the solvent evaporated, and the residue separated by CC (silica gel (60–120 mesh, 20 g), packed in hexane, then hexane/AcOEt 9:1): **15a** (0.90 g, 94%). Dark brown semisolid. UV (MeOH): 231.6, 270, 282, 305. IR ($CHCl_3$): 1670, 1630, 1580, 1560, 1508, 1466, 1417. ^{1}H-NMR ($CDCl_3$, 200 MHz): 10.17 (*s*, H–C=O); 8.19 (*d*, *J* = 6.46, H–C(5)); 7.58 (*t*, *J* = 7.5, H–C(7)); 7.39–7.18 (*m*, 7 arom. H); 6.0–5.8 (*m*, H–C(2′)); 5.32–5.20 (*m*, 2 H–C(3′)); 4.72 (*s*, PhCH_2); 4.11 (*d*, *J* = 4.10, 2 H–C(1′)). EI-MS: 319 (10, M^+), 278 (10), 250 (14), 145 (5), 111 (32), 91 (100). Anal. calc. for $C_{20}H_{17}NO_3$: C 75.22, H 5.37, N 4.39; found: C 75.41, H 5.63, N 4.62.

*2-{Benzyl[(2*E*)-but-2-enyl]amino}-4-oxo-4*H-*1-benzopyran-3-carboxaldehyde* (**15b**). As described for **15a**, with **14b** (0.84 g, 3.0 mmol), crotyl bromide (0.68 g, 5.0 mmol), anh. K_2CO_3 (2.0 g), and dry acetone (100 ml). CC (silica gel (60–120 mesh, 20 g), column packed in hexane, then hexane/AcOEt gradient) gave **15b** (0.96 g, 96%). Dark brown solid. M.p. 113–115° ($CHCl_3$/hexane 1:2). UV (MeOH): 237, 269, 275, 290, 300. IR ($CHCl_3$): 1672 (H–C=O), 1633 (C=O), 1614, 1576, 1540, 1496, 1466, 1440, 1388, 1340, 1313, 1215. ^{1}H-NMR ($CDCl_3$, 200 MHz): 10.27 (*s*, H–C=O); 8.34–8.18 (*m*, 2 arom. H); 7.68–7.28 (br. *m*, 7 arom. H); 5.75–5.71 (*m*, *J* = 5.3, H–C(3′)); 5.60–5.58 (*m*, H–C(2′)); 4.86 (*s*, PhCH_2); 4.15 (*d*, *J* = 4.84, 2 H–C(1′)); 1.84 (br. *d*, *J* = 6.8, Me). EI-MS: 304 (5, $[M-29]^+$), 250 (54, $[M-84]^+$), 242 (10), 241 (5), 234 (3), 188 (10), 183 (8), 171 (22), 170 (5). Anal. calc. for $C_{21}H_{19}NO_3$: C 75.66, H 5.74, N 4.20; found: C 75.52, H 5.85, N 4.49.

*2-{Benzyl[(2*E*)-3-phenylprop-2-enyl]amino}-4-oxo-4*H-*1-benzopyran-3-carboxaldehyde* (**15c**). As described for **15a**, with **14b** (0.84 g, 3.0 mmol), dry acetone (100 ml), crotyl bromide (0.98 g, 5.0 mmol), and anh. K_2CO_3 (2.0 g). CC (silica gel (60–120 mesh, 20 g); hexane/AcOEt gradient) gave **15c** (1.15 g, 97%). Brownish semisolid. UV (MeOH): 243, 283, 296, 308. IR ($CHCl_3$): 1670 (H–C=O), 1633 (C=O), 1580, 1508, 1558, 1508, 1500, 1462, 1450, 1416, 1360, 1340, 1325. ^{1}H-NMR ($CDCl_3$, 200 MHz): 10.23 (*s*, H–C=O); 8.24 (*d*, *J* = 7.70, H–C(5)); 7.64 (*t*, *J* = 7.61, H–C(7)); 7.43–7.21 (*m*, 12 arom. H); 6.53 (*d*, *J* = 15.90, H–C(3′)); 6.28 (*dt*, *J* = 15.90, 6.40, H–C(2′)); 4.63 (*s*, PhCH_2); 4.28 (*d*, *J* = 6.40, 2 H–C(1′)). EI-MS: 355 (1, $[M-40]^+$), 278 (1.5), 250 (10), 159 (3), 145 (5), 111 (40), 94 (30). Anal. calc. for $C_{26}H_{21}NO_3$: C 78.97, H 5.35, N 3.54; found: C 78.71, H 5.56, N 3.33.

*Ethyl (2*E*)-3-{2-[Benzyl(prop-2-enyl]amino}-4-oxo-4*H-*1-benzopyran-3-yl}prop-2-enoate* (**16a**). To a soln. of **15a** (0.64 g, 2.0 mmol) in dry benzene (100 ml), under protection from moisture, was added ethyl (triphenylphosphoranylidene)acetate (0.70 g, 2.0 mmol), and the mixture was refluxed with stirring to completion of the reaction (10 h). After evaporation the residue was purified by CC (silica gel (20 g, 60–120 mesh), packed in hexane, then hexane/AcOEt gradient): **16a** (0.75 g, 96%). Light brown solid. M.p. 80–82° ($CHCl_3$/hexane 1:2). UV (MeOH): 238, 279, 292, 318, 320. IR ($CHCl_3$): 1697 (CO_2Et), 1635 (C=O), 1620, 1616, 1541, 1508, 1456, 1420, 1350, 1340, 1288. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.17 (*dd*, *J* = 7.38, 1.26, H–C(5)); 7.52 (*t*, *J* = 8.36, H–C(7)); 7.48 (*d*, *J* = 15.69, C*H*=CHCOOEt); 7.35–7.20 (*m*, 9 arom. and olef. H); 6.05–5.91 (*m*, H–C(2′)); 5.37–5.24 (*m*, 2 H–C(3′)); 4.67 (*s*, PhCH_2); 4.20 (*q*, *J* = 7.12, MeCH_2O); 4.01 (*d*, *J* = 5.94, 2 H–C(1′)); 1.31 (*t*, *J* = 7.12, *Me*CH_2O). EI-MS: 389 (20, M^+), 344 (5), 316 (26), 275 (6), 170 (48), 144 (8), 111 (25), 91 (100). Anal. calc. for $C_{24}H_{23}NO_4$: C 74.02, H 5.95, N 3.69; found: C 74.23, H 6.27, N 3.47.

*Ethyl (2*E*)-3-{2-{Benzyl[(2*E*)-but-2-enyl]amino}-4-oxo-4*H-*1-benzopyran-3-yl}prop-2-enoate* (**16b**). As described for **16a**, with **15b** (0.67 g, 2.0 mmol), ethyl (triphenylphosphoranylidene)acetate (0.70 g, 2.0 mmol), and dry benzene (100 ml): **16b** (0.77 g, 95%). Off-white solid. M.p. 83–85° ($CHCl_3$/hexane 1:2). UV (MeOH): 235.4, 290, 305, 323. IR ($CHCl_3$): 1696 (CO_2Et), 1662 (C=O), 1633, 1614, 1576, 1540, 1496, 1464, 1440, 1388, 1346, 1313, 1215. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.30 (*d*, *J* = 7.77, H–C(5)); 7.77–7.70 (*m*, H–C(7)); 7.53–7.17 (*m*, 9 arom. and olef. H); 5.88–5.52 (*m*, H–C(2′)); 5.50–5.43 (*m*, H–C(3′)); 4.77 (*s*, PhCH_2); 4.12 (*q*, *J* = 7.12, MeCH_2O); 4.04 (*d*, *J* = 5.14, 2 H–C(1′)); 1.77 (*d*, *J* = 6.16, Me(4′)); 1.28 (*t*, *J* = 7.12, *Me*CH_2O). EI-MS: 403 (0.82, M^+), 375 (0.56), 374 (1.5), 330 (8), 304 (5), 283 (12), 278 (22), 242 (26). Anal. calc. for $C_{25}H_{25}NO_4$: C 74.42, H 6.25, N 3.47; found: C 74.66, H 6.42, N 3.40.

*Ethyl (2*E*)-3-{2-{Benzyl[(2*E*)-3-phenylprop-2-enyl]amino}-4-oxo-4*H-*1-benzopyran-3-yl}prop-2-enoate* (**16c**). As described for **16a**, with **15c** (0.79 g, 2.0 mmol), ethyl (triphenylphosphoranylidene)acetate (0.70 g, 2.0 mmol), and dry benzene (100 ml) (12 h): **16c** (0.89 g, 96%). Yellowish solid. M.p. 60–62° ($CHCl_3$/hexane

1:2). UV (MeOH): 235.4, 289.4, 327.6. IR ($CHCl_3$): 1699 (CO_2Et), 1643 (C=O), 1616, 1537, 1496, 1466, 1423, 1354, 1288, 1230. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.23 (*dd*, *J* = 7.8, 1.6, H–C(5)); 7.57 (split *t*, *J* = 7.58, 2.62, H–C(7)); 7.56 (*d*, *J* = 15.60, C*H*=CHCOOEt); 7.42–7.25 (*m*, 13 arom. and olef. H); 6.50 (*d*, *J* = 15.81, H–C(3′)); 6.41–6.30 (*m*, H–C(2′)); 4.74 (*s*, PhCH_2); 4.72–4.16 (*m*, MeCH_2O, 2 H–C(1′)); 1.27 (*t*, *J* = 7.08, *Me*CH_2O). EI-MS: 465 (1, M^+), 419 (1), 378 (1), 273 (5), 182 (8), 156 (10), 142 (8), 111 (40). Anal. calc. for $C_{30}H_{27}NO_4$: C 77.40, H 5.85, N 3.01; found: C 77.59, H 5.98, N 3.24.

*1-Benzyl-3-(prop-2-enyl)-2*H*-[1]benzopyrano[2,3-*b*]pyridine-2,5(1*H*)-dione* (**17a**). A soln. of **16a** (0.39 g, 1.0 mmol) in xylene (10 ml) was sealed in a glass tube which was heated to 220° for 6 h. The tube was chilled and cut, the solvent evaporated, and the residue separated by prep. TLC (silica gel *G*, 2-mm layer, 6 plates, eluent $CHCl_3$, extraction with $CHCl_3$/MeOH): **17a** (0.29 g, 84%). Brownish solid. M.p. 90–92° (benzene). UV (MeOH): 219, 229, 290, 320, 325, 340. IR ($CHCl_3$): 1674.4 (N–C=O), 1649 (C=O), 1614.6, 1585.7, 1552.9, 1460, 1430, 1350, 1280, 1242, 1211. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.26 (*d*, *J* = 7.08, H–C(6)); 8.01 (*s*, H–C(4)); 7.69 (*t*, *J* = 7.88, H–C(8)); 7.48–7.41 (*m*, 3 arom. H); 7.39–7.26 (*m*, 4 arom. H); 6.12–5.90 (*m*, H–C(2′)); 5.53 (*s*, PhCH_2); 5.23 (*d*, *J* = 6.80, 1 H–C(3′)); 5.18 (*d*, *J* = 10.11, 1 H–C(3′)); 3.36 (*d*, *J* = 6.68, 2 H–C(1′)). EI-MS: 343 (50, M^+), 302 (12), 285 (13). Anal. calc. for $C_{22}H_{17}NO_3$: C 76.95, H 4.99, N 4.08; found: C 77.78, H 4.84, N 4.26.

*1-Benzyl-3-[(2*E*)-but-2-enyl]-2*H*-[1]benzopyrano[2,3-*b*]pyridine-2,5(1*H*)-dione* (**17b**). As described for **17a**, with **16b** (0.4 g, 1.0 mmol) and xylene (10 ml): **17b** (0.285 g, 81%). Dark-brown semisolid. UV (MeOH): 235.4, 255, 280, 325, 348. IR ($CHCl_3$): 1665 (N–C=O), 1647.4 (C=O), 1612.7, 1585, 1552.9, 1510, 1495, 1464.1, 1394.7, 1370, 1348, 1304, 1220, 1211. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.27 (*d*, *J* = 7.64, H–C(6)); 7.96 (*s*, H–C(4)); 7.70 (distorted *t*, *J* = 8.46, H–C(8)); 7.46–7.13 (*m*, 7 arom. H); 5.75–5.54 (*m*, H–C(2′), H–C(3′)); 5.50 (*s*, PhCH_2); 3.26 (br., 2 H–C(1′)); 1.72 (br., Me(4′)). EI-MS: 357 (6), 283 (15), 265 (4), 266 (18), 238 (8), 286 (10). Anal. calc. for $C_{23}H_{19}NO_3$: C 77.29, H 5.36, N 3.92; found: C 77.15, H 5.51, N 3.75.

*1-Benzyl-3-[(2*E*)-3-phenylprop-2-enyl]-2*H*-[1]benzopyrano[2,3-*b*]pyridine-2,5(1*H*)-dione* (**17c**). As described for **17a**, with **16c** (0.47 g, 1.0 mmol) and xylene (10 ml). Prep. TLC with 8 plates: **17c** (0.35 g, 83%). Light brown solid. M.p. 70–72° (hexane/$CHCl_3$ 1:5). UV (MeOH): 235, 289, 320, 327, 345. IR ($CHCl_3$): 1666 (N–C=O), 1650 (C=O), 1583.7, 1551, 1464.1, 1450, 1400, 1350, 1296, 1211. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.25 (*dd*, *J* = 1.19, 8.12, H–C(6)); 8.04 (br. *s*, H–C(4)); 7.68 (*t*, *J* = 7.68, H–C(8)); 7.49–7.17 (*m*, 12 arom. H); 6.54 (*d*, *J* = 15.87, H–C(3′)); 6.40 (*dt*, *J* = 15.87, 6.59, H–C(2′)); 5.52 (*s*, PhCH_2); 3.50 (*d*, *J* = 6.59, 2 H–C(1′)). ^{13}C-NMR ($CDCl_3$, 50 MHz): 173.36 (C(5)); 161.48 (C(2)); 154.81 (C(10a)); 153.39 (C(9a)); 137.15 (quat. arom. C); 135.69 (quat. arom. C); 133.76 (CH); 132.60 (CH); 131.74 (CH); 128.77 (CH); 128.59 (CH); 128.34 (CH); 128.27 (C(3)); 128.06 (CH); 127.89 (CH); 127.13 (CH); 126.78 (CH); 126.20 (CH); 125.94 (CH); 125.69 (C(5a)); 117.04 (C(9)); 102.17 (C(4a)); 45.21 (CH_2N); 33.86 (C(1′)). EI-MS: 420 (0.6, $[M+1]^+$), 419 (4, M^+), 342 (1), 329 (10), 302 (5), 286 (15), 195 (3). Anal. calc. for $C_{28}H_{21}NO_3$: C 80.17, H 5.05, N 3.34; found: C 80.38, H 4.84, N 3.55.

*2-[Benzyl(phenyl)amino]-4-oxo-4*H*-1-benzopyran-3-carboxaldehyde* (**21**). As described for **8a**, with **6** (1.0 g, 3.8 mmol), dry acetone, benzyl bromide (1.0 g, 6.0 mmol), and anh. K_2CO_3 (2.0 g): **21** (1.30 g, 97%). Cream-colored solid. M.p. 157° (benzene). UV (MeOH): 331, 292, 247.5. IR ($CHCl_3$): 1672 (H–C=O), 1648 (C=O), 1602, 1576, 1478, 1462, 1443, 1413, 1391, 1318, 1306, 1234, 1201. ^{1}H-NMR ($CDCl_3$, 200 MHz): 10.20 (*s*, H–C=O); 8.41 (*dd*, *J* = 7.78, 1.70, H–C(5)); 7.78 (*dt*, *J* = 7.68, H–C(7)); 7.64–7.39 (*m*, 12 arom. H); 5.43 (*s*, PhCH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): 186.09 (CHO); 177.90 (C(4)); 163.06 (CH); 153.38 (quat. C); 144.26 (quat. C); 135.96 (quat. C); 133.34 (CH); 129.27 (CH); 128.81 (CH); 127.87 (quat. C); 127.23 (CH); 126.72 (CH); 126.31 (CH); 125.32 (CH); 124.54 (CH); 123.54 (quat. C); 116.51 (CH); 103.24 (quat. C); 57.59 (Ph*C*H_2). EI-MS: 355 (20, M^+), 354 (40), 283 (97), 284 (98), 171 (100).

*Ethyl (2*E*)-3-[2-[Benzyl(phenyl)amino]-4-oxo-4*H*-1-benzopyran-3-yl]prop-2-enoate* (**22**). As described for **16a**, with **21** (0.35 g, 1.0 mmol), dry benzene (100 ml), and ethyl (triphenylphosphoranylidene)acetate (0.35 g, 1.0 mmol) (7 h). FC (silica gel (200–400 mesh, 20 g); hexane/Et_2O 9:1) gave **22** (0.40 g, 96%). Cream-colored solid. M.p. 112° (benzene). UV (MeOH): 331.5, 252.5. IR ($CHCl_3$): 1697 (CO_2Et), 1635 (C=O), 1597, 1582, 1498, 1479, 1457, 1442, 1412, 1348, 1276, 1264, 1230. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.13 (br. *d*, *J* = 7.37, H–C(5)); 7.52 (*dt*, *J* = 7.74, H–C(7)); 7.35–7.16 (*m*, 8 arom. and olef. H); 7.14–6.99 (*m*, 6 arom. and olef. H); 5.16 (*s*, PhCH_2); 4.03 (*q*, *J* = 7.16, MeCH_2O); 1.18 (*t*, *J* = 7.16, *Me*CH_2O). EI-MS: 426 (8, $[M+1]^+$), 425 (29, M^+), 380 (24), 352 (50), 171 (21), 91 (100). Anal. calc. for $C_{27}H_{23}NO_4$: C 76.22, H 5.45, N 3.29; found: C 76.51, H 5.65, N 3.40.

*Ethyl (2*E*)-3-[4-Oxo-2-(phenylamino)-4*H*-1-benzopyran-3-yl)prop-2-enoate* (**23a**). As described for **16a**, with **6** (0.53 g, 2.0 mmol), CH_2Cl_2 (50 ml) instead of benzene, and ethyl (triphenylphosphoranylidene)acetate (0.70 g, 2.0 mmol) at r.t. for 12 h (TLC monitoring). FC (silica gel (200–400 mesh, 20 g); hexane/Et_2O 9:1)

gave **23a** (0.65 g, 98%). Colorless crystalline solid. M.p. 118–119° ($CHCl_3$/hexane 3:1). UV (MeOH): 322.9, 226.4, 209. IR ($CHCl_3$): 2950, 1700 (CO_2Et), 1644 (C=O), 1607, 1562, 1553, 1482, 1458. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.19 (*dd*, *J* = 7.80, 1.46, H–C(5)); 8.03 (br. *s*, NH); 7.73 (*d*, *J* = 15.51, C*H*=CHCOOEt); 7.51 (split *t*, *J* = 7.47, 1.58, H–C(7)); 7.43–7.21 (*m*, 8 arom. H, CH=C*H*COOEt); 4.15 (*q*, *J* = 7.09, MeCH_2O); 1.26 (*t*, *J* = 7.09, *Me*CH_2O). EI-MS: 335 (2.5, M^+), 262 (80), 261 (30), 170 (15), 144 (5).

*1-Phenyl-2*H*-[1]benzopyrano[2,3-*b*]pyridine-2,5(1*H*)-dione* (**24a**). As described for **16a**, with **6** (0.53 g, 2.0 mmol), dry benzene (100 ml), and ethyl (triphenylphosphoranylidene)acetate (0.7 g, 2.0 mmol) (12 h, TLC monitoring). After concentration to *ca.* 10 ml, the soln. was chilled for 1 h; cream-colored crystals separated out and were recrystallized from benzene: **24a** (0.56 g, 96%). Off-white solid. M.p. 284–285°. UV (MeOH): 336.5, 321.5, 292, 247.5. IR ($CHCl_3$): 1678, 1663, 1647, 1630, 1600, 1560, 1517, 1481, 1458, 1404, 1353, 1281, 1224. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.27 (overlapping *d*s, *J* = 9.19, H–C(4), H–C(6)); 7.60–7.27 (*m*, 7 arom. H); 7.11 (*d*, *J* = 8.22, H–C(9)); 6.60 (*d*, *J* = 9.61, H–C(3)). ^{13}C-NMR ($CDCl_3$, 50 MHz): 173.60 (C(5)); 161.66 (C(2)); 155.99 (C(10a)); 153.43 (C(9a)); 135.96 (CH); 134.03 (CH); 133.56 (C_{ipso}-N); 129.65 (CH); 129.54 (CH); 128.14 (CH); 126.33 (CH); 125.65 (CH); 121.92 (C(5a)); 117.52 (C(9)), 116.88 (CH), 102.18 (C(4a)). EI-MS: 290 (10, $[M+1]^+$), 289 (49, M^+), 288 (29), 171 (100). Anal. calc. for $C_{18}H_{11}NO_3$: C 74.73, H 3.83, N 4.84; found: C 74.59, H 3.94, N 4.98.

*1-Benzyl-2*H*-[1]benzopyrano[2,3-*b*]pyridine-2,5(1*H*)-dione* (**24b**). As described for **16a**, with **14** (0.42 g, 1.5 mmol), ethyl (triphenylphosphoranylidene)acetate (0.52 g, 1.5 mmol), and dry benzene (100 ml) (16 h). After concentration to 1/10th of the original volume, the soln. was chilled for 1 h; colorless crystals separated out and were recrystallized from benzene: **24b** (0.45 g, 98%). M.p. 186–187°. UV (MeOH): 336, 319.5, 290, 245. IR ($CHCl_3$): 1684 (N–C=O), 1662 (C=O), 1634, 1596, 1545, 1472, 1373, 1297, 1260, 1238, 1209, 1130. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.25 (br. *d*, *J* = 7.75, H–C(6)); 8.17 (*d*, *J* = 9.54, H–C(4)); 7.69 (*t*, *J* = 6.79, H–C(8)); 7.48–7.45 (*m*, 4 arom. H); 7.36–7.16 (*m*, 3 arom. H); 6.56 (*d*, *J* = 9.55, H–C(3)); 5.50 (*s*, PhCH_2). ^{13}C-NMR ($CDCl_3$, 50 MHz): 173.07 (C(5)); 161.46 (C(2)); 156.07 (C(10a)); 153.45 (C(9a)); 135.60 (CH); 135.46 (C_{ipso}-CH_2N); 133.96 (CH); 128.78 (CH); 126.22 (CH); 128.10 (CH); 126.74 (CH); 125.66 (CH); 122.16 (C(5a)); 117.07 (C(9)); 116.37 (CH); 102.46 (C(4a)); 44.78 (CH_2N). EI-MS: 304 (8, $[M+1]^+$), 303 (24, M^+), 169 (56), 111 (27), 91 (100). Anal. calc. for $C_{19}H_{13}NO_3$: C 75.24, H 4.32, N 4.62; found: C 75.48, H 4.43, N 4.48.

Pyridinone **24a** was also obtained in near quant. yield by refluxing **23a** in benzene for 10 h (TLC, ^{1}H-NMR of crude product).

*Ethyl (2*E*)-3-[2-[Methyl(phenyl)amino]-4-oxo-4*H*-1-benzopyran-3-yl]prop-2-enoate* (**20a**). As described for **16a**, with **13** (0.56 g, 2.0 mmol), dry benzene (100 ml), and ethyl (triphenylphosphoranylidene)acetate (0.7 g, 2.0 mmol) (7 h, TLC monitoring). FC (silica gel (200–400 mesh, 20 g); hexane/Et_2O 9:1) gave **20a** (0.67 g, 96%). Cream-colored solid. M.p. 99–100° ($CHCl_3$/hexane 1:2). UV (MeOH): 335, 248, 292.5. IR ($CHCl_3$): 1700 (CO_2Et), 1639.7 (C=O), 1616.5, 1527.8, 1493.1, 1398.6, 1360, 1292.5. ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.21 (*dd*, *J* = 6.34, 1.65, H–C(5)); 7.61 (*dt*, *J* = 7.63, 1.48, H–C(7)); 7.42–7.33 (*m*, 5 arom. and olef. H); 7.17–7.09 (*m*, 4 arom. and olef. H); 4.09 (*q*, *J* = 7.14, MeCH_2O); 3.61 (*s*, MeN); 1.21 (*t*, *J* = 7.14, *Me*CH_2O). EI-MS: 349 (2, M^+), 171 (29), 71 (49), 58 (100).

*2-[Benzyl(methyl)amino]-4-oxo-4*H*-1-benzopyran-3-carboxaldehyde* (**13b**). As described for **8a**, with **14** (0.84 g, 3.0 mmol), dry acetone (100 ml), MeI (2 ml, excess), and anh. K_2CO_3 (2.0 g): **13b** (0.84 g, 95%). Light brown semisolid. UV (MeOH): 296, 281.6, 246. IR ($CHCl_3$): 1672.5 (H–C=O), 1650 (C=O), 1556.7, 1483.4, 1466.1, 1842.6, 1327.2, 1228.1. ^{1}H-NMR ($CDCl_3$, 200 MHz): 10.40 (*s*, H–C=O); 8.13 (*dd*, *J* = 7.73, 1.26, H–C(5)); 7.54 (*dt*, *J* = 7.40, 1.48, H–C(7)); 7.36–7.17 (*m*, 7 arom. H); 4.77 (*s*, PhCH_2); 3.07 (*s*, MeN). EI-MS: 293 (11, M^+), 264 (41), 174 (98), 171 (88), 91 (90), 71 (100).

*Ethyl (2*E*)-3-[2-[Benzyl(methyl)amino]-4-oxo-4*H*-1-benzopyran-3-yl]prop-2-enoate* (**20b**). As described for **16a**, with **13b** (0.59 g, 2.0 mmol), dry benzene (100 ml), and ethyl (triphenylphosphoranylidene)acetate (0.7 g, 2.0 mmol) (15 h, TLC monitoring). FC (silica gel (200–400 mesh, 20 g); hexane/Et_2O 9:1) gave **20b** (0.70 g, 96%). Light brown semisolid. UV (MeOH): 332.6, 291, 244.4. IR ($CHCl_3$): 1699.5 (CO_2Et), 1637.8 (C=O), 1616, 1601.1, 1545.2, 1435.2, 1406.2, 1288.6, 1157.4, 1035.9. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.24 (*dd*, *J* = 7.07, 1.67, H–C(5)); 7.61 (*dt*, *J* = 6.99, 1.19, H–C(7)); 7.59 (*d*, *J* = 13.32, olef. H); 7.46–7.28 (*m*, 8 arom. H and olef. H); 4.78 (*s*, PhCH_2); 4.25 (*q*, *J* = 7.08, MeCH_2O); 3.17 (*s*, MeN); 1.34 (*t*, *J* = 7.08, *Me*CH_2O). EI-MS: 363 (1.5, M^+), 318 (2.0), 290 (1.8), 199 (12), 184 (12), 144 (5). Anal. calc. for $C_{22}H_{21}NO_4$: C 72.71, H 5.82, N 3.85; found: C 72.59, H 5.97, N 3.67.

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