Benzotriazole-Mediated 4-Position Derivatization of 2,6-Diarylpyrylium Cations by Electrophiles

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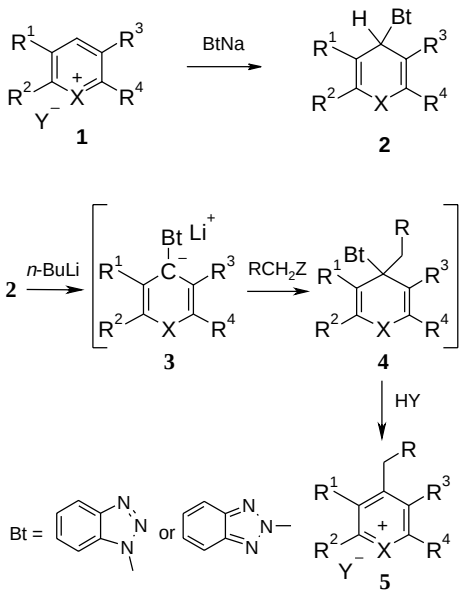
Abstract. 2,6-Diaryl-4*H*-(benzotriazolyl)pyrans (**7a**–**c**) on treatment with *n*-butyllithium undergo smooth lithiation at the position α to the benzotriazolyl moiety. In contrast to fused and bridged pyranyl derivatives, these pyranyl anions react with electrophiles by two routes: i) the expected electrophilic substitution resulting in various 4-alkyl- and 4-(ω-alkylfunctionalized)-pyrylium salts (**12**–**19**) or ii) pyrylium ring rearrangement of 2,6-diarylpyrylium anions (**8a**–**c**), leading to 1,2-diaryl-2,4-cyclopentadien-1-ols (**10a**–**c**).

Recently, we introduced new methodology for the easy indirect electrophilic derivatization of π-electron-deficient heteronium salts [1], utilizing the properties of benzotriazole as an efficient synthetic auxiliary [2]. Benzo[*b*]pyrylium, xanthylium, thioxanthylium, acridinium and 2',3-bridged pyrylium salts in this two pot, three step procedure yield the corresponding heterocycles, substituted at position 4 to the heteroatom (Scheme 1).



Scheme 1

The success of this strategy was demonstrated [1] by the preparation of a series of long chain (up to 22 carbons) alkyl-, ω-arylalkyl-, ω-halogenalkyl-,(α,ω-alkylidene)bisheteronium salts, which are of interest for synthetic, physico-organic and pharmaceutical applications [3]. Significantly, only a few short-chain 4-alkyl derivatives of simple, non-bridged pyrylium salts are known; they were synthesized in low yield by condensations of either acetaldehyde or alkyl acetates with aryl methylene ketones [4, p. 884]. Isolated examples of 4-(arylmethyl)- and 4-(hetarylmethyl)-2,6-diarylpyrylium salts were obtained by reaction of pyranylphosphonate carbanions with corresponding aldehydes [5]. 4-Alkylpyrylium salts with a long-chain alkyl group were not previously described. During our expansion of the new methodology to the synthesis of 4-alkyl-2,6-diarylpyrylium cations (**6**) we found that in some cases the intermediate 2,6-diaryl-4-benzotriazolylpyran-4-yl anions undergo rearrangement by ring contraction, and we now report on this alternative reaction pathway.

Results and Discussion

Following our normal procedure we prepared 2,6-diaryl-4-benzotriazolylpyran analogues of compound **2** and investigated the behavior of 2,6-diaryl-4-benzotriazolylpyranyl anions in reaction with electrophiles. Easily accessible 2,6-diarylpyrylium tetrafluoroborates (**6a**–**c**) [6] underwent facile regiospecific addition of the ben-

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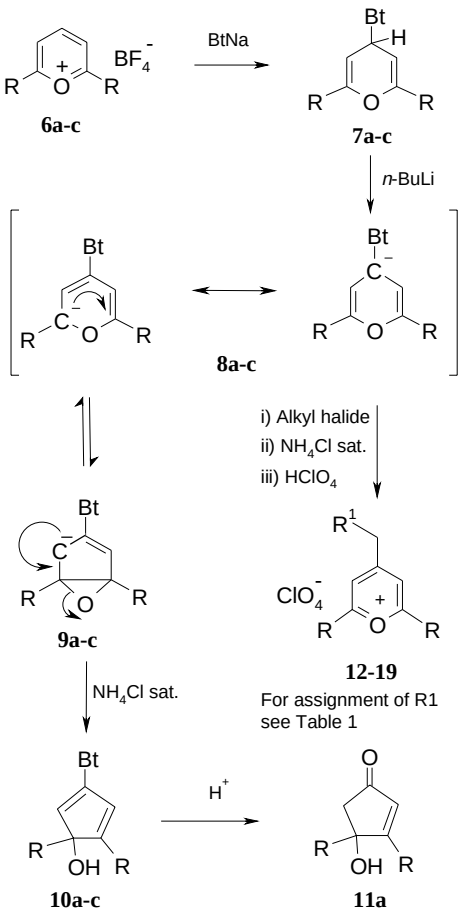
zotriazolyl anion in position 4 at room temperature in THF (Scheme 2) to give the benzotriazole derivatives **7a**–**c**. The mixtures of Bt-1 to Bt-2 isomers (ratio 9 to 1 by ^{1}H NMR) were used without further purification, but for analytical purposes the Bt-1 isomers were isolated and characterized. Compounds **7a**–**c** are colorless, crystalline, and stable to neutral and basic conditions, but easily eliminate benzotriazole to regenerate the highly fluorescent cations **6** upon treatment with weak acids.

Conversions of **7a**–**c** to the carbanion **8a**–**c** proceed at low temperature (–78 °C) in THF with *n*-butyllithium. In contrast to earlier investigations [1] the reactivity of anions **8a**–**c** is more complex than that of other fused or bridged anions of type **3**, and the products of their reaction with electrophiles depend dramatically on the alkyl halide type. Alkyl and arylalkyl halides, or alkylene dihalides with four or less carbon atoms in the aliphatic chain give the normal products of substitution **12–19** in moderate to high yields (Scheme 2, Table 1). However, aliphatic halides with a chain longer than 6 carbons unexpectedly gave the new products **10a**–**c** instead of alkyl substituted salts of type **5**. Quenching the reaction mixtures with ammonium chloride solution gave only **10a**–**c**, according to the NMR spectra of crude reaction mixture, which were isolated in yields of 57% to 66%. A mixture of both substitution and rearrangement products was obtained for the reaction of **7a** with 1-bromohexane. Lithiation of benzotriazole adducts **7a**–**c** in absence of an electrophile followed by quenching the reaction mixtures with ammonium chloride solution leads to the same rearrangement products **10a**–**c** in yields of 54% to 66% (first three line in Table 1). The products **10a**–**c** are isomeric with the starting benzotriazole derivatives **7a**–**c** according to the CHN analysis, but the NMR spectra no longer show a plane of symmetry. Treatment of **10a** with perchloric acid, or reflux in ethanol in the presence of *p*-toluenesulphonic acid as catalyst affords 4-hydroxy-3,4-diphenyl-2-cyclopenten-1-one (**11a**) in high yield (Scheme 2).



a: R = Ph, **b**: R = *p*-C_6H_4OMe, **c**: R = *p*-C_6H_4F

Scheme 2

The structure of compound **11a** was confirmed by X-ray analysis and is shown in Figure 1 along with selected bond lengths and angles. In this structure the conjugated phenyl ring is approximately coplanar with the enone system (angle between planes = 18.1(1)°), whereas the C4 phenyl ring is approximately orthogonal to the cyclopentenone ring (angle between planes = 103.4(1)°). The molecular packing is controlled by hydrogen bonds between the OH hydrogen and the carbonyl oxygen of an adjacent molecule. The NMR spectra and melting point are in agreement with literature data for this compound [7].

The tendency to form products of type **10** increases with the electron-withdrawing nature of the *para* sub-

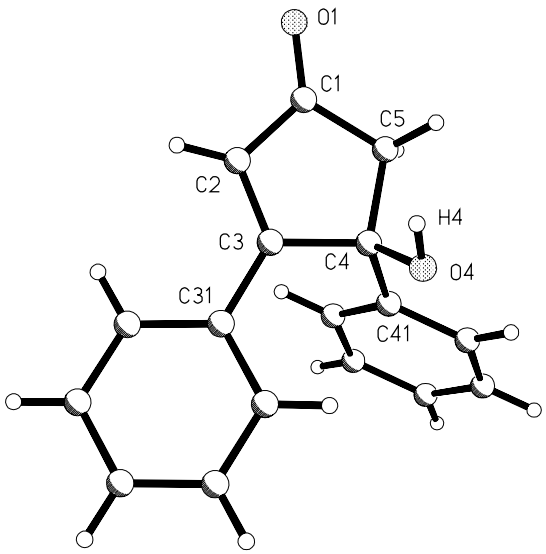
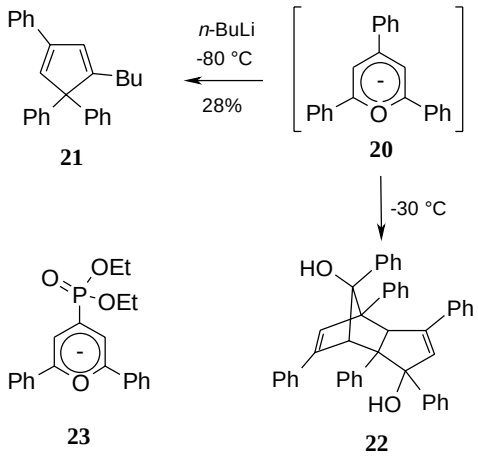


Fig. 1 Perspective view of the X-ray crystal structure of **11a**. Selected bond lengths (Å) and angles (°): C1–O1 1.225(2); C1–C2 1.455(2); C2–C3 1.341(2); C3–C4 1.542(2); C4–C5 1.544(2); C1–C5 1.504(2); C3–C31 1.469(2); C4–C41 1.521(2); C4–O4 1.428(2); C2–C1–C5 108.1(1); C1–C2–C3 111.4(1); C2–C3–C4 111.1(1); C3–C4–C5 103.2(1); C1–C5–C4 105.8(1).

stituent in the aromatic ring at positions 2 and 6 of pyran **7**. 2,6-(4'-Fluorophenyl)-4-benzotriazolylpyran (**7c**) following lithiation with *n*-butyllithium and treatment with an electrophile forms exclusively **10c** even if a very active electrophile such as benzyl bromide was used. Furthermore, we found that the anionic species **8b**,**c** on lithiation with *n*-butyllithium in the presence of HMPA did not react with electrophiles but rearrange to **10b**,**c**. However, under these conditions the reactivity of anion **8a** is greatly enhanced by the addition of two equivalents of HMPA, so that reaction with weakly electrophilic bromododecane gave the corresponding 2,6-diphenyl-4-dodecylpyrylium perchlorate (**18a**) in 44% yield.

The formation of cyclopentadienols **10a**–**c** originates from a rearrangement of anion **8a**–**c** through bicyclic intermediates **9a**–**c** followed by intramolecular oxirane ring opening (Scheme 2). We conclude that most active electrophiles attack anion **8** at the 4-position to form substitution products (**12**–**19**), but, in the presence of less reactive electrophiles, anion **8** transforms to **9** and subsequently to **10** (Scheme 2). The mechanism proposed is consistent with the fluoro-substituted pyran (**7c**) rearranging in preference to treating with an electrophile. Electron withdrawing substituents stabilize both the n_C and π^*_{CC} MOs involved in the formation of new (C-2)–(C-6) bond. In the same time the energy gap between n_C and σ^*_{C-Hal} MOs becomes larger and cause the inconvenience for substitution process.

A similar rearrangement has been described for the 2,4,6-triphenyl-substituted pyranyl anion **20** [6a] (Scheme 3). The action in of *n*-butyllithium large excess on 2,4,6-triarylpyran in THF at between –80 and –120 °C gave less than 3% of the pyranyl anion **20** [8] with 28% rearranged to product **21**. An intermediate of type **10** was postulated, and at a higher temperature (–30 °C) the cyclopentadiene dimer **22** was isolated in unspecified yield (Scheme 3). The present rearrangement differs by the absence of migration of phenyl groups and no introduction of alkyl residue from *n*-butyllithium into compound **21**.



Scheme 3

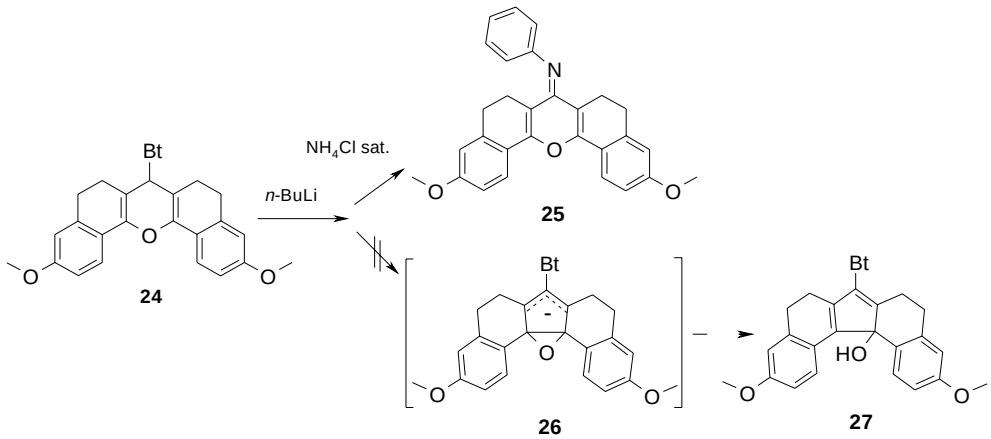
Anions of type **8** also behave differently from pyranyl anion (**23**) stabilized by a diethyl phosphonate moiety. Anion **23** does not rearrange but condenses with a variety of aryl ketones and aldehydes to form exomethylene substituted pyrans [5, 9].

In contrast to the pyran derivatives **7**, the 2',3-bridged pyran **24** on lithiation, in the absence of electrophile, gave the imine **25** instead of the expected **27** (Scheme 4).

Table 1 Synthesis of 4-substituted 2,6-diaryl-pyrylium perchlorates **12**–**19** or rearrangement products **10** by indirect electrophilic substitution

Pyran educt		Electrophile	Substitution product			Rearrangement product	
No	R		No	R^1	Yield (%)	No	Yield (%)
7a	Ph	– [a]	–	–	–	**10a**	66
7b	*p*-C_6H_4OMe	– [a]	–	–	–	**10b**	54
7c	*p*-C_6H_4F	– [a]	–	–	–	**10c**	66
7a	Ph	CH_3I	**12a**	H	28 [b]		– [e]
7a	Ph	$PhCH_2Br$	**13a**	Ph	81 [b]		– [e]
7c	*p*-C_6H_4F	$PhCH_2Br$	**13c**	Ph	0	**10c**	62
7a	Ph	$Cl(CH_2)_4Br$	**14a**	$(CH_2)_3Cl$	60		– [e]
7a	Ph	$I(CH_2)_4I$	**15a**	$(CH_2)_3I$	40		– [e]
7a	Ph	*n*-$C_4H_{10}I$	**16a**	*n*-C_3H_8	32		– [e]
7a	Ph	*n*-$C_6H_{13}Br$	**17a**	*n*-C_5H_{11}	57	**10a**	43
7c	*p*-C_6H_4F	*n*-$C_6H_{13}Br$	**17c**	*n*-C_5H_{11}	0	**10c**	60
7a	Ph	*n*-$C_{12}H_{25}I$	**18a**	*n*-$C_{11}H_{23}$	0	**10a**	57
7a	Ph	*n*-$C_{12}H_{25}I$	**18a**	*n*-$C_{11}H_{23}$	44 [c]		– [e]
7b	*p*-C_6H_4OMe	*n*-$C_{12}H_{25}I$	**18b**	*n*-$C_{11}H_{23}$	0	**10a**	60
7c	*p*-C_6H_4F	*n*-$C_{12}H_{25}I$	**18c**	*n*-$C_{11}H_{23}$	0	**10c**	66
7c	*p*-C_6H_4F	*n*-$C_{12}H_{25}I$	**18c**	*n*-$C_{11}H_{23}$	0	**10c**	22 [c]
7a	Ph	$I(CH_2)_4I$	**19a**	$(CH_2)_3R^2$ [d]	56		– [e]

[a] No electrophile was added. [b] Literature yield for **12a** 19% [12], 24–36% [4, p. 884], **13a** – 16% [4, p. 885], 60% [5]. [c] In the presence of HMPA (2 equiv). [d] R^2 = 2,6-diphenylpyrylium perchlorate. [e] No attempt to isolate the rearrangement product was undertaken.



Scheme 4

In this case, steric compression in the polycyclic intermediate **26** disfavors rearrangement to **27**. Instead, the carbanion derived from **24** eliminates nitrogen as known for numerous examples of benzotriazole stabilized anions [2a].

Conclucion

We have described a novel rearrangement together with further examples of simple indirect electrophilic substitutions of alkyl groups into position 4 of 2,6-diarylpyrylium cation **6**. These include the synthesis of hitherto inaccessible pyrylium derivatives with new, tailored properties of potential interest in polymer chemistry, solid phase methods, *Langmuir-Blodgett* methodology and for other applications in analytical or sensor chemistry [10].

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Experimental

Melting points were determined on a Koefler hot stage apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz respectively on a Varian XL 300 spectrometer in $CDCl_3$, $CDCl_3$/DMSO–d_6 or $CDCl_3$/CF_3CO_2D referenced to Me_4Si for the proton spectra and $CDCl_3$ for the carbon spectra. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. Tetrahydrofuran (THF) was distilled under nitrogen from sodium–benzophenone immediately before use. All reactions with water-sensitive compounds were carried out in dry nitrogen atmospheres. 2,6-Diarylpyrylium tetrafluoroborates **6a**–**c** were prepared according to a literature procedure [6], 3,11-dimethoxy-5*H*,6*H*,8*H*,9*H*–dibenzo[*c*,*h*]xanthenium perchlorate for synthesis of **24** was prepared according to a literature procedure [11].

Preparation of the 4*H*-(1H-Benzotriazol-1-yl)-2,6-diarylpyrans (7a–c, 24) (General Procedure)

To a solution of benzotriazole (1.19 g, 10 mmol) dissolved in dry THF (50 mL) was added NaH (0.40 g of 60% in mineral oil, 10 mmol). The reaction mixture was stirred at rt for 20 min before adding the 2,6-diarylpyrylium tetrafluoroborate (**6**) (10 mmol) portionwise. The reaction mixture was left stirring for 20 min before the precipitating inorganic by–product was filtered off. Evaporation of the solvent yields almost quantitative amount of the crude product containing Bt-1 and Bt-2 isomers in ratio 9:1. The crude mixture was used for further transformations without purification. Analytically pure samples of Bt-1 isomer were obtained by crystallization.

4H-(1H-Benzotriazol-1-yl)-2,6-diphenylpyran (**7a**)

Yield 82%, *m.p.* 212–214 °C (from ethyl acetate/hexane). – ^{1}H NMR ($CDCl_3$): δ/ppm = 5.77 (d, J = 4.3 Hz, 2H), 6.73 (t, J = 4.3 Hz, 1H), 7.25–7.33 (m, 2H), 7.34–7.50 (m, 7H), 7.68–7.82 (m, 5H), 8.00–8.10 (m, 1H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 52.7, 94.9, 110.6, 120.0, 123.8, 125.1, 127.1, 128.6, 129.7, 132.8, 147.0, 152.3.

$C_{23}H_{17}N_3O$	calcd.:	C 78.61	H 4.88	N 11.96
(351.41)	found:	C 78.26	H 4.87	N 11.94.

4H-(1H-Benzotriazol-1-yl)-2,6-bis(4-methoxyphenyl) pyran (**7b**)

Yield 70%, *m.p.* 134–136 °C. –^{1}H NMR ($CDCl_3$): δ/ppm = 3.85 (s, 6H), 5.66 (d, J = 4.2 Hz, 2H), 6.70 (t, J = 4.2 Hz, 1H), 6.95 (d, J = 8.7 Hz, 4H), 7.28–7.42 (m, 2H), 7.42–7.55 (m, 1H), 7.68 (d, J = 8.7 Hz, 4H), 8.06 (m, 1H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 53.0, 55.3, 93.2, 110.8, 114.0, 119.9, 123.8, 125.4, 126.5, 127.0, 131.8, 146.9, 152.2, 160.7.

$C_{25}H_{21}N_3O_3$	calcd.:	C 72.97	H 5.15	N 10.21
(411.46)	found:	C 72.83	H 5.24	N 10.04.

4H-(1H-Benzotriazol-1-yl)-2,6-bis(4-fluorophenyl)pyran (**7c**)

Yield 95%, *m.p.* 120–124 °C (from ether/ethyl acetate). – ^{1}H NMR ($CDCl_3$): δ/ppm = 5.74 (d, J = 4.2 Hz, 2H), 6.72 (t, J = 4.2 Hz, 1H), 7.05–7.20 (m, 4H), 7.30–7.40 (m, 2H), 7.40–7.48 (m, 1H), 7.65–7.80 (m, 4H), 8.05–8.13 (m, 1H). –

^{13}C NMR ($CDCl_3$): δ/ppm = 52.5, 94.8, 110.3, 115.8 (d, J = 21.7 Hz), 120.2, 123.9, 127.1 (d, J = 8.7 Hz), 127.2, 128.9 (d, J = 3.2 Hz), 131.8, 147.0, 151.5, 163.6 (d, J = 250.6 Hz).
$C_{23}H_{15}F_2N_3O$ calcd.: C 71.31 H 3.91 N 10.85
(387.39) found: C 71.08 H 3.73 N 10.87.

1-(3,11-Dimethoxy-5,7,8,9-tetrahydro-6H-dibenzo [c,h] xanthen-7-yl)-1H-1,2,3-benzotriazole (**24**)

Yield 65%, *m.p.* 164–166 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.76–2.00 (m, 2H), 2.31–2.48 (m, 2H), 2.50–2.67 (m, 2H), 2.72–2.87 (m, 2H), 3.83 (s, 6H), 6.38 (s, 1H), 6.69 (s, 2H), 6.87 (d, J = 8.7 Hz, 2H), 7.27 (t, J = 2.1 Hz, 2H), 7.42 (d, J = 6.9 Hz, 1H), 7.80 (d, J = 8.7 Hz, 2H), 8.05 (d, J = 6.9 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ/ppm = –23.4, 27.8, 55.3, 59.9, 101.8, 110.5, 111.5, 113.5, 119.9, 122.0, 123.3, 123.9, 127.1, 131.5, 138.3, 145.3, 146.9, 160.0.
$C_{29}H_{25}N_3O_3$ calcd.: C 75.14 H 5.45 N 9.07
(463.54) found: C 74.99 H 5.48 N 9.07.

Preparation of the Salts 12–19 (General Procedure)

To a solution of the 2,6-diphenyl-4*H*-(1*H*-benzotriazol-1-yl)pyran (**7**) (1.25 mmol) in dry THF (30 mL), at –78 °C, was added *n*-BuLi (0.78 mL, 1.25 mmol, 1.6M in hexane). The solution was stirred at –78 °C for 0.5 h, before adding the electrophile (1.25 mmol) as a solution in dry THF (10 mL). The reaction mixture was stirred overnight and allowed to warm up to rt, before being quenched with saturated aqueous NH_4Cl-solution (40 mL), and extracted with diethyl ether (2 × 30 mL). The combined organic extract was washed with brine and water and dried with $MgSO_4$. The solvent was removed *in vacuo* and to the resulting oil, acetic acid (20 mL) and $HClO_4$ (0.4 mL, 70%) added. The precipitate separating after addition of water (50 mL) is filtered off and recrystallized from glacial acetic acid/nitromethane (10/1, v/v).

4-Methyl-2,6-diphenylpyrylium Perchlorate (**12a**)

Yield 28%, *m.p.* 288 °C (lit. [12] 268 °C). – ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ/ppm = 2.89 (s, 3H), 7.67–7.74 (m, 4H), 7.77–7.84 (m, 2H), 8.17–8.24 (m, 6H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ/ppm = 24.1, 120.0, 127.9, 128.4, 130.5, 136.1, 170.9, 180.0.
$C_{18}H_{15}ClO$ calcd.: C 62.35 H 4.36
(346.77) found: C 62.47 H 4.27.

4-Benzyl-2,6-diphenylpyrylium Perchlorate (**13a**)

Yield 81%, *m.p.* 218 °C (lit. [5] 220 °C). – ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ/ppm = 4.45 (s, 2H), 7.31–7.42 (m, 5H), 7.62–7.69 (m, 4H), 7.72–7.78 (m, 2H), 8.11–8.16 (m, 6H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ/ppm = 43.2, 118.7, 127.9, 128.4, 128.5, 129.7, 130.3, 134.1, 136.0, 171.2, 175.6.
$C_{24}H_{19}ClO_5$ calcd.: C 68.17 H 4.53
(422.86): found: C 67.96 H 4.44.

4-(4-Chlorobutyl)-2,6-diphenylpyrylium Perchlorate (**14a**)

Yield 60%, *m.p.* 174–175.5 °C. – ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ/ppm = 1.90–2.20 (m, 4H), 3.18–3.30 (m, 2H), 3.60–3.72 (m, 2H), 7.70–7.90 (m, 6H), 8.35 (d, J = 7.5 Hz, 4H), 8.63 (s, 2H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D) : δ/ppm = 25.7, 31.1, 36.0, 43.7, 118.6, 127.5, 127.9, 129.6, 135.0, 169.9, 176.4.
$C_{21}H_{20}Cl_2O_5$ calcd.: C 59.59 H 4.76
(423.29) found: C 59.52 H 4.70.

4-(4-Iodobutyl)-2,6-diphenylpyrylium Perchlorate (**15a**)

Yield 40%, *m.p.* 177–180 °C. – ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ/ppm = 1.90–2.08 (m, 4H), 3.10–3.20 (m, 2H), 3.22–3.30 (m, 2H), 7.64–7.75 (m, 4H), 7.79 (d, J = 7.5Hz, 2H), 8.22 (d, J = 7.8 Hz, 4H), 8.26 (s, 2H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ/ppm = 5.5, 29.6, 32.4, 36.5, 118.7, 128.0, 128.5, 130.4, 136.1, 171.1, 176.9. – HRMS: calcd. for $C_{21}H_{20}IO$: 415.0559 (M–ClO_4); found: 415.0558.

4-n-Butyl-2,6-diphenylpyrylium Perchlorate (**16a**)

Yield 32%, *m.p.* 203 °C. – ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ/ppm = 1.00 (t, J = 7.2 Hz, 3H), 1.45–1.57 (m, 2H), 1.79–1.90 (m, 2H), 3.13 (t, J = 7.8 Hz, 2H), 7.68–7.74 (m, 4H), 7.78–7.84 (m, 2H), 8.17–8.25 (m, 6H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ/ppm = 13.4, 22.5, 31.3, 37.7, 118.7, 128.0, 128.4, 130.4, 136.1, 171.1, 178.1.
$C_{21}H_{21}ClO_5$ calcd.: C 64.87 H 5.44
(388.85) found: C 65.16 H 5.40.

4-Hexyl-2,6-diphenylpyrylium Perchlorate (**17a**)

Yield 57%, *m.p.* 149–153 °C. – ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ/ppm = 0.89 (t, J = 6.6 Hz, 3H), 1.25–1.40 (m, 4H), 1.42–1.54 (m, 2H), 1.78–1.92 (m, 2H), 3.07–3.18 (m, 2H), 7.65–7.74 (m, 4H), 7.74–7.82 (m, 2H), 8.21 (d, J = 5.1 Hz, 4H), 8.22 (s, 1H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ/ppm = 13.8, 22.3, 29.0, 29.2, 31.3, 38.0, 116.8, 128.0, 128.4, 130.4, 135.9, 170.9, 178.1.
$C_{23}H_{25}ClO_5$ calcd.: C 66.26 H 6.06
(416.91) found: C 66.31 H 5.83.

4-Dodecyl-2,6-diphenylpyrylium Perchlorate (**18a**)

Yield 44%, *m.p.* 128–132 °C (from ethanol/ether). – ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ/ppm = 0.89 (t, J = 6.2 Hz, 3H), 1.10–1.50 (m, 16H), 1.57–1.75 (m, 2H), 1.78–1.93 (m, 2H), 3.19 (t, J = 6.7 Hz, 2H), 7.62–7.90 (m, 6H), 8.27 (d, J = 7.0 Hz, 4H), 8.37 (s, 2H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ/ppm = 14.0, 22.6, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9, 38.0, 118.8, 128.0, 128.4, 130.3, 135.9, 170.8, 178.1.
$C_{29}H_{37}ClO_5$ calcd.: C 69.51 H 7.46
(501.07) found: C 69.30 H 7.45.

4,4'-(1,4-Butyliden)-bis-2,6-diphenylpyrylium bis-Perchlorate (**19a**)

Yield 56%, *m.p.* 252.7–254 °C. – ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ/ppm = 2.06–2.22 (m, 4H), 3.08–3.35 (m, 4H), 7.57–7.71 (m, 8H), 7.71–7.82 (m, 4H), 8.22 (d, J = 7.5 Hz, 8H), 8.35 (s, 4H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ/ppm = 28.7, 37.2, 119.1, 128.0, 128.5,130.3, 135.9, 171.1, 176.9.
$C_{38}H_{32}Cl_2O_{10}$ calcd.: C 63.42 H 4.49
(719.58) found: C 63.51 H 4.56.

Transformation of the 4-(1H-Benzotriazol-1-yl)-2,6-diarylpyrans to 10a–c and 25 (General Procedure)

To a solution of 4*H*-(1*H*-benzotriazol-1-yl)-2,6-diarylpyran (0.63 mmol) in THF (15 mL) was added *n*-BuLi (0.45 mL, 1.41M solution in hexane, 0.63 mmol) at –78 °C under argon. After 30 minutes, the reaction mixture was allowed to warm up to rt and stirred overnight, quenched with water, extracted with ethyl acetate and dried over $MgSO_4$. The solvent was removed, and the residue was washed with diethyl ether to give pure product.

4-(1H-Benzotriazol-1-yl)-1,2-diphenyl-2,4-cyclopentadien-1-ol (**10a**)

Crude product was crystallized from ethyl acetate to give the title compound as colorless crystals (yield 66%), *m.p.* 218–219 °C. – ^{1}H NMR ($CDCl_3$/DMSO): δ/ppm = 5.38 (s, 1H), 5.66 (s, 1H), 5.94–6.16 (m, 6H), 6.26–6.39 (m, 3H), 6.47 (t, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 7.2 Hz, 2H), 6.60 (s, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H). – ^{13}C NMR ($CDCl_3$/DMSO): δ/ppm = 85.7, 110.6, 119.1, 120.5, 123.9, 124.7, 126.1, 126.1, 127.0, 127.3, 127.4, 127.5, 127.7, 130.5, 131.5, 135.3, 139.4, 145.3, 153.0.

$C_{23}H_{17}N_3O$	calcd.:	C 78.61	H 4.89	N 11.96
(351.41)	found:	C 78.30	H 4.83	N 11.97.

4-(1H-Benzotriazol-1-yl)-1,2-bis-(4-methoxyphenyl)-2,4-cyclopentadien-1-ol (**10b**)

Crude product was washed with diethyl ether to give the title compound as colorless crystals (yield 54%), *m.p.* 200–201 °C. – ^{1}H NMR ($CDCl_3$/DMSO): δ/ppm = 3.72 (s, 3H), 3.76 (s, 3H), 6.42 (s, 1H), 6.69 (s, 1H), 6.76–6.90 (m, 3H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.46–7.58 (m, 2H), 7.60–7.72 (m, 3H), 8.06 (d, *J* = 8.1 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 54.8, 54.9, 86.0, 111.9, 113.5, 113.6, 118.6, 119.7, 124.9, 125.1, 125.3, 125.9, 128.4, 128.7, 131.0, 132.5, 135.5, 145.7, 153.2, 158.1, 158.9.

$C_{25}H_{21}N_3O_3$	calcd.:	C 72.97	H 5.15	N 10.21
(411.46)	found:	C 73.15	H 5.41	N 9.98.

4-(1H-Benzotriazol-1-yl)-1,2-bis-(4-fluorophenyl)-2,4-cyclopentadien-1-ol (**10c**)

Crude product was washed with diethyl ether to give the title compound as colorless crystals (yield 66%), *m.p.* 201–202 °C. – ^{1}H NMR ($CDCl_3$/DMSO): δ/ppm = 6.26 (s, 1H), 6.57 (s, 1H), 6.91–7.05 (m, 4H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.52–7.64 (m, 4H), 7.64–7.74 (m, 2H), 7.83 (d, *J* = 7.8 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H). – ^{13}C NMR ($CDCl_3$/DMSO): δ/ppm = 85.6, 110.8, 114.5 (d, *J* = 21.6 Hz), 119.4, 120.5 (broad), 124.2, 124.3 (broad), 126.0 (d, *J* = 7.8 Hz), 128.0, 128.1 (d, *J* = 7.8 Hz), 130.7, 135.2, 135.6, 145.6, 152.0, 161.1 (d, *J* = 244 Hz), 161.5 (d, *J* = 247 Hz).

$C_{23}H_{15}F_2N_3O$	calcd.:	C 71.31	H 3.91	N 10.85
(387.39)	found:	C 70.86	H 3.94	N 10.56.

N-(3,11-Dimethoxy-5,6,8,9-tetrahydro-7H-dibenzo[c,h]xanthen-7-ylidene)-N-phenylamine (**25**)

Crude product was washed with diethyl ether to give the title compound as colorless crystals (yield 66%), *m.p.* 201–203 °C. – ^{1}H NMR ($CDCl_3$/DMSO): δ/ppm = 1.90–2.25 (broad, 2H), 2.40–2.75 (broad, 2H), 2.75–3.20 (broad, 4H), 3.84 (s, 6H), 6.60–7.10 (m, 7H), 7.20 (t, *J* = 7.7 Hz, 2H), 7.77 (d, 2H, *J* = 8.5 Hz). – ^{13}C NMR ($CDCl_3$/DMSO): δ/ppm = 28.06, 55.32, 112.02, 113.1 (broad), 120.08, 121.3, 122.2, 124.1 (broad), 128.2, 139.8 (broad), 151.8, 153.2, 160.8 (broad).

$C_{29}H_{25}NO_3$	calcd.:	C 79.97	H 5.80	N 3.22
(435.53)	found:	C 79.59	H 5.93	N 3.21.

3,4-Diphenyl-4-hydroxy-cyclopent-2-enone (**11a**)

The mixture of 4-(benzotriazol-1-yl)-1,2-diphenyl-2,4-cyclopentadien-1-ol (**10a**) (0.52 g, 1.48 mmol) and catalytic amount of *p*-toluenesulfonic acid monohydrate (30 mg) in acetic acid (10 mL) was refluxed for 30 min. The reaction mixture was cooled and diluted with water (50 mL), extracted with ethyl acetate (50 mL), washed with water, and dried over $MgSO_4$. The solvent was removed under vacuum, and the residue was chromatographed through a silica gel column using 10% (vol.) of ethyl acetate in hexanes to give pure product as colorless crystals (yield 51%), *m.p.* 149.0–150.0 °C, (Lit. [7] *m.p.* 147.0–148.0 °C). – ^{1}H NMR ($CDCl_3$): δ/ppm = 2.80–3.06 (m, 2H), 3.50 (s, 1H), 6.64 (s, 1H), 7.20–7.38 (m, 6H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 2H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ/ppm = 56.5, 81.5, 124.2, 127.4, 128.7, 128.8, 129.2, 130.8, 131.4, 144.1, 174.3, 205.3.

X–Ray Crystallography

Intensity data were collected with a Siemens SMART CCD area detector using monochromatized Mo K_α (λ = 0.71073 Å) radiation. The crystal used was a colorless wedge of dimensions 0.65 × 0.45 × 0.32 mm. A total of 10 500 reflections were collected, which after merging (R_{int} = 0.0456) gave 2 541 uniques reflections. The intensities were corrected for Lorentz and polarization effects and for absorption (T_{max} = 0.974, T_{min} = 0.948).

The structure was solved by direct methods using SHELXS90 [13], and refined on F^2 by full-matrix least-squares procedures using SHELXL96 [14]. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were included in calculated positions with isotropic displacement coefficients equal to 1.2 times the isotropic equivalent of their carrier carbons, except for the OH hydrogen whose position was refined. The function minimized was $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + 0.0396P^2 + 0.402P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]/3$. A final difference map showed no features greater or less than 0.25 $e^-/Å^3$. Full tabulations of atom coordinates, bond lengths and bond angles, anisotropic thermal parameters and structure factors are available from the author PJS.

Crystal data at –110 °C : $C_{17}H_{14}O_2$, Mr = 250.28, monoclinic, space group $P2_1/c$, *a* = 9.6253(5), *b* = 18.3036(9), *c* = 7.4087(3) Å, β = 93.108(1), U = 1 302.2(1) $Å^3$, F(000) = 528, Z = 4, D_c = 1.277 g cm^{-3}, μ(Mo–K_α) = 0.083 mm^{-1}, $2\theta_{max}$ = 53°, 175 parameters, wR_2 = 0.1086 for all 2541 data, R1 = 0.0450 for 2 336 data with $F_o > 4\sigma(F_o)$.

References

[1] a) A. R. Katritzky, P. Czerney, J. R. Levell, J. Org. Chem. **1997**, *62*, 8198; b) A. R. Katritzky, S. N. Denisenko, P. Czerney, Heterocycles **1997**, *45*, 2413; c) A. R. Katritzky, P. Czerney, J. R. Levell, W. Du, Eur. J. Org. Chem. **1998**,2623

[2] a) A. R. Katritzky, X. Lan, I. Z. Yang, O. V. Denisko, Chem. Rev. **1998**, *98*, 409; b) A. R. Katritzky, Z. Yang, D. T. Cundy, Aldrichimica Acta **1994**, *47*, 31

[3] a) G. R. Geen, J. M. Evans, A. K. Vong in 'Comprehensive Heterocyclic Chemistry II', (Eds. A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon 1996, vol. 5, p. 469; b) P. Czerney, G. Graness, E. Birckner, F. Vollmer, W. Rettig, J. Photochem. Photobiology A: Chemistry **1995**, *89*, 31; c) A. T. Balaban, G. W. Fischer, A. Dinculescu, A. V. Koblik, G. N. Dorofeenko, V. V. Mezheritskii, W. Schroth in 'Advances

in Heterocyclic Chemistry' (Ed. A. R. Katritzky), Academic Press New York 1982, Supplement 2
[4] W. Schroth, W. Dölling, A. T. Balaban in 'Methoden der Organischen Chemie (Houben Weyl)', 4. Aufl., Georg Thieme Verlag Stuttgart – New York 1992, vol. E7b, p.755
[5] S. V. Krivun, S. N. Baranov, O. F. Voziyanova, Zh. Obshch. Khim. **1973**, *43*, 359
[6] a) G. A. Reynolds, C. H. Chen, J. A. Van Allan, J. Org. Chem. **1979**, *44*, 4456; b) V. V. Mezheritskii, G. N. Dorofeenko, Zh. Org. Khim. **1967**, *3*, 1533
[7] T. J. Clark, J. Org. Chem. **1973**, *38*, 1749
[8] a) R. R. Schmidt, Angew. Chem. Int. Ed. Engl. **1975**, *14*, 581; b) R. R. Schmidt, U. Burkert, R. Prewo, Tetrahedron Lett. **1975**, 3477
[9] C. H. Chen, G. A. Reynolds, J. Org. Chem. **1980**, *45*, 2449
[10] R. P. Haugland 'Handbook of Fluorescent Probes and Research Chemicals', Sixth Edition, Molecular Probes Inc. Eugene OR 1996
[11] J. Andrieux, J.-P. Battioni, M. Giraud, D. Molho, Bull. Soc. Chim. Fr. **1973**, 2093
[12] G. N. Dorofeenko, S. M. Lukyanov, L. N. Etmetchenko, A. V. Koblik, O.A. Rakina, Zh. Org. Khim. **1976**, *12*, 685
[13] G. M. Sheldrick, Acta Crystallogr., Sect. A **1990**, *46*, 467
[14] G. M. Sheldrick, SHELXL-96, University of Göttingen 1996

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