DOI: 10.1002/ejoc.200500631

3-Substituted Cyclopenta[*c*]pyrans: Synthesis and Electrophilic Substitutions

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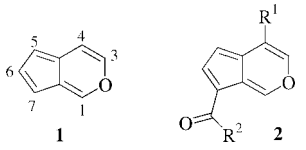
Dedicated to Professor Johann Mulzer in friendship and with admiration

Keywords: Electrophilic substitution / Fluorescence / Heterocycles / Olefination / α-Pyrones

The literature procedure for the preparation of the parent cyclopenta[*c*]pyran (**1**) was shown to provide only a low yield on mechanistic grounds. Intended as an alternative starting material for the synthesis of **1**, the cyclopenta[*c*]pyran-3-ones **10** were prepared. However, their conversion into **1** could be achieved at best in 1 % yield. Derivatives of **1** with an oxygen functionality in the 3-position were obtained by deprotonation, silylation and benzoylation of **10b**, giving rise to the lithium enolate **15**, the ketene acetals **16**–**18** and the ketene hemiacetal ester **19**, respectively. The olefination of **10b** with substituted methylenetriphenylphosphoranes furnished cyclopenta[*c*]pyran-3-ylacetonitrile (**21**) and methyl cyclopenta[*c*]pyran-3-ylacetate (**22**) in modest yields. These compounds as well as the primary alcohol **23**, which resulted from **22** on reduction with $LiAlH_4$, underwent an electrophilic aromatic substitution reaction with trifluoroacetic anhydride to form the 7-(trifluoroacetyl)cyclopenta[*c*]pyrans **24**–**27**. In the case of the acetonitrile **27**, a second and a third trifluoroacetyl group were readily introduced, giving rise to the highly resonance-stabilised anions **28** and **29**, the latter exhibiting a strong green fluorescence.

Introduction

The formal replacement of the C-6–C-7 vinylene group of azulene by an oxygen atom leads to cyclopenta[*c*]pyran (**1**) (Scheme 1), which thus belongs to the pseudoazulene class of compounds.[1] The parent compound **1** was synthesised by Seitz and co-workers,[2] who also obtained the 6-*tert*-butyl derivative. Entirely different synthetic approaches have yielded 6-*tert*-butyl-1,3-diphenyl-[3] and 1,3,4-triphenylcyclopenta[*c*]pyran.[4] A number of 1,4-disubstituted cyclopenta[*c*]pyrans and 3-methyl-1,4-diphenylcyclopenta[*c*]-pyran have been prepared in three-step procedures starting from 6*H*-1,3,4-oxadiazin-6-ones.[5] These cyclopenta[*c*]pyrans have been shown to undergo electrophilic aromatic substitution reactions at the 7-position under mild conditions. In particular, the Vilsmeier–Haack formylation gave rise to the corresponding cyclopenta[*c*]pyran-7-carboxaldehydes.[5] These compounds are related to naturally occurring derivatives of **1**, which are found in certain plants and are represented by the general formula **2** (Scheme 1), where R^2 is a hydrogen atom in most cases.[6–10] Synthetic routes to two of the compounds **2** have been developed.[11,12]



1 **2**

Scheme 1. Cyclopenta[*c*]pyran (**1**) and the general structure **2** of its naturally occurring derivatives.

In order to gain more knowledge about the reactivity of the cyclopenta[*c*]pyran system, we undertook to improve the preparation of **1**, to synthesise some of its simple derivatives and to study their behaviour towards electrophiles.

Results and Discussion

The Synthesis of Cyclopenta[*c*]pyran (1) by the Method of Seitz and Co-workers[2]

The sole synthesis of **1** was achieved in 1988 by Seitz and co-workers.[2] Although only a low yield was obtained, the simplicity of the reaction sequence (Scheme 2) was attractive. They deprotonated (trimethylsilyl)cyclopentadiene and treated the resulting anion with bromoacetaldehyde dimethyl acetal to obtain a mixture of the tautomers **3** in 55% yield, with **3a** forming the major component. For the conversion of **3** into the (dimethylamino)fulvene **4** by heating with *N*,*N*-dimethylformamide dimethyl acetal, a yield of

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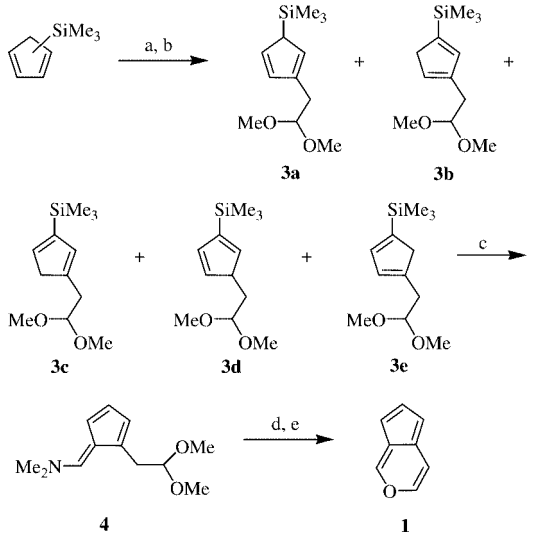
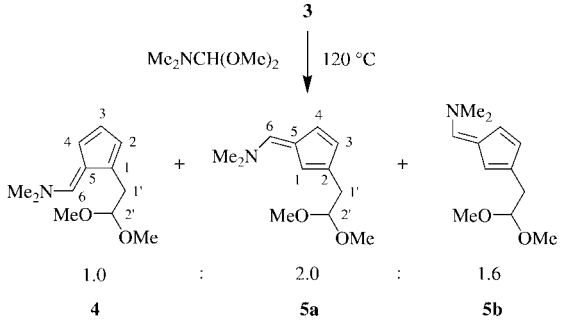
86% was claimed, whereas the hydrolysis of **4**, carried out in two steps, was reported to give **1** in only 5% yield.



Scheme 2. Synthesis of cyclopenta[*c*]pyran (**1**) according to the method of Seitz and co-workers.[2] Reagents and conditions: a: NaH, THF, 20 °C; b: $BrCH_2CH(OMe)_2$, THF, 66 °C (55%); c: $Me_2NCH(OMe)_2$, 120 °C (86%); d: 4 M NaOH, 100 °C; e: 1 M H_2SO_4 (pH = 5–6), 5 °C (5%).

In an attempt to improve the yield of **1**, we repeated the reaction sequence and found the origin of the low yield to be in the reaction of **3**, which gave not only **4** but its regioisomers **5a** and **5b** as well, with the ratio of **4/5a/5b** being 1.0:2.0:1.6 (Scheme 3).

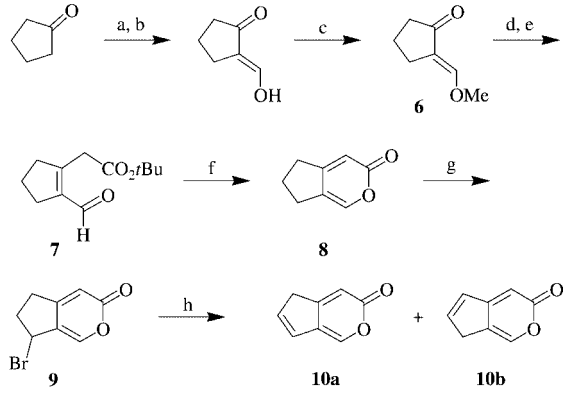


Scheme 3. The reaction of **3** with *N*,*N*-dimethylformamide dimethyl acetal.

Variation of the reaction conditions and the reagent, inter alia the use of (dimethylamino)(methoxy)methylium methyl sulfate ($Me_2NCHOMe^+MeOSO_3^-$)[13] instead of $Me_2NCH(OMe)_2$, which allowed the conversion to proceed at lower temperatures, did not change the outcome. Presumably, the trimethylsilyl group of **3** is replaced by a proton at an early stage in the reaction by the action of methanol, which is formed en route to **4**, and hence can no longer exert the intended steric effect of directing the entry of the (dimethylamino)methylene group next to the acetaldehyde acetal side-chain. As a consequence, the last step in the synthesis of **1** can have a maximum yield of just 22%, which is why we turned to another approach.

The Preparation of the Cyclopenta[*c*]pyran-3-ones 10

Several 1,4-disubstituted cyclopenta[*c*]pyrans have previously been prepared from the correspondingly substituted cyclopenta[*c*]pyran-3-ones by reduction with diisobutylaluminium hydride (DIBAL-H).[5] In order to apply this transformation to a new route to **1**, we had to develop a synthesis for the hitherto unknown α-pyrones **10**. This was achieved in six steps from cyclopentanone, as shown in Scheme 4. Dieter and Fishpaugh[14] had previously prepared the dihydro derivative **8** of **10** by treatment of *tert*-butyl (2-formylcyclopent-1-en-1-yl)acetate (**7**) with a mixture of trifluoroacetic acid (TFA) and its anhydride (TFAA). Since their route to **7** using 2-[(methylsulfanyl)-methylene]cyclopentanone as immediate precursor proved not to be very efficient in our hands, we took advantage of the corresponding methoxy compound **6**, which was conveniently obtained in two steps from cyclopentanone according to literature procedures.[15,16]



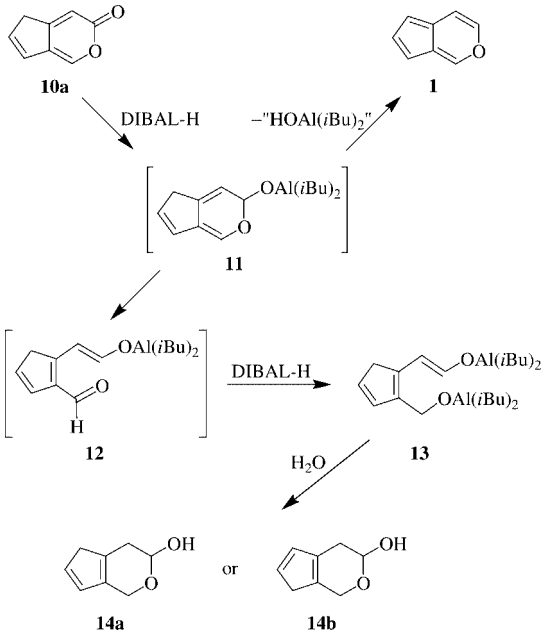
Scheme 4. Synthesis of α-pyrones **10a** and **10b**. Reagents and conditions: a: KH, HCO_2Et, Et_2O, 0 °C; b: NaH_2PO_4, 12 M HCl (63%); c: Me_2SO_4, acetone, 56 °C (ca. 95% crude product, used in the next step without purification); d: $LiCH_2CO_2tBu$, THF, –78 °C; e: 2 M HCl, 20 °C (52%); f: TFA, TFAA, 0–20 °C (76%); g: NBS, CCl_4, *hv*, 76 °C (62%); h: $CaCO_3$, DMAA, 110 °C (65%).

Several methods were examined for the conversion of **8** into **10**. Only the bromination of **8** with *N*-bromosuccinimide (NBS) followed by the elimination of hydrogen bromide from the resulting bromo-α-pyrone **9** was successful. The best base for the last step proved to be calcium carbonate in dimethylacetamide (DMAA), which had been found useful previously if dehydrohalogenation reactions with more conventional bases gave only poor results.[17] That **10a** and **10b** were isolated in yields of 12 and 53%, respectively, shows the greater thermodynamic stability of **10b**. Apparently, **10b** emerged from **10a** under the influence of the base required for the conversion of **9** into **10a**. It was not tested, however, whether the above **10a/10b** ratio corresponds to the equilibrium value.

Reactions of the Cyclopenta[*c*]pyran-3-ones 10

Our anticipation that **10** could be transformed to **1** in good yield by DIABL-H did not come true. Starting from **10b**, we obtained **1** in a yield of only 1% in the best case in

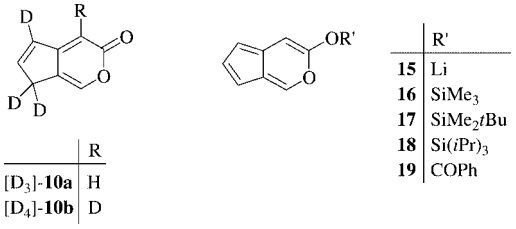
addition to **10b**, **10a**, **8**, a hemiacetal **14** and some unidentified material. The use of **10a** furnished traces of **1** as well, and a 9% yield of a hemiacetal **14**, which provides a clue as to why the formation of **1** is an unimportant pathway. Scheme 5 summarizes the mechanistic proposal.



Scheme 5. Mechanistic proposal for the reaction of the cyclopenta[*c*]pyran-3-one **10a** with diisobutylaluminium hydride (DIBAL-H).

After the addition of DIBAL-H to the carbonyl group of **10a**, the resulting compound **11** undergoes the desired elimination of "HOAl(iBu)$_2$", which is the major process in the reduction of 1,4-disubstituted cyclopenta[*c*]pyran-3-ones,[5] only to an insignificant extent. Apparently, opening of the six-membered ring of **11** is preferred by far, giving rise to the aldehyde **12**, which reacts with DIBAL-H to afford **13** and after hydrolysis a hemiacetal **14**, whose exact structure, either **14a** or **14b**, was not determined. The reason for the difference in the behaviour of **11** and its analogue emerging from **10b** on the one hand and the corresponding intermediates arising from 1,4-disubstituted cyclopenta[*c*]pyran-3-ones[5] on the other could be a buttressing effect of the substituents, which would have to approach the five-membered ring on opening of the six-membered one. Thus, the elimination of "HOAl(iBu)$_2$" with aromatisation would be the favoured step.

The use of DIBAL-H in the presence of triethylamine did not change the outcome. Instead of DIBAL-H, a number of other reducing agents were employed, but none of them gave even a trace of **1** from **10a** or **10b**. Some transferred a hydride ion to the five-membered ring of **10b** and, after hydrolysis, the dihydro derivative **8** of **10a** and **10b** was produced. Others just led to the formation of the enolate of **10a** and **10b** by abstraction of a proton. The high acidity of the methylene group of **10b** was demonstrated by its treatment with triethylamine in the presence of D_2O. After 4 d at room temperature, the major products obtained were [D_3]-**10b** and [D_4]-**10b** in a ratio of 2:3 (Scheme 6), indicating a virtually total H/D exchange in the 5- and 7-positions of **10b**. Somewhat surprisingly, a significant amount of the 4-H atoms of **10b** underwent exchange as well.



Scheme 6. Products obtained by treatment of **10b** with a base and, except for **15**, an electrophile.

We also employed the conditions of H/D exchange in an attempt to prepare cyclopenta[*c*]pyrans with an oxygen functionality in the 3-position. Thus, the treatment of **10b** in dichloromethane with triethylamine in the presence of chlorotrimethylsilane afforded a 32:6:1 mixture of ketene acetal **16**, **10a** and **10b**. With chlorotriisopropylsilane instead of chlorotrimethylsilane, only a small quantity of **10b** was converted into **18**, whereas in the case of *tert*-butylchlorodimethylsilane the reaction did not proceed at all. The ketene hemiacetal ester **19** was obtained in 65% yield from a mixture of **10b**, triethylamine and benzoyl chloride in acetonitrile. However, analogous experiments with 4-nitrobenzoyl chloride, pivaloyl chloride, acetyl chloride, ethyl chloroformate, methanesulfonyl chloride and toluenesulfonyl chloride were unsuccessful.

We then turned to the preparation of the lithium enolate **15** (Scheme 6), which was achieved by the action of either methyllithium or lithium diisopropylamide on **10b**. The complete formation of **15** was clearly demonstrated by ^{1}H and ^{13}C NMR spectroscopy (Table 1 and Table 2). When chlorotriisopropylsilane was added to a solution of **15** at –78 °C, workup led to a 60% yield of **18**. Under the same conditions, a 40:1:7 mixture of ketene acetal **17**, **10a** and **10b** was formed with *tert*-butylchlorodimethylsilane as electrophile, but no reactions were observed with diethyl chlorophosphate, diphenyl chlorophosphate or *N*,*N*-bis(trifluoromethylsulfonyl)aniline.

The ketene acetals **16**–**18** and the enol ester **19** were found to be rather sensitive compounds, which could not be rigorously purified and were hence characterised only by ^{1}H and ^{13}C NMR spectroscopy (Table 1 and Table 2). At room temperature, they decomposed within hours or days to give mixtures of **10a** and **10b**.

Several experiments were carried out in an effort to prepare cyclopenta[*c*]pyrans with a carbon substituent in the 3-position. Only two of them were successful. According to procedures for the olefination of lactones,[18,19] we obtained the acetonitrile **21** and the methyl acetate **22** (Scheme 7). The reaction of **10b** with the respective ylides should initially generate a species **20**, which is either a derivative of acrylonitrile or methyl acrylate, but which could not be observed. Instead, **21** and **22** were isolated as crystalline solids in 29 and 15% yields, respectively. Probably catalysed by

Table 1. ^{1}H NMR spectroscopic data for 3-substituted cyclopenta[*c*]pyrans in $CDCl_3$ (**16**–**19**, **21**, **22**), [D_8]THF (**15**) or [D_6]acetone (**23**); chemical shifts (δ) are given in ppm [$\delta(CHCl_3)$ = 7.26 ppm, δ(OCHD of [D_8]THF) = 3.58 ppm, δ([D_5]acetone) = 2.05 ppm]; representative signal multiplicities are given for **16** and **21**; the coupling constants are absolute values and are given in Hz.

Compd.	3-Subst.	1-H	4-H	5-H	6-H	7-H	Subst.	$J_{1,4}$	$J_{1,5}$	$J_{1,6}$	$J_{4,7}$	$J_{5,6}$	$J_{5,7}$	$J_{6,7}$
15	OLi	7.72	5.37	5.46	6.70	5.97	–	[a]	[a]	[a]	[a]	2.5	[a]	4.7
16	$OSiMe_3$	7.93	6.17	6.18	7.10	6.52	0.36 (9 H)	0.8	1.0	0.4	0.9	2.5	1.0	4.8
		br. s	t	dt	ddd	dt	s							
17	$OSiMe_2tBu$	7.93	6.16–6.19		7.10	6.52	0.29 (6 H), 1.02 (9 H)	[b]	[b]	0.5	0.9	2.5	0.9	4.8
18	$OSi(iPr)_3$	7.93	6.22	6.16	7.10	6.52	[c]	0.8	1.1	0.4	0.8	2.5	1.1	4.8
19	OCOPh	8.12	6.84	6.49	7.22	6.73	[d]	0.7	1.1	0.4	0.7	2.5	1.2	4.8
21[e]	CH_2CN	8.23	7.10[f]	6.50	7.21	6.75	3.78 (2 H)	0.9	1.1	[g]	0.9	2.6	1.1	4.8
		t	quint	dt	dd	dt	br. s							
22	$CH_2CO_2CH_3$	8.26	6.99[f]	6.42	7.18	6.70	3.69 (2 H), 3.73 (3 H)	0.8	1.0	0.4	0.8	2.7	1.0	4.7
23	CH_2CH_2OH	8.46	6.97[f]	6.26	7.06	6.61	2.88 (2 H),[h] 3.81–3.91 (m, 3 H)	0.8	1.0	0.4	0.8	2.5	1.0	4.7

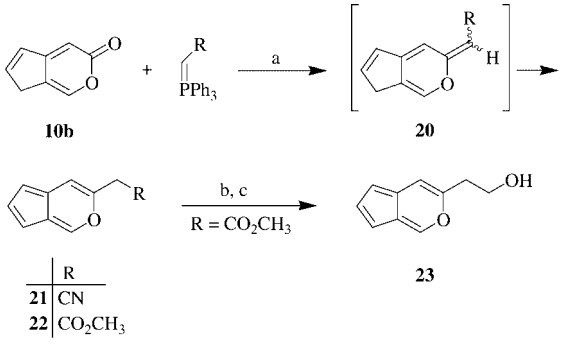
[a] Not resolved due to rather broad lines. [b] Not determined. [c] δ = 1.12 or 1.14 (d, J = 7 Hz, Me), 1.18–1.38 (one of several m, C*H*Me) ppm; the uncertainties are due to impurities. [d] δ = 7.55 (*m*-H), 7.69 (*p*-H), 8.22 (*o*-H) ppm. [e] The assignments are based on an H,H-COSY spectrum. [f] Coupling constant with CH_2: J = 0.7–0.9 Hz. [g] Not resolved. [h] Apparent t, line distance 6.4 Hz.

Table 2. ^{13}C NMR chemical shifts of 3-substituted cyclopenta[*c*]pyrans in $CDCl_3$ (**16**–**19**, **21**, **22**), [D_8]THF (**15**) or [D_6]acetone (**23**); chemical shifts (δ) are given in ppm [$\delta(CDCl_3)$ = 77.0 ppm, $\delta(OCD_2$ of [D_8]THF) = 67.6 ppm, $\delta(CD_3$ of [D_6]acetone) = 29.8 ppm].

Compd.	3-Subst.	C-1	C-3	C-4	C-4a	C-5	C-6	C-7	C-7a	Subst.
15[a]	OLi	142.2	163.4	80.6	138.5[b]	98.2	135.3	102.5	127.3[b]	–
16[a]	$OSiMe_3$	142.4	152.3	88.9	130.6[b]	106.2	136.1	107.2	126.2[b]	0.0
17[a]	$OSiMe_2tBu$	142.4	152.5	89.0	130.8[b]	106.0	136.1	107.1	126.1[b]	–4.6 (SiMe), 18.1 (C*Me*), 25.4 (*C*Me)
18[a]	$OSi(iPr)_3$	142.0	152.5	88.6	131.1[b]	105.8	136.2	107.0	126.2[b]	12.4 or 13.7 (Me), 17.6 or 17.7 (CH)[c]
19[a]	OCOPh	143.2	147.5	97.3	127.77[b]	110.3	136.3	109.5	126.5[b]	127.85 (*i*-C),[b] 128.8 (*m*-C), 130.5 (*o*-C), 134.4 (*p*-C), 163.8 (C=O)
21[a]	CH_2CN	145.6	138.7	108.4	125.2[b]	110.7	135.6	110.5	125.8[b]	22.6 (CH_2), 115.1 (CN)
22[a]	$CH_2CO_2CH_3$	146.1	143.3	109.5	125.7[b]	109.1	135.1	109.1	126.3[b]	39.3 (CH_2), 52.4 (CH_3), 169.6 (C=O)
23[a]	CH_2CH_2OH	147.6	150.0	108.1	126.7[b]	108.2	135.0	109.5	127.8[b]	37.9 (*C*H_2CH$_2$OH), 60.6 (CH_2OH)

[a] As far as specified, the assignments are based on a C,H-COSY spectrum. [b] The assignments of these signals may be exchanged. [c] The uncertainties are due to impurities.

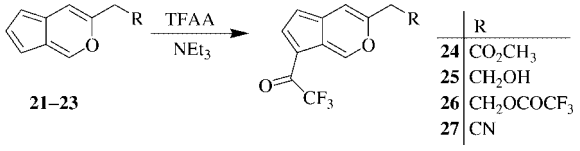
the ylide, acting as a base, **20** underwent tautomerism to afford **21** or **22**, demonstrating that these, most likely due to their aromatic character, are thermodynamically more stable than **20**. The reduction of **22** by $LiAlH_4$ was expected to furnish the primary alcohol **23** (Scheme 7). Indeed, this came true, but only at low temperatures, since the cyclopenta[*c*]pyran system is also attacked at room temperature.



Scheme 7. Synthesis of the cyclopenta[*c*]pyrans **21**–**23** from the α-pyrone **10b**. Reagents and conditions: a: 140–145 °C, xylene; b: $LiAlH_4$, THF, –70 °C; c: H_2O, NaOH, –70 to 20 °C.

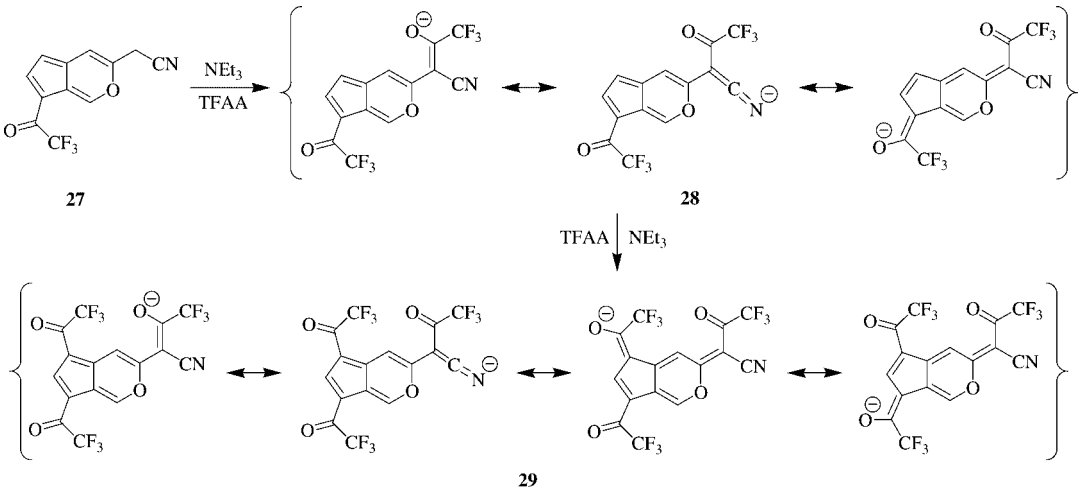
Trifluoroacetylation of the Cyclopenta[*c*]pyrans 21–23

Based on our experience with electrophilic aromatic substitution reactions of 1,4-disubstituted cyclopenta[*c*]pyrans,[5] we exposed **21**–**23** to trifluoroacetic anhydride (TFAA) in the presence of triethylamine (Et_3N) and anticipated the replacement of the proton in the 7-position. In the event, the methyl acetate **22** gave rise exclusively to the 7-(trifluoroacetyl)cyclopenta[*c*]pyran **24** (Scheme 8) in 43% yield. Also, the primary alcohol **25** was formed from **23**, but the trifluoroacetate **26** was isolated as the major product. Apparently, the aromatic system undergoes trifluoroacetylation somewhat faster than the alcohol functionality. The corresponding acetonitrile **27** was obtained from **21** in 25% yield.



Scheme 8. Reactions of the cyclopenta[*c*]pyrans **21**–**23** with trifluoroacetic anhydride (TFAA) in the presence of triethylamine (Et_3N).

However, the amount of TFAA applied to **21** had to be administered carefully because products with two and three trifluoroacetyl groups were formed preferentially on addition of more than 1.7 equiv. of TFAA. These compounds were shown to be salts with the anions **28** and **29** (Scheme 9). Their formation is a consequence of the acidification of the methylene group of **27** caused by the presence



Scheme 9. Reaction of 7-(trifluoroacetyl)cyclopenta[*c*]pyran **27** with trifluoroacetic anhydride (TFAA) in the presence of triethylamine (Et_3N).

of the trifluoroacetyl substituent. Thus, the anion of **27** should react with TFAA at the carbon atom bearing the CN group, giving rise to the neutral precursor of **28**, in which the exocyclic CH group is activated by three acceptor groups and hence transfers a proton to Et_3N. Although highly stabilised by resonance, **28** is still sufficiently nucleophilic to attack TFAA, resulting in the formation of the anion **29** after loss of a proton. The sequence of introduction of the trifluoroacetyl groups into **27** has been proven by the characterisation of the anion **28**, which is an intermediate en route to **29**.

The location of the trifluoroacetyl group in **24**, **25** and **27** was deduced from its substituent effects in the ^{13}C NMR spectra relative to those of **21**–**23**, respectively. Significant downfield shifts are observed for the signals of C-1 (5.8–5.9 ppm), C-3 (6.9–9.2 ppm), C-4a (11–15 ppm), C-6 (10.7–10.9 ppm) and C-7 (4.8–5.9 ppm), whereas the other absorptions are much less affected. This pattern matches perfectly that found by comparing the chemical shifts of 1,4-diphenylcyclopenta[*c*]pyran with those of its 7-trifluoroacetyl derivative.[5,20]

The longest-wavelength absorptions in the UV/Vis spectra of **21** (λ = 401 nm) and **22** (λ = 407 nm) are extremely broad and display a significant intensity even at 500 nm ($\log\varepsilon$ = 2.38 and 2.61, respectively). The introduction of a trifluoroacetyl group, that is, the conversion of **21** and **22** into **27** and **24**, respectively, causes not only an increase to the six- and nine-fold value of the molecular extinction coefficient of this band, but also a bathochromic shift of 38 and 34 nm, respectively. Whereas an enhancement in the intensity of the corresponding absorption was also observed on going from 1,4-diphenylcyclopenta[*c*]pyran to its 7-(trifluoroacetyl) derivative, the position of the maximum remained virtually unchanged.[5]

The trifluoroacetylation products of **27** were characterised as salts with the anions **28** and **29** by their behaviour on purification by chromatography and by attempts to obtain mass spectra. While the retention factor (R_f) of **27** on TLC on silica gel with *tert*-butyl methyl ether/light petroleum ether (4:1) is 0.55, the corresponding values of the trifluoracetylation products are only 0.06 and 0.10. In order to considerably increase their R_f values, we had to raise the polarity of the solvent by the addition of a substantial amount of ethanol. The EI mass spectra of the products show neither an M^+ signal nor intense fragment peaks that could originate from M^+ by successive loss of small groups. However, the FAB mass spectra clearly display signals from the anions **28** and **29** and their adducts with sodium ions. In particular, the ESI mass spectrum of the tris(trifluoroacetylation) product contains only one signal, namely that of **29**.

The detailed structures of **28** and **29** were derived from their ^1H, ^{13}C and ^{19}F NMR spectra. Two or three ^{19}F NMR absorptions of equal intensity prove the number of CF_3 groups. This information is extended to the number of CF_3CO groups by the respective ^{13}C NMR signals with their typical fine structure due to ^{13}C–^{19}F couplings. The location of these groups is obvious from the splitting of the ^1H NMR signals. Similar to the situation in **27**, 6-H in **28** experiences a coupling of 2.2 Hz to only one CF_3 group, while the second CF_3 group shows no interaction with any protons, supporting its position at the acetonitrile subunit. In contrast, 6-H in **29** is coupled [J(H,F) = 2.0 Hz] to two CF_3 groups, indicating that the third CF_3CO group occupies the 5-position. The chemical shifts of the carbon atoms bearing the nitrile groups of **28** and **29** are worthy of note as the values of δ = 69.3 and 72.2 ppm lie far upfield of the range characteristic of the resonances of trigonal carbon atoms. These values probably reflect the localisation of a rather large part of the charge of these anions at the respective carbon atoms.

The counterion to the anions **28** and **29** has to be a triethylammonium ion in the reaction mixtures, but it should be subject to exchange during workup operations. Thus, the missing NMR signals of the triethylammonium ion after dichloromethane solutions of the salts were extracted with brine suggest the presence of sodium salts. When an ether solution of Na^+**29** was treated with an aqueous solution

of potassium chloride, the major signals in the FAB mass spectrum originated from **29** associated with K^+.

The configurations of **28** and **29** shown in Scheme 9 have been drawn arbitrarily. Most probably, the real configurations are not very persistent since the exocyclic double bonds should adopt a significant single-bond character due to efficient delocalisation of the negative charge. Therefore, low barriers to rotation about the bonds that attach the substituents to the cyclopenta[*c*]pyran core and the acetonitrile subunit are expected.

The most remarkable feature of **29** is its strong green fluorescence. The UV/Vis absorption spectrum is depicted in Figure 1, together with the fluorescence spectrum on excitation at λ = 450 nm. The fluorescence quantum yield (Φ_f) was determined to be 0.55.

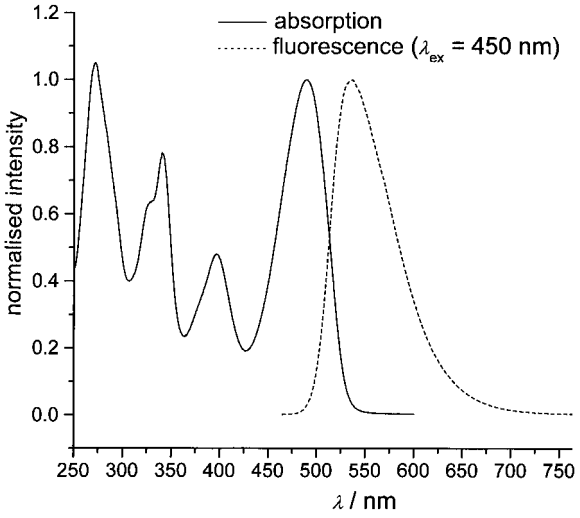


Figure 1. UV/Vis and fluorescence spectra of **29**, the latter on excitation at λ = 450 nm.

In order to prepare further substitution products, we exposed **21** to electrophiles other than TFAA. Having been utilised successfully with two 1,4-disubstituted cyclopenta[*c*]-pyrans,[5] tetranitromethane was to no avail. The Vilsmeier–Haack reagent, which gave rise to the 7-carboxaldehydes of a number of 1,4-disubstituted cyclopenta[*c*]pyrans and a 1,3,4-trisubstituted one in good yields,[5] furnished a product that contained a dimethylamino group, but it could not be characterised completely.

Conclusions

We have shown that the literature synthesis of the parent cyclopenta[*c*]pyran (**1**) is inefficient on mechanistic grounds. For a new approach to **1**, the α-pyrones **10a** and **10b** were prepared. However, attempts to convert them into **1** provided only traces of the target. Because of the difficult access to **1**, its reactivity cannot be studied at present. On the other hand, **10b** proved to be a useful starting material for the synthesis of a number of 3-substituted cyclopenta[*c*]pyrans. In particular, cyclopenta[*c*]pyran-3-ylacetonitrile (**21**) and -3-ylacetic acid methyl ester (**22**) are promising models for probing the properties of the pseudoazulene nucleus. The selective reduction of the ester functionality of **22** to give the primary alcohol **23** was possible only at low temperatures, whereas the ring system was attacked at room temperature as well. As an example of an electrophilic aromatic substitution, the reactions of **21**–**23** with trifluoroacetic anhydride (TFAA) in the presence of triethylamine (Et_3N) were studied. The electrophile was introduced selectively into the 7-position, as expected from the behaviour of 1,4-disubstituted cyclopenta[*c*]pyrans.[5] Surprisingly, 7-(trifluororacetyl)cyclopenta[*c*]pyran-3-ylacetonitrile (**27**) reacted readily with a TFAA/Et_3N mixture, eventually giving rise to the highly resonance-stabilised anion **29**, which is the first member of a new class of fluorescing compounds.

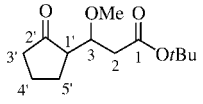
Experimental Section

General Remarks: NMR: Bruker Avance 400 and DMX 600 spectrometers. IR: JASCO FT/IR-410 spectrometer. UV/Vis: JASCO V-570 UV/VIS/NIR Spectrophotometer. Fluorescence: Photon Technology International QuantaMaster Model QM-2000-4 spectrometer. The fluorescence quantum yield was determined relative to rhodamine 101, having a quantum yield of 1.00, and was corrected for the refractive index of the solvent. MS: Finnigan MAT 8200 and MAT 90, Bruker Daltonics micrOTOF spectrometer. Elemental analyses: LECO Elemental Analyzer CHNS 932. Melting points: Kofler hot stage apparatus from C. Reichert, Optische Werke AG, Vienna, Austria. Frequently used solvents: DCM = dichloromethane, PE = light petroleum ether (b.p. 40–65 °C), MTBE = *tert*-butyl methyl ether.

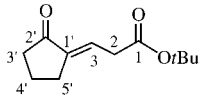
Reaction of the [(Trimethylsilyl)cyclopentadienyl]acetaldehyde Dimethyl Acetals 3a–e with *N*,*N*-Dimethylformamide Dimethyl Acetal: The reaction was conducted as described by Seitz and co-workers,[2] and the product obtained was characterised as a 1.0:2.0:1.6 mixture of the isomers **4**, **5a** and **5b** by ^1H and ^{13}C NMR spectroscopy at 600 and 151 MHz, respectively. Seitz and co-workers[2] did not specify whether they had recorded their ^1H NMR spectrum at 60, 100 or 400 MHz. Attempts to separate the mixture of **4**, **5a** and **5b** by column chromatography were met with no success. ^1H NMR (600 MHz, $CDCl_3$): **4**: δ = 2.92 (d, $J_{1',2'}$ = 5.5 Hz, 2 H, 1′-H), 3.27 (br. s, 6 H, NMe), 3.37 (s, 6 H, OMe), 4.51 (t, $J_{1',2'}$ = 5.5 Hz, 1 H, 2′-H), 6.20 (br. s, 1 H, 2-H), 6.42 (dd, $J_{3,4}$ = 5.0, $J_{2,3}$ = 2.6 Hz, 1 H, 3-H), 6.54 (dd, $J_{3,4}$ = 5.0, $J_{2,4}$ = 1.6 Hz, 1 H, 4-H), 7.27 (s, 1 H, 6-H) ppm; **5a**: δ = 2.88 (d, $J_{1',2'}$ = 5.7 Hz, 2 H, 1′-H), 3.231 (br. s, 6 H, NMe), 3.383 (s, 6 H, OMe), 4.64 (t, $J_{1',2'}$ = 5.7 Hz, 1 H, 2′-H), 6.27 (dd, $J_{3,4}$ = 4.5, $J_{1,3}$ = 1.6 Hz, 1 H, 3-H), 6.37 (dd, $J_{3,4}$ = 4.5, $J_{1,4}$ = 2.3 Hz, 1 H, 4-H), 6.40 (br. s, 1 H, 1-H), 7.03 (s, 1 H, 6-H) ppm; **5b**: δ = 2.83 (d, $J_{1',2'}$ = 5.8 Hz, 2 H, 1′-H), 3.227 (br. s, 6 H, NMe), 3.379 (s, 6 H, OMe), 4.61 (t, $J_{1',2'}$ = 5.8 Hz, 1 H, 2′-H), 6.21 (br. s, 1 H, 1-H), 6.48 (br. dd, $J_{3,4}$ = 4.8, $J_{1,3}$ = 1.5 Hz, 1 H, 3-H), 6.55 (dd, $J_{3,4}$ = 4.8, $J_{1,4}$ = 2.3 Hz, 1 H, 4-H), 7.05 (s, 1 H, 6-H) ppm; the assignments are based on H,H-COSY and ROESY experiments. ^{13}C NMR (151 MHz, $CDCl_3$): **4**: δ = 32.1 (C-1′), 38–47 (very broad, NMe), 53.6 (OMe), 106.4 (C-2′), 114.0 (C-4), 115.3 (C-1), 119.5 (C-2), 122.9 (C-3), 130.4 (C-5), 146.6 (C-6) ppm; **5a**: δ = 34.1 (C-1′), 38–47 (very broad, NMe), 52.7 (OMe), 105.0 (C-2′), 112.0 (C-1), 116.5 (C-2), 121.1 (C-3), 124.9 (C-4), 135.7 (C-5), 147.3 (C-6′) ppm; **5b**: δ = 33.3 (C-1′), 38–47 (very broad, NMe), 52.7 (OMe), 105.1 (C-2′), 114.4 (C-4), 116.4 (C-2), 121.8 (C-1), 126.9 (C-3), 129.6 (C-5), 147.3 (C-6) ppm; for the hydrogen-bearing carbon atoms, the assignments are based on a C,H-COSY spectrum,

whereas the signals of the quaternary carbon atoms were assigned by guessing.

***tert*-Butyl (2-Formylcyclopent-1-en-1-yl)acetate (7):** Under nitrogen, butyllithium (523 mmol, 351 mL of 1.49 M in hexane) was added dropwise to a stirred solution of diisopropylamine (73.5 mL, 523 mmol) in anhydrous THF (500 mL) kept at –30 °C over 10 min. Stirring was continued at –30 °C for 30 min. Then the temperature was lowered to –78 °C, *tert*-butyl acetate (60.8 g, 523 mmol) was added to the stirred mixture over 10 min and the resulting mixture was stirred at –78 °C for 1 h. (*E*)-2-(Methoxymethylene)cyclopentanone (**6**) (55.0 g, 436 mmol), dissolved in anhydrous THF (500 mL), was then added over 15 min and the mixture was stirred at –78 °C for a further 2.5 h. Thereafter, hydrochloric acid (1.5 L, 2 M) was added at –78 °C over 5 min and vigorous stirring was continued at room temperature for 14 h. The phases were then separated and the aqueous layer was extracted with diethyl ether (3 × 250 mL). After treatment with saturated aqueous $NaHCO_3$ (2 × 200 mL), the combined organic layers were dried with $MgSO_4$ and concentrated in vacuo to give 83.7 g of an orange oil, 1.66 g of which was subjected to flash chromatography (SiO_2; PE/MTBE, 5:1). The first fraction consisted of 947 mg of **7** as a colourless oil, corresponding to a yield of 47.7 g (52%). The second fraction was a 3.6:1.0 mixture (317 mg) of *tert*-butyl β-methoxy-β-(2-oxocyclopentyl)propionate (**30**) and *tert*-butyl (*E*)-β-(2-oxocyclopentylidene)propionate (**31**) which also contained small amounts of other components.



30



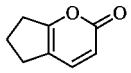
31

We found the ^1H NMR spectrum of **7** to be in agreement with the data given by Dieter and Fishpaugh,[14] whereas the ^{13}C NMR chemical shifts seem to have been confused, which is why we present our values here. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 21.3 (C-4), 27.9 (Me), 30.2 and 38.9 (C-3, C-5), 35.7 (CH_2CO), 81.7 (Me_3C), 140.4 (C-2), 156.6 (C-1), 168.4 (CO_2CMe_3), 187.9 (CHO) ppm; as far as specified, the assignments are based on a C,H-COSY spectrum.

30: ^1H NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 9 H, *t*Bu), 1.72 (m, 1 H, 4′-H), 1.87–2.23 (m, 4 H, 3′-H, 4′-H, 5′-H), 2.19 (dddd, $J_{1',5'}$ = 10.7 and 8.3, $J_{3,1'}$ = 3.2, $J_{1',3'}$ = 1.1 Hz, 1 H, 1′-H), 2.28 (m, 1 H, 3′-H), 2.33 (dd, $J_{2,2}$ = 14.8, $J_{2,3}$ = 6.7 Hz, 1 H) and 2.54 (dd, $J_{2,2}$ = 14.8, $J_{2,3}$ = 7.0 Hz, 1 H) (2-H), 3.28 (s, 3 H, OMe), 4.08 (td, average of $J_{2,3}$ = 6.9, $J_{3,1'}$ = 3.2 Hz, 1 H, 3-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 20.7 (C-4′), 23.2 (C-5′), 28.0 (C*Me*), 38.9 (C-3′), 39.4 (C-2), 52.8 (C-1′), 58.4 (OMe), 76.2 (C-3), 80.7 (*C*Me), 170.4 (C-1), 219.2 (C-2′) ppm; as far as specified, the assignments are based on C,H-COSY and HMBC spectra.

31: ^1H NMR (600 MHz, $CDCl_3$): δ = 1.43 (s, 9 H, *t*Bu), 1.93 (apparent quint, line distance 7.6 Hz, 2 H, 4′-H), 2.32 (apparent t, line distance 7.9 Hz, 2 H, 3′-H), 2.58 (apparent tdt, line distance 7.3, $J_{3,5'}$ = 2.7, $J_{2,5'}$ = 1.7 Hz, 2 H, 5′-H), 3.07 (dt, $J_{2,3}$ = 7.4, $J_{2,5'}$ = 1.7 Hz, 2 H, 2-H), 6.62 (tt, $J_{2,3}$ = 7.4, $J_{3,5'}$ = 2.7 Hz, 1 H, 3-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 19.5 (C-4′), 26.8 (C-5′), 28.0 (Me), 36.5 (C-2), 38.5 (C-3′), 81.4 (*C*Me), 127.1 (C-3), 139.5 (C-1′), 169.2 (C-1), 206.4 (C-2′) ppm; the assignments are based on a C,H-COSY spectrum.

6,7-Dihydrocyclopenta[*c*]pyran-3(5*H*)-one (8): The procedure of Dieter and Fishpaugh[14] was somewhat modified. Thus, the crude product of the preceding experiment [82.0 g, corresponding to 46.8 g (223 mmol) of **7** and 58.8 mmol of **30** and **31**] was dissolved in trifluoroacetic anhydride (600 mL) under nitrogen at 0 °C and trifluoroacetic acid (222 g, 1.95 mol) was added to the solution. The black mixture was stirred at 0 °C for 2 h and then at room temperature for 34 h. The volatile components were then removed by distillation in vacuo. The remaining black oil (118 g) was purified by flash chromatography (SiO_2; PE/MTBE, 1:1) to give, in the order of elution, 7.10 g (89%) of **32**, formed from **30** and **31**, and 27.8 g (91%) of **8**, both as brown crystals. The recrystallisation of **8** from PE/MTBE afforded 23.2 g (76%) of beige needles, m.p. 65–67 °C. The ^1H and ^{13}C NMR spectra are in agreement with published data.[14] The α-pyrone **32** had previously been prepared by a different route.[21] Whereas our ^1H NMR spectrum corresponds to the data reported, at least one chemical shift of our ^{13}C NMR spectrum is markedly different and so our data is presented here. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 20.7, 27.8, 31.0, 112.2, 115.9, 142.7, 163.9, 164.9 ppm.



32

7-Bromo-6,7-dihydrocyclopenta[*c*]pyran-3(5*H*)-one (9): A suspension of *N*-bromosuccinimide (21.4 g, 120 mmol) in anhydrous tetrachloromethane (500 mL), containing **8** (14.8 g, 109 mmol), was refluxed under nitrogen and simultaneously irradiated with a light bulb (200 W) for 7 h. After cooling to room temperature, the brown mixture was left for 14 h and then kept at 0 °C for 30 min for completion of the precipitation. The solid was removed by filtration and the reddish-orange filtrate was concentrated in vacuo at room temperature to one third of the original volume. This gave rise to a precipitate that was collected by filtration with suction and washed with cold PE to afford 14.5 g (62%) of **9** as a slightly pink solid, m.p. 80 °C. This product could be stored at –35 °C for prolonged periods, but decomposed at room temperature within a week. ^1H NMR (600 MHz, $CDCl_3$): δ = 2.47 (dddd, $J_{6,6}$ = 14.3, $J_{5,6}$ = 8.0 and 3.1, $J_{6,7}$ = 2.5 Hz, 1 H) and 2.49 (dddd, $J_{6,6}$ = 14.3, $J_{5,6}$ = 9.8 and 7.3, $J_{6,7}$ = 5.7 Hz, 1 H) (6-H$^\alpha$, 6-H$^\beta$), 2.79 (dddt, $J_{5,5}$ = 17.6, $J_{5,6}$ = 7.3 and 3.1, $J_{4,5}$ = 1.3, average of $J_{1,5}$ and $J_{5,7}$ = 0.6 Hz, 1 H) and 3.08 (br. dddd, $J_{5,5}$ = 17.6, $J_{5,6}$ = 9.8 and 8.0, $J_{4,5}$ = 2.1 Hz, 1 H) (5-H$^\alpha$, 5-H$^\beta$), 5.28 (br. dd, $J_{6,7}$ = 5.7 and 2.5 Hz, 1 H, 7-H), 6.19 (dtd, $J_{4,5}$ = 2.1, $J_{1,4}$ = $J_{4,5}$ = 1.3, $J_{4,7}$ = 0.6 Hz, 1 H, 4-H), 7.64 (m, 1 H, 1-H) ppm; the assignments are based on H,H-COSY and NOESY experiments. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 29.9 (C-5), 38.2 (C-6), 45.7 (C-7), 109.5 (C-4), 126.2 (C-7a), 147.8 (C-1), 161.4 (C-3), 162.0 (C-4a) ppm; the assignments are based on C,H-COSY and HMBC experiments. IR (KBr): $\tilde{\nu}$ = 1721 (C=O) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 216 (7), 214 (7) $[M]^+$, 136 (19), 135 (100), 134 (19), 107 (16), 79 (35), 78 (29), 77 (53), 51 (24). $C_8H_7BrO_2$ (215.1): calcd. C 44.68, H 3.28; found C 44.55, H 3.56.

Cyclopenta[*c*]pyran-3(5*H*)-one (10a) and Cyclopenta[*c*]pyran-3(7*H*)-one (10b): A solution of **9** (5.00 g, 23.2 mmol) in anhydrous *N*,*N*-dimethylacetamide (100 mL) was added over 5 min to a vigorously stirred suspension of calcium carbonate (14.0 g, 140 mmol) in anhydrous *N*,*N*-dimethylacetamide (100 mL), kept at 110 °C under nitrogen. Stirring was continued under these conditions for 4 h. After cooling to room temperature, the solid components were removed by filtration and washed several times with dichloromethane (a total of 100 mL). The filtrate was concentrated in vacuo (up to 70 °C/0.15 mbar) to give a black solution (15 g), which was subjected to flash chromatography (SiO_2; PE/MTBE, 1:2). In the order of elution, **10a** (714 mg, 24%) and **10b** (1.90 g, 61%) were obtained as brown solids. Recrystallisation from MTBE afforded **10a** (385 mg,

12%) as a light-brown solid, m.p. 61–63 °C, and **10b** (1.65 g, 53%) as light-beige needles, m.p. 95 °C.

10a: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.41 (q, average of $J_{4,5}$, $J_{5,6}$ and $J_{5,7} \approx$ 2.0 Hz, 2 H, 5-H), 6.23 (dt, $J_{6,7}$ = 5.8, $J_{5,6}$ = 2.2 Hz, 1 H, 6-H), 6.32 (quint, average of $J_{1,4}$, $J_{4,5}$ and $J_{4,7} \approx$ 1.3 Hz, 1 H, 4-H), 6.47 (dtd, $J_{6,7}$ = 5.8, $J_{5,7}$ = 2.1, $J_{4,7}$ = 0.9 Hz, 1 H, 7-H), 7.50 (d, $J_{1,4}$ = 1.1 Hz, 1 H, 1-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 37.8 (C-5), 110.0 (C-4), 125.6 (C-7), 127.0 (C-7a), 133.4 (C-6), 141.2 (C-1), 161.8 and 162.0 (C-3 and C-4a) ppm; as far as specified, the assignments are based on a C,H-COSY spectrum. IR (KBr): $\tilde{\nu}$ = 1716 (C=O) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 134 (100) $[M]^+$, 106 (69), 105 (35), 78 (99), 77 (66), 52 (21), 51 (48), 50 (25), 39 (17), 38 (10). HRMS (70 eV, EI): calcd. for $C_8H_6O_2$ $[M]^+$ 134.0368; found 134.0368.

10b: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.39 (td, average of $J_{5,7}$ and $J_{6,7} \approx$ 2.2, $J_{1,7} \approx$ 1.2 Hz, 2 H, 7-H), 6.16 (d, $J_{1,4}$ = 1.1 Hz, 1 H, 4-H), 6.61 (dtd, $J_{5,6}$ = 5.6, $J_{5,7}$ = 2.2, $J \approx$ 0.6 Hz, 1 H, 5-H), 6.87 (dt, $J_{5,6}$ = 5.6, $J_{6,7}$ = 2.3 Hz, 1 H, 6-H), 7.47 (br. quint, $J \approx$ 1.1 Hz, 1 H, 1-H) ppm; the assignment of the signals to 5-H and 6-H is based upon comparison with the spectra of [D_3]-**10b** and [D_4]-**10b** (see below). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 34.2 (C-7), 104.2 (C-4), 120.4 (C-7a), 130.1 (C-5), 144.2 (C-1), 147.2 (C-6), 161.7 (C-4a), 163.3 (C-3) ppm; the assignments are based on C,H-COSY and HMBC experiments. IR (KBr): $\tilde{\nu}$ = 1710 (C=O) cm^{-1}. UV/Vis (CH_3CN): λ_{max} (log ε) = 349 (sh, 3.43), 329 (sh, 3.81), 318 (3.87), 271 (3.49), 260 (3.65), 252 (3.67), 235 (4.13), 228 (4.29), 223 (4.25) nm. MS (70 eV, EI): *m*/*z* (%) = 134 (100) $[M]^+$, 106 (38), 105 (25), 78 (80), 77 (53), 52 (15), 51 (34), 50 (19). $C_8H_6O_2$ (134.1): calcd. C 71.64, H 4.51; found C 71.48, H 4.65.

Reaction of α-Pyrone 10a with DIBAL-H: Diisobutylaluminium hydride (DIBAL-H) (5.74 mmol, 5.74 mL of 1 M in dichloromethane) was added dropwise over 10 min to a stirred solution of **10a** (350 mg, 2.61 mmol) in anhydrous dichloromethane (20 mL), kept at –78 °C under nitrogen. The mixture was stirred at –78 °C for a further 8 h, allowed to warm to room temperature over 15 h, diluted with dichloromethane (100 mL) and treated with a 10% aqueous solution of potassium sodium tartrate (100 mL). The phases were separated and the aqueous phase was extracted with dichloromethane (2 × 50 mL). The combined organic layers were dried with $MgSO_4$ and [D_6]DMSO (1 mL) was added. Thus, by concentration in vacuo at 0 °C, a solution of the crude product in [D_6]DMSO was obtained, of which an NMR spectrum was recorded. The spectrum showed the presence of a very small amount of cyclopenta[*c*]pyran (**1**) in addition to isobutyl alcohol as the major component and a compound assumed to be 3-hydroxy-1,3,4,5- (**14a**) or -1,3,4,7-tetrahydrocyclopenta[*c*]pyran (**14b**). The signals of **1** were identified on the basis of the data of Seitz and co-workers.[2] Flash chromatography of the NMR solution (SiO_2; PE/MTBE, 2:1) gave a yellow resin (31 mg, 9%) of a compound to which structure **14a** or **14b** was assigned. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (ddt, *J* = 17.1, 4.6, 2.6 Hz, 1 H) and 2.70 (dq, *J* = 17.1, *J* ≈ 3 Hz, 1 H) (4-H$^{\alpha}$, 4-H$^{\beta}$), 2.90–2.94 (m, 2 H, CH_2 of the five-membered ring), 3.44 (d, *J* = 4.9 Hz, 1 H, OH), 4.49 (dquint, *J* = 15.3, 2.6 Hz, 1 H) and 4.62 (dquint, *J* = 15.3, 2.6 Hz, 1 H) (1-H$^{\alpha}$, 1-H$^{\beta}$), 5.26 (q, average of *J* = 4.3 Hz, 1 H, 3-H), 6.30 (dt, *J* = 5.6, 1.2 Hz, 1 H) and 6.31 (br. d, *J* = 5.6 Hz, 1 H) (CH=CH) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 32.4 (C-4), 43.1 (CH_2 of the five-membered ring), 61.7 (C-1), 92.2 (C-3), 129.7 and 131.8 (CH=CH), 133.6 and 136.0 (C-4a, C-7a) ppm; as far as specified, the assignments are based on a C,H-COSY spectrum.

Reaction of the α-Pyrone 10b with DIBAL-H: The reaction of **10b** was conducted as for **10a** (see above), giving complex mixtures of products that contained at best traces of cyclopenta[*c*]pyran (**1**). The use of toluene as solvent also led to a complex mixture, in which the yield of **1** was determined to be 1% by NMR spectroscopy using pentachlorobenzene as internal standard.

Treatment of the α-Pyrone 10b with D_2O in the Presence of Triethylamine: A solution of **10b** (200 mg, 1.49 mmol) in anhydrous THF (8 mL) was admixed with D_2O (2 mL) and triethylamine (5 drops). The resulting solution was stirred at room temperature for 4 d and then concentrated in vacuo at room temperature to dryness. The remaining light-brown solid was recrystallised from MTBE giving rise to a 1.5:1.0 mixture of 4,5,7,7-tetradeuterio- ([D_4]-**10b**) and 5,7,7-trideuteriocyclopenta[*c*]pyran-3(7*H*)-one ([D_3]-**10b**) (168 mg, 82%), which was only slightly contaminated by other isotopomers of **10b**, isotopomers of **10a** and a component stemming from triethylamine. The ratio of [D_4]-**10b** and [D_3]-**10b** was determined from the integrals of the signals of 4-H and 6-H. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.16 (dd, $J_{1,4}$ = 1.3, $J_{4,6}$ = 0.4 Hz, 4-H of [D_3]-**10b**), 6.86 (s, 6-H), 7.47 (s, 1-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): [D_4]-**10b**: δ = 33.6 (quint, $J_{C,D}$ = 20.4 Hz, C-7), 103.7 (t, $J_{C,D}$ = 26.4 Hz, C-4), 120.3 (s, C-7a), 129.85 (t, $J_{C,D}$ = 26.1 Hz, C-5), 144.1 (s, C-1), 147.1 (s, C-6), 161.6 (s, C-4a), 163.3 (s, C-3) ppm; [D_3]-**10b**: δ = 33.6 (quint, $J_{C,D}$ = 20.4 Hz, C-7), 104.0 (s, C-4), 120.3 (s, C-7a), 129.89 (t, $J_{C,D}$ = 25.7 Hz, C-5), 144.1 (s, C-1), 147.1 (s, C-6), 161.7 (s, C-4a), 163.3 (s, C-3) ppm. MS (70 eV, EI): *m*/*z* (%) = 138 (100) $[M]^+$, 137 (74) $[M]^+$, 110 (39), 109 (48), 108 (23), 82 (70), 81 (98), 80 (45), 55 (11), 54 (25), 53 (36), 52 (25), 51 (14). HRMS (70 eV, EI): calcd. for $C_8D_4H_2O_2$ $[M]^+$ 138.0619, $C_8D_3H_3O_2$ $[M]^+$ 137.0556; found 138.0620, 137.0560.

3-(Trimethylsilyloxy)cyclopenta[*c*]pyran (16): Chlorotrimethylsilane (44.5 mg, 0.410 mmol), triethylamine (189 mg, 1.87 mmol) and the α-pyrone **10b** (50.0 mg, 0.373 mmol) were combined in anhydrous dichloromethane (4 mL) under nitrogen. The solution was stirred at room temperature for 2.5 h, during which time a reddish-orange colour developed, and then concentrated in vacuo at 0 °C. After the addition of PE (20 mL) to the residue, the mixture was stirred vigorously at room temperature for 10 min. Solid components were then quickly removed by filtration and the solvent of the filtrate was evaporated in vacuo at 0 °C. The residue was a reddish-orange oil (0.5 mL) consisting mainly of PE and containing **16**, **10a** and **10b** in a ratio of 32:6:1. In this mixture, **16** converted completely into **10a** and **10b** at room temperature over a few hours. Attempts to isolate **16** either by short-path distillation in vacuo or by chromatography also resulted in its complete decomposition to **10a** and **10b**. Dissolved in $CDCl_3$, **16** decomposed in about one week. ^{1}H (400 MHz) and ^{13}C NMR (101 MHz): see Table 1 and Table 2.

Cyclopenta[*c*]pyran-3-yl Benzoate (19): Benzoyl chloride (52.4 mg, 0.373 mmol), triethylamine (41.5 mg, 0.410 mmol) and the α-pyrone **10b** (50.0 mg, 0.373 mmol) were combined in anhydrous acetonitrile (4 mL) under nitrogen. The solution was stirred at room temperature for 3 h, during which time a reddish-orange colour developed, and then concentrated in vacuo at 0 °C. After the addition of PE (20 mL) to the residue, the mixture was stirred vigorously at room temperature for 10 min. Solid components were then quickly removed by filtration and the solvent of the filtrate was evaporated in vacuo at 0 °C. The brownish-yellow residue was purified by flash chromatography (neutral Al_2O_3 of activity IV; PE/MTBE, 5:1; –12 °C) to give a yellow-orange solid (58 mg), which was shown by NMR spectroscopy to consist mainly of **19** but contained ca. 20% of an impurity with a benzoyl group. In the absence of a solvent, **19** decomposed to **10a** and **10b** at room temperature within a few days. Solutions in $CDCl_3$ could be stored without a change at –35 °C for several days. ^{1}H (400 MHz) and ^{13}C NMR

(101 MHz): see Table 1 and Table 2. IR (KBr): $\tilde{\nu}$ = 1758 (C=O), 1642 (C=C) cm^{-1}.

Lithium Cyclopenta[*c*]pyran-3-olate (15): Methyllithium (0.373 mmol, 0.266 mL of 1.40 M in diethyl ether) was added to a solution of the α-pyrone **10b** (50.0 mg, 0.373 mmol) in anhydrous THF (4 mL), kept at –78 °C under nitrogen. The deep-red solution was stirred at –78 °C for 15 min prior to further processing.

Alternatively, lithium diisopropylamide was used as the base. It was prepared by the addition of butyllithium (0.131 mmol, 0.095 mL of 1.38 M in hexane) to a solution of diisopropylamine (13.3 mg, 0.131 mmol) in anhydrous THF (3 mL), kept at 0 °C under nitrogen. The solution was stirred at 0 °C for 10 min and then cooled to –78 °C, at which temperature **10b** (16.0 mg, 0.119 mmol) was added. The mixture was stirred at –78 °C for 20 min prior to further processing.

NMR samples of **15** were prepared by conducting the above experiments in a flask with a fused-on NMR tube and a frit between the flask and the NMR tube. The solutions of **15** were allowed to warm to room temperature and then concentrated in vacuo at 20 °C as thoroughly as possible. The residue was treated with anhydrous [D_8]THF and the resulting mixture was passed through the frit into the NMR tube by immersing the tube step-by-step into liquid nitrogen. Finally, the tube was evacuated (0.04 mbar) and sealed. ^{1}H (400 MHz) and ^{13}C NMR (101 MHz): see Table 1 and Table 2.

3-(*tert*-Butyldimethylsilyloxy)cyclopenta[*c*]pyran (17): A solution of the lithium enolate **15** (0.373 mmol) was prepared from **10b** and methyllithium as described above. At –78 °C, *tert*-butylchlorodimethylsilane (56.2 mg, 0.373 mmol), dissolved in anhydrous THF (4 mL), was added. The mixture was then stirred at –78 °C for 1 h, allowed to warm to 0 °C, stirred at 0 °C for 1 h and concentrated in vacuo at 0 °C. After the addition of PE (20 mL) to the residue, the suspension was stirred vigorously at room temperature for 10 min. The solid was quickly removed by filtration and the solvent of the filtrate was evaporated in vacuo at 0 °C. An orange-red oil (55 mg) remained, which was shown by NMR spectroscopy to consist of **17**, **10a** and **10b** in a ratio of 40:1:7. On storing of the NMR sample ($CDCl_3$) at 5 °C for 7 d, the ratio changed to 12:1:4. In the absence of a solvent, **17** decomposed completely at room temperature in 1 d. Attempts to purify **17** either by short-path distillation or flash chromatography led to the instantaneous conversion of **17** into **10a** and **10b**. ^{1}H (400 MHz) and ^{13}C NMR (101 MHz): see Table 1 and Table 2.

3-(Triisopropylsilyloxy)cyclopenta[*c*]pyran (18): A solution of the lithium enolate **15** (0.373 mmol) was prepared from **10b** and methyllithium as described above. At –78 °C, chlorotriisopropylsilane (71.9 mg, 0.373 mmol) was added. The mixture was then stirred at –78 °C for 3 h, warmed to 0 °C and concentrated in vacuo at 0 °C. After the addition of PE (20 mL) to the residue, the suspension was stirred vigorously at room temperature for 10 min. The solid was quickly removed by filtration and the solvent of the filtrate was evaporated in vacuo at 0 °C. An orange-red, viscous oil remained, which was dissolved in MTBE (30 mL). The solution was extracted with saturated aqueous $NaHCO_3$ (2 × 20 mL), dried with $MgSO_4$ and concentrated in vacuo at 0 °C. The residue was purified by flash chromatography (basic Al_2O_3 of activity IV; PE/MTBE, 20:1; –10 °C) to give **18** (65 mg, 60%) as an orange-red resin, which was contaminated by products containing triisopropylsilyl groups. ^{1}H (400 MHz) and ^{13}C (101 MHz): see Table 1 and Table 2.

Cyclopenta[*c*]pyran-3-ylacetonitrile (21): A stirred suspension of the α-pyrone **10b** (900 mg, 6.71 mmol) and (cyanomethylene)triphenylphosphorane (20.2 g, 67.1 mmol) in anhydrous xylene (250 mL) was heated under nitrogen at 145 °C for 23 h. Then further (cyanomethylene)triphenylphosphorane (4.04 g, 13.4 mmol) was added and the mixture was stirred as well as heated for a further 4 h. Analysis by TLC showed that **10b** had now been consumed completely. The dark-brown mixture was allowed to cool to room temperature and filtered. The solvent of the filtrate was evaporated in vacuo and the residue was treated with diethyl ether (4 × 70 mL). After filtration of the extracts, the filtrate was concentrated in vacuo and the dark-brown residue (3.90 g) was purified by flash chromatography (SiO_2; PE/MTBE, 3:1) to give **21** (383 mg, 36%) as an orange-brown solid. A further purification step was carried out by sonication of the product with PE/MTBE (10:1; 15 mL) for 5 min, whereby a black solid separated which was filtered off. The filtrate was stored at –35 °C for 20 h and this gave rise to pure **21** (306 mg, 29%) as yellow-orange needles, m.p. 52–54 °C. ^{1}H (400 MHz) and ^{13}C NMR (101 MHz): see Table 1 and Table 2. IR (KBr): $\tilde{\nu}$ = 2257 (CN), 1635 (C=C) cm^{-1}. UV/Vis (CH_3CN): λ_{max} (log ε) = 401 (3.08), 312 (sh, 3.28), 293 (3.48), 260 (4.16), 250 (4.24), 237 (4.15), 229 (4.15), 217 (4.25) nm. MS (70 eV, EI): *m*/*z* (%) = 157 (100) $[M]^+$, 156 (24), 129 (25), 128 (22), 103 (9), 102 (39), 101 (12), 77 (9), 63 (10), 51 (9). $C_{10}H_7NO$ (157.2): calcd. C 76.42, H 4.49, N 8.91; found C 76.25, H 4.72, N 8.83.

Methyl Cyclopenta[*c*]pyran-3-ylacetate (22): A stirred suspension of the α-pyrone **10b** (650 mg, 4.85 mmol) and (methoxycarbonylmethylene)triphenylphosphorane (11.4 g, 34.1 mmol) in anhydrous xylene (180 mL) was heated under nitrogen at 140 °C for 19 h. Then further (methoxycarbonylmethylene)triphenylphosphorane (3.43 g, 10.3 mmol) was added to the dark-brown mixture, which was stirred as well as heated for a further 6 h. Analysis by TLC showed that **10b** had now been consumed completely. After cooling to room temperature, the mixture was filtered to remove solid components, which were washed with dichloromethane (DCM, 50 mL). The filtrate was concentrated in vacuo to dryness and the residue was digested with diethyl ether (7 × 50 mL). The combined diethyl ether extracts were filtered and the solvent was evaporated in vacuo leaving behind a brown residue (6.50 g), which was subjected to flash chromatography (SiO_2; PE/MTBE, 6:1) resulting in the isolation of a yellow oil. Its storage at –35 °C gave rise to yellow crystals (135 mg, 15%), m.p. 46–47 °C, which were shown by ^{1}H (400 MHz) and ^{13}C NMR spectroscopy (101 MHz) (see Table 1 and Table 2) to be **22**. IR (KBr): $\tilde{\nu}$ = 1725 (C=O), 1636 (C=C) cm^{-1}. UV/Vis (DCM): λ_{max} (log ε) = 407 (3.26), 295 (3.86), 262 (4.28), 252 (4.34) nm. MS (70 eV, EI): *m*/*z* (%) = 190 (26) $[M]^+$, 132 (10), 131 (100), 103 (27), 102 (11), 77 (31), 51 (17). HRMS (70 eV, EI): calcd. for $C_{11}H_{10}O_3$ $[M]^+$ 190.06245; found 190.06246.

2-(Cyclopenta[*c*]pyran-3-yl)ethanol (23): A solution of **22** (80 mg, 0.42 mmol) in anhydrous THF (8 mL) was added over 5 min to a stirred suspension of $LiAlH_4$ (64 mg, 1.69 mmol) in anhydrous THF (5 mL), kept at –70 °C under nitrogen. Analysis by TLC showed that **22** had been consumed completely at –70 °C after 20 min. At this temperature, water (0.065 mL) was then added and, under continued stirring, the cooling bath was removed. At –30 °C, NaOH (0.065 mL of a 15% aqueous solution) and, at 0 °C, water (1.95 mL) were added. When the mixture reached a temperature of 20 °C, the solid components were removed by filtration and washed with diethyl ether (2 × 4 mL). The yellow-orange filtrate was dried with $MgSO_4$ for a short time and concentrated to dryness in vacuo at 5 °C. The dark-red residue, a viscous oil (57 mg, 84%), was characterised by ^{1}H (400 MHz) and ^{13}C NMR spectroscopy (151 MHz) (see Table 1 and Table 2) to be rather pure **23** and was used for trifluoroacetylation without purification since attempts to subject the product to flash chromatography, even on basic Al_2O_3, led to

decomposition. HRMS (ESI$^+$, CH_3CN): calcd. for $C_{10}H_{10}O_2$ $[M]^+$ 162.06753; found 162.06818.

Methyl 7-(Trifluoroacetyl)cyclopenta[*c*]pyran-3-ylacetate (24): Anhydrous triethylamine (Et_3N, 26 mg, 0.26 mmol) and trifluoroacetic anhydride (TFAA, 46 mg, 0.22 mmol) were added in this order to a stirred solution of **22** (40 mg, 0.21 mmol) in anhydrous dichloromethane (DCM, 5 mL), kept at 0–5 °C under nitrogen. The mixture turned dark-reddish-brown immediately and, according to TLC analysis, only a small amount of **22** was left after 10 min. In addition, the formation of a new compound was indicated. After 2 h, further Et_3N (7 mg, 0.07 mmol) and TFAA (15 mg, 0.07 mmol) were added at 5–10 °C. All **22** had been consumed 30 min later. The mixture was then diluted with DCM (15 mL) and washed with water (2×20 mL). The combined aqueous layers were extracted with DCM (2×10 mL) and the combined DCM layers were dried with $MgSO_4$. After evaporation of the solvent in vacuo at 25 °C, a dark-red residue (75 mg) remained, the purification of which by flash chromatography (SiO_2; MTBE/PE, 3:1) afforded almost pure **24** as a yellow solid (25 mg, 42%), m.p. 99–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.77 (s, 3 H, CH_3), 3.86 (s, 2 H, CH_2), 6.56 (d, $J_{5,6}$ = 3.5 Hz, 1 H, 5-H), 7.30 (s, 1 H, 4-H), 8.04 (dq, $J_{5,6}$ = 3.5, $J_{6,F}$ = 2.0 Hz, 1 H, 6-H), 9.31 (s, 1 H, 1-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 39.3 (CH_2), 52.7 (CH_3), 110.9 (C-4), 111.8 (C-5), 115.0 (C-7), 117.4 (q, $J_{C,F}$ = 290 Hz, CF_3), 125.2 (C-7a), 138.8 (C-4a), 145.7 (q, $J_{C,F}$ = 3.3 Hz, C-6), 150.4 (C-3), 152.0 (q, $J_{C,F}$ = 0.6 Hz, C-1), 168.3 (CO_2CH_3), 173.8 (q, $J_{C,F}$ = 34 Hz, $COCF_3$) ppm; the assignments are based on C,H-COSY and HMBC spectra as well as on the comparison with the spectra of 1,4-diphenylcyclopenta[*c*]pyran and its 7-(trifluoroacetyl) derivative.[5,20] ^{19}F NMR (376 MHz, $CDCl_3$, internal reference: $CFCl_3$, δ = 0.0 ppm): δ = –72.4 (d, $J_{H,F}$ = 2.0 Hz) ppm. UV/Vis (DCM): λ_{max} (log ε) = 441 (4.18), 328 (sh, 4.13), 315 (4.24), 300 (4.27), 258 (4.21) nm. IR (KBr): $\tilde{\nu}$ = 1732 (H_3CO–C=O), 1650 (F_3C–C=O), 1639 (C=C) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 286 (33) $[M]^+$, 227 (11), 218 (15), 217 (100), 185 (10), 158 (33), 130 (25), 102 (15). HRMS (ESI$^+$, CH_3CN): calcd. for $C_{13}H_9F_3NaO_4$ $[M + Na]^+$ 309.03451; found 309.03453.

Reaction of 2-(Cyclopenta[*c*]pyran-3-yl)ethanol (23) with Trifluoroacetic Anhydride: Anhydrous Et_3N (64 mg, 0.63 mmol) and TFAA (113 mg, 0.54 mmol) were added in this order to a stirred solution of **23** (39 mg, 0.24 mmol) in anhydrous DCM (10 mL), kept at –60 °C under nitrogen. The colour of the solution changed from orange-red to dark-red immediately. According to TLC analysis (SiO_2; MTBE/PE, 3:1), **23** had been consumed completely and two products had been formed after 10 min. After stirring at –60 °C for a total of 50 min, water (5 mL) was added to the mixture, which, while stirred, was now allowed to warm to 10–15 °C. The layers were separated and the organic layer was washed with water (2×5 mL). The combined aqueous layers were extracted with DCM (2×5 mL). After the combined organic layers had been dried with $MgSO_4$ for a short time, the solvent was evaporated in vacuo at 25 °C. The NMR analysis of the dark-brown residue (67 mg) indicated the formation of two products in a ratio of 2.4:1. Separation by flash chromatography (SiO_2; MTBE/PE, 4:1) furnished, in this order, pure 2-{7-(trifluoroacetyl)cyclopenta[*c*]pyran-3-yl}ethyl trifluoroacetate (**26**) (25 mg, 29%) as a yellow solid, m.p. 73–76 °C, and 2-{7-(trifluoroacetyl)cyclopenta[*c*]pyran-3-yl}ethanol (**25**) (7 mg, 11%) as a yellow solid, m.p. 76–81 °C, which contained some minor impurities.

25: ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 3.11 (apparent t, line distance 6.1 Hz, 2 H, CH_2CH$_2$OH), 3.99 (br. apparent t, line distance 6.1 Hz, 2 H, CH_2OH), 4.01 (very broad, 1 H, OH), 6.61 (dd, $J_{5,6}$ = 3.7, $J_{1,5}$ = 0.8 Hz, 1 H, 5-H), 7.52 (dt, $J_{1,4}$ = 1.0, $J_{4,CH2}$ = 0.5 Hz, 1 H, 4-H), 8.03 (dq, $J_{5,6}$ = 3.7, $J_{6,F}$ = 2.2 Hz, 1 H, 6-H), 9.38 (≈t, average of $J_{1,4}$ and $J_{1,5}$ = 0.9 Hz, 1 H, 1-H) ppm. ^{13}C NMR (101 MHz, [D$_6$]acetone): δ = 38.1 (*C*H$_2$CH$_2$OH), 60.2 (CH$_2$OH), 110.8 (C-4), 111.7 (q, $J_{C,F}$ = 0.8 Hz, C-5), 114.3 (C-7), 118.6 (q, $J_{C,F}$ = 290 Hz, CF_3), 126.1 (C-7a), 141.7 (C-4a), 145.9 (q, $J_{C,F}$ = 3.4 Hz, C-6), 153.4 (q, $J_{C,F}$ = 0.8 Hz, C-1), 159.2 (C-3), 173.0 (q, $J_{C,F}$ = 33.6 Hz, *C*OCF$_3$) ppm; the assignments are based on a C,H-COSY spectrum and the comparison with the spectra of 1,4-diphenylcyclopenta[*c*]pyran and its 7-(trifluoroacetyl) derivative.[5,20] ^{19}F NMR (376 MHz, [D$_6$]acetone, internal reference: $CFCl_3$, δ = 0.0 ppm): δ = –71.3 (d, $J_{H,F}$ = 2.2 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3423 (br., OH), 1638, 1626 (C=O, C=C) cm^{-1}. UV/Vis (DCM): λ_{max} (log ε) = 445 (4.27), 326 (4.14), 314 (4.28), 299 (4.30), 261 (4.13) nm. MS (70 eV, EI): *m*/*z* (%) = 258 (50) $[M]^+$, 227 (11), 190 (13), 189 (100), 171 (28), 158 (32), 130 (23), 102 (15). HRMS (ESI$^+$, CH_3CN): calcd. for $C_{12}H_9F_3NaO_3$ $[M + Na]^+$ 281.03960; found 281.03774.

26: ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 3.48 (apparent t, line distance 6.2 Hz, 2 H, CH_2CH$_2$O), 4.89 (apparent t, line distance 6.2 Hz, 2 H, CH$_2$O), 6.66 (dd, $J_{5,6}$ = 3.7, $J_{1,5}$ = 0.8 Hz, 1 H, 5-H), 7.61 (m, 1 H, 4-H), 8.06 (dq, $J_{5,6}$ = 3.7, $J_{6,F}$ = 2.1 Hz, 1 H, 6-H), 9.38 (m, 1 H, 1-H) ppm. ^{13}C NMR (101 MHz, [D$_6$]acetone): δ = 33.4 (*C*H$_2$CH$_2$O), 66.2 (CH$_2$O), 111.1 (C-4), 112.4 (q, $J_{C,F}$ = 0.8 Hz, C-5), 114.9 (C-7), 115.5 (q, $J_{C,F}$ = 285 Hz, OCO*C*F$_3$), 118.5 (q, $J_{C,F}$ = 290 Hz, CCO*C*F$_3$), 126.0 (C-7a), 140.8 (C-4a), 146.1 (q, $J_{C,F}$ = 3.5 Hz, C-6), 153.4 (q, $J_{C,F}$ = 0.8 Hz, C-1), 155.9 (C-3), 157.6 (q, $J_{C,F}$ = 41.9 Hz, O*C*OCF$_3$), 173.3 (q, $J_{C,F}$ = 33.7 Hz, C*C*OCF$_3$) ppm; the assignments are based on a C,H-COSY spectrum and the comparison with the spectra of 1,4-diphenylcyclopenta[*c*]pyran and its 7-(trifluoroacetyl) derivative.[5,20] ^{19}F NMR (376 MHz, [D$_6$]acetone, internal reference: $CFCl_3$, δ = 0.0 ppm): δ = –74.9 (s, 3 F, OCOCF$_3$), –71.5 (d, $J_{H,F}$ = 2.1 Hz, 3 F, CCOCF$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 1778 (O–C=O), 1639, 1629 (C=O, C=C) cm^{-1}. UV/Vis (DCM): λ_{max} (log ε) = 443 (4.28), 327 (4.16), 313 (4.30), 300 (4.34), 258 (4.21) nm. MS (70 eV, EI): *m*/*z* (%) = 354 (44) $[M]^+$, 285 (60), 240 (17), 172 (16), 171 (100), 158 (11), 130 (13), 115 (17), 69 (11). HRMS (70 eV, EI): calcd. for $C_{14}H_8F_6O_4$ $[M]^+$ 354.03213; found 354.03231.

Reaction of Cyclopenta[*c*]pyran-3-ylacetonitrile (21) with Trifluoroacetic Anhydride

{7-(Trifluoroacetyl)cyclopenta[*c*]pyran-3-yl}acetonitrile (27): Anhydrous Et_3N (39 mg, 0.38 mmol) and TFAA (67 mg, 0.32 mmol) were added in this order to a stirred solution of **21** (50 mg, 0.32 mmol) in anhydrous DCM (7 mL) at room temperature under nitrogen. The mixture turned dark-reddish-brown immediately and, according to TLC analysis, a new compound had formed within 10 min. However, a significant amount of **21** was still present, which is why more Et_3N and TFAA were added after 1 and 2 h [7 mg (0.07 mmol) and 15 mg (0.07 mmol), respectively, each time]. Since still some **21** was left after a total of 3.5 h, further Et_3N (7 mg, 0.07 mmol) and TFAA (15 mg, 0.07 mmol) were added, which led to the total consumption of **21**. After a total of 4 h, the mixture was diluted with DCM (15 mL) and washed with water (2×25 mL). The combined aqueous layers were extracted with DCM (2×30 mL) and the combined DCM layers were dried with $MgSO_4$. After evaporation of the solvent in vacuo at 30 °C, a black residue (150 mg) remained, which was subjected to flash chromatography (SiO_2). Elution with MTBE/PE (3:1) furnished **27** (20 mg, 25%) as yellow crystals, m.p. 132–135 °C. By changing the eluant to MTBE/PE/ethanol (3:2:1), fractions of 15 and 7 mg were obtained, which mainly consisted of salts with the anions **29** and **28**, respectively.

27: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.98 (d, $J_{4,CH2}$ = 0.9 Hz, 2 H, CH_2), 6.65 (dd, $J_{5,6}$ = 3.5, $J_{1,5}$ = 0.9 Hz, 1 H, 5-H), 7.44 (q, $J_{1,4}$ = $J_{4,CH2}$ = 0.9 Hz, 1 H, 4-H), 8.08 (dq, $J_{5,6}$ = 3.5, $J_{6,F}$ = 2.0 Hz, 1 H, 6-H), 9.27 (td, $J_{1,4}$ = $J_{1,5}$ = 0.9, $J_{1,6}$ = 0.4 Hz, 1 H, 1-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 22.9 (CH_2), 109.8 (C-4), 112.9 (q, $J_{C,F}$ = 0.9 Hz, C-5), 113.8 (CN), 116.0 (C-7), 117.2 (q, $J_{C,F}$ = 291 Hz, CF_3), 125.2 (C-7a), 137.1 (C-4a), 145.6 (C-3), 146.3 (q, $J_{C,F}$ = 3.5 Hz, C-6), 151.5 (C-1), 174.2 (q, $J_{C,F}$ = 34.9 Hz, *C*OCF_3) ppm; the assignments are based on C,H-COSY and HMBC spectra as well as on a comparison with the spectra of 1,4-diphenylcyclopenta[*c*]pyran and its 7-(trifluoroacetyl) derivative.[5,20] ^{19}F NMR (376 MHz, $CDCl_3$, internal reference: $CFCl_3$, δ = 0.0 ppm): δ = –72.6 (d, $J_{H,F}$ = 2.0 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2262 (CN), 1655 (C=O), 1638 (C=C) cm^{-1}. UV/Vis (DCM): λ_{max} (log ε) = 439 (3.87), 328 (sh, 3.74), 314 (sh, 3.92), 300 (3.99), 256 (3.95) nm. MS (70 eV, EI): *m*/*z* (%) = 253 (29) $[M]^+$, 185 (14), 184 (100), 156 (19), 101 (13). HRMS (70 eV, EI): calcd. for $C_{12}H_6F_3NO_2$ $[M]^+$ 253.03451; found 253.03471. $C_{12}H_6F_3NO_2$ (253.2): calcd. C 56.93, H 2.39, N 5.53; found C 56.68, H 2.58, N 5.39.

A Salt of [Hydroxy(trifluoromethyl)methylene]{7-(trifluoroacetyl)cyclopenta[*c*]pyran-3-yl}acetonitrile (a Salt with Anion 28): Anhydrous Et_3N (77 mg, 0.76 mmol) and TFAA (134 mg, 0.64 mmol) were added in this order to a stirred solution of **21** (50 mg, 0.32 mmol) in anhydrous DCM (7 mL) at room temperature under nitrogen. The mixture turned dark-reddish-brown immediately and, according to TLC analysis, two new compounds had been formed in addition to **27** within 10 min. After 1 h, **21** had been consumed almost completely and the major product was **27**. After a further 3 h, again Et_3N (7 mg, 0.07 mmol) and TFAA (15 mg, 0.07 mmol) were added and, 30 min later, the mixture was diluted with DCM (15 mL) and washed with water (2×25 mL). The combined aqueous layers were extracted with DCM (2×30 mL) and the combined DCM layers were dried with $MgSO_4$. After evaporation of the solvent in vacuo at 30 °C, the black residue (140 mg) was subjected to flash chromatography on SiO_2 (2×30 cm). With MTBE/PE (4:1, 600 mL) as eluant, **27** (20 mg, 25%) was obtained. A change to MTBE/PE/ethanol (4:1:2, 600 mL) as eluant then yielded, in the order of elution, **29** (30 mg, as a salt with an unknown cation) and a 1:9 mixture of **29** and **28** (40 mg, as salts with unknown cations), as dark-red resins.

28: ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 6.37 (dd, $J_{5,6}$ = 4.0, $J_{1,5}$ = 0.7 Hz, 1 H, 5-H), 7.88 (dq, $J_{5,6}$ = 4.0, $J_{6,F}$ = 2.2 Hz, 1 H, 6-H), 8.55 (d, $J_{1,4}$ = 1.0 Hz, 1 H, 4-H), 9.16 (≈t, average of $J_{1,4}$ and $J_{1,5}$ ≈ 0.8 Hz, 1 H, 1-H) ppm. ^{13}C NMR (101 MHz, [D$_6$]acetone): δ = 69.3 (*C*CN), 104.7 (C-4), 110.2 (q, $J_{C,F}$ = 0.8 Hz, C-5), 111.9, 119.3, 125.9, 145.5, 160.0 (CN, C-3, C-4a, C-7, C-7a), 119.2 and 119.6 (each q, $J_{C,F}$ = 291 Hz, 2 CF_3), 145.9 (q, $J_{C,F}$ = 3.6 Hz, C-6), 149.6 (C-1), 169.9 (q, $J_{C,F}$ = 31 Hz) and 170.4 (q, $J_{C,F}$ = 33 Hz) (2 *C*OCF_3) ppm; the assignment of the signals to C-1, C-4, C-5, C-6 is based on a C,H-COSY spectrum. ^{19}F NMR (376 MHz, [D$_6$]acetone, internal reference: $CFCl_3$, δ = 0.0 ppm): δ = –71.1 (s, 3 F), –70.6 (d, $J_{H,F}$ = 2.2 Hz, 3 F) ppm. MS (8.0 kV, Ar, FAB^+, 3-nitrobenzyl alcohol): *m*/*z* (%) = 394 (12) [**28** + 2 $Na]^+$, 213 (79) $[C_{10}H_4F_3O_2]^+$, 176 (100) [3-nitrobenzyl alcohol + $Na]^+$. MS (8.0 kV, Ar, FAB^-, 3-nitrobenzyl alcohol): *m*/*z* (%) = 719 (3) [2 **28** + $Na]^-$, 348 (100) $[\mathbf{28}]^-$.

A Salt of [Hydroxy(trifluoromethyl)methylene]{5,7-bis(trifluoroacetyl)cyclopenta[*c*]pyran-3-yl}acetonitrile (a Salt with Anion 29): Anhydrous Et_3N (97 mg, 0.96 mmol) and TFAA (134 mg, 0.64 mmol) were added in this order to a stirred solution of **21** (100 mg, 0.64 mmol) in anhydrous DCM (10 mL) at room temperature under nitrogen. After 10 min, TLC analysis (SiO_2; MTBE/PE, 4:1) of the dark-reddish-brown mixture indicated three products (R_f = 0.55, 0.10, 0.06), the major one of which was **27**, and still some **21**. Again Et_3N and TFAA were added after 3 and 3.5 h [150 mg (1.5 mmol) and 230 mg (1.1 mmol), respectively, each time], whereby the mixture became still darker. After a total of 4 h, **21** had been consumed completely and only a small amount of **27** was left. Then the mixture was diluted with DCM (20 mL) and washed with water (2×25 mL) as well as brine (40 mL). The combined aqueous layers were extracted with DCM (2×60 mL) and the combined DCM layers were dried with $MgSO_4$. After evaporation of the solvent in vacuo at 25 °C, the black residue (410 mg) was subjected to flash chromatography (SiO_2, 2×30 cm; MTBE/PE/ethanol, 3:1:1, 300 mL, and then 2:1:2, 600 mL) to afford pure **29** (60 mg, 20%, as calculated for the sodium salt) and a fraction (110 mg) of **29** contaminated with impurities as red-brown resins, which showed a green fluorescence in solution. When a layer of hexane was put on top of a concentrated solution of the pure substance in ethyl acetate in an NMR tube, long and thin orange needles, m.p. 201–205 °C, grew at room temperature within days. ^{1}H NMR (400 MHz, [D$_6$]DMSO, the values in brackets refer to a [D$_6$]-acetone solution): δ = 8.09 [8.21] (sept, $J_{6,F}$ = 2.0 Hz, 1 H, 6-H), 9.22 [9.29] (d, $J_{1,4}$ = 1.3 Hz, 1 H, 4-H), 9.40 [9.43] (d, $J_{1,4}$ = 1.3 Hz, 1 H, 1-H) ppm. ^{13}C NMR (101 MHz, [D$_6$]DMSO): δ = 72.2 (*C*CN), 105.8 (C-4), 111.2, 112.9, 117.5, 124.4, 146.9, 165.0 (CN, C-3, C-4a, C-5, C-7, C-7a), 116.90 (q, $J_{C,F}$ = 292 Hz), 116.95 (q, $J_{C,F}$ = 291 Hz) and 117.7 (q, $J_{C,F}$ = 292 Hz) (3 CF_3), 143.6 (sept, $J_{C,F}$ = 3.6 Hz, C-6), 150.6 (C-1), 169.8 (q, $J_{C,F}$ = 31.4 Hz), 172.1 (q, $J_{C,F}$ = 33.7 Hz) and 172.8 (q, $J_{C,F}$ = 33.7 Hz) (3 *C*OCF_3) ppm; the assignment of the signals to C-1, C-4, C-6 is based on a C,H-COSY spectrum. ^{19}F NMR (376 MHz, [D$_6$]DMSO, the values in brackets refer to a [D$_6$]acetone solution, internal reference: $CFCl_3$, δ = 0.0 ppm): δ = –71.3 [–72.3] (d, $J_{H,F}$ = 2.0 Hz, 3 F), –71.0 [–72.0] (s, 3 F), –70.4 [–71.4] (d, $J_{H,F}$ = 2.0 Hz, 3 F) ppm. IR (KBr): $\tilde{\nu}$ = 2213 (CN), 1644, 1626 (C=O, C=C) cm^{-1}. UV/Vis (ethyl acetate): λ_{max} (log ε) = 490 (4.27), 397 (3.95), 341 (4.16), 327 (sh, 4.10), 272 (4.29) nm. Fluorescence (ethyl acetate) on excitation at λ = 450 nm: λ_{max} = 537 nm, quantum yield Φ_f = 0.55. MS (8.0 kV, Ar, FAB^+, 3-nitrobenzyl alcohol): *m*/*z* (%) = 957 (21) [2 **29** + 3 $Na]^+$, 490 (67) [**29** + 2 $Na]^+$, 176 (100) [3-nitrobenzyl alcohol + $Na]^+$. MS (8.0 kV, Ar, FAB^-, 3-nitrobenzyl alcohol): *m*/*z* (%) = 911 (8) [2 **29** + $Na]^-$, 444 (100) $[\mathbf{29}]^-$. HRMS (ESI^-, CH_3CN): calcd. for $C_{16}H_3F_9NO_4$ $[\mathbf{29}]^-$ 443.99238; found 443.99364; the spectrum contains no further signals.

A solution of Na^+**29** (20 mg) in diethyl ether (15 mL) was extracted with saturated aqueous KCl (2×7 mL). After drying of the ether solution with $MgSO_4$ and evaporation of the solvent in vacuo, an FAB^+ mass spectrum (8.0 kV, Ar, 3-nitrobenzyl alcohol) was recorded: *m*/*z* (%) = 1005 (16) [2 **29** + 3 $K]^+$, 989 (14) [2 **29** + 2 K + $Na]^+$, 973 (4) [2 **29** + K + 2 $Na]^+$, 522 (75) [**29** + 2 $K]^+$, 506 (25) [**29** + K + $Na]^+$, 490 (7) [**29** + 2 $Na]^+$, 192 (100) [3-nitrobenzyl alcohol + $K]^+$, 176 (40) [3-nitrobenzyl alcohol + $Na]^+$.

Acknowledgments

We are grateful to Prof. Christoph Lambert and his group for recording the UV/Vis spectra and determining the fluorescence data. Dr. Elena Bogdan thanks the Alexander von Humboldt Foundation and the Hertie Foundation for a Roman Herzog Research Fellowship.

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Received: August 18, 2005
Published Online: November 15, 2005

