Pergamon

Tetrahedron 54 (1998) 12807–12822

TETRAHEDRON

Stannylated α-Pyrones: Synthesis, Halogenation and Destannylation Reactions

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Dedicated to Prof. Dr. Gernot Boche on the occasion of his 60th birthday.

Received 7 July 1998; accepted 3 August 1998

Abstract

Ethynyltributyltin undergoes inverse type [4+2] cycloadditions with various 1,3,4-oxadiazin-6-ones to afford two regioisomeric stannylated α-pyrones, which can be separated by flash column chromatography. Exposure of the stannanes to elemental halogens in chloroform or THF as solvent yields the corresponding halogeno pyrones. A general exception of this reaction type is also described. Destannylation with dry hydrogen chloride furnishes 3,6-disubstituted α-pyrones.

Keywords: *Cycloadditions; Tin and compounds; Alkynes; Pyrones*

INTRODUCTION

The cycloaddition of alkynes to 1,3,4-oxadiazin-6-ones with subsequent loss of nitrogen in a cycloreversion reaction offers a way to highly substituted α-pyrones [1, 2]. But, due to the inverse-type character of these Diels-Alder reactions, their usefulness was restricted to highly reactive alkynes like angle strained dienophiles, e.g. benzyne and cyclooctyne, and the electron-rich N,N-dimethylaminopropyne. During these investigations Christl et al. reported the use of norbornadiene in the presence of boron trifluoride-diethyl ether or trifluoroacetic acid as a synthetic equivalent for acetylene in this reaction [3].

We had recently found that organotin alkynes are reactive dienophiles in inverse-type Diels-Alder reactions with 1,2,4,5-tetrazines [4, 5, 6]. A combination with the less electron deficient 1,2,4-triazines is also possible, but requires forcing reaction conditions [7]. The increasing

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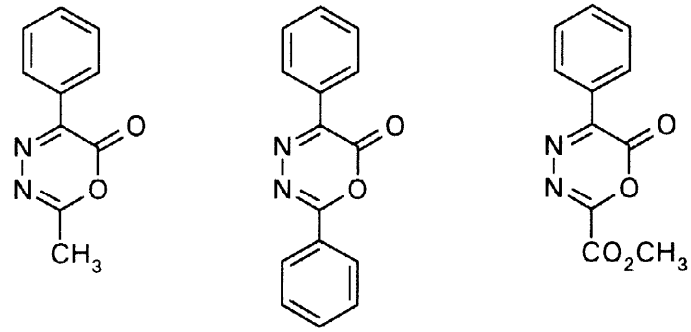
** X-ray crystal structure analysis

0040-4020/98/$ - see front matter
PII: S0040-4020(98)00754-6

importance of organostannanes as synthetic intermediates [8, 9] prompted us to investigate the reactivity of organotin alkynes in Diels-Alder reactions with 1,3,4-oxadiazin-6-ones **1-3** (Figure 1). The low-lying LUMO's of these compounds are responsible for their ability to serve as electron poor dienes in inverse-type Diels-Alder reactions. Hence, **3** should be the most reactive (-I, -M-effect), followed by **2** (-M-effect) and **1** (+I-effect). The substituent effects were also confirmed qualitatively by semiempirical calculations [10]: The important LUMO energy levels decrease as expected from **1** (-1.39 eV) to **2** (-1.59 eV) and again to -1.85 eV for **3**. For comparison, the calculated LUMO energy for 1,2,4,5-tetrazine (-1.30 eV) is found in the same range. In addition, the different size of $-CH_3$, $-C_6H_5$ and $-CO_2CH_3$ should have a considerable influence on these [4+2] cycloadditions.



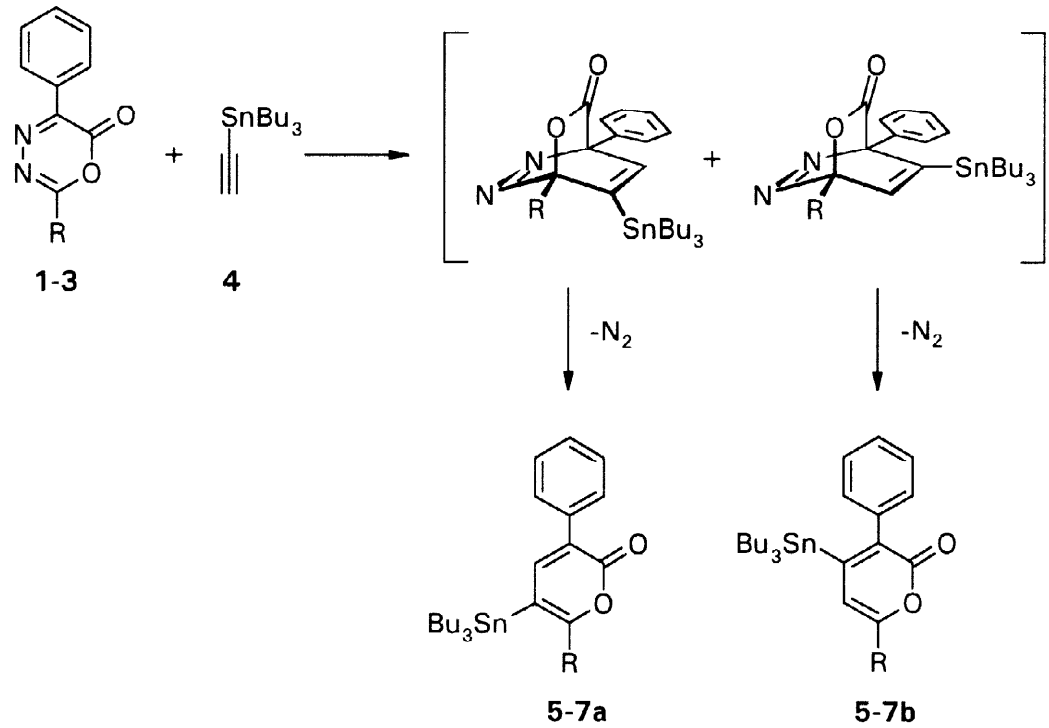
1 2 3

Figure 1. 1,3,4-Oxadiazin-6-ones used in this study.

Results and Discussion

In the exploratory studies we had to recognize, that generally high reaction temperatures were necessary for successful reactions in contrast to the tetrazines. Apparently steric interactions play a major part and decrease the reaction rate drastically. This is not bewildering when the proposed bicyclic intermediate formed in the cycloaddition is considered. Strong steric interactions between the bulky tributyltin group of the alkyne and the substituents of the 1,3,4-oxadiazin-6-one have to be overcome in the transition state leading to the bicyclic intermediate (Scheme 1). However, the stability of the organotin alkynes tolerated drastic conditions up to reflux in 1,2-dichlorobenzene at 180°C for 16h to compensate for this lack of reactivity. In agreement with earlier reports [1, 2] the bicyclic intermediates lose rapidly molecular nitrogen in a cycloreversion and can not be isolated. Hence, always α-pyrones and never pyridazine derivatives were obtained, which would be the products resulting from the cycloaddition with subsequent loss of carbon dioxide. A further cycloaddition of a second equivalent of ethynyltributyltin to the 1,3-diene system of the α-pyrone could not be observed, too. For all cases, the cycloaddition with the unsymmetrical ethynyltributyltin afforded two regioisomers, which could be separated by flash column chromatography.

Heating **2** and ethynyltributyltin **4** (1.5 fold excess) in refluxing 1,2-dichlorobenzene at 180°C overnight (16h) afforded a mixture of regioisomeric α-pyrones in a ratio of approximately 2:1. The progress of the reaction was monitored by volumetric methods and thin layer chromatography. After chromatographic work-up of the crude mixture pure α-pyrones **6a** and **6b** were isolated in 49 respectively 31% yield. Likewise **1** afforded in an identical procedure the α-pyrones **5a** and **5b** (yield 33 and 23%). The more reactive ester substituted 1,3,4-oxadiazin-6-one **3** combined with ethynyltributyltin **4** more smoothly in refluxing toluene at 110°C (>95% complete after 10h). This corresponds to an approximately onehundred-fold increase in reactivity in comparison with heterocycles **1** and **2**. The two isomers **7a** and **7b** were isolated in 50% and 31% yield. Reaction conditions and yields are summarized in Scheme 1 and Table 1.



Scheme 1. Synthesis of stannylated α-pyrones by cycloaddition reactions.

Table 1. Reaction conditions and yields for Scheme 1.

Diene	Solvent	T [°C]	t [h]	R	Yield [%]		Yield [%]	
1	1,2-dichlorobenzene	180	16	$-CH_3$	**5a**	33	**5b**	23
2	1,2-dichlorobenzene	180	16	$-C_6H_5$	**6a**	49	**6b**	31
3	toluene	110	10	$-CO_2CH_3$	**7a**	50	**7b**	31

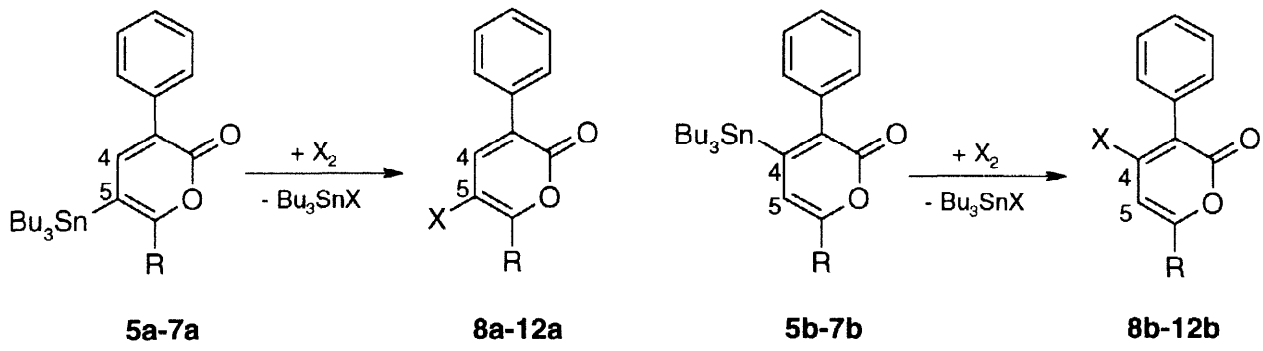
The regiochemistry of the cycloadditions studied leading to compounds **5-7** could be easily assigned by comparing the ^{1}H-chemical shifts of the α-pyrone hydrogens in 4- or 5- position with

the parent compounds **17-19**. The hydrogen atom at carbon 4, which is part of an electron withdrawing lactone system, suffers a downfield shift of about 0.5 ppm in comparison with the hydrogen atom attached to carbon-5.

The mass spectra of the compounds **5-7** showed a weak molecular ion peak (rel. int. between 0.2 and 2%). The first characteristic fragment radical cation (100% peak for **5** and **7**) resulted from the loss of one butyl group from the tin atom. **6** seems to be much less stable compared with **5** and **7**. The MS showed numerous additional fragments. Correct elemental analyses were obtained for all stannyl compounds except **6b**, showing that even the oily compounds can be obtained in analytically pure form by flash column chromatography.

The stannylated α-pyrones obtained in these cycloadditions are useful synthetic intermediates. Halodemetallation with halogens offers the possibility to synthesize 3,4,6- or 3,5,6-trisubstituted α-pyrones which are regiospecifically halogenated in 4- or 5-position. This method furnishes the products of the hypothetic cycloaddition of halogeno alkynes to 1,3,4-oxadiazin-6-ones. Chloro-, bromo-, and iodoalkynes are unstable, difficult to handle and may decompose explosively upon heating. Furthermore, these alkynes are also deactivated towards inverse-type Diels-Alder reactions due to the electron withdrawing halogen substituent, so the direct cycloaddition will not be possible.

When the partial charges in the α-pyrone ring system are considered, the 4-position in **5-7** is deactivated towards electrophilic substitution because of the electron withdrawing lacton fragment. In contrast, an attack of an electrophile in position 5 should take place more smoothly. The more reactive halogens (chlorine in CCl_4 or bromine in $CHCl_3$) showed no reactivity difference between trialkyltin groups in 4- or 5-position and replaced these immediately and regiospecifically in good yields. But, the less reactive iodine reacted with **6a** in THF at RT within 3h to afford 3,6-diphenyl-5-iodo-pyran-2-one **10a**, whereas the reaction time for the conversion of **6b** to 3,6-diphenyl-4-iodo-pyran-2-one **10b** increased to three weeks at ambient temperature, as indicated by the disappearance of the brownish iodine colour. It seems that the reaction rate can be increased by changing the solvent from THF to $CHCl_3$. For example, the reaction time required for the conversion of **5b** to **12b** amounted only 4d in $CHCl_3$. Our results are summarized in Scheme 2, Table 2 gives further details.



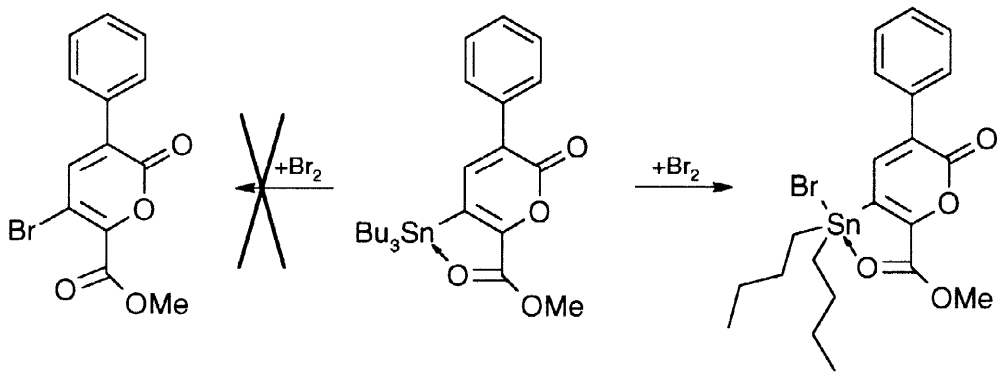
Scheme 2. Regiospecific electrophilic displacement of the tributyltin substituent by halogens.

Table 2. Reaction conditions and yields for the reactions of Scheme 2.

Starting material	R	Position $SnBu_3/X$	X_2	Reaction conditions and time	Product	Yield [%]	M.p. [°C]
6a	**Ph**	5-	Cl_2	CH_2Cl_2/CCl_4, RT	**8a**	82	147
6a	Ph	5-	Br_2	$CHCl_3$, -60°C	**9a**	87	145-146
6a	Ph	5-	I_2	THF, RT, 3h	**10a**	61	130
5a	CH_3	5-	Br_2	$CHCl_3$, -60°C	**11a**	80	91
5a	CH_3	5-	I_2	$CHCl_3$, RT, 1h	**12a**	69	107-108
6b	Ph	4-	Cl_2	CH_2Cl_2/CCl_4, RT	**8b**	51	148-150
6b	Ph	4-	Br_2	$CHCl_3$, -60°C	**9b**	78	162
6b	Ph	4-	I_2	THF, RT, 21d	**10b**	69	158-160
5b	CH_3	4-	Br_2	$CHCl_3$, -60°C	**11b**	55	119
5b	CH_3	4-	I_2	$CHCl_3$, RT, 4d	**12b**	52	132
7b	CO_2CH_3	4-	Br_2	$CHCl_3$, -60°C	**13b**	65	148

The hitherto unknown compounds exhibited the expected ^1H and ^{13}C spectra. The iodopyrones show the expected upfield shift of the iodinated carbon in the ^{13}C NMR spectra, whereas for the brominated and chlorinated carbons a downfield shift is observed. The EI mass spectra invariably showed correct molecular peaks (100% for most cases). Extrusion of CO leads to the first fragment radical cation. Further fragments are in full concordance with reasonable dissociation pathways.

A totally different outcome was observed for the reaction of **7a** with bromine. Combining **7a** with one equivalent of bromine at -60°C in chloroform, a rapid disappearance of the red-brownish bromine colour was observed indicating an immediate reaction. But, after work-up the crystalline colourless product still showed intense signals for aliphatic hydrogens in the IR and ^1H NMR spectra.



7a **13a**

Scheme 3. Unexpected substitution at tin caused by an ester function adjacent to the tin group.

Something unexpected had happened: Apparently the oxygen of the carbonyl group exerts a strong interaction on the tin atom. Therefore, the normal reactivity sequence is reversed and substitution of a butyl group instead of the unsaturated pyrone ring system takes place (Scheme 3). The proposed structure of **13a** was unambiguously proven by X-ray analysis (Figure 2). Figure 2 shows that the pyrone ring system and the ester function are arranged nearly in a plane (dihedral angles: O1-C6-C7-O71 175.47°, C5-C6-C7-O72 172.46°), which is due to a non covalent interaction of the carbonyl oxygen (O71) with the tin atom (Sn1). The O71-Sn1 distance of only 2.61 Å is very short. The geometric arrangement (relevant bond angles: C5-Sn1-Br2 94.75°, C15-Sn1-Br2 101.56°, C19-Sn1-Br2 101.48°, C19-Sn1-C15 119.07°, C19-Sn1-C5 115.00°, C15-Sn1-C5 118.22°) at the tin center resembles an intermediate between a trigonal bipyramidal structure and the originally expected tetrahedral arrangement, if the carbonyl oxygen (O71) is considered as additional substituent. Further bond lengths and angles show no exceptional values, e.g. the two planes formed by the phenyl and the pyrone ring are tilted (dihedral angle C4-C3-C9-C14 38.99°, C2-C3-C9-C10 40.36°).

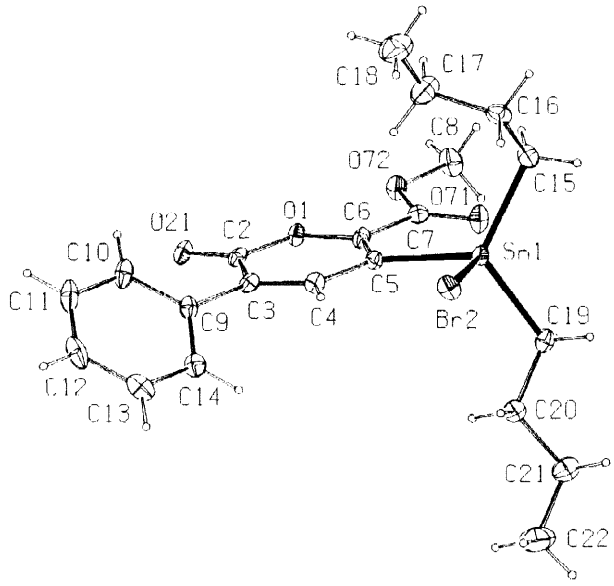
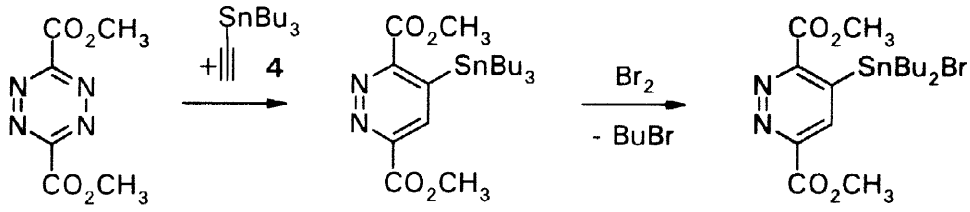


Figure 2. ORTEP-plot of compound **13a** with crystallographic numbering system. Ellipsoids are drawn at the 50% probability level while isotropic H-atom thermal parameters are represented by spheres of arbitrary size.

This reactivity reversal has already been reported in the literature for a similar case [11]. These observations show, that this effect of the ester group, similar to a neighbouring group effect, is of general importance and has to be taken into account for all analogous transformations of related structures.

To underline this statement, we synthesized an additional similar compound **16**. In contrast to the data reported [12], in our hands the organotin alkyne **4** reacted smoothly at room temperature with the very electron-deficient 1,2,4,5-tetrazine **14** to give the stannylated pyridazine **15**, with the

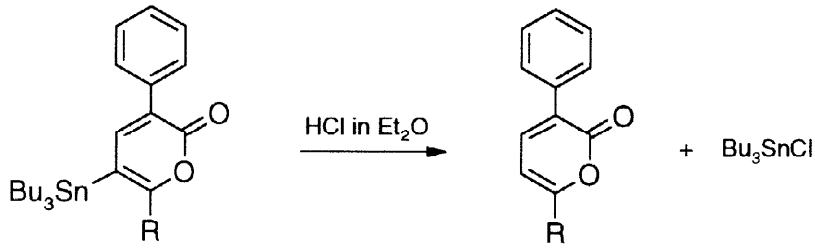
ester function in ortho position to the tributyltin substituent. Product **16** was obtained by the same procedure given above and unambiguously characterized by its spectroscopic data (Scheme 4).



14 **15** **16**

Scheme 4. A further example for the influence of an ester group on the reactivity of trialkyltin substituents.

The stannyl group could be replaced in the pyrone derivates **5a-7a** by hydrogen using dry hydrogen chloride in diethyl ether to furnish 3,6-disubstituted α-pyrones **17-19** in good yields (47-80%) without any complications. For this case, ethynyltributyltin serves as a synthetic equivalent for acetylene in a straightforward combination of cycloaddition and subsequent proto-destannylation (Scheme 5).



5a-7a **17-19**

Scheme 5. Protodestannylation of **5a-7a** with hydrogen chloride to 3,6-disubstituted α-pyrones (**17**: R = –CH_3, 48%, **18**: R = –Ph, 80%, **19**: R = –CO_2CH_3, 49%).

This procedure was also used for the selective deuterium labelling of the 5-position with deuterated trifluoroacetic acid (chemical yield 83%, but only 70% deuterium content). Probably due to the partial charge distribution discussed above, selective deuterium labelling of **5b** proceeded very slowly. Yield and deuterium content were very low (each about 30%, deuterium content determined by ^1H NMR spectroscopy). Low incorporation of deuterium has already been reported in the literature [13], and these authors blamed the purity of the acid used for these discouraging results. This is at least not true for our work, because of the different deuterium contents incorporated in 4- and 5 position. However, reasons for an explanation of these unsatisfactory results remain unclear to us.

CONCLUSION

The direct cycloaddition between electron poor and unstable halogenated alkynes and electron poor 1,3,4-oxadiazin-6-ones is not possible, but can be achieved by the two-step sequence of a cycloaddition and a subsequent halodemetallation. Organotin alkynes react with electron poor 1,3,4-oxadiazin-6-ones in good yields to furnish stannylated cycloadducts, which can be easily halogenated in a subsequent step, albeit an exception exists for compounds with an ester function in ortho position to the trialkyltin substituent. Nevertheless, this combination provides an easy access to a variety of hitherto unknown α-pyrones not otherwise available from Diels-Alder reactions or other synthetic strategies.

EXPERIMENTAL SECTION

General: IR spectra were recorded with a Beckmann Acculab 1. NMR spectra were obtained with a Bruker AC250 (250 MHz for ^1H and 63 MHz for ^{13}C). All NMR spectra were taken in $CDCl_3$ with TMS as an internal standard. The degree of substitution of the C atoms was determined by the DEPT-135 method. Mass spectra were recorded at an ionizing voltage of 70 eV by electron impact with a Varian MAT311A instrument. Melting points were determined with a Büchi melting point apparatus and are uncorrected. Elemental analyses were performed in the microanalytical laboratory of the Chemical Institute of the University of Regensburg. For analytical thin layer chromatography precoated plastic sheets (POLYGRAM SIL G/UV254, Macherey-Nagel) were used. Silicagel 60 (particle size 0.040-0.063 mm, Merck) was used for flash column chromatography (fcc). Reactions were carried out under a nitrogen atmosphere. Solvents for reactions were dried according to standard procedures. Compounds **1** [14], **2** [1, 15], **3** [16], **4** [17] (purity 97.5%, GC) and **14** [18] were prepared according to literature procedures.

Reaction of ethynyltributyltin (**4**) *and 2-methyl-5-phenyl-1,3,4-oxadiazin-6-one* (**1**)*:* A mixture of **4** (3.88 ml, 13.4 mmol) and **1** (1.68 g, 8.94 mmol) in 1,2-dichlorobenzene (35 ml) was stirred at 180°C for 14 h. After removal of the solvent under reduced pressure a crude mixture of **5a** and **5b** was obtained as a brown oil. Isomers were separated by fcc (silicagel 60, 200 g, petroleum ether 40/60 : ethyl acetate 97 : 3).

6-Methyl-3-phenyl-5-tributylstannyl-pyran-2-one (**5a**): The first fraction gave pure **5a** as a yellow oil (1.41 g, 33%), R_f = 0.47 (petroleum ether 40/60 : ethyl acetate 85 : 15). – IR (film): ν = 3070, 3030, 2965, 2930, 2880, 2860, 1710, 1590, 1540, 1450, 1180, 1070, 1030, 930, 790, 695. – ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.91 (t, J = 7.1 Hz, 9 H, $-CH_2-CH_3$), 1.07-1.15 (m, 6 H, $-CH_2-$), 1.21-1.42 (m, 6 H, $-CH_2-$), 1.47-1.67 (m, 6 H, $-CH_2-$), 2.31 (s, 3 H, $-CH_3$), 7.31-7.44 (m, 3 H, aromatic H), 7.33 (s, 1 H, $=C^4-H$, pyranone), 7.60-7.65 (m, 2 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 10.16 (3C), 13.56 (3C), 22.25, 27.19 (3C), 28.96 (3C), 110.47, 124.76, 128.02,

128.13 (2C), 128.35 (2C), 135.43, 146.89, 162.54, 164.75. – MS (70eV, EI); *m/z* (%): 476 (2) [M^+], 419 (30) [M^+-C_4H_9], 293 (79), 186 (92) [M^+-$SnBu_3$+H], 179 (36), 177 (38), 158 (100) [186-CO], 115 (72) [158-CH_3CO], 105 (45) [$PhCO^+$], 77 (24) [Ph^+], 57 (19) [$C_4H_9^+$], 43 (85) [CH_3CO^+]. – $C_{24}H_{36}O_2Sn$ (475.2): calcd. C 60.66, H 7.64; found C 60.33, H 7.57.

6-Methyl-3-phenyl-4-tributylstannyl-pyran-2-one (**5b**): The second fraction gave **5b** as a yellow oil (974 mg, 23%), R_f = 0.37 (petroleum ether 40/60 : ethyl acetate 85 : 15). – IR (film): ν = 3060, 3030, 2950, 2920, 2870, 2850, 1700, 1610, 1510, 1455, 1435, 1370, 1350, 1065, 1015, 925, 780, 740, 690. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.66-0.92 (m, 15 H, –C*H*$_2$–, –C*H*$_3$), 1.14-1.46 (m, 12 H, –C*H*$_2$–), 2.26 (d, *J* = 1.0 Hz, 3 H, –C*H*$_3$), 6.10 (q, *J* = 1.0 Hz, 1 H, =C^5–*H*), 7.33-7.40 (m, 5 H, aromatic H). – The compound was to unstable for correct elemental analysis within ± 0.4%. The structure proof relies on the following reaction products.

Reaction of ethynyltributyltin (**4**) *with 2,5-diphenyl-1,3,4-oxadiazin-6H-one* (**2**)*:* **4** (2.25 ml, 7.55 mmol) was added to **2** (1.50 g, 6.00 mmol) dissolved in dry 1,2-dichlorobenzene (15 ml). The reaction mixture was stirred at 180°C for 16h. After cooling, the solvent was removed under reduced pressure (50°C, 0.1 Torr) to give a brown oil. The regioisomers were separated by means of fcc (silicagel 60, 100 g, CH_2Cl_2).

3,6-Diphenyl-5-tributylstannyl-pyran-2-one (**6a**): The first fraction consisted of pure **6a** (1.56 g, 49%), R_f = 0.26 (CH_2Cl_2), bright yellow crystals, m.p. 55-56°C. – IR (KBr): ν = 3075, 3040, 2960, 2930, 2880, 2860, 1710, 1595, 1580, 1510, 1490, 1450, 870, 700, 690. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.76-1.00 (m, 15 H, –C*H*$_2$–, –C*H*$_3$), 1.12-1.35 (m, 6 H, –C*H*$_2$–), 1.35-1.53 (m, 6 H, –C*H*$_2$–), 7.33-7.48 (m, 6 H, aromatic H), 7.51 (s, 1 H, =C^4–*H*), 7.54-7.59 (m, 2 H, aromatic H), 7.67-7.72 (m, 2 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 11.16 (3C), 13.55 (3C), 27.18 (3C), 28.85 (3C), 112.05, 125.67, 128.27, 128.31 (4C), 128.45 (2C), 128.49 (2C), 130.19, 135.38, 135.86, 147.30, 162.06, 165.43. – MS (70eV, EI); *m/z* (%): 538 (2) [M^+], 481 (100) [M^+-C_4H_9], 367 (28) [M^+-3C_4H_9], 233 (17), 220 (16), 105 (26) [$PhCO^+$], 77 (14) [Ph^+]. – $C_{29}H_{38}O_2Sn$ (537.3): calcd. C 64.83, H 7.13; found C 64.82, H 7.24.

3,6-Diphenyl-4-tributylstannyl-pyran-2-one (**6b**): Fcc yielded **6b** (990 mg, 31%) as an yellow oil, R_f = 0.20 (CH_2Cl_2). – IR (film): ν = 3070, 3040, 2960, 2930, 2880, 2860, 1710, 1600, 1570, 1510, 1450, 1375, 1355, 1100, 1075, 1050, 1025, 925, 905, 770, 700, 690. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.77 (m, 6 H, Sn–C*H*$_2$–), 0.86 (t, *J* = 7.1 Hz, 9 H, –C*H*$_3$), 1.20-1.32 (m, 6 H, –C*H*$_2$–), 1.34-1.51 (m, 6 H, –C*H*$_2$–), 6.81 (s, $J_{Sn\text{-}H}$ = 27.8 Hz, 1 H, =C^5–*H*), 7.33-7.56 (m, 8 H, aromatic H), 7.82-7.88 (m, 2 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 11.04 (3C), 13.53 (3C), 27.18 (3C), 28.89 (3C), 108.04, 125.61 (2C), 128.29, 128.35 (2C), 128.89 (2C), 129.64 (2C), 130.28, 131.90, 135.29, 138.87, 156.46, 160.12, 162.37. – MS (70eV, EI); *m/z* (%): 538 (0.6) [M^+], 481 (100) [M^+-C_4H_9], 367 (7) [M^+-3C_4H_9], 339 (20) [367-CO], 233 (14), 105 (32) [$PhCO^+$], 77 (15) [Ph^+]. – $C_{29}H_{38}O_2Sn$ (537.3): calcd. C 64.83, H 7.13; found C 64.90, H 7.25.

Reaction of ethynyltributyltin (**4**) *and 6-oxo-5-phenyl-1,3,4-oxadiazin-2-carboxylic acid methyl ester* (**3**)*:* A mixture of **4** (0.68 ml, 2.35 mmol) and **3** (439 mg, 2.19 mmol) in toluene (5 ml) was refluxed for 10 h to yield after evaporation of the solvent a crude mixture of **7a** and **7b** as an orange oil (69:31 determined by means of ^{1}H NMR spectroscopy). Isomers were separated by fcc (silicagel 60, 100 g, CH_2Cl_2 : ethyl acetate 100 : 0 → 50 : 50).

6-Oxo-5-phenyl-3-tributylstannyl-6H-pyran-2-carboxylic acid methyl ester (**7a**): The first fraction gave **7a** as pale yellow crystals (462 mg, 50%), m.p. 69-70°C. – IR (film): ν = 3060, 3040, 2960, 2930, 2880, 2860, 1730, 1710, 1450, 1320, 1270, 1190, 1070, 790, 780, 695. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.89 (t, *J* = 7.2 Hz, 9 H, –C*H*$_3$), 1.08-1.19 (m, 6 H, –C*H*$_2$–), 1.22-1.42 (m, 6 H, –C*H*$_2$–), 1.46-1.59 (m, 6 H, –C*H*$_2$–), 3.95 (s, 3 H, –OC*H*$_3$), 7.40-7.47 (m, 3 H, aromatic H), 7.57 (s, 1 H, =C^4–*H*, pyranone ring, Sn side bands), 7.67-7.71 (m, 2 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 11.26 (3C), 13.64 (3C), 27.29 (3C), 29.01 (3C), 53.15, 123.55, 128.46 (2C), 128.57 (2C), 129.23, 131.56, 134.53, 144.81, 149.89, 160.22, 162.15. – MS (70eV, EI); *m/z* (%): 520 (0.2) [M$^+$], 463 (100) [M$^+$-C_4H_9], 349 (12), 321 (8), 150 (13). – $C_{25}H_{36}O_4Sn$ (519.3): calcd. C 57.83, H 6.99; found C 57.88, H 6.95.

6-Oxo-5-phenyl-4-tributylstannyl-6H-pyran-2-carboxylic acid methyl ester (**7b**): The second fraction gave **7b** as yellow oil (287 mg, 31%). IR (film): ν = 3070, 3040, 2960, 2920, 2880, 2860, 1720, 1620, 1440, 1370, 1310, 1260, 1230, 1070, 930, 765, 695. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.73-0.88 (m, 15 H, –C*H*$_2$–, –C*H*$_3$), 1.15-1.50 (m, 12 H, –C*H*$_2$–), 3.94 (s, 3 H, –OC*H*$_3$), 7.24 (s, 1 H, =C–H, pyranone ring, Sn side bands), 7.29-7.34 (m, 2 H, aromatic H), 7.38-7.44 (m, 3 H, Phenyl-H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 11.06 (3C), 13.46 (3C), 27.08 (3C), 28.77 (3C), 52.83, 116.72, 128.40 (2C), 128.88, 129.26 (2C), 138.10, 142.08, 144.95, 158.27, 160.54 (2C). – MS (70eV, EI); *m/z* (%): 463 (100) [M$^+$-C_4H_9], 205 (41), 151 (29), 77 (19) [Ph$^+$]. – $C_{25}H_{36}O_4Sn$ (519.3): calcd. C 57.83, H 6.99; found C 57.35, H 7.07.

General procedure A for the chlorination of stannyl compounds 6a and 6b: The organotin compound was dissolved in dry CH_2Cl_2 (app. 0.05 mmol/ml). Chlorine (1.1 eq.) in CCl_4 (app. 0.075 mmol/ml) was added at RT over a period of approximately 5 min. After completion of the addition, the reaction mixture was stirred for further 30 min at RT. Removal of the solvent under reduced pressure gave the crude product, which was purified by recrystallization from cyclohexane.

5-Chloro-3,6-diphenyl-pyran-2-one (**8a**): Following the *general procedure A* **6a** (215 mg, 0.40 mmol) yielded 93 mg (0.33 mmol, 82%) of **8a**, yellow plates, m.p. 147°C. – IR (KBr): ν = 3060, 1725, 1615, 1550, 1490, 1440, 1100, 1000, 900, 780, 690. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.40-7.51 (m, 6 H, aromatic H), 7.54 (s, 1 H, =C^4–*H*, pyranone ring), 7.69-7.74 (m, 2 H, aromatic H), 7.90-7.98 (m, 2 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 111.74, 126.68, 128.24 (2C), 128.41 (2C), 128.61 (2C), 128.75 (2C), 129.20, 130.53, 130.81, 133.39, 142.55, 155.46,

159.98. – MS (70eV, EI); *m/z* (%): 282 (83) [M^+], 254 (100) [M^+-CO], 191 (24), 189 (17), 149 (32) [M^+-CO-PhCO],127 (13), 114 (11) [149-Cl^+], 105 (58) [$PhCO^+$], 77 (68) [$C_6H_5^+$]. – $C_{17}H_{11}O_2Cl$ (282.7): calcd. C 72.22, H 3.92; found C 71.91, H 4.10.

4-Chloro-3,6-diphenyl-pyran-2-one (**8b**): Following the *general procedure A* **6b** (120 mg, 0.22 mmol) yielded 50 mg (0.18 mmol, 51%) of **8b**, pale yellow crystals, m.p. 148-150°C. – IR (KBr): ν = 3065, 1710, 1610, 1550, 1490, 1450, 1350, 1320, 1060, 930, 825, 765, 695, 685. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 6.84 (s, 1 H, =C^5–*H*, pyranone ring), 7.39-7.50 (m, 8 H, aromatic H), 7.84-7.89 (m, 2 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 104.75, 123.91, 125.81 (2C), 128.24 (2C), 128.79, 129.10 (2C), 130.03 (2C), 130.39, 131.42, 132.14, 147.79, 158.35, 160.68. – MS (70eV, EI); *m/z* (%): 282 (58) [M^+], 254 (100) [M^+-CO], 149 (23), 114 (13), 105 (47) [$PhCO^+$], 77 (60) [Ph^+]. – $C_{17}H_{11}O_2Cl$ (282.7): calcd. C 72.22, H 3.92; found C 71.97, H 4.35.

*General procedure **B** for the bromination of stannyl compounds:* The organotin compound was dissolved in $CHCl_3$ (0.05 mmol/ml) and cooled to -60°C under an atmosphere of dry nitrogen. Bromine (1 eq.) in $CHCl_3$ (0.05 mmol/ml) was added over a period of approximately 10 min. After completion of the addition, the cooling bath was removed and the reaction mixture was allowed to reach ambient temperature. Stirring was continued for further 2h. The solvent was removed under reduced pressure and the residue purified by fcc (silicagel 60, 10-15 g, petroleum ether 40/60 : ethyl acetate) unless otherwise stated. Final recrystallization from the indicated solvent gave analytically pure product.

5-Bromo-3,6-diphenyl-pyran-2-one (**9a**): Following the *general procedure **B*** **6a** (180 mg, 0.335 mmol) yielded after recrystallization from cyclohexane 96 mg (0.29 mmol, 87%) of **9a**, pale yellow crystals, m.p. 145-146°C. – IR (film): ν = 3030, 1720, 1600, 1540, 1470, 1430, 1040, 880, 770, 680. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.36-7.60 (m, 6 H, aromatic H), 7.66 (s, 1 H, =C^4–*H*, pyranone ring), 7.68-7.83 (m, 2 H, aromatic H), 7.85-7.92 (m, 2 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 98.51, 126.90, 128.27 (2C), 128.31 (2C), 128.60 (2C), 129.04 (2C), 129.18, 130.81, 131.55, 133.35, 144.63, 156.87, 160.15. – MS (70eV, EI); *m/z* (%): 326 (94) [M^+], 298 (62) [M^+-CO], 189 (30), 114 (15), 105 (100) [$PhCO^+$], 77 (77) [Ph^+] – $C_{17}H_{11}O_2Br$ (327.2): calcd. C 62.41, H 3.39; found C 62.58, H 3.48.

4-Bromo-3,6-diphenyl-pyran-2-one (**9b**): Following the *general procedure **B*** **6b** (141 mg, 0.262 mmol) yielded after recrystallization from cyclohexane 67 mg (0.21 mmol, 78%) of **9b**, colourless needles, m.p. 162°C. – IR (KBr): ν = 3060, 1715, 1600, 1565, 1540, 1385, 1445, 1435, 1345, 1305, 1190, 1050, 905, 760, 750, 700, 685, 635. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.00 (s, 1 H, =C^5–*H*, pyranone ring), 7.37-7.55 (m, 8 H, aromatic H), 7.83-7.88 (m, 2 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 107.37, 125.85 (2C), 126.76, 128.28 (2C), 128.80, 129.10 (2C), 129.84 (2C), 130.25, 131.40, 134.17, 139.17, 157.99, 159.82. – MS (70eV, EI); *m/z* (%): 326 (44)

[M^+], **298** (56) [M^+-CO], 191 (21), 114 (21), 105 (100) [$PhCO^+$], 77 (93) [Ph^+]. – $C_{17}H_{11}O_2Br$ (327.2): **calcd.** C 62.41, H 3.39; found C 62.43, H 3.37.

5-Bromo-6-methyl-3-phenyl-pyran-2-one (**11a**): Following **the *general procedure B*** **5a** (205 mg, 0.43 mmol) yielded after recrystallization from hexane 92 mg (0.35 mmol, 80%) of **11a**, colourless plates, m.p. 91-91.5°C. – IR (KBr): ν = 3070, 3050, 2980, 1710, 1615, 1550, 1435, 1320, 1210, 1075, 1030, 925, 790, 740, 700, 615. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.42 (s, 3 H, $-CH_3$), 7.39-7.45 (m, 3 H, aromatic H), 7.48 (s, 1 H, $=C^4-H$, pyranone ring), 7.60-7.65 (m, 2 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.64, 99.44, 126.25, 128.14 (2C), 128.52 (2C), 128.94, 133.52, 143.27, 158.63, 160.61. – MS (70eV, EI); *m/z* (%): 264 (100) [M^+], 236 (98) [M^+-CO], 193 (30) [236-CH_3CO], 157 (29) [236-Br], 129 (22) [157-CO], 128 (25), 115 (52), 105 (28), 88 (14), 77 (16) [Ph^+], 63 (20), 43 (97) [CH_3CO^+]. – $C_{12}H_9O_2Br$ (265.1): calcd. C 54.37, H 3.42; found C 54.07, H 3.68.

4-Bromo-6-methyl-3-phenyl-pyran-2-one (**11b**): Following the *general procedure B* **5b** (147 mg, 0.31 mmol) yielded after recrystallization from hexane/cyclohexane (2:1) 45 mg (0.17 mmol, 55%) of **11b**, colourless needles, m.p. 119°C. – IR (KBr): ν = 3100, 3030, 2920, 1705, 1620, 1600, 1560, 1440, 1350, 1300, 1230, 940, 825, 775, 750, 700. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.28 (d, J = 0.7 Hz, 3 H, $-CH_3$), 6.36 (d, J = 0.7 Hz, 1 H, $=C^5-H$, pyranone ring), 7.33-7.47 (m, 5 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.40, 109.69, 125.99, 128.25 (2C), 128.65, 129.76 (2C), 134.14, 139.11, 159.85, 160.52. – MS (70eV, EI); *m/z* (%): 264 (51) [M^+], 236 (63) [M^+-CO], 193 (11) [236-CH_3CO], 157 (8) [238-Br], 129 (18) [157-CO], 114 (52) [157-CH_3CO], 43 (100) [CH_3CO^+]. – $C_{12}H_9O_2Br$ (265.1): calcd. C 54.37, H 3.42; found C 54.09, H 3.52.

4-Bromo-6-oxo-5-phenyl-6H-pyran-2-carboxylic acid methyl ester (**13b**): Following the *general procedure B* **7b** (212 mg, 0.41 mmol) yielded after recrystallization from petroleum ether 40/60 : ethyl acetate (50 : 50) 82 mg (0.27 mmol, 65%) of **13b**, colourless crystals, m.p. 148°C. – IR (KBr): ν = 3070, 2940, 1705, 1610, 1540, 1420, 1345, 1290, 1240, 1100, 1070, 990, 950, 940, 920, 915, 870, 820, 750,735, 690. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.96 (s, 3 H, $-OCH_3$), 7.41 (s, 1 H, $=C^5-H$, pyranone ring), 7.36-7.50 (m, 5 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 53.33, 116.20, 128.37 (2C), 129.37 (2C), 129.43, 133.28, 133.31, 136.63, 146.07, 157.98, 159.05. – MS (70eV, EI); *m/z* (%): 308 (52) [M^+], 280 (6) [M^+-CO], 249 (100) [280-OCH_3], 221 (5) [249-CO], 193 (58) [221-CO], 114 (76) [193-Br], 88 (16). – $C_{13}H_9O_4Br$ (309.1): calcd. C 50.51, H 2.93; found C 50.49, H 3.14.

3-(Bromo-dibutyl-stannyl)-6-oxo-5-phenyl-6H-pyran-2-carboxylic acid methyl ester (**13a**): Following the *general procedure B* **7a** (169 mg, 0.325 mmol) yielded crude crystals after evaporation of the solvent, which were purified without fcc by two recrystallizations from cyclohexane to afford **13a** (102 mg, 0.19 mmol, 58%), colourless crystals, m.p. 108°C. – IR (KBr):

ν = 3050, 3010, 2950, 2920, 2860, 2840, 1725, 1580, 1530, 1435, 1350, 1330, 1285, 1075, 1020, 785, 775, 705, 695. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.91 (t, J = 7.2 Hz, 6 H, –CH_3), 1.32-1.70 (m, 12 H, –CH_2–CH_2–CH_2–), 4.07 (s, 3 H, –OCH_3), 7.40-7.50 (m, 3 H, aromatic H), 7.74-7.77 (m, 2 H, aromatic H), 8.19 (s, 1 H, =C^4–H, pyranone ring). – MS (70eV, EI); *m/z* (%): M^+ not detectable, 485 (100) [M^+-C_4H_9], 463 (11) [M^+-Br], 349 (15) [M^+-2C_4H_9-Br], 321 (14) [349-CO], 171 (16). – $C_{21}H_{27}BrO_4Sn$ (542.0): calcd. C 46.53, H 5.02; found C 46.11, H 5.00.

X-Ray structural analysis of compound **13a** [19-21]: – *Crystal Data*: $C_{21}H_{27}BrO_4Sn$, M_r = 542.03, monoclinic, $P2_1/c$, a = 15.7430(10), b = 7.2327(4), c = 19.4470(10) Å, α = 90.00, β = 101.744(7), γ = 90.00°, V = 2168.0(2) Å^3, Z = 4, D_x = 1.661 g/cm^3, Mo-K_α radiation (λ = 0.71069 Å), graphite monochromator, μ = 3.044 mm^{-1}, F(000) = 1080, colourless prisms (0.8 × 0.4 × 0.2 mm). – *Data Collection*: Stoe IPDS diffractometer, 13164 measured reflections, 4050 independent reflections, 3137 observed reflections [$I \geq 2\sigma(I)$], Θ = 1.65 - 26.05°, h = -19 → 19, k = -8 → 8, l = -23 → 23. – *Refinement:* Full matrix least-squares refinement on F^2, $wR(F^2)$ = 0.0463, R = 0.0337, S = 0.841, 4050 reflections used for refinement of 259 parameters, $(\Delta/\sigma)_{max}$ < 0.001, H atoms riding, $\Delta\rho_{max}$ = 0.802 e Å^{-3}, $\Delta\rho_{min}$ = -0.879 e Å^{-3}, program(s) used to solve structure: *SIR92* (Altomare et al., **1993**), program(s) used to refine structure: *SHELXL-93* (Sheldrick, **1993**), software used to prepare material for publication: *PLATON* (Spek, **1990**). – Further details of the crystal structure investigation have been deposited at the Cambridge Crystallographic Data Centre.

General procedure C for the iodination of stannyl compounds: The organotin compound (ca. 0.3 mmol) was dissolved in THF or $CHCl_3$ (5 ml). Iodine (1 eq.) in THF (5 ml) or $CHCl_3$ (saturated solution, app. 10 ml) was added over a period of approximately 10 min. The reaction mixture was stirred in the dark until the iodine colour disappeared. Removal of the solvent under reduced pressure was followed by fcc (silicagel 60) and recrystallization to give the analytically pure product.

5-Iodo-3,6-diphenyl-pyran-2-one (**10a**): Following the *general procedure C* (THF, 16h) **6a** (183 mg, 0.34 mmol) yielded after recrystallization from cyclohexane 78 mg (0.21 mmol, 61%) of **10a**, pale yellow crystals, m.p. 130°C. – IR (KBr): ν = 3060, 3040, 1700, 1590, 1530, 1485, 1440, 1050, 980, 800, 780, 770, 690. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.36-7.52 (m, 6 H, aromatic H), 7.65-7.72 (m, 2 H, aromatic H), 7.77-7.84 (m, 2 H, aromatic H), 7.79 (s, 1 H, =C^4–H, pyranone ring). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 67.23, 127.25, 128.25 (2C), 128.28 (2C), 128.58 (2C), 129.10 (2C), 129.35, 130.79, 133.31, 133.37, 149.23, 159.75, 160.42. – MS (70eV, EI); *m/z* (%): 374 (100) [M^+], 346 (40) [M^+-CO], 247 (8) [M^+-I], 219 (12) [M^+-I-CO], 191 (26) [219-CO], 128 (12) [HI], 114 (9) [219-PhCO], 105 (67) [PhCO$^+$], 77 (44) [$C_6H_5^+$]. – $C_{17}H_{11}O_2I$ (374.2): calcd. C 54.57, H 2.96; found C 54.39, H 2.87.

4-Iodo-3,6-diphenyl-pyran-2-one (**10b**): Following the *general procedure C* (THF, 21d) **6b** (120 mg, 0.22 mmol) yielded after recrystallization from cyclohexane 58 mg (0.15 mmol, 69%) of

10b, colourless crystals, m.p. 163°C. – IR (KBr): ν = 3050, 1715, 1600, 1565, 1530, 1485, 1440, 1345, 1300, 760, 740, 690. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.21 (s, 1 H, =C^5–*H*, pyranone ring), 7.34-7.49 (m, 8 H, aromatic H), 7.80-7.88 (m, 2 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 112.66, 117.52, 125.86 (2C), 128.40 (2C), 128.85, 129.08 (2C), 129.56 (2C), 130.04, 131.28, 132.18, 137.83, 157.66, 157.76. – MS (70eV, EI); *m/z* (%): 374 (44) [M^+], 346 (26) [M^+-CO], 191 (13), 105 (100) [$PhCO^+$], 77 (52) [Ph^+]. – $C_{17}H_{11}O_2I$ (374.2): calcd. C 54.57, H 2.96; found C 54.58, H 3.03.

5-Iodo-6-methyl-3-phenyl-pyran-2-one (**12a**): Following the *general procedure* ***C*** ($CHCl_3$, 1h) **5a** (241 mg, 0.51 mmol) yielded after recrystallization from hexane 89 mg (0.35 mmol, 69%) of **12a**, colourless crystals, m.p. 107-108°C. – IR (KBr): ν = 3060, 3030, 2920, 1700, 1590, 1530, 1185, 1075, 1010, 930, 920, 775, 690. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.51 (s, 3 H, –C*H*$_3$), 7.33-7.45 (m, 3 H, aromatic H), 7.58 (s, 1 H, =C^4–*H*, pyranone ring), 7.60-7.65 (m, 2 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 23.15, 68.67, 126.54, 128.13 (2C), 128.50 (2C), 128.87, 133.45, 147.79, 160.86, 161.35. – MS (70eV, EI); *m/z* (%): 312 (100) [M^+], 284 (51) [M^+-CO], 241 (7) [284-CH_3CO], 185 (9) [M^+-I], 157 (19) [185-CO], 115 (32), 105 (21), 77 (7) [Ph^+], 63 (8), 43 (18) [CH_3CO^+]. – $C_{12}H_9O_2I$ (312.1): calcd. C 46.18, H 2.91; found C 45.90, H 3.07.

4-Iodo-6-methyl-3-phenyl-pyran-2-one (**12b**): Following the *general procedure* ***C*** ($CHCl_3$/4d) **5b** (239 mg, 0.50 mmol) yielded after recrystallization from hexane/cyclohexane (5:1) 82 mg (0.26 mmol, 52%) of **12b**, colourless needles, m.p. 132°C. – IR (KBr): ν = 3080, 3020, 2910, 1700, 1610, 1590, 1530, 1430, 1370, 1340, 1285, 1215, 925, 760, 740, 685. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.51 (d, *J* = 1.0 Hz, 3 H, –C*H*$_3$), 6.58 (d, *J* = 1.0 Hz, 1 H, =C^5–*H*, pyranone ring), 7.27-7.34 (m, 2 H, aromatic H), 7.38-7.47 (m, 3 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.04, 114.81, 117.61, 128.36 (2C), 128.71, 129.51 (2C), 131.42, 137.82, 158.44, 159.47. – MS (70eV, EI); *m/z* (%): 312 (91) [M^+], 284 (30) [M^+-CO], 185 (5) [M^+-I], 157 (50) [284-I], 142 (10) [157-CH_3], 129 (33) [157-CO], 114 (29) [157-CH_3CO], 88 (10), 63 (11), 43 (100) [CH_3CO^+]. – $C_{12}H_9O_2I$ (312.1): calcd. C 46.18, H 2.91; found C 46.27, H 3.14.

4-Tributylstannyl-pyridazine-3,6-dicarboxylic acid dimethyl ester (**15**): 1,2,4,5-Tetrazine-3,6-dicarboxylic acid methyl ester **14** (395 mg, 2.0 mmol) was dissolved in dry CH_2Cl_2 (16 ml) at ambient temperature. Ethynyltributyltin **4** (600 µl, 660 mg, 2.1 mmol) was added with stirring. The red tetrazine colour disappeared during one hour. The solvent was evaporated under reduced pressure and the resulting orange oil subjected to fcc (silicagel 60, 30 g, petroleum ether 40/60 : EtOH 6:1, R_f=0.48) to furnish **15** as yellow oil (833 mg, 1.72 mmol, 86%), which solidified at +4°C. – IR (KBr): ν = 2960, 2920, 2860, 2840, 1740, 1715, 1430, 1345, 1280, 1240, 1170, 1130, 1060, 950, 850, 810, 760. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.88 (t, 9 H, CH_2–C*H*$_3$), 1.10-1.23 (m, 6 H, –C*H*$_2$–), 1.25-1.39 (m, 6 H, –C*H*$_2$–), 1.43-1.63 (m, 6 H, –C*H*$_2$–), 4.09 (s, 6H, O–C*H*$_3$), 8.44 (s, $^3J_{Sn\text{-}H}$=34.1 Hz, 1 H, =C–*H*). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 11.31 (3C), 13.51 (3C),

27.17 (3C), 28.93 (3C), 53.30, 53.60, 136.93, 148.50, 150.31, 157.29, 164.85, 167.03. – MS (70eV, EI); *m/z* (%): 486 (0.2) [M^+], 455 (1) [M^+-OCH_3], 429 (100) [M^+-C_4H_9], 315 (15) [M^+-3 C_4H_9], 271 (8) [315-CO_2], 177 (3), 151 (9), 57 (8), 41 (17). $C_{20}H_{34}N_2O_4Sn$ (481.8): calcd. C 49.51, H 7.06, N 5.77; found C 49.40, H 7.17, N 4.99.

4-(Bromo-dibutyl-stannyl)-pyridazine-3,6-dicarboxylic acid dimethyl ester (**16**): Following the *general procedure B* **15** (300 mg, 0.62 mmol) and bromine (99 mg, 32 µl, 0.62 mmol) yielded after evaporation of the solvent crude **16**, which was purified by fcc (silicagel 60, 15 g, ethyl acetate) and recrystallization from petroleum ether 40/60 to furnish yellow plates (138 mg, 0.27 mmol, 44%), m.p. 72-73°C. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.86 (t, *J* = 7.2 Hz, 6 H, –CH_2–CH_3), 1.23-1.71 (m, 12 H, –CH_2–), 4.12 (s, 3 H, –CO_2CH_3), 4.24 (s, 3 H, –CO_2CH_3), 9.07 (s, 1 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.40 (2C), 21.04 (2C), 26.27 (2C), 28.06 (2C), 53.52, 55.30, 137.40, 148.82, 152.13, 154.72, 164.16, 170.56. – MS (70eV, EI); *m/z* (%): 451 (65) [M^+-C_4H_9], 335 (15), 315 (20), 199 (22), 57 (100) [$C_4H_9^+$], 41 (41). – $C_{16}H_{25}BrN_2O_4Sn$ (508.2): calcd. C 37.83, H 4.35, N 5.51; found C 38.26, H 4.83, N 5.54.

6-Methyl-3-phenyl-pyran-2-one (**17**): **5b** (150 mg, 0.316 mmol) was dissolved in dry cyclohexane (2 ml). 1.0M HCl in Et_2O (0.5 ml) was added dropwise to the stirred solution at RT. After stirring for further 15 min, the solvent was removed in a stream of dry nitrogen. The residue was purified by chromatography (silicagel 60, 20 g, petroleum ether 40/60 : ethyl acetate 95:5). The product solidified overnight at -20°C and was recrystallized from petroleum ether 40/60 to give colourless needles of **17** (28 mg, 0.15 mmol, 48%), m.p. 67-68°C; m.p. 67°C [3]. – IR (KBr): ν = 3080, 3020, 2940, 1705, 1625, 1560, 1345, 1105, 980, 930, 910, 840, 790, 695. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.31 (d, *J* = 0.9 Hz, 3 H, –CH_3), 6.11 (qd, *J* = 0.9 Hz, *J* = 7.0 Hz, 1 H, =C^5–*H*), 7.39 (d, *J* = 7.0 Hz, 1 H, =C^4–*H*), 7.31-7.44 (m, 3 H, aromatic H), 7.61-7.66 (m, 2 H, aromatic H). – $C_{12}H_{10}O_2$ (186.2): calcd. C 77.40, H 5.41; found C 77.08, H 5.61.

3,6-Diphenyl-pyran-2-one (**18**): **6b** (143 mg, 0.27 mmol) was dissolved in dry Et_2O (10 ml). 1.0M HCl in Et_2O (0.3 ml, 0.3 mmol) was added dropwise at RT within 3 min to the stirred solution. The crude product crystallized quantitatively from the reaction mixture and was filtered off with suction. Recrystallization from abs. EtOH yielded **18** (51 mg, 78%, 0.21 mmol), m.p. 161.5°C; m.p 162°C [3]. – IR (KBr): ν = 3060, 1705, 1620, 1550, 1485, 1440, 1350, 1160, 960, 770, 760, 685. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 6.80 (d, *J* = 7.2 Hz, 1 H, =C^5–*H*), 7.34-7.50 (m, 6 H, aromatic H), 7.54 (d, *J* = 7.2 Hz, 1 H, =C^4–*H*), 7.71-7.74 (m, 2 H, aromatic H), 7.87-7.91 (m, 2 H, aromatic H). – $C_{17}H_{12}O_2$ (248.3): calcd. C 82.24, H 4.87; found C 82.17, H 4.91.

6-Oxo-5-phenyl-6H-pyran-2-carboxylic acid methyl ester (**19**): **7b** (136 mg, 0.26 mmol) was dissolved in petroleum ether 40/60 (1 ml) and 1.0M HCl in Et_2O (1 ml) was added. The yellow reaction mixture was allowed to stand at RT for 3d. The long, colourless needles were collected by filtration and recrystallized from MeOH. Yield 48 mg (56%, 0.15 mmol), m.p. 123.5°C; m.p.

127°C [3]. – IR (KBr): ν = 3060, 2960, 1725, 1705, 1550, 1440, 1360, 1300, 1270, 1100, 925, 790, 760. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.96 (s, 3 H, $-OCH_3$), 7.23 (d, J = 7.0 Hz, 1 H, $=C^3-H$), 7.39-7.48 (m, 3 H, aromatic H), 7.54 (d, J = 7.0 Hz, 1 H, $=C^4-H$), 7.67-7.72 (m, 2 H, aromatic H). Spectral data agree with those reported in reference [3].

ACKNOWLEDGEMENTS

D.H. thanks the Fonds der Chemischen Industrie for a doctoral fellowship. Financial support by the Deutsche Forschungsgemeinschaft and the BASF AG is gratefully acknowledged.

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