Tetrahedron Vol. 49, No. 18, pp. 3793-3800, 1993
Printed in Great Britain

0040-4020/93 \$6.00+.00

Alkylation of 2,6-Diphenylpyrylium and 2,6-Di-*t*-butylpyrylium Ions by Photochemical Reaction with Tetraalkylstannanes

Enrico Baciocchi,* Giancarlo Doddi,* Marcella Ioele,

Dipartimento di Chimica and Centro C.N.R. di Studio sui Meccanismi di Reazione, Università "La Sapienza",
Piazzale Aldo Moro 5, 00185 Roma (Italy).

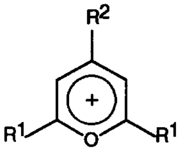
Gianfranco Ercolani

Istituto di Chimica Agraria, Università di Catania, Via Valdisavoia 5, 95123 Catania (Italy).

(*Received in UK* 2 *February* 1993)

Abstract: 2,6-diphenylpyrylium and 2,6-di-*t*-butylpyrylium perchlorates are easily converted into a number of the corresponding 4-alkyl derivatives by photochemical reaction with tetraalkylstannanes, in MeCN at room temperature. The mechanism of the process is discussed.

The excellent properties of 2,4,6-triphenylpyrylium ion, **1a**, as sensitizer of photochemical processes are well known;[1] the excited form of this species is a very strong oxidant ($E^\circ = 2.53$ V) capable of converting neutral substrates into cation radicals which then can undergo a variety of useful processes.



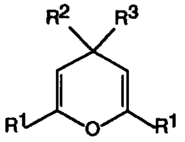
1a $R^1 = R^2 = Ph$

1b $R^1 = Ph$; $R^2 = H$

1c $R^1 = Ph$; $R^2 = alkyl$

1d $R^1 = Bu^t$; $R^2 = H$

1e $R^1 = Bu^t$; $R^2 = alkyl$



2a $R^1 = R^2 = Ph$; $R^3 = alkyl$

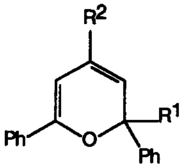
2b $R^1 = Ph$; $R^2 = R^3 = alkyl$

2c $R^1 = Ph$; $R^2 = R^3 = H$

2d $R^1 = Ph$; $R^2 = H$; $R^3 = alkyl$

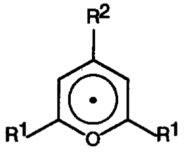
2e $R^1 = Bu^t$; $R^2 = R^3 = H$

2f $R^1 = Bu^t$; $R^2 = H$; $R^3 = alkyl$



3a $R^1 = alkyl$; $R^2 = Ph$

3b $R^1 = R^2 = alkyl$



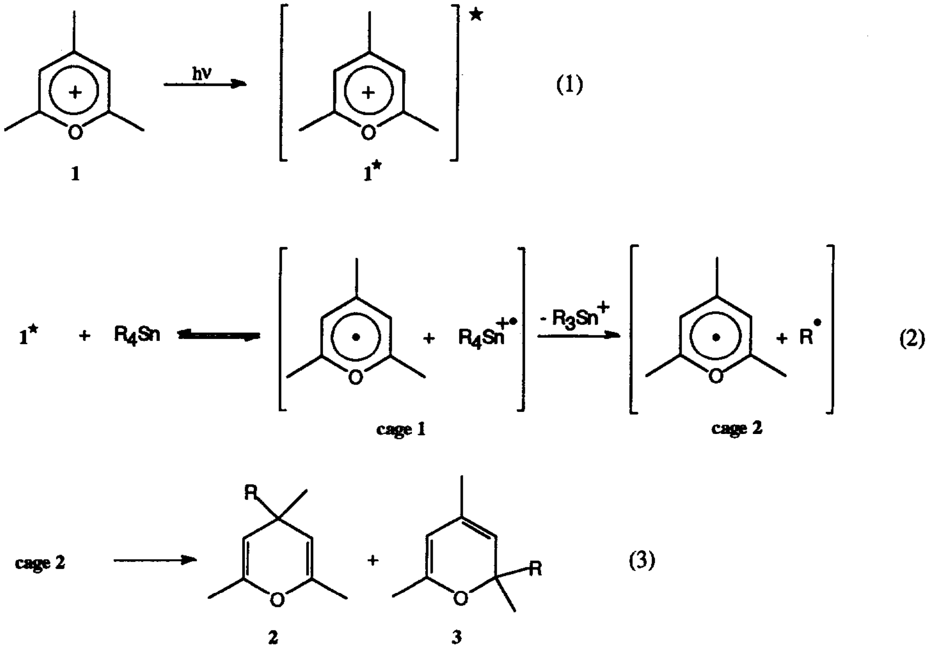
4a $R^1 = Ph$; $R^2 = H$

4b $R^1 = R^2 = Ph$

4c $R^1 = Bu^t$; $R^2 = H$

In this respect, it has been recently reported that **1a**, when irradiated in the presence of a tetraalkylstannane, forms a mixture of 2,4,6-triphenyl-4-alkyl-4*H*-pyran **2a** and 2,4,6-triphenyl-2-alkyl-2*H*-pyran **3a**.[2] According to the proposed mechanism (eqs. 1-3 with **1** = **1a**) the excited form of the pyrylium ion oxidizes the stannane producing a radical cation. This undergoes a fragmentation reaction leading to an alkyl radical, which in **cage 2** gives a coupling reaction.

Owing to our interest in the synthetic aspects of free radical chemistry,[3] and in the search of new methods for the functionalization of pyrylium ions,[4] we have felt that the application of the above process to unsubstituted pyrylium cations, could provide a simple method for the synthesis of alkylated pyrylium ions,[5] since 4*H*-pyrans with a hydrogen atom in 4 position can easily be oxidized to the corresponding pyrylium



ions.[6] Thus, in this paper we report on the synthesis of 4-alkyl-2,6-diphenyl- and 4-alkyl-2,6-di-*t*-butylpyrylium salts, **1c** and **1e** respectively, by photochemical reaction of 2,6-diphenyl and 2,6-di-*t*-butylpyrylium cations, **1b** and **1d** with dialkyldibutylstannanes. The main aspects of the mechanism of these processes are also discussed.

RESULTS AND DISCUSSION

In line with the above prediction, we found that external irradiation centered at 350 nm of acetonitrile solutions of 2,6-diphenylpyrylium **1b**, dialkyldibutylstannane[7] R_2Bu_2Sn with R = Bu, $PhCH_2$, Pr^i, Cyhex (cyclohexyl), Bu^t, and perchloric acid afforded the expected 4-alkyl-2,6-diphenylpyrylium perchlorates **1c**, even though in relatively low yields (20-35%, Table 1). It can be noted that the alkylation always involves the R group of R_2Bu_2Sn, in that fragmentation of the stannane radical cation occurs so as to form the more stable alkyl radical.[2,8] No variation was observed when the reaction was run under argon, or when tetrafluoroboric acid, instead of perchloric acid, was used. No reaction took place in the dark.

When the same procedure was applied to the 2,6-di-*t*-butylpyrylium cation **1d**, with the irradiation centered at 300 nm, i.e. in proximity of its absorption maximum (λ_{max}= 292 nm), no alkylation occurred and the substrate was recovered unchanged.[9] This finding suggests that the singlet-excited-state lifetime of **1d** is exceedingly short, and therefore difficult to quench by tetraalkylstannanes. On the contrary, good yields of pure 4-alkyl-2,6-di-*t*-butylpyrylium salts **1e** were obtained when **1d** and the tetraalkylstannanes were irradiated at 350 nm in the presence of **1b** (Table 2). Shorter irradiation times than those indicated in Table 2 afforded not only **1e** but also **1c**, i.e. the alkylation product of **1b**, together with the unreacted starting cations **1b** and **1d**. This indicates that on prolongued irradiation times **1c** is photochemically excited and converted into neutral products (*vide infra*). An exception, however, was the reaction with $(PhCH_2)_2Bu_2Sn$, where the only benzylation product was **1c** (R^2 = $PhCH_2$), which was formed along with bibenzyl and benzaldehyde.

Worse results were obtained when **1d** was irradiated at 350 nm in the presence of **1a** as photosensitizer.

Table 1. Photoalkylation of 2,6-Diphenylpyrylium Ion **1b** with Tetraalkylstannanes in CH_3CN at 45 °C

Stannane	Irradiation Time, min	Product	Yield %
Bu_4Sn	150	**1c**, R^2 = Bu	32[a]
$(PhCH_2)_2Bu_2Sn$[b]	90	**1c**, $R^2 = PhCH_2$	18[c]
$Pr^i_2Bu_2Sn$	90	**1c**, $R^2 = Pr^i$	30[a]
$Cyhex_2Bu_2Sn$	120	**1c**, R^2 = Cyhex	33[a]
$Bu^t_2Bu_2Sn$	60	**1c**, $R^2 = Bu^t$	34[a]

[a] Yield of isolated pyrylium perchlorate. [b] Reaction performed in the absence of $HClO_4$. [c] Yield measured by ^{1}H-NMR in the presence of $PhCH_2Cl$ as internal standard (see Experimental Section).

In this case, a clean alkylation occurred only with $Pr^i_2Bu_2Sn$, whereas with Bu_4Sn and $Bu^t_2Bu_2Sn$, the product was contaminated by significant amounts of unreacted **1a** and **1d** (Table 3). Again, no benzylation of **1d** was observed. A quantum yield determination was also carried out for the reaction of **1d** and $Bu^t_2Bu_2Sn$ with **1a** as photosensitizer.[10] A very low value ($\Phi = 0.035$) was obtained.

The above results clearly show that these reactions can usefully be exploited as a one-pot procedure for the alkylation of 2,6-disubstituted pyrylium salts. In this respect, it is important to note that previous attempts to introduce either a benzyl group or a linear alkyl group, other than methyl or ethyl, in 2,6-disubstituted pyrylium salts, by direct homolytic substitution, were unsuccessful.[4]

The mechanism of the reaction of **1b** with tetraalkylstannanes probably involves the same steps suggested for the photoalkylation of **1a** (i.e., eqs. 1-3 with **1** = **1b**). In the present case, however, 4*H*-pyran

Table 2. Photoalkylation of 2,6-Di-*t*-butylpyrylium Ion **1d** with Tetraalkylstannanes, in the Presence of **1b** (1:1), in CH_3CN at 45 °C

Stannane	Irradiation Time, min	Product	Yield %
Bu_4Sn	160	**1e**, R^2 = Bu	70[a]
$Pr^i_2Bu_2Sn$	120	**1e**, $R^2 = Pr^i$	70[b]
$Cyhex_2Bu_2Sn$	150	**1e**, R^2 = Cyhex	75[a]
$Bu^t_2Bu_2Sn$	90	**1e**, $R^2 = Bu^t$	72[a], 40[b]

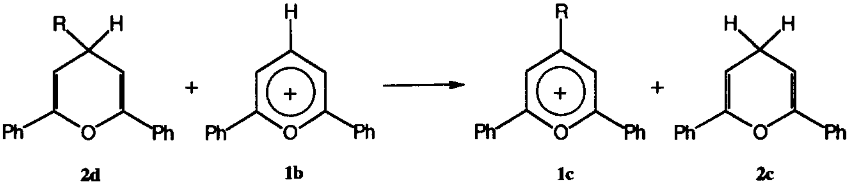
[a] Yield measured by ^{1}H-NMR in the presence of $PhCH_2Cl$ as internal standard (see Experimental Section). [b] Yield of isolated pyrylium perchlorate.

Table 3. Photoalkylation of 2,6-Di-*t*-butylpyrylium Ion **1d** with Tetraalkylstannanes, in the Presence of **1a** (1:1), in CH_3CN at 45 °C

Stannane	Irradiation Time, min	Product	Yield %
Bu_4Sn	330	**1e**, $R^2 = Bu$	$60^{a,b}$
$Pr^i_2Bu_2Sn$	360	**1e**, $R^2 = Pr^i$	75^c
$Bu^t_2Bu_2Sn$	420	**1e**, $R^2 = Bu^t$	$70^{a,d}$

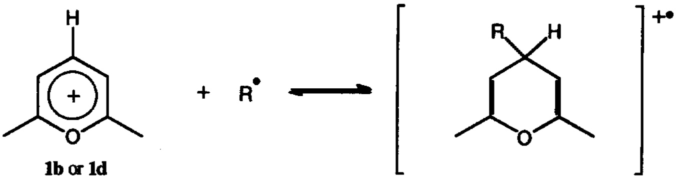
[a] Yield measured by ^{1}H-NMR in the presence of $PhCH_2Cl$ as internal standard (see Experimental Section). [b] The product is contaminated by cations **1a** (14 %) and **1d** (4 %). [c] Yield of isolated pyrylium perchlorate. [d] The product is contaminated by cations **1a** (12 %) and **1d** (2 %).

2d, which forms by collapse of the radicals in **cage 2**, undergoes further oxidation under the reaction conditions to give cation **1c**. This oxidation could be accomplished, at least in part, by cation **1b** itself, *via* a hydride transfer mechanism leading to the more stable 2,4,6-trisubstituted cation **1c** (eq. 4).[11,12] Since in this process the substrate is consumed, this would also account for the low yields of alkylated pyrylium salts **1c** (Table 1). To find some evidence for this mechanism, and hence for the formation of pyran intermediates, we carried out some experiments in the absence of acid, because under this condition pyrans show a higher stability.[6,13] Accordingly, the ^{1}H-NMR analysis of the hexane extracts obtained in these experiments (see Experimental Section) showed, besides organotin residues, the pres7 Experimental Section) showed, besides amounts of the pyrans **2b** and **3b**. The presence of **2c** is consistent with the occurrence of the process described in eq. 4. This is also supported by the finding that when equimolar amounts of **1b** and authentic samples of pyrans **2d** are mixed under irradiative conditions, quantitative formation of **1c** and **2c** is observed.[14,15] The presence of **2b** and **3b** indicates that 2,6-diphenyl-4-alkylpyrylium ion **1c**, once formed, participates in the photochemical process leading to the formation of 4*H*- and 2*H*-alkylpyrans (eqs. 1-3 with **1** = **1c**). This further contributes to diminish the yields of alkylpyrylium salts **1c**.

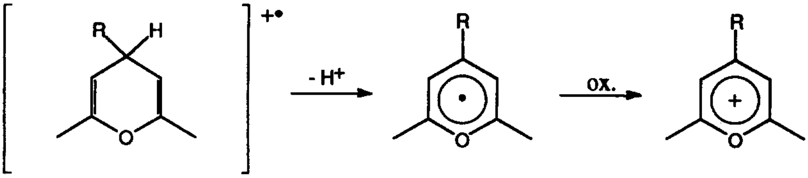


(4)

More intriguing is the mechanism of the reaction of 2,6-di-*t*-butylpyrylium salt **1d** in the presence of **1b** (or **1a**). Since only cation **1b** (or **1a**) can directly be excited, the first step is certainly the electron transfer process between **1b*** (or **1a***) and the tetraalkylstannane leading to the pyranyl radical **4a** (or **4b**) and alkyl radical, as described in eq. 2 (**1*** = **1b*** or **1a***). Of course, the two species can collapse in **cage 2** to form **2d** (or pyrans **2a** and **3a**, *vide infra*) which in turn, as already mentioned, gives **1c**. However, the formation of **1e** as the main reaction product clearly indicates that another process besides collapse in **cage 2** must occur. The most likely possibility is that alkyl radicals in part escape from the cage and attack the substrate **1d**, according to the accepted mechanism for homolytic heteroaromatic substitutions under oxidative conditions (eqs. 5 and 6 with **1d** as the substrate).[4,16] An alternative possibility involving an electron transfer reaction between the pyranyl radical **4a** (or **4b**) and **1d** to give the pyranyl radical **4c**, which then couples with alkyl radical to form **1c**, can be ruled out since the former process is largely endoergonic.[17]



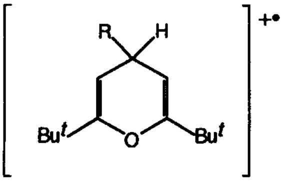
(5)



(6)

Further information comes from ^{1}H-NMR analysis of the hexane extracts obtained in the reaction of **1d** in the presence of **1b** and in the absence of acid, which shows the formation of 2,6-di-*t*-butyl-4*H*-pyrans **2e** and **2f**, along with 2,6-diphenyl substituted pyrans **2b**, **2c** and **3b**.[18] The formation of **2f** suggests the occurrence of the electron-transfer process indicated in eq. 7.[19] Pyran **2f** is subsequently oxidized to 2,6-di-*t*-butyl-4-alkylpyrylium cation **1e** under the reaction conditions. The presence of pyran **2e** suggests that cation **1d** participates in a hydride transfer reaction with **2d** and **2f**, analogous to that indicated in eq. 4.[20] Moreover, the formation of **2b** and **2c** is in agreement with the already mentioned participation of **1c** in the photochemical process (eqs 1-3, with **1** = **1c**), and explains why this cation is not found in the reaction product (with the only exception of the reaction with $(PhCH_2)_2Bu_2Sn$) if the irradiation times are sufficiently long. In addition, **1c** can also act as the sensitizer for the conversion of cation **1d** to **1e**, in line with the results of independent experiments where **1d** and Bu_4Sn were irradiated in the presence of **1c** (R^2 = Me).

4a (or **4b**) +



⟶ **1b** (or **1a**) + **2f** (7)

Since cations **1b** and **1d** should have similar reactivity toward nucleophilic radicals,[21] it is likely that the pathway described by eqs. 5 and 6 plays a role also in the reaction of **1b** alone with tetraalkylstannanes, to form **1c**. It follows, therefore, that both in cage and out of cage processes should be possible for cation **1b**. An exception, however, seems to be the benzylation reaction, which is effective with **1b** but not with **1d**, thus indicating that **1c** (R^2 = $PhCH_2$) can exclusively be produced by radical collapse in **cage 2**. The scarcely nucleophilic benzyl radical,[22] once escaped from **cage 2**, prefers to dimerize producing bibenzyl or to react with oxygen yielding benzaldehyde, rather than to attack a heterocyclic cation.

Finally the reactivity toward nucleophilic radicals of cations **1a** and **1c**, with the γ position occupied by a phenyl and an alkyl group, respectively, should be lower than the reactivity of the γ-unsubstituted pyrylium ions **1b** and **1d**,[21] therefore an out of cage process for these cations appears to be unlikely.

EXPERIMENTAL SECTION

^{1}H-NMR spectra (acetone-d6) were recorded on a Bruker WP-80 SY spectrometer. UV-vis spectra (CH_3CN) were recorded on a Cary 1 spectrophotometer. FAB mass spectra were obtained on a VG 4 mass spectrometer. Melting point are uncorrected. Acetonitrile (Carlo Erba RS reagent) was used without further purification.

The stannanes R_2Bu_2Sn were prepared according to literature methods (R = Pr^i,[23] Cyhex,[23] Bu^t,[24] $PhCH_2$[25]), whereas tetrabutylstannane was a commercial product (Aldrich). Methods described in the literature were also used for the synthesis of the perchlorates of 2,6-diphenylpyrylium **1b** (λ_{max}= 400 nm, 276 nm),[26,27] 2,6-di-*t*-butylpyrylium **1d** (λ_{max}= 294 nm),[28] 2,4,6-triphenylpyrylium **1a** (λ_{max}= 406 nm, 356 nm, 276 nm),[29] and 4-methyl-2,6-diphenylpyrylium **1c** (R^2 = Me. λ_{max}= 388 nm, 274nm, 238nm).[4]

Photochemical Experiments. Photolyses were performed at 45 °C, under air, by external irradiation (see Tables 1-3 for the irradiation times), in a Rayonet photoreactor with a bank of 16 x 24 W black light phosphor lamps (λ_{max} = 350 nm), of an acetonitrile solution (40 ml) of the pyrylium salt(s) (0.6 mmol, each), organotin derivative (0.9 mmol) and 65 % perchloric acid (2.4 mmol), contained in a pyrex vessel. The solution was evaporated under reduced pressure, the residue was then repeatedly washed with hexane to remove most of the organotin derivatives, dissolved in CH_3CN (CH_3CO_2H for **1e** R^2 = Bu^t), and precipitated by addition of diethyl ether. The solid was collected and washed with ether. This procedure, however, failed to completely precipitate **1e** (R^2 = Bu, Cyhex, Bu^t) as solid perchlorate, and therefore the yields of these salts, reported in Tables 2 and 3, were determined by ^{1}H-NMR. These samples were prepared by dissolution in acetone-d6 of the reaction residue obtained after hexane washing, and added with $PhCH_2Cl$ as internal standard.

The preparation of **1c** (R^2 = $PhCH_2$) was carried out in the absence of the strong acid, since in the acid medium worse yields were obtained, probably because of decomposition of the corresponding stannane.

The pyrylium salts **1c** and **1e** were characterized by ^{1}H-NMR and FAB mass spectra (glycerol).[30]

1c (R^2 = Bu) δ 0.9-1.0 (3H, m), 1.2-2.0 (6H, m), 3.3 (2H, m), 7.6-8.0 (6H, m), 8.4-8.7 (4H, m), 8.84 (2H, s). *m/e* = 289 (M^+).

1c (R^2 = Pr^i) δ 1.55 (6H, d, J= 7.0 Hz), 3.57 (1H, m, J= 7.0 Hz), 7.6-8.0 (6H, m), 8.4-8.6 (4H, m), 8.84 (2H, s). *m/e* = 275 (M^+).

1c (R^2 = Bu^t) δ 1.65 (9H, s), 7.6-8.0 (6H, m), 8.4-8.7 (4H, m), 8.83 (2H, s). *m/e* = 289 (M^+).

1c.(R^2 = $PhCH_2$) δ 4.60 (2H, s), 7.2-7.6 (5H, m), 7.6-8.0 (6H, m), 8.4-8.7 (4H, m), 8.85 (2H, s).

1c (R^2 = Cyhex)[31] δ 3.6 (1H, m), 7.7-8.0 (6H, m), 8.4-8.7 (4H, m), 8.81 (2H, s). *m/e* = 315 (M^+).

1e (R^2 = Bu)[32] δ 1.56 (s), 3.1 (2H, m), 8.18 (2H, s). *m/e* = 249 (M^+).

1e (R^2 = Pr^i) δ 1.41 (6H, d, J = 6.95 Hz), 1.59 (18 H, s), 3.43 (1H, m, J = 6.95 Hz, 0.04 Hz), 8.19 (2H, d, J = 0.04 Hz). *m/e* = 235 (M^+).

1e (R^2 = Bu^t) δ 1.51 (9H, s), 1.60 (18 H, s), 8.22 (2H, s).

1e (R^2 = Cyhex)[32] δ 1.57 (s), 3.7 (1H, m), 8.16 (2H, s).

^{1}H-NMR of the pyrans mixtures were recorded dissolving in $CDCl_3$ the residue obtained by evaporation of the hexane extracts of the reactions performed in the absence of acid. The spectra were compared with those of authentic samples prepared according literature methods.[2, 33, 34]

ACKNOWLEDGMENTS

This work was supported in part by C.N.R. Progetto Finalizzato Chimica Fine II. We thank Dr. T. Del Giacco for assistance in the quantum yield measurement, and Mr. G. D'Arcangelo for the FAB-mass spectra.

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