Synthesis and photochemistry of 2,2-di-tert-butyl-6-(4,4-di-tert-butylbuta-1,3-dienyl)-2H-pyran

Pinar Kilickiran*, Sethuraman Sankararamanb*, Henning Hopf*

*Institut für Organische Chemie, Universität Braunschweig, Hagenring 30, D-38106, Braunschweig, Germany
bDepartment of Chemistry, Indian Institute of Technology, Madras 600 036, India

Received 18 January 2001; accepted (revised) 11 July 2001

E,E-1,1,9,9-tetra-tert-butylnona-1,3,6,8-tetraen-5-one 7 undergoes cyclization under both basic and acidic conditions to yield 2,2-di-tert-butyl-6-(4,4-di-tert-butylbuta-1,3-dienyl)-2H-pyran 6. Upon photolysis of the 2H-pyran derivative ring opening to the ketone is observed. The 2H-pyran derivative is fluorescent and its fluorescence quantum yield and lifetime have been measured in cyclohexane and acetonitrile.

The valence isomerization (electrocyclic ring opening) of 2H-pyran 1 to the Z-diene 2 (Eqn 1) is an interesting reaction for several reasons. It allows one to understand the effect of a heteroatom (oxygen) on a prototypical electrocyclization, the ring closure of 1,3,5-hexatriene to 1,3-cyclohexadiene.1 From the synthetic organic chemists’ point of view it is useful for the stereoselective synthesis of Z,E-dienones from 2H-pyrans, because 2-substituted 2H-pyrans are readily obtained by the addition of organometallic reagents to the corresponding pyrilium salts.2,3 In this paper we describe the synthesis and photochemistry of a new 2H-pyran derivative, namely, 2,2-di-tert-butyl-6-(4,4-di-tert-butylbuta-1,3-dienyl)-2H-pyran 6.

Results and Discussion
Formation of 2H-pyran 6

During the course of the synthesis of 3-tert-butyl-4,4-dimethyl-2-pentenal 4 from the chloride 3 (Eqn 2) by Hass Bender procedure4 using 2-nitropropane and potassium hydroxide under refluxing conditions, we serendipitously discovered the formation of two new by-products which were isolated and characterized as the ketone 5 and the 2H-pyran derivative 6 (Eqn 2). Formation of 5 and 6 in this reaction can only be rationalized by invoking an aldol condensation of the aldehyde 4 with acetone that is formed during the reaction. When aldehyde 4 was deliberately allowed to react with acetone under basic condition at room temperature two products, ketones 5 and 7 were formed and none of the pyran derivative 6 could be observed in the crude product (Eqn 3). However, when ketone 7 was refluxed under basic condition in isopropyl alcohol (Hess Bender reaction condition) formation of 6 could readily be observed (Eqn 4). An analogous base-catalyzed isomerization of an allenic ketone to a 2H-pyran derivative has recently been reported.5 Formation of 6 could be explained by the Michael addition of hydroxide ion to 7 followed by the ring closure of the resulting enolate ion with the concomitant loss of the hydroxide ion (Scheme I). The conversion of the ketone 7 to the pyran derivative 6 can also be accomplished under acidic conditions. Thus,
when a solution of the ketone 7 in benzene-$d_6$ was heated at 60 °C in the presence of catalytic amount of $p$-toluenesulfonic acid (PTSA) the conversion of 7 to 6 could be conveniently observed by $^1$H NMR spectroscopy (Eqn4). Under acidic conditions the formation of 6 could be explained by the initial protonation of 7 at the carbonyl oxygen followed by the cyclization of the intermediate carbenium ion, followed by the loss of proton (Scheme II).

**Photochemistry of 2H-pyran 6**

Pyran 6 is a greenish yellow solid and in the solid state it is very stable and does not decompose or undergo thermal isomerization even upon melting (150 °C). Also, a solution of 6 in chloroform is thermally stable for several days at room temperature. However, exposure of the solution to room light for extended period of time or deliberate photolysis of the solution resulted in the conversion of 6 to the trans ketone 7 (Scheme III). The retrocyclization of 6 to 7 occurs by an electrocyclic ring opening of the former under photochemical conditions, presumably through the formation of the intermediate Z,E-dienone 8 which further undergoes a photochemical cis-trans isomerization to 7. When the photolysis was carried out in CDCl$_3$ and the reaction followed by $^1$H NMR spectroscopy the disappearance of signals due to 6 with the concomittent appearance of signals due to 7 could be observed. During the course of the reaction, apart from the signals due to 6 and 7 we also observed signals of very low intensity in the NMR spectrum which we assign to 8 based on the signal multiplicity and coupling constant values. However, 8 was not formed in significant amount for isolation and characterization, presumably due its further isomerization to 7 under the photolytic conditions. After prolonged photolysis the conversion of 6 to 7 was complete and only signals due to 7 could be observed in the NMR spectrum. Thermal and photochemical ring opening of derivatives of 2H-pyran$^3$ and 2H-pyran-2-one$^6$ are well known in literature and in the former case the reaction is known to proceed via the intermediacy of the Z,E-dienone and in the latter case via a ketene intermediate. It should be mentioned that photolysis of the trans ketone 7 did not lead to the formation of 6.$^7$

The 2H-pyran derivative 6 is highly fluorescent which prompted us to investigate its photophysical properties. The absorption and the fluorescence emission spectra were measured in cyclohexane and acetonitrile, solvents of widely differing polarity. In both the solvents the absorption spectrum of compound 6 exhibited $\pi-\pi^*$ transitions in the region 300-400 nm (Figure 1). Several partially resolved vibrational fine structure could be observed in both solvents although the resolution of the vibrational fine structures was better in cyclohexane than in acetonitrile. Compound 6 did not exhibit any significant solvatochromism as the absorption maxima in these two solvents were nearly the
same. Therefore we conclude that the solvent polarity did not have significant effect on the ground state of 6.

The fluorescence spectra were measured by the excitation of the sample at 350 nm, corresponding to the most intense vibrational band ($v_{0.3}$). The excitation and the emission spectra in cyclohexane and acetonitrile are shown in Figure 2. It is apparent from Fig.2 that there is a significant solvent effect on the emission spectrum of 6. In cyclohexane (Figure 2A) the fluorescence spectrum shows vibrational fine structure and the mirror image relationship of the absorption and the emission spectra is evident in Figures 1A and 2A. The $v_{0.0}$ vibrational bands nearly overlap in the excitation and the emission spectra indicating no significant Stoke shift. The $v_{0.0}$ vibrational band in the absorption spectrum appears at 3.048 eV (405 nm) whereas the same band in the emission spectrum appears at 3.105 eV (398 nm). Moreover, the spacing of the vibrational bands in the absorption and the emission spectra are nearly the same indicating that the spacing of the vibrational energy levels in both $S_0$ and $S_1$ states of 6 are nearly the same. The emission spectrum measured in acetonitrile is quite different from that in cyclohexane (Figure 2B). The intensity of the higher vibrational levels ($v_{0.2}$ and above) is much lower in both the excitation and the emission spectra. For example, the most intense band in the excitation and the emission spectra correspond to the $v_{0.1}$ vibrational state whereas in the absorption spectrum it is $v_{0.3}$ vibrational band that is most intense (compare Figures 1B and 2B). It is evident from Figure 2B that the resolution of the vibrational bands is poor in both the excitation and the emission spectra measured in acetonitrile compared to the absorption spectrum in the same solvent. The band width of the excitation and the emission spectra in acetonitrile are also smaller than that in cyclohexane. Nevertheless a mirror image relationship exists between the excitation and the emission spectra measured in acetonitrile (Figure 2B). The decrease in the intensity of the higher vibrational levels is generally associated with an efficient chemical

![Figure 1 - Absorption spectrum of pyran 6 in cyclohexane (A) and acetonitrile (B)](image)

![Figure 2 - Excitation and fluorescence emission spectra of pyran 6 in cyclohexane (A) and acetonitrile (B). ($\lambda_{ex} = 350$ nm.)](image)
reaction taking place from these states which effectively competes with the fluorescence emission. A decrease in the fluorescence quantum yield with the decreasing wavelength of excitation, which is observed in the present system, is a measure of such competing pathways by which the higher vibrational excited states decay. The chemical transformation that competes with the fluorescence emission in the present system is the ring opening reaction of 6 to give 7. This process occurs more efficiently from the higher vibrational states of the excited state. Such wavelength dependent efficiency of the competing photochemical/photophysical processes is well known in many other systems.

The fluorescence quantum efficiency \( \Phi_f \) was measured by a comparative method using quinine sulfate as the reference. For compound 6 the \( \Phi_f \) in cyclohexane is 0.011 and that in acetonitrile is 0.027. The fluorescence lifetime \( \tau_f \) in these two solvents was measured by the time correlated single photon counting technique using a picosecond laser spectrometer. The lifetime in cyclohexane is 98 pS where as in acetonitrile it is 200 pS. Since the instrument detector response is limited to 53 pS, the measured life times are associated with 10-15% error.

**Conclusions**

The serendipitous discovery of the 2H-pyran derivative 6 led to its isolation and characterization. Upon photolysis, compound 6 underwent an electrocyclic ring opening reaction to yield the trans ketone 7 through the intermediacy of ketone 8. However, the reverse reaction, namely the photolysis of ketone 7 did not lead to the formation of 6. Compound 6 can be conveniently prepared from ketone 7 either by a base induced cyclization or an acid catalysed cyclization reaction. Compound 6 is fluorescent and its fluorescence spectrum, the quantum yield and lifetime of fluorescence emission from these states.

**Experimental Section**

Emission spectra were measured on a Hitachi F-4500 spectrometer. The quantum yield of fluorescence was measured using a quinine sulfate solution in 0.1 N \( \text{H}_2\text{SO}_4 \) as the reference system. The concentration of quinine sulfate and the substrate in the respective solutions was adjusted such that the optical density was 0.1 at the excitation wavelength of 350 nm. The areas under the fluorescence spectra were taken for the calculation of the quantum yields.

The fluorescence lifetime was measured using a laser spectrometer (IBH Instruments) fitted with a Ti-Sapphire laser (Tsunami, Spectra Physics). The pulse width of the laser output was 1.2 pS. The average output of the fundamental wavelength (750 nm) was 680 mW with a pump power of 4.5 W. The fundamental output was frequency doubled to 375 nm using a second harmonic generator and the second harmonic output was used for the excitation of the sample. The fluorescence was detected at 480 nm using a two stage microchannel plate photomultiplier (MCP-PMT R3809U, Hamamatsu) which has a detection response of 53 pS. The fluorescence decay was measured using the IBH Instruments software library which includes an interactive shift of the fitted function as part of \( \chi^2 \) goodness of the fit criterion.

**Isolation of 2,2-di-tert-butyl-6-(4,4-di-tet-butylbuta-1,3-dienyl)-2H-pyran 6.** 2-Nitropropane (10.1 mL, 0.1mole) was added dropwise to a stirred solution of KOH (4.48 g, 80 mmole) in water (16 mL) and 2-propanol (58 mL). After 30 min a solution of chloride 3 (11.0 g, 58 mmole) in 2-propanol (30 mL) was added dropwise. The reaction mixture was refluxed for 5.5 hr and cooled to room temperature. It was diluted with water (250 mL) and extracted with ether (4 x 100 mL). The combined organic layer was dried over MgSO4, solvent was evaporated and the residue was purified by column chromatography over silica gel by 1:7 (v/v) ethyl acetate and hexane mixture as the eluant to give 4 as a colorless liquid (7.60 g, 80%), 5 as a light yellow oil (0.6 g, 5%) and the pyran 6 as a greenish yellow solid (0.15 g, 0.7%). The aldehyde 4 and the chloride 3 have been synthesized in our laboratory earlier and they have been thoroughly characterized.

**6.** mp 128-30 °C; IR (KBr): 2958s, 1642m, 1542m, 1481m, 1388m, 1365m, 1332m, 1060s, 1007m, 716 cm -1; UV-Vis (CHCl3) \( \lambda_{max} \) (log \( \varepsilon \)): 310 (3.89), 330 (4.08), 350 (4.23), 365 (4.22), 405 (3.56); \(^{1}H\) NMR (200 MHz, CDC13, Me4Si) \( \delta_h \): 7.35 (1H, dd, J = 12.0 and 14.6 Hz), 6.11 (1H, dd, J = 12.0 Hz), 5.91 (1H, dd, J = 6.0 and 10.4 Hz), 5.70 (1H, d, J = 14.6 Hz), 5.42 (1H, d, J = 10.4 Hz), 4.89 (1H, d, J = 6.0 Hz), 1.41 (9H, s), 1.23 (9H, s), 1.08 (18H, s); \(^{13}C\) NMR (50 MHz, CDCl3) \( \delta_c \): 158.31 (s), 152.40 (s), 128.09 (d), 125.02 (d), 123.19 (d), 120.76 (d), 119.73 (d), 98.48 (d), 89.02 (s), 43.50 (s), 38.93 (s), 37.92 (s), 32.63 (q), 31.77 (q), 25.55 (q); MS (70 eV, El) m/z: 358 (M +, 2), 302 (24), 301 (100), 245 (32), 244 (34), 230 (4), 189 (36), 139 (48), 123 (90), 99 (58), 77 (100), 65 (100), 53 (100), 41 (88), 39 (100), 37 (100), 35 (74), 33 (48), 31 (45), 29 (46), 27 (46), 25 (46), 23 (46), 21 (46), 19 (46), 17 (46), 15 (46), 13 (56), 11 (68), 9 (98), 7 (100), 5 (100), 3 (100), 1 (100).
Synthesis of *E,E*-1,1,9,9-tetra-tert-butylnona-1,3,6,8-tetraen-5-one 7. A mixture of aldehyde 4 (0.2 g, 1.19 mmoles) and acetone (44 mL) was heated at 60 °C in an oil bath and the reaction was monitored by IR spectroscopy. After 16 hr the ketone 7 and the *2H*-pyran 6 were present in the ratio 3:1 as determined by the peak integration in the NMR spectrum.

Acknowledgement

Financial support from Hans Boeckler Stiftung (P K) and Alexander von Humboldt Stiftung (SS) is gratefully acknowledged. The fluorescence life-time measurements were made at the National Centre for Ultrafast Processes, University of Madras and we thank Dr P Ramarunthy and V K Indira Priyadarshini for their help. We thank Dr A K Mishra and J Shobini (IIT, Madras) for their help with the steady state fluorescence studies and helpful discussions. The support of this work by the Fonds der Chemischen Industrie is gratefully acknowledged.

References