Synthesis and spectroscopic properties of novel cinnamate derivatives of thioxanthone: photocuring activity *versus* photodimerization

Norman S. Allen* and Deborah Mallon
Chemistry Department, Faculty of Science and Engineering, Manchester Polytechnic, Chester Street, Manchester M1 5GD, UK

and Alan Timms and Arthur W. Green
International Biosynthetics Ltd, Halebank Industrial Estate, Widnes, Cheshire WA8 8NS, UK

and Fernando Catalina
Instituto de Ciencia y Technologia de Polimeros, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

(Received 23 June 1992; revised 11 September 1992)

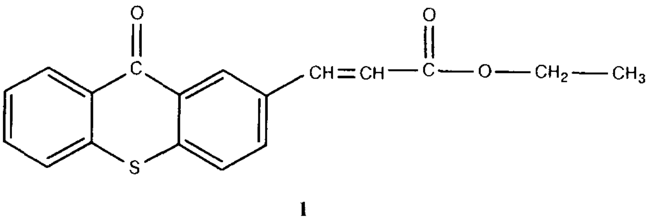
Two novel 2-substituted derivatives of thioxanthone-containing cinnamate (ethyl ester of 2-propenoic acid) and cinnamamide (*N,N*-dimethylacrylamide) groups are synthesized and characterized. The spectroscopic properties of these two new photoinitiators are examined and related to their photocuring behaviour in an epoxy acrylate resin and compared with those of commercial 2-isopropylthioxanthone. Despite an increase in the longest wavelength absorption maximum and corresponding extinction coefficient, most of the derivatives showed little improvement in photocuring activity when compared with 2-isopropylthioxanthone. Their lower activities were reflected in reduced fluorescence quantum yields and reduced phosphorescence quantum yields. Photolysis quantum yields of the cinnamate esters, however, were found to be increased compared with those of 2-isopropylthioxanthone. In this case photoreaction was observed in both nitrogen-saturated and oxygen-saturated 2-propanol. Using *FT*i.r. and *FT*h.m.r. analysis, the cinnamate groups were found to undergo a primary reaction involving (2+2) cycloaddition via the lowest excited singlet excited state. The cycloaddition reaction is found to compete effectively with hydrogen atom abstraction. This is confirmed on microsecond flash photolysis by the absence of any ketyl radical formation in nitrogen-saturated 2-propanol. The role of the cycloaddition reaction in controlling the photochemical activity of the thioxanthone chromophore is discussed.

(Keywords: synthesis; spectroscopic properties; thioxanthone)

INTRODUCTION

Modification of the structure of conventional photoinitiator chromophores for improved property requirements continues to be a subject of much interest and activity. For example, water-soluble benzophenone initiators have been prepared through the use of sulfonate and sulfonium groups for the curing of water-based inks and silk-screen emulsions[1,2], while increased photochemical activity has been sought through the use of tertiary amine groups[3,4] and peresters[5,6]. In the latter two cases, more active alkylamino and benzoyl radicals are produced, respectively, on irradiation in order to induce the crosslinking of acrylated systems. To reduce migration rates and improve compatibility, copolymerizable photoinitiators have also been synthesized, 2-acryloyloxythioxanthone being a typical example[7].

In our efforts to produce copolymerizable photoinitiators with enhanced activity, we have synthesized two novel 2-substituted derivatives of thioxanthone with a cinnamate (ethyl ester of 2-propenoic acid) and a cinnamide (*N,N*-dimethylacrylamide) group, structures **1** and **2**. Poly(vinyl cinnamate) for example, has long been known as a useful photoresist material and is known to undergo a primary 2+2 photocycloaddition reaction which results in crosslinking[8]. Polymers containing styrylpyridinium[9] and styrylthiazolium groups[10] are also known to undergo a 2+2 cycloaddition reaction resulting

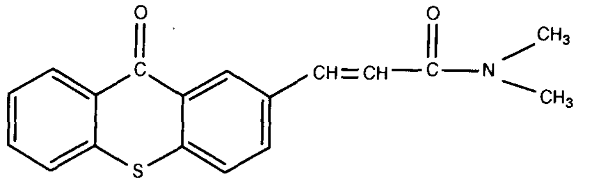


1

---

*To whom correspondence should be addressed

0032-3861/93/112401-06



2

in crosslinking. However, more recent evidence has shown that some aryl cinnamates may also undergo a photo-Fries rearrangement[11].

EXPERIMENTAL

Materials

Ethyl acrylate, *N*,*N*-dimethylacrylamide, palladium acetate, triphenyl phosphine, triethylamine, *N*-methyldiethanolamine, methyl ethyl ketone, methanol, dimethyl formamide and charcoal were obtained from the Aldrich Chemical Company, UK, as standard laboratory reagents. Ethanol, chloroform, methanol and 2-propanol were obtained from the same company in spectroscopic grade, while 2-bromothioxanthone and 2-isopropylthioxanthone were obtained from International Biosynthetics, Widnes, UK. The 2-isopropylthioxanthone was recrystallized twice from ethanol. The Synocure 3105 (an epoxy-acrylate prepolymer) was supplied by Cray Valley Products, Orpington, Kent, UK.

Synthesis

Thioxanthyl-2-propenoic acid (ethyl ester), 1. Ethyl acrylate (0.8 cm^3), 2-bromothioxanthone (1.95 g), palladium acetate (0.017 g), triphenyl phosphite (0.078 g), triethylamine (5 cm^3) and dimethyl formamide (10 cm^3) were placed in a round-bottomed flask (100 cm^3) and flushed with nitrogen. The mixture was then refluxed for 24 h at 115°C. The reaction was then quenched with hydrochloric acid (2M) (200 cm^3) and the product filtered. The crude material was then recrystallized from ethanol to give a 30% yield of pure product (0.69 g) with a melting point of 136–137°C. Calculated carbon, hydrogen and sulfur values are 69.66, 4.56 and 10.33%, respectively; found C = 69.49%, H = 4.59% and S = 10.29%.

(N,N-*dimethyl)thioxanthyl-2-acrylamide, 2.* *N*,*N*-dimethyl acrylamide (1.3 cm^3), 2-bromothioxanthone (2.92 g), triphenyl phosphite (0.054 g), palladium acetate (0.024 g), triethylamine (5 cm^3) and dimethylformamide (10 cm^3) were placed in a round-bottomed flask (100 cm^3) and flushed with nitrogen. The mixture was then refluxed for 24 h at 115°C. The reaction was then quenched with hydrochloric acid (2M) (200 cm^3) and the product filtered. The crude material was recrystallized twice from methanol:methyl ethyl ketone (50:50 v/v) to give a 34.3% yield of pure product (1.3 g) with a melting point of 230–233°C. Calculated carbon, hydrogen, sulfur and nitrogen values are 69.9, 4.85, 10.36 and 4.53%, respectively; found C = 69.72%, H = 4.95%, S = 10.35% and N = 4.49%.

Structural analysis of the compounds was also confirmed using *FT*i.r., *FT*n.m.r. and mass spectrometry.

Photocuring

The equipment used during this study was a Mini-cure apparatus available from Primarc (Jigs and Lamps), UK. The lamp was medium-pressure mercury with a rating of 80 W cm^{-1}. Depth of cure was assessed using the pencil hardness method at 2H, while surface cure was simply monitored using the thumb twist method. In both cases cure speeds were assessed in metres per minute. Laboratory curing studies were also carried out using a 100 W high-pressure mercury lamp set at a distance of 5 cm from the sample surface. Curing efficiencies were evaluated using the Sheenan Pendulum Hardness Instrument (Sheenan, London, UK). The average of 10 sample measurements was taken in each case within ±10%.

The photoinitiators and amine synergist (*N*-methyldiethanolamine) were incorporated into the Synocure 3105 at 2% w/w each and coated at 6 μm thickness onto aluminized card.

Spectroscopic measurements

Normal and second-order derivative absorption spectra were obtained using a Perkin-Elmer Lambda 7 absorption spectrometer. Phosphorescence excitation and emission spectra were obtained using a Perkin-Elmer LS-5 luminescence spectrometer. Phosphorescence quantum yields were obtained in ethanol at 77 K using the relative method with benzophenone as a standard[12] assuming a quantum yield of 0.74 in ethanol. All spectra were corrected using a Perkin-Elmer 3600 data station with an appropriate OBEY file for this purpose.

*FT*i.r. spectra were recorded in KBr discs using a Biorad *FT*i.r. spectrometer (model FTS-7) coupled to an SPC-3200 data station. *FT*n.m.r. analysis was carried out using a Jeol 270 MHz GSX instrument in $CDCl_3$ using tetramethylsilane as the internal standard. Typical conditions for ^1H spectral analysis were: 16 k data points zero filled to 32 k; a pulse time of 3.2 μs (30°); and an acquisition time of 1.37 s. Spectra were obtained with water suppression via homo-gated decoupling. Typical conditions for ^{13}C spectral acquisition were: 16 k data points zero filled to 32 k; a pulse time of 5.9 μs (60°); and an acquisition time of 0.41 s with a 2 s pulse delay. Mass spectrometry was carried out using a VG 30/70 instrument.

Photoreduction quantum yields

Absolute quantum yields of photolysis (θ_r) for the initiators were determined in 2-propanol at 10^{-5} M using an irradiation wavelength of 365 nm selected from a Philips high-pressure Hg lamp (HB-CS 500 W) and a Kratos GM252 monochromator. Sample cells were thermostatted at 30°C and the solutions were oxygen- and nitrogen- (<5 ppm O_2) saturated. The absorbed light intensity was measured using an International Light radiometer (model 700) previously calibrated by the Aberchrome 540 actinometer[13,14]. Photolysis of the thioxanthones was monitored by measuring the change in the main u.v. absorption maximum at ~390 nm.

Flash photolysis

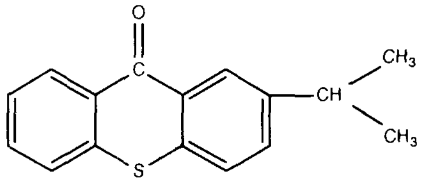
Transient absorption spectra were recorded using a microsecond kinetic flash photolysis apparatus utilizing two 16 kV xenon-filled flash lamps with 300 J energy output (operated at 10 kV) and a 150 W tungsten/halogen monitoring source. Transient decay profiles were stored using a Gould storage oscilloscope (model 1425) and solutions were degassed using white spot nitrogen gas (<5 ppm O_2).

Irradiation

Samples of the initiators were irradiated in a Microscal Unit as both powders and in KBr discs utilizing a 500 W high-pressure Hg/tungsten lamp (MBTF) and also daylight conditions.

RESULTS AND DISCUSSION

The new cinnamate and cinnamamide thioxanthone compounds are shown as structures **1** and **2**, with compound **3** being the control chromophore, namely 2-isopropylthioxanthone. The ability of the two new derivatives to induce the photocuring of a commercial epoxy acrylate resin, Synocure 3105, is shown in *Table 1*. Here the data compare the efficiencies of the photoinitiators in terms of both surface and depth of cure. Surface cure was determined by the thumb twist method and the number of standard passes through the Mini-cure apparatus are interpreted as metres per minute. The same interpretation is placed on the measurement of depth of cure, where the rating is based on marking ability by a 2H grade pencil. Also shown are standard pendulum hardness data. As may be seen from the data, different tests gave different degrees of efficiency for each initiator structure. Thus, while both the surface and depth of cure data showed compound **3** to be the most effective initiator, the pendulum hardness method showed compound **1** to be the most effective initiator. This variation in photoactivity was also found when we examined their curing efficiencies by using the *FT*i.r. method for loss of acrylic unsaturation. In general, therefore, there appears to be little or no improvement in photocuring efficiency by incorporating cinnamate or cinnamamide groups onto the thioxanthone chromophore, i.e. by having the double bond directly attached to the ring structure. Some of the cured coatings became cloudy on curing, due to precipitation. Cinnamate esters are known to undergo a primary photochemical process of 2 + 2 cycloaddition[8,15] and this may compete with any hydrogen atom abstraction or crosslinking mechanisms for the acrylic functionality in the resin. Solid state analysis of the initiators, which will be discussed later, confirms this mechanism.



3

Absorption maxima and extinction coefficients of the three thioxanthones are compared in *Table 2* in three solvents, namely cyclohexane, chloroform and 2-propanol. It is seen that in the case of the two novel compounds **1** and **2**, there is a small shift in the longest wavelength absorption maximum. This is a mixed $n–\pi/\pi–\pi^*$ transition for the thioxanthone chromophore, as noted by the variable solvent shift data. This transition is the one of most significance in terms of absorption of the u.v. radiation for photocuring. Thus, despite the small red shift in the absorption wavelength, as well as the small increase in the extinction coefficients, the photocuring efficiencies are not enhanced.

Fluorescence and phosphorescence analysis of the initiators showed that they exhibit both types of emission. The fluorescence emission wavelength maxima and quantum yields are shown in *Table 3* for three solvents, namely cyclohexane, chloroform and 2-propanol. All three exhibit significant red shifts in their emission wavelength maximum with increasing solvent polarity, as well as a corresponding increase in quantum yields. This is indicative of their lowest excited singlet state being $\pi–\pi^*$ in character. Phosphorescence emission wavelength maxima and quantum yields for the two novel initiators are compared in *Table 4* with those of 2-isopropylthioxanthone in ethanol. Again, both the quantum yields are seen to be significantly lower than that of the 2-isopropyl derivative. These data are interesting, as they clearly indicate that the rate of intersystem crossing from the lowest excited singlet to

Table 2 Absorption maxima and extinction coefficients of cinnamate derivatives of thioxanthone in different solvents

	Cyclohexane		Chloroform		2-Propanol	
Compound	λ_{max} (nm)	Log *E*	λ_{max} (nm)	Log *E*	λ_{max} (nm)	Log *E*
1	384.1	3.70	390.6	3.77	384.3	3.95
2	387.4	3.58	393.7	3.75	386.2	3.59
3	380.8	3.83	386.9	3.95	381.8	3.63

Table 3 Fluorescence emission maxima and quantum yields of cinnamate derivatives of thioxanthone in different solvents

	Cyclohexane		Chloroform		2-Propanol	
Compound	λ_{max} (nm)	ϕ_f	λ_{max} (nm)	ϕ_f	λ_{max} (nm)	ϕ_f
1	400	0.0005	422	0.0230	433	0.0340
2	420	0.0012	426	0.0320	439	0.0360
3	410	0.0007	422	0.0540	432	0.1300

Table 1 Photocuring efficiencies of cinnamate derivatives of thioxanthone in an epoxy-acrylate resin (Synocure 3105) at 2% w/w concentration and 2% w/w of *N*-methyldiethanolamine using a 100 W high-pressure Hg lamp and Mini-cure equipment

Compound	Surface passes	Cure (m $\min^{-1}$)	Depth of passes −2H	Cure (m $\min^{-1}$)	Pendulum hardness oscillations
1	4	0.58	10	0.23	199
2	6	0.39	13	0.18	130
3	3	0.78	7	0.33	189

Table 4 Phosphorescence emission maxima and quantum yields of cinnamate derivatives of thioxanthone in ethanol

Compound	Phosphorescence	
	λ_{max} (nm)	ϕ_p
1	445.8	0.014
2	451.6	0.038
3	485.1	0.140

Table 5 Quantum yields of photolysis at 365 nm irradiation for cinnamate derivatives of thioxanthone in 2-propanol at 10^{-5} M

Compound	ϕ_r Nitrogen	ϕ_r Nitrogen/amine	ϕ_r Oxygen
1	0.098	0.104	0.083
2	0.189	0.529	0.397
3	0.015	–	<0.001

the corresponding triplet state for the two new derivatives must be low and would certainly contribute to their lower photocuring activity. In this case, deactivation via *trans–cis* isomerism and subsequent 2+2 cycloaddition is highly probable, as will be shown below.

Photolysis quantum yields of the initiators were also measured and the data are shown in *Table 5*. It is seen that the quantum yields of the cinnamate derivatives are higher than that of 2-isopropylthioxanthone. Furthermore, some degree of photoreaction also occurs in oxygenated 2-propanol, suggesting that hydrogen atom abstraction is not the only important mechanism for these initiators. The increased photoreaction therefore would suggest the importance of some degree of 2+2 cycloaddition to give a cyclobutane-type product. Photoreaction in oxygen also indicates that some of the reaction may be occurring via the lowest excited singlet state. The tertiary amine also increases the photolysis quantum yield.

Microsecond flash photolysis was also carried out on the photoinitiators in order to provide an understanding of the nature of possible intermediates in their photoreactions. All the initiators were studied in nitrogen and air-equilibrated 2-propanol, and found to exhibit the end-of-pulse transient absorption spectra shown in *Figure 1* for initiator **1** as an example. An absorption maximum is observed in the region 300–400 nm with a peak at 380 nm. This is not significantly quenched by the presence of dissolved oxygen. There was no evidence for ketyl radical or radical anion formation above 400 nm due to hydrogen atom abstraction or respective electron abstraction from the solvent, unlike that obtained earlier for thioxanthones (including the 2-isopropyl derivative). Thus, the cinnamate and cinnamamide esters appear to have different behaviour to that of other thioxanthone structures[2,3]. Since the same transient was observed with both the derivatives, we can only assume at this stage that *trans–cis* isomerism must be responsible for the absorption change and/or intermediate species responsible for the 2+2 cycloaddition reaction. Furthermore, in agreement with the photolysis quantum yields, the reaction would appear to occur primarily from the lowest excited singlet state.

As discussed previously, photodimerization reactions are well established in the literature[8,15]. To ascertain whether 2+2 cycloaddition is occurring with these initiators, we carried out an *FT*i.r. and *FT*h.m.r. analysis of the pure compound in the solid phase before and after irradiation in a KBr disc and as a powder. The samples were irradiated for 1 h in a Microscal unit. Expanded *FT*i.r. spectra of the chromophore before and after irradiation in the region 2000–400 cm^{-1} are shown in *Figure 2* for initiator **1** as an example. Several distinct changes are seen in this fingerprint region of the i.r. spectrum, which are indicative of the loss of the vinyl group and the formation of cyclobutyl structures[16]. Peaks for the product after irradiation are shown in this figure only to avoid congestion. In the region 2000–400 cm^{-1} (*Figure 2*), the >C=O stretch at 1707 cm^{-1} has been reduced and is shifted to higher frequencies at 1731.8 cm^{-1}, due to removal of the vinyl conjugation with the phenyl ring and consequent formation of an ester group. The vinyl stretches at 1638.2 and 1589.2 cm^{-1} have also markedly reduced due to the loss of *trans* vinyl conjugation with the phenyl ring. The latter is confirmed by loss of the absorption at 972.2 cm^{-1}. Weak >C–H absorptions are observed between 1480 and 1310 cm^{-1}, with some evidence for a weak cyclobutyl peak at 825.1 cm^{-1} which has shifted from the original 817.7 cm^{-1}. A new alkyl C–H has appeared at 1317.3 cm^{-1}. As expected, there are also marked changes in the >C–O stretch region, with all the main peaks decreasing. A new >C–O peak is also observed at 1069.9 cm^{-1}, which is probably alkyl >C–H. Thus, the *FT*i.r. analysis indicates definite photocycloaddition to give cyclobutyl derivatives. It is interesting to note that there is no evidence here for *cis* product formation. This will obviously depend on the conditions and time of irradiation.

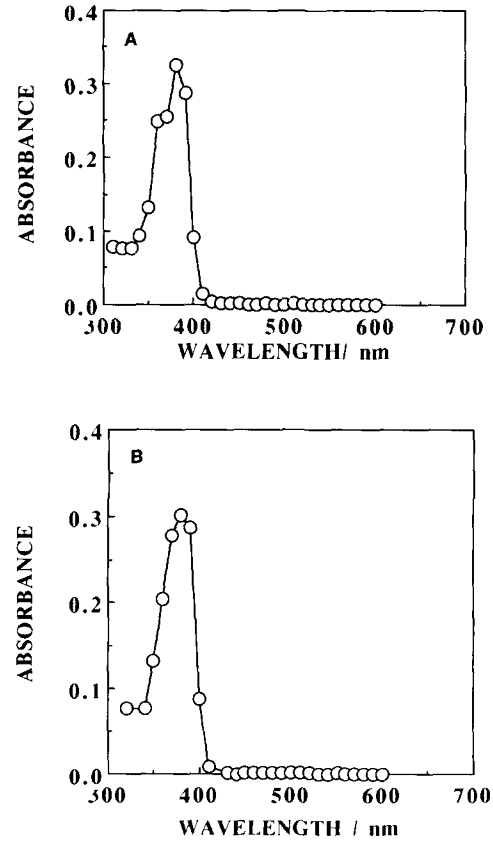


Figure 1 End-of-pulse transient absorption spectra of thioxanthyl-2-propenoic acid (ethyl ester) in (a) nitrogen and (b) air-saturated 2-propanol at 5×10^{-5} M

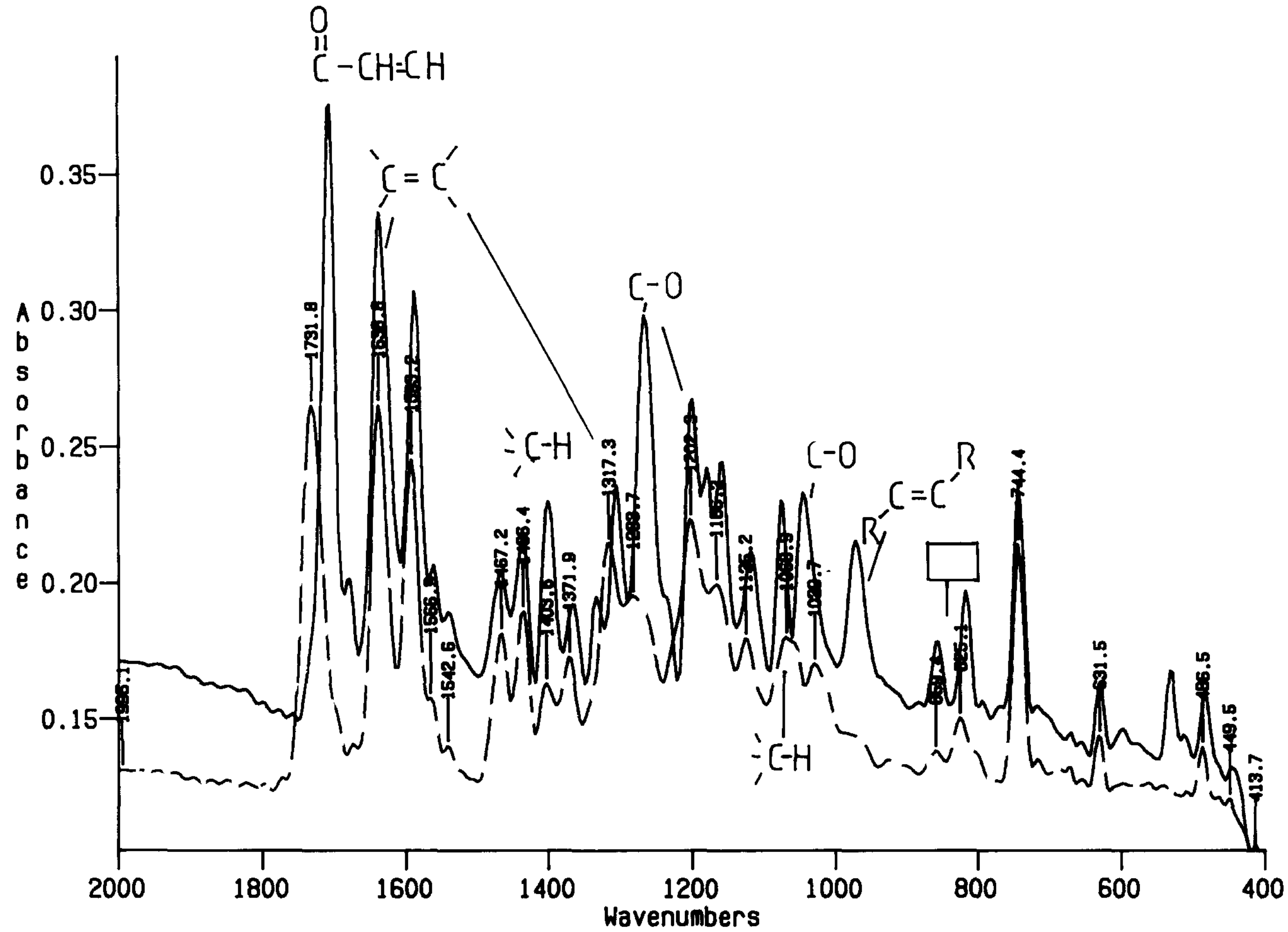


Figure 2 *FT*i.r. spectra of thioxanthyl-2-propenoic acid (ethyl ester) in a KBr disc in the region 2000–400 cm^{-1} before (——) and after (- - -) irradiation for 1 h in the Microscal unit

^{1}H *FT*n.m.r. spectral analysis of the chromophore, before and after irradiation as the solid powder for 1 h, confirms the conclusions from the *FT*i.r. spectral analysis. The ^{1}H *FT*n.m.r. spectral analysis was undertaken on structure **1**. The unirradiated initiator in deuterated chloroform showed a typical vinyl AB quartet with the first two peaks at $\delta = 7.7$–7.8 ppm and the second two peaks at $\delta = 6.5$–6.6 ppm. Both were reduced after irradiation. The initiator also showed a quadruplet at $\delta = 4.1$–4.4 ppm due to the alkyl protons. After irradiation the quartet changed to an octet and produced two new peaks with a doublet at $\delta = 4.05$ ppm and $\delta = 4.6$ ppm. Such a change is typical for cyclobutyl group formation, with the octet being associated with a number of possible *cis* and *trans* isomers. The doublet at 4.05 ppm would be due to the C–H group adjacent to the aromatic substitution on the cyclobutyl ring, while the doublet at 4.6 ppm would be due to that adjacent to the substituted ester functionality.

CONCLUSIONS

The results show that substitution of either cinnamate ester or cinnamamide groups into the thioxanthone chromophore has little influence on photoinitiator activity for photocuring of acrylated resins. In many cases there is a significant reduction in photoactivity due to hydrogen atom abstraction, as evidenced by the flash photolysis data. Deactivation of the lowest excited triplet state, as evidenced by the reduced phosphorescence quantum yields, is associated with a facile *trans–cis* isomerization process and subsequent 2 + 2 cycloaddition to give a mixture of cyclobutane isomers.

ACKNOWLEDGEMENTS

The authors thank SERC for a CASE Award to D.M.

REFERENCES

1 Green, P. N. *Polym. Paint Resins* 1985, **175**, 246
2 Allen, N. S., Chen, W., Catalina, F., Green, P. N. and Green, W. A. *J. Photomchem. Photobiol., Chem. Edn* 1988, **44**, 349
3 Allen, N. S., Lam, E., Howells, E. M., Green, P. N., Green, A., Catalina, F. and Peinado, C. *Eur. Polym. J.* 1990, **26**, 1345
4 Allen, N. S., Lam, E., Kotecha, J. L., Green, W. A., Timms, A., Navaratnam, S. and Parsons, B. J. *J. Photochem. Photobiol., Chem. Edn* 1990, **54**, 367
5 Allen, N. S., Hardy, S. J., Jacobine, A. F., Glaser, D. M., Yang, B. and Wolf, D. *Eur. Polym. J.* 1990, **26**, 1041
6 Allen, N. S., Hardy, S. J., Jacobine, A. F., Glaser, D. M., Yang, B., Wolf, D., Catalina, F., Navaratnam, S. and Parsons, B. J. *J. Appl. Polym. Sci.* 1991, **42**, 1169
7 Allen, N. S., Peinado, C., Lam, E., Kotecha, J. L., Catalina, F., Navaratnam, S. and Parsons, B. J. *Eur. Polym. J.* 1990, **26**, 1237
8 Turner, S. R. and Daly, R. C. in 'Photopolymerisation and Photoimaging Science and Technology' (Ed. N. S. Allen), Elsevier Science Publishers, London, 1989, Ch. 3, p. 75
9 Ichimura, K. *J. Polym. Sci., Polym. Chem. Edn* 1982, **20**, 1411
10 Allen, N. S., Barker, I. C., Edge, M., Williams, D. A. R., Sperry, J. A. and Batten, R. J. *J. Photochem. Photobiol., Chem. Edn* 1992, **68**, 227

11 Subramanian, P., Creed, D., Griffin, A. C., Hoyle, C. E. and Venkataram, K. *J. Photochem. Photobiol., Chem Edn* 1991, **61**, 317

12 Demas, J. N. and Crosby, G. A. *J. Phys. Chem.* 1971, **75**, 91

13 Heller, H. G. and Lanagan, J. R. *J. Chem. Soc., Perkin Trans. I* 1981, 341

14 Heller, H. G. British Patent, 7/1464603

15 Bottcher, H., Bendig, J., Fox, M. A., Hopf, G. and Timpe, H. J. 'Technical Applications of Photochemistry', Deutscher Verlag fur Grundstoffindustrie, Leipzig, 1992, Ch. 2, p. 68

16 Kemp, W. 'Organic Spectroscopy' 3rd Edn, MacMillan Publishers, London, 1991