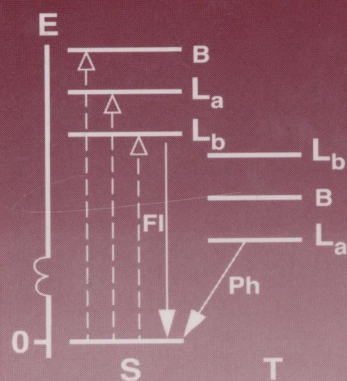


**SPECIALIST PERIODICAL
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Photochemistry

Volume 35

senior reporter I. DUNKIN

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A Specialist Periodical Report

Photochemistry

Volume 35

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Introduction and Review of the Year

BY IAN R. DUNKIN

We are pleased to welcome a new reporter to the team for this volume, Niall Geraghty. He has taken over from Andrew Gilbert the chapter on photo-oxidation and -reduction.

As usual, my selection of photochemical highlights of the period reviewed in this volume is as subjective and personal as ever. It is a sign of the times in which we live, perhaps, but I continue to believe that photochemistry needs to 'earn its living' in the chemical world and not just be a subject of interest for a relatively closed group of specialists. Of course, photochemistry already has a long history of successful and important commercial applications. Traditional photographic techniques come to mind immediately, although these now seem to be on the verge of replacement by digital electronics. Nevertheless, lithography for printing and for microchip manufacture continues to be a strong area of well established economic activity involving photochemistry, and there are a few industrial manufacturing processes also.

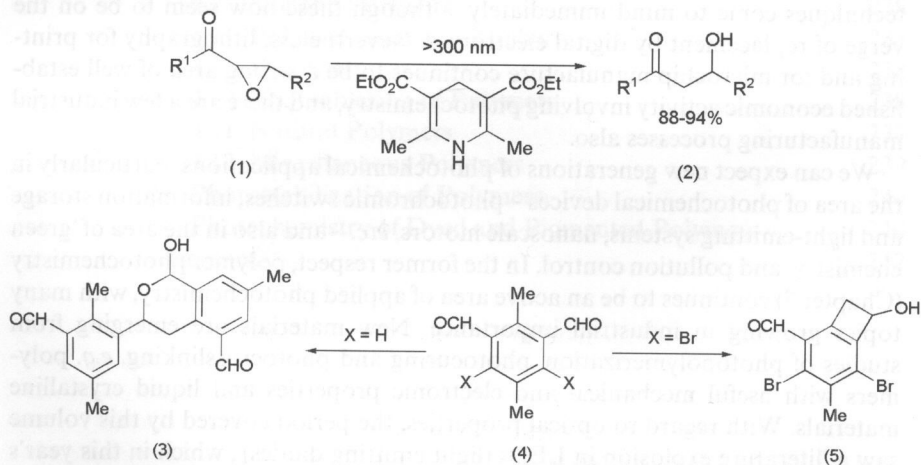
We can expect new generations of photochemical applications, particularly in the area of photochemical devices – photochromic switches, information storage and light-emitting systems, nanoscale motors, *etc.* – and also in the area of 'green chemistry' and pollution control. In the former respect, polymer photochemistry (Chapter 7) continues to be an active area of applied photochemistry, with many topics growing in industrial importance. New materials are emerging from studies of photopolymerization, photocuring and photocrosslinking, *e.g.* polymers with useful mechanical and electronic properties and liquid crystalline materials. With regard to optical properties, the period covered by this volume saw a 'literature explosion in LEDs (light emitting diodes)', which in this year's review form one of the largest specialized topics in photochemistry and photophysics. Another growth area is the photochemical oxidation of organic waste in the control of pollution (Chapter 5).

Despite these important examples of the commercialization of photochemistry and photophysics, synthetic photoreactions still seem to remain underexploited in chemicals manufacture. We know that photons are relatively expensive, so that may be one reason; but another factor, I believe, is that so many photochemical reactions seem to have disappointingly poor chemical yields or quantum yields, or give rather too many by-products. I was pleased therefore to see a selection of efficient photoreactions which – by virtue of high chemical yields or interesting selectivity – could compete with the best thermal processes in the

design of syntheses.

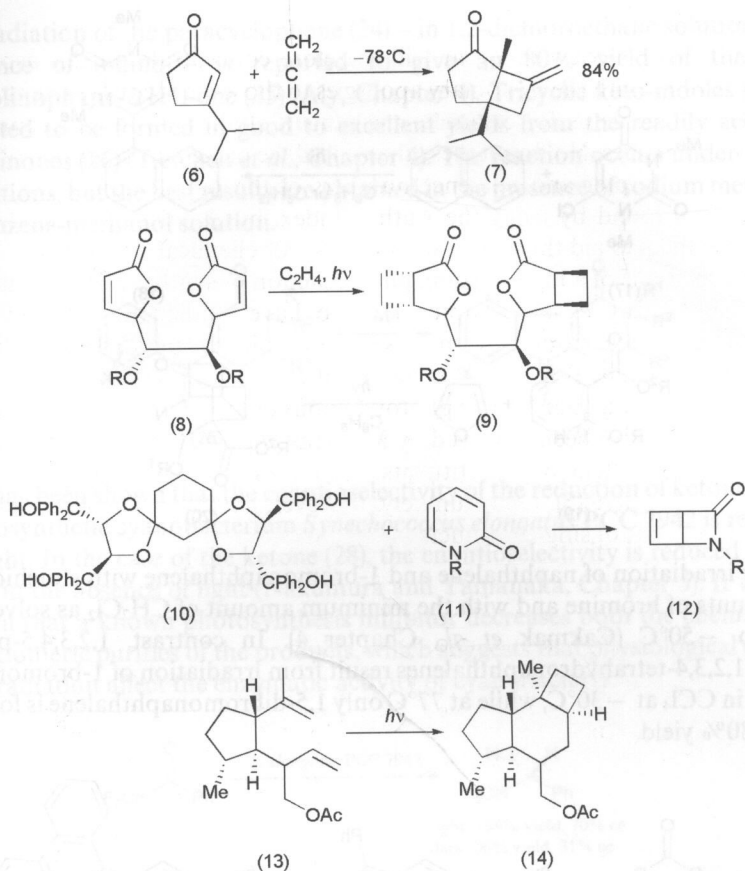
The rest of my review this year will therefore concentrate on this aspect of photochemistry, with the customary apologies to those who would prefer to read about developments in, for example, mechanistic studies, ultrafast reactions or photoaffinity probes. No doubt these themes will be picked up in future volumes. As usual, the chapter and reference numbers of the publications cited in this review can be found by using the Author Index, but I have also included the chapter numbers to aid those who wish to scan for chemical structures.

A good example of a high-yielding photoreaction of synthetic utility has been reported by Zhang *et al.* (Chapter 1), who have studied the photolysis of acyloxiranes (1) in acetonitrile – in presence of a dihydropyridine derivative as hydrogen donor. The β -hydroxyketone products (2) were obtained in yields of 88–94%. Interesting quantitative photoreactions of aromatic dialdehydes in the crystalline state have been observed by Moorthy *et al.* (Chapter 1) and found to be critically dependent on substituents. Examples are (4; X=H) yielding (3), while (4; X=Br) gave (5). Unfortunately, however, not all analogues of (4) gave quantitative yields of single products.



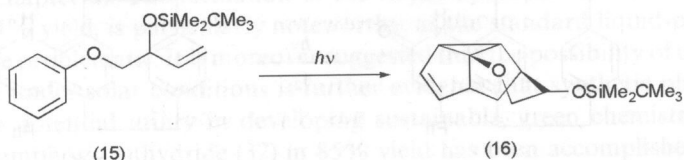
Photocycloaddition of allene to the cyclopentenone derivative (6) in methylene chloride solution at -78°C afforded a cycloadduct (7) in 84% yield, which was a key intermediate for the construction of the AB ring core of Taxol (Shimada *et al.*, Chapter 2). Similarly, photocycloadditions of ethene to enantiopure butenolides (8) at -78°C have been studied by de March *et al.* (Chapter 2). The product distribution was found to depend on the protecting group R, but with R = TMS, the product stereoisomer (9) was obtained in 83% yield, and an efficient synthesis of (+)-grandisol was developed.

An example of efficient chiral induction in a photoreaction is provided by the irradiation of inclusion compounds of pyridones (11) with the chiral host (10) (Tanaka *et al.*, Chapter 2). This process afforded optically active β -lactams (12) with ee in the range 91–99%. The intramolecular 2 + 2 alkene photocycloaddition of (13) catalysed by Cu(I) afforded the tricyclic compound (14) in 89% yield,

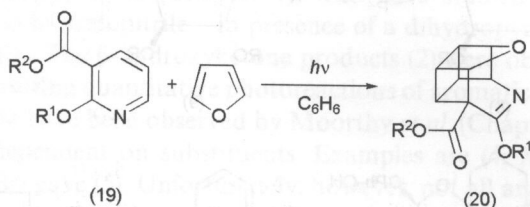
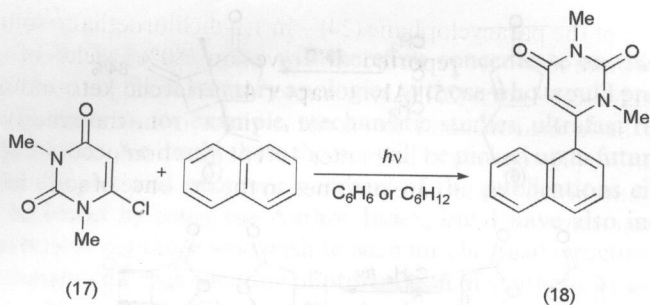


which was a key intermediate in a synthesis of kelsoene (Bach and Spiegel, Chapter 3).

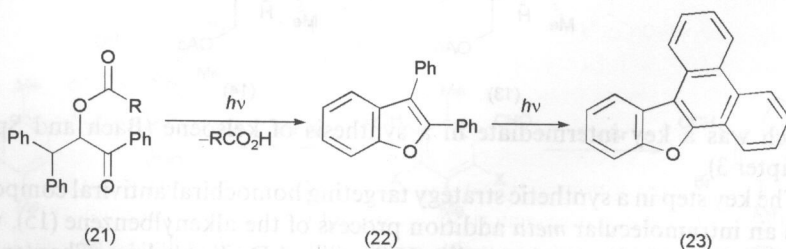
The key step in a synthetic strategy targeting homochiral antiviral compounds was an intramolecular *meta* addition process of the alkenylbenzene (15), which yielded the 1,6-bridged adduct (16) (Hillaert and De Keukeleire, Chapter 4). In what seems an interesting means of introducing substituents into aromatic rings (Ohkura *et al.*, Chapter 4), irradiation of the chlorinated uracil derivative (17) and naphthalene in cyclohexane or benzene afforded exclusively the photosubstitution product (18). Diastereoselective photoaddition of nicotinic esters (19) and furan has been shown to give caged products (20) in 73–84% yield (Sakamoto *et al.*, Chapter 4).



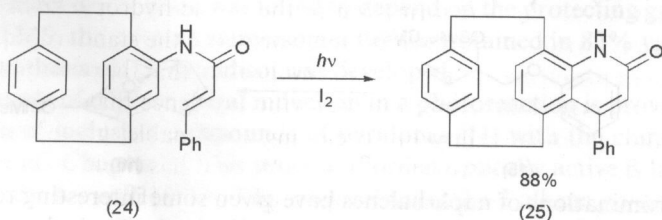
Photobrominations of naphthalenes have given some interesting results. It is reported that 1,4-dibromonaphthalene can be formed selectively and in 90%



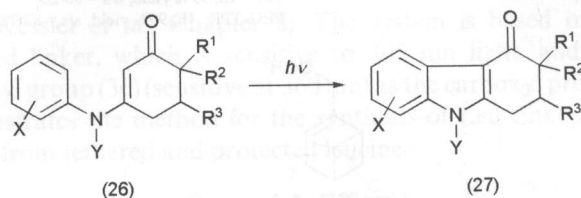
yield by irradiation of naphthalene and 1-bromonaphthalene with stoichiometric amounts of bromine and with the minimum amount of CH_2Cl_2 as solvent at -30 to -50°C (Cakmak *et al.*, Chapter 4). In contrast, 1,2,3,4,5-pentabromo-1,2,3,4-tetrahydronaphthalenes result from irradiation of 1-bromonaphthalene in CCl_4 at -30°C , while at 77°C only 1,5-dibromonaphthalene is formed and in 80% yield.



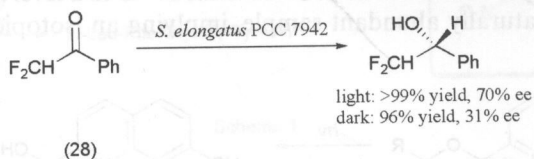
Esters (21), readily formed from 2-hydroxy-1,2,2-triphenylethanone and carboxylic acids, undergo efficient photocyclization to the benzofuran (22), which then yields the benzophenanthro[9,10-d]furan (23) by the usual 6π -oxidative closure process of the *cis* stilbene moiety (Ashraf *et al.*, Chapter 4). The overall reaction is so convenient that the authors propose the triphenylethanone as a new photolabile protecting group for carboxylic acids.



Irradiation of the paracyclophane (24) – in 1,2-dichloroethane solution in the presence of iodine – is reported to give an 80% yield of the novel quinolinophane-2(1H)-one (25) (Aly, Chapter 4). Tricyclic keto-indoles (27) are reported to be formed in good to excellent yields from the readily accessible enaminoxones (26) (Tietcheu *et al.*, Chapter 4). The reaction occurs under various conditions, but the best results are obtained in the presence of sodium methoxide in benzene-methanol solution.

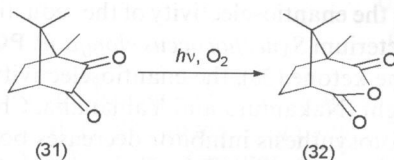
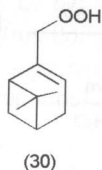
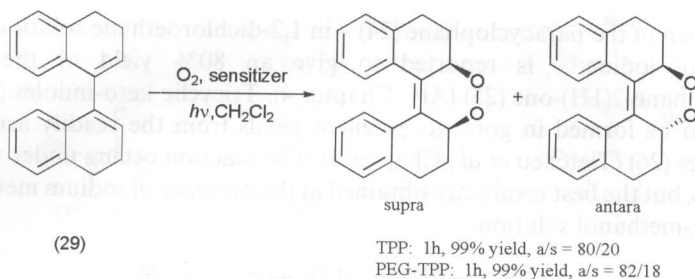


It has been shown that the enantioselectivity of the reduction of ketones by the photosynthetic cyanobacterium *Synechococcus elongatus* PCC 7942 is regulated by light. In the case of the ketone (28), the enantioselectivity is reduced by over 50% in the absence of light (Nakamura and Yamanaka, Chapter 5). It was also shown that a known photosynthesis inhibitor decreases both the chemical and enantiomeric purities of the products, which suggests that physiological changes on irradiation affect the enzymatic activity of cyanobacteria.

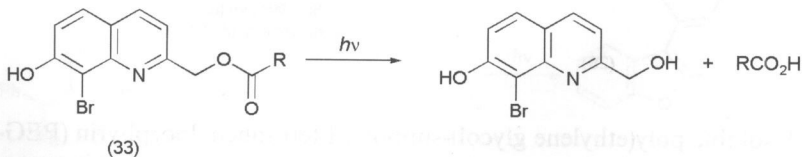


A soluble poly(ethylene glycol)-supported tetraphenylporphyrin (PEG-TPP) has been prepared, whose reactivity in singlet oxygen generation is comparable to that of an unanchored sensitizer (Benaglia *et al.*, Chapter 5). Its use is exemplified by the oxidation of (29) in essentially quantitative yield. The advantage of the PEG-TPP is that it can be recovered by simple filtration during workup and used again up to six times with no loss of efficiency. Other singlet oxygen reactions have been carried out using a novel solvent-free procedure, which involves loading a porphyrin into solvent-swollen polystyrene beads and carrying out the photo-oxidation in the neat liquid substrate (Griesbeck and Bartoschek, Chapter 5). The formation of the allylic hydroperoxide (30) from β -pinene in 84% yield, is particularly noteworthy, as the standard liquid-phase reaction can be problematic. It is moreover suggested that the possibility of using this approach under solar conditions is further evidence that synthetic photochemistry has potential utility in developing sustainable, green chemistry. A synthesis of camphoric anhydride (32) in 85% yield has been accomplished by the *unsensitized* photo-oxidation of camphorquinone (31) (Ji *et al.*, Chapter 5).

The IR multiphoton dissociation of CF_3H , pre-excited to the second C–H

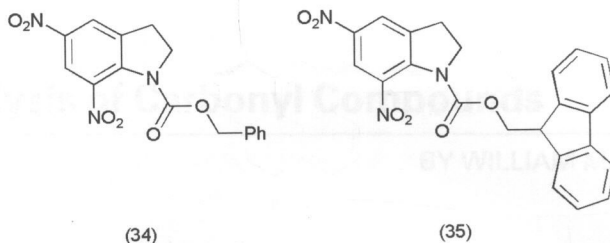


stretch overtone, has been examined with a view to developing a laser isotope-separation method for ^{13}C (Boyarkin *et al.*, Chapter 6). This single stage process resulted in a C_2F_4 product that had been enriched in ^{13}C to a level as high as 99% starting from a naturally abundant sample, implying an isotopic selectivity of >9000.

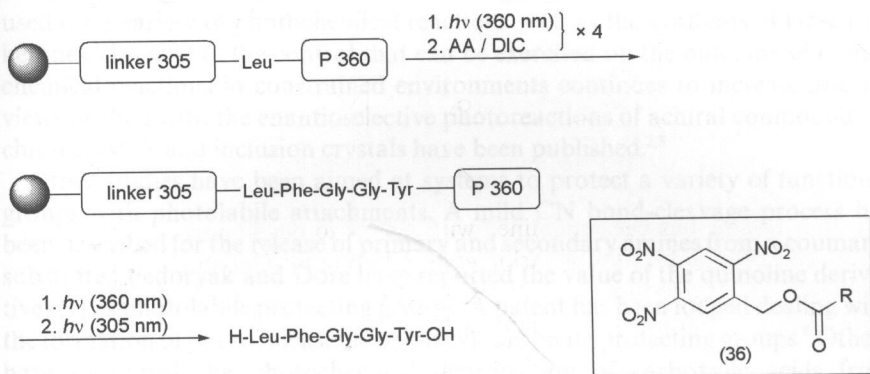


The 8-bromo-7-hydroxyquinoline moiety, as in (33), has been proposed as a novel photolabile protecting group for carboxylic acids (Fedoryak and Dore, Chapter 6). This system has a greater single photon quantum efficiency than other commonly used photocleavable protection for carboxylic acids, but also has sufficient sensitivity to multiphoton-induced photolysis to be used *in vivo*. Rather unusually, a method has been developed for the *photoprotection* of amines using the *N*-benzyloxycarbonyl (*N*-Cbz) and *N*-9-fluorenylmethoxycarbonyl (*N*-Fmoc) derivatives of 5,7-dinitroindoline (34) and (35) (Helgen and Bochet, Chapter 6). These reagents allow efficient protection of primary and secondary amines, as carbamate (*N*-Cbz or *N*-Fmoc) derivatives in neutral conditions, by UV irradiation (350nm) of a mixture of the amine with either reagent. It is possible, moreover, to premix the reagents and then photolytically trigger the acylation reaction later.

Finally, a sequential solid-phase peptide synthesis has been developed which makes use of both a photolabile linker and a photolabile protecting group



(Scheme 1) (Kessler *et al.*, Chapter 6). The system is based on a *tert*-butyl ketone-derived linker, which is sensitive to 305 nm light, and a nitroveratryloxycarbonyl group (36) (sensitive at 360 nm) as the carboxyl protecting group. Scheme 1 illustrates the method for the synthesis of Leu-Enkephalin (in 55% overall yield) from tethered and protected leucine.



Scheme 1

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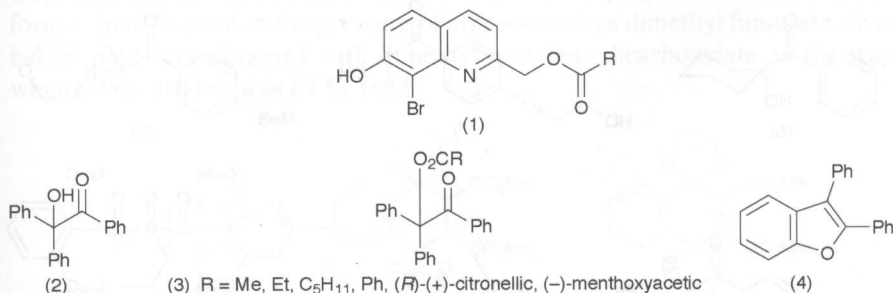
Photolysis of Carbonyl Compounds

BY WILLIAM M. HORSPOOL

The focus of organic photochemistry continues to change. Over the years considerable research devoted to simple carbonyl compounds was published, however, this emphasis has been diminishing on an annual basis and continues to diminish in the period of this review.

Reviews of general interest in this area highlights microreactors that can be used for a variety of photochemical reactions such as the synthesis of large ring ketones.¹ Interest in the control that can be exercised on the outcome of photochemical reactions in constrained environments continues to increase and reviews dealing with the enantioselective photoreactions of achiral compounds in chiral crystals and inclusion crystals have been published.^{2,3}

Other studies have been aimed at systems to protect a variety of functional groups with photolabile attachments. A mild CN bond-cleavage process has been described for the release of primary and secondary amines from a coumarin substrate.⁴ Fedoryak and Dore have reported the value of the quinoline derivatives (1) as photolabile protecting groups.⁵ A patent has been lodged dealing with the formation of photo releasable phenacyl carbonate protecting groups.⁶ Others have examined the photochemical deprotection of carboxylic acids from phenacyl and 2,5-dimethylphenacyl esters that can be carried out in a two-phase system. The results indicate, in benzene-water with added cetyltrimethylammonium bromide, that the yield of liberated acid is enhanced.⁷ Ashraf *et al.*⁸ have described the use of the hydroxyketone (2) as a further example of molecules that can be used as photoactivatable protecting groups for acids. The hydroxy group is readily esterified with a variety of acids to afford the esters (3). These, on excitation in methanol or ethanol with no need to exclude air, release the free acid in excellent yields and afford the furan (4) as the by-product. This furan is



photochemically active under the reaction conditions and undergoes *cis*-stilbene type cyclization. Klan and Zabadal have reviewed the area of photoremovable protecting groups.⁹

1 Norrish Type I Reactions

The photochemical decomposition of methanal in a solid Xe matrix has been studied.¹⁰ Work has also been reported dealing with the photodissociation dynamics of methanal,¹¹ and *ab initio* calculations have been carried out on the photochemical decomposition of acetaldehyde into methane and CO.^{12,13} The photocatalytic decomposition of acetaldehyde to yield carbon dioxide has also been reported.¹⁴ The threshold for CC bond fission in propanal and the release of the CHO fragment has been shown to be at a wavelength of 326.26 nm.¹⁵ Chowdhury¹⁶ has reported the dissociation of propynal using multiphoton irradiation. Gas-phase photolysis of butyraldehyde in the 280-330 nm range has shown that the CHO radical is produced.¹⁷

Laser-flash irradiated benzaldehyde in ethylene glycol has been examined using TRESR and CIDEF techniques. Benzoyl radicals and α -hydroxybenzyl radicals were detected.¹⁸ The photochemical dehalogenation and decarbonylation of 2-, 3- and 4-chlorobenzaldehydes has been studied.¹⁹

Induced pre-dissociation is reported to be a photochemical path to ethane during the irradiation of acetone in the gas phase.²⁰ Irradiation at 193 nm of ethyl vinyl ketone results in the formation of a variety of products such as *n*-butane, but-1-ene and buta-1,3-diene. The study was used to determine the rate of combination of ethyl radicals to yield butane and of vinyl radicals to afford buta-1,3-diene.²¹

Supramolecular complexes of benzyl radicals are formed upon irradiation of the ketones (5) in supramolecules.²² Turro²³ has reviewed some aspects of the decarbonylation of dibenzyl ketone derivatives in supercages.

