

Introduction and Review of the Year

BY IAN R. DUNKIN

Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, G1 1XL, Glasgow, UK

This is a very special volume of *Photochemistry*, because it is to be the last in the current format. It has been apparent in recent years that we are experiencing a profound change in the way in which information of all types is disseminated. In particular, more-or-less universally available on-line searching for scientific papers and data has greatly speeded up the task of searching the literature for material relevant to any area of interest. So much so, that the inevitable time delay inherent in the production of review serials, such as the *Specialist Periodical Reports*, now seems excessive. Moreover, the nature of some other RSC publications has changed in the past few years. *Chemical Society Reviews*, for example, has moved from being a vehicle for the comprehensive or historical coverage of selected topics to being more of a collection of updates on the research of individual groups. This has left a niche in the review coverage of the RSC, and the intention is to fill this with a new style of *Specialist Periodical Reports*. In the future, from Volume 37 onwards, *Photochemistry* will aim at providing a critical analysis of recently published research in photochemistry, with less of an attempt at comprehensiveness. It also is intended to emphasize applications of photochemistry in, for example, synthesis, fabrication of new devices and materials, medicine, pollution control, *etc.*

At the same time, we must bid farewell to three reporters who have contributed indefatigably to the publication over many years. First of all, William Horspool, who has written the first three chapters on organic photochemistry – covering carbonyl compounds, enones and alkenes – for many volumes. The sum of William's contributions represents an enormously valuable and continuous review of these topics, which will, I am sure, continue to be of benefit for many years to come. Secondly, Norman Allen has carried out the Gargantuan task of reviewing the field of polymer photochemistry, also for many years. His contribution to the present volume, containing 949 references, is no exception and well illustrates the size of this job. I am pleased to acknowledge the sustained and enthusiastic contributions made by both William and Norman, and thank them for their support during the brief time I have assumed this responsibility of editorship.

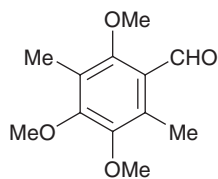
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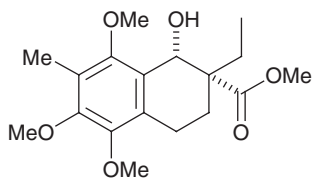
Deserving special recognition for his contribution is Andrew Gilbert, the third of our current contributors who is leaving at this time. Not only has he written the chapters on aromatic photochemistry and photo-oxidation and reduction for a good many years, but was also the Senior Reporter until I took over for Volume 34. He has now passed over the photo-oxidation and reduction chapter into the capable hands of Neil Geraghty, but continues with his contribution on aromatic photochemistry in the current volume. Most of all, though, Andrew merits our gratitude for maintaining both the quality and breadth of coverage of Photochemistry in his long-held position of Senior Reporter. As I am beginning to discover, finding the right authors, with the necessary expertise and the willingness to commit to writing a review annually for a considerable period, is no mean task, one which Andrew has always managed with characteristic tact and persistence. I speak therefore not only for myself but also on behalf of the RSC in thanking him for all the years of dedication which he has brought to the direction of *Photochemistry*.

Having, with great pleasure, made these preliminary acknowledgements, I move to my selection of photochemical highlights of the period reviewed in this volume, which is as subjective and personal as ever. I continue to believe that photochemistry needs to 'earn its living' in the chemical world and not be just a subject of interest for a relatively closed group of specialists, a point of view which will inform the new format *Photochemistry* in future volumes. I have therefore looked especially to highlight work in which photochemistry has accomplished something of real utility: efficient syntheses, the manufacture of commercially useful devices, and biological, medical or environmental applications, for example. 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.

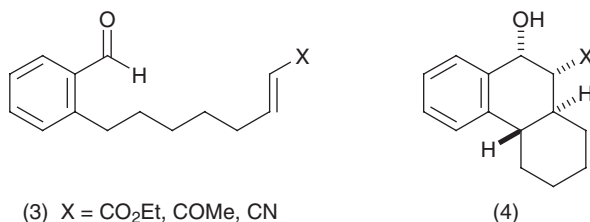
A good example of a high-yielding photoreaction of synthetic utility is provided by the photoenol of the benzaldehyde (1), which can be trapped in very good yield (81%) by methyl 2-ethylacrylate, acting as a dienophile, to give the tetrahydronaphthalene derivative (2) (Nicolaou and Gray, Chapter 1). Related, intramolecular reactions of photoenols have provided routes to polycyclic carbon frameworks, such as the conversion of (3) into (4) (Nicolau *et al.*, Chapter 1).



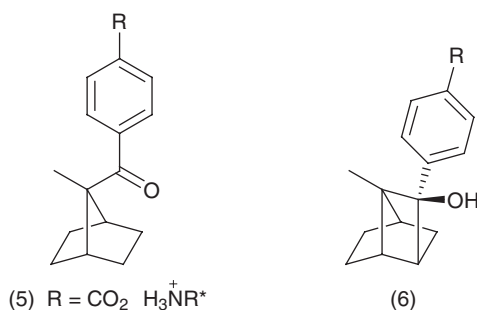
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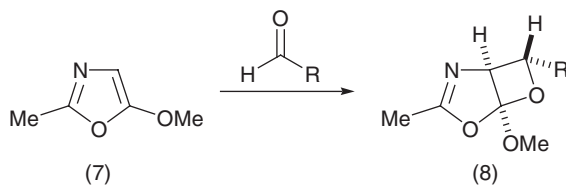
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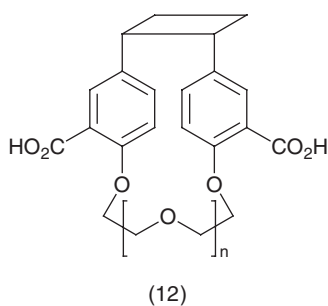
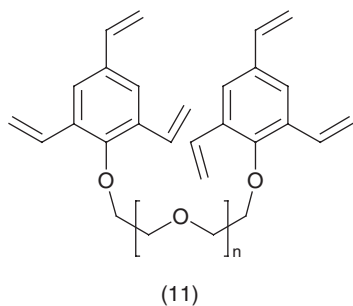
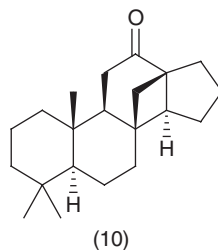
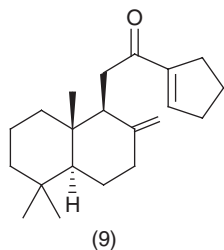


Scheffer *et al.* (Chapter 1) have shown how the use of ionic chiral auxiliaries as a means of immobilizing ketoacids (5) within crystals results in excellent yields of cyclized products upon irradiation, and with high ee. With (*S*)-(+)-1-phenylethylamine as the salt-forming amine, for example, a quantitative yield of (6) with 98% ee was obtained. The corresponding *R* amine similarly gave a quantitative yield of the enantiomer of (6) with an ee of 97%, and other chiral amines were also tried with success.

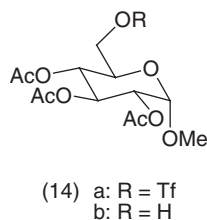
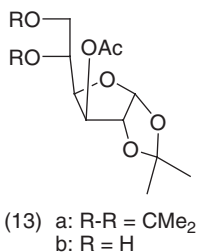


The photocycloaddition of aldehydes to the 5-methoxyoxazole (7) has been developed by Griesbeck *et al.* (Chapter 1) as a path to esters of *erythro*- α -amino- β -hydroxycarboxylic acids. The photoaddition, giving the intermediate bicyclic oxetanes (8: R = Ph, 2-naphthyl, BnCH₂, Et, *i*-Pr, *i*-Bu), occurs with excellent *exo*-diastereoselectivity (dr > 98:2) and chemical yields are >85%. An intramolecular 2 + 2 photocycloaddition has been exploited as the key step in the synthesis of pentacyclic terpene systems, such as the formation of (10) from (9) (de la Torre *et al.*, Chapter 2). The yield of 63% for this example seems reasonable in view of the complexity of the system. Nishimura and co-workers (Chapter 3) have described the synthesis of a series of interesting crownopaddlans by intramolecular photocycloadditions of the compounds (11: n = 2–4), while new crownophanes (12: n = 2–4) were prepared by irradiation of the corresponding divinyl derivatives. Pyridine analogues of (12) were also prepared.

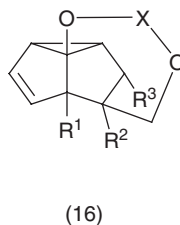
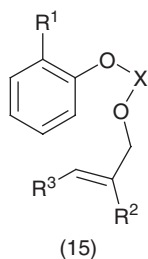




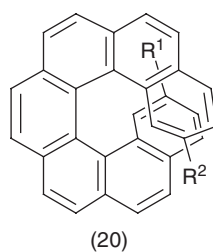
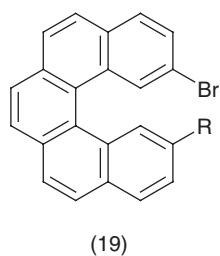
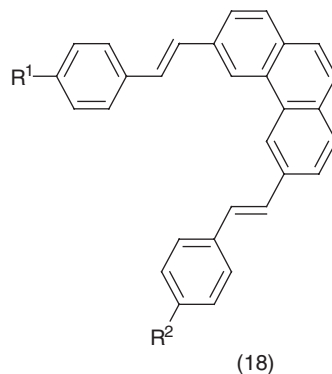
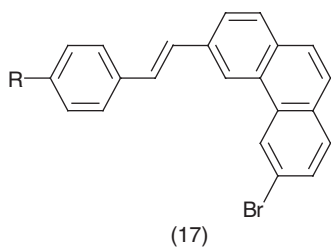
The irradiation of CBr_4 in MeOH has been reported as an efficient photochemical means of removing protecting groups (Chen *et al.*, Chapter 3). Examples are the release of (13b) from (13a) in 89% yield, and (14b) from (14a) in 86% yield.

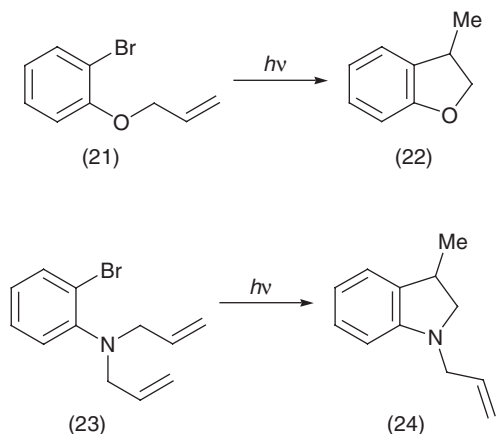


Potentially useful synthetic reactions may not always proceed in high yields. The intramolecular *meta* photocycloadditions of (15: X = CH_2 , SiMe_2 ; R^1 , R^2 , R^3 = H, Me), for example, gave the corresponding 1,6-bridged dihydrosemibullvalene adducts (16) in yields of only 7–19%, but starting with relatively simple precursors provide an approach to complex molecular systems not readily accessible by conventional means (Penkett *et al.*, Chapter 4).



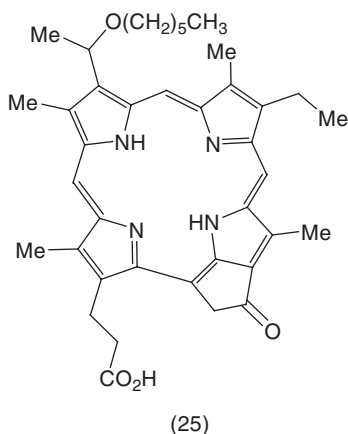
Photocyclizations of mono- and distyryl substituted polynuclear arenes in the synthesis of helicenes have been reported by El Abed *et al.* (Chapter 4). In this work, irradiation of toluene solutions of (17: R = H, OMe, CN, Me, OH) and (18: R¹, R² = H, OMe, Me) with iodine in the presence of propylene oxide as an HI scavenger, afforded 62–96% and 70–90% of the [5]- and [7]carbohelicenes (19) and (20), respectively, depending on the substituents. A remarkable enhancement has been observed for the photocyclizations of 1-allyloxy- and 1-allylamino-2-halogenoarenes, giving dihydrofurans and indoles respectively, when an enolate ion is added as an entrainment reagent (Vaillard *et al.*, Chapter 4). The dihydrofuran (22), for example, was obtained in 55% yield from irradiation of (21) but this was increased to 91% when the CH₃COCH₂⁻ ion was present; and similarly under the latter conditions the yield of (24) from (23) was greater than 96%.

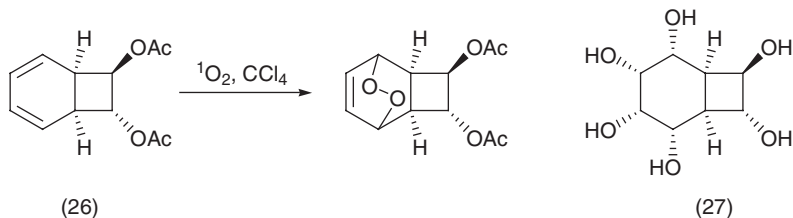




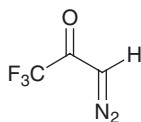
A microreactor has been described, based on SiO_2 capillaries with the inner walls covered with TiO_2 -coated colloidal SiO_2 particles (Li *et al.*, Chapter 5). The reduction of methylene blue was carried out by injecting a solution of the reactant through the microcapillary using a syringe pump, while irradiating at 254 nm, and a 150-fold increase in the reduction rate was obtained relative to a comparable batch system.

The potential of using ceramic-based nanoparticles as carriers of photosensitizers for photodynamic therapy (PDT) has been described (Roy *et al.*, Chapter 5). As an example, the anticancer drug 2-devinyl-2-(1-hexyloxyethyl)pyropheophorbide (25) has been encapsulated in the non-polar core of micelles by hydrolysis of triethoxyvinylsilane. The resulting particles were uniform in size, having an average diameter of 30 nm, and were stable in an aqueous medium. The uptake of the nanoparticles by tumour cells, and significant cell death following $^1\text{O}_2$ generating irradiation at 650 nm, was then demonstrated *in vitro*. The photooxygenation of *trans*-8-(acetyloxy)bicyclo[4.2.0]octa-2,4-dien-7-yl acetate (26) was a key step in the stereospecific synthesis of a new inositol analogue (27) (Kara and Balci, Chapter 5).

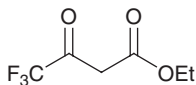




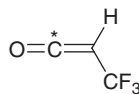
The trifluoromethyl group has long been considered as having a low tendency to migrate to a carbene centre, and this seemed to explain why, for example, photolysis of the diazoester (28) results in hydrogen abstraction to give (29), rather than rearrangement. An investigation of the photolysis of a ^{13}C -labelled isotopomer of (28), however, has now shown that an estimated 93.5% of the rearranged product (30) was produced by trifluoromethyl migration (Haiss and Zeller, Chapter 6). Meldrum's acid (31) undergoes isomerization to the corresponding diazirine when irradiated at 355 nm, but loss of N_2 and Wolff rearrangement at 254 nm; the two processes clearly occur from two different electronic excited states (Bogdanova and Popik, Chapter 6).



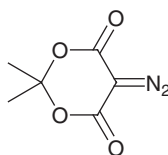
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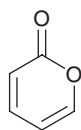


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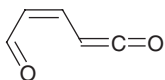


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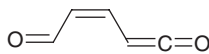
A very good example of the enormous benefits that DFT computations of IR spectra have brought to matrix-isolation studies – giving the technique a veritable new lease of life in the study of organic reactive intermediates – has been provided by a study of the photolysis of α -pyrone (32) and its 4,6-dimethyl derivative (Breda *et al.*, Chapter 6). The photochemistry of α -pyrone was the subject of some of the earliest matrix-isolation studies of organic species, but the use of DFT computations has now allowed a virtually complete identification of the individual rotamers of the ring opened aldehyde-ketene (33)–(36).



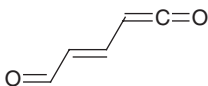
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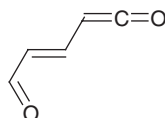
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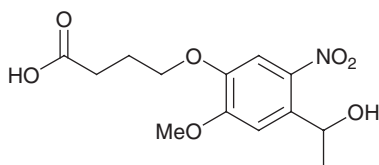


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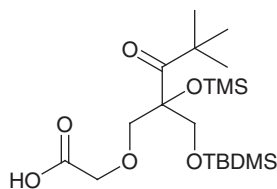


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Wavelength dependent differential release of compounds from a solid-phase resin has been demonstrated, using beads bifurcated with nitroveratryl (37) and pivaloyl glycol (38) photo-linkers (Ladlow *et al.*, Chapter 6). A narrow bandwidth tuneable pulsed laser was used for photolysis, and it was found that the nitroveratryl linker undergoes cleavage over a wide range of wavelengths, with maximum cleavage rates at 320 and 340 nm, while the pivaloyl glycol linker is photo-stable at wavelengths above 340 nm.



(37)



(38)

Finally, it must be remarked that, as is so often the case, the real highlight in polymer photochemistry (Chapter 7) for the review period is the sheer volume of work in this field. Polymer photochemistry continues to be an active area of applied photochemistry, with many topics growing in commercial and industrial importance. New materials are constantly emerging from studies of photopolymerization, photocuring and photocrosslinking, *e.g.* polymers with useful mechanical and electronic properties and liquid crystalline materials. Last year, for example, saw a virtual literature explosion in LEDs (light emitting diodes), and in this year's review it still represents one of the largest specialized topics in photochemistry and photophysics.