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# PHOTOCYCLOADDITION OF CYCLOHEXENE AND MALEIC ANHYDRIDE SENSITIZED BY INSOLUBLE BENZOYLATED POLYSTYRENE

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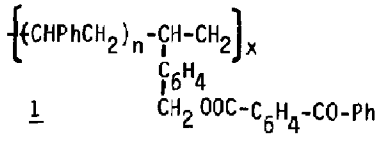
Abstract: Friedel-Crafts benzoylation of styrene - 2% DVB copolymer beads yielded insoluble benzoylated polystyrene which was successfully used as sensitizer in the |2+2| photocycloaddition of cyclohexene with maleic anhydride.

Several insoluble polymeric sensitizers have been in use to perform some types of photochemical reactions. Thus, polystyrene-bound dyes, such as Rose Bengal, sensitize singlet oxygen formation[1] and oxidations derived from it, while poly-p-styrylmethyl 4-benzoylbenzoate 1 has been claimed[2] to mimic the behaviour of benzophenone in sensitized |2+2| photocycloadditions. Surprisingly, however, the simplest insoluble polymeric benzophenone analog, namely cross-linked poly-p-benzoylstyrene 2, was not considered as a good candidate "because of the problem with $AlCl_3$ incorporation when Polystyrene-divinylbenzene beads are benzoylated under Friedel-Crafts conditions"[2]. We have already performed some photochemical reactions on polymer-bound substrates[3], and in the present report we show that $AlCl_3$-free 2 can be easily prepared and advantageously used as sensitizer in the title photocycloaddition.

Benzoylation of polystyrene - 2% DVB copolymer beads, 200-400 mesh, by PhCOCl (10% excess) and $AlCl_3$ (1 equiv.) in $CS_2$ at 25°C for 20 hrs, followed by thorough washings with 2% HCl, $H_2O$, $H_2O$ - acetone (1:1), acetone, acetone-methanol (1:1), methanol, methanol-dioxane (1:1), dioxane, dioxane-ether (1:1) and finally ether yielded, after drying (60°C, 1-2 mmHg, 7-15 days), either 2 (n=1) or 2 (n=15), both of them free of halogen (elemental analysis). The degree of functionalization of 2 was determined by oximation and elemental analysis of nitrogen in the washed and dried polymeric oximes.

The |2+2| photocycloaddition of cyclohexene 3 and maleic anhydride 4 sensitized by benzophenone 5 is a well known reaction[4], and gives a mixture of diastereomeric anhydrides of constitution 6, in yields up to 67% when carried out at -80°C in acetone[4b]. In the absence of sensitizer and of solvent, direct irradiation of the charge-transfer complex between 3 and 4 gives also[4c] small amounts (<12%) of 6.



$\left[(CHPhCH_2)_n\text{-}\underset{\substack{C_6H_4\\ CH_2\,OOC\text{-}C_6H_4\text{-}CO\text{-}Ph}}{CH}\text{-}CH_2\right]_x$

1

$\left[(CHPhCH_2)_n\text{-}CH(C_6H_4COPh)CH_2\right]_x$

2

We have studied the photocycloaddition between 3 and 4 at room temp., with Pyrex filter (λ>310 nm) under sensitization by either 5 or 2, as well as without sensitizer. A typical run was as follows: in a small conventional photochemical reactor vessel (50 ml capacity) with a Pyrex immersion well and a medium pressure mercury lamp Philips HPK-125, were introduced 20.4 mmole of 4, 1.5 mmole of 5 (or the equivalent number of carbonyl groups in the form of 2), 3.0 mmole of diethyl adipate as internal standard and 10 ml (99.0 mmole) of 3, and the volume was completed to 30.0 ml with either 3 or acetonitrile. Irradiations were carried out under $O_2$-free dry $N_2$. Fig. 1 shows the formation of 6, quantitatively determined as a function of irradiation time by g.l.c. By-products formed under sensitization by 5 were: 3-(cyclohex-2-en-1-yl)cyclohexene 7, cyclohex-2-en-1-yldiphenylmethanol 8 and 7,7-diphenylhept-6-enal 9, as well as benzopinacol and benzhydrol. Compounds 7 and 8 had already been found[5] during photolysis of 5 in 3, together with the oxetane, 8,8-diphenyl-7-oxabicyclo[4.2.0]octane 10. We could not find 10 in our experiments, but it probably was formed and converted into the aldehyde 9 found by us. In the reactions sensitized by 2 the only by-product found after filtration was 7 (all others, if present, should remain anchored to the polymer). One additional by-product in these polymeric runs was 11, also anchored to the polymer, formed by photocycloaddition of 4 on the unsubstituted phenyl rings of 2, followed by Diels-Alder addition of a second molecule of 4, as is known to happen for benzene[6] and soluble polystyrene[7].

Formation of 7 demonstrates the photooxidant properties of our polymeric benzophenone 2. Therefore, a new series of irradiations was performed as above, but omitting 4. Fig. 2 gives the results of these irradiations.

As seen in the figures, both the soluble (5) and the insoluble (2) sensitizers achieve the photocycloaddition to 6 and the photooxidation of 3 to its dimer 7. The efficiency of 2 (n = 15) is roughly 75% that of 5 while, surprisingly, for the more functionalized 2 (n=1) it is only 50%. It must be pointed out here that polymeric benzophenones 2 recovered after their use as sensitizers no longer exhibit a carbonyl stretching band in their i.r. spectra, hydroxyl stretching being observed instead. This disappearance of carbonyl groups in the polymers takes place before the complete exhaustion of maleic anydride (Fig. 1). We conclude that hydrogen atom abstraction by the excited triplet carbonyls from either cyclohexene or benzylic positions in the polymer itself can explain these facts. In the latter case, formation of a new C-C bond by combination of the polymeric diradical formed after hydrogen atom transfer should produce additional cross-linking on the polymeric sensitizer, as has been found[8] for 1. In the case of the highly loaded polymer 2 (n=1), this photo-induced cross-linking process would quickly render the polymer unswellable, thus preventing the arrival of ground state molecules of 4 near the triplet carbonyls of the sensitizer, and therefore the transfer of triplet character to 4 and subsequent photocycloaddition would be slowed down and eventually suppressed. The lightly loaded 2 (n=15) would be less deactivated by this process.

Because of this photoinduced cross-linking, polymeric benzophenone 2 is not reusable as a sensitizer. Polyester 1, however, in spite of previous claims[2], cannot be reused, since it

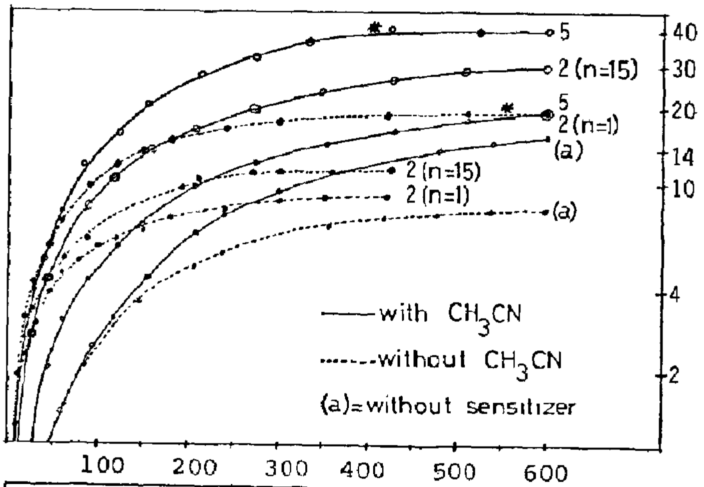


Fig. 1. Percent yield of 6 against minutes of irradiation. Points marked ✱ indicate exhaustion of 4.

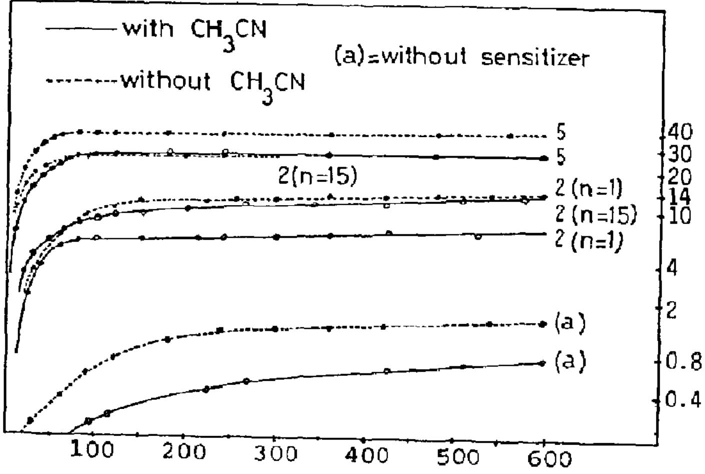
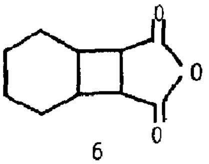


Fig. 2. Percent yield of 7 (based on initial 5) against minutes of irradiation.



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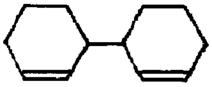

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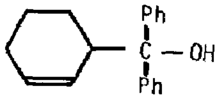

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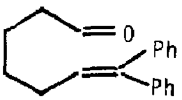

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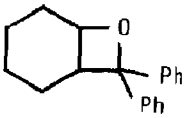

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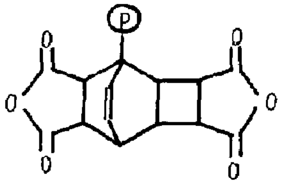

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undergoes the same process[8]. Moreover, this polymeric ester has been found to release benzophenone when irradiated[8], so part of the sensitization observed when it is used can be due to benzophenone itself. In our experiments with 2 there is no possibility of a benzophenon release and, accordingly, we could not find any benzophenone by g.l.c. analysis of the crude reaction mixtures. Therefore, sensitization by 2 is definitely a sensitization in solid phase.

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