

CONCERNING THE USE OF POLYMER BASED PHOTSENSITIZERS

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As part of a program designed to study the useful features of polymer based reagents in synthetic processes, we have investigated the use of benzoylated polystyrene-divinylbenzene copolymer beads as sensitizers for certain photocycloaddition reactions. Our results demonstrate that under certain conditions, benzoylated polystyrene-divinylbenzene (hereafter referred to as P)-Benzoyl) can be used effectively as a photosensitizer. We report these results in preliminary form now.

Benzoylated polystyrene-divinylbenzene is prepared by the reaction of chloromethyl polystyrene-divinylbenzene (1.8%) copolymer beads³ with para-benzoyl benzoic acid using ethyl acetate as a solvent and triethyl amine as a catalyst. In a typical preparation, 10.0 g of chloromethylated styrene-divinylbenzene copolymer (1.38 meq.Cl/g) and 3.18 g (14 meq.) of para-benzoyl benzoic acid were refluxed overnight with 70 ml. of ethyl acetate and 2.0 ml of triethyl amine. The beads were then filtered and carefully washed with various solvents using Merrifield's procedure to insure that all the free acid was removed from the polymer matrix.⁴ The remaining copolymer possessed both an ester absorption (5.75 μ) and a benzophenone absorption (6.01 μ) in the infrared spectrum. The attached benzoyl benzoic acid could be quantitatively removed from the polymer by trans-esterification with triethyl amine in methanol.

P)-Benzoyl was used successfully as a heterogeneous sensitizer⁵ for the conversion of coumarin to its dimers, to sensitize the cycloaddition of

tetrachloroethylene to cyclopentadiene and to sensitize the dimerization of indene. Results are detailed in Tables I and II.

TABLE I

Use of P -Benzoyl as a Photosensitizer^a

Reactants (in mmoles)	Sensitizer	Temp.	Time	Products (%) ^b
Indene (No solvent)	Benzophenone (5 mmoles)	25 ^o	20 h.	(1) 4% (2) 38%
Indene (NO Solvent)	P -Benzoyl (1.0 g) ^c	25 ^o	20 h.	(1) 0.5% (2) 12.0%
Indene (17.2 mmoles in 15 ml. benzene)	Benzophenone (2.75 mmoles)	25 ^o	24 h.	(2) 97%
Indene (17.2 mmoles in 15 ml. benzene)	P -Benzoyl (1.0 g.)	25 ^o	11 h.	(2) 61%
Indene 17.2 mmoles in 15. ml. of benzene)	none			none
TCE ^d (37.2 mmoles) + CPD ^e (15.7 mmoles)	Benzophenone (0.55 mmoles)		10 ^o 11 h.	2.7% ^h
TCE (37.2 mmoles) + CPD (15.7 mmoles)	P -Benzoyl ^f		10 ^o 11 h.	3.3%
TCE (37.2 mmoles) + CPD (15.7 mmoles)	P -Benzoyl ^g		10 ^o 11 h.	3.5%
TCE (37.2 mmolâs) + CPD (15.7 mmoles)	none		10 ^o 11 h.	-----

- a. Experiments were carried out in standard photoreaction vessels with a 450 watt Hanovia medium pressure lamp.
- b. Percentages were determined by g.c. IN the case of indene, both products are reported when they were formed, They are dimers.^{6,7}
- c. The amount of benzophenone residues attached to the polymer is, at the maximum, 1.38 meq/g
- d. Tetrachloroethylene
- e. Cyclopentadiene
- f. Not stirred
- g. Soluble polystyrene was used instead of insoluble beads and the attaching support.
- h. Adducts are formed.⁹

The most dramatic results were obtained with coumarin. Purer product was obtained, without purification, using the polymer sensitizer beads, (P)-Benzoyl, than could be obtained from the use of benzophenone as a sensitizer after several purifications. The results are given in Table II.

TABLE II

(P)-Benzoyl as a Sensitizer for Coumarins

<u>Reactant</u>	<u>(Amts. in mmoles)</u>	<u>Sensitizer</u>	<u>Time</u>	<u>Photoproducts^a</u>
Coumarin	(5 mmoles in 10 ml. benzene)	Benzophenone (15 mmoles)	72 h.	oil ^b
Coumarin	(5 mmoles in 10 ml. benzene)	(P)-Benzoyl (1.4 meq)	72 h.	m 171-174 ^o
Coumarin	(5 mmoles in 10 ml. benzene)	(P)-Benzoyl (1.1 meq)	72 h.	m 164-172 ^o

- The photoproducts obtained were those observed by Hammond⁸ and by Schenck⁶ from the benzophenone sensitized dimerization of coumarin.
- The photodimer can be isolated from this oil only after chromatography or repeated recrystallization⁸.

The use of (P)-benzoyl as a sensitizer has several advantages over conventional sensitizers in cases where (P)-benzoyl works well. Among the advantages of the polymer based sensitizer are the ease by which it can be separated from the excess reactants and products and the fact that it can be reused. Since the sensitizer is always attached to the polymer, it can always be recovered and accounted for and there is no danger that it be lost in the reaction mixture. We are certain, in cases where separation of the sensitizer from the products is for some reason difficult, (P)-benzoyl will be both useful and advantageous on a synthetic photoreaction.

Other uses of polymer based photosensitizers and photoreagents are being investigated and will be described in subsequent communications.

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* A referee justifiably questioned the propriety of this name. It was chosen because it is shorter than the more appropriate polystyryl-4-benzoyl benzoate, and about as accurate.