

Oxetane Formation by Addition of *N*-Substituted Imidazoles to Benzophenone and Poly(4-Vinylbenzophenone)s

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SYNOPSIS

Photochemical oxetane formation by addition of 1-methyl-2,4,5-triphenylimidazole (**1a**), 1,2-dimethyl-4,5-diphenylimidazole (**1b**), and 1-acetylimidazole (**1c**) to benzophenone (BP), poly(4-vinylbenzophenone) (PVBP), and poly(styrene-co-4-vinylbenzophenone) (PSVBP) was studied in the solution and solid phases. In solution, BP underwent the photoaddition smoothly to all three imidazoles **1a–1c**. On the other hand, the photoaddition of PVBP and PSVBP depended on the imidazole employed, that is, **1b** and **1c** produced the corresponding oxetane, but **1a** did not. The lack of oxetane formation from the polymeric BP and **1a** is probably due to a rapid triplet-sensitized decomposition of a once-formed oxetane ring as a result of the intramolecular triplet energy transfer from a pendant benzophenone group. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Several years ago, we reported an efficient [2 + 2] photoaddition of benzophenone (BP) to 1-methyl-2,4,5-triphenylimidazole (**1a**) giving oxetane **2a** in acetonitrile solution.¹ The photoaddition likewise went on for substituted BPs when their triplet energies (E_T 's) are below 70 kcal/mol.¹ A polymeric BP poly(4-vinylbenzophenone) (PVBP) with the E_T almost equal to that of BP, however, was found to undergo no photoaddition with **1a**. The present study was initiated to understand this curious polymer effect on the oxetane formation.

We used BP, PVBP, and a copolymer of styrene and 4-vinylbenzophenone (PSVBP) as the ketone component and **1a**, 1,2-dimethyl-4,5-diphenylimidazole (**1b**), and 1-acetylimidazole (**1c**) as the imidazole component [eqs. (1) and (2)]. Photochemical oxetane formation in the polymer system has long been known.^{2–4}

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EXPERIMENTAL

General

NMR spectra were taken on a Varian T-60 or a JEOL GX-400 spectrometer, with TMS as an internal standard. IR spectra were measured on a JASCO IRA-1 spectrometer by using polystyrene film as a calibration standard. UV spectra were measured on a Shimadzu UV-200 spectrometer. Thin-layer chromatography (TLC) and column chromatography were done on Merck precoated TLC (or PLC) plates (silica gel 60 F₂₅₄) and Wako-gel C-200, respectively.

Irradiation was done with a 400-W high-pressure mercury lamp through a Pyrex filter, unless otherwise specified. During the irradiation, a sample was cooled with an ice-water bath and nitrogen was passed through the reaction vessel.

Samples

PVBP was prepared as follows. A mixture of 4-vinylbenzophenone⁵ (3.0 g, 14 mmol) and recrystallized α,α' -azobisisobutyronitrile (30 mg, 0.18 mmol) in 60 mL of benzene was flushed with bub-

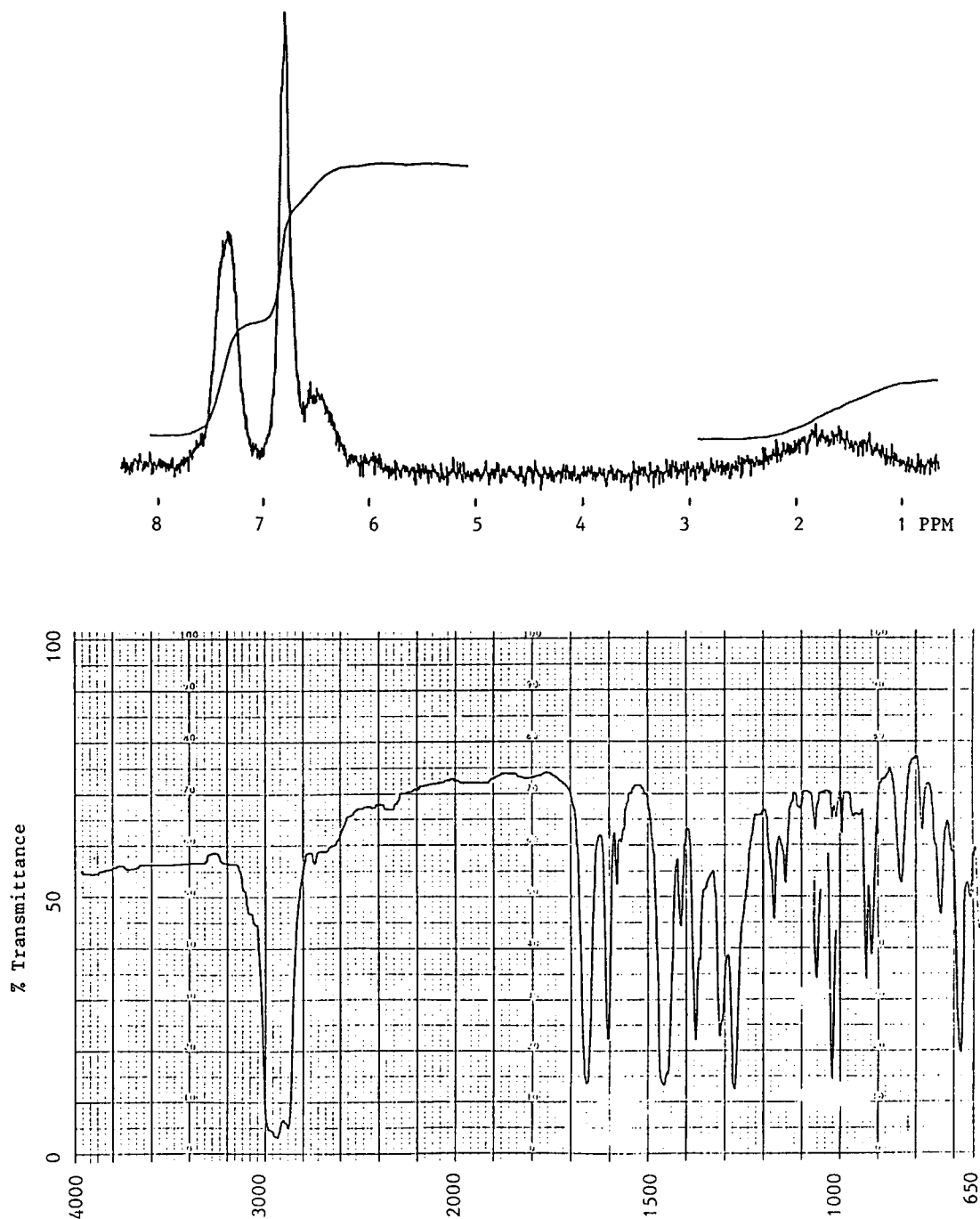


Figure 1 The NMR (in C_6D_6) and IR (in nujol) spectra of poly(4-vinylbenzophenone) (PVBP).

bling nitrogen. Then, the polymerization was carried out at $70 \pm 2^\circ C$ for 25 h under gentle stirring. After precipitation three times from benzene (20 mL) into methanol (200 mL), 1.51 g (51%) of the polymer was obtained as a white solid. Its NMR and IR spectra are displayed in Figure 1. The molecular weight

determined by osmometry (CORONA 117 Molecular Weight Apparatus) was 25,000.

PSVBP was similarly prepared from styrene (8.0 g, 77 mmol) and 4-vinylbenzophenone (2.0 g, 9.6 mmol). The styrene/4-vinylbenzophenone molar ratio in the polymer was estimated by NMR and UV

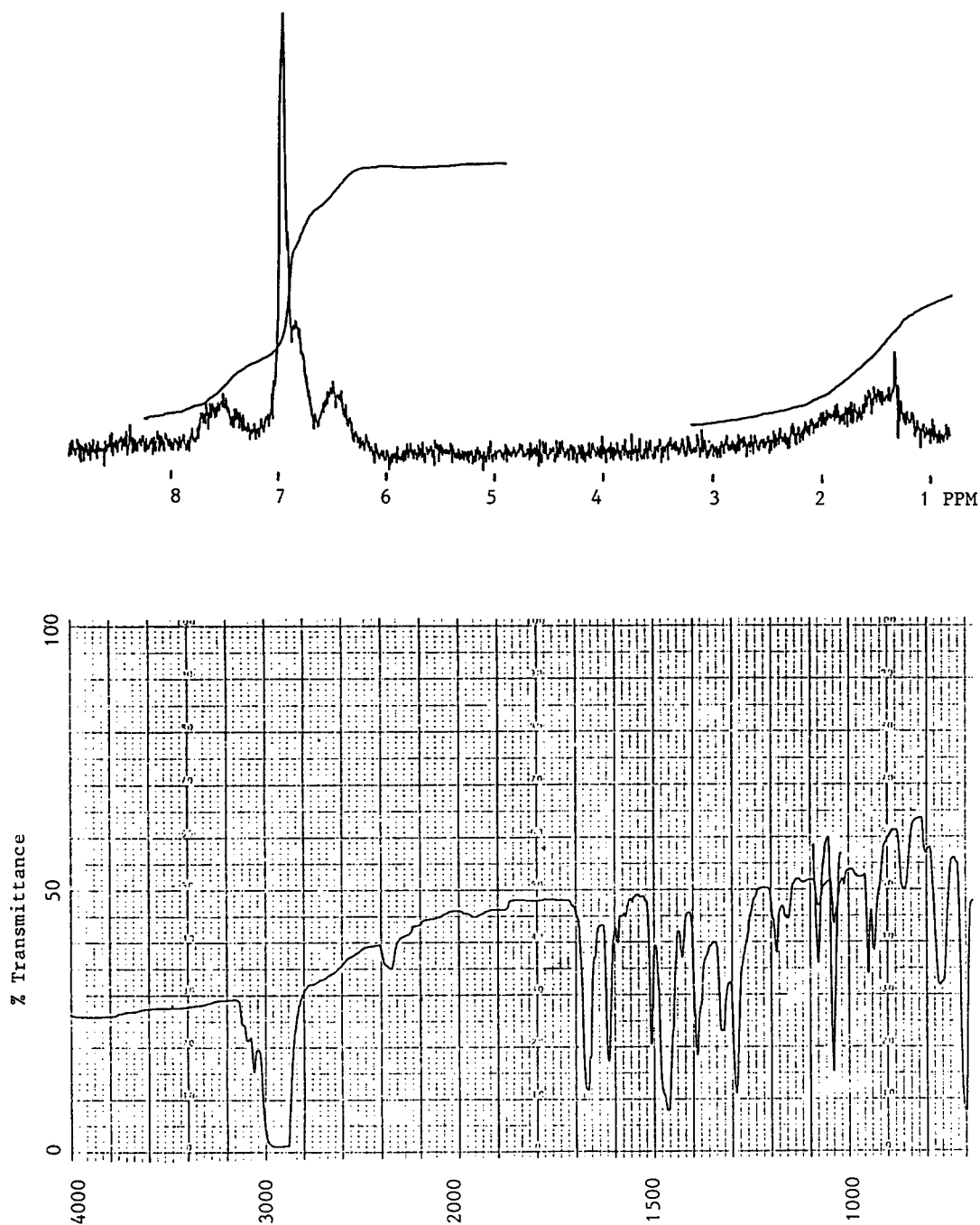


Figure 2 The NMR (in C_6D_6) and IR (in nujol) spectra of poly(styrene-co-4-vinylbenzophenone) (PSVBP).

to be 2.6, that is, styrene \approx 56 wt. % and 4-vinylbenzophenone \approx 44 wt. %. The NMR and IR spectra are shown in Figure 2.

1-Methyl-2,4,5-triphenylimidazole (**1a**) and 1,2-dimethyl-4,5-diphenylimidazole (**1b**) were prepared as described previously.⁶ 1-Acetylimidazole (**1c**) is commercially available.

Photolyses

Photolyses of **1a** With BP

A typical procedure is as follows. A solution containing 1.7 g (5.5 mmol) of **1a** and 5.7 g (31 mmol) of BP in acetonitrile (230 mL) was irradiated for 1.5 h. After rotary evaporation, the residue was

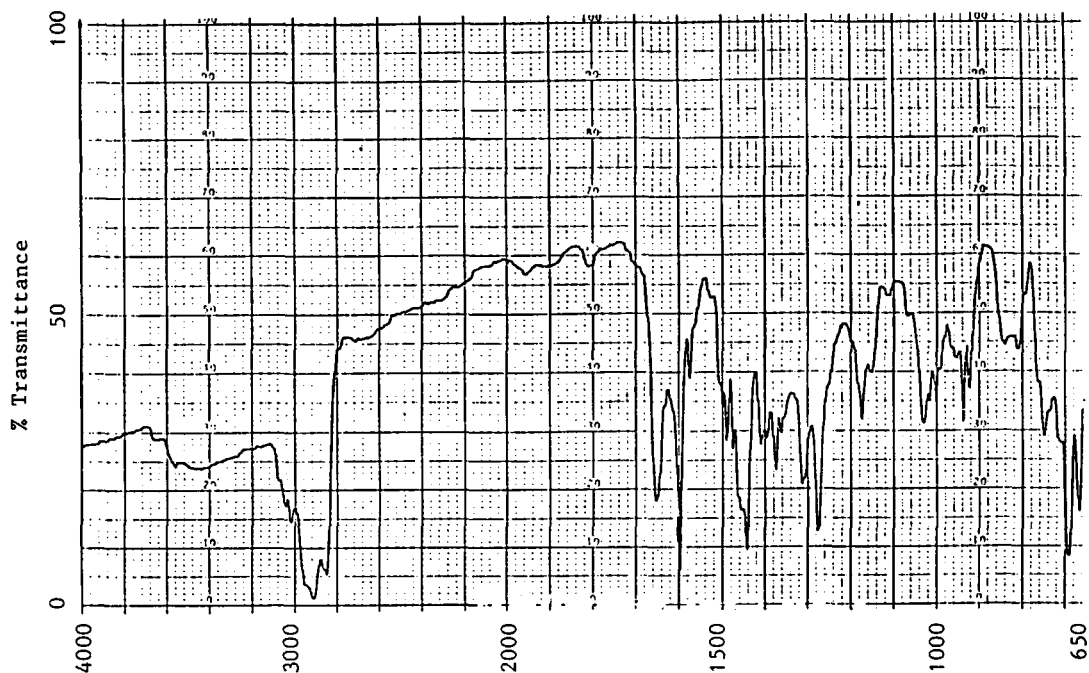


Figure 3 The IR spectrum of poly-oxetane **3b** (in nujol).

found by the NMR analysis to be a mixture of **2a** 64%, **5a** 3%, and **1a** 33%. Isolation of **5a**, which had already been characterized,⁶ was done with preparative TLC (ethyl acetate–hexane, 1 : 4 v/v) in a separate experiment. Oxetane **2a** was isolated by low-temperature (–20 to –30°C) column chromatography on silica gel, using ethyl acetate–hexane (1 : 4 v/v) as eluent. On silica gel at room temperature, **2a** decomposed in a few hours to produce, quantitatively, **1a** and BP. After recrystallization from hexane, 540 mg (20%) of **2a** was obtained as white crystals: mp 169–170°C; NMR (CDCl₃) δ 7.8–6.8 (25 H, m, phenyl), 2.60 (3 H, s, N–CH₃); IR (nujol) 960 cm⁻¹ (oxetane ring⁷); UV (acetonitrile) λ 260 (ϵ 4600), 200 (61000) nm; MS m/e 492 (M⁺, 0.5), 310 (100), 182 (67), 105 (89). For the X-ray structure of **2a**, see Ito et al.¹

ANAL: Calcd for C₃₃H₂₈N₂O: C, 85.33%; H, 5.73%; N, 5.69%. Found: C, 84.99%; H, 5.57%; N, 5.59%.

A solution containing **2a** (50 mg, 0.1 mmol) in dry (with K₂CO₃) *tert*-butylbenzene (2 mL) was heated at 120°C for 2.5 h. Quantitative decomposition of **2a** into **1a** and BP was observed by TLC and NMR.

Photolyses of **1a** With PVBP or PSVBP

Solutions containing 50–150 mg of **1a** and 50–100 mg of the polymer in benzene (10 mL) or benzene/acetonitrile (16 mL, 15 : 1 v/v) were irradiated for

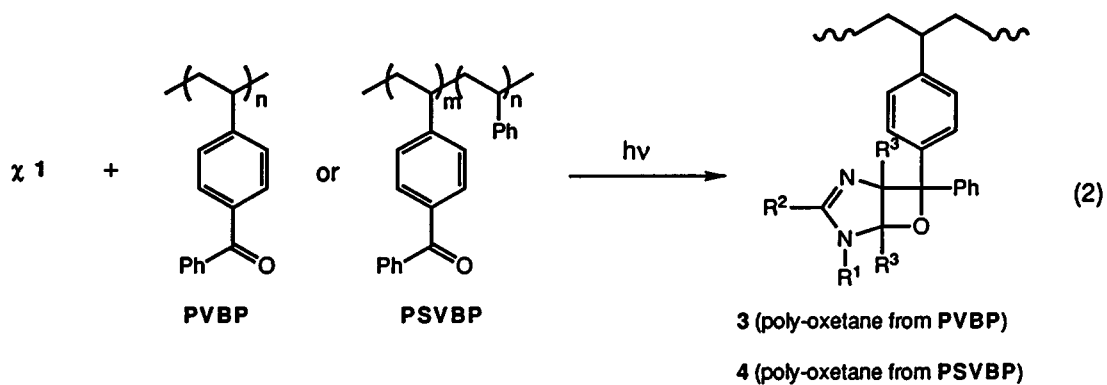
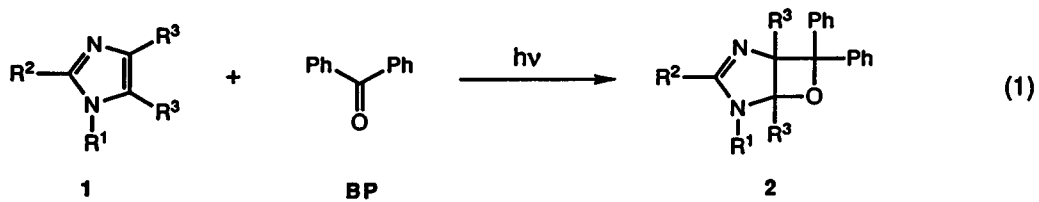
6–16 h. Each reaction mixture was concentrated and was poured into methanol (50 mL). The resultant precipitate was further purified by precipitation twice from benzene to methanol. NMR, IR, TLC, and UV analyses of both the precipitate and the methanol layer were done. The precipitate was found to be an unchanged PVBP or PSVBP.

Photolyses of **2a**

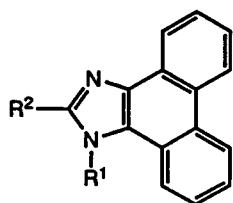
Both the BP-sensitized and direct photolyses were performed. In the sensitization experiment, a solution containing **2a** (50 mg) and BP (100 mg) in acetonitrile (20 mL) was irradiated for 7 h. In the direct photolysis, a solution containing **2a** (50 mg) in acetonitrile (20 mL) was irradiated with a 10-W low-pressure mercury lamp through a Vycor filter (mainly 254 nm) for 7 h. The NMR analyses of the reaction mixtures gave results shown in eq. 3.

Photolyses of **1b** With BP

A solution containing **1b** (0.80 g, 3.2 mmol) and BP (2.2 g, 12 mmol) in acetonitrile 150 mL was irradiated for 2 h. After rotary-evaporation, the residue was analyzed with NMR. Oxetane **2b** was detected as an almost exclusive product, while the signals for **1b** and **5b** were not observed. Compound **2b** was isolated by low-temperature (–20 to –30°C) silica gel column chromatography by using ethyl acetate-



For 1 - 4
 a; $R^1 = \text{Me}, R^2 = R^3 = \text{Ph}$
 b; $R^1 = R^2 = \text{Me}, R^3 = \text{Ph}$
 c; $R^1 = \text{COMe}, R^2 = R^3 = \text{H}$



5a, $R^1 = \text{Me}, R^2 = \text{Ph}$
 5b, $R^1 = R^2 = \text{Me}$

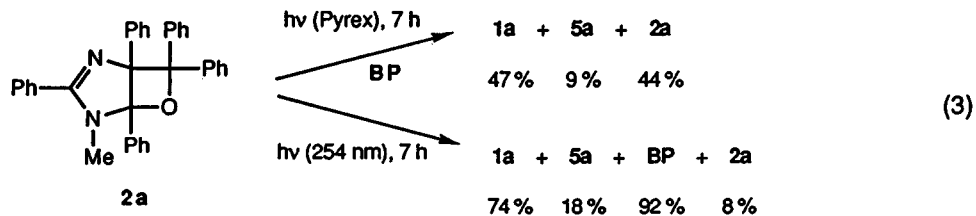


Table I Photolyses of Benzophenones With Imidazoles

Expt.	Imidazole (mM)	Ketone (mM)	Solvent	Irradiation Time (h)	Product (%)		Recovered 1 (%)
					Oxetane ^a	Phenanthrene	
1	1a (24)	BP (135)	MeCN	1.5	2a, 64	5a, 3	33 ^b
2	1a (24)	BP (41)	MeCN	3	2a, 38	5a, 13	49 ^b
3	1a (24)	BP (135)	C ₆ H ₆	1.5	2a, 22	5a, 1	77 ^b
4	1a (17)	PVBP (25) ^c	C ₆ H ₆	6	None	None	100
5	1a (30)	PVBP (16) ^c	C ₆ H ₆ -MeCN (15 : 1)	16	None	5a, 11	89
6	1a (32)	PSVBP (21) ^c	C ₆ H ₆	10	None	None	100
7	1a (0.2) ^d	BP (1.2) ^d	None	4	2a, 47	None	53 ^b
8	1a (0.16) ^d	PVBP (0.28) ^d	None	6	None	None	100
9	1b (22)	BP (81)	MeCN	2	2b, 70	None	None
10	1b (25)	PVBP (15) ^c	C ₆ H ₆ -MeCN (15 : 1)	17	3b, 28	5b, 23	52
11	1b (25)	PSVBP (6.6) ^c	C ₆ H ₆ -MeCN (15 : 1)	18	4b, 36	5b, 21	70
12	1c (66)	BP (196)	C ₆ H ₆	25	2c, 92	—	8
13	1c (14)	PVBP (5.9) ^c	C ₆ H ₆	20	3c, 50	—	46
14	1c (1.0) ^d	BP (0.50) ^d	None	24	None	—	100

^a The oxetane yields were calculated on the basis of the initial amount of the limiting reagent, that is, imidazole for Experiments 1–3, 7, 9, and 12 and ketone for Experiments 10, 11, and 13.

^b Data from Ito et al.¹

^c The concentration of 4-vinylbenzophenone unit.

^d In mmol.

hexane (1 : 2 v/v) as eluent and was recrystallized from acetone: mp 140–145°C; NMR (CDCl₃) δ 7.7–6.85 (20 H, m, phenyl), 2.61 (3 H, s, Me-N), 1.66 (3 H, s, Me-C); IR (nujol) 995 cm⁻¹ (split, oxetane ring⁷); UV (ethanol) λ 255 (ϵ 4100), 204 (43000) nm; MS *m/e* 430 (M⁺, 0.5), 248 (100), 182 (37), 105 (60). The elemental analysis gave the correct C : H : N ratio.

A solution containing **2b** (20 mg) in *tert*-butylbenzene (1 mL) was heated at 150°C for 1 h. An NMR analysis of the reaction mixture showed that it was an equimolar mixture of **1b** and BP.

Photolyses of **1b** With PVBP

A solution containing **1b** (201 mg, 0.81 mmol) and PVBP (100 mg, 0.48 mmol vinylbenzophenone unit) in 32 mL of benzene/acetonitrile (15 : 1 v/v) was irradiated for 17 h. A resultant white precipitate (101 mg) was collected by filtration. The filtrate was concentrated and poured into methanol to get 25 mg of another precipitate. The IR spectra of both precipitates were essentially the same and they were assigned as poly-oxetane adducts between PVBP and **1b** (**3b**) because a band observed at 1030 cm⁻¹ (Fig. 3) corresponds to the oxetane structure.⁷ The yield of oxetane was estimated in two ways. First, from the nitrogen content of the elemental analysis for **3b** (C, 84.03%; H, 6.08%; N, 2.85%), it was cal-

culated to be 28% on the basis of the vinylbenzophenone unit. Second, from the weight gain of the polymer (26 mg), it was calculated to be 21% on the basis of the vinylbenzophenone unit. The value estimated by the first method is listed in Table I (Experiment 10; this statement is also valid for Experiments 11 and 13). The filtrate of the second precipitate was evaporated to dryness to give 164 mg of the residue and the NMR analysis showed that it was a mixture of **1b** (71%) and **5b** (29%). They were separated by preparative TLC (benzene-AcOEt, 1 : 6 v/v). Phenanthrene **5b** was already characterized.⁶

Poly-oxetane **3b** (56 mg) suspended in *tert*-butylbenzene (2.5 mL) was heated at 150°C for 5 h. The reaction mixture was filtered and washed with benzene to give 45 mg of a solid, whose IR spectrum was indistinguishable from that of PVBP. PVBP thus recovered was insoluble in benzene, although the original PVBP was soluble in benzene. The filtrate was evaporated to give 11 mg of the residue, which was subjected to preparative TLC (AcOEt) to afford 2 mg of **1b**.

Photolyses of **1b** With PSVBP

A solution containing **1b** (200 mg, 0.81 mmol) and PSVBP (100 mg, 0.21 mmol vinylbenzophenone unit) in 32 mL of benzene/acetonitrile (15 : 1 v/v)

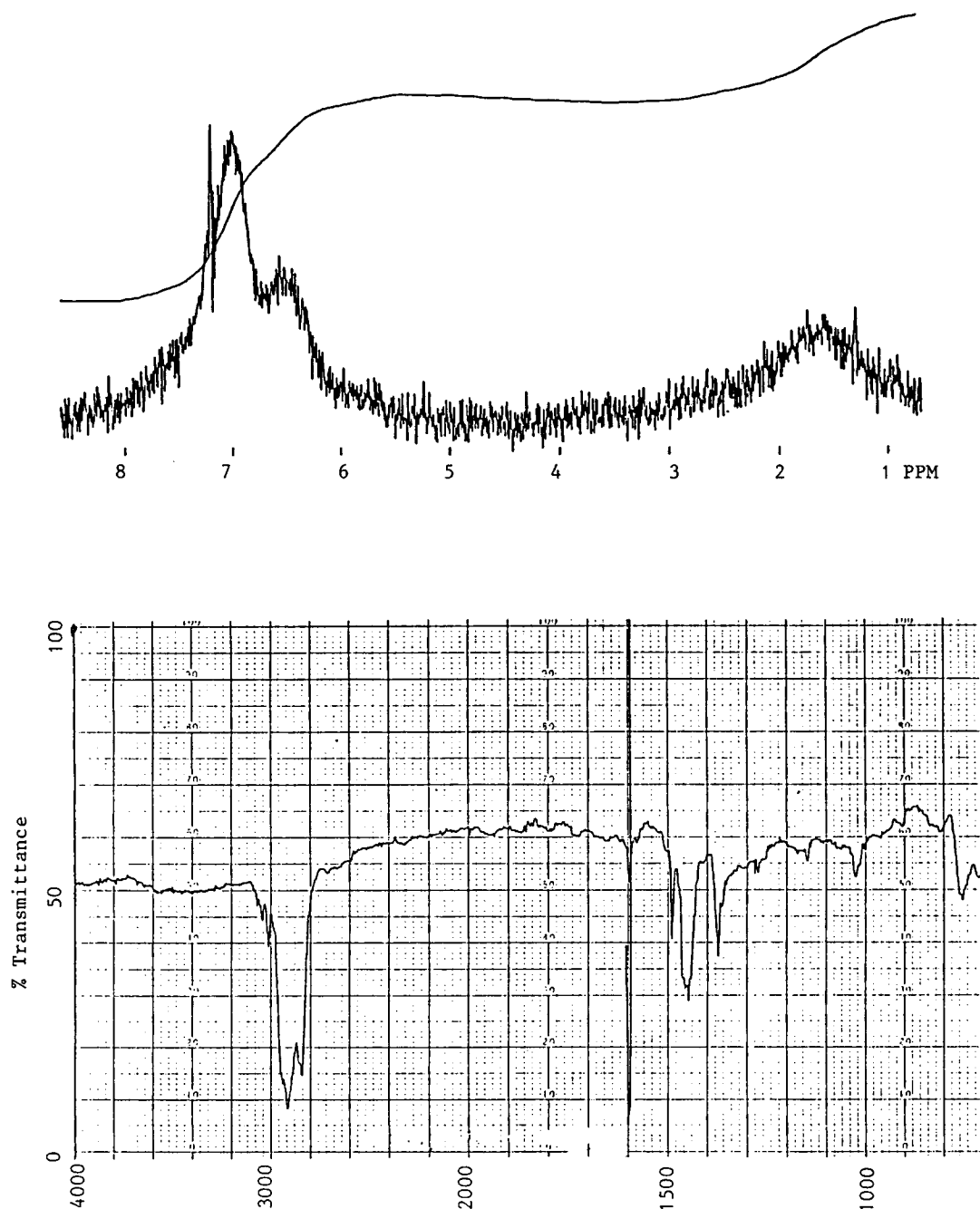


Figure 4 The NMR (in CDCl_3) and IR (in nujol) spectra of poly-oxetane **4b**.

was irradiated for 18 h. The reaction mixture was concentrated and poured into methanol. The precipitate formed was collected by filtration, weighing 116 mg. It was purified by repeated precipitation from benzene into methanol and analyzed by NMR, IR, and elemental analyses. In the NMR and IR spectra (Fig. 4), absorption bands that are ascribable to the carbonyl group are unobservable and the IR peak at 1030 cm^{-1} corresponds to the oxetane

structure,⁷ demonstrating that the precipitate is a poly-oxetane **4b**. From the nitrogen content of the elemental analysis (C, 87.08%; H, 7.07%; N, 1.78%), the yield of oxetane was calculated to be 36% on the basis of the vinylbenzophenone unit. The oxetane yield estimated from the weight gain of the polymer (16 mg) was 28% on the basis of the vinylbenzophenone unit. The filtrate, which was a mixture of **1b** (77%) and **5b** (23%) by NMR, was characterized

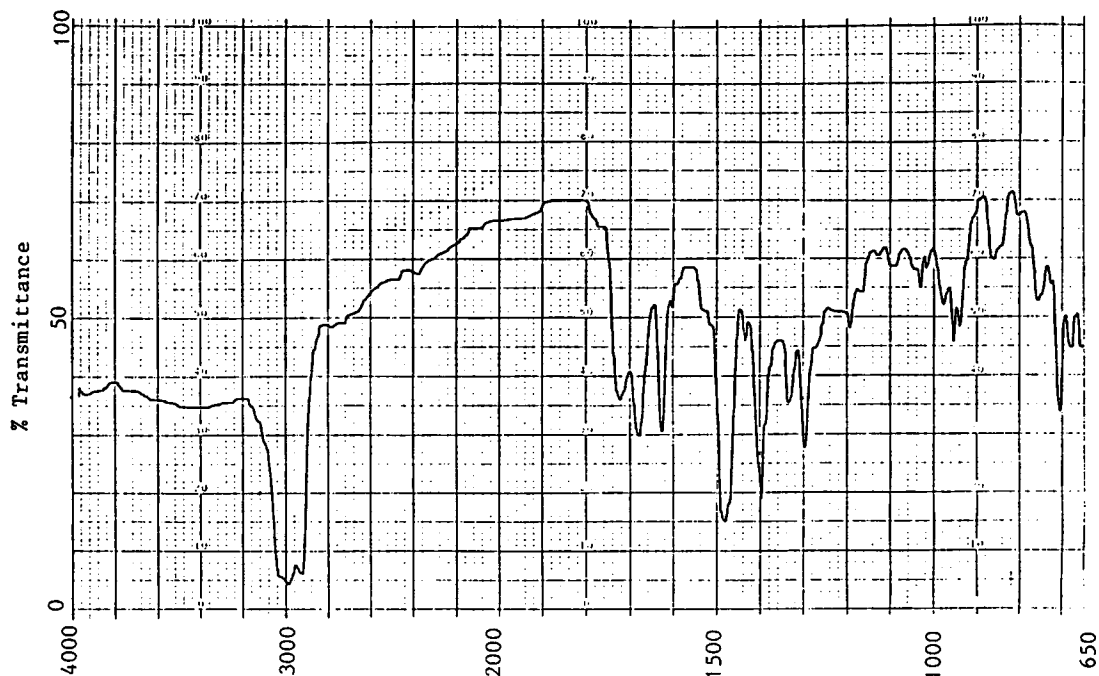


Figure 5 The IR spectrum of poly-oxetane **3c** (in nujol).

after separation by preparative TLC (benzene–AcOEt, 1 : 6 v/v).

A solution of **4b** (44 mg) in *tert*-butylbenzene (2.5 mL) was heated at 150°C for 5 h. The solvent was removed and then methanol was added. The resultant precipitate was filtered to afford 35 mg of a solid, whose NMR and IR spectra were indistinguishable from those of PSVBP. The filtrate was evaporated to dryness to afford 7 mg of a residue, which was shown to be a crude **1b** (80% from NMR).

Photolyses of **1c** With BP

A solution containing 1.02 g (9.2 mmol) of **1c** and 4.99 g (27.4 mmol) of BP in benzene (140 mL) was irradiated for 25 h. The reaction mixture (92% **2c** and 8% **1c** by NMR) was rotary evaporated to remove the solvent and then a small amount of ether was added. The resultant pale brown crystals were collected by filtration and were found to be an essentially pure **2c**: 1.04 g (39%), mp 129–136°C (lit.⁸ mp 137°C). The NMR and IR spectra were identical with those of the authentic sample.⁸

A solution containing **2c** (40 mg, 0.14 mmol) in *tert*-butylbenzene (2.5 mL) was heated at 150°C for 5 h. After column chromatography of the reaction mixture (hexane–benzene, 1 : 2 v/v), 22 mg (86%) of BP was isolated.

Photolyses of **1c** With PVBP

A solution containing **1c** (61 mg, 0.55 mmol) and PVBP (49 mg, 0.23 mmol vinylbenzophenone unit) in 40 mL of benzene was irradiated for 20 h. The resultant brown precipitate was separated by filtration and washed with benzene. From the benzene filtrate, 28 mg of **1c** was recovered after removing the solvent. The brown precipitate (71 mg) had IR absorption bands at 1715 (C=O of acetyl), 1020, and 970 (oxetane⁷) cm⁻¹ (Fig. 5). This indicates that the precipitate is a poly-oxetane **3c**. The yield of oxetane calculated from the nitrogen content of the elemental analysis (C, 75.63%; H, 5.76%; N, 5.56%) is 50% on the basis of the vinylbenzophenone unit. The yield of oxetane calculated from the weight gain of the polymer (10 mg) is 36%.

Poly-oxetane **3c** (104 mg) suspended in *tert*-butylbenzene (5 mL) was heated at 150°C for 5 h. The insoluble polymer was filtered and was washed with benzene to give 87 mg of a solid. Its IR spectrum was essentially identical with that of PVBP. Thus, PVBP recovered from thermolysis of **3c** was insoluble in benzene, although the original PVBP was soluble in benzene.

Solid-State Photolyses

In each case, a mixture of crystals of imidazole (**1a** or **1c**) and ketone (BP or PVBP) was ground in a

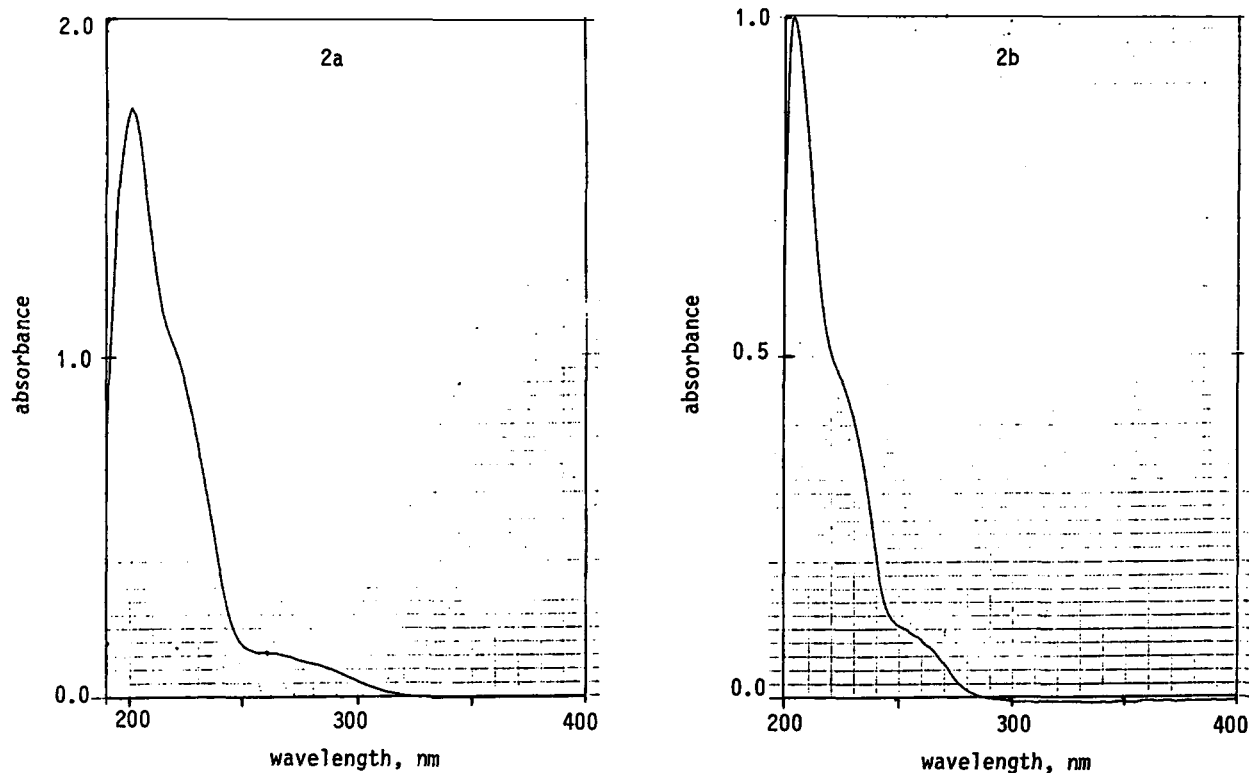


Figure 6 The UV spectra for oxetanes **2a** and **2b**: **2a**, $2.79 \times 10^{-5} M$ in acetonitrile; **2b**, $2.33 \times 10^{-5} M$ in ethanol.

mortar to a fine powder with a pestle. The powder was spread between two Pyrex plates in a thin layer and irradiated under a nitrogen atmosphere at an ice-water temperature. The reaction mixture was analyzed by NMR.

RESULTS AND DISCUSSION

Table I summarizes irradiation conditions and photoproducts. As already reported,¹ photolyses of imidazole **1a** and BP in solution gave mainly oxetane **2a** along with a minor amount of a dehydrocyclization product **5a** (Experiments 1–3). On the other hand, irradiation of **1a** with a polymeric BP, PVBP or PSVBP afforded no corresponding oxetane, **3a** or **4a**, respectively (Experiments 4–6).

It seems well established that intramolecular triplet energy migration in polymeric BP systems occurs very efficiently.^{9,10} For example, the energy migration rate k_{mig} in PVBP is reported⁹ to be $8 \times 10^{10} \text{ s}^{-1}$. The quenching rate k_q of the BP triplet by **1a** is also rapid and was estimated by us to be $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile,¹ that is, nearly diffusion controlled. In the reaction of the polymeric

BP with **1a**, several pendant benzophenone groups will always be present close to an oxetane structure if it is produced. Therefore, we suspected that the observed lack of formation of oxetanes **3a** and **4a** could be due to a facile photosensitized cleavage of the oxetane ring into the starting components as a result of triplet energy transfer from a pendant benzophenone group in its triplet excited state. In fact, upon photolysis in the presence of BP, oxetane **2a** was cleaved to give the original imidazole **1a** besides a small amount of phenanthrene **5a** [eq. (3)]. The cycloreversion of **2a** also occurred by direct irradiation at 254 nm [eq. (3)].

Photolyses of the copolymer PSVBP with **1a** were performed with the intention of seeing an effect of the lesser number (relative to that in the homopolymer PVBP) of the benzophenone group surrounding an oxetane structure. As aforementioned, however, oxetane formation was not observed (Experiment 6).

In order to demonstrate that oxetanes can indeed be formed from the polymeric BP, imidazoles **1b** and **1c** were employed instead of **1a**. In these cases, the corresponding oxetanes were formed not only from BP (**2b** and **2c**, Experiments 9 and 12) but

also from PVBP and PSVBP (**3b**, **4b**, and **3c**, Experiments 10, 11, and 13). Figure 6 displays the UV spectra for **2a** and **2b**. The spectrum of **2b**, which does not bear the Ph group at the amidine moiety, is considerably blue-shifted as compared with that of **2a**. Oxetane **2c** does not have a chromophore that is responsible for long-wavelength absorption. Therefore, E_T for oxetanes **2b** and **2c** will be considerably higher than that of **2a**. As a result, the photosensitized decomposition of the poly-oxetanes **3b**, **4b**, and **3c** through the intramolecular triplet energy transfer from a pendant benzophenone group is expected to be much slower than the analogous photosensitized decomposition of the elusive poly-oxetanes **3a** and **4a**.

In connection with the oxetane formation from the polymeric BP, it is interesting to consider the results for the solid-state photolysis (Experiments 7, 8, and 14). Under the solid-state reaction condition, a sensitizer molecule (a BP molecule or a pendant benzophenone group) should be always present near an oxetane formed. Photolysis of BP with **1a** produced oxetane **2a** both in the solid state (Experiment 7) and in solution (Experiments 1–3). In contrast, in the case of the photolysis of BP and **1c**, the corresponding oxetane was produced only in solution (Experiment 12), but not in the solid state (Experiment 14). The same situation was observed for the photoaddition of **1a** to 4,4'-dimethylbenzophenone, 4-methylbenzophenone, or 4-benzoylpyridine.¹

We consider that the photochemical solid-state oxetane production from BP and **1a** (Experiment 7) is unexpected, because a photosensitized decomposition of oxetane **2a** in the solid state will be rapid owing to a presumably efficient triplet energy transfer from BP to **2a**. The absence of oxetane production from the solid-state photolysis of BP and **1c** (Experiment 14) is also unexpected, because the triplet energy transfer from BP to **2c** is probably slower than BP to **2a**. We are as yet unable to rationalize these inconsistent facts. It has been sug-

gested that, in the solid state, BP and **1a** can probably take a mutual molecular geometric arrangement that is suitable for the oxetane formation to occur.¹¹

CONCLUSION

In solution, whereas imidazoles **1b** and **1c** produced the corresponding oxetanes by photoaddition with PVBP and PSVBP, **1a** did not. This lack of oxetane formation from the polymeric BP and **1a** is probably due to a rapid triplet-sensitized decomposition of a once-formed oxetane ring as a result of the intramolecular triplet energy transfer from a pendant benzophenone group.

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