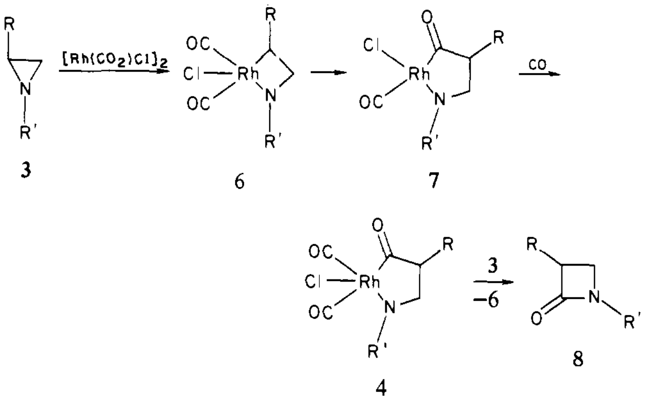
**Table I.** $\beta$-Lactams (4) Obtained by the Rhodium(I)-Catalyzed Carbonylation of Aziridines

| 4: R, R' | $^1$H NMR, ppm$^a$ | $^{13}$C NMR, ppm$^{a,b}$ | MS, *m/e* |
|---|---|---|---|
| Ph, $C(CH_3)_3$ | 1.36 (s, 9 H, $C(CH_3)_3$), 3.07 (dd, 1 H, $H_b$, $J_{AB} = 2$, $J_{BC} = 6$ Hz), 3.52 (dd, 1 H, $H_c$, $J_{ac} =$ 5 Hz), 4.06 (dd, 1 H, $H_a$), 7.23 (s, 5 H, Ph) | 27.78 (q, $CH_3$), 44.70 (t, $CH_2$), 52.28 (s, $C(CH_3)_3$), 53.24 (d, *CH*Ph), 128.79, 127.26 (d each, CH of Ph), 136.39 (s, quaternary carbon of Ph), 167.14 (s, CO) | 203, $[M]^+$ |
| Ph, 1-adamantyl | 1.68–2.05 (m, 15 H, adamantyl protons), 3.11 (dd, 1 H, $H_b$, $J_{ab} = 2$, $J_{bc} = 5.5$ Hz) 3.55 (dd, 1 H, $H_c$, $J_{ac} = 5.0$ Hz), 4.06 (dd, 1 H, $H_a$), 7.23 (s, 5 H, Ph) | 29.06 (d), 36.21 (t), 40.83 (t) (secondary and tertiary adamantyl carbons), 43.75 (t, $CH_2$), 52.06 (d, *CH*Ph), 53.97 (s, quaternary C of adamantane group), 127.29, 128.75 (d each, CH of Ph), 136.45 (s, quaternary carbon of Ph), 167.12 (s, CO) | 281, $[M]^+$ |
| *p*-$PhC_6H_4$, $C(CH_3)_3$ | 1.33 (s, 9 H, $C(CH_3)_3$), 3.13 (dd, 1 H, $H_b$, $J_{ab} = 2$, $J_{bc} = 5.5$ Hz), 3.53 (dd, 1 H, $H_c$, $J_{ac} = 6$ Hz), 4.10 (dd, 1 H, $H_a$), 7.16–7.56 (m, 9 H, aromatic ring protons) | 27.77 (q, $CH_3$), 44.63 (t, $CH_2$), 51.94 (d, *CH*Ph), 53.28 (s, $C(CH_3)_3$), 127.01, 127.26, 127.51, 127.66, 128.76 (d each, aromatic CH), 135.31, 140.26, 140.78 (s each, quaternary carbons of *p*-$PhC_6H_4$), 167.05 (s, CO) | 279, $[M]^+$ |
| *p*-$PhC_6H_4$, 1-adamantyl | 1.70–2.05 (m, 15 H, adamantyl protons), 3.15 (dd, 1 H, $H_b$, $J_{ab} = 2$, $J_{bc} = 5.5$ Hz), 3.56 (dd, 1 H, $H_c$, $J_{ac} = 5$ Hz), 4.10 (dd, 1 H, $H_a$), 7.15–7.65 (m, 9 H, aromatic ring protons) | 29.04 (d), 36.19 (t), 40.82 (t) (secondary and tertiary adamantyl carbons), 43.63 (t, $CH_2$), 51.72 (d, *CH*Ph), 54.00 (s, quaternary C of adamantane group), 127.01, 127.25, 127.50, 127.68, 128.75 (d each, aromatic CH), 135.44, 140.25, 140.81 (s each, quaternary carbons of *p*-$PhC_6H_4$), 167.03 | 357, $[M]^+$ |
| *p*-$BrC_6H_4$, $C(CH_3)_3$ | 1.38 (s, 9 H, $C(CH_3)_3$), 3.06 (dd, 1 H, $H_b$, $J_{ab} = 2$, $J_{bc} = 5.5$ Hz), 3.53 (dd, 1 H, $H_c$, $J_{ac} =$ 5.0 Hz), 4.05 (dd, 1 H, $H_a$), 7.00–7.60 (m, 4 H, aromatic protons) | | 283, 281, $[M]^+$ |

$^a$ $CDCl_3$ with tetramethylsilane as internal standard. $^b$ Multiplicity of signals observed when C-13 spectra were recorded in the partially decoupled mode.

Scheme I



rhodium(I) chloride and rhodium acetate are incapable of catalyzing the desired transformation.

A possible mechanism for the formation of $\beta$-lactams is outlined in Scheme I. Oxidative addition of rhodium(I) to the more substituted carbon–nitrogen bond of the aziridine would give the rhodium(III) complex **6**. Ligand migration to **7** and subsequent carbonylation would give **8**. The $\beta$-lactam would then be formed by reductive elimination of **8**, with or without the assistance of another molecule of the aziridine. Analogy to the proposed mechanism is found in the elegant work done on the stoichiometric rhodium(I)-induced cleavage and carbonylation of certain polycyclic hydrocarbons such as cubane[6] and the photolytic reaction of chromium carbene complexes with imines to give $\beta$-lactams.[7] Unfortunately, the latter reaction, as well as the use of cyclopentadienyliron dicarbonyl complexes to prepare $\beta$-lactams[8] are both *stoichiometric* methods and not catalytic as in the present case.

The following procedure is typical: a mixture of **3**, R = Ph, R' = $C(CH_3)_3$ (1.00 g, 5.71 mmol), and $[Rh(CO)_2Cl]_2$ (0.11 g, 0.28 mmol) in dry benzene (30 mL) was stirred under carbon monoxide for 2 days at 20 atm and 90 °C. The solvent was removed by rotary evaporation, and the analytically pure $\beta$-lactam was obtained by silica gel chromatography using ethyl acetate–hexane as the eluant.

In conclusion, aziridines can be carbonylated to $\beta$-lactams in a completely regiospecific manner. This constitutes the first example of direct ring expansion and carbonylation of an aziridine.

**Acknowledgment.** We are grateful to the Natural Sciences and Engineering Research Council for support of this work.

**Registry No. 3** (R = Ph; R' = $C(CH_3)_3$), 18366-49-9; **3** (R = Ph; R' = 1-adamantyl), 87461-58-3; **3** (R = *p*-$PhC_6H_4$; R' = $C(CH_3)_3$), 87451-10-3; **3** (R = *p*-$PhC_6H_4$; R' = 1-adamantyl), 87451-11-4; **3** (R = *p*-$BrC_6H_4$; R' = $C(CH_3)_3$), 87451-12-5; **4** (R = Ph; R' = $C(CH_3)_3$), 87451-13-6; **4** (R = Ph; $R^1$ = 1-adamantyl), 87451-14-7; **4** (R = *p*-$PhC_6H_4$; R' = $C(CH_3)_3$), 87451-15-8; **4** (R = *p*-$PhC_6H_4$; R' = 1-adamantyl), 87451-16-9; **4** (R = *p*-$BrC_6H_4$; Rr' = $C(CH_3)_3$), 87451-17-0; $[Rh(CO)_2Cl]_2$, 14523-22-9; 1,5-cyclooctadienerhodium(I) chloride dimer, 12092-47-6.

---

(6) Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 3515.

(7) McGuire, M. A.; Hegedus, L. S. *J. Am. Chem. Soc.* **1982**, *104*, 5538.

(8) Wong, P. K.; Madhavarao, M.; Marten, D. F.; Rosenblum, M. *J. Am. Chem. Soc.*, **1977**, *99*, 2823.

---

# Photophysics of the Second Excited Singlet States of Xanthione and Related Thiones in Perfluoroalkane Solvents

A. Maciejewski[1] and R. P. Steer*

*Department of Chemistry, University of Saskatchewan*
*Sakatoon, Saskatchewan, Canada S7N OWO*

*Received June 20, 1983*

Xanthione and related molecules have been adopted as model compounds for the study of the remarkable photophysics and spectroscopy of aromatic thiones in a variety of media.[2-5] On the basis of measurements of low quantum yields of net photodecomposition ($\phi_d$) it has been assumed that xanthione itself does

---

(1) On leave from A Mickiewicz University, Poznan, Poland.

(2) Mahaney, M.; Huber, J. R. *Chem. Phys.* **1975**, *9*, 371-378.

(3) Capitanio, D. A.; Pownall, H. J.; Hüber, J. R. *J. Photochem.* **1974**, *3*, 225-236.

(4) Anderson, R. W.; Hochstrasser, R. M. Pownall, H. J. *Chem. Phys. Lett.* **1976**, *43*, 224-227.

(5) Taherian, M. R.; Maki, A. H. *Chem. Phys.* **1982**, *68*, 179-189.

Table I. Spectral Data for $S_2 \leftrightarrow S_0$ Transitions in Several Aromatic Thiones[a]

| compd | $E_{abs}^{0-0}(S_2)$, cm$^{-1}$ | $E_{S_2} - E_{S_1}$, cm$^{-1}$ | $\Delta\bar{\nu}_{1/2}$(abs), cm$^{-1}$ | $\Delta\bar{\nu}_{1/2}$(em), cm$^{-1}$ | Stokes shift, cm$^{-1}$ |
|---|---|---|---|---|---|
| 1 | 23 990 | 7970 | 2650 | 3900 | 1300 |
| 2 | 25 540 | 8590 | 3330 | 3650 | 2390 |
| 3 | 27 490 | 9280 | 5000 | 5000 | 4000 |
| 4 | 29 400 | 11000 | 3250 | 5900 | 2960 |

[a] In perfluoro-*n*-hexane.

Table II. $S_2 \rightarrow S_0$ Fluorescence Quantum Yields and $S_2$ Decay Parameters of Several Aromatic Thiones

| compd | solvent | $\phi_f$ | $\tau_{S_2}$, ps | $10^{-9}k_{nr}$, s$^{-1}$ | $10^{-7}k_r$, s$^{-1}$ | $k_r^{calcd}$, s$^{-1}$ | $\frac{\phi_f^{PFMCH}}{\Phi_f^{solvent}}$ | $\frac{\phi_{S_2}^{PFMCH}}{\Phi_{S_2}^{solvent}}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | PFMCH | 0.014 ± 0.002 | 175 ± 5 | 5.7 | 8.0 | 8.0 | 1 | 1 |
|  | 3-MP | $(3.0 \pm 0.3) \times 10^{-3}$ | 38 ± 7 | 25 | 7.5 | 7.6 | 4.7 | 4.6 |
|  | $C_6H_6$ | $(1.0 \pm 0.2) \times 10^{-3}$ | 12 ± 3[a] | 83 | 8.3 | 9.5 | 14 | 15 |
| 2 | PFMCH | 0.023 ± 0.002 | 210 ± 5 | 4.8 | 11 | 9.0 | 1 | 1 |
|  | 3-MP | $(2.3 \pm 0.2) \times 10^{-3}$ | 24 ± 7 | 40 | 9.6 | 10 | 10 | 8.8 |
| **3** | PFMCH | $(1.0 \pm 0.2) \times 10^{-4}$ | <20 |  |  | 22 | 1 | 1 |
|  | 3-MP | $(2.3 \pm 0.2) \times 10^{-4}$ | <20 |  |  | 20 | 0.43 |  |
| 4[b] | PFMCH | 0.14 ± 0.015 | 880 ± 10 | 0.97 | 16 |  | 1 | 1 |
|  | 3-MP | 0.013 ± 0.002 | 77 ± 10 | 13 | 17 |  | 10.8 | 11.4 |

[a] Reference 4. [b] Reference 7.

not undergo any photochemical reaction that significantly affects its second excited singlet-state decay rate in dilute degassed 3-methylpentane, acetonitrile, or methanol solutions at room temperature.[2,3,6] We recently showed[7] that the second excited singlet state of 2,2,3,3-tetramethylindanethione in perfluoroalkane solvents is quenched by saturated hydrocarbons such as 3-methylpentane at near diffusion-controlled rates, perhaps suggesting an important chemical interaction between the excited thione and the alkane, despite negligibly small values of $\phi_d$. This communication describes the results of experiments which indicate that the solvent is not a passive spectator in the decay and that it may not be possible to measure exclusively photophysical decay parameters of the second excited singlet states of xanthione and related molecules in many common solvents at room temperature.

$S_2 \rightarrow S_0$ fluorescence of xanthione (**1**), 4*H*-1-benzopyran-4-thione (**2**), and 4*H*-pyran-4-thione (**3**) was excited by means of a synchronously pumped, cavity dumped, rhodamine-6G dye laser, the output of which was frequency doubled to give <20-ps pulses of tunable UV light at a repetition rate of 4 MHz. Time-correlated single-photon counting of monochromator-dispersed emission was used to accumulate decay profiles, and the previously described[8] excitation pulse mimic technique was used to deconvolute the instrument response function from the fluorescence profile. All fluorescence decays could be described adequately by single exponential functions, and no evidence of emission from vibrationally unrelaxed molecules[9] was found on the time scales investigated. Absorption, emission, and excitation spectra and fluorescence quantum yields were measured as described previously.[7]

Important spectral parameters for **1**, **2**, **3**, and 2,2,3,3-tetramethylindanthione (**4**) in perfluoro-*n*-hexane at room temperature are summarized in Table I. Both emission and absorption spectra are better resolved in perfluoroalkane than in hydrocarbon solvents, and for **1** the vibronic structure is better resolved in perfluoroalkanes at room temperature than in 3-methylpentane glasses[2] at 77 K for comparable spectral resolution. In fluid perfluoroalkanes the origin bands of the absorption and emission spectra are nearly coincident but are separated by >200 cm$^{-1}$ in 3-methylpentane. Neither the spectra nor the excited-state lifetimes change significantly upon substituting one perfluoroalkane solvent for another. All observations are indicative of extremely weak solute–solvent interaction in perfluoroalkane solutions.[10]

The Stokes shift and the widths of the $S_2 \leftrightarrow S_0$ absorption and emission band systems (Table I, $\Delta\bar{\nu}_{1/2}$) increase in the order **1** < **2** < **3**, indicative of progressively larger distortions and displacements of the second excited singlet-state potential surfaces of these molecules relative to their ground states. Such observations are consistent with the expectation that the pyran-4-thione ring is capable of progressively greater distortion in the excited state as one and then both of the stabilizing benzo groups are removed.

$S_2 \rightarrow S_0$ fluorescence quantum yields ($\phi_f$) and $S_2$ excited-state lifetimes ($\tau_{S_2}$) of **1**–**4** in 3-methylpentane and perfluoromethylcyclohexane are given in Table II. Radiative ($k_r$) and total nonradiative ($k_{nr}$) rate constants for $S_2$ decay, calculated from $k_r = \varphi_f/\tau_{S_2}$ and $k_{nr} = (1 - \phi_f)/\tau_{S_2}$, together with values of $k_r$ calculated from the $S_2 \leftarrow S_0$ absorption spectrum[11] ($k_r^{calcd}$) are shown in Table II. Excellent agreement between the observed and calculated $k_r$, expected for electric dipole-allowed transitions to relatively undistorted excited states, is found for all but **3**. For the latter there is considerable evidence of both a large geometry change and photodecomposition subsequent to excitation to $S_2$. The total nonradiative decay rate is markedly solvent dependent for both **1** and **2**, in agreement with previous results[7] for **4**.

Both 3-methylpentane[12] and benzene[4] have been used previously as solvents in experiments in which the lifetime of xanthione $S_2$ has been determined. In order to examine the extent of interaction of excited **1** with these solvents, $10^{-5}$ M solutions of the thione in perfluoromethylcyclohexane were spiked with hydrocarbon and the $S_2$ lifetimes measured. The results conform to standard Stern–Volmer kinetics for quencher concentrations up to 0.3 M, yielding bimolecular quenching rate constants of $6.5 \times 10^9$ M$^{-1}$ s$^{-1}$ and $1.1 \times 10^{10}$ M$^{-1}$ s$^{-1}$ for 3-methylpentane and benzene respectively. The magnitudes of these rate constants together with the absence of large solvent deuterium isotope effects for heteroatom-containing solvents[13] suggest that a *chemical interaction* leading to $S_2$ relaxation is taking place. Quenching by singlet–singlet energy transfer is ruled out because such processes would be highly endothermic, and quenching by charge transfer seems unlikely due to the failure of the quenching rate constants to correlate with ionization energies or electron affinities of the interacting species. Because $\phi_d$ of **1** monitored by UV absorption is $<10^{-2}$ in degassed 3-methylpentane and $<10^{-3}$ in degassed

---

(6) Bruhlmann, U.; Huber, J. R. *J. Photochem.* **1979**, *10*, 205–213.

(7) Maciejewski, A.; Steer, R. P. *Chem. Phys. Lett.*, in press.

(8) James, D. R.; Demmer, D. R. M.; Verrall, R. E.; Steer, R. P. *Rev. Sci. Instrum.* **1983**, *54*, 1121–1130.

(9) Lin, H.-B.; Topp, M. R. *Chem. Phys. Lett.* **1977**, *48*, 251–255.

(10) See also: Lawson, C. W.; Hirayama, F.; Lipsky, S. *J. Chem. Phys.* **1969**, *51*, 1590–1596. Mauser, H.; Kretschmer, R. *Z. Phys. Chem.* **1972**, *80*, 21–28. Parker, C. A.; Joyce, T. A. *Trans. Faraday Soc.* **1969**, *65*, 2823–2829. Hara, K.; Ware, W. R. *Chem. Phys.* **1980**, *51*, 61–68.

(11) Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, *37*, 814–822.

(12) Mahaney, M.; Huber, J. R. *J. Mol. Spectrosc.* **1981**, *87*, 438–448.

(13) Maciejewski, A.; Steer, R. P. *J. Photochem.*, submitted for publication.

benzene at the low thione concentrations employed, excited-state deactivation by irreversible hydrogen abstraction would appear not to be dominant despite the possibility of efficient solvent cage recombination.

On the assumption that (1) photodissociation, atom abstraction, and exciplex formation do not occur in perfluoroalkane solvents[10] and (2) internal conversion to $S_1$ is the major $S_2$ radiationless decay process, $k_{nr}$ of **1**, **2**, and **4** may be correlated with the $S_2$–$S_1$ electronic energy difference (Table I) according to the "energy-gap law".[14] A plot of ln $k_{nr}$ vs. $(E_{S_2} - E_{S_1})$ for the three thiones is linear if data taken in perfluoroalkane solvents are used. This supports the proposals that $S_2$ decays primarily by internal conversion and that perfluoroalkane solvents are sufficiently chemically inert to permit the characterization of the photophysical properties of these excited thiones in fluid solutions at room temperature.

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada for their continuing support.

**Registry No. 1**, 492-21-7; **2**, 6005-15-8; **3**, 1120-93-0; **4**, 74768-62-0.

---

(14) Engleman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145-164.

---

# Radiation-Induced Reduction of Thymidine in Aqueous Solution: Isolation and Characterization of a Novel Dimeric Product

Sei-ichi Nishimoto, Hiroshi Ide, Kikumi Nakamichi, and Tsutomu Kagiya*

*Department of Hydrocarbon Chemistry*
*Faculty of Engineering, Kyoto University*
*Kyoto 606, Japan*

*Received June 3, 1983*

The radiation chemistry of DNA constituents has been a subject for intensive studies, because the DNA is considered to be one of the most vital targets of ionizing radiation that leads to lethal damage of bacterial and mammalian cells.[1,2] It is suggested by a number of workers that radiolyses of pyrimidine bases and related nucleosides in aqueous solution under deaerated conditions give the possible dimeric products[3-7] as well as those from the C5–C6 double-bond saturation with hydrogen and/or hydroxyl groups.[2,5,8] Although chemistries of the hydrogenation and hydroxylation were well established, only a few attempts[3] have been made to characterize the dimeric products, which appears to be of not only radiation chemical but also biological interest. We report here the successful characterization of a novel dimeric product of 5,5′-bi-5,6-dihydrothymidine (**2**) produced on γ-irradiation of a deaerated aqueous solution of thymidine (**1**) in the presence of formate. The reported dimer **2** is apparently distinct from typical cyclobutane-type dimers produced in the photochemical reaction of pyrimidine derivatives.[9]

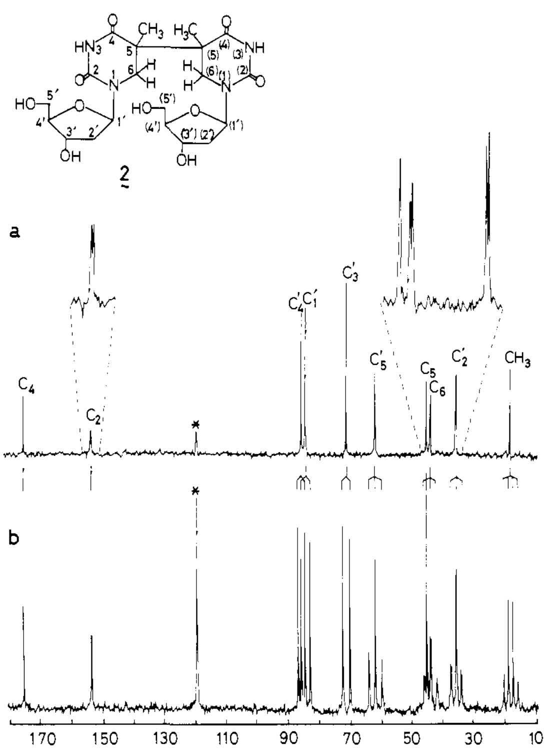
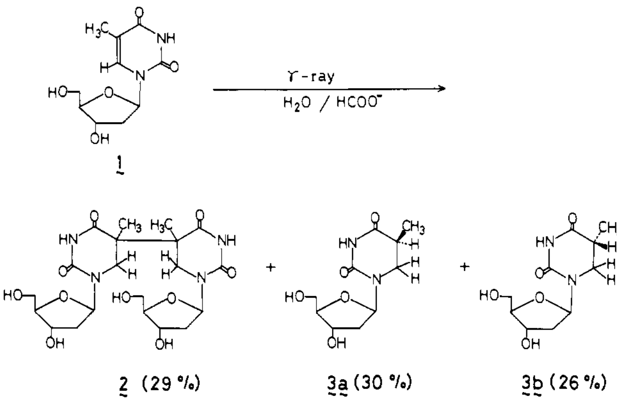


**Figure 1.** Observed critical temperatures plotted against values calculated through eq 5.

Scheme I



Typically, a solution of **1** (1 mM) in 3 mL of triply distilled water containing sodium formate (0.1 M) was buffered at pH 7.0 ± 0.1 with sodium phosphate (2 mM) and deaerated ($<3 \times 10^{-3}$ mmHg). Irradiation was performed at room temperature with a $^{60}$Co γ-ray source (0.38 kGy $h^{-1}$).

Conversion of **1** increased linearly with irradiation dose up to 1.52 kGy, from which the *G* value[10] for the conversion was derived as $G(-\mathbf{1}) = 2.97$. An HPLC analysis (monitored by UV absorption at 210 nm) showed that the dimer **2** (relative retention volume:[11] $k' = 3.79$) and hydrogenated products[12] of 5(*S*)-(−)-5,6-dihydrothymidine (**3a**, $k' = 1.34$) and 5(*R*)-(+)-5,6-dihydrothymidine (**3b**, $k' = 1.61$) are among the major products. The hydrogenated products **3a,b** are analogous to 5,6-dihydrothymine as a major product in the radiolytic reduction of thy-

---

(1) Altman, K. I., Gerber, G. B., Okada, S., Eds. "Radiation Biochemistry"; Academic Press: New York/London, 1970; Vol. I, Chapter 3.

(2) Hütterman, J., Köhnlein, W., Teoule, R., Bertinchamps, A. J., Eds. "Effects of Ionizing Radiation on DNA. Physical, Chemical and Biological Aspects"; Springer-Verlag: Berlin/Heidelberg/New York, 1978.

(3) (a) Shragge, P. C.; Verghese, A. J.; Hunt, J. W.; Greenstock, C. L. *J. Chem. Soc., Chem. Commun.* **1974**, 736; (b) *Radiat. Res.* **1974**, *60*, 250.

(4) Ali, K. M.; Scholes, G. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 449.

(5) (a) Infante, G. A.; Jirathana, P.; Fendler, J. H.; Fendler, E. J. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 1585; (b) *Ibid.* **1974**, *70*, 1162.

(6) Cadet, J.; Teoule, R. *Int. J. Appl. Radiat. Isot.* **1971**, *22*, 273.

(7) Cadet, J.; Balland, A.; Berger, M. *Int. J. Radiat. Biol.* **1981**, *39*, 119.

(8) (a) Ekert, B. *Nature (London)* **1962**, *194*, 278. (b) Scholes, G. *Prog. Biophys. Mol. Biol.* **1963**, *13*, 59. (c) Khattak, M. N.; Green, J. H. *Int. J. Radiat. Biol.* **1966**, *11*, 131; (d) *Ibid.* **1966**, *11*, 577. (e) Wada, T.; Ide, H.; Nishimoto, S.; Kagiya, T. *Chem. Lett.* **1982**, 1041.

(9) Wang, S. Y., Ed. "Photochemistry and Photobiology of Nucleic Acids"; Academic Press: New York, 1976; Vol. 1, p 169.

(10) The number of molecules produced or changed per 100 eV of energy absorbed by the reaction system.

(11) The relative retention volume is defined by $k' = (V - V_0)/V_0$ where $V$ is the retention volume at a given peak and $V_0$ is the void volume of the system. The analysis was carried out on an ODS-type column and 90% water/10% methanol was delivered at a flow rate of 0.6 mL $min^{-1}$. Under these conditions **1** was eluted with $k' = 2.87$.

(12) **3a** and **3b** were confirmed by comparison of their retention volumes with those of authentic samples (see also ref 7, 14).

0002-7863/83/1505-6740$01.50/0