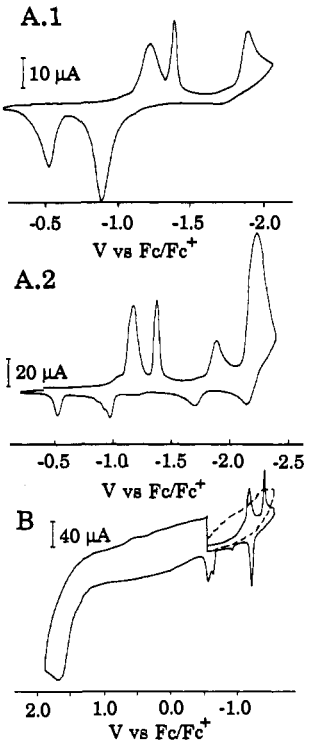


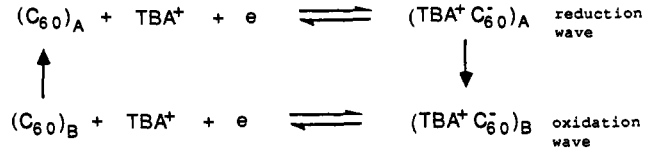
Figure 2. Cyclic voltammograms of a film of C_{60} on a platinum electrode (1-mm diameter) in a solution of MeCN [supporting electrolyte: 0.1 M (TBA)BF_4] showing (A) (1) third reduction; (2) fourth reduction; and (B) oxidation processes. Solid curve, first scan; dashed curve, second scan; v = 200 mV/s.

electrode. This amount represents 2.7×10^{-8} mol of C_{60}, or about 16 monolayers (assuming a 10-Å diameter of the molecule).[9] The integrated areas of the first reduction and reoxidation waves were 2.56 and 2.37 mC/cm^2, respectively, near the values expected for a one-electron transfer. Similarly the second reduction and reoxidation waves were 1.19 and 1.34 mC/cm^2, i.e., about 50% of the first waves. For a number of different electrodes, the integrated second-wave areas were typically 50–70% of the first waves. For $v \leq 200$ mV/s, the E_{pc} values were essentially independent of v, while E_{pa} shifted toward less negative values by about 90 mV (first peak) and 50 mV (second peak) with increasing v. At higher v, i_{pc} and i_{pa} increased more slowly with v and the peaks broadened, suggesting the onset of kinetic limitations in the electrode processes.

The CV behavior depended upon the nature of the cation in the supporting electrolyte. In the presence of Na^+, Cs^+, or TEA^+ (tetraethylammonium) the waves decreased markedly after a few scans over the first reduction and reoxidation waves. However, with THA^+ (tetra-*n*-hexylammonium) or TOA^+ (tetra-*n*-octylammonium) very stable films were obtained.

A scan of the C_{60} film in 0.1 M (TBA)BF_4/MeCN toward positive potentials showed an oxidation wave at about +1.6 V vs Fc/Fc^+ (Figure 2B). No cathodic wave was associated with this oxidation wave, and after cycling over this wave, the electroactivity of the film was diminished, suggesting instability of the oxidized C_{60}.

The first reduction and reoxidation waves are separated by about 0.5 V, are narrower than the usual surface waves, and shift relatively little at small v. Similar waves showing hysteresis, although with significantly smaller splittings, have been found for several systems, e.g., TTF-TCNQ films,[10-13] and were attributed to large structural rearrangements of the surface films following the electron-transfer process. Resistance changes in the films occurring during the redox processes may also be important. Thus we propose the following scheme for the first reduction and reoxidation waves:



A and B represent two different structural forms, where B is more stable for the reduced film and A is the stable form of the C_{60} film. The large splitting between the waves implies significant energies of reorganization for both forms and suggests that the C_{60} films are highly organized. A similar mechanism could be proposed for the second reduction and reoxidation waves, which show smaller splittings. C_{60} deposited on indium tin oxide displays a UV band (344 nm) slightly shifted from that in solution.[2] Upon reduction [at the first wave in MeCN/(TBA)BF_4] the band shifts by 6 nm to longer wavelengths. The C_{60} film is not stable after extended reduction at the first and second waves, or briefer reduction at the third and fourth waves, or upon oxidation of C_{60}. These preliminary studies also suggest that tetra-*n*-alkylammonium cations are important in stabilization of the reduced film. Additional studies are under way to probe the properties of C_{60} films and elucidate the mechanism of their redox processes.

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Template-Directed Modification of Single-Stranded DNA by Psoralen-Tethered Oligonucleotides: Sites of Photoadduct Formation Analyzed by Sequence-Specific and Sequence-Random Cleavage

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Numerous agents have been targeted to react sequence specifically with single-stranded[1] or double-stranded[2] nucleic acids

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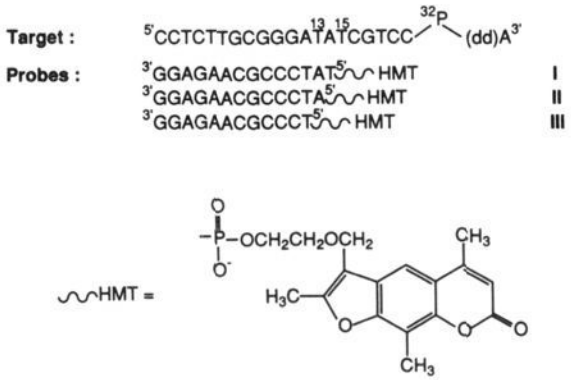
by tethering to a complementary, probe oligodeoxynucleotide.[3] The degree to which chemical reactivity can be spatially focused on the target strand and the chemical transformations that can be achieved are of general interest. The photochemical [2 + 2] cycloaddition reaction of psoralens with the 5,6-double bond of thymidine residues in DNA has been widely exploited to study nucleic acid structure.[4] Oligonucleotide-tethered derivatives of psoralen[5-7] have been shown to undergo photochemical cross-linking with a complementary target strand; the yield and rate of cross-linking are a function of the position of a lone thymidine in the target strand.[7] Using a general method for determining the site of cross-linking at nucleotide resolution, we demonstrate herein that psoralen–oligonucleotide conjugates can deliver the photoreactivity of psoralens primarily to one of several thymidine residues in close spatial proximity in a target. By combining this precise targeting technology with a known photoadduct-triggered DNA cleavage reaction,[8,9] we further demonstrate that these conjugates can serve as stoichiometric, site-specific endonucleases.

We selected a 3′-end-radiolabeled, 21-nucleotide (nt) DNA fragment bearing six thymidine residues as a target single strand.[10] Conjugates I, II, and III of 4′-(hydroxymethyl)-4,5′,8-trimethylpsoralen (HMT) at the 5′-termini of three oligodeoxynucleotides were synthesized by the method of Pieles and Englisch.[6] In hybrids of I, II, and III with the target strand, the position of the photoreactive HMT moiety relative to thymidine residues in the target strand was expected to vary in 1-nt increments. Two molar equivalents of I, II, or III was independently annealed to the target strand and then irradiated (351.1 nm) at 25 °C. Denaturing polyacrylamide gel electrophoresis (DPAGE) with autoradiographic detection of products revealed, in addition to recovered target DNA, lower mobility, presumably photo-cross-linked DNA (hereafter called target·I, target·II, and target·III) in 50–70% yield (Cerenkov counting).[11]



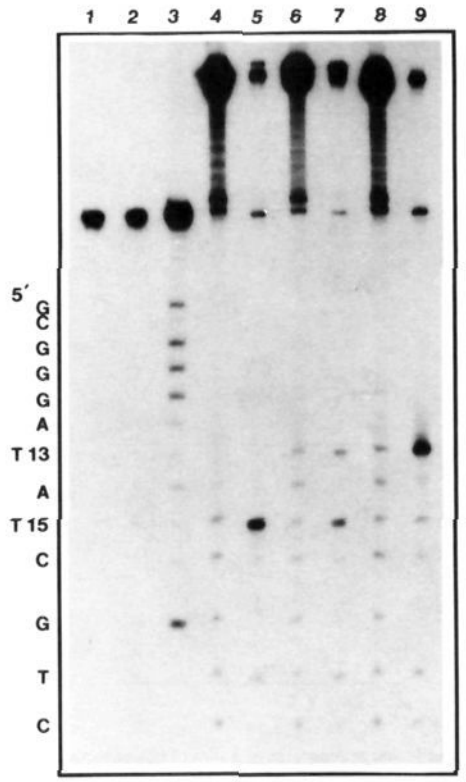


Figure 1. Analysis of cross-link position in photoadducts of oligodeoxynucleotide–HMT conjugate probes I, II, and III with 3′-end-radiolabeled target DNA on a polyacrylamide gel. The target DNA was prepared by end labeling 2 nmol of the appropriate synthetic oligodeoxynucleotide using [α-^{32}P]ddATP/terminal deoxynucleotidyl transferase followed by ethanol precipitation. Target DNA was admixed with 4 nmol of probe I, II, or III in 20 μL of 50 mM Tris (pH 8.0) containing 10 mM NaCl, 10 mM $MgCl_2$, and 0.1 mM EDTA, then incubated at 70 °C for 5 min, and then cooled over 0.5 h to 25 °C. The mixture was irradiated at 25 °C for 0.33 h in a silanized Pyrex test tube at 351.1 nm (100 mW, Spectra-Physics argon laser Model 2025-05). DNA was isolated by ethanol precipitation, and cross-linked DNA was isolated from 25% denaturing PAGE (19:1 acrylamide/bisacrylamide). Cleavage conditions: lane 1, target DNA; lanes 2, 5, 7, and 9, sequential $NaBH_4$ and $C_6H_5NH_2/CH_3CO_2H$,[17] on target DNA, target·I, target·II, and target·III, respectively; lane 3, target DNA, Maxam–Gilbert G-specific reaction;[18] lanes 4, 6, and 8, Fe(II) on target·I, target·II, and target·III, respectively.

The cross-link positions in the target strand for all three isolated cross-linked products were individually analyzed by two methods, the first involving sequence-specific and the second sequence-random cleavage. The unique reactivity of 5,6-unsaturated pyrimidines[8] was exploited to achieve sequence-specific cleavage: the cross-linked DNAs were exposed sequentially to excess aqueous $NaBH_4$ and aqueous $C_6H_5NH_2$ (pH 4.5).[9] DPAGE analysis (Figure 1) revealed extensive cleavage and, by inference, predominant cross-linking at T15 in target·I (lane 5) and T13 in target·III (lane 9). For the case of target·III, quantitation (densitometry and Cerenkov counting) revealed a 1:1 molar ratio of the two major products, the intact cross-link and the fragment representing cleavage at T13. In contrast, target·II was relatively unreactive toward this reagent combination, returning mostly the cross-linked species along with minor amounts of fragments representing cleavage at both T13 and T15 (lane 7). The results of an independent evaluation of cross-link position using single-hit, sequence-random cleavage[12] with iron(II)/EDTA/ascorbic

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acid/H_2O_2[13] were for target·I (lane 4) and target·III (lane 8) fully consistent with the results of sequence-specific cleavage. For target·II, sequence-random cleavage afforded approximately equimolar quantities (densitometry) of radiolabeled fragments shorter than full-length target strand representing cleavage at and to the radiolabeled side of T13 (lane 6).[12] This suggests that T13 is the predominant site of cross-linking in target·II, implying that this lesion must be resistant to $NaBH_4/C_6H_5NH_2$ cleavage.[14]

These data demonstrate conclusively that a psoralen can be targeted to react with a selected thymidine in a target single strand. With the present system, it is apparent that the first extrahelical residue in the target strand to the 3'-side of the hybrid duplex is especially susceptible to photoreaction. The absence of appreciable photoreaction at the proximal 5'-TA site in the hybrid of probe I with the target DNA is especially impressive. Furthermore, this study demonstrates that the $NaBH_4/C_6H_5NH_2$-promoted cleavage reaction of the photoadducted thymidine is a preparatively useful reaction.[15] The combination of these two selective processes renders psoralen–oligonucleotide conjugates sequence-tunable, site-specific endonucleases.

The results herein pinpoint for the first time at nucleotide resolution the sites of photo-cross-links afforded by a psoralen covalently tethered to the terminus of a probe oligodeoxynucleotide. Although demonstrated with a single-stranded-DNA target, the methods herein, with minor modification, should be applicable to the definition of cross-link location in DNA–RNA hybrid structures of interest in studies of antisense repression of mRNA translation[16] and cross-links or even ternary linkages in triplex structures of interest in repression of gene transcription.[2]

Acknowledgment. This work was supported by the National Institutes of Health (GM 35466 and GM 32681), National Science Foundation (DIR-8220099), and Graduate School Research Fund of the University of Washington. P.B.H. is a Sloan Fellow (1988–1992) and NIH Research Career Development Award recipient (AG 00417). We thank Susan Ribeiro, Dr. Margaret Weidner, Dr. Julie T. Millard, and James Clendenning for technical assistance and Professor J. M. Schurr for the use of equipment.

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(15) A 5'-^{32}P-radiolabeled analogue of the target strand (lacking the 3'-terminal radioactive 3'-ddAMP residue) which had been photo-cross-linked to probe I was also studied. Random (iron(II) EDTA) cleavage was fully consistent with cross-linking through T15 (as for target·I). The sequence-specific ($NaBH_4/C_6H_5NH_2$) cleavage conditions afforded, in addition to the fragment of electrophoretic mobility consistent with cleavage at T15, comparable quantities of at least three other substances with mobilities 1–2-nt slower, suggesting that the new 3'-terminus is structurally heterogeneous.

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Chromium-Mediated Cyclizations of Cross-Conjugated Ketoketenes in 8- and 10e⁻ Processes

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The reaction of Fischer carbene complexes with alkynes is one of great utility in the synthesis of substituted quinones and phenols.[1] Recently we reported that the reactions of ketoalkynes with alkoxyalkenyl carbene complexes of the type **1a** give bicyclic lactones of the type **3a** (Scheme I) that arise from double cyclizations of cross-conjugated ketoketene intermediates in an overall process that involves an 8e⁻ reorganization.[2] We report here a demonstration that these cyclizations can be effected in other possible 8e⁻ configurations, the first examples of 10e⁻ processes in this system, and evidence which suggests that the selectivity for the formation of the two possible isomeric η^1,η^3-vinyl carbene and η^4-vinyl ketene complexed intermediates is under stereoelectronic control.[3]

A possible mechanism for the formation of lactones of the type **3** has been previously proposed to involve cross-conjugated ketoketenes of the type A that is complexed to chromium.[2,4] The overall process for the formation of lactone **3a** can be envisioned as the stitching together of the carbene ligand, a CO ligand, and the ketoalkyne as indicated in structure A. Permutation of the vinyl group in A about the cross-conjugated ketoketene unit produces four configurations that would be expected to lead to bicyclic lactones in similar 8e⁻ ring closures. These are indicated by structures A–D (Chart I) where the labels R_1–R_4 define the

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