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Norrish Type II Photochemical Reaction of an Aryl Ketone on a Monolayer-Protected Gold Nanocluster. Development of a Probe of Conformational Mobility

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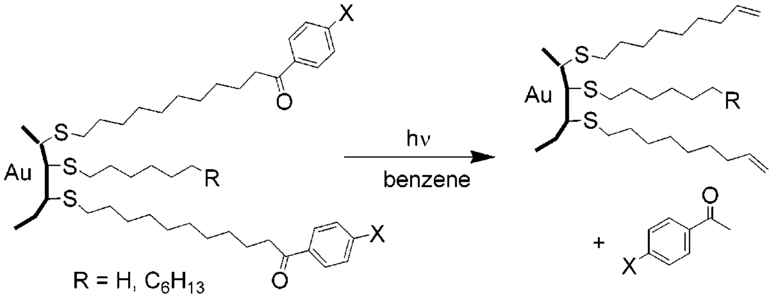
ABSTRACT



A Norrish type II reaction of an aryl ketone monolayer-protected colloid was investigated for the first time. Photolysis of mercaptoundecanophenone-modified gold colloid, MUP-MPC, generates free acetophenone in solution and the nonene-modified MPC via the triplet excited state and the 1,4-biradical intermediate. The reaction is being developed as a probe of conformational mobility in these unique environments.

The Norrish−Yang type II reaction is a very well understood and studied photochemical reaction of carbonyl compounds.[1] Norrish−Yang type II photoreactivity is influenced by both environmental and structural factors and is also sensitive to the conformational flexibility of the molecule. As such, it has been used extensively as a photoreaction to probe the properties of a variety of ordered media including cyclodextrins, zeolites, liquid crystals, micelles, crystalline state, and others.[2] Self-assembled monolayers of organic molecules on metal surfaces offer another type of ordered environment, and there are a great number of studies whose goals are to prepare these with the appropriate organic functionality at the interface to provide a site for molecular recognition or modulation of electronic factors for a sensing action.[3] Because of the power of photochemistry to provide careful control of surface modifications of organic functionality through photopatterning techniques, a number of photochemical reactions on modified planar gold surfaces were studied to explore the properties of these monolayers; the types of reactions investigated include photoextrusion of

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[1] (a) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168. (b) Wagner, P. J. In *CRC Handbook of Organic Photochemistry and Photobiology*; Hoorspool, W. R., Ed.; CRC Press, Inc.: Boca Raton, FL; Chapters 38, 449 and Chapter 39, 471.

[2] (a) *Photochemistry in Organized and Confined Media*; Ramamurthy, V., Ed.; VCH Publishers: New York, 1991. (b) Workentin, M. S.; Leigh, W. J.; Jeffrey, K. R. *J. Am. Chem. Soc.* **1990**, *112*, 7329. (c) Ihmels, H.; Scheffer, J. R. *Tetrahedron* **1999**, *55*, 885. (d) Ramamurthy, V.; Corbon, D. R.; Johnston, L. J. *J. Am. Chem. Soc.* **1992**, *114*, 3870. (e) Baldvins, J. E.; Cui, C. Weiss, R. G. *Photochem. Photobiol.* **1996**, *63*, 726. (f) Takagi, K.; Harata, E.; Schichi, T.; Kanoh, T.; Sawaki, Y. *J. Photochem. Photobiol. A: Chem.* **1997**, *105*, 47.

[3] For a general introduction to self-assembled monolayers, see: Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.

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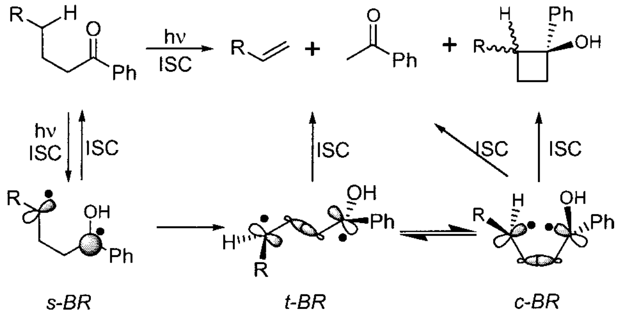
nitrogen from aryl azide[4] and diazoketones,[5] *E*−*Z* photoisomerization of stilbenes[6] and azo compounds[7] and other photochromic materials, and photodimerization reactions.[8] Similar studies of organic monolayers on Au nanoclusters (so-called monolayer-protected Au clusters or MPC's) are less well known despite the interest in these new chemical materials and the putative parallels to the planar gold surfaces.[9]

Our group's approach is to develop photoreactive monolayer surfaces to serve as a template for further surface modifications and as probes of the conformational mobility of molecules as self-assembled monolayers on planar and colloid metals. In this study, we report the first example of a photochemical Norrish type II reaction of an aryl ketone incorporated at the interface of a self-assembled monolayer on a gold nanocluster. Norrish II reactivity of aryl ketones involves γ-hydrogen abstraction by the n,π* triplet excited state of the carbonyl group.[1] Products are derived from fragmentation and/or cyclization of the ensuing 1,4-biradical, namely, acetophenone enol/alkene and/or cyclobutanols, respectively (Scheme 1). Product formation and distribution is influenced greatly by the conformational flexibility of the triplet 1,4-biradical. Herein we report that photolysis of aryl ketone MPC's undergo Norrish type II fragmentation to yield alkene-modified clusters via the carbonyl triplet excited state. We suggest that development of this reaction will provide a useful probe for mobility in these unique environments.

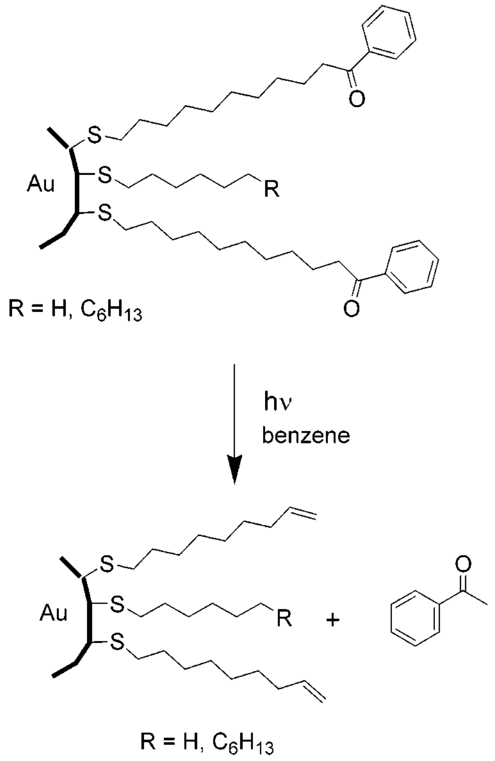
Scheme 1. Norrish Type II Photochemical Reaction



The Norrish type II mercaptoundecanophenone monolayer precursor, MUP, was synthesized from 11-bromoundecanoyl chloride by Friedel−Crafts acylation of benzene followed by thio-esterification of the 11-position by reaction with potassium thioacetate and, finally, hydrolysis of the thioester to the thiol. MUP was obtained analytically pure by repeated column chromatography and recrystallization. The structure was confirmed by ^{1}H and ^{13}C NMR, infrared, and mass spectroscopy.[10]

Simple alkylthiolate-protected gold clusters are prepared from $HAuCl_4 \cdot H_2O$ and alkylthiol under reducing conditions, however this procedure is incompatible with MUP since it leads to reduction of the carbonyl group. Therefore, MPC's of MUP were prepared by the place-exchange method developed by Murray and co-workers[11] starting from well-defined hexanethiolate and dodecanethiolate Au MPC's synthesized using published protocols.[12,13] Proton NMR spectroscopy was used to determine the purity and the extent of exchange (stoichiometry) of the resulting mixed MPC's (MUP-C_6MPC and MUP-C_{12}MPC, respectively; see Scheme 2). Figure 1a shows an ^{1}H NMR spectrum of the MUP-C_{12}-MPC isolated after place exchange. The spectrum exhibits distinctive broad resonances that are assigned to MUP-bound colloid. Distinctive resonances include those of the aromatic

Scheme 2. Cartoon Representation Illustrating the Photolysis of MUP-MPC[a]



[a] MUP-C_6MPC, R = H; MUP-C_{12}MPC, R = C_6H_{13}.

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(10) 11-Mercatoundecanophenone: mp 49−50 °C; ^{1}H NMR (200 MHz) $CDCl_3$ δ 7.95 (2H, d), 7.5 (3H, m), 2.94 (2H, t), 2.51 (2H, q), 1.73 (2H, m), 1.61 (2H, m), 1.2−1.5 (12H, br, m); ^{13}C NMR (75 MHz) $CDCl_3$ δ 24.4, 24.7, 28.4, 29.0, 29.3, 29.4, 29.5, 34.0, 38.6, 128.0, 128.5, 132.8, 137.1, 200.5; IR (dropcast on NaCl) 2918.1, 2849.5, 1681.1 cm^{-1}.

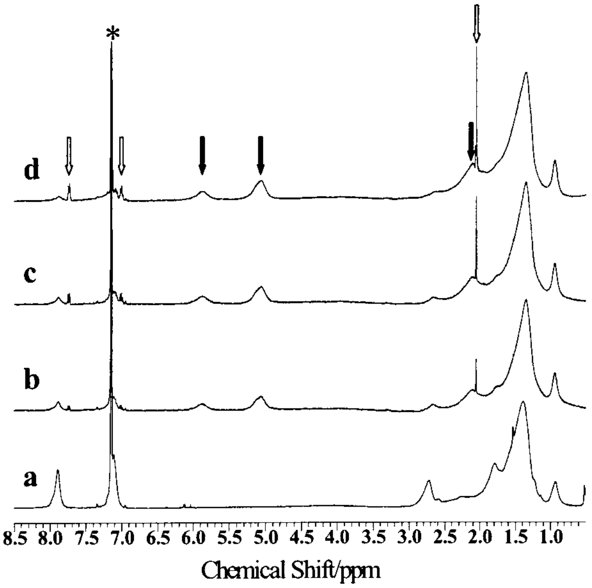

Figure 1. Proton NMR spectra of MUP-C_{12}MPC measured in benzene-d_6 (C_6D_6 indicated by *****: **a**, isolated MPC, prior to photolysis; **b**, **c**, and **d**, intermediate photolysis times, illustrating the spectral changes characteristic of the Norrish type II reaction with the extent of reaction. Hollow arrows indicate free acetophenone liberated during photolysis. Filled arrows indicate characteristic signals due to formation of nonene-MPC.

protons at 7.90 and 7.11 ppm and the CH_2 protons α and β to the carbonyl function at 2.72 and 1.78 ppm, respectively. No free thiol in solution, which would appear as sharp resonances at the same chemical shifts, is evident, suggesting the sample is pure MUP-MPC. Using the procedures of Murray,[14] the ratio of the CH_3 resonance of nonexchanged hexanethiolate ligand (at 0.88 and 0.92 ppm, for C_6 and C_{12}, respectively) to that of the exchanged **MUP** ligand (resonance of protons on ring *ortho* to carbonyl at 7.90 ppm) was used to determine the extent of exchange to be 1:3 hexanethiolate:MUP. Because the stoichiometry of the original hexanethiolate MPC is known[13] and the place-exchange reaction maintains that of the original colloid,[13] the average stoichiometry of the MUP-C_6MPC is estimated to be $(MUP)_{82}(C_6H_{13}S)_{26}Au_{314}$. For the dodecanethiolate, the stoichiometry was determined to be $(MUP)_{76}(C_{12}H_{25}S)_{32}Au_{314}$. These stoichiometries were confirmed by I_2 reduction[14b] of the MUP-MPC's and integration of the NMR spectra of the resulting disulfides.[15]

Irradiation of an Ar-saturated solution of MUP-MPC's in benzene-d_6 between 300 and 400 nm using an appropriately filtered medium-pressure Hg lamp gave products consistent with the Norrish type II photoreaction (Scheme 2). This is illustrated for MUP-C_{12}MPC in the ^{1}H NMR spectrum, measured at intermediate photolysis time, shown in Figure 1b−d. Sharp proton resonances at 7.75 and 7.06 ppm and the singlet at 2.06 ppm indicated by hollow arrows provide evidence for the liberation of free acetophenone (from the enol); this is confirmed by isolation and characterization of acetophenone from the photolysis solution. Furthermore, concomitant with the generation of acetophenone is a decrease in the broad aromatic resonances and the appearance of new broad resonances at 5.07, 5.88, and 2.11 ppm, respectively. The signals at 5.07 and 5.88 ppm are consistent with the olefinic protons of the nonene-modified MPC and that at 2.11 with the corresponding allyl methylene protons. As expected the nonene-MPC was formed along with acetophenone on Norrish II fragmentation. To verify that the broad resonances at 5.07 and 5.88 ppm are the result of an alkene-MPC, an authentic sample of a Au-undecenethiolate MPC was prepared[16] and its proton NMR spectrum matched that from the photolysis (see Supporting Information).

Because the protons α to the S−Au functionality are not observed, it is very easy to detect the generation of free thiol or disulfide cleaving from the colloid. These would appear as sharp peaks in the 2.50−2.65 ppm region of the ^{1}H spectrum. Notably, no evidence for generation of thiol or disulfide during the photolysis was found, indicating that the Au−S bond is stable under these conditions. Additionally, there is no evidence (no OH stretch in the IR spectrum and no ^{1}H NMR resonances in the NMR spectrum of the photolyzed MPC) for formation of any cyclobutanol that would arise from cyclization of the 1,4-biradical.

Parallel photolyses of MUP-MPC were carried out in the presence 1 M *trans*-1,3-pentadiene in benzene-d_6. The presence of the diene clearly quenches the photoreaction, and no significant product formation is observed after exhaustive irradiation, indicating that the reaction of the MUP-MPC proceeds via the triplet excited state of the carbonyl, similar to solution studies on the free MUP. Further evidence for triplet quenching is provided by the formation of *cis*-1,3-pentadiene formed by the photosensitized geometric isomerization.

Because the alkene and the acetophenone are generated in a 1:1 ratio, the amount of acetophenone generated can be quantified and serve as an "internal standard" to quantify the extent of reaction on the MPC. The concentration of acetophenone was determined by gas chromatography.[17] The moles of acetophenone generated in an extensive photolysis of MUP-C_6MPC were thus quantified; the stoichiometry of the resulting photolyzed colloid was $(MUP)_{41}(alkene)_{41}$-

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(15) Stoichiometries are determined by integration of the relevant signals in ^{1}H NMR spectra and carry the relevant error in the measurement. Product stoichiometries are based on the stoichiometry of starting colloid before photolysis.

(16) Mercaptoundecene was used for preparation of a model alkene-MPC instead of mercaptononene because the former is readily available from commercially available 11-bromoundecene.

(17) A Hewlett-Packard 5890 GC with a 15 m DB-5 capillary column and a FID detector was used. A calibration curve was made using concentrations of an acetophenone solution in hexane varying from 0.98×10^{-3} to 3.31×10^{-3} M using hexadecane as an internal standard.

$(C_6H_{13}S)_{26}Au_{314}$, on the basis of the original stoichiometry above. Therefore, the photolysis proceeds to approximately 50% conversion. Further conversion efficiency is limited by the inner filter effect of the competitive absorption by the acetophenone liberated. Washing away liberated acetophenone and re-irradiating the remaining MPC verified this; in this way essentially all the MUP-MPC could be converted, the reaction could be taken to greater than 80% completion with a reasonable photolysis time, and the final stoichiometries were $(MUP)_{15}(nonene)_{67}(C_6H_{13}S)_{26}Au_{314}$ and $(MUP)_9(nonene)_{67}(C_{12}H_{25}S)_{32}Au_{314}$, respectively.[15]

In MUP, the Norrish II reaction proceeds via the n,π* triplet state to yield the triplet 1,4-biradical initially in a skew conformation (*s-BR*); Scheme 1. Two families of biradical conformers are considered important in product formation: the transoid (*t-BR*) and cisoid (*c-BR*) biradicals, both of which are derived from the skew biradical via rotations around the central $C_\alpha-C_\beta$ σ-bond or the $C^\bullet-OH$ and C_α bond. Orbital overlap requirements preclude cyclization from the *t-BR*. In principle, fragmentation and cyclization can both occur from the *c-BR*; however, cyclization is the preferred pathway.[18] Thus, the majority of fragmentation products arise from *t-B*R. In either case, products are derived from the conformation of the biradical on ISC from the triplet to the singlet. To achieve the geometry for cyclization, considerable movement of either the alkyl or the phenyl-ketyl portion of the *s-BR* is required and such motions require a large volume to be swept.[19] Since the alkyl portion is anchored and subject to considerable van der Waals interactions, the motions may mainly involve the large ketyl-phenyl moiety that is at the interface. The alternative pathway available to the *s-BR* is conversion to the *t*-BR. This conversion can occur with less motion, particularly if it occurs by ¨crankshaft" twisting motions[2d] of the alkyl chain and not larger motion of the ancillary groups, to achieve the geometry. Regardless, the *t-BR* should in fact lead to less disruption of the molecules at the interface and is overall less sterically demanding. The fact that there is only evidence for fragmentation products from the MPC's suggests that the environment of the MUP-MPC is affecting the equilibrium of the conformers and that reactivity is from the *t*-BR. There appears to be little difference on the photochemistry of having the short (C_6) or longer (C_{12}) dilutent with the MUP.

The present results illustrate for the first time that the Norrish type II reaction of aryl ketones occurs efficiently on MPC via the excited state triplet of the ketone. The extent of reaction can be easily quantified. Of particular note is that photolysis of the MUP-MPC does not lead to any Au−S cleavage, namely, these colloids are stable to photolysis. The alkene-modified MPC's undergo typical olefin chemistry, such as electrophilic addition reactions, and can thus serve as a template for further chemical modification. This aspect will appear in the full account of this work. With these promising preliminary results we plan on developing this reaction further to investigate the mobility in MPC by altering the structure of MUP by lengthening both the thiolate alkyl portion to move the photoreactive moiety away from the metal and also by adding alkyl groups to the aryl ring to embed the photoreactive fragment into the monolayer surface away from the interface. These studies are currently in progress.

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Supporting Information Available: ^{1}H NMR spectra of MUP-C_6MPC, MUP-C_{12}MPC, and mercaptoundecene-MPC and spectra of the photolyzed MPCs, where the liberated acetophenone has been removed. This information is available free of charge via the Internet at http://pubs.acs.org.

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