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PHOTOLYSIS OF NITRO-β,γ-ALKENES: NITRO-2,5-CYCLOHEXADIENES

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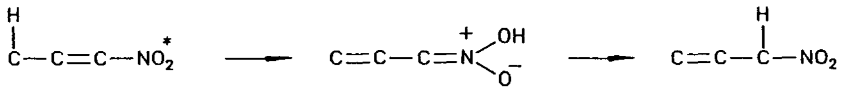
Abstract: Photolysis of 3-fluoro-4-methyl-, 3-chloro-4-methyl-, and 3,4-dimethyl-4-nitro-2,5-cyclohexadienyl acetate, in methanol, gives 3-fluoro-4-methyl-, 3-chloro-4-methyl-, and 3,4-dimethyl-4-hydroxy-2,5-cyclohexadienyl acetate, respectively. The replacement of nitro by hydroxyl is stereospecific. Photolysis of 1,4-dimethyl-4-nitro-2,5-cyclohexadienyl acetate in methanol gives 1,4-dimethyl-4-hydroxy-2,5-cyclohexadienyl methyl ether. Photolysis in ether gives 1,4-dimethyl-4-hydroxy-2,5-cyclohexadienyl acetate, with retention of configuration, and *p*-xylene. Photolysis of 1,4-dimethyl-4-nitro-2,5-cyclohexadienyl methyl ether in methanol gives 1,4-dimethyl-4-hydroxy-2,5-cyclohexadienyl methyl ether, with retention. Photolysis in ether gives 1,4-dimethyl-4-hydroxy-2,5-cyclohexadienyl methyl ether, with retention, and *p*-xylene.

Introduction

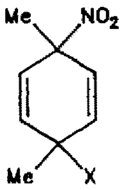
Photochemical studies of nitro compounds have largely involved aromatic nitro compounds, nitroalkanes, and α,β-unsaturated nitro compounds as substrates.[1] A common reaction of α,β-unsaturated nitro compounds is double bond migration to form the β,γ-unsaturated compound by a process involving γ-hydrogen abstraction and tautomerization of the resulting nitronic acid:[2,3]



$$\overset{H}{\overset{|}{C}}{-}C{=}C{-}NO_2^{*} \longrightarrow C{=}C{-}C{=}\overset{+}{N}\begin{smallmatrix}OH\\O^-\end{smallmatrix} \longrightarrow C{=}C{-}\overset{H}{\overset{|}{C}}{-}NO_2$$

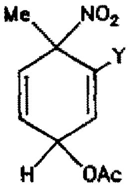
However, the further photochemistry of the product α-nitro-β,γ-alkene has not been investigated. In the reaction mixture in which it is formed photochemically it is likely that most of the light is absorbed by the conjugated starting substrate and by other conjugated products (e.g. the α,β-unsaturated ketone)[3] thus masking the photochemistry of the non-conjugated product.

Nitromethane exhibits its longer wavelength absorption at 270 nm (ϵ = 2 m^2mol^{-1}), attributed to an $n-\pi^*$ transition.[4] It is this transition which is assumed to give the excited state responsible for the photochemistry of nitroalkanes and other non-conjugated nitro compounds. There is good evidence that the primary photochemical process in nitroalkanes is dissociation of the C-N bond to form an alkyl radical and nitrogen dioxide.[5-8] These subsequently recombine to form the nitroalkane and the alkyl nitrite.[9] Formation of the alkyl nitrites can only be observed in the solid or liquid phases at low temperatures.[1,6,9] Under other conditions the excess vibrational energy results in rapid dissociation of the nitrite into an alkoxy radical and nitric oxide. Secondary photolysis of the alkyl nitrite to give these intermediates can also occur.[1] Thus the products that would be expected to be observed from the photolysis of nitroalkanes and non-conjugated unsaturated nitro compounds are those which would be formed by the further reaction of the corresponding alkoxy radicals.

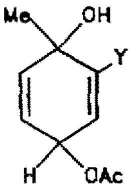


1

a, X = OAc
b, X = OMe

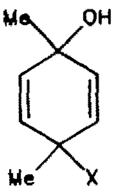


2



3

m, Y = F
n, Y = Cl
o, Y = Me



7

a, X = OAc
b, X = OMe

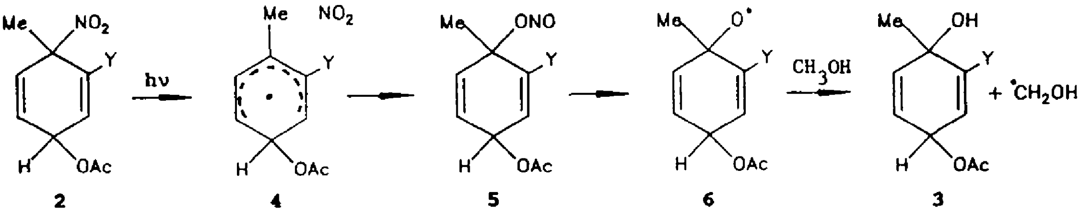
The one reported investigation of the photochemistry of an α-nitro-β,γ-alkene is that by Shosenji and co-workers on the photosolvolysis of the diastereomers of 1,4-dimethyl-4-nitro-2,5-cyclohexadienyl acetate (**1a**).[10] They reported the formation of the corresponding nitrocyclohexadienyl alkyl ethers (e.g **1b**), with a significant amount of stereoselection, when alcohols (e.g. methanol) were used as solvents. Photolysis in pentane and in ether gave p-xylene. In the present work we have investigated the photochemistry of 3-fluoro-4-methyl- (**2m**), 3-chloro-4-methyl- (**2n**), and 3,4-dimethyl-4-nitro-2,5-cyclohexadienyl acetate (**2o**), and have reinvestigated the photolysis of **1a**, the last with rather different results than reported by Shosenji et al.

Results and Discussion

Photolysis of **2n** in aqueous acetonitrile gave 3-chloro-4-hydroxy-4-methyl-2,5-cyclohexadienyl acetate (**3n**) and 3-chloro-4-methylphenyl acetate. The photoreaction is stereospecific since, in methanol, (*E*)-**2n** gave (*E*)-**3n**. The aryl acetate is the product that would be expected on (thermal) solvolysis of the nitro group.[11] It is to be noted that in the reactions in both aqueous acetonitrile and methanol the nitro group is replaced by hydroxyl. Thus **3n** cannot be formed by the solvolytic replacement of the nitro group in **2n**, a reaction that does occur thermally with tertiary acetate adducts under carefully controlled conditions.[12] It is apparent that **3n** is a genuine photoproduct. The aryl acetate was obtained as a minor product in the photolyses carried out at 254 nm but not in those at 300 nm. The assignment of the structure of **3n** (and **3m**, below) is based on the spectral data. The presence of the hydroxyl and acetate groups is established by the ir and the ^1H and ^{13}C nmr establish the 1,4-diene structure. These assignments are supported by comparison with the spectral data for **2** and **7a**.

Photolysis of (*E*)-**2m** in methanol gave (*E*)-**3m** and, likewise, (*Z*)-**2m** gave (*Z*)-**3m**. The reactions were carried out at 254 nm and aryl acetate was not formed in significant amount. Photolysis of **2o** gave **3o** and 3,4-dimethylphenyl acetate.

Scheme 1



The foregoing reactions of the tertiary nitrocyclohexadienes parallel those of the nitroalkanes. The mechanism of these reactions (Scheme 1) would thus appear to involve fission of C-N bond to form the cyclohexadienyl radical **4** and nitrogen dioxide, recombination to form the nitrite ester **5**, followed by fission of the nitrite to form alkoxy radical **6** and nitric oxide. Hydrogen abstraction by the alkoxy radical, from methanol, would give the observed hydroxy acetate **3**. Reaction between the hydroxymethylene radical (produced in step 4) and the nitric oxide (from step 3) would give formaldehyde and nitroxyl.[6,13] Formation of the resonance-stabilized cyclohexadienyl radical **4**, by fission of the C-N bond at the tertiary centre, should be much more facile than, e.g., formation of the methyl radical from nitromethane. What is surprising about our observations is that the conversion of nitro to hydroxyl is completely stereospecific. This implies that the recombination of **4** and the nitrogen dioxide must be extremely fast, faster than the members of the radical pair can relocate within the solvent cage. Recombination involving an even more reactive alkyl radical and nitrogen dioxide must be at least as fast - an unsuspected facet of the photolysis of nitroalkanes.

Photolysis of the *p*-xylene adduct **1a** is more complex than photolysis of **2** since 1,4-dimethyl-4-hydroxy-2,5-cyclohexadienyl methyl ether (**7b**) was formed in methanol rather than the acetate **7a**. Furthermore the reaction was not stereospecific, (*E*)-**1a** giving a mixture of the diastereomers of **7b**. Some 4-methoxymethyl toluene and 2,5-dimethylphenol were also formed. There are thermal pathways to these minor products and they will not be discussed further.[14] It seems obvious that formation of the hydroxycyclohexadienyl methyl ether must involve the normal conversion of nitro to hydroxyl and the replacement of acetate by methoxyl. The question arises as to which step occurs first and whether the conversion of nitro to hydroxyl is stereospecific. Either **7a** or **1b** will be an intermediate in the reaction, depending upon whether the conversion of nitro to hydroxyl occurs before or after the conversion of acetate to methoxyl. Both of these compounds were synthesized and photolyzed in methanol. (*E*)-**1b** gave (*E*)-**7b** and (*Z*)-**1b** gave (*Z*)-**7b**. These reactions thus parallel those of the acetates **2** and exhibit the same replacement of nitro by hydroxyl with retention of stereochemistry. On photolysis diene **7a** gave **7b**, and it also underwent the same reaction thermally, although more slowly. However, in the short time photolysis of **1a**, the intermediate formation of **7a**, but not **1b**, could be detected by NMR. Thus it appears that photolysis of **1a** gives **7a** (nitro to hydroxyl conversion) which gives in turn **7b** (solvolysis of acetate) and this was confirmed when the photolysis was carried out in ether, in which the solvolysis reaction is suppressed. Acetate (*E*)-**1a** gave acetate (*E*)-**7a** and (*Z*)-**1a** gave (*Z*)-**7a**. In both cases *p*-xylene was also formed in a slightly greater amount than **7**.

Our results on photolysis of **1a** differ substantially from Shosenji et al.[10] They claim to have detected photosolvolysis to **1b** in methanol and apparently did not observe the formation of the dienol(s) **7a** or **7b**. Furthermore, they noted the formation of *p*-xylene in ether but did not observe the formation of dienol **7a** in this solvent either. The conversion of **1a** to **1b** is a well-established and a particularly facile example of a common acid-catalyzed thermal reaction of acetyl nitrate adducts.[14] It is possible that Shosenji's results were confused by the competing thermal exchange. Our results are consistent for all of the dienes investigated. It is easy to understand why the photolysis of **1a** in methanol is complicated by the subsequent solvolysis of **7a** to **7b** whereas this complication does not occur in the cases of **2m** and **2n**. Solvolysis of **7a**, for which the intermediate cyclohexadienyl cation should be much more stable, should be faster than solvolysis of **3m** or **3n**.

A surprising feature of our results is that there is competition between the formation of **7a** and *p*-xylene, and of **7b** and *p*-xylene, in the photolysis in ether of **1a** and **1b**, respectively. We have commented above on the extremely rapid recombination of the cyclohexadienyl radical and nitrogen dioxide. We cannot envisage a competing reaction with ether which would divert the initially formed radicals from the recombination, as the recombination is faster than even intra-cage migration. We suggest that the explanation for the absence of the competing reaction in methanol lies in the fact that **1a** (**1b**) is hydrogen bonded to the methanol through the carbonyl (methoxyl) group. When the cyclohexadienyl radical is generated in methanol it can rapidly disperse its excess vibrational energy to the solvent in virtue of its association with the solvent. This does not happen in ether and the vibrationally excited cyclohexadienyl radical thus rapidly fragments at the C-O bond to form *p*-xylene and an acetoxy (methoxy) radical.

Experimental

Melting points are uncorrected and were determined on a Reichert 7905 melting point apparatus. IR spectra, of chloroform solutions or nujol mulls for solids, and thin films between sodium chloride plates for liquids, were recorded on a Perkin-Elmer 283 spectrometer. UV spectra were recorded on a Perkin-Elmer Lambda-4B spectrophotometer using methanol as solvent. ^1H NMR spectra were recorded on a Perkin-Elmer R-32 (90 MHz) or a Bruker WM 250 (250 MHz) spectrometer. Tetramethylsilane (90 MHz) or the solvent deuterium signal (250 MHz) was used as the lock signal. ^{13}C NMR spectra (62.9 MHz) were recorded on the Bruker spectrometer using solutions in chloroform-d and the peak at 77.0 ppm for calibration. ^{19}F NMR spectra were recorded on the Bruker spectrometer using $CFCl_3$ as the external standard. Mass spectra (MS) were recorded on a Perkin-Elmer Hitachi RMU-6E spectrometer. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Vancouver, British Columbia.

Petroleum ether (b p. 30-60 °C, reagent grade, Fisher), and ether (BDH, dried over sodium), were distilled before use for chromatography. Tetrahydrofuran (THF) (Anachemia), used for alkyl lithium addition reactions, was freshly distilled, under nitrogen, from potassium metal and benzophenone. Spectral grade solvents from Aldrich were used for spectroscopy and photolysis experiments. Alumina was from Camag. AnalTech Silica Gel GF plates were used for TLC.

4-Methyl-4-hydroxy-2,5-cyclohexadienone was obtained from Dr. G. N. Henderson[15]. 1,4-Dimethyl-4-nitro-2,5-cyclohexadienyl acetate (**1a**),[14,16] the corresponding methyl ether (**1b**)[14] and 3,4-dimethyl-4-nitro-2,5-cyclohexadienyl acetate (**2o**)[17] were prepared according to the literature descriptions. 3-Fluoro- (**2m**) and 3-chloro-4-methyl-4-nitro-2,5-cyclohexadienyl acetate (**2n**) were obtained by nitration of 2-fluoro- and 2-choro-toluene, respectively.[18]

1,4-Dimethyl-4-hydroxy-2,5-cyclohexadienyl acetate (**7a**). *4-Methyl-4-trimethylsilyloxy-2,5-cyclohexadienone.* O,N-Bis(trimethylsilyl)acetamide (BSA) (20 cm^3, 0.08 mol) was added from a syringe to a stirred solution of 4-methyl-4-hydroxy-2,5-cyclohexadienone (3.1 g, 0.025 mol) in dry acetonitrile (125 cm^3), under a nitrogen atmosphere, and the mixture was then heated under reflux. The reaction was monitored by NMR. After refluxing for 17 h 90% of the starting material was silylated. The reaction mixture was cooled and the acetonitrile was evaporated below 10 °C with the receiver flask cooled by solid carbon dioxide. Addition of petroleum ether (50 cm^3), filtration of the precipitated acetamide, and evaporation of the filtrate below 10 °C gave the crude silyloxydienone. Chromatography on basic alumina (100 g) deactivated with 5% v/v of 10% aqueous acetic acid, at 0 °C and using 5% ether-petroleum ether as eluent, gave colourless crystals of the pure dienone (3.5 g, 71%), mp 57 °C; IR (nujol): 1665 (C=O), 1620 (C=C) cm^{-1}; MS (70 eV) *m/z* (relative intensity) 196 (*M*, 23), 181 (*M* - CH_3, 74); ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 0.04 (s, 9, $Si(CH_3)_3$), 1.38 (s, 3, CH_3), 6.07 (d, *J* = 10 Hz, 2, 2-H and 6-H), and 6.83 (d, *J* = 10 Hz, 2, 3-H and 5-H) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C: 1.9 ($Si(CH_3)_3$), 29.5 (CH_3), 69.6 (C-4), 126.8 (C-2 and C-6), 153.5 (C-3 and C-5), and 185.4 (C-1) ppm. *Anal*. calcd. for $C_{10}H_{16}O_2Si$: C 61.23, H 8.16; found: C 61.56, H 8.20.

1,4-Dimethyl-4-silyloxy-2,5-cyclohexadienyl acetate. Methyl lithium in diethyl ether (26 cm^3, 36 mmol) was added over a period of 5 min to a stirred solution of the silyloxydienone (1.18 g, 6 mmol) in THF (18 cm^3), at -78 °C, under a nitrogen atmosphere. Stirring was continued for 30 min at -78 °C and for 15 min at -40 °C. The reaction was quenched by adding acetic anhydride (5.7 cm^3, 54 mmol) and stirring was continued at -40 °C for another 5 min. Ether (50 cm^3) at -40 °C was added and the excess acetic anhydride was neutralized by adding aqueous ammonia (50 cm^3) cooled to -60 °C. The mixture was warmed to 0 °C and the organic layer was separated. The aqueous layer was extracted with cold ether (2 x 10 cm^3). The combined organic layers were washed with saturated sodium chloride solution (2 x 10 cm^3) followed by distilled water, dried ($MgSO_4$) and evaporated at 5 °C to give the silyloxycyclohexadienyl acetate (2.6 g, *E*:*Z* = 4.3:1). The (*E*) isomer had ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 0.06 (s, 9, $Si(CH_3)_3$), 1.22 (s, 3, 4-CH_3), 1.45 (s, 3, 1-CH_3), 1.94 (s, 3, $OCOCH_3$), 5.81 (d, *J* = 10.3 Hz, 2), and 5.96 (d, *J* = 10.3 Hz, 2) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C: 2.1 ($Si(CH_3)_3$), 22.1 ($OCOCH_3$), 26.9 (1-CH_3), 31.5 (4-CH_3), 68.0 (C-4), 75.0 (C-1), 127.8 (C-2 and C-6), 134.4 (C-3 and C-5), and 169.9 ($OCOCH_3$) ppm. The (*Z*) isomer had ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 0.04 (s, 9, $Si(CH_3)_3$), 1.32 (s, 3, 4-CH_3), 1.48 (s, 3, 1-CH_3), 1.92 ($OCOCH_3$), 5.78 (d, *J* = 10.2 Hz, 2), and 5.88 (d, *J* = 10.2 Hz, 2) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C: 2.3 ($Si(CH_3)_3$), 22.1 ($OCOCH_3$), 26.4 (1-CH_3), 29.5 (4-CH_3), 68.8 (C-4), 75.0 (C-1), 127.8 (C-2 and C-6), 136.4 (C-3 and C-5) and 169.8 ($OCOCH_3$) ppm.

Hydroxy acetate **7a**. A solution of tetra-n-butylammonium fluoride in THF (5 cm^3, 5 mmol) was added to a stirred solution of the silyloxycyclohexadienyl acetate (640 mg, 2.5 mmol) in freshly distilled THF (6 cm^3) at 0 °C, under a nitrogen atmosphere, and stirring was continued for 30 min. The mixture was added to ether (10 cm^3) at 0 °C, followed by cold saturated sodium chloride solution (10 cm^3). The organic layer was separated and washed with distilled water (2 x 10 cm^3), dried ($MgSO_4$) and evaporated at 5 °C with the receiver flask cooled with solid carbon dioxide. Residual THF was removed on a vacuum line (the sample flask was cooled with ice-salt). The residue was dissolved in pentane and stored at -20 °C for 18 h. Colorless crystals of (*E*)-**7a** (147 mg) were obtained, mp 50-51 °C; MS (70 eV) *m/z* (relative intensity): 123 (*M* - OAc, 83) and 122 (*M* - HOAc, 100); IR ($CDCl_3$): 3600-3360 (O-H), 1710 (br, C=O and C=C), 1250 and 1050 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ: 1.26 (s, 3, 4-CH_3), 1.32 (s, 3, 1-CH_3), 1.93 (s, 3, $COCH_3$), 5.66 (d, *J* = 10 Hz, 2) and 5.89 (d, *J* = 10 Hz, 2) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C: 22.3 ($OCOCH_3$), 27.3 and 27.9 (1-CH_3 and 4-CH_3), 64.4 (C-4), 73.8 (C-1), 128.0 (C-2 and C-6), 134.8 (C-3 and C-5), and 170.2 ($OCOCH_3$) ppm. Anal. calcd. for $C_{10}H_{14}O_2$: C 65.93, H 7.69, found: C 65.98, H 7.69.

(*Z*)-**7a**, in the residual mixture with (*E*)-**7a**, had ^1H NMR ($CDCl_3$, 250 MHz) δ: 1.40 (4-CH_3), 1.45 (1-CH_3), 1.92 ($OCOCH_3$), 5.75 (d, *J* = 10.3 Hz, 2), and 5.83 (d, *J* = 10.3 Hz, 2) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C: 22.1 ($OCOCH_3$), 26.9 and 28.0 (1-CH_3 and 4-CH_3), 66.2 (C-4), 74.6 (C-1), 129.2 (C-2 and C-6), 134.9 (C-3 and C-5), and 169.9 ($OCOCH_3$) ppm.

Photochemical reactions

Photolyses were carried out in a Rayonet Photochemical Reactor (The Southern New England Ultraviolet Company) using either 254 nm or 300 nm radiation. The diene solution, generally 100 mg in 100 cm^3, was contained in a quartz tube fitted with a side arm and a cold finger, through which cold water was circulated. Argon was bubbled through the solution for 10 min before starting the photolysis, to deoxygenate the solution, and the bubbling was continued during the photolysis to stir the solution. The products were obtained by evaporation of the solvent at -5°C. For each substrate a dark reaction was carried out under the same conditions as the photolysis.

3-Chloro-4-methyl-4-nitro-2,5-cyclohexadienyl acetate (**2n**). A solution of diene **2n** (100 mg) in acetonitrile (140 cm^3) and water (60 cm^3) was photolyzed for 60 min at 254 nm. The solution was evaporated to 70 cm^3, sodium chloride was added and the solution was extracted with dichloromethane. The organic layer was dried ($MgSO_4$) and the solvent evaporated to give a mixture (50 mg) of unreacted **2n** (42%), 3-chloro-4-methylphenyl acetate (25%), and **3n** (32%). The products from a larger scale experiment were separated by TLC (silica) using 25% ether-petroleum ether as the eluent. (*E*)-**3n** was obtained as a colorless oil, IR (CCl_4): 3590 (O-H), 1740 (C=O), and 1220 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ: 1.44 (s, 3, CH_3), 2.08 (s, 3, $OCOCH_3$), 5.65 (ddd, *J* = 3.2, 3.2, 1.4 Hz, 1, 1-H), 5.80 (ddd, *J* = 10, 3.2, 1.8 Hz, 1, 6-H), 5.99 (dd, *J* = 3.2, 1.8 Hz, 1, 2-H), and 6.04 (dd, *J* = 10, 1.4 Hz, 1, 5-H) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C: 21.0 ($OCOCH_3$), 27.3 (CH_3), 66.0 (C-1), 67.8 (C-4), 122.6 and 123.0 (C-2 and C-6), 135.3 (C-5), 141.5 (C-3), and 170.5 ($OCOCH_3$) ppm. (*Z*)-**3n** was also obtained as a colorless oil, ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 1.52 (s, 3, CH_3), 2.09 (s, 3, $OCOCH_3$), 5.72 (br t, J = 3.8 Hz, 1, 1-H), 5.87 (ddd, J = 9.8, 3.8, 1.7 Hz, 1, 6-H), 6.06 (dd, J = 3.8, 1.7 Hz, 1, 2-H), and 6.10 (br d, J = 9.8 Hz, 1, 5-H) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C: 21.0 ($OCOCH_3$), 27.2 (CH_3), 66.2 (C-1), 68.0 (C-4), 122.9 and 123.3 (C-2 and C-6), 136.7 (C-5), 142.8 (C-3), and 170.4 ($OCOCH_3$) ppm.

Diene (*E*)-**2n** in methanol at 0 °C was photolyzed for 2 h at 300 nm and was converted (50%) into (*E*)-**3n**. When the photolysis was carried out at 254 nm some aryl acetate was also formed.

3-Fluoro-4-methyl-4-nitro-2,5-cyclohexadienyl acetate (**2m**). Photolysis of (*Z*)-**2m** in methanol for 4 h at 254 nm gave 3-fluoro-4-hydroxy-4-methyl-2,5-cyclohexadienyl acetate ((*Z*)-**3m**). Repetition (x 3) of the solvolysis on a 340 mg scale gave, after work up, a mixture (400 mg, in total) of (*Z*)-**2m** and (*Z*)-**3m**. Diene (*Z*)-**3m** was obtained as a colourless oil from TLC (silica) and elution with 10% ether-petroleum ether. It had ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 1.46 (s, 3, CH_3), 2.07 (s, 3, $OCOCH_3$), 5.43 (ddd, J = 14.9, 3.8, 1.8 Hz, 1, 2-H), 5.80 (m, 2, 1-H, 6-H), and 5.93 (dd, J = 9.4, 8.8 Hz, 1, 5-H) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C: 21.1 ($OCOCH_3$), 25.1 (CH_3), 65.8 (C-4, J = 25.8 Hz), 66.6 (d, C-1, J = 11.1 Hz), 101.4 (d, C-2, J = 18.1 Hz), 123.8 (d, C-6, J = 2.9 Hz), 134.7 (d, C-5, J = 5.1 Hz), 162.9 (d, C-3, J = 266.1 Hz), and 170.5 ($OCOCH_3$) ppm; ^{19}F NMR ($CDCl_3$, 235.36 MHz) δ_F: -124.5 ppm.

Photolysis of (*E*)-**2m** in methanol for 4 h at 254 nm gave, after work-up, (*E*)-**3m** (40 mg) as a colorless oil, IR ($CDCl_3$): 3580 (OH), 1730 (C=O), and 1240 (C-O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 1.50 (s, 3, CH_3), 2.05 (s, 3, $OCOCH_3$), 5.46 (ddd, J = 15.5, 3.6, 2 Hz, 1, 2-H), 5.82 (m, 2, 1-H, 6-H), and 5.93 (ddd, J = 9, 9, 2.3 Hz, 1, 5-H) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C: 21.1 ($OCOCH_3$) 25.3 (CH_3), 65.9 (d, J = 23.7 Hz, C-4), 66.9 (d, J = 12.6 Hz, C-1), 102.0 (d, J = 17.5 Hz, C-2), 124.2 (C-6), 135.5 (d, C-5, J = 3.8 Hz), and 170.5 ($OCOCH_3$) ppm; ^{19}F NMR ($CDCl_3$, 235.36 MHz) δ_F: -124.4 ppm.

3,4-Dimethyl-4-nitro-2,5-cyclohexadienyl acetate (**2o**). Photolysis of diene **2o** in methanol at 10 °C, for 2 h at 300 nm, gave a mixture of 3,4-dimethylphenyl acetate (41%) and 3,4-dimethyl-4-hydroxy-2,5-cyclohexadienyl acetate (**3o**, 59%). In the product mixture **3o** had ^{1}H NMR (two diastereomers) δ: 1.30 and 1.40 (4-CH_3), 1.75 and 1.85 (3-CH_3), 1.90 ($OCOCH_3$), 5.6-6.1 (m) ppm. Attempted separation of the products by TLC (silica) resulted in the decomposition of **3o**. The aryl acetate was separated as a colorless oil, ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 2.22, 2.24 (s, 6, 3- and 4-CH_3), 2.27 (s, 3, $OCOCH_3$), 6.80 (dd, 1, J = 8.1, 2.2 Hz, 6-H), 6.84 (br s, 1, 2-H), and 7.1 (d, 1, J = 8.1 Hz, 5-H) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C: 19.1, 19.8 (3-, 4-CH_3), 21.1 ($OCOCH_3$), 118.6 (C-6), 122.5 (C-2), 130.4 (C-5), 134.2 (C-4), 137.9 (C-3), 148.7 (C-1), and 169.9 ($OCOCH_3$) ppm.

1,4-Dimethyl-4-nitro-2,5-cyclohexadienyl acetate (**1a**). Photolysis of **1a** in methanol at 10 °C, for 4 h at 300 nm, gave 4-methoxymethyltoluene (15%), 2,5-dimethylphenol (19%), and 1,4-dimethyl-4-hydroxy-2,5-cyclohexadienyl methyl ether (**7b**, 65%).

(*E*)-**1a** in ether at 5 °C was photolyzed for 3 h at 300 nm and gave a mixture of *p*-xylene (52%), diene (*E*)-**7a** (44%), and unreacted (*E*)-**1a** (4%). (*Z*)-**1a** similarly gave a mixture of *p*-xylene (56%) and (*Z*)-**7a** (44%). The product dienes were identical with authentic samples (vide supra).

1,4-Dimethyl-4-nitro-2,5-cyclohexadienyl methyl ether (**1b**). (*E*)-**1b** in methanol was photolyzed for 2 h at 300 nm and gave a mixture (70 mg) of 4-methoxymethyltoluene (17%) and (*E*)-**7b** (83%). TLC (silica) using 30% ether-petroleum ether as the eluent gave 4-methoxymethytoluene as a colorless liquid, ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 2.32 (s, 3, CH_3), 3.37 (s, 3, OCH_3), 4.43 (s, 2, CH_2), 7.17 (d, J = 7.1 Hz, 2, 2-H, 6-H), 7.23 (d, J = 7.1 Hz, 2, 3-H, 5-H) ppm. Diene (*E*)-**7b** was obtained as a colorless crystals, mp 95-96^0 C (lit.[12,19] 94-95^0 C); IR (Nujol): 3415 (O-H), 2830 (OCH_3), 1120, 1065 (C-O) cm^{-1}; ^{1} NMR ($CDCl_3$, 250 MHz) δ: 1.31 (s, 3, CH_3), 1.36 (s, 3, CH_3), 3.05 (s, 3, OCH_3), 5.60 (d, J = 10.2 Hz, 2, 2-H, 6-H), and 6.02 (d, J = 10.2 Hz, 2, 3-H, 5-H) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C: 27.9 (CH_3), 28.1 (CH_3), 51.6 (OCH_3), 65.7 (C-4), 71.0 (C-1), 131.2 (C-2, C-6), and 136.2 (C-3, C-5) ppm.

(*Z*)-**1b** in methanol at 10 °C, on photolysis for 2 h at 300 nm, gave a mixture (57 mg) of (*Z*)-**7b** with a small amount of 4-methoxymethyltoluene. On TLC (silica) using 30% ether-petroleum ether as the eluent diene (*Z*)-**7b**[12,19] was obtained as an oil, IR (neat): 3410 (O-H), 2830 (OCH_3), 1135, 1085 (C-O) cm^{-1}: ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 1.26 (s, 3, CH_3), 1.32 (s, 3, CH_3), 3.13 (s, 3, OCH_3), 5.63 (d, J = 10.2 Hz, 2, 2-H, 6-H), and 5.99 (d, J = 10.2 Hz, 2, 3-H, 5-H) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C: 28.1 (CH_3), 28.8 (CH_3), 52.0 (OCH_3), 65.7 (C-4), 71.0 (C-1), 131.1 (C-2, C-6), and 135.4 (C-3, C-5) ppm.

(*E*)-**1b** in ether at 5 °C was photolyzed for 90 min at 300 nm and gave a mixture of *p*-xylene (29%), diene (*E*)-**7b** (31%), and unreacted (*E*)-**1b** (40%).

1,4-Dimethyl-4-hydroxy-2,5-cyclohexadienyl acetate (**7a**). Diene **7a** in methanol at 5 °C was photolyzed for 30 min at 300 nm and was converted (50%) into diene **7b**. No reaction occurred when a solution of diene **7a** in ether was photolyzed for 1 h at 300 nm. When the photolysis was carried out for 4 h 2,4-dimethylphenol was obtained.

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