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Conformational Effects and Regiospecificity in Conjugated Dienone Photoisomerization

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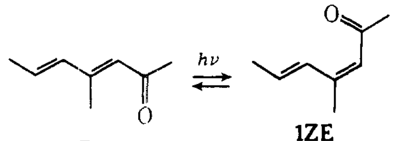
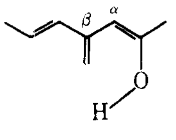
Regiospecific photoisomerization of rhodopsin at its 11-cis double bond is the key photochemical event in vision,[1] and regiospecific triplet-sensitized isomerization of trienones and related compounds has been reported.[2] Regiospecific dienone photoisomerization is rare, however. Quantum yield studies reveal that singlet or triplet excitation of any of the known 3,5-heptadienone isomers, *E,E*, *E,Z*, or *Z,E*, gives *directly* the other two.[3-6] Of a series of aliphatic and δ-phenyl dienones, only 4-methyl-3,5-heptadienone (**1**) undergoes regiospecific photoisomerization.[7]



Several causes for the unique behavior of **1** can be proposed. Effecient enolization of excited dienone could lead to exclusive α,β isomerization via the enol (**2**). Alternatively the cause may be conformational. For example, 1,3-diene triplets undergo rapid rotation about their 1,2 and 3,4 bonds, but are incapable of rotation about their central (2,3) bonds.[8] This leads to separate s-cis and s-trans excited dienes which exhibit distinct chemical properties.[9,10] Excited dienones may behave similarly.[4] Infrared and UV data reveal that all the α,β-*E* dienones which we photoisomerized[3] existed as mixtures of s-cis and s-trans enone conformers with the exception of **2**.[11] These 4-methyl-substituted dienones have exclusively s-cis enone units owing to steric destabilization of their s-trans conformers.[12] The unique behavior of their excited states of **1** may derive from the absence of s-trans enone units.



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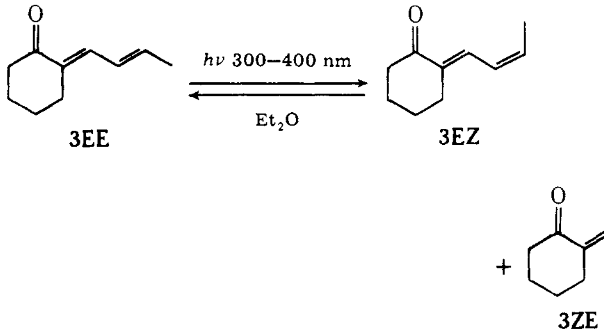
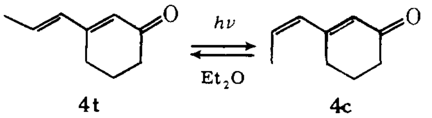
Reinvestigation of the photoisomerization of 4-methyl-3,5-heptadienone confirmed our initial report of this unusual regiospecific photoisomerization. An attempt to prepare the "missing" *E,Z* isomer so that its photochemical behavior could be studied was unsuccessful.[13] Tests for photoenolization were carried out by irradiation of **1EE** in deuterated solvents. Photoenolization would lead to deuterium incorporation into the dienone at the 4-methyl group under these conditions.[14] Irradiation of **1EE** in methanol-*O*-d_1 and in diethyl ether saturated with deuterium oxide proceeded normally and was continued for 1 h after the photostationary state had been reached. Control reactions in methanol and water-saturated ethyl ether were also carried out. Analysis of the photoproducts by GLC–mass spectrometry showed the same M + 1/M signal intensity ratio for samples of **1EE** and of **1ZE** from both deuterated and undeuterated media. Thus, no deuterium incorporation has taken place, and we can conclude that photoenolization does not occur.

The possible effect of the s-cis enone conformation on photoisomerization was tested by studying 2-butenylidenecyclohexanone (**3**).[15,16] This compound lacks the β substituent of **2**, but the ring locks its enone unit in the s-cis conformation. Irradiation of **3EE** gave a photostationary mixture of three isomers. The same photostationary mixture was produced starting from the photoisomers. Structures were assigned on the basis of IR, NMR, and UV spectra which are well known for sets of isomeric dienones.[11,17] Thus, locking the enone unit into the s-cis conformation did not lead to regiospecific photoisomerization.



Conformational influence on quantum yields for photoisomerization was studied using 3-(1-propenyl)-2-cyclohexenone (**4**),[3,18] which possesses a locked s-trans enone unit.



Enone unit isomerism, far more than diene unit isomerism, seems the possible cause of such an effect.[4] Quantum yields for photoisomerization of **4** in ether, determined at three wavelengths, are presented in Table I. The 254- and 313-nm values for trans to cis photoisomerization are different at a high level of confidence. Thus, conformational isomerism of the enone unit cannot be the only factor which contributes to the observed wavelength dependence.[4]

Beyond photoenolization and enone conformational effects, now eliminated, several other possible causes for regiospecific photoisomerization of **1** should be assessed. Depletion of the photostationary concentration of the missing *E,Z* isomer owing to preferential excitation is unlikely. Nonplanarity caused by relief of a 1,3-dimethyl interaction should lead to reduced, not enhanced, UV absorption by this isomer.[11] The steric destabilization of the *E,Z* isomer would be expected to bias decay ratios of nonplanar excited dienones against *E,Z* formation. However, behavior of isomeric 1,3-pentadiene triplets, which possess "allyl methylene" geometry, suggests

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Table I. Quantum Yields for 3-(1-Propenyl)-2-cyclohexenone Photoisomerization in Ether[a]

λ, nm	$\phi_{t\to c}$	$\phi_{c\to t}$ (calcd)[b]	$\Sigma\phi$[c]
254	0.32 ± 0.02[d]	0.72 ± 0.06	1.04 ± 0.06
313	0.20 ± 0.02[e]	0.24 ± 0.04	0.44 ± 0.04
334	0.26 ± 0.02[f]		

[a] Analysis of errors was made according to D. V. Huntsberger, "Elements of Statistical Inference", 2nd ed., Allyn and Bacon, Boston, Mass., 1967, p 285. [b] Calculated as $\phi_{c\to t} = (T_{pss}\epsilon_t\phi_{t\to c})/C_{pss}\epsilon_c$ where T_{pss}/C_{pss} is the photostationary state ratio. [c] $\phi_{t\to c} + \phi_{c\to t}$. [d] Seven determinations. [e] Five determinations. [f] Three determinations. The back reaction correction was not applied owing to uncertainty in the photostationary state composition. A reasonable estimate of this correction gives a value of $\phi_{t\to c} = 0.30$.

that significant amounts of the missing dienone isomer would be formed by such decay.[19] Finally, equilibrating planar excited states, used to explain regiospecific isomerization of trienone triplets,[2] cannot be reconciled easily with the known properties of dienone singlets. Dienone singlets do not fluoresce[4] nor do they undergo efficient intersystem crossing.[5] These observations seem inconsistent with the relatively long singlet lifetimes required for equilibrating planar singlets. Thus, the cause(s) of regiospecific photoisomerization of 1 remains unidentified.

The quantum yields for photoisomerization of 4 are relevant to excited state geometry. A common excited state, twisted about the γ,δ bond, requires that $\Sigma\phi = 1$. The data at 313 nm ($n\pi^*$ and $\pi\pi^*$ excitation) are inconsistent with such a common excited state while the 254-nm data ($\pi\pi^*$ excitation) allow it. A possible interpretation is that the $\pi\pi^*$ singlet is twisted about the γ,δ bond while the $n\pi^*$ singlets are planar.[20]

Experimental Section

General. Spectra were determined using Beckman IR-10 infrared, Cary-14 ultraviolet, Varian A-60 and Perkin-Elmer R-12 nuclear magnetic resonance, and Hitachi Perkin-Elmer RMU-6L mass spectrometers. Tetramethylsilane was employed as an internal standard for all NMR spectra. Irradiations were carried out in Pyrex vessels under nitrogen using a Rayonet reactor equipped with 3500 Å lamps. The solvent was degassed ethyl ether unless otherwise specified.

4-Methyl-3,5-heptadienone (1). Irradiation of a 7.6 × 10^{-4} M solution of **1EE** produced only one other isomer, **1ZE,** with VPC retention times (5 ft. × 1/8 in., 10% SE-30 on 60–80 mesh Anakrom ABS, 70 °C,He flow 44 mL/min) of 10.6 and 8.5 min, respectively. Use of several other VPC columns revealed two compounds only. Extended irradiation resulted in gradual formation of volatile products (retention time <2 min) at the expense of dienones. The spectral properties (IR and NMR) of the pure components separated by preparative TLC were in accord with those previously reported for **1EE** and **1ZE**.[9]

Photoenolization was tested using ca. 5 × 10^{-3} M solutions of **1EE** in methanol, methanol-*O-d*, and ethyl ether saturated with deuterium oxide and with water. The samples were placed in Pyrex tubes and degassed by three freeze-pump-thaw cycles prior to irradiation.

2-Butenylidenecyclohexanone (3). Preparation by the method of Normant[15] using 1-bromopropene (30% cis) gave a 34% yield of light yellow prisms, mp 54.5–55 °C (lit.[16] mp 56 °C), that was a 3:1 mixture of **3EE** and **3EZ**. Pure **3EE** was obtained by preparative VPC: IR (film) 1680 (C=O), 1630, 1580 (C=C), 815 cm^{-1} ($RCH{=}CR_2$); NMR (CCl_4) τ 8.10 (d, 3, J = 4 Hz, CH_3–), 7.50 (m, 8, $(CH_2)_4$), 3.79 (m, 1, H_γ), 3.68 (m, 1, H_δ), 2.95 (d, J = 9 Hz, H_β); UV (ether) λ_{max} 282 nm (ϵ 24 300). Comparison with the 3:1 mixture shows that **3EZ** must have very similar spectral properties.

A 3.2 × 10^{-4} M ether solution of pure **3EE** produced a three-component photostationary mixture when irradiated. VPC analysis (5 ft. × 1/8 in. 10% SE-30 on 60–80 mesh Anakron ABS, 130 °C, 40 mL/min) revealed **3EE**, 6.9 min, **3EZ**, 6.4 min (shoulder on **3EE** peak), and a third isomer with a retention time of 4.3 min identified as **3ZE** (see below). The photostationary composition was 52% *E,E*, 14% *E,Z*, and 34% *Z,E*. The *Z,E* isomer was separated from this mixture using preparative TLC (silica gel/10% ether in pentane) as an oil: IR (film) 1680 (C=O), 1630, 1585 cm^{-1} (C=C); NMR (CCl_4) τ 8.25 (d, 3, J = 7 Hz, CH_3), 7.71 (m, 8, ring CH_2's), 4.0 (m, 2, H_β and H_δ), 3.25 (m, 1, H_γ); UV (ether) λ_{max} 279 nm (ϵ 15 800).

Pure **3EE** and **3ZE** as well as a 3:1 mixture of **3EE** and **3EZ** exhibited identical mass spectral fragmentation patterns: *m/e* (rel intensity) 150 (95) (M), 149 (80), 148 (60), 136 (75), 135 (100) $M - CH_3$, 122 (50) M – CO and $M - C_2H_4$, 121 (40), 120 (50), 107 (75), 105 (30). Irradiations of pure **3ZE** and a **3EE–3EZ** mixture produced the same photostationary isomer mixture described above.

3-(1-Propenyl)-2-cyclohexenone (4). Preparation by a modification of the method of Crison and Normant[18] gave a **4t–4c** mixture from which **4t** was isolated by chromatography on alumina. The cis isomer was isolated in 99% purity by irradiation of an ether solution of **4t** at 254 nm and subsequent preparative TLC. IR and NMR absorption of these materials were identical to those reported previously.[9]

Stock solutions rich in **4t** were prepared for photostationary state determinations in degassed ether under nitrogen. Aliquots were withdrawn under nitrogen and sealed in tubes (Vycor for 254-nm radiation, Pyrex for 313-nm radiation). Irradiation at 254 nm was carried out in a Rayonet photochemical reactor equipped with RPR2537 lamps. Irradiation at 313 nm was carried out in a "merry-go-round" apparatus equipped with a Hanovia 450W type 267A mercury arc and a 1-cm filter containing a solution of 1.2 g of potassium chromate in 0.5% (w/v) aqueous potassium carbonate. The isomer ratio was monitored as irradiation proceeded by VPC. At 254 nm (dienone concentration 0.0391 M) the photostationary mixture was 44.7 ± 0.2% cis while at 313 nm (dienone concentration 0.0408 M) it was 53.4 ± 1.2% cis.

Molar absorptivities were determined using Cary 14 and Beckman DU (equipped with a Gilford detector) instruments: **4t**, ϵ_{254} = 18 000 ± 600 and ϵ_{313} = 134.5 ± 3.4; **4c**, ϵ_{254} = 9810 ± 30 and ϵ_{313} = 97 ± 13.

Quantum Yield Measurements. Quantum yields were determined using the method and apparatus described previously.[4] Isolation of the 334-nm region was accomplished using the filters described by Calvert and Pitts.[21] Samples were prepared by dissolving freshly distilled dienone in anhydrous ether and adding dodecane as an internal GLC standard. They were degassed by a minimum of three freeze–pump–thaw cycles, sealed with a flame, wrapped in aluminum foil, and stored in a freezer until use. VPC analysis used a 10 ft. × 1/8 in. 11% FFAP on 100/120 mesh Anakrom ABS at 185 °C. Actinometer values were taken as the average of three determinations before and three after each run.

Acknowledgment. We wish to thank the National Science Foundation for a grant in partial support of this work and the referees for helpful comments.

Registry No.—**1EE,** 29178-97-0; **1ZE,** 29178-98-1; **3EE,** 68492-45-5; **3EZ,** 68492-46-6; **3ZE,** 68492-47-7; **4t,** 29179-03-1; **4c,** 68492-48-8.

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(2) Cf. V. Ramamurthy and R. S. H. Liu, *J. Am. Chem. Soc.*, **96,** 5625 (1974).

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(7) We previously reported that irradiation of 1-aryldienones gave photostationary mixtures which contained the *E,E* and *Z,E* isomers only. A reinvestigation of sorbophenone by R.A.G. revealed the *E,Z* isomer as a shoulder on the VPC peak for the *E,E* isomer. Examination of an 80% *E,Z*–20% *E,E* mixture showed that the *E,Z* isomer had IR absorption similar to that of *E,E* and a mass spectrum identical to that exhibited by the other two isomers. Thus, sorbophenone does not exhibit regiospecific photoisomerization.

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(17) Salient points are: **3EE**, H_β which appears at τ 2.95 as a doublet $J_{\beta\gamma} = 9$ Hz, shifted far downfield by the resonance and long-range anisotropic effects of the carbonyl group and intense UV absorption $\epsilon_{max} = 24\,300$; **3ZE**, H_γ appears farthest downfield (characteristic of α,β-cis dienones) at τ 3.25 split into a broad multiplet ($J_{\beta\gamma}$ and $J_{\gamma\delta} > 10$ Hz, virtual coupling with methyl) and UV absorption is less intense, $\epsilon_{max} = 15\,800$, than for **3EE**. The third component, **3EZ**, has spectral properties which are very similar to those of **3EE**.

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Regioselective Substitution in Hindered Aromatics. 4-Nitrophthalic Acid from Nitration and Nitric Acid Oxidation of Indene, 1,2-Dihydronaphthalene, and Their Polymers

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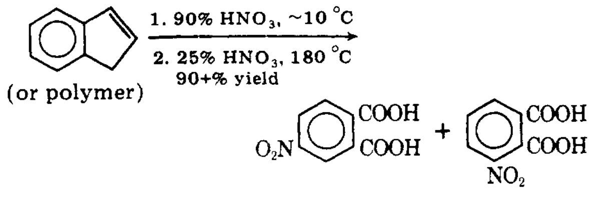
Renewed interest in the chemistry of 4-aminophthalic anhydride[1-4] prompts us to report on an efficient synthesis of 4-nitrophthalic acid, one of its precursors, from indene, 1,2-dihydronaphthalene, and polyindene.

Results and Discussion

Nitrophthalic acids are conventionally prepared by nitration of phthalic anhydride (or acid).[5,6] An approximately 50:50 mixture of 4-nitro and 3-nitro isomers (I and II, respectively) is then separated by fractional crystallization. This procedure is not applicable to large-scale production of a single isomer as availability of one isomer would always depend on an outlet for the other. Selective synthesis of 3-nitrophthalic acid can be accomplished via nitration of naphthalene, followed by subsequent oxidation of 1-nitronaphthalene.[7] To our knowledge, however, there is no procedure available to selectively prepare the more useful 4-nitrophthalic acid (or anhydride) from inexpensive raw materials. Earlier we reported that selective para substitution on an aromatic nucleus can be attained if polymeric or oligomeric substrates are used.[8] Nitration of styrene or polystyrene, followed by oxidation of their nitro intermediates, gave good yields of nitrobenzoic acids, with 90% selectivity to the para isomer. Extending this work, we now report on the selective synthesis of 4-nitrophthalic acid from indene, polyindene, and 1,2-dihydronaphthalene (eq 1).



(1)

I

II (I/II = 97/3)

Table I. Preparation of Nitrophthalic Acids

	expt no. 1	2	3
substrate, RH	indene[i]	polyindene[h,j]	1,2-dihydronaphthalene[h,k,o]
nitration[a]			
HNO_3 concn (wt %)	90	90	90
HNO_3,[b] g (mol)	162.5 (2.58)	162.5 (2.58)	162.5 (2.58)
RH, g (mol)[c]	30 (0.26)	30 (0.26)	30 (0.225)
time, h[d]	4.5	3.5	3.5
temp, °C (±2 °C)	−6	10	10
HNO_3 consumed, mol	0.39	0.40	N.D.
HNO_3 consumed, mol/mol of RH	1.51	1.55	N.D.
product, g (%)[e]	44.8 (94.1)	48.0 (100)	N.D.
oxidation			
nitro-RH, g (mol)[e]	30 (0.154)	48 (0.26)	N.D.
HNO_3 concn (wt %)	25	25	25
HNO_3,[b] g (mol)	94.8 (1.5)	137.3 (2.2)	N.D.
HNO_3, mol/mol of nitro-RH	9.7	8.4	N.D.
time, h	1	1	1
temp, °C (±1 °C)	180	175	175
pressure, psig	250	260	265
HNO_3 consumed, mol	0.82	1.17	N.D.
HNO_3 consumed, mol/mol of nitro-RH	5.32	4.53	N.D.
product, g (%)[e,f]	53.1 (101)	50.4 (92.5)	41.7 (86.0)
anal, %[g] (4/3/P/O)	93.0[l]/2.8[m]/0.7[n]/3.5	80.2/1.6/0.5/17.7	68.4/6.0/3.5/22.1
ratio 4-nitro/3-nitrophthalic acids	97.1/2.9	98.0/2.0	91.9/8.1

[a] Atmospheric pressure. [b] As 100% HNO_3. [c] Assume 100%. [d] Include 30 min post-addition stirring period. [e] Calculated, assume HNO_3 forms mono- and dinitro-RH. [f] Weight percent calculated vs. maximum moles of 4-nitrophthalic acid possible using assumed molecular weight of nitro-RH. [g] Mole percent 4-nitrophthalic acid/3-nitrophthalic acid/phthalic acid/others (unknowns, GLC). [h] Single experiments only; not optimized. [i] Registry no. 95-13-6. [j] Registry no. 9003-64-9. [k] Registry no. 447-53-0. [l] Registry no. 610-27-5. [m] Registry no. 603-11-2. [n] Registry no. 88-99-3. [o] N.D. is not determined.

Nitration can be carried out with nitric acid alone or in combination with sulfuric acid. Best results were obtained with 90% nitric acid since polyolefin and the nitrated intermediate were completely soluble in this medium. Use of mixed acid (HNO_3–H_2SO_4) resulted in product precipitation, incomplete nitration, and lower yields of nitrophthalic acids. Use of additional solvent such as acetic acid or chlorinated hydrocarbons could also facilitate the reaction.[9] As nitric acid is used as well for the ensuing oxidation, it was most convenient to use nitric acid alone in the first step. Following nitration with fuming nitric acid, sufficient water was added to dilute the acid down to the level needed for oxidation. The nitration with 90% nitric acid has been studied in the temperature range of −10 to 30 °C, with comparable results. Temperatures of around 170–185 °C, nitric acid concentrations of around 25%, and holding times of 1 h typify our best oxidation conditions.

Experiment 1 (Table I) represents a typical result with indene. Indene, an abundant coproduct of ethylene manufacture via steam cracking of naphtha, is the feedstock of choice for