and 11.61. After warming to room temperature, ^1H NMR indicated a 2.3:1.0:1.5 equilibrium mixture of **5**/**6**/**7**.

We now know that both monosubstituted alkenes and 1,2-disubstituted alkenes react with **1** via a concerted C–H addition pathway. Only when this pathway is blocked by steric hinderance (1-methylcyclohexene and *trans*-stilbene)[8] or when a carbocation can be greatly stabilized (1,1-diphenylethylene)[9] have we seen reactions of **1** with alkenes that involve carbocation intermediates.

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Supplementary Material Available: Spectral and analytical characterizations of compounds **3**-*d* and **5**-*d* to **11**-*d* (2 pages). Ordering information is given on any current masthead page.

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(8) *trans*-Stilbene reacts with **1** to give a μ-alkenyl compound via exclusive phenyl migration.[3]

(9) 1,1-Diphenylethylene reacts with **1**-*d* to give a μ-alkenyl product with the deuterium exclusively at the vinyl position ($^2H\{^1H\}$ NMR, δ 12.39). Casey, C. P.; Colborn, R. E.; Meszaros, M. W., unpublished results.

Double-Bond Isomerization Barrier in the 2^1A_g Excited Singlet State of *cis,trans*-1,3,5,7-Octatetraene[†]

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The unsubstituted linear polyene 1,3,5,7-octatetraene readily photoisomerizes, even in a crystalline matrix maintained at 4.2 K.[1-3] This photochemical activity opens new opportunities to determine the properties of the potential energy surfaces that control the fate of electronic excitation in the linear polyenes. Activation energies for isomerization on ground- and excited-state potential energy surfaces are of particular interest.

In the dark, a hexane solution of *cis,trans*-octatetraene is stable at room temperature. However, when excited to its lowest energy singlet state, *cis,trans*-octatetraene in *n*-hexane reverts to the trans,trans isomer at a rate of approximately 10^7 s^{-1} at 55 K. This establishes that the isomerization of *cis,trans*-octatetraene to trans,trans-octatetraene can take place on the 2^1A_g excited-state potential energy surface over a barrier of order 1.1 kcal mol^{-1}.

A solution containing roughly equal amounts of *cis,trans*-octatetraene and *trans,trans*-octatetraene in *n*-hexane was prepared from a solution of the *trans,trans* isomer by photolysis and HPLC purification as has been described previously.[1] A 2-μL quartz capillary cell filled with this solution was mounted in a closed-cycle helium refrigerator that has been modified so as to maintain an atmosphere of cold helium gas over the sample and the final cold stage. Fluorescence in the region of the origin of the 2^1Ag to 1^1A_g (S_1 to S_0) transition was excited at 313 nm by a 100-W Hg lamp dispersed through a JY-DH20 double monochromator equipped with 1-mm slits giving a bandwidth of approximately 2 nm. After recording the fluorescence at 8 K, the sample was shielded from the exciting light, heated to an elevated temperature, and then exposed to the photolyzing light source (same as the fluorescence source except that the light flux was quadrupled by doubling the slit width) for 10 min. The intensity of the photolysis source was such that in 10 min the number of photons absorbed was comparable to the number of octatetraene molecules in the sample. After photolysis the sample was recooled to 8 K and the fluorescence was rescanned. Below 10 K the fluorescence spectra of these molecules are well resolved and distinct providing an unambiguous assay for the relative amounts of the cis,trans and trans,trans isomers.[1]

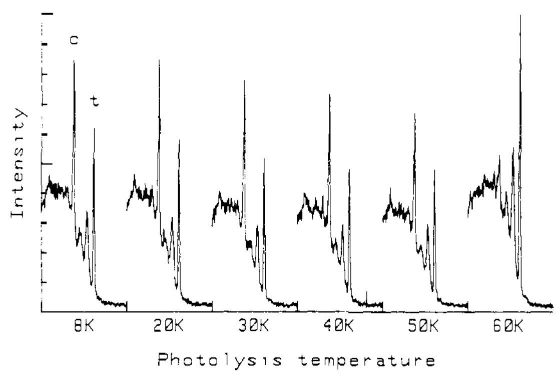

Figure 1. Repeated scans of the fluorescence at 8 K from a hexane solution containing *cis,trans*- and *trans,trans*-octatetraene. In the first scan the fluorescence origin for the cis,trans isomer at 28 646 cm^{-1} is labeled c and that of the trans,trans isomer at 28 737 cm^{-1} is labeled t. Prior to taking each scan the sample temperature was raised to the value that labels that scan and irradiated at 313 nm until roughly one photon had been absorbed for each octatetraene molecule.

The initial fluorescence spectrum and the spectra at 8 K following photolyses at 20, 30, 40, 50, and 60 K are shown in Figure 1. The fluorescence origins for the cis,trans (28646 cm^{-1}) and trans,trans (28737 cm^{-1}) isomers are labeled in the intial scan. The decrease in intensity of both of these features in subsquent spectra is due in part to a slow drift in excitation lamp intensity. For the photolyses at temperatures up to 50 K, the relative intensities of the fluorescence origins of the cis,trans and trans,trans isomers remains nearly constant. After photolysis at 60 K, the cis,trans origin vanishes while the intensity of the fluorescence origin of the trans,trans isomer increases significantly. Clearly, the rate of cis to trans photoisomerization has increased dramatically with increasing temperature. Similar behavior has been observed for octatetraene in *n*-octane.

This dramatic increase in the efficiency of cis to trans photoisomerization with increasing temperature must come from a thermally activated isomerization process on the excited state potential energy surface. We have shown that within 10 ps excitation to vibrationally excited levels of the 1^1Bu state (S_2) is relaxed to a thermal distribution in the vibrational levels of the 2^1A_g state (S_1).[4] Thus, this thermally assisted photoisomerization takes place on the 2^1A_g potential energy surface. The data in Figure 1 show that the rate for this isomerization channel begins to compete effectively with the decay of the excited state at temperatures between 50 and 60 K. At 10 K the lifetime of the 2^1A_g state of *cis,trans*-octatetraene in *n*-hexane is 70 ns and does not strongly depend on temperature between 10 and 30 K.[5] Thus, to good approximation we may set the isomerization rate equal to (70 ns)$^{-1}$ at 55 K. Assuming an Arrhenius preexpontential factor of 10^{10}–10^{13}, the activation energy for this excited state isomerization channel is 1.1 ± 0.4 kcal mol^{-1}. This is approximately a factor of 50 smaller than estimates of the isomerization barrier on the ground-state potential energy surface.[6-8]

From the observed spectra it is clear that, with respect to torsional coordinates, minima on the excited-state potential energy surface are not displaced from the ground-state equilibrium

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(1) Granville, M. F.; Holtom, G. R.; Kohler, B. E. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 31–33.

(2) Hossain, M; Kohler, B. E.; West, P. *J. Phys. Chem.* **1982**, *86*, 4918–4920.

(3) Ackerman, J. R.; Forman, S. A.; Hossain, M.; Kohler, B. E. *J. Chem. Phys.* **1984**, *80*, 39–44.

(4) Ackerman, J. R.; Kohler, B. E.; Huppert, D.; Rentzepis, P. M. *J. Chem. Phys.* **1982**, *77*, 3967–3973.

(5) Ackerman, J. R. Ph.D. Thesis, Wesleyan University, middletown, CT, 1984.

(6) Frey, H. M.; Lamont, A. M.; Walsh, R. *J. Chem. Soc. A* **1971**, 2642–2646.

(7) Orchard, S. W.; Thrush, B. *Proc. R. Soc. London, Ser. A* **1974**, *337*, 257–274.

(8) Lasaga, A. C.; Aerni, R. J.; Karplus, M. *J. Chem. Phys.* **1980**, *73*, 5230–5243.

0002-7863/84/1506-3681$01.50/0

values.[9,10] While the spectra unambiguously indicated the presence of a barrier on the excited-state surface, they give no information about the height of that barrier.

The tremendous decrease in isomerization barrier height upon excitation is consistent with almost complete reversal of bond alternation in the lowest energy excited singlet state. Calculations of bond orders for the polyene 2^1A_g state[11,12] predict significant weakening of the ground-state double bonds in the 2^1A_g state. Bond order changes in going from the ground state to the 1^1B_u state are predicted to be much smaller as is born out by the observed spectra.[13,14]

These data unequivocably identify a thermally activated isomerization channel on the excited state surface that proceeds over a 1 kcal mol^{-1} barrier. They do not, of course, specify the trajectory for this isomerization. While it reasonable to associate this barrier with simple twisting about the isomerizing bond, a detailed microscopic interpretation will require more extensive experimental and theoretical work.

Registry No. *cis,trans*-1,3,5,7-Octatetraene, 1871-51-8; *trans,trans*-1,3,5,7-octatetraene, 3725-31-3.

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(9) Granville, M. F.; Holtom, G. R.; Kohler, B. E. *J. Chem. Phys.* **1980**, *72*, 4671-4675.

(10) Spiglanin, T. A.; Kohler, B. E. *J. Chem. Phys.* **1984**, *80*, 3091-3096.

(11) Schulten, K.; Ohmine, I.; Karplus, M. *J. Chem. Phys.* **1976**, *64*, 4422-4441.

(12) Ducasse, I. R.; Miller, T. E.; Soos, Z. G. *J. Chem. Phys.* **1982**, *76*, 4094-4104.

(13) Granville, M. F.; Kohler, B. E.; Snow, J. B. *J. Chem. Phys.* **1981**, *75*, 3765-3769.

(14) Kohler, B. E.; Spiglanin, T. A.; Hemley, R. J.; Karplus, M. *J. Chem. Phys.* **1984**, *80*, 23-30.

A New Method for the Synthesis of Organic Nitro Compounds

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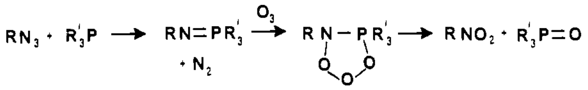
In connection with recent studies in this laboratory on the synthesis of tunicamycin, the nitro galactose derivative **1** was required as a key intermediate.[1,2] Numerous attempts at its synthesis by known methods[1] ended in complete failure. In particular, synthesis from the corresponding 6-iodogalactose derivative **2** using the Kornblum silver nitrite displacement method,[1c] which seemed most appropriate in this case, led to no detectable amount of **1** under a variety of conditions.[3] Motivated by these results, we have devised a new route from halides and sulfonates to nitro compounds.

The hypothesis leading to the method described herein is depicted by the overall equation:



The azides required for this process are generally readily available by S_N2 displacement and their conversion to phosphine imines occurs smoothly under mild conditions (Staudinger reaction[4]). Cycloaddition of ozone to the phosphine imine would provide an unstable adduct, which we speculated could decompose to phosphine oxide and the desired nitro compound, although the mechanism by which such decomposition would occur may not be simple.

The azide **3**, readily prepared by reaction of the corresponding iodide (**2**) with excess lithium azide in dimethylformamide (4 mL/g of LiN_3, 75 °C, 16 h), upon stirring with 1.1 equiv of triphenylphosphine in methylene chloride (CH_2Cl_2) at 35 °C for 16 h under nitrogen was converted to the phosphine imine **4** cleanly. Slow addition of this solution of **4** in CH_2Cl_2 to a saturated solution of ozone (3.3-4 equiv) in CH_2Cl_2 at -78 °C, nitrogen purging to remove excess ozone, and chromatography on silica gel afforded the desired nitro compound **1** as a colorless oil in 61% yield. Reaction of **3** with tri-*n*-butylphosphine (CH_2Cl_2, 23 °C, 4 h) produced the phosphine imine, which was ozonized in the same manner to form nitro sugar **1** in ca. 50% yield. 2,2,2-Trichloroethyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranoside (**5**) was similarly converted to a phosphine imine (tri-*n*-butylphosphine, 6 h at 23 °C and 0.5 h at 40 °C in CH_2Cl_2),[5] which was ozonized to form 2,2,2-trichloroethyl 3,4,6-tri-*O*-acetyl-2-nitro-2-deoxy-α-D-galactopyranoside (**6**) in 54% overall yield. In another example the azide **7** was transformed into nitro sugar **8** in 57% yield.

For each of the above cases the ozonolytic conversion of phosphine imine to nitro compound required at least *3 equiv* of ozone and proceeded in better yield if the solution of phosphine imine was added to the cold solution of ozone rather than inversely.

The conversion of a number of other primary and secondary azides to the corresponding nitro compounds was studied to ascertain the scope of the phosphine imine → nitro transformation. The following nitro compounds were obtained in the overall percent yields indicated from the corresponding azides via the tri-*n*-butylphosphine imines (from secondary azides) or triphenylphosphine imines (from primary azides): 3-phenylpropyl (60%), *n*-octyl (70%), 2-octyl (71%), *trans*-4-*tert*-butylcyclohexyl (50%), cyclooctyl (41%).

Benzyl azide proved to be an exceptional case since it afforded under standard conditions no α-nitrotoluene but instead benzaldehyde as major product (53%).[6]

The following procedure for the preparation of 1-nitrooctane is illustrative:

To a stirred solution of 1-azidooctane (200 mg, 1.29 mmol) in dry CH_2Cl_2 (0.5 mL) under nitrogen in a flame-dried flask was added a solution of triphenylphosphine (372 mg, 1.42 mmol) in 0.5 mL CH_2Cl_2 with stirring. Evolution of nitrogen was visible within 5 min after the addition of phosphine. Stirring was continued at room temperature for 5.0 h. The reaction mixture was then diluted with dry CH_2Cl_2 (4.0 mL) and added dropwise by cannula into 106 mL of a saturated solution of ozone (4.23 mmol) in CH_2Cl_2. After the addition of the phosphine imine was complete, the reaction mixture was stirred at -78 °C for 10 min and purged of ozone at -78 °C with argon or nitrogen until the blue color was completely discharged. Concentration of the reaction mixture under reduced pressure at room temperature and flash chromatography (30:70, petroleum ether:diethyl ether) of the residual oil yielded 143 mg (70%) of 1-nitrooctane,[7] bp 66-68 °C (2 mm). 1-Octanal was eluted as a minor component (22 mg, 13%).

The synthesis of nitro compounds from azides via the ozonolysis of phosphine imines is obviously limited to those substrates that are tolerant of ozone at -78 °C. Apart from this restriction, the process seems to be both predictable and reliable. It is obviously

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(1) For reviews, see: (a) Schickh, O. v.; Apel, G.; Padeken, H. G.; Schwarz, H. H.; Segnitz, A.; Houben-Weyl-Müller. "Methoden der Organischen Chemie;" Georg Thieme Verlag: Stuttgart, **1971**; Vol. X/1. (b) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734. (c) Kornblum, N. *Org. React.* **1962**, *12*, 101. (d) Gilbert, K. E.; Borden, W. T. *J. Org. Chem.* **1979**, *44*, 659.

(2) Ito, T.; Takatsuki, A.; Kawamura, K.; Sato, K.; Tamura, G. *Agric. Biol. Chem.* **1980**, *44*, 695.

(3) Various 6-nitro-D-glucopyranoside derivatives have been prepared successfully by silver nitrite displacement in this laboratory and previously. See: (a) Sugihara, J. M.; Teerlink, W. T.; MacLeod, R.; Dorrence, S. M.; Springer, C. H. *J. Org. Chem.* **1963**, *28*, 2079. (b) Richardson, A. C. *MTP Int. Rev. Sci.: Org. Chem., Ser. One* **1973**, *7*, 105. The failure of the silver nitrite displacement process to generate the 6-nitrogalactopyranoside **1** (nitrite ester is the main byproduct) seems to correlate with the slowness of backside displacement in the galacto series relative to the gluco series.

(4) Gololobov, Yu. G.; Zhmurova, I. N.; Kasukhin, L. F. *Tetrahedron* **1981**, *37*, 437.

(5) In general phosphine imine formation from an azide occurs at a faster rate with tri-*n*-butylphosphine than with the less nucleophilic triphenylphosphine.

(6) The formation of aldehyde or ketone as byproduct (0-13%) was observed in the ozonolysis of phosphine imines derived from 1° or 2° azides, respectively.

(7) Kornblum, N.; Powers, J. W. *J. Org. Chem.* **1957**, *22*, 455.

0002-7863/84/1506-3682$01.50/0