(5 mL) was allowed to stand at room temperature for 10 min, and the solution was then concentrated to a final volume of 1 mL. Acetone (30 mL) was added, and the precipitate was removed by suction filtration. The filtrate was taken to dryness, and the product was obtained as a powder from EtOH–C_6H_6: mp 109–111 °C; yield 63 mg (58%).

Anal. Calcd for $C_{14}H_{22}N_6O_6 \cdot H_2O$: C, 45.82; H, 5.60; N, 23.01. Found: C, 45.40; H, 5.99; N, 22.70.

N^6-[(Dimethylamino)carbamoyl]adenosine (26). A solution of **22** (317 mg, 0.5 mmol) in a mixture of MeOH (20 mL) and 0.25 N $NaHCO_3$ (20 mL) was allowed to stand at room temperature for 1 h. The solution was concentrated to a final volume of 5 mL, acetone (50 mL) was added, and the precipitate was then removed by suction filtration. The filtrate was taken to dryness, and the residue was then washed with water that contained a relatively small amount of acetone: yield 89 mg (50%); mp 143 °C (H_2O).

Anal. Calcd for $C_{13}H_{19}N_7O_5 \cdot H_2O$: C, 42.04; H, 5.70; N, 26.40. Found: C, 42.23; H, 5.58; N, 26.51.

N^6-[[1-(Ethoxycarbonyl)ethyl]carbamoyl]adenosine (27). A solution of **23** (410 mg, 0.76 mmol) in a mixture of MeOH (20 mL) and 0.25 N $NaHCO_3$ (20 mL) was allowed to stand at room temperature for 1 h. The solution was concentrated to a final volume of 3 mL, acetone was added, and the precipitate was then removed by suction filtration. The filtrate was taken to dryness, and the residual material was then precipitated from EtOH–EtOAc. A satisfactory elemental analysis could not be obtained: ^{13}C NMR (25 MHz) δ 16.15 (α-CH_3), 19.67 (CH_3CH_2O), 64.20 (CH_3CH_2), 65.41 (C-5′), 73.24, 76.57, and 88.39 (C-2′, C-3′, and C-4′, specific resonances were not assigned), 82.31 (α-C), 91.14 (C-1′), 144.99 (C-8), 152.07 (C-4), 153.48 (C-2), 157.42 [NC(O)N]; the remaining carbons were not observed due to their long T_1 relative to the pulse-repetition rate.

Acknowledgment. This investigation was supported in part by Research Grant GM24664 to J.B.H. and G.Z. from the National Institutes of Health. We thank Dr. Jun Uzawa (Institute of Physical and Chemical Research, Japan) for help in analyzing the LSPD ^{13}C NMR spectra, and we also thank Dr. James Wheeler (Howard University) for assistance with mass spectral analyses and Dr. Kurt L. Loening (Chemical Abstracts Service) for assistance with nomenclature. ^{13}C NMR spectra at 25 and 75 MHz were recorded with instrumentation at the Bureau of Biologics. We are especially grateful to a reviewer who suggested the possibility of our having obtained the $O^{5'}$,8-cycloadenosine compounds reported herein.

Registry No. 1, 15888-38-7; 2, 362-75-4; 3, 82838-77-5; 4, 82838-78-6; 5, 82838-79-7; 6, 82838-80-0; 7, 82838-81-1; 8, 82838-82-2; 9, 7387-57-7; 10, 66386-42-3; 11, 82838-83-3; 12, 82838-84-4; 13, 82848-98-4; 14, 82848-99-5; 15, 82838-85-5; 16, 82838-86-6; 17, 82838-87-7; 18, 15180-53-7; 19, 82838-88-8; 20, 82838-89-9; 21, 82838-90-2; 22, 82838-91-3; 23, 82838-92-4; 24, 82838-93-5; 24 AcOH, 82838-94-6; 25, 66781-63-3; 26, 82849-00-1; 27, 82838-95-7; EtOC(O)Cl, 541-41-3; PhOCC(O)Cl, 1885-14-9; 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy, 14691-88-4; 4-amino-2,2,6,6-tetramethylpiperidine, 36768-62-4; propyl amine, 107-10-8; 1,1-dimethylhydrazine, 57-14-7; L-alanine ethyl ester hydrochloride, 1115-59-9.

Photochemistry of (*o*-Methylphenyl)alkenes and the Stereospecific Trapping of the Resulting *o*-Xylylenes[1a]

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Received April 20, 1982

The photochemical behavior of a series of *o*-methylstyrenes with simple alkyl groups in the α or β positions was investigated in order to determine the synthetic potential of the resulting *o*-xylylenes. The major photochemical product of all the styrenes employed (**1**, **9**, **10**, and **11**) was the corresponding *o*-xylylene. The *o*-xylylenes were trapped in acceptable yields by maleic anhydride to give the Diels–Alder adducts. In the case of **9** or **10** and **11** the *o*-xylylenes were produced stereoselectively and trapped stereospecifically to give **15** or **16**, respectively. In the absence of a dienophile or in the presence of a weak dienophile, such as cyclohexene, a slower isomerization of the *o*-methylstyrenes to the meta isomers was observed, presumably via a benzvalene intermediate. In addition, the *o*-xylylene produced from **9** or **10** and **11** underwent geometrical isomerization in the absence of maleic anhydride, resulting in the formation of **10** and **11** upon irradiation of **9** and vice versa.

There has been considerable recent interest in the application of *o*-xylylenes (*o*-quinodimethanes) in organic synthesis.[2] These reactive intermediates are excellent dienes for Diels–Alder cycloadditions and allow the construction of six-membered rings fused to benzene rings. The transient *o*-xylylenes have been generated by a number of methods, including the thermolysis of benzocyclobutenes,[2] Vollhardt's method based on the cobalt-catalyzed preparation of the benzocyclobutenes,[2b,3] various 1,4-eliminations,[2b,d–f,h,4] and the photoenolization of *o*-alkylphenyl ketones.[5] Our interest in this area is the synthetic use of *o*-xylylenes generated photochemically from *o*-alkylstyrene derivatives.[6] We have recently demonstrated that several phenyl-substituted *o*-xylylenes generated by this method can be trapped as Diels–Alder adducts in good yields.[7] Our ultimate goal is to use this method to generate *o*-xylylenes from *o*-alkylstyrenes substituted in the α position

(1) (a) Presented in part at the American Chemical Society and Chemical Society of Japan Chemical Congress, Honolulu, Hawaii, April, 1979. (b) Boettcher Foundation Fellow, 1979–1980.

(2) For reviews and a few leading references, see: (a) Oppolzer, W. *Synthesis* **1978**, 793–802. (b) Funk, R. L.; Vollhardt, K. P. C. *Chem. Soc. Rev.* **1980**, *9*, 41–61. (c) Kametani, T.; Nemoto, H. *Tetrahedron* **1981**, *37*, 3–16. (d) Kerdesky, F. A. J.; Ardecky, R. J.; Lakshmikantham, M. V.; Cava, M. P. *J. Am. Chem. Soc.* **1981**, *103*, 1992–1996. (e) Djuric, S.; Sarkar, T.; Magnus, P. *Ibid.* **1980**, *102*, 6885–6886. (f) Wiseman, J. R.; Pendery, J. J.; Otto, C. A.; Chiong, K. G. *J. Org. Chem.* **1980**, *45*, 516–519. (g) Grieco, P. A.; Takigawa, T.; Schillinger, W. J. *Ibid.* **1980**, *45*, 2247–2251. (h) Nicolaou, K. C.; Barnette, W. E.; Ma, P. *Ibid.* **1980**, *45*, 1463–1470.

(3) Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1980**, *102*, 5245–5253; **1980**, *102*, 5253–5261.

(4) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1981**, *103*, 476–477.

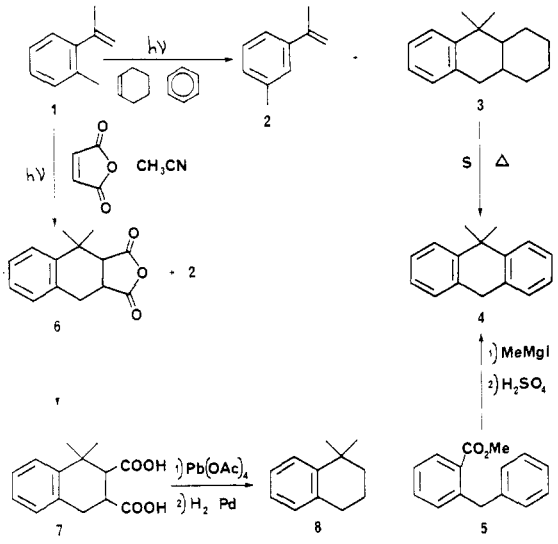
(5) Sammes, P. G. *Tetrahedron* **1976**, *32*, 405–422.

(6) (a) Scully, F.; Morrison, H. *J. Chem. Soc., Chem. Commun.* **1973**, 529–530. (b) Pratt, A. C. *Ibid.* **1974**, 183–184.

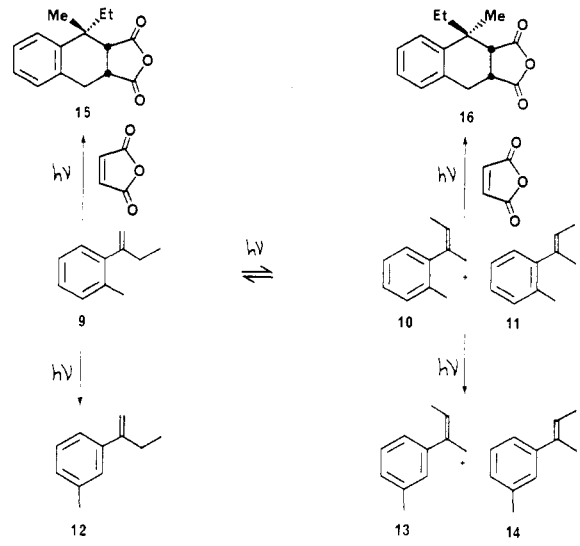
(7) Hornback, J. M.; Mawhorter, L. G.; Carlson, S. E.; Bedont, R. A. *J. Org. Chem.* **1979**, *44*, 3698–3703.

0022-3263/82/1947-4285$01.25/0

Scheme I



Scheme II



with groups containing dienophiles so that an intramolecular Diels–Alder reaction can occur. In light of this goal, we initiated a study of the photochemistry of some *o*-methylstyrenes with simple alkyl groups in the α position as models for the more complicated systems. We report here the results of this study, which show the presence of several competing pathways.

Results and Discussion

Irradiation of 2-(2-methylphenyl)propene (**1**)[8] in a solution of 20% cyclohexene in benzene gave two major photoproducts, **2** and **3**,[9] along with cyclohexene photodimers and small amounts of several unidentified photoproducts (Scheme I). The yields varied and decreased with increasing conversion of **1**, but a typical yield was 55% of **2** and 45% of **3** at 30% conversion of **1**. Styrene derivative **2** was identified by comparison with an authentic sample prepared by a modification of the procedure of Tiffenau.[10] Octahydroanthracene **3** was identified on the basis of its spectral properties and its conversion by dehydrogenation with sulfur to dihydroanthracene **4**. The sample of **4** thus obtained was identical with a sample obtained by reaction of ester **5** with 2 equiv of methylmagnesium iodide followed by acid-catalyzed cyclization of the resulting alcohol.

When **1** was irradiated in benzene in the absence of cyclohexene, **2** was the only product. Experiments employing varying concentrations of cyclohexene showed that the amount of **3** produced increased until the cyclohexene concentration reached about 20% and then began to decrease. The amount of **2** produced in these experiments decreased continuously as the cyclohexene concentration was increased. Neither **2** nor **3** were produced when **1** was irradiated through Pyrex with xanthone as a photosensitizer.

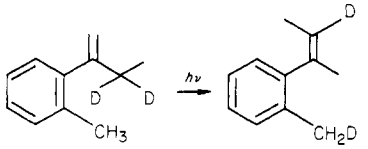
Irradiation of **1** in acetonitrile containing ca. 0.02 M maleic anhydride, a more reactive dienophile, resulted in a more rapid disappearance of **1**. In this case the major product was anhydride **6** (59%) along with a substantially decreased amount of **2** (9%) at 57% conversion of **1** (Scheme I). The structure of **6**[9] was assigned on the basis of its mass spectrum, which showed it to be a 1:1 adduct of maleic anhydride and **1**, and its spectral properties. The structural assignment was confirmed by hydrolysis of **6** to diacid **7** followed by decarboxylation and reduction to give **8**, which was identical with an independently synthesized sample.[11] In this case also the amount of **2** produced in the reaction decreased as the initial concentration of the maleic anhydride was increased. The yield of **6** increased as the initial concentration of maleic anhydride was increased up to ca. 0.02 M and then decreased as a new product began to appear.

The photochemical behavior of 2-(2-methylphenyl)-1-butene (**9**) was also investigated. Styrene derivative **9** was prepared from 1-(2-methylphenyl)-1-propanone[12] by a Wittig reaction. Irradiation of **9** in benzene gave **10** (9%), **11** (8%), and **12** (21%) at 48% conversion of **9** (Scheme II). Sensitized irradiation (xanthone) of **9** gave **10** (18%) and **11** (5%) at 87% conversion of **9** with no **12** detectable. Compound **12** was identified by comparison with a sample prepared independently from 1-(3-methylphenyl)-1-propanone[13] by a Wittig reaction. Isomers **10** and **11** were also identified by comparison with samples prepared independently by the reaction of 1-(2-methylphenyl)-1-ethanone with ethylenetriphenylphosphorane in Me_2SO. This reaction gave a 1.7:1 mixture of **10** and **11**, which were separated by preparative GC. The stereochemistries of **10** and **11** were assigned on the basis of their NMR and UV spectra. The *o*-methyl groups of **10** and **11** cause the planes of the benzene ring and the butene to be rotated with respect to each other. In such systems the proton cis to the phenyl ring should be shielded with respect to the proton trans to the phenyl ring.[14] The NMR signal for the vinyl proton of **11** is at δ 5.34, while that of **10** is at δ 5.44. In addition, the planes should be twisted more in the case of *Z*-isomer **10** than *E*-isomer **11**. This should cause the UV absorption maximum of **10** (235 nm) to be shifted to shorter wavelengths than that of **11** (243 nm) as seen in the case of (*Z*)-2-phenyl-2-butene (235 nm) and the corresponding *E* isomer (243 nm).[15]

(8) Sadler, I. H. *J. Chem. Soc. B.* **1969**, 1024–1031.
(9) Based on mechanistic considerations (vide infra) **3**, **6**, **15**, and **16** are presumed to have cis-ring junctions.
(10) Tiffenau, M. *Ann. Chim.* **1907**, *10*, 145–198.
(11) Khalaf, A. A.; Roberts, R. M. *J. Org. Chem.* **1966**, *31*, 89–95. Bogert, M. T.; Davidson, D.; Apfelbaum, P. M. *J. Am. Chem. Soc.* **1934**, *56*, 959–963.
(12) Birch, S. F.; Dean, R. A.; Fidler, F. A.; Lowery, R. A. *J. Am. Chem. Soc.* **1949**, *71*, 1362–1369.
(13) Grammaticakis, P. *Bull. Soc. Chim. Fr.* **1940**, 527–540.
(14) Martin, G. J.; Martin, M. L. "Progress in Nuclear Magnetic Resonance Spectroscopy"; Emsley, J. W., Feeney, J.; Sutcliffe, L. H., Eds.; Pergamon: Oxford, 1972; Vol. 8, pp 175–176. Uijttewall, A. P.; Joukers, F. L.; van der Gen, A. *J. Org. Chem.* **1979**, *44*, 3157–3168.
(15) Cram, D. J. *J. Am. Chem. Soc.* **1949**, *71*, 3883–3889.

The formation of **10** and **11** upon irradiation of **9** suggested that the photochemistry of these two alkenes also be investigated. Irradiation of either **10** or **11** in benzene resulted in the rapid production of a mixture of the two isomers (ca. 1 *Z*:1.4 *E*). Continued irradiation of this mixture gave **9** (12%), **13** (38%), **14** (23%), and a trace of **12** at 36% conversion of the starting alkenes. Sensitized irradiation (xanthone) of either **10** or **11** also resulted in the rapid production of a mixture of the two isomers (ca. 1 *Z*:4 *E*) followed by a slower production of **9** (4% at 76% conversion of the starting alkenes). No **13** or **14** could be detected in the sensitized photolysis mixture. Isomers **13** and **14** were identified by comparison with authentic samples. The authentic samples were prepared by the reaction of 1-(3-methylphenyl)-1-ethanone with ethylenetriphenylphosphorane in Me_2SO, which gave a mixture of **13** and **14** (2:1, respectively), which was separated by preparative GC. The stereochemistries of **13** and **14** were assigned on the basis of their NMR and UV spectra. These compounds are more planar than **10** and **11**, and here it is expected that the proton cis to the phenyl ring in **14** (δ 5.80) should be deshielded with respect to the proton trans to the phenyl ring in **13** (δ 5.48).[14] In addition, for the same reason mentioned previously, the UV absorption maximum of **13** (235 nm) should occur at shorter wavelength than that of **14** (240 nm).[15]

In order to determine whether the sensitized irradiation of **9** was producing **10** via a 1,3 hydrogen migration or via two successive 1,5 hydrogen migrations, we prepared labeled derivative **17** from the correspondingly labeled ketone by a Wittig reaction (see Experimental Section). Irradiation of **17** in benzene with xanthone as photosensitizer gave **18**. The positions of the labels in **18** were assigned by NMR.

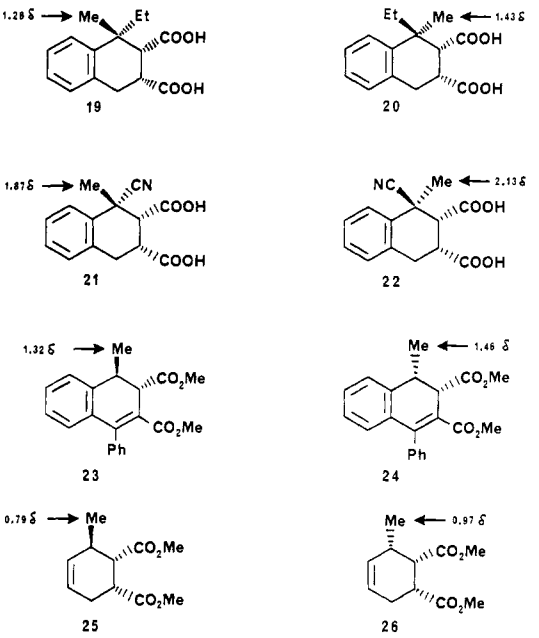


17 **18**

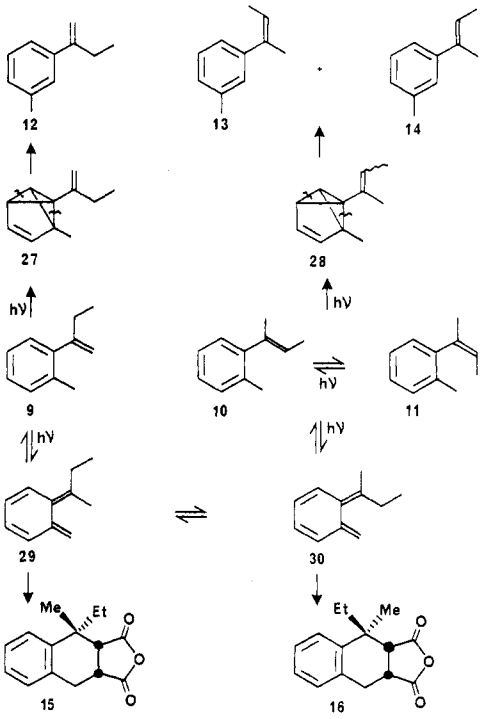
Irradiation of **9** in acetonitrile containing ca. 0.03 M maleic anhydride gave a single photoproduct (43% yield at 56% conversion of **9**). The mass spectrum of this photoproduct showed it to be a 1:1 adduct of **9** and maleic anhydride. The photoproduct was assigned structure **15**[9] by comparison of its IR and NMR spectra with those of **6**. Similar irradiation of either **10** or **11** or a mixture of the two gave a single adduct, **16**, along with a small amount of **9**. The structure of **16**[9] was assigned as described for **15**. In both of these irradiations none of the meta isomers, **12**, **13**, and **14**, was observed. Irradiation of **9** in the presence of higher concentrations of maleic anhydride resulted in the formation of an additional photoproduct, which was detected by NMR.[16]

The assignment of the stereochemistry for **15** and **16** proved to be difficult. These compounds are expected to exist in boat conformations.[17] However, there are two possible boat conformations, one with the anhydride ring exo and one with the anhydride ring endo. Since it was difficult to decide which of these two conformations would be preferred,[17] it was not possible to assign the stereochemistry on the basis of the difference in the chemical shifts of the methyl groups in the NMR spectra. To circumvent this difficulty, **15** and **16** were gently hydrolyzed to the corresponding diacids, **19** and **20** (Chart I). These are expected to prefer a half-chair conformation with the carboxyl group on C-3 equatorial in order to avoid a 1,3-pseudoaxial–axial interaction. This is expected to cause the NMR signal for the methyl group cis to the carboxyl group on C-2 in **20** to appear downfield from the methyl trans to the carboxyl group in **19**. This assignment is in accord with the literature assignments of stereochemistry for model compounds **21** and **22**,[18] **23** and **24**,[17] and **25** and **26**[19] (Chart I).

Chart I



Scheme III



(16) Although this new photoproduct could not be obtained pure, due to its instability and contamination with **15**, its NMR spectrum still showed a methyl group on the benzene ring, suggesting that it might be a [2 + 2] adduct of **9** and maleic anhydride.

(17) Pfau, M.; Combrisson, S.; Rowe, J. E., Jr.; Heindel, N. D. *Tetrahedron* **1978**, *34*, 3459–3468.

(18) Kametani, T.; Tsubuki, M.; Shiratori, Y.; Kato, Y.; Nemoto, H.; Ihara, M.; Fukumoto, K. *J. Org. Chem.* **1977**, *42*, 2672–2676.

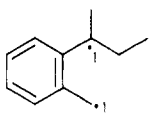
A mechanism for the photochemical behavior of **9**, **10**, and **11** is outlined in Scheme III. (A similar mechanism can be written for **1**.) The formation of **12** from **9** and **13** and **14** from **10** and **11** most likely proceeds via benzvalene intermediates **27** and **28**, respectively. Photoisomerization of benzene derivatives via benzvalenes is a known photochemical process.[20]

Irradiation of **9** also produces *o*-xylylene **29** by a 1,5 hydrogen migration. This *o*-xylylene must be produced stereoselectively since the reaction with maleic anhydride yields only **15**. Once the *o*-xylylene is produced, it has several reaction pathways available to it. If a dienophile is present, the *o*-xylylene can be trapped in a Diels–Alder reaction. The *o*-xylylene may also undergo a 1,5 hydrogen migration to regenerate the starting alkene (**29** → **9**). This is a known reaction of alkyl-substituted *o*-xylylenes and has been shown to occur both thermally and photochemically.[21] Finally, the *o*-xylylene may undergo a geometrical isomerization (**29** → **30**), which ultimately results in the formation of **10** and **11**.[22]

From the data presented above it is possible to draw some conclusions about the relative rates of these processes. First, the formation of the *o*-xylylenes from the excited styrenes must be substantially faster than the formation of the benzvalenes since it is possible to completely (or nearly completely) supress the latter process when a good dienophile is present to trap the *o*-xylylene. In the absence of a dienophile, or in the presence of a weak dienophile such as cyclohexene, the *o*-xylylene reverts to the starting alkene, allowing the less efficient benzvalene isomerization to occur. In addition, the Diels–Alder reaction of **29** or **30** with maleic anhydride is faster than the interconversion of **29** and **30** since the *o*-xylylenes are trapped stereospecifically and the formation of **10** and **11** from **9** (and the formation of **9** from **10** and **11**) is supressed in the presence of maleic anhydride.

The formation of **15** from **29** and **16** from **30** demonstrates that the Diels–Alder reactions of these *o*-xylylenes follow the endo-addition rule.[23,24] This is in accord with other studies of intermolecular Diels–Alder reactions of *o*-xylylenes,[25,26] although a minor amount of exo addition has also been reported.[27] The stereospecific trapping observed here contrasts with our previous results[7] where phenyl-substituted *o*-xylylenes gave mixtures of stereoisomeric adducts with cyclohexene. However, since one of these phenyl-substituted *o*-xylylenes was apparently trapped stereospecifically by maleic anhydride,[6b] it would appear that only weak dienophiles, such as cyclohexene, are unable to trap the *o*-xylylenes stereospecifically. This could be due to competing exo and endo addition with this dienophile or to the longer lifetime of the *o*-xylylene, allowing geometrical isomerization to compete.

In accord with our previous observations,[7] we were not able to obtain any Diels–Alder adducts upon sensitized irradiation of **1**, **9**, **10**, or **11**. However, the interconversion of **9** and **10** and **11** did occur upon sensitized irradiation and deuterium labeling demonstrated that this process involved a 1,5 hydrogen migration. If the sensitized irradiation does involve an *o*-xylylene, then the lifetime of the *o*-xylylene must be short under these conditions. An alternative explanation is that the sensitized irradiation involves the triplet biradical **31**, which never produces **29** or **30**, but instead reacts to give **9**, **10**, or **11**.



31

In summary, these studies have demonstrated that *o*-xylylenes can be produced stereoselectively from simple *o*-methylstyrene derivatives. Furthermore, these *o*-xylylenes can be trapped stereospecifically with reactive dienophiles in reasonable yields. However, two competing isomerizations of the styrene derivatives were observed, which may decrease the synthetic utility of the reaction, especially when less reactive dienophiles are employed.

Experimental Section

General Procedures. Boiling points are uncorrected; melting points are corrected. Nuclear magnetic resonance spectra were obtained on a Varian EM-360 or a Varian HA-100 spectrometer. Infrared spectra were obtained with a Perkin-Elmer 337 spectrophotometer. Ultraviolet spectra were obtained on a Beckman Acta V spectrophotometer. Elemental analyses were obtained from Atlantic Microlab, Inc., Atlanta, GA.

Preparative GC employed an Aerograph A-700 chromatograph. The following columns were used: column P, 3.7 m × 6.4 mm, 17% Silicone Gum Rubber UCW-982 on 30/60 Chromsorb P; column Q, 6.1 m × 9.5 mm, 30% SE-30 on 40/60 Chromsorb W. Analytical GC was performed with a Hewlett-Packard 5750 chromatograph coupled to a Columbia Scientific Industries CSI 38 digital integrator. The following columns were used: column A, 1.8 m × 3.2 mm, 10% Silicone Gum Rubber UCW-982 on 60/80 Chromsorb W; column B, 1.5 m × 3.2 mm, 10% butanediol succinate on 80/100 Chromsorb P; column C, 1.5 m × 3.2 mm, 3% SE-30 on 80/100 Chromsorb G; column D, 1.8 m × 3.2 mm, 3% OV-17 on 100/120 Chromsorb W.

2-(3-Methylphenyl)propene (2). Compound **2** was prepared by the procedure of Tiffenau[10] with the exception that the dehydration was conducted as described below.[28] A solution of crude 2-(3-methylphenyl)-2-propanol, obtained from the reaction of excess methylmagnesium iodide with methyl 3-methylbenzoate, in 20 mL of HMPA was heated to reflux for 1.5 h. The solution was poured into 100 mL of water and extracted with three 50-mL portions of pentane. The combined extracts were washed three times with water, with $NaHSO_3$ solution, and again with water, and dried over $MgSO_4$. Distillation gave 0.41 g of **2**; 54% from the ester; bp 94–95 °C (39 mm); NMR ($CDCl_3$) δ 7.1 (m, 4 H, Ar), 5.30 (narrow m, 1 H, C=CH), 4.99 (narrow m, 1 H, C=CH), 2.26 (s, 3 H, Ar CH_3), 2.07 (br s, 3 H, C=CCH_3).

Dehydrogenation of *cis*-9,9-Dimethyl-1,2,3,4,4a,9,9a,10-octahydroanthracene (3). A mixture of 0.160 g (1.75 mmol) of **3** and 0.091 g (2.8 mmol) of sulfur flowers was heated to 230–240 °C for 3 h. After cooling, the tarry reaction mixture was washed with ether and the solution was filtered to remove undissolved solids. After evaporation of the ether, the residue was chroma-

(19) Odinokov, V. N.; Galeeva, R. I.; Tolstikov, G. A.; Spirikhin, L. V.; Zaev, E. E. *Zh. Org. Khim.* **1977**, *13*, 1195–1200.

(20) Wilzbach, K. E.; Kaplan, L. *J. Am. Chem. Soc.* **1964**, *86*, 2307–2308. Kaplan, L.; Wilzbach, K. E.; Brown, W. G.; Yang, S. S. *Ibid.* **1965**, *87*, 675–676. Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1976**, *32*, 1309–1326.

(21) de Fonseka, K. K.; McCullough, J. J.; Yarwood, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 3277–3282. McCullough, J. J. *Acc. Chem. Res.* **1980**, *13*, 270–276, and references contained therein.

(22) We have no information as to whether this process is thermal, photochemical, or some combination of these two processes.

(23) Huisgen, R.; Grashey, R.; Sauer, J. "The Chemistry of Alkenes"; Patai, S., Ed.; Interscience: New York, 1964; pp 910–912.

(24) No **16** was detected by NMR in the reaction of **9** with maleic anhydride, nor was any **15** detected in the reaction of **10** or **11** with maleic anhydride. We estimate that 10% of **16** in **15**, or vice versa, would have been easily detectable.

(25) See ref 17 and references contained therein. In this study the endo addition was postulated to be due to hydrogen bonding.

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tographed on silica gel (2 × 88 cm column), using hexane as eluent, to give 0.036 g (23%) of 9,9-dimethyl-9,10-dihydroanthracene (4). This sample had an NMR spectrum identical with that of an authentic sample and its TLC and GC retention times were the same as those of the authentic sample.

9,9-Dimethyl-9,10-dihydroanthracene (4). To a solution of methylmagnesium iodide, prepared from 1.46 g (0.060 mol) of magnesium turnings and 8.5 g (0.060 mol) of methyl iodide in 50 mL of anhydrous ether, was added dropwise a solution of 6.33 g (0.0288 mol) of methyl 2-benzylbenzoate in 50 mL of anhydrous ether over a period of 10 min. The solution was then heated to reflux for 2 h. To the solution was added ca. 13 mL of saturated NH_4Cl solution. The ether was decanted from the resulting solids, and the solids were washed well with ether. The ether was removed in vacuo and the remaining oil was added dropwise to 30 mL of ice-cold 85% H_2SO_4 with stirring. The resulting orange solution was stirred at room temperature for 35 min and then poured into 500 mL of water and extracted with three 150-mL portions of ether. The combined extracts were washed with $NaHSO_3$ solution, $NaHCO_3$ solution, and water and then dried over $MgSO_4$. Distillation gave 3.52 g (59%) of 4, bp 143–155 °C (1.65 mm) [lit.[29] bp 183–185 °C (17 mm)]. Several recrystallizations from methanol gave a sample with mp 49.5–51 °C (lit.[29] mp 51.5–52 °C); NMR ($CDCl_3$) δ 7.1 (m, 8 H, Ar), 3.90 (s, 2 H, CH_2), 1.47 (s, 6 H, CH_3).

***cis*-1,1-Dimethyl-1,2,3,4-tetrahydro-2,3-naphthalenedicarboxylic Acid (7).** A mixture of 1.57 g (6.83 mmol) of 6 and 4 g (100 mmol) of NaOH in 50 mL of water was heated to reflux for 2 h. After cooling, the aqueous solution was washed twice with ether and the ether was discarded. The aqueous solution was boiled for several minutes and then cooled and acidified with HCl. After the solution was allowed to stand overnight at 5 °C, the resulting solid was collected and dried to give 1.07 g (63%) of 7. Two recrystallizations from acetone–hexane gave an analytical sample: mp 178.5–179.5 °C; NMR (Me_2SO-d_6) δ 12.0 (br s, 2 H, CO_2H), 7.1 (m, 4 H, Ar), 3.1 (m, 4 H, CH_2, CH, CH), 1.40 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3).

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.52; H, 6.56.

Bisdecarboxylation of *cis*-1,1-Dimethyl-1,2,3,4-tetrahydro-2,3-naphthalenedicarboxylic Acid (7). Oxygen was bubbled through 10 mL of pyridine (freshly distilled from barium oxide) for 20 min. To the pyridine were added 1.07 g (4.31 mmol) of 7 and 2.8 g (6.68 mmol) of lead tetraacetate, and the solution was heated to 60–68 °C for 10 min. After about 1 min of heating, gas evolution began and was complete after 5 min. The solution was poured into 200 mL of 10% HNO_3 and extracted with three 75-mL portions of ether. The combined extracts were washed with saturated $NaHCO_3$ solution and saturated NaCl solution and dried over $MgSO_4$. The solvent was removed in vacuo to leave 0.82 g of oil. This oil was dissolved in 50 mL of ethyl acetate and hydrogenated in a Parr apparatus, using 0.2 g of 10% Pd on C as catalyst. After the catalyst was removed by filtration, the residue was distilled to give 0.18 g (26%) of 8, bp 93 °C (5 mm) [lit.[11] bp 88 °C (8.1 mm), 98 °C (10 mm)]. The IR and NMR spectra of this material were identical with those of an authentic sample of 8.[11]

2-(2-Methylphenyl)-1-butene (9). A solution of 55.0 g (0.15 mol) of methyltriphenylphosphonium bromide in 50 mL of dry Me_2SO was added by a syringe to a solution of methyl sulfinyl carbanion [prepared[30] from 8.4 g (0.19 mol) of a 55% dispersion of NaH in mineral oil] in 75 mL of dry Me_2SO under a nitrogen atmosphere. After this solution was stirred for 10 min at room temperature, 20.0 g (0.14 mol) of 1-(2-methylphenyl)-1-propanone[12] was added via syringe and the solution was stirred at room temperature for 16 h. The solution was poured into 200 mL of water and extracted with pentane. The combined extracts were washed several times with 1:1 Me_2SO–water and then with water and dried over $MgSO_4$. The pentane solution was filtered through 3 g of neutral alumina (activity I) and the alumina was eluted with an additional 500 mL of pentane. Distillation yielded 18.0 g (93%) of 9: bp 35 °C (1.5 mm); NMR ($CDCl_3$) δ 6.98 (br s, 4 H, Ar), 5.06 (narrow m, 1 H, C=CH), 4.75 (narrow m, 1 H, C=CH), 2.7–2.0 (m, with singlet superimposed at 2.17, 5 H, $ArCH_3$ and CH_2), 0.93 (t, 3 H, CH_3); UV (heptane) λ_{max} <210 nm.

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.25; H, 9.71.

2-(3-Methylphenyl)-1-butene (12). Compound 12 was prepared from 3.6 g (0.024 mol) of 1-(3-methylphenyl)-1-propanone,[13] 9.9 g (0.028 mol) of methyltriphenylphosphonium bromide, and 1.5 g (0.034 mol) of a 55% dispersion of NaH in mineral oil in the same manner as described for the preparation of 9. Distillation yielded 1.8 g (51%) of 12: bp 42 °C (1.2 mm); NMR ($CDCl_3$) δ 7.1 (m, 4 H, Ar), 5.17 (br s, 1 H, C=CH), 4.93 (m, 1 H, C=CH), 2.63–2.07 (m with s superimposed at 2.20, 5 H, $ArCH_3$ and CH_2), 1.05 (t, J = 8 Hz, 3 H, CH_3).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.22; H, 9.71.

(*Z*)- and (*E*)-2-(2-Methylphenyl)-2-butene (10 and 11). Compounds 10 and 11 were prepared from 4.0 g (0.027 mol) of o-methylacetophenone,[8] 20.0 g (0.054 mol) of ethyltriphenylphosphonium bromide, and 2.4 g (0.054 mol) of a 55% dispersion of NaH in mineral oil in the same manner as described for the preparation of 9 with the exception that the reaction was stirred for 16 h at 50 °C. Distillation yielded 2.5 g (63%) of a 1.7:1 mixture of 10 and 11, bp 34 °C (1.1 mm).

Pure samples of 10 and 11 were obtained by preparative GC (column P, 110 °C). Compound 10 eluted first: NMR ($CDCl_3$) δ 7.0 (m, 4 H, Ar), 5.45 (br q, J = 7 Hz, 1 H, C=CH), 2.13 (s, 3 H, Ar CH_3), 1.87 (narrow m, 3 H, Ar CH_3C=C), 1.32 (br d, J = 7 Hz, 3 H, C=$CHCH_3$); IR (neat) 1690, 850, 770 cm^{-1}; UV (CH_3CN) λ_{max} 230 nm (ε 8400).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.07; H, 9.89.

Compound 11 eluted second: NMR ($CDCl_3$) δ 7.03 (s, 4 H, Ar), 5.34 (br q, J = 7 Hz, 1 H, C=CH), 2.20 (s, 3 H, Ar CH_3), 1.85 (narrow m, 3 H, Ar CH_3C=C), 1.69 (br d, J = 7 Hz, 3 H, C=$CHCH_3$); IR (neat) 1690, 850, 700 cm^{-1}; UV (CH_3CN) λ_{max} 245 nm (ε 7850), 250 (7900).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.01; H, 9.93.

(*Z*)- and (*E*)-2-(3-Methylphenyl)-2-butene (13 and 14). A mixture of 13 and 14 was prepared from 3.5 g (0.025 mol) of 3-methylacetophenone, 11.9 g (0.032 mol) of ethyltriphenylphosphonium bromide, and 1.6 g (0.036 mol) of a 55% dispersion of NaH in mineral oil in the same manner as described for the preparation of 10 and 11 with the exception that the reaction was stirred for 21 h at 31 °C. This gave 2.7 g (74%) of crude product, (Z/E = 2), bp 34 °C (1.1 mm).

Pure samples of 13 and 14 were obtained by preparative GC (column P, 125 °C). Compound 13 eluted first: NMR ($CDCl_3$) δ 7.0 (m, 4 H, Ar), 5.48 (br q, J = 7 Hz, 1 H, C=CH), 2.31 (s, 3 H, Ar CH_3), 2.00 (narrow m, 3 H, Ar CH_3C=C), 1.57 (d of m, J = 7 Hz, 3 H, C=$CHCH_3$); IR (neat) 810, 765, 685 cm^{-1}; (CH_3CN) λ_{max} 236 nm (ε 8010).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.37, H, 9.61.

Compound 14 eluted second; NMR ($CDCl_3$) δ 7.1 (m, 4 H, Ar), 5.80 (br q, J = 7 Hz, 1 H, C=CH), 2.27 (s, 3 H, Ar CH_3), 1.97 (narrow m, 3 H, Ar CH_3C=C), 1.74 (br d, J = 7 Hz, 3 H, C=$CHCH_3$); IR (neat) 810, 765, 685 cm^{-1}; UV (CH_3CN) λ_{max} 245 nm (ε 11 520).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.38; H, 9.61.

1-(2-Methylphenyl)-2,2-dideuterio-1-propanone (32). To a solution of 1.9 g (0.013 mol) of 1-(2-methylphenyl)-1-propanone[8] in 10 mL of dry THF was added a solution of 0.2 g of Na reacted with 20 mL of D_2O. After the solution was stirred at room temperature for 20 min, the THF was removed in vacuo and the residue was extracted with three 50-mL portions of CH_2Cl_2. The combined extracts were dried over Na_2SO_4, and the solvent was removed in vacuo. The residue was treated three times as above and then distilled to give 1.7 g of 32: bp 88–89 °C (10 mm); NMR ($CDCl_3$) δ 7.6–7.0 (m, 4 H, Ar), 2.43 (s, 3 H, Ar CH_3), 1.08 (s, 3 H, CH_3) with no detectable protons in the α position.

2-(2-Methylphenyl)-3,3-dideuterio-1-butene (17). To a stirring slurry of 12.4 g (0.035 mol) of methyltriphenylphosphonium bromide in 150 mL of dry THF, under a nitrogen

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atmosphere, was added 14.2 mL (0.035 mol) of 2.45 M *n*-butyllithium solution. After the solution had stirred at room temperature for 3.5 h, 2.6 g (0.017 mol) of **32** was added dropwise over a period of 5 min. The solution was heated to reflux for 14 h, then poured into 200 mL of water, and extracted with three 50-mL portions of pentane. The combined extracts were filtered, washed with four 50-mL portions of water, and dried over $MgSO_4$. After the solvent had been removed in vacuo, the residue was chromatographed on silica gel to give 1.2 g of clear oil. Distillation gave 1.0 g (40%) of **17**: bp 47 °C (3.0 mm); NMR ($CDCl_3$) δ 7.06 (br s, 4 H, Ar), 5.09 (d, J = 2 Hz, 1 H, C=CH), 4.80 (d, J = 2 Hz, 1 H, C=CH), 2.23 (s, 3 H, $ArCH_3$), 0.99 (br s, 3 H, CH_3).

Hydrolysis of 4α-Ethyl-4β-methyl-3aβ,4,9,9aβ-tetrahydronaphtho[2,3-*c*]furan-1,3-dione (15). To a solution of 4 mL of water and 30 mL of xylene was added 0.5 g (2.0 mmol) of **15** dissolved in 20 mL of xylene. The resulting solution was heated to reflux for 2 h and cooled, and the precipitate was collected. Two recrystallizations from acetone/hexane gave 0.31 g (60%) of 1α-ethyl-1β-methyl-1,2,3,4-tetrahydro-2α,3α-naphthalenedicarboxylic acid (**19**): mp 168–170 °C; NMR (acetone-d_6) δ 7.68 (br s, 2 H), 7.10 (m, 4 H), 3.71–2.80 (m, 4 H), 2.07 (q, J = 7 Hz, 2 H), 1.28 (s, 3 H) 1.07 (t, J = 7 Hz, 3 H); IR (Nujol) 1680 cm^{-1}. This compound was not stable enough for a C and H analysis to be obtained.

Hydrolysis of 4β-Ethyl-4α-methyl-3aβ,4,9,9aβ-tetrahydronaphtho[2,3-*c*]furan-1,3-dione (16). A solution of 1.1 g (4.5 mmol) of **16** in 25 mL of toluene was added to 10 mL of 1% aqueous NaOH solution and the resulting mixture was stirred for 1 h. The aqueous layer was separated and adjusted to a pH of 3. The milky aqueous layer was extracted with three 25-mL portions of ether, and the combined organic layers were dried over $MgSO_4$. Removal of the solvent gave 0.25 g (21%) of 1β-ethyl-1α-methyl-1,2,3,4-tetrahydro-2α,3α-naphthalenedicarboxylic acid (**20**), whose NMR spectrum was immediately measured: NMR (acetone-d_6) δ 9.41 (br s, 2 H), 7.06 (m, 4 H), 3.97–2.32 (m, 4 H), 1.82–1.10 (m, 5 H, with a singlet superimposed at 1.43), 0.70 (t, J = 7 Hz, 3 H); IR (neat) 1690 cm^{-1}. Any further attempts at purification (e.g., recrystallization, column chromatography, etc.) caused changes in the NMR spectrum. Allowing the sample to stand during any of the above stages of preparation caused similar results.

Photochemical Apparatus. Preparative irradiations were conducted with a quartz immersion well and a Hanovia 450-W, medium-pressure, mercury-vapor lamp. A Pyrex filter was employed for sensitized runs. Water-cooled vessels of 250 or 500 mL were used and the solutions were purged continuously with a stream of oxygen-free nitrogen.[31]

Analytical irradiations employed the same light source and immersion well combined with a "merry-go-round" type apparatus with quartz or Pyrex photolysis tubes of 10–15-mL capacity. Solutions (5–15 mL, ca. 0.02 M in compound under investigation) were degassed with oxygen-free nitrogen[31] prior to irradiation. Analyses were done by GC, using internal standards.

Irradiation of 2-(2-Methylphenyl)propene (1) in the Presence of Cyclohexene. A solution of 2.009 g (0.0152 mol) of **1**[8] and 57 mL of cyclohexene in 228 mL of benzene was irradiated through quartz in the preparative photochemical apparatus. After 21 h of irradiation, GC analysis (column A, temperature programmed from 124 to 249 °C) showed ca. 70% of **1** had reacted to give a mixture of **2**, **3**, cyclohexene photodimers, and small amounts of several unidentified compounds.

The solvent and the excess cyclohexene were removed in vacuo to leave 3.14 g of red-brown oil. Distillation of this oil gave the following fractions: fraction 1, 0.45 g, bp 83–90 °C (36 mm), predominantly a mixture of **1** and **2**; fraction 2, 1.52 g, bp 60–140 °C (1.6 mm), predominantly a mixture of **3** and cyclohexene photodimers. Preparative GC (column Q, 170 °C) of fraction 1 gave a pure sample of **2**, which had IR and NMR spectra identical with those of an independently prepared sample.

Preparative GC (column Q, 260 °C) of fraction 2 followed by distillation gave an analytically pure sample of **3**, bp 135 °C (1.75 mm); NMR ($CDCl_3$) δ 7.1 (m, 4 H, Ar), 3.0–1.0 (m, 18 H total, remaining protons, with singlets corresponding to the two methyls superimposed at 1.32 and 1.08); UV (cyclohexane) λ_{max} 257 nm (sh, ϵ 572), 264 (ϵ 744), 272 (ϵ 737), 285 (sh, ϵ 181).

Anal. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.74; H, 10.26.

Analytical photolyses were analyzed by GC on column A, temperature programmed from 110 to 220 °C, using naphthalene as an internal standard.

Irradiation of 2-(2-Methylphenyl)propene (1) in the Presence of Maleic Anhydride. A solution of 3.011 g (0.0228 mol) of **1** and 3.0 g (0.031 mol) of maleic anhydride in 275 mL of Spectrograde acetonitrile was irradiated through quartz in the preparative photochemical apparatus. After 43 h of irradiation, GC analysis (column A, temperature programmed from 127 to 250 °C) showed that ca. 73% of **1** had reacted. The solvent was removed in vacuo to leave 5.97 g of dark, viscous oil. Distillation gave, after a forerun of **1** and maleic anhydride, 1.83 g of *cis*-4,4-dimethyl-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1,3-dione (**6**), bp 176–185 °C (1.5 mm) (48% yield based on reacted **1**), which crystallized on standing. Several recrystallizations from hexane–benzene gave an analytical sample: mp 96–97.5 °C; NMR ($CDCl_3$) δ 7.25 (m, 4 H, Ar), 3.9–3.0 (m, 4 H, CH_2, CH, CH), 1.64 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3); UV (acetonitrile) λ_{max} 254 nm (sh, ϵ 220), 259 (ϵ 246), 264 (sh, ϵ 209), 268 (ϵ 167); MS, m/e 230.

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 73.01; H, 6.15.

Analytical photolyses were analyzed by GC on column A, temperature programmed from 110 to 220 °C, using naphthalene as an internal standard.

Direct Irradiation of 2-(2-Methylphenyl)-1-butene (9). A solution of 3.0 g (0.021 mol) of **9** in 500 mL of benzene was irradiated through quartz in the preparative photochemical apparatus for 29 h. Distillation gave 1.5 g of a mixture of **12**, **10**, and **11**, bp 34–38 °C (1.5 mm). Preparative GC (column P, 110 °C) gave pure samples of **12**, **10**, and **11** (first to last eluting, respectively). The IR and NMR spectra of these samples were identical with those of independently prepared samples.

Analytical photolyses were analyzed on column C, temperature programmed from 85 to 130 °C, using naphthalene as an internal standard.

Sensitized Irradiation of 2-(2-Methylphenyl)-1-butene (9). A solution (10 mL) of 0.057 M **9** and 0.09 M xanthone in benzene was irradiated through Pyrex for 10 h. GC analysis showed the presence of **10** and **11**, which had the same retention times as authentic samples on three different columns (column A, column C, column D, temperature programmed from 85 to 200 °C). Quantitation was done by GC, using *o*-toluenenitrile as an internal standard.

Sensitized Irradiation of 2-(2-Methylphenyl)-3,3-dideuterio-1-butene (17). A solution of 1.0 g (6.7 mmol) of **17** and 1.3 g of xanthone in 500 mL of benzene was irradiated through a Pyrex filter in the preparative photochemical apparatus for 36 h. The crude photolysis solution was concentrated to ca. 50 mL and diluted to 100 mL with hexane, and the precipitated xanthone was removed by filtration. This procedure was repeated three times and the resulting liquid was distilled to give 0.35 g of a mixture of deuterated photoproducts, bp 33–36 °C (1.5 mm). Preparative GC (column P, 120 °C) gave a pure sample of **18**: NMR ($CDCl_3$) δ 7.1 (m, 4 H, Ar), 2.13 (br s, 2 H, Ar CH_2D), 1.90 (br s, 3 H, Ar CH_3C=C), 1.35 (br s, 3 H, C=CCH_3).

Irradiation of 2-(2-Methylphenyl)-1-butene (9) in the Presence of Maleic Anhydride. A solution of 10.0 g (0.07 mol) of **9** and 11.5 g (0.12 mol) of maleic anhydride in 500 mL of acetonitrile was irradiated through quartz in the preparative photochemical apparatus for 41 h. The immersion well was cleaned several times during the irradiation to remove a polymer film that slowed the reaction. The solvent was removed in vacuo and the residue distilled. The fraction boiling around 175 °C (0.5 mm) was chromatographed on silica gel, using 40% ether in hexane as eluent, to give 2.3 g (13%) of **15**: mp 112–115 °C after recrystallization from hexane; NMR ($CDCl_3$) δ 7.23 (m, 4 H, Ar), 3.7–2.9 (m, 4 H, H's on C-2, C-3, and C-4), 1.8–1.3 (br q, J = 7 Hz, with a singlet superimposed at 1.69, 5 H, CH_2 of ethyl and CH_3), 0.60 (br t, J = 7 Hz, 3 H, CH_3 of ethyl); IR (neat) 1850, 1770, 740 cm^{-1}; MS, m/e 244 (molecular ion), 146 (base peak).

Anal. Calcd for $C_{15}H_{15}O_3$: C, 73.35; H, 6.60. Found: C, 73.68; H, 6.63.

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Analytical photolyses were analyzed by GC on column A, temperature programmed from 150 to 250 °C, using naphthalene as an internal standard.

Direct Irradiation of (*Z*)-2-(2-Methylphenyl)-2-butene (10). Ten milliliters of 0.019 M **10** in benzene was irradiated through quartz for 5 h. GC analysis showed the presence of **9**, **11**, **12**, **13**, and **14**, which had the same retention times as authentic samples on three different columns (column A, column C, column D). Quantitation was done by GC, using naphthalene as an internal standard.

Direct Irradiation of (*E*)-2-(2-Methylphenyl)-2-butene (11). Ten milliliters of 0.021 M **11** in benzene was irradiated and analyzed as described for **10**.

Sensitized Irradiation of (*Z*)- and (*E*)-2-(2-Methylphenyl)-2-butene (10 and 11). Ten milliliters of a solution of a 0.04 M mixture of **10** and **11** (5:3, respectively) and 0.041 M xanthone in benzene was irradiated through Pyrex for 5.5 h. GC analysis (column C, temperature programmed from 85 to 180 °C) showed the presence of **9**. Quantitative GC employed naphthalene as an internal standard.

Irradiation of (*Z*)- and (*E*)-2-(2-Methylphenyl)-2-butene (10 and 11) in the Presence of Maleic Anhydride. A solution of 1.0 g (6.8 mmol) of a mixture of **10** and **11** (5:3, respectively) and 1.5 g (15.0 mmol) of maleic anhydride in 250 mL of acetonitrile was irradiated through quartz in the preparative photochemical apparatus for 5.5 h. The immersion well was cleaned several times during the irradiation to remove a polymer film that slowed the reaction. Distillation gave 0.4 g (24%) of **16**: bp 147–148 °C (0.35 mm); NMR ($CDCl_3$) δ 7.18 (m, 4 H, Ar), 3.85–2.81 (m, 4 H, H's on C-2, C-3, and C-4), 1.9–1.1 (m with s superimposed at 1.49, 5 H, CH_2 of ethyl and CH_3), 0.70 (t, J = 7 Hz, 3 H, CH_3 of ethyl); IR (neat) 1870, 1780, 735 cm^{-1}; MS, m/e 244 (molecular ion), 146 (base peak).

Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.70; H, 6.63.

Analytical photolyses were analyzed by GC (column C, temperature programmed from 85 to 200 °C), using naphthalene as an internal standard.

Irradiation of (*Z*)-2-(2-Methylphenyl)-2-butene (10) in the Presence of Maleic Anhydride. A solution of 0.50 g (3.4 mmol) of **10** and 0.75 g (7.5 mmol) of maleic anhydride in 275 mL of acetonitrile was irradiated through quartz in the preparative photochemical apparatus for 4.1 h. Workup as described for the photoproduct obtained by irradiation of the mixture of **10** and **11** and maleic anhydride gave 0.23 g (28%) of **16** with spectral properties identical with those of the sample of **16** obtained above.

Acknowledgment. We gratefully acknowledge support of this research by a grant from the National Science Foundation (CHE77-07881 A01). R.B. thanks the Marathon Oil Co. for summer support and the Boettcher Foundation for a fellowship.

Registry No. 1, 7399-49-7; 2, 1124-20-5; *cis*-3, 82902-68-9; 4, 42332-94-5; 5, 6962-60-3; *cis*-6, 82902-66-7; *cis*-7, 82902-67-8; 8, 1985-59-7; 9, 82902-62-3; 10, 82902-63-4; 11, 82902-64-5; 12, 82902-69-0; 13, 82902-70-3; 14, 34815-66-2; 15, 82902-65-6; 16, 82949-87-9; 17, 82902-76-9; (*Z*)-18, 82902-77-0; 19, 82902-73-6; 20, 82902-74-7; 27, 82917-41-7; 28, 82917-42-8; 29, 82902-71-4; 30, 82902-72-5; 32, 82902-75-8; maleic anhydride, 108-31-6; cyclohexene, 110-83-8; 2-benzyl-α,α-dimethylbenzenemethanol, 57732-89-5; 2-(3-methylphenyl)-2-propanol, 5208-37-7; methyl iodide, 74-88-4; methyl 3-methylbenzoate, 99-36-5; methyltriphenylphosphonium bromide, 1779-49-3; 1-(2-methylphenyl)-1-propanone, 2040-14-4; 1-(3-methylphenyl)-1-propanone, 51772-30-6; ethyltriphenylphosphonium bromide, 1530-32-1; 2-methylacetophenone, 577-16-2; 3-methylacetophenone, 585-74-0; xanthone, 90-47-1.

Highly Stereo- and Regioselective Formation of 2-Oxazolone Telomers, Potential Synthetic Intermediates for Amino Sugars

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Received February 24, 1982

Free radical initiated reaction of 3-acyl-2-oxazolones proceeds smoothly in polyhalomethanes, which function as telogens, to give type **3** telomers of synthetic potential with high regio- and stereoselectivity, while the 3-alkyl derivatives failed to give such polyfunctional products. This particular telomerization can be controlled exclusively in the trans "head-to-tail" addition mode, as elucidated by ^1H and ^{13}C NMR and X-ray analysis of the products. Thus, the 3-benzoyl heterocycle **7** gave *trans*-4-chloro-5-(trichloromethyl)-2-oxazolidone (**8**) as a sole 1:1 adduct and two trans isomers of 4′-chloro-5-(trichloromethyl)[4,5′-bioxazolidinyl]-2,2′-dione (**9a,b**) as 2:1 telomers. Some characteristic reactions of the telomers are described.

Telomerization reactions capable of simultaneously attaining the stereoselective formation of carbon–carbon bonds and functionalization in a single step have great potential as a synthetic methodology for polyfunctional and complex molecules of biological interest.[1] Previously we explored a well-stereocontrolled telomerization reaction of vinylene carbonate with polyhalomethanes[2] and reported the synthetic utility of the polyfunctional products (viz., telomers) as versatile intermediates for stereoselective preparation of various monosaccharides including 2-deoxyaldoses.[1a,3] We next turned our attention to further application of such reactions to the 2-oxazolone heterocycle, which might serve as a building block for amino alcohols, including amino sugars.

Even though the 2-oxazolone skeleton was first reported in 1912,[4] 4,5-unsubstituted 2-oxazolones were not readily accessible until the practical synthesis reported by Scholz in 1976.[5] Such heterocycles were recently shown to be reactive enough to undergo smooth photocycloadditions and thermal cycloadditions to cyclobutane derivatives[6] and Diels–Alder products,[7] respectively, in contrast to the previous observation of extremely poor reactivities of the

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0022-3263/82/1947-4291$01.25/0