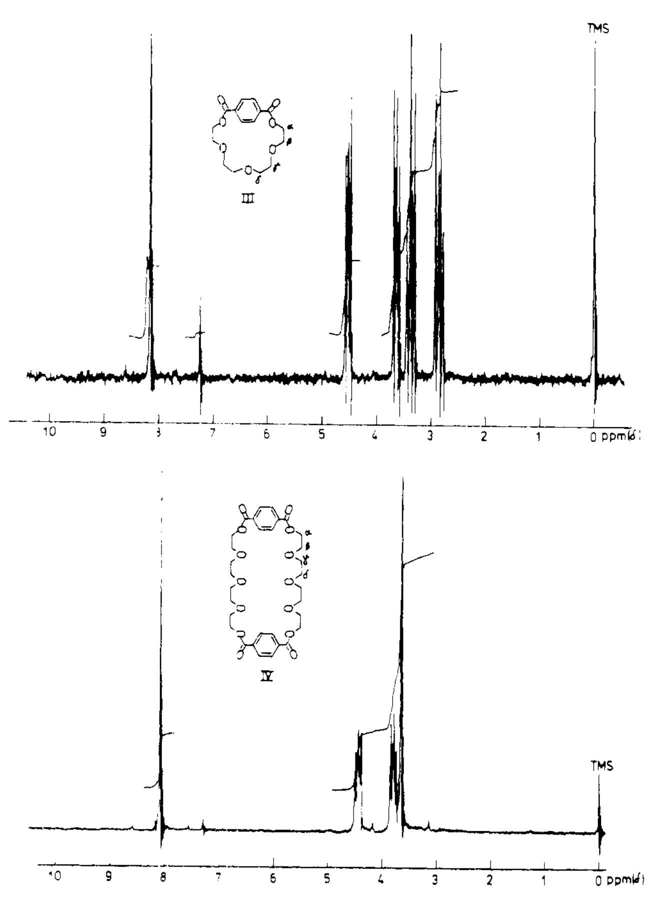

Figure 1. ${}^1H$ NMR spectra of III and IV ($CDCl_3/Me_4Si_{int}$, δ values (ppm), 90 MHz).

spectrometer. The molecular weight determinations were performed by Miss U. Loewe on a Knauer vapor pressure osmometer.

1,15,20,34-Tetraoxo-2,5,8,11,14,21,24,27,30,33-decaoxa-[15.15](1,4)benzenophane (IV). A 2.03-g (10-mmol) amount of terephthalic acid dichloride in 250 mL of benzene and 1.94 g (10 mmol) of tetraethylene glycol (II) and 1.58 g (20 mmol) of pyridine in 250 mL of benzene were simultaneously added within 12 h to 750 mL of boiling benzene stirred vigorously (two-component high dilution principle apparatus[5]). After cooling, the precipitated pyridinium hydrochloride was filtered off, and the solvent was removed in vacuo. The solid residue was recrystallized from *n*-heptane: yield 650 mg, 20%; mp 96 °C.

1,15-Dioxo-2,5,8,11,14-pentaoxa[15](1,4)benzenophane (III). A 1.01-g (5-mmol) amount of terephthalic acid dichloride (I) was dissolved in 250 mL of benzene and added simultaneously with a solution of 0.97 g (5 mmol) of tetraethylene glycol (II) and 0.79 g (10 mmol) of pyridine in 250 mL of benzene within 22 h to 2 L of boiling benzene stirred vigorously (two-component high dilution principle apparatus[5]). After cooling, the precipitated hydrochloride was filtered off. The solvent was removed in vacuo and the residue recrystallized from *n*-heptane. The first precipitate was filtered off and identified as the dimer IV (yield 65 mg, 2%). Concentration of the mother liquor afforded the monomer III (yield 211 mg, 13%), which was recrystallized from petroleum ether (50–70 °C), mp 98–99 °C.

Registry No.—I, 100-20-9; II, 112-60-7; III, 65745-85-9; IV, 65930-81-6.

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(5) This device allows the predilution of both cyclization components and their separate addition to the reaction medium: F. Vögtle, D.O.S. 2 205 712 (Aug 23, 1973); cf. D.B.P. 2 304 768 (Mar 2, 1973); *Chem. Ind.* (*London*), 346 (1972); *Chem.-Ztg.*, **96**, 396 (1972). The standardized apparatus is commercially available from Normag, Dr. Otto Ftitz GmbH, Apparatebau KG (Normag), D-6238 Hofheim/Taunus, Feldstr. 1 (vgl. Informationsheft Nr. 37, Normag), West Germany.

Photoepoxidation of Vinylallenes

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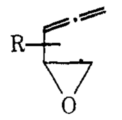
Previous work from both the Bertrand group and our own laboratory has shown that vinylallenic hydrocarbons **1** can be converted to cyclopentenones **2** either by treatment with peracid[1] or by acetoxymetallation (mercuric and thallic acetate in acetic acid).[2] We have also shown that vinylallenes **1** can easily be prepared by two different methods: (i) hydrolysis of vinylallenic Grignard reagents[3] and (ii) reaction of magnesiocuprates with the sulfonic esters of diversely substituted pent-4-en-2-yn-1-ols **3**.[2,4]

The ready availability of vinylallenes bearing different substituents together with the possibility of transforming these compounds to cyclopentenones suggested a new methodology for the preparation of several classes of natural products. The viability of this method was demonstrated by the synthesis of both jasmone and dihydrojasmone.[2,5,6]

There are two annoying problems associated with the methods used to induce cyclization of the vinylallene system. One is inherent with the structure of the vinylallene used and involves oxidation of the isolated double bond to give epoxide **4** when the reactivity of the allenic portion is low. The other inconvenience is related to the formation of a mixture of α-keto esters **5** which results by attack of carboxylic acid on the allene epoxide **6**. In some cases, the α-keto esters **5** were the major components of the epoxidation reaction.[7] Similar byproducts were detected in the acetoxymetallation reaction but these compounds could not be readily characterized as a result of their instability.[2]



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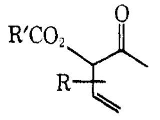
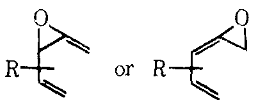


+ isomers

5



6

The formation of these byproducts decreases the yield of cyclopentenone **2** and limits the applicability of the method.

Recently, Shimizu and Bartlett[8] reported a new method for the epoxidation of double bonds which consists of irradiating an olefin in the presence of molecular oxygen and a α-diketone as sensitizer. These conditions were found to be very efficient for the synthesis of epoxides, even when deactivated alkenes were used. This new method seemed particularly promising to adapt to the vinylallenic system since it proceeds in the complete absence of nucleophiles and thus could avoid formation of the byproducts previously encountered. The only problem might be the ability of the eventually formed cyclopentenone to survive the experimental conditions. In order to probe the applicability of the Bartlett method, five diversely substituted vinylallenes **1a–e** were prepared (see Experimental Section) and were photooxygenated with a Hanovia medium pressure lamp (450 W) under the conditions described by Shimizu and Bartlett.[8] The reactions were carried out in each case using 0.01 mol of vinylallene dissolved in 500 mL of dry methylene chloride in the presence of 0.01 mol of biacetyl; dry molecular oxygen was continuously bubbled through the solution during irradiation. Starting material was completely consumed (TLC) in 10 to 15 min and the reaction products were isolated by column chromatography on silica gel. In each case, the major product isolated corresponded to cyclopentenone **2** (Scheme I). In only one case was there a

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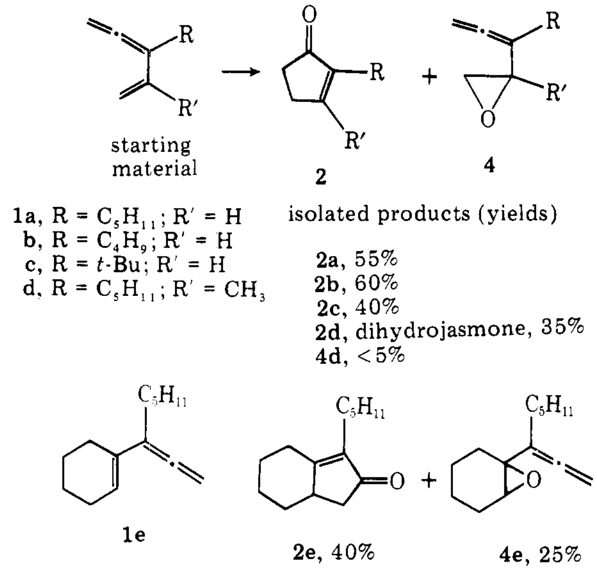
Scheme I



starting material

2

4

1a, R = C_5H_{11}; R′ = H
b, R = C_4H_9; R′ = H
c, R = *t*-Bu; R′ = H
d, R = C_5H_{11}; R′ = CH_3

isolated products (yields)

2a, 55%
2b, 60%
2c, 40%
2d, dihydrojasmone, 35%
4d, <5%

1e

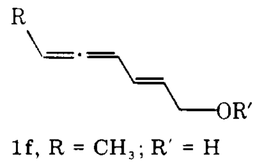
2e, 40%

4e, 25%

substantial amount of the α-allenic epoxide **4**. A complicated mixture (TLC) of more polar byproducts was also obtained (IR bands at 3350 cm^{-1} and between 1760 and 1740 cm^{-1}). However, all attempts to separate and identify the constituents of this mixture were unsuccessful. 2-Pentylcyclopent-2-en-1-one (**2a**) was also irradiated under similar conditions and afforded a mixture of products having similar properties to the polar byproducts obtained from the vinylallenes. Thus, it seems that vinylallenes are converted exclusively to cyclopentenones which are transformed to subsequent oxygenation products. Fortunately, the difference in the oxygenation rates allows for the isolation of the desired cyclopentenones in good yield.

Some attempts were carried out in order to improve the yield but without much success. Utilization of filters (Corex and Pyrex) had no effect on the product distribution and only decreased the oxidation rate (~30 min). Similar observations were made when the nature of the sensitizer was changed. For example, benzil leads to the same products as biacetyl but the yields of the cyclopentenones were slightly lowered (~10%) and the purification of these ketones was more difficult. Finally, the role of biacetyl concentration was briefly examined but seemed to have little effect upon the product distribution. The only characteristic fact that emerged from these studies was that 0.5 equiv of biacetyl was necessary for complete conversion of the vinylallene.

The results outlined in Table I clearly show that this photoepoxidation reaction is a fast and efficient way to convert vinylallenes to cyclopentenones. Although the yield is somewhat lower than that encountered with the peracid oxidation route,[1,5,6] purification of the product is much easier in many cases since the unknown byproducts are easily removed as a result of their high polarity. Unfortunately, this method does not work well with α-vinylallenic alcohols or ethers. Thus, when compounds **1f**, **1g**, and **1h** were submitted to the reaction conditions, starting material was completely consumed in about 30 min, but the crude reaction mixture consisted of a number of higher oxidation products analogous with those obtained in the photooxygenation of cyclopentenone **2a**.



1f, R = CH_3; R′ = H
g, R = R′ = CH_3
h, R = H; R′ = CH_3

Experimental Section

Infrared spectra were determined using a Perkin-Elmer Model 257; NMR spectra were measured in a Varian Associates Model A 60 or EM 360 with solvent as specified.

Preparation of Vinylallenes 1. Hydrocarbons **1a–e** were prepared according the procedures previously outlined.[2b]

3-*n*-Butylpenta-1,2,4-triene (1b) was isolated by column chromatography using petroleum ether as the eluent: 77%; IR (neat liquid) 3100, 3040, 3020, 1940, 1620, 990, 900, 855 cm^{-1}; NMR (CCl_4) δ 0.9 (t, 3 H, J = 7 Hz), 1.1–1.6 (m, 4 H), 1.8–2.2 (M, 2 H), 4.85 (broad s, 2 H), 4.9–5.2 (m, 2 H), 6.2 (dd, 1 H, J = 10 and 17 Hz).

3-*tert*-Butylpenta-1,2,4-triene (1c) was isolated by the same method: 43%; IR (neat liquid) same characteristic bands as that observed with **1b**; NMR (CCl_4) δ 1.2 (s, 9 H); 4.90 (broad s, 2 H), 4.85–5.2 (m, 2 H), 6.0 (dd, 1 H, J = 10 and 17 Hz).

Alcohol **1f** was prepared by the general procedure described in ref 9 and involved the reduction of hept-2-yne-4,5-dien-1-ol with lithium aluminum monomethoxhydride in THF (yield 80%): IR (neat liquid) 3350, 1945, 1640, 1000, 975, and 860 cm^{-1}; NMR (CCl_4) δ 1.7 (dd, 3 H, J = 3 and 7 Hz), 4.05 (m, 2 H), 5.1–6.0 (m, 4 H).

Ether **1g** was prepared from **1f** using the phase-transfer method recently described.[10] It was isolated by column chromatography over silica gel using a 95/5 petroleum ether–ether mixture as the eluent (80%): IR (neat liquid) 3040, 1940, 1640, 970 cm^{-1}; NMR (CCl_4) δ 1.7 (dd, 3 H, J = 3 and 7 Hz), 3.6 (s, 3 H), 4.1 (m, 2 H), 5.0–6.0 (m, 4 H).

Ether **1h** was prepared from hexa-2,5-diyne-1-ol[11] by (i) reduction with $LiAlH_4$ in the conditions previously described,[9] (ii) etherification by the phase transfer méthod,[10] and (iii) isomerization of the β-enyne to vinylallene using a 10% solution of NaOH in methanol.[12] **1h** was isolated by column chromatography over silica gel using a 95/5 petroleum ether–ether mixture as eluent: IR (neat liquid) same characteristic band as that observed with **1g**; NMR (CCl_4) δ 3.2 (s, 3 H), 3.6–5 (m, 2 H), 5.7–6.3 (m, 3 H).

Photoepoxidation of Vinylallenes. A 0.01-mol sample of vinylallene **1** and 0.01 mol of biacetyl were dissolved in 500 mL of dry methylene chloride and the solution was saturated with oxygen before irradiation. After the photolysis was completed, the solvent was evaporated in vacuo and the crude product, dissolved in ether, was washed until neutral with a saturated aqueous solution of sodium bicarbonate. After the usual workup the cyclopentenones were purified by column chromatography using petroleum ether–ether (70/30) as the eluent. In every case the homogeneity of the ketone was verified by TLC and VPC. Cyclopentenones **2a**, **2d**, and **2e** were identified by comparison of their spectra with those previously described.[2b,5]

2-*n*-Butylcyclopent-2-enone (2b): IR (neat liquid) 3045, 1705, 1635 cm^{-1}; NMR (CCl_4) δ 0.95 (t, 3 H, J = 7 Hz), 1.2–1.7 (m, 4 H), 1.9–2.6 (m, 6 H), 7.15 (m, 1 H).

2-*tert*-Butylcyclopent-2-enone (2c): IR (neat liquid) 3040, 1700, 1640 cm^{-1}; NMR (CCl_4) δ 1.15 (s, 9 H), 1.7–2.4 (m, 4 H), 7.1 (broad s, 1 H).

Epoxide 4e was identified by comparison of its spectra with those of previously described homologues:[1a] IR (neat liquid) 1950 and 850 cm^{-1}; NMR (CCl_4) δ 0.95 (t, 3 H, J = 7 Hz), 1.1–2.0 (m, 16 H), 3.0 (M, 1 H), 4.8 (t, 2 H, J = 3 Hz).

Registry No.—**1a**, 61779-54-2; **1b**, 57223-19-5; **1c**, 68630-30-8; **1d**, 62055-70-3; **1e**, 68630-31-9; **1f**, 68630-32-0; **1g**, 68630-33-1; **1h**, 68630-34-2; **2a**, 25564-22-1; **2b**, 5561-05-7; **2c**, 5682-67-7; **2d**, 1128-08-1; **2e**, 68630-35-3; **4d**, 68630-37-5; **4e**, 68630-36-4; hept-2-yne-4,5-dien-1-ol, 3589-09-1; hexa-2,5-diyn-1-ol, 28255-99-4.

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