appear to alter the selectivity for preferential attack of the anthryl system and allows for more convenient in situ generation of the nucleophilic species.[6] Similarly, the use of diphenylphosphoryl azide[7] in the conversion of acid **1** to carbamate **2** simplifies the procedure, but in this case, yields of carbamate are slightly lowered (~50%).

Experimental Section[8]

9'-Anthrylmethyl (±)-(*E*)-2-(3,4-Dibenzyloxyphenyl)cyclopropylcarbamate (2). A solution of 3.0 g (0.008 mol) of acid **1** in 15 mL of toluene and 15 mL of thionyl chloride was stirred at room temperature for 4 h. The reaction medium was then evaporated under reduced pressure leaving the acid chloride as an oil (IR γ_{max} 1775 cm^{-1}). The oil was taken up in 30 mL of acetone, cooled to 0–2 °C, and treated dropwise with 3 g (0.046 mol) of sodium azide in 15 mL of water. After the addition, the mixture was stirred for 1 h gradually attaining room temperature and then 25 mL of water was added and the mixture extracted with toluene (2 × 70 mL). The combined extracts were dried over Na_2SO_4 and evaporated under reduced pressure leaving the acyl azide as an oil. The oil was taken up in toluene and maintained at ~90 °C until bubbling ceased (1–4 h) and an IR indicated absence of the characteristic acyl azide absorptions (2140 and 1705 cm^{-1}). 9-Anthracenemethanol (1.7 g, 0.008 mol) was then added and heating at ~90 °C continued (24–48 h) until an IR indicated absence of the isocyanate absorption (2280 cm^{-1}) and maximal carbamate carbonyl absorption (1700 cm^{-1}). As the mixture attained room temperature, yellow crystals were produced which were collected and recrystallized from toluene to finally provide 2.9 g (64%) of yellow crystals: mp 166–167 °C; IR (KBr disk) 1680 cm^{-1}; NMR ($CDCl_3$) δ 6.1 (S, 3, $-CH_2An$ and $-NHCO_2-$ the latter of which disappears upon addition of CD_3OD and Et_3N). Anal. Calcd for $C_{39}H_{33}NO_4$: C, 80.80; H, 5.74; N, 2.42. Found: C, 80.54; H, 5.77; N, 2.34.

(±)-(*E*)-2-(3,4-Dibenzyloxyphenyl)cyclopropylamine Tosylate (3). To a mixture of 0.13 g (0.003 mol) of 57% sodium hydride in 5 mL of DMF under N_2 at room temperature was added 0.22 mL (0.003 mol) of ethanethiol in 1 mL of DMF. When the solution was clear (~15 min), 1.45 g (0.0025 mol) of carbamate **2** in 20 mL of DMF was added quickly via syringe. The resulting red-colored solution was stirred for 30 min and then dumped into 100 mL of water/25 mL of crushed ice. The resulting milky suspension was extracted with ether (3 × 100 mL), adding potassium carbonate to the aqueous phase during the first extraction. The combined ethereal extracts were washed with water (2 × 50 mL), dried over K_2CO_3, and concentrated to ~50 mL. To this phase was then added 0.475 g (0.0025 mol) of *p*-toluenesulfonic acid monohydrate dissolved in 25 mL of ether. Yellow crystals were obtained after standing at room temperature. Recrystallization was effected from ethanol–ether (1:1) and provided 0.95 g (74%) of yellow crystals: mp 163–164 °C; NMR ($CDCl_3$) δ 8.1 (broad S, 3, $-NH_3^+$, disappears upon addition of CD_3OD). Anal. Calcd for $C_{30}H_{31}NO_5S$: C, 69.63; H, 6.00; N, 2.71. Found: C, 69.83; H, 6.36; N, 2.62.

Registry No.—**1**, 68708-15-6; **2**, 68708-16-7; **3**, 68708-18-9; 9-anthracenemethanol, 1468-95-7.

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(6) To insure stoichiometry when employing repetitive methanethiol deblocking, it is most convenient to isolate the sodium salt as the hydrated crystalline material after its larger scale preparation from sodium ethoxide according to H. F. Backer and F. Stienstra, *Recl. Trav. Chim. Pays-Bas*, **52**, 1033 (1933); *Chem. Abstr.*, **28**, 4713 (1934), or as the anhydrous powder as more recently described by N. Kornblum, S. C. Carlson, and R. G. Smith, *J. Am. Chem. Soc.*, **100**, 289 (1978).
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(8) Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. IR spectra were obtained with a Perkin-Elmer 283 spectrophotometer either as thin films from reaction media, neat thin films, or KBr disks. NMR spectra were recorded on a Varian Associates T-60A spectrometer using $CDCl_3$/1% Me_4Si. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Selective Monomer/Dimer Formation in a Many-Membered Crown Ether Lactone Synthesis

Klaus Frensch and Fritz Vögtle*

Institut für Organische Chemie und Biochemie der Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn, West Germany

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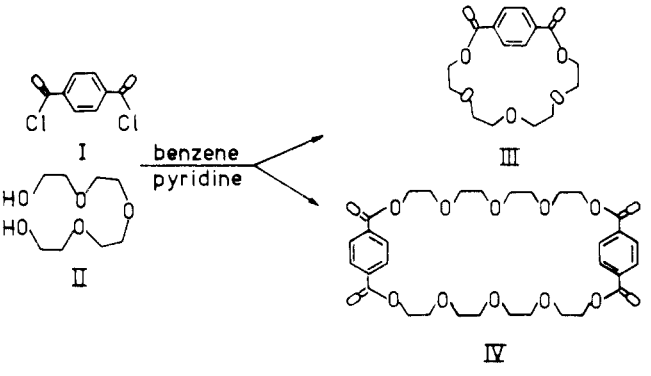
The existence of the monomeric terephthalic acid ester III,[1] which we synthesized in 1977, was recently questioned[2] since its melting point was similar to that of the dimeric tetralactone IV. In this communication, we give unequivocal



proof of the existence of both cycles and describe their syntheses in detail.

Reaction of terephthalic acid dichloride I with tetraethylene glycol II under high dilution conditions gave, in contrast to other reports,[2] the monomeric lactone III as well as the dimeric cyclic ester IV. The monomer/dimer ratio may be influenced by variation of the reaction conditions; reaction in more concentrated solution yields only the dimeric ester IV apart from polycondensed material, while more diluted conditions lead to the monomer ester III as main product besides polymeric material and some dimer product.

It is, in fact, a peculiarity of these cyclic compounds that the melting point of dimer IV (96 °C) is almost identical with that of monomer III (98–99 °C). While III forms large, colorless crystals (*n*-heptane/petroleum ether), IV always crystallized as a colorless powder (*n*-heptane).

By osmometric molecular weight determination we found a molecular weight of 632 for the dimer IV and 322 for the monomer III. Mass spectra show molecular ion peaks M^+ at *m/e* 648 for the dimer and at *m/e* 324 for the monomer. High-resolution mass spectra confirm the molecular formulas $C_{32}H_{40}O_{14}$ and $C_{16}H_{20}O_7$, respectively. The ^1H NMR spectra of III and IV (Figure 1) are significantly different. While the spectrum of the dimer shows a splitting into two multiplets and one singlet for the CH_2 protons lying α,β and γ,δ to the ester oxygen (α, 4.5 ppm; β, 3.8 ppm; γ, 3.65 ppm), the signals due to the γ- and δ-CH_2 protons of the monomer are further split so that a total of four multiplets results: α, 4.5 ppm; β, 3.65 ppm; γ, 3.35 ppm; δ, 2.85 ppm. The strong highfield shift of the bridge protons clearly indicates the presence of the *monomeric* ester since the γ and δ protons come close to the aromatic nucleus and are, therefore, expected to show signals at higher field strength as is known for other paracyclophanes.[3,4]

The ligand IV yields a 1:2 complex with NaSCN, mp 174–176.5 °C, formerly ascribed to III.[1] With pure III, only unstoichiometric salt-containing material could be isolated up to now.

Experimental Section

Melting points were taken on a Kofler Mikroskopheiztisch and are uncorrected. NMR spectra were recorded on a Bruker EM-390

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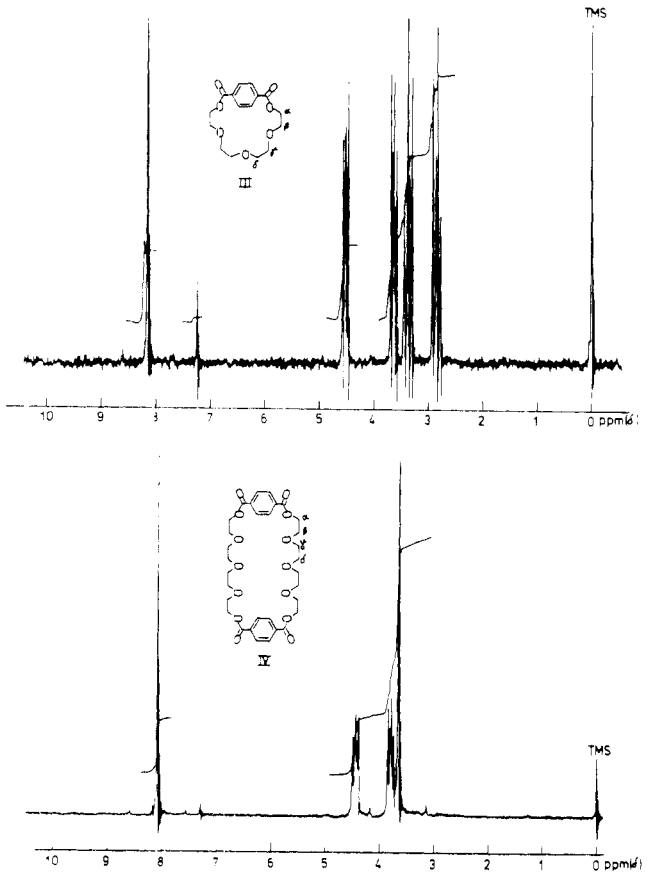

Figure 1. ^1H NMR spectra of III and IV ($CDCl_3/Me_4Si_{int}$, δ values (ppm), 90 MHz).

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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Photoepoxidation of Vinylallenes

Max Malacria and Jacques Goré*

Département de Chimie Organique, Université Claude Bernard, 69621 Villeurbanne, France

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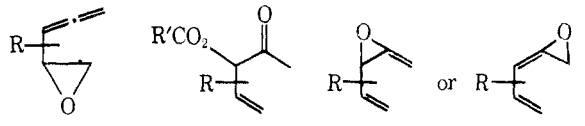
Previous work from both the Bertrand group and our own laboratory has shown that vinylallenic hydrocarbons **1** can be converted to cyclopentenones **2** either by treatment with peracid[1] or by acetoxymetallation (mercuric and thallic acetate in acetic acid).[2] We have also shown that vinylallenes **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 by-



4 + isomers **5** **6**

products were detected in the acetoxymetallation reaction but these compounds could not be readily characterized as a result of their instability.[2]

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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