of 3.6 g (0.02 mol) of 9 in 50 ml of dry ether was saturated with gaseous methylamine in a pressure bottle and the stoppered bottle was kept at room temperature for 5 days. The solvent was removed under reduced pressure and the oily residue was dissolved in chloroform, washed with dilute hydrochloric acid and water, and then dried ($MgSO_4$), Removal of the solvent under reduced pressure left 3.0 g (67%) of N-methyl-4-hydroxy-4-phenylbutyramide (12) as an oily residue: ir (neat) 3300 (broad) (NH and OH), 1640 (amide C=O), and 1510 cm⁻¹ (amide II).

A solution of 3.0 g (0.015 mol) of 12 in 50 ml of tetrahydrofuran was slowly added to a suspension of 3.8 g (0.01 mol) of powdered lithium aluminum hydride in 85 ml of tetrahydrofuran under an atmosphere of nitrogen. The reaction mixture was refluxed for 20 hr and then treated cautiously with 16 ml of water. The suspension was filtered and the filtrate was concentrated in vacuo to give an oily residue which was then dissolved in ether and extracted with dilute hydrochloric acid, and the acid solution was made basic with aqueous sodium bicarbonate. Extraction with ether followed by drying and removal of the solvent left an oily residue which gave an infrared spectrum and glpc identical in every respect with 8 prepared by method A.

 \hat{N} -(4-Acetoxy-4-phenylbutyl)-N-methylacetamide (7). A solution of 7.0 g (0.04 mol) of 8 in 20 ml of pyridine and 25 ml of acetic anhydride was heated on a steam bath overnight. The reaction mixture was poured into water and extracted with ether. The ether solution was washed with dilute hydrochloric acid, aqueous sodium bicarbonate, and water and then dried (MgSO₄). Removal of the ether under reduced pressure left 5.8 g (56%) of an oily residue: ir (neat) 1740 (ester C=O) and 1645 cm⁻¹ (amide C=O); nmr (CDCl₃), δ 7.28 (s, 5, ArH), 5.77 (t, 1, Ph-CH), 3.28 (q, 2, CH₂-N), 2.83 (d, 3, NHCH₃), 2.02 (s, 3, COCH₃), 1.98 (s, 3, COCH₃), and 1.70 (m, 4, O-C-CH₂CH₂).

3-Benzoyl-1-ethoxypropylurethane, (10). A solution of 300 g of 3 was refluxed overnight in 100 ml of absolute ethanol and the excess ethanol was removed under reduced pressure. The red oily residue was extracted with three 250-ml portions of petroleum ether (30-60°) and the combined extracts were cooled in a Dry Iceacetone bath to give the product as a pale yellow solid in 43% yield. Recrystallization from petroleum ether (60-110°) gave 10 as a white solid melting at 105-105.5°: ir (CHCl₃) 3440 and 3360 cm⁻¹ (NH), 1720 (carbamate C=O), and 1688 (ketonic C=O); nmr $(CDCl_3)$ δ 7.92 (m, 2, ArH), 7.62 (m, 3, ArH), 4.10 (q, 2, O-CH₂CH₃), 3.58 (m, 2, O-CH₂CH₃), 3.08 (t, 2, COCH₂), 2.08 (q, 2, CH2), 1.20 (t, 3, O-CH2CH3), and 1.15 (t, 3, O-CH2CH3).

Anal. Calcd for C15H21NO4: C, 64.50; H, 7.58; N, 5.01. Found: C, 64.49; H, 7.47; N, 5.22

Substituting compounds 4, 5, or 6 for 3 in the above reaction also gave 10 as the product. Yields ranged from 30 to 50%.

Propyl 3-Benzoyl-1-propoxypropyl Carbamate, (11). A solution of 30.0 g of 3 was refluxed overnight in 100 ml of propanol. The excess propanol was removed under reduced pressure at 60° (15 mm) leaving a red oil which crystallized on standing. The product was separated from an insoluble red oil by trituration with three 250-ml portions of petroleum ether (30-60°). The combined extracts were cooled in a Dry Ice-acetone bath to give a pale yellow solid in 20% yield which was recrystallized twice from petroleum ether (60-110°) to give 11 as a white solid melting at 66-67°: ir (Nujol) 3440 and 3360 (NH), 1720 (carbamate C=O), and 1688 cm^{-1} (keto C=O).

Anal. Calcd for C17H25NO4: C, 66.45; H, 8.20; N, 4.56. Found: C, 66.43; H, 8.09; N, 4.72.

The same product, 11, was obtained, as evidenced by an identical mp and ir spectrum, when 4, 5, or 6 was substituted for 3 in the above reaction. Yields ranged from 20 to 40%.

Registry No.-1, 15982-16-8; 2, 15982-30-6; 3, 53166-42-0; 4, 53166-43-1; 5, 53166-44-2; 6, 53166-45-3; 7, 24316-62-9; 8, 4266-01-7; 9, 1008-76-0; 10, 53166-46-4; 11, 53166-47-5; 12, 53166-48-6.

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Thermal [2 + 2] Cycloaddition of 1.1-Dimethoxyethene to the Carbonyl of 2-Ethoxy-3-indolone

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Although the photochemical [2 + 2] cycloaddition reaction of ketones and aldehydes to olefins (the Paterno-Büchi reaction) is a general reaction for the preparation of oxetanes,¹ analogous thermal cycloadditions are relatively rare. An exception is the thermal cycloadditions of cumulated systems (ketenes and ketenimines) to carbonyl compounds.² A few examples of thermal cycloadditions to strongly polarized ketones such as hexafluoroacetone³ and carbonyl cyanide⁴ have also appeared.

We wish to report on the thermal [2 + 2] cycloaddition of 2-ethoxy-3-indolone (1) to 1,1-dimethoxyethene (2). When a deuteriochloroform solution of 1 and 2 was heated at 40° in the probe of an nmr spectrometer for 2 hr, new peaks were observed in the nmr spectrum. The nmr absorptions (Experimental Section) indicated that the product was a [2 + 2] cycloadduct of 1 and 2, either an oxetane or an azetidine. A solution containing the product and approximately 10% residual starting materials was then examined by infrared spectroscopy. The ir spectrum revealed that the product possessed a carbon-nitrogen double bond (1600 cm^{-1}) but not a carbon-oxygen double bond. Hence the product was assigned an oxetane structure. The regiochemistry of the cycloadduct was tentatively predicted as shown in structure 3 from the chemical shifts of the ring methylene protons, δ 2.78 and 3.29 ppm, and the polarities of the carbonyl group of 1 and the double bond of 2. Although the cycloadduct could be separated from solvent by rotary evaporation, it was not stable to any standard methods of purification such as sublimation, glpc, or tlc.

The regiochemistry and overall structure of 3 was subsequently confirmed by a hydrolysis experiment. When a chloroform solution of 3 was extracted with water, methyl 3-(2-ethoxy-3-hydroxyindoleninyl)acetate (4) was isolated in 40% yield. The indoleninylacetate (4) was identified from OH, C=O, and C=N stretching bands at 3480, 1720, and 1625 cm⁻¹, respectively, in the ir spectrum, the nmr data reported in the Experimental Section, and a strong mass spectral parent ion at m/e 249. Oxetanes with regiochemistry identical with 3 from photochemical [2 + 2]cycloaddition of ketones to 1,1-diethoxyethene are similarly unstable with respect to hydrolysis.⁵



Symmetry considerations⁶ suggest that this cycloaddition occurs via an intermediate or via the 2s + 2a mode. The need for a strongly polar olefin capable of stabilizing charge and the regiochemistry of the cycloaddition are consistent with initial formation of a dipolar intermediate such

as 5. 2-Ethoxy-3-indolone (1) was not thermally reactive with less polar olefins such as styrene even at higher temperatures.

Experimental Section

The nmr spectra were obtained using Varian A-60A and HA100 spectrometers, and ir spectra were recorded with a Perkin-Elmer 337 spectrophotometer. Elemental analysis was performed by Atlantic Microlabs, Atlanta, Georgia.

2-Ethoxy-3-indolone (1). 2-Ethoxy-3-indolone was prepared by the reaction of ethyl iodide with the silver salt of isatin. Silver nitrate (200 g, 1.18 mol) was dissolved in 500 ml of water and added with stirring to 128 g (1.2 mol) of sodium carbonate dissolved in 500 ml of water. The yellow precipitate was collected by suction filtration, washed with water, and dried at 140° in the dark until the weight was constant. Isatin (160 g, 1.09 mol), the dry silver carbonate (156 g, 1.13 equiv of silver), 2 g of silver nitrate and 3 l. of ethanol were placed in a 5-l. three-neck flask equipped with a mechanical stirrer and condenser and refluxed for 14 days. The silver salt of isatin was then removed by vacuum filtration and washed several times with ethanol. The salt was dried at ambient temperature under vacuum to a constant weight of 214 g. Evaporation of the ethanol washes gave 89 g (0.6 mol) of recovered isatin.

The dried silver salt (125 g) and 2 l. of chloroform were placed in a 5 l. three-neck flask equipped as above and brought to reflux for 1 hr. The mixture was cooled and 79 g (0.5 mol) of ethyl iodide was added. The reaction was stirred for 10 days at ambient temperature, the precipitate was removed by vacuum filtration through Celite, and the red chloroform filtrate was evaporated to give 29.5 g of crude 2-ethoxy-3-indolone. The precipitate collected on Celite was dried as before and allowed to react with an additional 48 g (0.3 mol) of ethyl iodide under the same conditions as described above. Work-up gave an additional 29 g of crude product. The crude material was sublimed four times at 50° (0.01 mm) to yield 32 g (38% based on isatin consumed), mp 61-62° (lit.⁷ 52°). The purified 2-ethoxy-3-indolone gave the following spectral absorptions: nmr (CDCl₃) δ 1.49 (t, J = 7 Hz, 3 H), 4.53 (q, J = 7 Hz, 2 H), 7.01-7.42 ppm (m, 4 H); ir (CHCl₃) 1750 and 1600 cm⁻¹.

Thermal Reaction of 2-Ethoxy-3-indolone (1) with 1,1-Dimethoxyethene (2) in an Nmr Tube. 1,1-Dimethoxyethene (40 mg, 0.45 mmol) and 0.5 ml of deuteriochloroform were placed in an nmr tube and the 100-MHz spectrum was recorded, δ 3.06 (s, 2 H) and 3.59 ppm (s, 6 H). Then 60 mg (0.34 mmol) of 2-ethoxy-3-indolone was added to the above solution. Three minutes after the addition, the spectrum was taken and consisted simply of the sum of the spectra of 1,1-dimethoxyethene and 2-ethoxy-3-indolone. After 10 min at 40° shoulders appeared on the low-field side of each of the peaks of the methylene quartet of 2-ethoxy-3-indolone. After 30 min at 40° each peak of the methylene quartet appeared as distinct doublets, a shoulder appeared to the high-field side of the methoxy peak at 3.59 ppm, a new singlet appeared at 3.42 ppm, and an AB pattern appeared at 2.78 and 3.29 ppm (J = 12Hz). After 2 hr in the probe of the spectrometer, these new peaks, along with the methyl triplet and aromatic proton absorptions, were the only significant peaks in the spectrum, discounting the residual 1,1-dimethoxyethene absorptions.

Thermal Reaction of 2-Ethoxy-3-indolone (1) with 1,1-Dimethoxyethene (2) Observed in an Ir Cell. 2-Ethoxy-3-indolone (120 mg, 0.68 mmol), 1,1-dimethoxyethene (60 mg, 0.68 mmol), and 0.51 ml of chloroform were placed in an nmr tube and the thermal cycloaddition was followed by nmr until the reaction reached 90% completion as judged by observation of the change in the methylene quartet pattern of the spectrum at δ 4.53 ppm. An aliquot was then withdrawn from the nmr tube and diluted to a suitable concentration with chloroform. The ir spectrum contained a small absorbance at 1650 cm⁻¹ (A = 0.1) due to residual 1,1-dimethoxyethene in addition to the carbonyl absorbance at 1750 cm^{-1} (A = 0.15) and the carbon-nitrogen double bond stretching band at 1600 cm⁻¹ (A = 0.80) from residual 2-ethoxy-3-indolone and the cycloadduct (3). Thus, the ratio of the absorbances in the reaction mixture (C=O:C=N) was 0.19, whereas the ratio of absorbances (C=O:C=N) was 0.45 for pure 2-ethoxy-3-indolone in chloroform solution.

Thermal Reaction of 2-Ethoxy-3-indolone (1) with 1,1-Dimethoxyethene (2). A 100-ml three-neck flask equipped with a magnetic stirrer, condenser, and nitrogen inlet was charged with 0.50 g (2.9 mmol) of 2-ethoxy-3-indolone, 0.40 g (4.5 mmol) of 1,1dimethoxyethene, and 50 ml of chloroform. The flask was heated at 40° for 12 hr and an additional 0.40 g of 1,1-dimethoxyethene

was added. After the solution was heated for an additional 12 hr, it was transferred to a separatory funnel, 50 ml of water was added, and the mixture was shaken vigorously. The organic layer was separated and dried with magnesium sulfate, and the chloroform was removed by rotary evaporation. The residue solidified and was sublimed at 110° (0.01 mm). The sublimate was then recrystallized twice from ether-petroleum ether (bp 30-40°) to give 0.28 g of white crystals (40%), mp 108-110°. The product was identified as methyl 3-(2-ethoxy-3-hydroxyindoleninyl)acetate (4) from the following spectral absorptions: nmr (CDCl₃) δ 1.40 (t, J = 7 Hz, 3 H), 2.83 (s, 2 H), 3.71 (s, 3 H), 4.42 (q, J = 7 Hz, 2 H), 4.55 (broad, 1 H), and 7.25 ppm (m, 4 H); ir (CHCl₃) 3480, 1720, 1625, and 1590 cm^{-1} ; mass spectrum (70 eV) m/e 249 (41), 220 (4.9), 219 (15), 190 (6), 188 (6), 176 (21), 162 (10), 161 (14), 148 (21), 146 (base), 134 (6), 119 (8), 90 (23); (12 eV) m/e 250 (18), 249 (base).

Anal. Calcd for C13H15NO4: C, 62.64; H, 6.06; N, 5.62. Found: C, 62.62; H, 6.11; N, 5.51.

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Registry No.-1, 53153-60-9; 2, 922-69-0; 3, 53153-61-0; 4, 53153-62-1; ethyl iodide, 75-03-6; isatin silver salt, 5711-07-9.

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Bis Homologation of a Naphthalene to a Dihydroheptalene via Carbenoid Addition^{1a}

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The homologation of a bicyclo[4.4.0]decane, with simultaneous enlargement of both rings to a bicyclo[5.5.0]dodecane, was first demonstrated by Anderson and Barlow² and subsequently was exploited by Dauben and Bertelli in their elegant synthesis of heptalene.³ In a search for alternate approaches to heptalene derivatives, we have found that this double-ring expansion can be accomplished conveniently by a bis addition of dibromocarbene to a tetrahydronaphthalene.

Parham, et al., have shown that ring enlargement of a 1-alkoxycyclohexene (1) to alkoxycycloheptadienes 3a and 3b occurs when the derived endo-chlorocyclopropane 2 is heated in the presence of pyridine.⁴ The rigid requirement for the endo halide in this reaction implies firm control of the electrocyclic opening (disrotatory) of the cyclopropyl cation by orbital symmetry constraints.⁵ Application of this