triturated with methylene chloride. Evaporation of the methylene chloride left a residue of 1.34 g. This was heated at 170° until cessation of gas evolution (~30 min). The crude mixture of amino monoacids (1.0 g) was dissolved in 10 ml of absolute ethanol, saturated with HCl, and heated under reflux overnight. Neutralization with aqueous KOH followed by extraction with ether gave 0.70 g (62%) of amino ester mixture **5** and **6**.

Chromatography of 250 mg of this mixture on 10 g of Florisil gave 27 mg of essentially pure **5** (eluted with 1:1 ether–hexane): λ (CCl_4) 3.58, 5.78, 8.50, 9.66 μ; τ (CCl_4) 5.97 (2 H, q, J = 7 Hz), 7.3–9.4 (21 H, m, containing t at 8.77, J = 7 Hz); *m/e* 213 (parent), 84 (base peak).

Further elution with ether provided 63 mg of pure **6**, whose infrared, nmr, and mass spectra were identical with those of the same compound when obtained from pure 8 (see below).

Preparation of Pure Amino Diester 8 by Hydrogenation of 9. A solution of 1.003 g (3.53 mmol) of **9**[8,9] in ethanol was hydrogenated at atmospheric pressure with an uptake of 88 ml of gas (theoretical, 82 ml) in 1 hr. Filtration and removal of the solvent at reduced pressure gave 0.992 g of 8 distilling at 80° (0.005 mm): λ (CCl_4) 3.55, 5.71, 5.76 μ; τ (CCl_4) 5.87 (4 H, q, J = 7 Hz), 6.57 (1 H, t, J = 7 Hz), 7.2–9.3 (22 H, m, containing t at 8.77, J = 7 Hz); *m/e* 285 (parent), 112 (base peak).

Anal. (of picrate, mp 63–64°) Calcd for $C_{21}H_{30}N_4O_{11}$: C, 49.02; H, 5.88; N, 10.89. Found: C, 49.10; H, 6.03; N, 10.75.

Conversion of 8 to 6. A solution of 460 mg (1.62 mmol) of 8 in 2 ml of 20% aqueous HCl was heated under reflux for 20 hr. The residue remaining after removal of the water *in vacuo* was heated at 170° until cessation of gas evolution. This residue of crude amino monoacid was dissolved in absolute ethanol. The solution was saturated with anhydrous HCl and heated under reflux overnight. The ethanol solution was neutralized with 20% aqueous KOH. Extraction with methylene chloride followed by evaporation afforded a residue of 161 mg of crude amino ester. Distillation *in vacuo* at 100–110° (0.005 mm) gave 80 mg (24%) of **6**: λ (CCl_4) 3.59, 5.79, 8.51 μ; τ (CCl_4) 5.95 (2 H, q, J = 7 Hz), 7.3–9.3 (21 H, m, containing q at 8.84, J = 7 Hz); *m/e* 213 (parent), 112 (base peak).

Preparation of Diethyl 2,2-Dimethycyclopropane-1,1-dicarboxylate (2). To a 150-ml quartz immersion type photolysis cell, equipped with a Vycor filter and a Dry Ice condenser, was added 125 ml of isobutylene (bp −6°) and 3.6 g (0.0193 mmol) of diethyl diazomalonate. The system was purged with nitrogen and attached to a bubble counter. The solution was maintained at ±5° (circulating pump using ethanol coolant cooled by Dry Ice–acetone bath) and irradiated with a Hanovia 500-W high-pressure mercury immersion lamp until cessation of gas evolution (*ca.* 5 hr). The solution was concentrated by warming to room temperature and the residue was vacuum distilled to give 3.0 g (0.014 mol, 72%) of **2** collected at 46° (0.005 mm): λ (CCl_4) 5.79, 8.1, 9.1 μ; τ (CCl_4) 5.88 (4 H, J = 7 Hz), 8.71 (3 H, s), 8.79 (11 H, s and t, J = 7 Hz); *m/e* 214 (parent), 122 (base peak).

Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.74. Found: C, 61.84; H, 8.34.

Reaction of Compound 2 with Pyrrolidine. Formation of 11. To a 100-ml glass pressure flask was added 3.0 g (14.1 mmol) of **2** and 1.0 g (14.1 mmol) of pyrrolidine. The vessel was purged with nitrogen, sealed, and heated at 120° for 40 hr. The solution was diluted with ether and extracted with 5% aqueous HCl. The organic fraction was dried and concentrated *in vacuo* to give 1.82 g (60%) of recovered **2**. The aqueous fraction was carefully made basic with solid Na_2CO_3 and extracted with ether. The ether fraction was dried and concentrated *in vacuo.* The residue was distilled at 80–87° (0.005 mm) to give 0.47 g (1.65 mmol, 13%) of **11**: λ (CCl_4) 3.53, 5.72, 5.78 μ; τ (CCl_4) 5.95 (4 H, q, J = 7 Hz), 6.40 (1 H, t, J = 6 Hz), 7.3–7.8 (4 H, m), 8.0–8.9 (12 H, m, containing t, J = 7 Hz at 8.9), 9.04 (6 H, s); *m/e* 285 (parent), 112 (base peak).

Anal. (of methiodide, mp 92–94°) Calcd for $C_{16}H_3NO_4I$: C, 44.97; H, 7.07. Found: C, 44.68; H, 7.31.

Formation of Diethyl Tetramethylcyclopropane-1,1-dicarboxylate (3). To a 150-ml quartz immersion type photolysis cell, equipped with a reflux condenser, was added 125 ml of tetramethylethylene and 2.0 g (10.7 mmol) of diethyl diazomalonate. The system was purged with nitrogen and attached to a bubble counter. The solution was maintained at 18° (tap water) and irradiated until cessation of gas evolution (6 hr) with a Hanovia 500-W high-pressure mercury immersion lamp. The solution was concentrated under reduced pressure and distilled to give 1.9 g (7.75 mmol, 73%) of **3**: bp 64° (0.02 mm); λ (CCl_4) 5.79, 8.15 μ; τ (CCl_4) 5.91 (4 H, q, J = 7 Hz), 8.78 (t, J = 7 Hz), and 8.79 (s) (total = 18 H; *m/e* 242 (parent), 227 (base peak).

Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 64.84; H, 9.26.

Acknowledgments. This research was supported by Public Health Service Grant No. CA-12107-11. Facilities for nmr spectra were supported by Public Health Service Grant No. RR-00292-03.

Registry No. —**1,** 16783-06-5; **2,** 16783-05-4; **3,** 53166-31-7; **4,** 7686-78-4; **5,** 53166-32-8; **6,** 53166-33-9; **7,** 53166-34-0; **7** picrate, 53166-35-1; **8,** 53166-36-2; **8** picrate, 53166-37-3; **9,** 53166-38-4; **11,** 53166-39-5; **11** methiodide, 53166-40-8; pyrrolidine, 123-75-1; isobutylene, 115-11-7; diethyl diazomalonate, 5256-74-6; tetramethylethylene, 563-79-1.

References and Notes

(1) (a) W. A. Bone and W. H. Perkin, *J. Chem. Soc.*, **67**, 108 (1895); (b) R. H. Best and J. F. Thorpe, *ibid.*, 685 (1909); (c) J. M. Stuart and H. H. Westberg, *J. Org. Chem.*, **30**, 1951 (1965); (d) J. E. Dolfini, K. Menich, P. Corliss, R. Cavanaugh, S. Danishefsky, and S. Chalsrabartly, *Tetrahedron Lett.*, 4421 (1966).

(2) The only striking exceptions to this rule are found in an instance of mercaptide attack[3] and in situations where the cyclopropane is part of an even more strained system.[4a,b]

(3) W. E. Truce and L. B. Lindy, *J. Org. Chem.*, **26**, 1643 (1961).

(4) (a) J. Meinwald and J. K. Crandall, *J. Amer. Chem. Soc.*, **88**, 1292 (1966); (b) A. G. Cook, W. C. Meyer, K. E. Ungrodt, and R. H. Mueller, *J. Org. Chem.*, **31**, 14 (1966).

(5) R. W. Kierstead, R. P. Linstead, and B. C. L. Weedon, *J. Chem. Soc.*, 3610 (1952).

(6) S. R. Poulter and C. H. Heathcock, *Tetrahedron Lett.*, 5339 (1968).

(7) M. Jones, Jr., A. Kulczycki, and K. F. Hummel, *Tetrahedron Lett.*, 183 (1967).

(8) J. M. Stewart and G. M. Pagenkopf, *J. Org. Chem.*, **34**, 7 (1969).

(9) S. Danishefsky and G. Rovnyak, *J. Chem. Soc., Chem. Commun.*, 821 (1972).

(10) A. B. Chmurny and D. J. Cram, *J. Amer. Chem. Soc.*, **95**, 4237 (1973), and following papers.

(11) In the case of **1** 46% is recovered after 50 hr at 110°. In the case of **1** only 7% is recovered after 50 hr at 100°. However, a precise ratio for the relative rates of ring opening is complicated by the formation of decarbethoxylation products **5** and **6** from **1** and some deterioration of starting materials under these forcing conditions.

(12) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N.Y., 1962, pp 197–202, and references therein.

(13) Boiling points are uncorrected. Infrared spectra were measured on a Perkin-Elmer 137 infracord spectrophotometer. Nmr spectra were obtained from a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard. Mass spectra were obtained from an LKB-9000 system *via* direct insertion. Combustion analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Ring-Opening Reactions of 2-Benzoylcyclopropane Isocyanate

Robert L. Augustine* and Frank G. Pinto

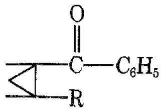
Department of Chemistry, Seton Hall University,
South Orange, New Jersey 07079

Received July 24, 1974

In an extension of some previous work it was felt that the mixed carbonic anhydrates of *cis-* (**1**) and *trans-* 2-benzoylcyclopropanecarboxylic acid (**2**)[1] could be used to prepare the benzoylcyclopropane isocyanates, **5** and **6**. These latter materials were required as intermediates in the synthesis of the benzoylcyclopropylamines which were to serve as models for the preparation of a series of azabicyclic compounds.

The anhydrides, **1** and **2**, were smoothly converted to the isomeric carboxazides, **3** and **4**, respectively, by reaction with sodium azide. These carboxazides rearranged to give the isomeric isocyanates, **5** and **6**, on refluxing in toluene.

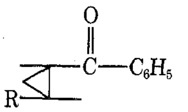
Reduction of either **5** or **6** with lithium aluminum hydride gave the same amino alcohol as shown by chromatographic and spectral comparisons of the two reduction products. The nmr spectrum of the diacetate of this compound was consistent with structure **7**, which was confirmed by direct synthesis. Reaction of phenylbutyrolactone (**9**) with methyl amine gave a hydroxyamide which on reduction with lithium aluminum hydride gave an amino alcohol, **8**, identical with that obtained on reduction of either **5** or **6**. Treatment of **8** with acetic anhydride gave **7**. This ring opening of **5** or **6** by lithium aluminum hydride was not unexpected since it had been shown previously that reaction of phenylcyclopropylamines with either lithium aluminum hydride[2] or base[3] caused ring cleavage. It was thought, though, that a phenyl substituent must be present on the cyclopropane ring in order for these reactions to occur.



$1,\ R = \underset{\overset{\|}{O}}{C}-O-\underset{\overset{\|}{O}}{C}-O-C_2H_5$

$3,\ R = \underset{\overset{\|}{O}}{C}-N_3$

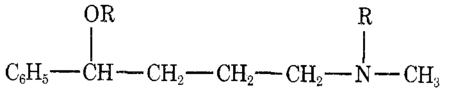
$5,\ R = N{=}C{=}O$



$2,\ R = \underset{\overset{\|}{O}}{C}-O-\underset{\overset{\|}{O}}{C}-O-C_2H_5$

$4,\ R = \underset{\overset{\|}{O}}{C}-N_3$

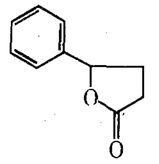
$6,\ R = N{=}C{=}O$



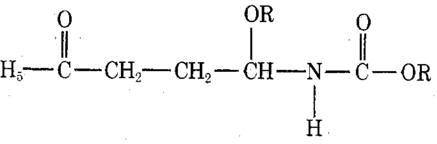
$C_6H_5-\overset{OR}{\overset{|}{C}}H-CH_2-CH_2-CH_2-\overset{R}{\overset{|}{N}}-CH_3$

7, R = $COCH_3$

8, R = H



9



$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{OR}{\overset{|}{C}}H-\underset{\underset{H}{|}}{N}-\overset{O}{\overset{\|}{C}}-OR$

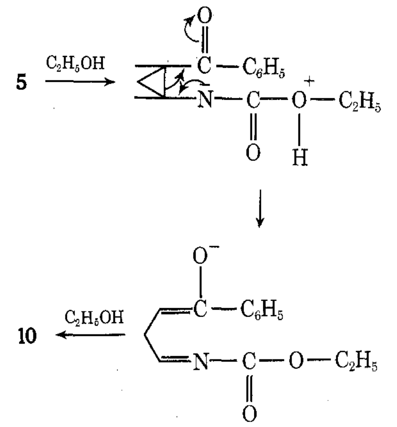
10, R = C_2H_5

11, R = C_3H_7

However, ring opening did not occur when either 2-phenoxycyclopropyl isocyanate[4] or 2-(2′,3′-methylenedioxyphenyl)cyclopropyl carboxazide[5] were converted to the corresponding carbamates on heating in alcohol. It was considered, then, that a similar reaction should be successful in converting either the carboxazide, **3** and **4**, or the isocyanates, **5** and **6**, into the corresponding cyclopropyl carbamates. When the carboxazide, **3**, was refluxed in ethanol a carbamate was obtained but the elemental analysis indicated that two molecules of alcohol were incorporated into the product. The nmr spectrum of this carbamate showed that the cyclopropane ring was no longer present but rather that the product was **10**. This was verified by lithium aluminum hydride reduction to the amino alcohol **8**. **10** was also obtained when either **4**, **5**, or **6** was refluxed in ethanol. The propyloxy carbamate, **11**, was obtained when the azides, **3** or **4**, or the isocyanates, **5** or **6**, were refluxed in *n*-propyl alcohol.

In contrast to the previous reports of ring stability during the reactions of cyclopropyl isocyanates[5] and carboxazides[4] with alcohol, this facile ring cleavage is due to the stabilization of the ring-opened anion by the carbonyl group as shown in Scheme I.

Scheme I



Experimental Section

All melting points are uncorrected. The infrared spectra were recorded using a Beckman IR-10 spectrophotometer and the nmr spectra were obtained using a Varian A-60A spectrometer with TMS as an internal standard.

***cis*-1-Benzoyl-2-cyclopropane Isocyanate (5).** *cis*-1-Benzoyl-2-cyclopropanecarboxylic ethylcarbonic anhydride (**1**) was prepared as previously described[1] from 4.08 g of *cis*-1-benzoyl-2-cyclopropanecarboxylic acid, 2.55 g of triethylamine, and 3.0 g of ethyl chloroformate in 75 ml of acetone. **1** was not isolated but was treated directly at 0° with a solution of 2.1 g of sodium azide in 8 ml of water. The resulting suspension was stirred for 1 hr at 0° and 1 hr at room temperature and then poured into cold water and extracted with ether. The dried ethereal solution ($MgSO_4$) was concentrated under reduced pressure to give ***cis*-1-benzoyl-2-cyclopropane carboxazide,** (**3**), as an oily residue: ir (toluene) 2140 cm^{-1} (CON_3).

A toluene solution of **3**, previously dried over $MgSO_4$, was slowly added to a flask heated on a steam bath. Decomposition was noted immediately with nitrogen being profusely evolved. The solution was heated until gas evolution ceased and then the toluene was removed under reduced pressure to give about 4 g of a red oil shown to be primarily **5** by its spectral properties: ir (neat) 2285 (N=C=O) and 1675 cm^{-1} (PhCO); no other carbonyl bands present.

***trans*-1-Benzoyl-2-cyclopropane isocyanate** (**6**) was prepared in very good yield from *trans*-1-benzoyl-2-cyclopropanecarboxylic ethylcarbonic anhydride (**2**)[1] using the procedure described for the preparation of the cis isomer, **5**: ir of **4** (toluene) 2140 cm^{-1} (CON_3).

The oil obtained from the decomposition of the carboxazide, **4**, was distilled and the product, **6**, collected at 103° (0.1 mm). Extensive decomposition occurred during the distillation. This distillate had an infrared spectrum identical with that of the crude material before distillation and was different from that of the cis isomer, **5**: ir (neat) 2280 cm^{-1} (N=C=O); nmr ($CDCl_3$) aromatic CH at δ 7.92 (m, 2) and 7.45 (m, 3) cyclopropyl CH at 3.28 (m, 1), 2.83 (m, 1), and 1.40 (m, 1).

***N*-Methyl-4-hydroxy-4-phenylbutylamine (8). Method A.** A solution of 17.0 g (0.073 mol) of **10** in 175 ml of tetrahydrofuran was added dropwise under an atmosphere of nitrogen to a suspension of 5.7 g (0.15 mol) of powdered lithium aluminum hydride in 300 ml of anhydrous ether at 0°. The reaction mixture was allowed to stir at room temperature overnight and for 3 hr at reflux. Twenty-five milliliters of water was then added dropwise and the resulting suspension was stirred for 0.5 hr and filtered. The filtrate was concentrated to an oil under reduced pressure, and the oil was dissolved in ether, dried ($MgSO_4$), and distilled to give 7.4 g (57.2%) of **8**: bp 99–108° (0.02 mm); ir (film) 3300 cm^{-1} (broad) (NH and OH).

Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.56; H, 9.50; N, 7.64.

8 was also obtained when **5**, **6**, or **11** was reduced with lithium aluminum hydride as described above.

Method B. Phenylbutyrolactone (**9**) was prepared according to the procedure described by Julia,[6] bp 97–98° (0.02–0.03 mm [lit,[6] bp 122° (0.1 mm)] ir (Nujol), 1780 cm^{-1} (lactone C=O). A solution 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.

***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 ($MgSO_4$). 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 ($CDCl_3$), δ 7.28 (s, 5, ArH), 5.77 (t, 1, Ph-CH), 3.28 (q, 2, CH_2-N), 2.83 (d, 3, $NHCH_3$), 2.02 (s, 3, $COCH_3$), 1.98 (s, 3, $COCH_3$), and 1.70 (m, 4, O-C-CH_2CH_2).

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 Ice–acetone 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 ($CHCl_3$) 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-CH_2CH_3), 3.58 (m, 2, O-CH_2CH_3), 3.08 (t, 2, $COCH_2$), 2.08 (q, 2, CH_2), 1.20 (t, 3, O-CH_2CH_3), and 1.15 (t, 3, O-CH_2CH_3).

Anal. Calcd for $C_{15}H_{21}NO_4$: 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 $C_{17}H_{25}NO_4$: 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.

References and Notes

(1) R. L. Augustine and F. G. Pinto, *J. Org. Chem.*, **33**, 1877 (1968).

(2) C. Kaiser, A. Burger, L. Zirngibl, C. S. Davis, and C. L. Zirkle, *J. Org. Chem.*, **27**, 768 (1962).

(3) H. M. Walborsky and P. E. Ronman, *J. Org. Chem.*, **38**, 4213 (1973).

(4) J. Finkelstein, E. Chiang, and J. Lee, *J. Med. Chem.*, **8**, 432 (1965).

(5) A. Burger, U. S. Patent 2,934,542 (1960); *Chem. Abstr.*, **54**, 16429 (1960).

(6) M. Julia, S. Julia, and B. Bemont, *Bull. Soc. Chim. Fr.*, 304 (1960).

Thermal [2 + 2] Cycloaddition of 1,1-Dimethoxyethene to the Carbonyl of 2-Ethoxy-3-indolone

Tad H. Koch,* John Olesen, and James Foy

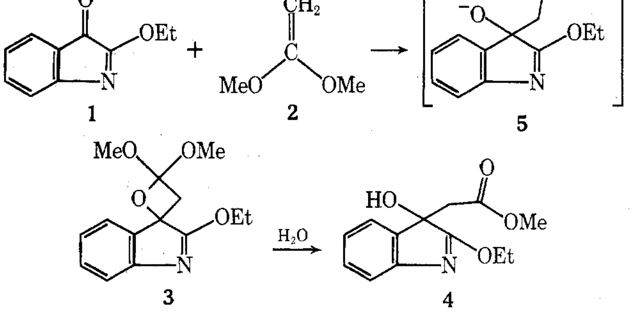
Department of Chemistry, University of Colorado, Boulder, Colorado 80302

Received August 9, 1974

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 hexafluoroacetone[3] and carbonyl cyanide[4] 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 considerations[6] 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