Photodecarbonylation of chiral cyclobutanones

Jailall Ramnauth and Edward Lee-Ruff

Abstract: Triplet photosensitized irradiation of 2(*S*),3(*R*)-bis[(benzoyloxy)methyl]cyclobutanone gave optically pure (−) *E*-1(*S*),2(*S*)-bis(benzoyloxymethyl)cyclopropane as a major product in the nonpolar fraction along with its stereoisomer and cycloelimination products. The absolute stereochemistry of the chiral cyclopropane was established by independent synthesis and X-ray crystal structure determination of a synthetic precursor. The distribution of decarbonylation and cycloelimination products was inversely dependent on the concentration of the substrate. Irradiation of the same ketone in tetrahydrofuran or benzene gave mostly cycloelimination products. Addition of Michler's ketone increased the ratio of photodecarbonylation, suggesting a triplet state pathway for this process. This was corroborated by the addition of dicyanoethylene, which showed significant quenching of photodecarbonylation. Irradiation of 2(*S*)-[(benzoyloxy)methyl]cyclobutane in acetone gave the corresponding cyclopropane as the principal product.

Key words: photodecarbonylation, chiral cyclopropanes, cyclobutanones, triplet sensitization.

Résumé : L'irradiation triplet photosensibilisée de la 2(*S*),3(*R*)-bis[(benzoyloxy)méthyl]cyclobutanone conduit au (−)-*E*-1(*S*),2(*S*)-bis(benzoyloxyméthyl)cyclopropane comme produit majeur de la fraction non polaire avec son stéréoisomère et des produits de cycloélimination. La stéréochimie absolue du cyclopropane chiral a été déterminée par une synthèse indépendante et par diffraction des rayons X d'un précurseur de synthèse. La distribution des produits de décarbonylation et de cycloélimination varie d'une façon inverse de la concentration du substrat. L'irradiation de la même cétone dans du tétrahydrofurane ou le benzène conduit principalement à des produits de cycloélimination. L'addition de la cétone de Michler augmente le rapport de photodécarbonylation; ceci suggère que le processus se produit par le biais d'un état triplet. Cette conclusion est corroborée par l'addition de dicyanoéthylène qui provoque une désactivation importante de la photodécarbonylation. L'irradiation du 2(*S*)-[(benzoyloxy)méthyl]cyclobutane dans l'acétone conduit au cyclopropane correspondant comme produit principal.

Mots clés : photodécarbonylation, cyclopropanes chiraux, cyclobutanones, sensibilisation triplet.

[Traduit par la rédaction]

Introduction

The photochemistry of cyclobutanones has been thoroughly investigated during the last three decades (1, 2). The primary process involves α-cleavage to a short-lived 1,4-acylalkyl diradical that can undergo one of three independent transformations: cycloelimination to ketene and olefin; ring expansion to a cyclic oxacarbene (2-tetrahydrofuranylidene); and decarbonylation, the latter normally representing a minor process unless structural features permit stabilization of a 1,3-diradical (e.g., presence of a 3-alkylidene group). Furthermore, sensitization experiments with simple cyclobutanones suggest that cyclopropane formation is a dominant pathway from the triplet state (3). Of the three photodecomposition pathways, the solution photodecarbonylation of cyclobutanones has received scant attention. This is largely due to the inefficiency of this process from direct irradiation, with singlet excited states giving rise to efficient cycloelimination and ring expansion as the result of strain effects. Triplet sensitized photochemistry of cyclobutanones appears to take a completely different course of events and is an area that has been relatively unexplored. The triplet sensitized photochemistry of a series of α-vinylcyclobutanones using either acetone or Michler's ketone (4,4′-bis(dimethylamino)benzophenone) as triplet sensitizers gave products derived from a 1,4-acyl alkyl diradical but different from the direct irradiation, in which case the usual cycloelimination and ring expansion pathways are observed (4). Chiral cyclobutanones are now readily accessible by a number of routes (5). The decarbonylation of these derivatives would involve a 1,4-acyl alkyl diradical whose lifetime would influence the extent of epimerization of the resultant cyclopropanes formed. It was of interest to investigate conditions under which chiral cyclopropanes could be produced from photodecarbonylation of chiral cyclobutanones. Chiral cyclopropanes are important intermediates in natural product synthesis and a variety of methods are available for their synthesis (6); however, only a few of these have been reported from ring contraction of chiral cyclobutane derivatives. With the availability of 2(*S*),3(*R*)-bis[(benzoyloxy)methyl] cyclobutanone **1**(*a*) and 2(*S*)-[(benzoyloxy)methyl]cyclobutanone **1**(*b*) in optically pure form (7, 8), we were interested in carrying out exploratory studies on the conditions under which cyclopropanes are efficiently produced by sensitized photodecarbonylation. We

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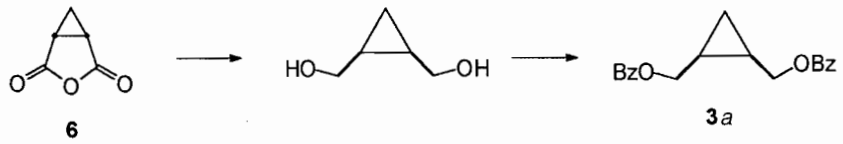
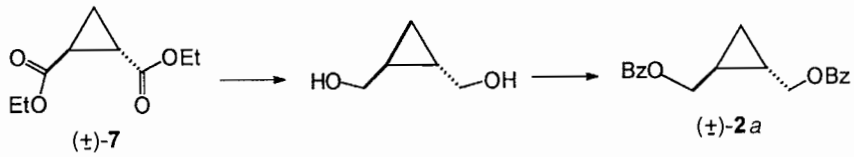
Scheme 1.



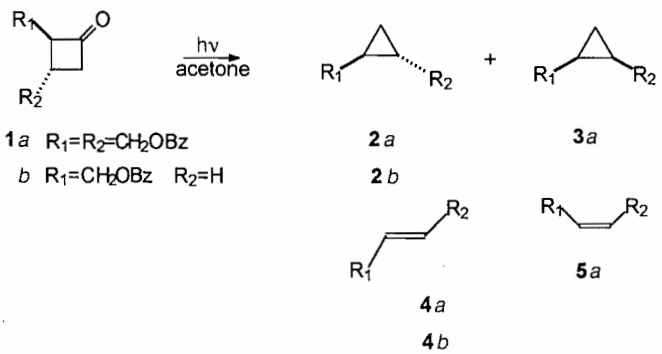
Scheme 2.



have reported the photochemistry of these derivatives under direct irradiation in the presence of purine bases as a novel method for producing ribonucleosides (8, 9). Decarbonylation of **1**(*a*) would produce two diastereomeric cyclopropanes **2**(*a*) and **3**(*a*), the latter derived from epimerization. The *E* isomer **2**(*a*) would be expected to be optically pure. Decarbonylation of **1**(*b*) would give achiral cyclopropane **2**(*b*).

Results and discussion

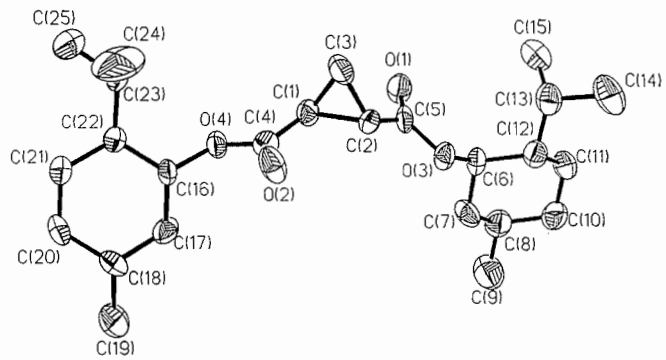
Cyclobutanone derivatives **1**(*a*) and **1**(*b*) were prepared according to literature methods (7, 8). The key step for the asymmetric synthesis of **1**(*a*) was the cycloaddition of dimen-



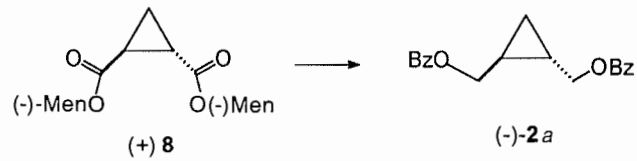
thyl fumarate with 1,1-dimethoxyethylene in the presence of a Lewis acid catalyst (7) giving greater than 98% diastereomeric enrichment. The preparation of optically pure **1**(*b*) was based on the enantioselective synthesis of a cyclobutane precursor from cycloaddition of 3-acryloyl-1,3-oxazolidin-2-one with 1,1-bis(methylthio) ethylene using a chiral titanium catalyst (10). This step occurred with an enantiomeric excess of greater than 98% (10).

Irradiation of a 6×10^{-3} M solution of **1**(*a*) in acetone for 4 h using a medium-pressure mercury lamp with unfiltered light gave a 25% conversion to a mixture of nonpolar compounds consisting of cyclopropanes **2**(*a*) (53%), **3**(*a*) (17%) and olefins **4**(*a*) (19%) and **5**(*a*) (11%). The structures of all photoproducts were assigned based on spectral data, elemental analysis, and independent synthesis. Olefin **5**(*a*) was prepared from benzoylation of *Z*-2-butene-1,4-diol. Its isomer **4**(*a*) was prepared by double nucleophilic substitution of *E*-1,4-dibromo-2-butene with potassium benzoate. Preparation of *Z*-1,2-bis(benzoyloxymethyl) cyclopropane (**3**(*a*))was based on

Fig. 1. X-ray crystal structure of (−) dimenthyl 1(*S*),2(*S*)-cyclopropanedicarboxylate (**+8**).



reduction of 1,2-cyclopropanedicarboxylic acid anhydride (**6**) followed by benzoylation (Scheme 1), whereas the racemic *E* isomer **2**(*a*) was prepared from commercially available diethyl *E*-cyclopropane-1,2-dicarboxylate (**7**) according to Scheme 2. That optically pure cyclopropane **2**(*a*) was produced in the photolysis of **1**(*a*) was established by the observed optical rotation of the nonpolar fraction. The measured specific rotation of **2**(*a*) was −7.5. To confirm the absolute configuration, cyclopropane (−)-**2**(*a*) was prepared from the known (−)-dimenthyl 1(*S*),2(*S*)-cyclopropane-1,2-dicarboxylate (**8**) (11).



We were not able to reproduce the literature procedure for the preparation of (+)-**8** from the methylenation of dimenthyl succinate with bromochloromethane under basic conditions (11). Our method for preparing (+)-**8** was based on the esterification of (±)-cyclopropane-1,2-dicarboxylic acid via the diacid chloride and separation of the diastereomeric diester by recrystallization from methanol. The optical purity of (+)-**8** was verified by matching the specific rotation ($[\alpha]_D$ = +17.5) with that reported in the literature ($[\alpha]_D$ = +17.8). Furthermore, the absolute configuration of (+)-**8** was confirmed by X-ray crystallographic analysis (Fig. 1). Reduction of (+)-**8** with lithium aluminum hydride followed by benzoylation gave

Table 1. Concentration dependence on the distribution (%) of products in acetone[a]

Conc. (10^{-3} M)	**2**(*a*)	**3**(*a*)	**4**(*a*)	**5**(*a*)	Cycl./olefin
5.6	12.4	3.9	4.4	2.8	2.3
3.0	16.5	5.1	3.4	3.4	3.2
1.5	20.3	5.1	3.3	1.6	5.2

[a]Yields were determined by HPLC analysis and calibration with standard solutions.

(±)-**2**(*a*) having identical spectral features with racemic (α)-**2**(*a*) and a specific rotation $[\alpha]_D = -7.5$ that was identical with the specific rotation for the sample obtained from photolysis.

A photostability study of each of the nonpolar photoproducts **2**(*a*)–**5**(*a*) under the irradiation conditions for **1**(*a*) indicated that cyclopropanes **2**(*a*) and **3**(*a*) were inert whereas olefins **4**(*a*) and **5**(*a*) underwent photoisomerization to give a 60:40 photoequilibrium mixture of **4**(*a*) and **5**(*a*). Thus olefin **5**(*a*) is a likely secondary photoproduct from the initially formed *E* isomer **4**(*a*). This photoequilibrium distribution of **4**(*a*) and **5**(*a*) was observed for all photolysis of **1**(*a*), indicating that photoequilibration competes with the primary photodecomposition.

The extent of photodecarbonylation as affected by substrate concentrations and nature of solvent was investigated. Decreasing concentrations led to increasing yields of cyclopropanes as seen in Table 1. This trend is what would be expected for solvent photosensitized processes. Direct excitation of ketone **1**(*a*) would be minimized under dilute conditions favouring triplet sensitized processes. Photolysis of **1**(*a*) in either tetrahydrofuran or benzene gave predominantly cycloelimination products **4**(*a*) and **5**(*a*) in the nonpolar fraction (Table 2). This latter observation further supports the speculation that decarbonylation of cyclobutanone is the consequence of triplet state decomposition. The formation of *cis*-olefin **5**(*a*) was somewhat surprising in view of the stereoselectivity of photocycloeliminations observed in other cyclobutanone derivatives (1). Further evidence for the intervention of the triplet state in the decarbonylation was obtained from irradiation of **1**(*a*) in THF in the presence of Michler's ketone (4,4′-dimethylamino)benzophenone) a known triplet photosensitizer for cyclobutanones (4). A significant increase in cyclopropane formation was observed under the photosensitized conditions (Table 2).[3] Quenching studies using dicyanoethylene (DCE) (13) showed significant reduction of photodecarbonylation dependent on the DCE concentration in the acetone photolysis (see Table 2). However, addition of DCE under the nonsensitized photolysis in THF did not supress the small amounts of cyclopropanes, indicating a minor singlet state route for photodecarbonylation.

Irradiation of ketone **1**(*b*) in acetone (6×10^{-3} M) gave efficient conversion to cyclopropane **2**(*b*) (86%) and olefin **4**(*b*) (10%). The identity of cyclopropane **2**(*b*) was established from its spectral data and independent synthesis from cyclopropane carboxylic acid as outlined in Scheme 3. The predominance for photodecarbonylation in ketone **1**(*b*) is probably associated with inefficient cycloelimination from β-cleavage of a secondary C—C bond as compared to a tertiary C—C bond in **1**(*a*).

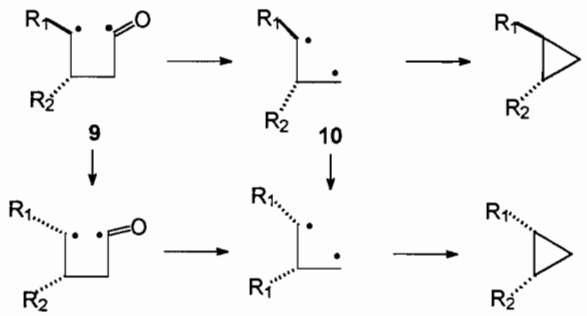
Table 2. Solvent dependence on distribution (%) of products[a]

Solvent	**2**(*a*)	**3**(*a*)	**4**(*a*)	**5**(*a*)	Cycl./olefin
Acetone	12.4	3.9	4.4	2.8	2.3
Acetone + 6×10^{-3} M DCE	10.2	3.6	6.2	3.5	1.43
Acetone + 2×10^{-2} M DCE	5.3	1.9	11.5	4.7	0.44
THF	1.8	0.2	8.7	6.4	0.13
Benzene	2.6	0.81	19.3	11.1	0.11
THF + MK[b]	5.4	2.2	8.1	5.2	0.57

[a]Yields were detemined by HPLC analysis and calibration with standard solutions. Concentration of **1**(*a*) was 5.6×10^{-3} M for all solutions.
[b]MK = Michler's ketone.

Scheme 3.

Scheme 4.



It has been shown that chiral cyclopropanes can be prepared from chiral cyclobutanones using acetone as a triplet sensitizer and solvent. The extent of epimerization at the α-carbon in the decarbonylation of cyclobutanones will depend on the lifetimes of the intermediate acyl-alkyl diradical **9** and the 1,3-diradical **10** (Scheme 4). Thermodynamic equilibration of these intermediates would give an epimeric mixture of cyclopropanes. However, 1,3-diradicals (trimethylene) generated from other precursors such as optically active pyrazolines retain their optical activity in the products (14, 15). These observations are rationalized in terms of the stereoselective ring-closure of these triplet trimethylenes. It would be expected that diradical **10** would be formed in the triplet state by spin conservation. Our results show that some epimerization takes place at the stereogenic radical site. Further studies on the triplet sensitized photochemistry of other chiral 2,4-disubstituted cyclobutanones are in progress.

[3] Although triplet-type photoreactions have been reported for cyclobutanones in the presence of Michler's ketone, energy transfer is endothermic. Evidence suggests an electron transfer process operating under these conditions (12).

Experimental

Melting points (mp) were determined on a Reichert melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker ARX 400 (400 MHz) spectrometer in $CDCl_3$ solutions containing 1% TMS. Optical rotations were measured using a Perkin–Elmer 241 polarimeter. HPLC analysis was performed on a Waters M-6000A instrument with a Lambda-Max model 481 LC detector using UV detection (254 mm), a Hewlett–Packard integrator, and a Spherisorb Silica analytical column from Sigma–Aldrich. Photolyses were carried out using a Hanovia 450 W medium-pressure mercury arc lamp in a water-cooled immersion well. Quartz tubes containing the samples were strapped around this well and the assembly immersed in an ice–water bath. The samples were degassed with argon for 30 min prior to irradiation. The X-ray crystal structure was performed on a Siemens R 3 m/v diffractometer using 1591 observed reflections. All solvents used in these reactions were dried and distilled. Analytical thin-layer chromatography (TLC) was done on commercially prepared silica gel 60F 254 plastic sheets (E. Merck & Co.). Preparative TLC was conducted on Aldrich silica gel 60F 254 precoated glass plates. Elemental analyses were performed by Guelph Chemical Laboratories Limited. The starting cyclobutanones **1**(*a*) and **1**(*b*) were synthesized according to literature methods (7, 8).

General photolysis procedures

A solution of ketone **1**(*a*) or **1**(*b*) in 70 mL of solvent ($\sim 10^{-3}$ M) was irradiated for 4 h (13 h for **1**(*b*)). The solvent was removed by rotoevaporation under reduced pressure. The residue was chromatographed on TLC plates (hexane:ethyl acetate, 95:5) to give a nonpolar fraction. The polar fraction was not analyzed but consisted of unreacted ketone and products containing an alcohol function. The nonpolar fraction was analyzed by analytical HPLC and comparison with synthesized samples as detailed below. Quenching studies with DCE were carried out under the same conditions using 6×10^{-3} M and 1.2×10^{-2} M solutions of DCE.

(±) E-1,2-Bis(benzoyloxymethyl)cyclopropane ((±) 2(a))

To a stirred suspension of $LiAlH_4$ (0.25 g, 6.44 mmol) in anhydrous ether (15 mL) at 0°C under argon was added diethyl *E*-1,2-cyclopropanedicarboxylate ((±)-**7**) (0.5 g, 2.7 mmol) in 20 mL ether. After 1 h, 3 mL of water was added and the solution filtered. To the filtrate was added anhydrous $MgSO_4$ and the solution was concentrated. ^{1}H NMR analysis of the residue showed the presence of the diol. Most of the diol remained in the filter cake. To the dry filter cake was added pyridine (10 mL), and benzoyl chloride (0.9 g, 6.0 mmol) was added dropwise with constant stirring. After 2 h, water (10 mL) was added to the reaction mixture and the organic layer was extracted with 50 mL ether, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was subjected to preparative TLC (benzene) to yield 70 mg (8.4%) of a white solid; mp 48–50°C; IR (KBr): 1715, 1600 cm^{-1}; ^{1}H NMR δ: 8.01–7.34 (m, 10H), 4.40–4.36 (dd, 2H, J = 5.8, 5.5 Hz), 4.48–4.04 (dd, 2H, J = 7.8, 4.0 Hz), 1.42–1.37 (m, 2H), 0.77–0.73 (t, 2H, J = 6.9 Hz). Anal. calcd. for $C_{19}H_{18}O_4$: C 73.55, H 5.81; found: C 73.42, H 5.71.

(−) Dimenthyl E-1(S), 2(S)-cyclopropanedicarboxylate ((+)8)

The title compound was prepared from (±)-cyclopropanedicarbonyl chloride which was prepared using the following procedures. A solution of diethyl *E*-1,2-cyclopropanedicarboxylate (±)-**7** (10 g, 53.7 mmol) in 100 mL of an aqueous methanol solution (9:1 methanol: H_2O) of 10% KOH was heated to reflux for 4 h. After cooling to room temperature, the mixture was diluted with 20 mL of H_2O and acidified with 50 mL of cold 6 M HCl. The solution was saturated with NaCl and extracted with 5 × 40 mL ether. The ether extract was dried over Na_2SO_4 and evaporated to yield 5.7 g of a white crystalline solid, mp 175–177°C (lit. (16) mp for *E*-1,2-cyclopropanedicarboxylic acid 175–177°C). To 4.6 g (38.4 mmol) of the dicarboxylic acid in 15 mL benzene was added 17 g (143 mmol) of $SOCl_2$. The mixture was heated to reflux for 4 h. The mixture was evaporated under reduced pressure. The residue was distilled (88°C, 10 Torr (1 Torr = 133.3 Pa) to give a colourless liquid of the acid chloride. ^{1}H NMR δ: 2.93–2.89 (t, 2H, J = 7.0 Hz), 1.91–1.88 (t, 2H, J = 7.2 Hz).

A solution of (−)-menthol (4.0 g, 25 mmol) in 3 g pyridine and 20 mL benzene was cooled in an ice–water bath. To this solution was added *E*-1,2-cyclopropanedicarbonyl chloride (2.0 g, 12.0 mmol) over a period of 20 min. The mixture was stirred for an additional 20 min at this temperature and for another 2 h at room temperature. After this time 50 mL of H_2O was added. The organic layer was extracted with 50 mL of ether and washed with 100 mL H_2O, dried over Na_2SO_4, and evaporated to yield 3 g (61%) of a white solid. This solid was dissolved in 50 mL of warm methanol. Colourless needles were obtained (1.2 g). An additional three recrystallizations gave optically pure (+)-**8** in 0.82 g (16.7%) yield; mp 94–95°C; $[\alpha]_D$ = +17.5 ($CHCl_3$, *c* 0.1), (lit. (11) $[\alpha]_D$ = +17.8 ($CHCl_3$, *c* 1.0)); IR (KBr): 1724 cm^{-1}. The absolute structure was confirmed by X-ray crystallography (Fig. 1).

(−) E-1(S),2(S)-Bis(benzoyloxymethyl)cyclopropane ((−)-2(a))

To a stirred suspension of $LiAlH_4$ (0.27 g, 1.1 mmol) in 20 mL of dry THF at 0°C under argon was added (−) dimenthyl *E*-1(*S*),2(*S*)-cyclopropanedicarboxylate ((+)-**8**) (0.7 g, 1.7 mmol) in 20 mL THF, dropwise over a period of 20 min. The reaction mixture was then heated to reflux for 4 h. After cooling in an ice–water bath the following were added sequentially:(1) 0.7 mL H_2O, (2) 0.7 mL of 15% aqueous NaOH, and (3) 2.1 mL of H_2O. The mixture was filtered and the precipitate washed with 200 mL of ether. The precipitate was subjected overnight to Soxhlet extraction with ether. The ether extracts were combined and evaporated and to the residue was added 20 mL H_2O, 1 mL methanol, and 20 mL hexane. The organic layer was separated and the aqueous layer was extracted with additional hexane (4 × 20 mL). The combined organic fractions were then washed with 10 mL H_2O. The combined aqueous layers were saturated with NaCl and extracted with ether (5 × 20 mL). The organic extract was dried over Na_2SO_4 and concentrated to give 50 mg (28.4%) of a colourless oil. To this material was added 1 mL of pyridine and the solution cooled to 0°C. Benzoyl chloride (0.25 mL) was added with constant stirring. The reaction mixture was allowed to warm to room temperature and stirred for an additional 2 h. After this time, 20 mL of H_2O was added. The mix-

ture was extracted with 50 mL ether, and the ether extract was washed with 2 × 40 mL of H_2O, 2 × 40 mL of a 5% aqueous HCl solution, 2 × 40 mL of a saturated $NaHCO_3$ solution, 2 × 100 mL H_2O, and dried over Na_2SO_4. The ether was evaporated to give 70 mg (13.1%) of a white solid identical in all respects (except for specific rotation) with racemic **2**(*a*) prepared above; mp 49–50°C; $[\alpha]_D = -7.5$ ($CHCl_3$, *c* 0.042).

*Z-1,2-Bis(benzoyloxymethyl)cyclopropane (**3**(a))*

To a stirred suspension of $LiAlH_4$ (0.16 g, 4.2 mmol) in 20 mL of THF at 0°C under argon, was added *Z*-1,2-cyclopropanedicarboxylic acid anhydride (**6**) (0.14 g, 1.25 mmol) in 10 mL THF, dropwise over a period of 20 min. The reaction mixture was stirred for an additional 20 min at this temperature and then heated to reflux for 3 h. After cooling to 0°C, the following were added sequentially: (1) 0.17 mL H_2O, (2) 0.17 mL of 15% aqueous NaOH, (3) 0.51 mL H_2O. The mixture was stirred for 20 min. To this mixture was added dropwise 10 mL of pyridine and 1.0 g of benzoyl chloride over a period of 10 min. The mixture was stirred at room temperature for 24 h. After this time, 20 mL of H_2O was added to quench the excess benzoyl chloride. The reaction mixture was then filtered and the filter cake was washed with 50 mL of ethyl acetate. The filtrate was washed with 200 mL of H_2O, 200 mL of saturated $NaHCO_3$, 200 mL of a 5% aqueous HCl solution, and 200 mL of H_2O. The organic layer was dried over Na_2SO_4 and evaporated to give 0.2 g (52%) of a yellow oil. The residue was chromatographed on two preparative TLC plates to give 0.1 g of an oil (benzene); IR: 1717, 1602 cm^{-1}; ^1H NMR δ: 8.10–7.41 (m, 10H), 4.66–4.62 (dd, 2H, J = 6.1, 6.8 Hz), 4.23–4.18 (dd, 2H J = 8.6, 3.0 Hz), 1.57–1.51 (m, 2H). Anal. calcd. for $C_{19}H_{18}O_4$: C 73.55, H 5.81; found: C 73.21, H 5.77.

E-*1,4-Bis(benzoyloxy)-2-butene (**4**(a))*

Potassium benzoate (8.0 g, 50 mmol) was dissolved in 25 mL of 0.1 M NaOH and 200 mL acetonitrile. The solution was heated to reflux. To this solution was added *E*-1,4-diromo-2-butene (5.0 g, 23 mmol) in one portion. The mixture was heated under reflux with constant stirring for 4 h. After this time, the mixture was poured into 25 mL of a 0.1 M HCl solution with constant stirring. The diester was filtered off and washed several times with a 5% $NaHCO_3$ aqueous solution. The solid was recrystallized from methanol to afford 3.4 g (50%) of a white crystalline solid; mp 102–103°C (lit. (17) mp 100–101°C); ^1H NMR δ: 8.08–7.43 (m, 10H), 6.08–6.07 (t, 2H), 4.88–4.87 (d, 4H).

*Z-1,4-Bis(benzoyloxy)-2-butene (**5**(a))*

A solution containing *Z*-2-butene-1,4-diol (3 g, 34 mmol) in pyridine (6 g, 76 mmol) was cooled to 0°C. Benzoyl chloride (10.5 g, 75 mmol) was added dropwise over a period of 30 min. The mixture was allowed to warm to room temperature and stirring continued for an additional 2 h. After this time, 50 mL of water was added. The diester was filtered and recrystallized from 95% ethanol giving 7.0 g (70%) of a white crystalline solid; mp 66–67°C (lit. (17) mp 66–67°C); ^1H NMR δ: 8.06–7.41 (m, 10H), 5.96–5.95 (t, 2H), 5.04–5.00 (d, 4H).

*Benzoyloxymethylcyclopropane (**2**(b))*

A suspension of $LiAlH_4$ (0.57 g, 15.0 mmol) in 50 mL of anhydrous ether was cooled to 5°C. To this suspension was added dropwise a solution of cyclopropanecarboxylic acid (1 g, 11.6 mmol) in 20 mL ether over a period of 30 min. The reaction mixture was stirred at this temperature for an additional 30 min, then heated to reflux for 2 h. After cooling to 5°C the following were added sequentially: (1) 0.6 mL H_2O, (2) 0.6 mL of 15% aqueous NaOH, (3) 1.8 mL of water. The mixture was stirred for an additional 30 min and filtered. The precipitate was washed with 200 mL ether. The combined ether solution was concentrated to give 0.78 g of cyclopropane-methanol, which was used for the next step without purification. The crude alcohol was dissolved in 15 mL pyridine and cooled to 5°C. To this solution was added dropwise 2.3 g (16.4 mmol) of benzoyl chloride over a period of 15 min. This mixture was allowed to warm to room temperature and stirred overnight. After this time, 2 mL of H_2O was added. The solution was concentrated under reduced pressure and partitioned using 100 mL ethyl acetate and 200 mL H_2O. The organic layer was washed with 2 × 100 mL H_2O, 4 × 100 mL saturated $NaHCO_3$, and 2 × 100 mL of water. After drying over Na_2SO_4 the organic layer was concentrated under reduced pressure to give 1.4 g (68%) of the title compound as an oil; IR: 1718, 1602 cm^{-1}; ^1H NMR δ: 8.08–7.41 (m, 5H), 4.16 (d, 2H, J = 7.4 Hz), 1.28–1.24 (m, 1H), 0.63–0.59 (m, 2H), 0.38–0.35 (m, 2H). Anal. calcd. for $C_{11}H_{12}O_2$: C 74.97, H 6.86; found: C 75.00, H 6.97.

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