by photochemical reduction of 1-benzyl-3-carbamoylpyridinium cation have obtained a dimer, to which they assigned a 6,6′-linked structure by comparison with the product reported by Wallenfels.[14] Consequently, the Kano's photoproduct as well is identical to **2** and therefore must be regarded as a 4,4′-linked dimer.

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Facile Preparation of Optically Active *c*-2,*t*-3-Dimethyl-*r*-1-methoxycyclopropane

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The thermal chemistry of cyclopropane and its derivatives has attained considerable theoretical importance.[3] Elegant experimental studies[4] have complemented and supported the earlier conceptual insights. Mechanistic attention is now shifting to an understanding of substituent and activation effects on reaction stereochemistry as well as the correspondence of observed kinetic parameters with the thermochemical estimates.

For the detailed investigation of the rearrangement chemistry of 2,3-dimethyl-*r*-1-methoxycyclopropane[5,6] and an eventual determination of the dynamic stereochemistry of the stereomutation process, we required each enantiomer of the chiral isomer (**7**). In this note we present a convenient as well as reliable synthesis of optically active *c*-2,*t*-3-dimethyl-*r*-1-methoxycyclopropane (**7**).

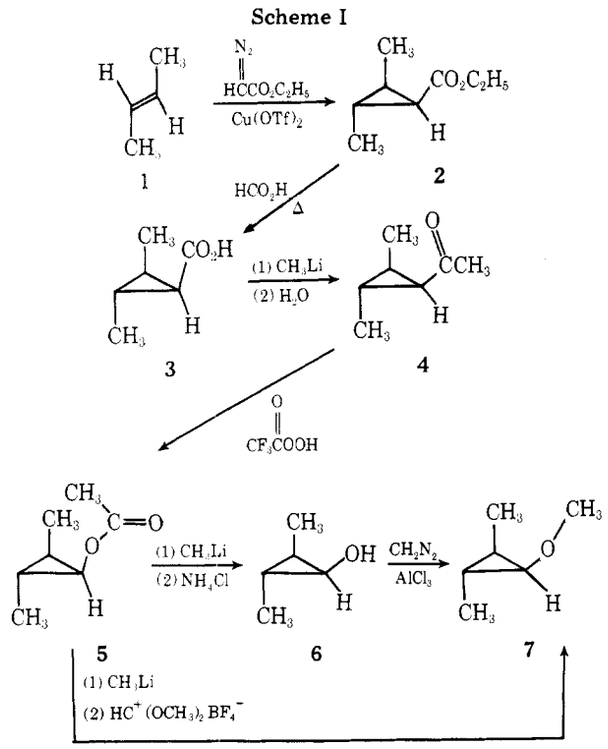
Results and Discussion

Our approach to the preparation of optically active cyclopropane **7** was patterned after the generalized DePuy synthesis[7] of cyclopropanols as illustrated in Scheme I.

The cupric trifluoromethanesulfonate catalyzed cyclopropanation of *trans*-2-butene (**1**) was accomplished in 33% isolated yield.[9,10] Basic saponification of the ethyl *c*-2,*t*-3-dimethyl-*r*-1-cyclopropanecarboxylate (**2**) was found to be unreliable, but transesterification with formic acid[11] afforded *c*-2,*t*-3-dimethylcyclopropane-*r*-1-carboxylic acid (**3**) in 82% yield. The resolution of **3** was achieved through fractional recrystallization of the diastereomeric quinine salts.[12] Optically active carboxylic acid **3** was then transformed into optically active *c*-2,*t*-3-dimethyl-*r*-1-methoxycyclopropane (**7**) through a sequence beginning with a methyllithium treatment and subsequent hydrolysis. Baeyer–Villiger oxidation of the resulting methyl ketone with trifluoroperacetic acid, treatment with methyllithium to produce the cyclopropanol **6**, and immediate methylation with diazomethane catalyzed by boron trifluoride etherate or aluminum trichloride[13] completed the synthesis. An alternate direct conversion of the acetate **5** into the ether **7** employing methyllithium treatment and subsequent reaction with dimethoxycarbonium tetrafluoroborate[14] was less effective.

The overall yield of **7** was 2.7% based on ethyl diazoacetate. The optically active cyclopropyl ether **7**, with $[\alpha]^{22}_{237}$ +13.4°, was found to be chromatographically and spectroscopically identical with an authentic sample obtained from the Schöllkopf reaction between *trans*-2-butene, dichloromethyl methyl ether, and methyllithium.[15]

Scheme I



Experimental Section

^{1}H NMR spectra were obtained on a Varian T-60 instrument. Infrared spectra were recorded on a Beckman IR-20 spectrophotometer. Mass spectra were secured on a Finnigan 1015D quadrupole mass spectrometer with a variable leak inlet, an ion source temperature of 55 °C, and an ionization potential of 70 eV. Analytical and preparative gas chromatographic separations were achieved on Varian Model A90-P and 1400 instruments. Optical rotations were obtained on a Perkin-Elmer Model 241 polarimeter.

Cupric Trifluoromethanesulfonate.[16] In a 750-mL conical flask was placed 12.5 g (101 mmol) of cupric carbonate in 280 mL of acetonitrile. To the stirred suspension, 25.0 g (167 mmol) of trifluoromethanesulfonic acid was cautiously added over 10 min. The reaction mixture was stirred an additional 30 min, filtered into a 1-L round-bottom flask, and concentrated under reduced pressure to give a blue solid which was dried by heating in the same vessel with a Fisher burner at 0.1 Torr to give 28.9 g (96%) of cupric trifluoromethanesulfonate.

(±)-Ethyl *c*-2,*t*-3-Dimethyl-*r*-1-cyclopropanecarboxylate (2).[9,10] *trans*-2-Butene (1.2 L) was condensed in a 5-L round-bottom flask fitted with an addition funnel, a dry ice–acetone cooled condenser,[17] a nitrogen inlet, and a paddle stirrer. Anhydrous ethyl ether (1 L) and finely ground cupric trifluoromethanesulfonate (20.0 g, 55 mmol) were added to the flask before ethyl diazoacetate[8] (82.0 g, 720 mmol) in ethyl ether was added dropwise over 1.5 h. The solution was allowed to reflux as it was stirred for 4.5 h. It was then stirred without the reflux condenser for 2 h as the alkene was boiled off. A solution of 50% ammonium hydroxide was added to the dark residue until two distinct phases were formed. Ammonium hydroxide washes were continued until clear. After washing with water (3 × 75 mL), the ethereal solution was dried ($MgSO_4$), filtered, and concentrated by distillation [bp 34–37 °C (9 Torr)] to give 34.0 g (33%) of **2**, which was identified from its ^{1}H NMR [(60 MHz, $CDCl_3$) δ 4.18 (ester methylene, q, J = 7 Hz, 2 H) and 1.60–0.93 (methyl and cyclopropyl, m, 12 H)], IR [(neat film) $\bar{\nu}_{CH}$ 3010–2885, $\bar{\nu}_{C=O}$ 1755, and $\bar{\nu}_{C-O}$ 1240 cm^{-1}], and electron impact mass spectra [(70 eV) *m/e* 142 (M^+), 127 ($M^+ - CH_3$), 97 ($M^+ - C_2H_5O$), and 69 ($M^+ - C_2H_5CO_2$)].

(±)-*c*-2,*t*-3-Dimethyl-*r*-1-cyclopropanecarboxylic Acid (3). A 500-mL three-neck round-bottom flask was fitted with an addition funnel and a nitrogen inlet, as well as with a distillation head and condenser. The flask was charged with 63.0 g (440 mmol) of (±)-ethyl *c*-2,*t*-3-dimethyl-*r*-1-cyclopropanecarboxylate (**2**), formic acid (5.1 g, 110 mmol), and 2 drops of concentrated sulfuric acid. Ethyl formate was distilled from the mixture at 54 °C while additional formic acid (25.3 g, 550 mmol) was added at a rate equal to the distillation throughput rate. The distillation was continued until only formic acid was being collected. Vacuum distillation [bp 52–54 °C (0.2 Torr)] afforded 41.3 g (82%) of (±)-*c*-2,*t*-3-dimethyl-*r*-1-cyclopropanecarboxylic acid (**3**), whose structure was confirmed from its ^{1}H NMR [(60

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MHz, $CDCl_3$) δ 12.04 (carboxyl, s, 1 H) and 1.41–0.62 (methyl and cyclopropyl, m, 9 H)] and IR spectra [(neat film) $\bar{\nu}_{OH}$ 3520–3160, $\bar{\nu}_{C-H}$ 2880, $\bar{\nu}_{C=O}$ 1695, and $\bar{\nu}_{C-O}$ 1240 cm^{-1}], as well as from the electron impact mass spectrum (70 eV) of the corresponding methyl ester (from a diazomethane treatment) [*m/e* 128 (M^+), 113 ($M^+ - CH_3$), 97 ($M^+ - CH_3O$), and 69 ($M^+ - CH_3CO_2$)].

(−)-*c*-2,*t*-3-Dimethyl-*r*-1-cyclopropanecarboxylic Acid [(−)-3]. Diastereomeric salts were prepared from (±)-*c*-2,*t*-3-dimethyl-*r*-1-cyclopropanecarboxylic acid (**3**; 32.0 g, 280 mmol) and quinine monohydrate (50.0 g, 150 mmol) in 400 mL of absolute ethanol in a 3-L round-bottom flask. The mixture was heated at reflux for 1 h before 1.6 L of water was added. After 24 h, the crystals were collected (60.5 g; mp 124–126 °C) and redissolved in 2:1 water/ethanol. After an additional 60 h, the crystals were collected (36.0 g; mp 134–136 °C), redissolved in 1:1 water/ethanol, and allowed to stand for an additional 48 h. The collected crystals (34.4 g; mp 137–138 °C) were heated with aqueous methanol at 70 °C. After removing the methanol by distillation, the aqueous solution was made acid with dilute hydrochloric acid. The product was extracted into ether (5 × 50 mL), washed with water (3 × 30 mL), dried ($MgSO_4$), filtered, and distilled [bp 74–76 °C (6–8 Torr)] to give 5.5 g (17%) of (−)-*c*-2,*t*-3-dimethyl-*r*-1-cyclopropanecarboxylic acid (**3**), $[\alpha]^{22}_{589}$ −23.72° (*c* 0.0137, C_2H_5OH).[12,19]

(−)-*c*-2,*t*-3-Dimethyl-*r*-1-cyclopropane Methyl Ketone [(−)-4]. To a 2-L three-neck round-bottom flask fitted with a magnetic stirring bar, addition funnel, and reflux condenser was added (−)-*c*-2,*t*-3-dimethyl-*r*-1-cyclopropanecarboxylic acid [(−)-**3**; 6.1 g, 54 mmol] and 250 mL of anhydrous ether. Methyllithium (370 mmol) in ethyl ether was rapidly added, and the reaction mixture was subsequently heated at reflux for 1 h. The reaction was quenched with saturated ammonium chloride solution and extracted into ether. After washing with water (3 × 50 mL), drying ($MgSO_4$), and filtering, the optically active product[20] (4.68 g, 82%) was isolated by distillation: bp 44–48 °C (32 torr); $[\alpha]^{22}_{589}$ −27.17° (*c* 0.0138, C_2H_5OH). The structure of the product was confirmed from its ^1H NMR [(60 MHz, $CDCl_3$) δ 2.08 (methyl, s, 3 H), 1.57 (methine, m, 1 H), and 1.28–0.90 (methyl and cyclopropyl, m, 8 H)], IR [(neat film) $\bar{\nu}_{C-H}$ 3010–2880 and $\bar{\nu}_{C=O}$ 1685 cm^{-1}], and electron impact mass spectra [(70 eV) *m/e* 112 (M^+), 97 ($M^+ - CH_3$), and 69 ($M^+ - CH_3CO$)].

(−)-*c*-2,*t*-3-Dimethyl-*r*-1-cyclopropyl Acetate [(−)-5]. In a 250-mL three-neck round-bottom flask fitted with a magnetic stirring bar, addition funnel, and reflux condenser was placed (−)-*c*-2,*t*-3-dimethyl-*r*-1-cyclopropyl methyl ketone (4.7 g, 42 mmol), sodium hydrogen phosphate (28.3 g, 200 mmol), and methylene chloride (50 mL). Freshly prepared trifluoroperacetic acid [from freshly distilled trifluoroacetic anhydride (20.8 g, 104 mmol) and 90% hydrogen peroxide (4 mL)] was added to the mixture at a rate which produced a steady reflux. The reaction mixture was stirred and heated at reflux for 8 h. After washing with saturated ammonium chloride (3 × 15 mL) and water (3 × 15 mL), the product was extracted into ether (5 × 25 mL), dried ($MgSO_4$), filtered, and distilled [bp 46–48 °C (30 torr)] to yield 3.6 g (67%) of the optically active acetate, $[\alpha]^{22}_{589}$ −44.88° (*c* 0.0088, C_2H_5OH). The product structure was confirmed from its ^1H NMR [(60 MHz, $CDCl_3$) δ 3.65 (methine, m, 1 H), 1.98 (acetate methyl, s, 3 H), 1.2–0.9 (ring methyls, m, 6 H), and 0.9–0.4 (cyclopropyl, m, 2 H)], IR [(neat film) $\bar{\nu}_{C-H}$ 3020–2890, $\bar{\nu}_{C=O}$ 1755, and $\bar{\nu}_{C-O}$ 1240 cm^{-1}], and electron impact mass spectra [(70 eV) *m/e* 128 (M^+), 113 ($M^+ - CH_3$), and 69 ($M^+ - CH_3CO_2$)].

(+)-*c*-2,*t*-3-Dimethyl-*r*-1-methoxycyclopropane (7). To a 250-mL three-neck round-bottom flask fitted with a magnetic stirring bar and an addition funnel containing (−)-*c*-2,*t*-3-dimethyl-*r*-1-cyclopropyl acetate (**5**; 3.0 g, 24 mmol) in 100 mL of anhydrous ether was added freshly prepared methyllithium (52 mmol) in ether. After stirring the reaction mixture for 1 h at room temperature, saturated boric acid solution was added (30 mL) and the organic phase was dried ($MgSO_4$), filtered, and analyzed by infrared spectroscopy; $\bar{\nu}_{C=O}$ at 1755 cm^{-1} had disappeared and a $\bar{\nu}_{O-H}$ at 3650–3150 cm^{-1} had appeared, indicating the presence of the cyclopropanol **6**. Aluminum chloride (50 mg) was added to the ethereal solution before diazomethane[18] was bubbled through in a stream of nitrogen. The reaction was followed by infrared spectroscopy, where the disappearance of $\bar{\nu}_{O-H}$ after 10 h signaled the end of the reaction. (+)-*c*-2,*t*-3-Dimethyl-*r*-1-methoxycyclopropane was isolated in 18% yield by preparative gas chromatography utilizing a 4.6 m × 3.2 mm, 10% SE-30 on Chromosorb W stainless steel column operated at 75 °C, $[\alpha]^{22}_{237}$ +13.4° (*c* 0.095, C_2H_5OH). The optically active product was found to be identical both chromatographically and spectroscopically with authentic racemic material.[15]

(±)-*c*-2,*t*-3-Dimethyl-*r*-1-methoxycyclopropane (7). An authentic sample of the cyclopropyl ether was prepared by the method of Schöllkopf.[15]

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Registry No.—**1**, 624-64-6; **2**, 56711-67-2; (±)-**3**, 02431-63-4; (−)-**3**, 20431-71-4; (−)-**3** quinine salt, 66791-91-1; (+)-**3**, 20431-72-5; (+)-**3** quinine salt, 66791-92-2; (−)-**4**, 66769-48-0; (+)-**4**, 66791-93-3; (−)-**5**, 66769-49-1; **6**, 13830-35-8; (+)-**7**, 66791-94-4; cupric trifluoromethanesulfonate, 34946-82-2; cupric carbonate, 36386-77-3; trifluoromethanesulfonic acid, 1493-13-6; ethyl diazoacetate, 623-73-4; quinine, 130-95-0.

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(20) An identical procedure from (+)-**3** gave (+)-**4**,[19] $[\alpha]^{22}_{589}$ +5.38°.

A Novel and Convenient Synthesis of Dibenz[*a*,*c*]anthracene

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Dibenz[*a*,*c*]anthracene (**1**) is a relatively rare and expensive polycyclic hydrocarbon available synthetically only through complex multistep procedures.[1] Consequently, relatively little is known concerning its chemistry or that of its derivatives, few of which are known.[1] However, **1** has been found to be a weak tumor initiator,[2] stimulating interest in its chemical and biological properties and the nature of its potentially activated metabolite(s).

We now wish to report an unexpectedly simple and conve-

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