TABLE II
REACTION OF ESTER WITH ALKYL HALIDE[a]

Ester[d] (mmol)	Halide[d] (mmol)	Cu_2O, mmol	*t*-BuNC, mmol	Time, hr	Product yield,[b] %
CH_3COOPh (10) (122-79-2)	$PhCH_2Cl$ (10) (100-44-7)	5	20	12	CH_3COOCH_2Ph 43[c] $PhOCH_2Ph$ 45[c]
CH_3COOPh (10)	*n*-BuBr (40) (109-65-9)	10	20	5	CH_3COO-*n*-Bu 40 PhO-*n*-Bu 41
$PhCOOCH_2Ph$ (10) (120-51-4)	*n*-BuBr (50)	10	15	8	PhCOO-*n*-Bu 38 $PhCH_2O$-*n*-Bu 36

[a] A mixture of ester with alkyl halide was heated at 80° in 10 ml of benzene under nitrogen. [b] Yield was determined by glpc analysis and calculated on the basis of ester. [c] Calculated on the basis of benzyl chloride. [d] Registry numbers are in parentheses.

In the two reactions of eq 5–7 and 8, a stoichiometric amount of Cu_2O is converted into Cu(I) halide. The formation of Cu(I) alkoxide requires alkyl halide.

Experimental Section

Materials.—Cu_2O and Cu(II) acetate were commercial reagents of analytical grade and were dried under nitrogen prior to use. Cu(I) acetate was prepared under nitrogen according to Calvin's method.[4,5] *tert*-Butyl isocyanide was prepared according to Ugi's procedure.[11] (−)-(*S*)-Phenethyl alcohol, $[\alpha]^{25}D$ −45.6° (*c* 3.29, cyclohexane) (lit. $[\alpha]^{23}D$ −45.5°),[12] was prepared according to Kenyon's method,[12] and was converted to (+)-(*R*)-phenethyl bromide, $[\alpha]^{25}D$ +58.6° (*c* 3.94, cyclohexane) (lit. $[\alpha]^{22}D$ +130.96°)[8] (optical purity 45%), according to a published method of Gerrard.[8]

Preparation of 1:1 Complex of Cu(I) Acetate–*t*-BuNC (3).—All the reagents were carefully dried and distilled under nitrogen. Under nitrogen, a mixture of acetic acid (34 mmol), Cu_2O (17 mmol), and *t*-BuNC (34 mmol) was heated in 24 ml of benzene at 80° for 2.5 hr. During the reaction, the production of water was observed. After filtration, the filtrate was subjected to evaporation *in vacuo* (10 mm). Then 20 ml of benzene was added and recrystallization was carried out by warming the mixture up to 80°. This procedure was repeated three times. The white residue was dried *in vacuo* (2–3 mm) at 80° for 12 hr (**3**, 1.85 g, 53% on the basis of Cu_2O). **3** was sensitive to air. When **3** was exposed to air in solid state, it turned light blue gradually, and in benzene solution it turned greenish blue immediately. Cu(I) acetate–*t*-BuNC (**3**) had nmr (CD_3CN) τ 8.51 (singlet, CH_3– and *tert*-butyl protons at the same position); ir (KBr) 2169 (C≡N), 1585, 1560 (COO), 1410, 1235, 1210 cm^{-1} (*tert*-butyl group).

Anal. Calcd for $C_7H_{12}NO_2Cu$: C, 40.87; H, 5.88; N, 6.81; Cu, 30.98. Found: C, 40.83; H, 6.13; N, 6.80; Cu, 30.40.

Preparation of 1:1 Complex of Cu(I) Benzoate–*t*-BuNC Complex.—A similar procedure was carried out with benzoic acid. The 1:1 complex was obtained: nmr (CD_3CN) τ ~2.6 (5 H), 8.55 (9 H); ir (KBr) 3060 (phenyl), 2168 (C≡N), ~1600, 1570 cm^{-1} (COO and phenyl).

Reaction of 3 or Cu(I) Acetate with (+)-(*R*)-Phenethyl Bromide. A.—Under nitrogen, **3** (4 mmol) was mixed with *t*-BuNC (2 mmol) in 5 ml of benzene. The solution became clear by the addition of *t*-BuNC. To this mixture, (+)-(*R*)-phenethyl bromide (2.35 mmol) was added dropwise at room temperature. The reaction mixture was stirred for 30 min at room temperature. Then it was elevated up to 45° and allowed to react for 2 hr. After the reaction, 30 ml of *n*-pentane was added to remove Cu-Br–*t*-BuNC by filtration. The filtrate was condensed at room temperature by evaporation *in vacuo* (10 mm). Analysis by glpc showed that the reaction was quantitative. The product ester was purified by preparative glpc. The specific rotation of the ester was $[\alpha]^{25}D$ −41.6° (*c* 6.27, cyclohexane), being opposite in sign to the original halide. This sign was the same as that obtained from the reaction of (−) alcohol with acetic acid anhydride.[7]

B.—The reaction of Cu(I) acetate with (+)-(*R*)-phenethyl bromide was carried out at 50° for 3 hr by a similar procedure. Yield of the ester was over 90%. The specific rotation of the product ester was $[\alpha]^{25}D$ −0.3° and $[\alpha]^{25}_{350}$ −1.5° (*c* 6.62, cyclohexane). By a reference experiment, it was confirmed that the optical active ester obtained in the above reaction (A) was not racemized under the reaction conditions.

Reaction of Ester with Alkyl Halide by Cu_2O–*t*-BuNC.—A typical procedure is as follows. Under nitrogen, a mixture of Cu_2O (5 mmol), phenyl acetate (10 mmol), and *t*-BuNC (20 mmol) in benzene was stirred at 80° for 5 min, and then benzyl chloride (10 mmol) was added dropwise and heated for 12 hr. Then 20 ml of petroleum ether was poured into the cooled reaction mixture. The precipitated CuCl–*t*-BuNC and some unreacted Cu_2O were removed by filtration. The yields of products were determined by glpc analysis of the filtrate. Benzyl acetate and benzyl phenyl ether were obtained in the yield of 42.5 and 44.5%, respectively. Dibenzyl ether was not detected in the reaction mixture. The product structures were determined by comparison of nmr and ir with those of the authentic sample.

Reaction of Benzyl Chloride by Cu_2O–*t*-BuNC.—Under nitrogen, a mixture of benzyl chloride (20 mmol), Cu_2O (10 mmol), and *t*-BuNC (20 mmol) was heated at 80° for 12 hr. *n*-Pentane was added to remove CuCl–*t*-BuNC and the unreacted Cu_2O by filtration. The yield of product was determined by glpc analysis of filtrate. Dibenzyl ether was obtained in a yield of 51% (on the basis of Cu_2O).

Registry No.—Acetic acid, 64-19-7; Cu_2O, 1317-39-1; *t*-BuNC, 7188-38-7; benzoic acid, 65-85-0; Cu(I) benzoate–*tert*-butyl isocyanide complex, 38641-30-4; benzyl ether, 103-50-4.

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Nucleophilic Methanolysis of 1-Acetyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (2-Acetylquadricyclene) and Methyl 1-Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane carboxylate (2-Carbomethoxyquadricyclene)

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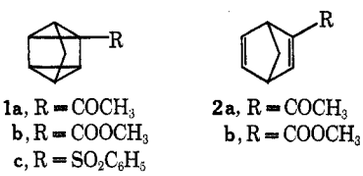
Although electrophilic additions to saturated, strained carbocyclic systems are commonplace, the corresponding nucleophilic additions are rare. Thus, such reactions as the alcoholysis of strained carbon linkages are usually feasible only in the presence of electrophilic catalysts (*e.g.*, H^+, Ag^+, etc.). We wish to report, however, that α-carbanion stabilizing substituents, such as the acetyl group, render the quadricyclene skeleton exceedingly reactive toward methanolysis not only under basic conditions but even in neutral solvent.

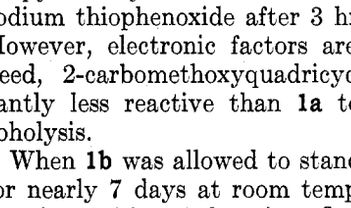
2-Acetylquadricyclene (**1a**), previously unreported, was prepared in nearly quantitative yield by sensitized

irradiation of 2-acetybicyclo[2.2.1]heptadiene (**2a**),[1] and characterized by its elemental composition, spectra, and Pd(II)-catalyzed cycloreversion to **2a**. When **1a** was treated with absolute methanol, a rapid, exothermic reaction ensued. Subsequent removal of excess solvent left crude 3-acetyl-5-methoxynortricyclene (**3a**, 95%) as a mixture (*ca.* 50:50) of C-3 epimers. The structure assigned to **3a** was inferred from its spectral and analytical data. In particular, the nmr spectrum exhibits two acetyl proton singlets at τ 7.87 and 7.93, one for each epimer, and two methoxy proton singlets at 6.77 and 6.79. The near-infrared spectrum of **3a** between 1.6 and 1.8 μ, the first C–H stretching vibration overtone region, closely resembles the published spectrum of parent nortricyclene,[2] while the infrared spectrum shows characteristic nortricyclene skeletal absorption at 12.35 μ.[3a-c]

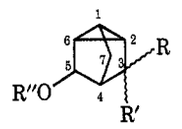
The assignment of C-3 rather than C-5 as the epimeric carbon atom was confirmed by treatment of *ca.* 50:50 *exo*:*endo*-**3a** with sodium methoxide in methanol-*O*-*d*. All hydrogen atoms α to the carbonyl function, including H-3, underwent complete deuterium exchange, while the epimers of the resulting tetradeuterionortricyclene **3b** were simultaneously equilibrated to a 35:65 ratio. No new isomers of **3b** were detected by nmr analysis. Had **3a** been epimeric at C-5 and of a single configuration (*i.e.*, exo or endo) at C-3, two additional isomers should have formed upon treatment with base.



1a, R = $COCH_3$
b, R = $COOCH_3$
c, R = $SO_2C_6H_5$



2a, R = $COCH_3$
b, R = $COOCH_3$

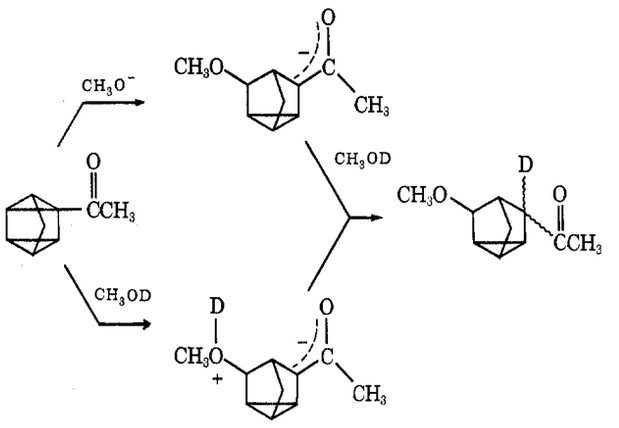


3

3	R	R′	R″
a	$COCH_3$	H	CH_3
b	$COCH_3$	D	CD_3
c	$COCH_3$	D	CH_3
d	CO_2CH_3	H	CH_3
e	$SO_2C_6H_5$	H	$C(CH_3)_3$

When quadricyclene **1a** was allowed to react with methanol-*O*-*d*, an 87% yield of crude 3-deuterio-3-acetyl-5-methoxynortricyclene (**3c**) was obtained. The position of the deuterium atom was fixed by the absence of a one-proton multiplet at τ 7.49 in its nmr spectrum. Preliminary nmr rate studies showed methoxide ion to be an active catalyst. Thus, the deuteriomethanolysis of 1.87 *M* **1a** was complete within 42 min at probe temperature (*ca.* 30°) in neutral solvent but required no more than 6 min to go to completion in the presence of 10 mol % sodium methoxide. In one experiment, addition of 1.95 *M* sodium methoxide in methanol to neat quadricyclyl methyl ketone initiated a near explosion.

It seems likely that the methanolysis of **1a** proceeds as depicted below. Catalysis by methoxide ion is consistent with rate-determining nucleophilic cleavage of the cyclopropane ring bonded to the acetyl function. Also, protonation of the indicated intermediates would be expected to afford epimeric C-3 product.



The reactivity of cyclopropanes toward nucleophilic addition is clearly enhanced by internal strain. Truce and Linday found, for example, that cyclopropyl methyl ketone had incompletely reacted with sodium thiophenoxide after 3 hr in refluxing ethanol.[4] However, electronic factors are also important. Indeed, 2-carbomethoxyquadricyclene (**1b**)[5] is significantly less reactive than **1a** toward nucleophilic alcoholysis.

When **1b** was allowed to stand in absolute methanol for nearly 7 days at room temperature, there was no reaction. After 4 days in refluxing methanol, **1b** was partially isomerized to diene **2b** (14%) and largely converted to 3-carbomethoxy-5-methoxynortricyclene (**3d**, 72%). Methoxide ion effectively catalyzes the addition of methanol to **1b**. In one experiment, **1b** and sodium methoxide (110 mol %) were mixed in methanol at room temperature. After 5 days, the reaction mixture was poured into water and extracted with dichloromethane. Ultimately, a 47:53 mixture of 3-*exo*,*endo*-carbomethoxy-5-*exo*-methoxynortricyclene (**3d**) was obtained in 72% yield. The structure assigned to **3d** was based on spectral comparison (ir, near-ir, nmr) with authentic material prepared by the action of sulfuric acid on methanolic **1b** and confirmed by comparison of chemical shift parameters to those published[3c] for known *exo*- and *endo*-**3d**.

The facility with which **1a** and **1b** add methanol contrasts with the severe conditions often necessary to promote nucleophilic additions to appropriately substituted, strained carbocycles.[4,6a-d] We note, however, that *uncatalyzed*, room-temperature methanolyses of spiro[2.5]octa-4,7-dien-6-one[7] and the photobicyclobutane derived from $\Delta^{3,5}$-cholestadiene[8] have been

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(8) W. G. Dauben and F. G. Willey, *Tetrahedron Lett.*, 893 (1962).

reported. Also, 1-cyanobicyclo[1.1.0]butane[9] and 1-cyano-3-methylbicyclo[1.1.0]butane[6d] have been found to undergo methoxide-catalyzed addition of methanol at room temperature. The reactions of **1a** and **1b** described herein corroborate the earlier finding of Cristol and Singer that treatment of quadricyclyl phenyl sulfone (**1c**) with potassium *tert*-butoxide and *tert*-butyl alcohol in dimethyl sulfoxide gave, after 18 hr at room temperature, a 34% yield of 3-*exo*,*endo*-phenylsulfonyl-5-*exo*-*tert*-butoxynortricyclene (**3e**).[6d,10] Finally, the lesser reactivity of **1b** relative to **1a** must reflect the superior ability of the acetyl group over the carbomethoxy group to stabilize adjacent negative charge.

Experimental Section

General.—The photoisomerizations described herein were conducted in a Rayonet photochemical reactor equipped with 16 3500-Å lamps and an RQV-118 quartz reaction vessel. Nmr spectra were recorded on a Varian Model A-60 nmr spectrometer (relative to internal TMS), infrared spectra on a Perkin-Elmer Model 337 spectrophotometer, and near-infrared spectra on a Cary-17 uv-vis-ir spectrophotometer. Boiling points are uncorrected. Glpc analyses were performed on a Hewlett-Packard Model 5750 gas chromatograph, a 6-ft column of 10% UCON W-98 on 80–100 mesh silica being utilized. Elemental compositions were determined by Galbraith Laboratories, Inc., Knoxville, Tenn. Sodium methoxide was obtained from the J. T. Baker Chemical Co. and methanol-*O*-*d* (99%) from Diaprep Inc.

2-Acetylquadricyclene (1a).—A solution of diene **2a** (20.0 g, 149 mmol) and bis(dimethylamino)benzophenone (0.6 g, 2.2 mmol) in ether (125 ml) was irradiated for 28 hr. The solvent and sensitizer were subsequently removed and the crude product was distilled, giving 17.9 g (89%) of **1a** as a colorless liquid: bp 45–47° (0.5 mm); ir (neat) 3.25 (cyclopropyl CH), 6.02 μ (C=O); nmr (CD_3COCD_3) τ 7.30–7.65 (m, 2), 7.8–8.1 (m, 3), 8.21 (s, 3, $COCH_3$), 8.25–8.45 (m, 2).

Anal. Calcd for $C_9H_{10}O$: C, 80.60; H, 7.46. Found: C, 80.50; H, 7.46.

A 0.3-g sample of the presumed quadricyclene (from a benzophenone-sensitized run) was dissolved in chloroform-*d* (0.5 ml) and treated with bis(benzonitrile)palladium(II) chloride (0.025 g). An nmr spectrum recorded shortly thereafter was, except for minor impurities, identical with that of diene **2a**.

Under ambient conditions, **1a** rapidly becomes colored and is eventually transformed into a red gum. It can, however, be stored for long periods at low temperatures.

Methanolysis of 1a.—To 7.58 g (56 mmol) of **1a** was added 10 ml of absolute methanol. Within several minutes, there was heat evolution sufficient to cause the solvent to reflux. After 19 hr, the excess methanol was evaporated *in vacuo*, leaving 8.85 g (95%) of crude **3a** as a yellow oil which was then distilled to a colorless liquid: bp 50.5–53.5° (0.05–0.07 mm); ir (neat) 3.27 (cyclopropyl CH), 5.86 (C=O), 9.05 (COC), 12.35 μ (nortricyclene skeleton); near-ir (CCl_4) λ_{max} 1.659 μ (ε 1.233) (first CH stretching vibration overtone characteristic of the nortricyclene skeleton); nmr (CD_3COCD_3) τ 7.87 and 7.93 (singlets, O=C-CH_3), 7.68 (m, H-4), 7.49 (m, H-3), 6.77 and 6.79 (singlets, OCH_3), 6.55 (broad singlet, H-5), 8.0–9.1 (complex multiplets, H-1,2,6,7,7′). The acetyl proton singlets are of nearly equal intensity, as are the methoxy proton singlets, consistent with the formulation of **3a** as an equimolar mixture of C-3 epimers.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.02; H, 8.52.

Deuteriomethanolysis of 1a.—Quadricyclene **1a** (1.34 g, 10 mmol) was dissolved in methanol-*O*-*d* (10 ml) and stirred at room temperature for *ca.* 22 hr. Vacuum evaporation of the solvent left 1.45 g (87%) of crude deuterionortricyclene (**3c**) as a clear, yellow oil: ir (neat) 3.26 (cyclopropyl CH), 5.87 (C=O), 9.05 (COC), 12.26 μ (nortricyclene skeleton); nmr (CD_3COCD_3) τ 7.87 and 7.93 (*ca.* 1:1 singlets, O=CCH_3), 7.72 (m, H-4), 6.77 and 6.80 (*ca.* 1:1 singlets, OCH_3), 6.55 (broad singlet, H-5), 8.0–9.1 (complex multiplets, H-1,2,6,7,7′). Except for the absence of a one-proton multiplet at τ 7.49 (H-3), the nmr spectrum of **3c** is nearly identical with that of **3a**.

Methoxide-Catalyzed Epimerization and α-Hydrogen Exchange in 3a.—To 1.67 g (10 mmol) of *ca.* 50:50 *exo*:*endo*-**3a** was added 10 ml of 0.16 *M* sodium methoxide in methanol-*O*-*d*. After stirring at room temperature for *ca.* 2.35 hr, the reaction mixture was poured into 50 ml of water and extracted with three 100-ml portions of dichloromethane. The combined extracts were dried ($MgSO_4$) and concentrared *in vacuo*, leaving 1.50 g (88%) of tetradeuterionortricyclene (**3b**) as a clear, colorless liquid: ir (neat) 3.27 (cyclopropyl CH), 5.89 (C=O), 9.04 (COC), 12.3 μ (nortricyclene skeleton). Except for the absence of singlets at τ 7.87 and 7.93 (O=CCH_3) and a multiplet at τ 7.49 (H-3), the nmr spectrum of **3b** is nearly identical with that of **3a**. However, the methoxy resonances at τ 6.77 and 6.79 are no longer of equal intensity but are in a 65:35 ratio.

Preliminary Rate Studies.—The deuteriomethanolysis of quadricyclene **1a** was followed by nmr spectroscopy at instrument probe temperature (*ca.* 30°). Owing to the large solvent proton resonance (~τ 6.7), the spectral region between τ 7.5 and 10.0 was isolated for analysis.

A. Uncatalyzed.—Three 50-μl portions of **1a** (164 mg, 1.22 mmol) were injected into methanol-*O*-*d* (0.5 ml), and nmr spectra were recorded *ca.* 7, 16, 26, 40, and 49 min after the time of mixing. Reaction progress was monitored by the disappearance of the acetyl singlet of **1a** and the appearance of the acetyl singlets of **3c**. The conversion of **1a** to **3c** was more than 70% complete within 7–8 min and 100% complete within 40 min.

B. Catalyzed.—Three 50-μl portions of **1a** were injected into 0.5 ml of 0.25 *M* sodium methoxide in methanol-*O*-*d*. By the time an nmr spectrum was recorded (within 4–7 min from the time of mixing), the alcoholysis of **1a** was complete. The spectrum of the reaction mixture was identical with that of tetradeuterionortricyclene **3b**.

2-Carbomethoxyquadricyclene (1b).—Although the synthesis of **1b** has appeared in the literature,[5] preparative details and spectral parameters were not described. Thus, we include herein our synthesis and characterization of **1b**.

A solution of diene **2b** (20.0 g, 133 mmol) and bis(dimethylamino)benzophenone (0.6 g, 2.2 mmol) in ether (125 ml) was irradiated for 24 hr. Removal of the solvent and sensitizer and distillation of the crude product gave 16.6 g (83%) of **1b** as a clear, colorless liquid: bp 40–42° (0.5 mm); ir (neat) 3.28 (cyclopropyl CH), 5.83 μ (C=O); nmr (CD_3COCD_3) τ 6.44 (s, $COOCH_3$), 7.58 (complex multiplet, 7).

Anal. Calcd for $C_9H_{10}O_2$: C, 72.00; H, 6.67. Found: C, 71.97; H, 6.85.

When 0.3-g samples of neat **1b** were heated at *ca.* 103° (oil bath), isomerization to diene **2b** was effected (as determined by nmr analysis).

Reaction time, hr	Approximate mole ratio **1b**:**2b**
21	50:50
24	54:46
24	46:54
25	52:48

Acid-Catalyzed Methanolysis of 1b.—A solution of **1b** (7.50 g, 50 mmol) in methanol (40 ml) was treated with 1 ml of concentrated sulfuric acid. After several hours, the reaction mixture was poured into dichloromethane (200 ml), washed with two 50-ml portions of saturated aqueous sodium bicarbonate and two 50-ml portions of water, dried ($MgSO_4$), and concentrated at reduced pressure. Distillation of the crude product gave 6.74 g (74%) of 3-*exo*,*endo*-carbomethoxy-5-*exo*-methoxynortricyclene (**3d**): bp 70–72° (0.5 mm) [lit.[3c] bp 60° (0.3 mm)]; ir (neat) 5.77 (C=O), 12.3 μ (nortricyclene skeleton); near-ir (CCl_4) λ_{max} 1.658 μ (ε 1.312) (nortricyclene skeleton, first CH stretching vibration overtone); nmr (CD_3COCD_3) τ 6.37 (s, $COOCH_3$ of *endo*-**3d**), 6.41 (s, $COOCH_3$ of *exo*-**3d**), 6.58 (m, H-5 of *exo*-**3d**), 6.78 (s, $-OCH_3$ of *exo*- and *endo*-**3d**), 7.65–8.90 (several complex multiplets, H-1,2,4,6,7,7′ of *exo*- and *endo*-**3d** (the H-5 resonance of *endo*-**3d** is buried under the 6.37 singlet); glpc 65:35 *endo*:*exo*-**3d**.

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.93; H, 7.69. Found: C, 66.48; H, 7.47.

Methoxide-Catalyzed Methanolysis of 1b.—A solution of **1b** (1.50 g, 10 mmol) in methanol (5 ml) and a solution of sodium methoxide (0.54 g, 10 mmol) in methanol (5 ml) were mixed and allowed to stir for 5 days at room temperature. The reaction

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(10) M. S. Singer, Ph.D. Thesis, University of Colorado, 1966, pp 71–73.

mixture was then poured into water (100 ml) and extracted with three portions (100 ml each) of dichloromethane. The combined extracts were dried ($MgSO_4$) and concentrated at reduced pressure, leaving 1.32 g (72%) of a clear oil with spectra (ir, near ir, nmr) identical with those described for authentic 5-*exo*-methoxy-3-*exo*,*endo*-carbomethoxynortricyclene (**3d**): glpc 47:53 endo:exo.

In a control experiment, a solution of **1b** (1.53 g, 10 mmol) in methanol (10 ml) was allowed to stir at room temperature for nearly 7 days. Vacuum evaporation of the solvent left 1.45 g (95%) of product with an nmr spectrum identical with that of unreacted starting material.

Uncatalyzed Methanolysis of 1b.—A solution of **1b** (1.50 g, 10 mmol) in methanol (10 ml) was refluxed mildly over a period of 4 days. Reduced pressure evaporation of the solvent left 1.61 g of crude product found by nmr analysis to consist primarily of diene **2b** (14%), nortricyclene **3d** (72%), and unreacted **1b** (13%). The product ratios were estimated by integration of appropriate carbomethoxy proton resonances. However, owing to significant peak overlap, they may be somewhat in error.

Registry No.—**1a**, 38739-89-8; **1b**, 24161-47-5; **2a**, 38739-91-2; **2b**, 3604-36-2; *endo*-**3a**, 38739-93-4; *exo*-**3a**, 38822-43-4; *endo*-**3b**, 38822-44-5; *exo*-**3b**, 38822-45-6; *endo*-**3c**, 38822-46-7; *exo*-**3c**, 38734-70-2; *endo*-**3d**, 28298-03-5; *exo*-**3d**, 35193-30-7; bis(dimethylamino)benzophenone, 90-94-8.

Synthesis of Cyclodec-3-en-1-ols by Acid-Catalyzed Two-Carbon Ring Expansion

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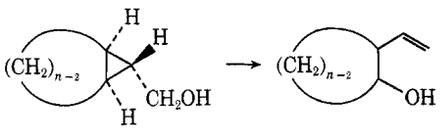
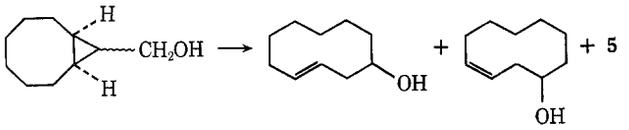
Acid-catalyzed rearrangement of bicyclo[*n*.1.0]alkyl methanols (**1**) represents an effective synthetic route to 2-vinylcycloalkanols (**2**) for certain ring sizes.[1]



1 **2**

$n = 4, 5, 6$

In an effort to use this reaction with an eight-membered ring (**3**), we discovered that the major products



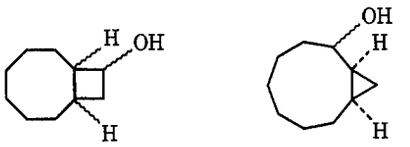
3 *trans*-**4** *cis*-**4**

of the reaction are not analogous to **2** but rather are the result of an interesting two-carbon ring expansion.[2,3] The rearrangement provides a convenient synthetic route to 3-cyclodecenols.

Compound **3** is readily prepared from cyclooctene by addition of ethyl diazoacetate followed by hydride reduction. This results in a 66:34 mixture of exo and endo isomers. Acid-catalyzed rearrangement of the mixture gave a 74:19:7 ratio of *trans*-**4**, *cis*-**4**, and **5** in an overall yield of 95%. Products *cis*-**4** and *trans*-**4** were identified by retention time comparisons of the alcohols and their trimethylsilyl derivatives and by spectral comparisons with authentic samples. The minor component (**5**) is an isomeric alcohol of unknown structure.

The isomers of **3** (*syn*-**3** and *anti*-**3**) were separated by gas chromatography and examined separately. Acid-catalyzed rearrangement of *anti*-**3** gave only the trans ring-expanded product, *trans*-**4**. Rearrangement of *syn*-**3** gave a 46:40:9:4 ratio of *trans*-**4**, *cis*-**4**, **5**, and another unknown compound.

No cyclobutanol products **6** were detected. A mixture of cyclobutanols (**6**) was prepared and coinjected



6 **7**

on gc and was found not to enhance any of the product peaks. It was also established that the cyclobutanols are stable to the acid catalysis conditions.

It should be noted that a stereospecific synthesis of *cis*-**4** or *trans*-**4** is best accomplished by the Winstein–Poulter method[4] involving stereospecific rearrangement of bicyclo[7.1.0]decan-2-ols, **7**. Although the syntheses of *cis*,*syn*- or *cis*,*anti*-**7** are lengthy, they are formed with high stereoselectivity and require no difficult separations. Although *anti*-**3** rearranges cleanly to *trans*-**4**, the synthesis of *anti*-**3** is nonselective and the separation is difficult.

The rearrangement of **3** is more useful where the stereochemistry of the double bond is not crucial, *e.g.*, in making compounds where the double bond is to be removed.[5] For those cases the sequence requires fewer steps than the Winstein–Poulter method and gives a higher overall yield (35% *vs.* 19%).

Experimental Section

Spectral measurements utilized Beckman IR-8, Varian Associates A-60 or HA-100, and Atlas CH7 instruments. Analyses were performed by Alfred Bernhardt Microanalytisches Laboratorium or Galbraith Laboratories, Analytical gas chromatography (gc) was carried out with a Wilkens Aerograph Model 1200 instrument with flame ionization detector and the 0.01-in. capillary columns listed: (A) 125 ft UCONLB550X, (B) 75 ft DEGS, (C) 100 ft Apiezon N. Samples were collected using an

(1) (a) T. L. Bond, *Tetrahedron Lett.*, 4255 (1965); (b) K. B. Wiberg and A. J. Ashe, *J. Amer. Chem. Soc.*, **90**, 63 (1968).

(2) Solvolysis of the analogous seven-membered ring dinitrobenzoate has recently been reported: K. B. Wiberg and T. Nakihara, *ibid.*, **93**, 5193 (1971).

(3) Unpublished work of E. Walton in these laboratories has shown that the analogous [5.1.0] bicyclic system does not give this two-carbon ring expansion. The syn (endo) isomers of the analogous [3.1.0] and [2.1.0] systems favor the ring expansion while the anti (exo) isomers show none of that process.[1a]

(4) S. Winstein and C. D. Poulter, *J. Amer. Chem. Soc.*, **92**, 4282 (1970), and references cited therein.

(5) Hydrogenation of the 3-cyclodecenols in ether over Adams catalyst is essentially quantitative (determined by internal glc standard).