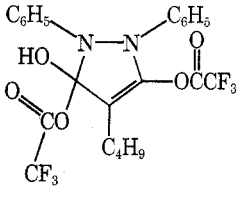
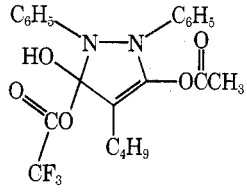
hydride and the volatiles were removed in vacuo to give a crystalline adduct assigned structure **4**. Compound **2a** was then obtained by extracting a dichloromethane solution of **4** with 1 equiv of aqueous base and crystallizing **2a** from heptane; **2f** was prepared by the same method.

The infrared spectrum of **4** shows two carbonyl absorptions. One absorption at 1800 cm^{-1} is at the same position as the acetate carbonyl in **2a** and it has been assigned to the acetate carbonyl. The other carbonyl absorption at 1780 cm^{-1} is broad and shifted to longer wavelengths, which suggests that the trifluoroacetate carbonyl is involved in a hydrogen bond. Taken together, these assignments suggest the following structure for the adduct **4**. By analogy one may also infer a similar structure for **3**.



3



4

Experimental Section

General. All melting points were uncorrected. Microanalyses were performed by Midwest Microlab, Ltd., Indianapolis, Ind., and all analyses were within ±0.3%. TLC were run on Brinkmann polygram sil G/uv_{254}. NMR spectra were recorded on a Varian T-60 spectrometer using Me_4Si as an internal standard. Infrared spectra were recorded on a Beckman IR-33. Trifluoroacetic anhydride and thallium(I) ethoxide were obtained from Aldrich Chemical Co.

1,2-Diphenyl-4-butyl-5-acetyloxy-4-pyrazolin-3-one (2a). Phenylbutazone (5.0 g, 0.016 mol) was dissolved in 15.0 g (0.081 mol) of trifluoroacetic anhydride which was cooled with an ice bath; it usually took about 0.25 hr for all of the phenylbutazone to go into solution. Then the reaction mixture was concentrated in vacuo at room temperature to give **3** as a viscous, clear oil which crystallized when it was cooled in the refrigerator. The crystals were too hygroscopic to handle but NMR and ir spectra of the oil were recorded: ir (neat) 3000–2200 (broad, moderate) (O–H), 1830 (strong, sharp) (C=O), and 1780 cm^{-1} (broad, strong) (C=O); NMR ($CDCl_3$) δ 13.6 (1, 2, OH), 7.5–7.10 (10, m, aromatic H), 2.55–2.2 (2, m, CH_2C=), and 2.2–0.75 (7, m, CH_3 and CH_2). The oil was then allowed to react with 10 ml of acetic anhydride overnight in a tightly sealed flask under a nitrogen atmosphere. The volatile materials were evaporated at room temperature to give a white solid (mp 50–60°), a portion of which was recrystallized from CH_2Cl_2–heptane to give white crystals (mp 63–66°) of **4** whose spectral properties were identical with those of the crude solid: mp 50–60°; ir (KBr) 2800–2200 (broad, moderate) (O–H), 1800 (strong, sharp) (C=O), and 1780 cm^{-1} (broad, strong) (C=O); NMR ($CDCl_3$) δ 11.5 (1, s, OH), 7.55–7.0 (10, m, aromatic H), 2.5–2.1 (s, m, CH_2C=), 2.13 (3, s, CH_3C=O), and 2.1–0.75 (7, m, CH_3 and CH_2).

Anal. Calcd for $C_{23}H_{23}F_3N_2O_5$: C, 59.47; H, 4.99; N, 6.03; F, 12.27. Found: C, 59.54; H, 5.02; N, 6.18; F, 12.24.

The rest of the white solid, mp 50–60°, was dissolved in 120 ml of CH_2Cl_2 and extracted with 75 ml of water containing 1.7 g (0.017 mol) of $KHCO_3$. The CH_2Cl_2 layer was separated and dried over Na_2SO_4 and the CH_2Cl_2 was evaporated in vacuo to give a viscous light-yellow oil. The oil was crystallized from CH_2Cl_2–heptane (20:650) which was concentrated to 350 ml on a hot plate and then cooled in a refrigerator overnight to give 2.10 g (mp 49–51°) of **2a** as fine needles. The mother liquor was concentrated to 200 ml and cooled overnight to give an additional 0.93 g (mp 46–49°) of **2a** as fine needles for a total yield of **2a** of 54%: ir (KBr) 1800 and 1700 cm^{-1} (strong, sharp) (C=O); NMR ($CDCl_3$) δ 7.6–7.0 (10, m, aromatic H), 2.45–2.1 (2, m, CH_2-C=), 2.13 (3, s, CH_3C=O), and 2.0–0.7 (7, m, CH_3 and CH_2).

Anal. Calcd for $C_{21}H_{22}N_2O_3$: C, 71.97; H, 6.33; N, 7.99. Found: C, 71.79; H, 6.19; N, 8.16.

1,2-Diphenyl-4-butyl-5-pivaloxy-4-pyrazolin-3-one (2c). Thallium(I) ethoxide (2.24 g, 0.009 mol) was dissolved in anhydrous ether (100 ml) and allowed to react with 2.84 g (0.0092 mol) of phenylbutazone. The resulting white suspension was stirred at room temperature for 1 hr, and then it was filtered. The residue was dried in a vacuum desiccator to give 4.55 g (mp 194–202° dec) of the thallium(I) salt of phenylbutazone (1).

Anal. Calcd for $C_{19}H_{19}N_2O_2Tl$: C, 44.59; H, 3.74. Found: C, 44.26; H, 3.93.

A suspension of 1 (5.12 g, 0.01 mol) in anhydrous ether (100 ml) was then allowed to react with 1.20 g (0.01 mol) of pivalyl chloride. The resulting suspension was stirred at room temperature for 6 hr. Then it was filtered and the filtrate was concentrated in vacuo. The residue from the concentration of the filtrate was titrated with petroleum ether (bp 30–60°) to give 2.95 g (mp 114–115°, 75% yield) of **2c**: ir (KBr) 1790 and 1660 cm^{-1} (strong, sharp) (C=O); NMR ($CDCl_3$) δ 7.6–6.95 (10, m, aromatic H), 2.40–2.10 (2, m, CH_2C=C), 1.95–0.7 (7, m, CH_3 and CH_2), and 1.20 [9, s, $(CH_3)_3C$].

Anal. Calcd for $C_{24}H_{28}N_2O_3$: C, 73.44; H, 7.19; N, 7.14. Found: 73.40; H, 7.06; N, 7.18.

Registry No.—**1**, 57091-21-1; **2a**, 57091-22-2; **2b**, 16006-72-7; **2c**, 57091-23-3; **2d**, 57091-24-4; **2f**, 57091-25-5; **2g**, 42177-40-2; **3**, 57091-26-6; **4**, 57091-27-7; phenylbutazone, 50-33-9; trifluoroacetic anhydride, 407-25-0; acetic anhydride, 108-24-7; thallium(I) ethoxide, 20398-06-5; pivalyl chloride, 3282-30-2; benzoyl chloride, 98-88-4; tosyl chloride, 98-59-9; 3-pyridinecarboxylic anhydride, 16837-38-0; 2-acetoxybenzoyl chloride, 5538-51-2.

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Electrolytic Decarboxylation Reaction. III. Anodic Acetoxylation of Tricyclo[4.4.0.0^{1,5}]decan-4-ones

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The conversion of carboxyl function to acetoxy group has been the subject of many investigations in recent years.[1-5] One of the major difficulties in the reaction is associated with lack of effective methods for preparing carbonium ion at the site of carbon atom attached to carboxyl group. Our interest in exploring the utility of the electrolytic decarboxylation method[6] enables us to investigate the electrochemical acetoxylation to carbonium ion at the C-2 carbon of the tricyclo[4.4.0.0^{1,5}]decan-4-one system. In this report we describe an application of the anodic acetoxylation method to the 2-carboxytricyclo[4.4.0.0^{1,5}]decan-4-ones (**1b** and **7**).

Electrolysis of **1b** in a mixed solvent of AcOH–*t*-BuOH–Et_3N (2:1:0.1) using platinum electrodes at a constant cur-

Table I
Electrolytic Decarboxylation of 1b in Various Solvents

Run	Electrode	Supporting electrolyte (ml)	Solvent (ml)	Current, A/cm²	Applied voltage, V	Temp, °C	Time, hr	Product, %[a] 2	3	4	5	6
1	C	Et_3N (0.04)	Py–H_2O (9:1)	0.03–0.02	20–25	3–5	5	25	10			
2	Pt	Et_2NH (0.03)	MeOH (8)	0.07–0.08	12–15	5–10	2				64	14
3	Pt	Et_3N (0.6)	AcOH-*t*-BuOH (12:6)	0.08	20	5–10	20			67		

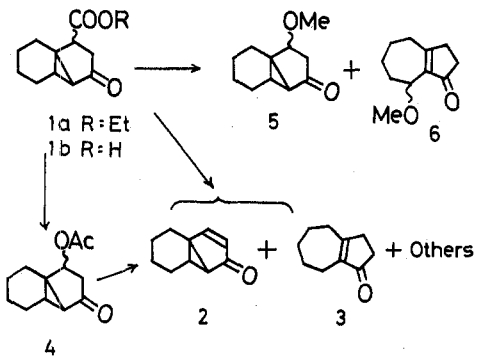
[a] Yields are calculated on isolated products.

Table II
Physical Properties and Elemental Analyses of the Products 2, 3, 4, 5, and 6 obtained by Electrolysis of 1b

Compd	Bp, °C (mm)	Ir, cm⁻¹ $\nu_{C=O}$	$\nu_{C=C}$	NMR, ppm, δ	Peak, *m/e* (rel intensity)	Formula	Calcd, % C	H	Found, % C	H
2	153–155 (11)	1697	1569	5.43 (d, 6 Hz, HC=) 7.35 (d, 6 Hz, HC=)	148 (M^+ 47) 91 (100)	$C_{10}H_{12}O$	81.04	8.16	81.05	8.19
3	135–137 (11) [lit.[a] 136 (12)]	1692	1642		150 (M^+, 91), 122 (100)					
4	145–147 (2)	1734		2.06 (s, 3 H, CH_3CO) 2.08 (s, 3 H, CH_3CO)	208 (M^+, 7), 120 (100)	$C_{12}H_{16}O_3$	69.21	7.74	69.33	7.82
5	119–120 (2)	1730		3.21 (s, 3 H, CH_3O) 3.28 (s, 3 H, CH_3O)	180 (M^+, 5) 122 (100)	$C_{11}H_{16}O_2$	73.30	8.95	73.30	9.00
6	118–120 (2)	1695	1642	3.14 (s, 3 H, CH_3O)	180 (M^+, 2) 164 (100)	$C_{11}H_{16}O_2$	73.30	8.95	73.51	8.84

[a] P. Plattner and G. Büchi, *Helv. Chim. Acta*, **29**, 1608 (1946).

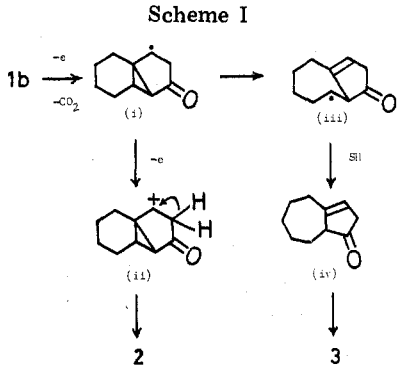
rent of 0.08 A/cm², applied voltage ca. 20 V (1.6–1.7 V vs. SCE), at 5–10° for 20 hr afforded 67% of the acetate **4** as a sole product. The conditions and results of electrolyses of **1b** using diethyl- and/or triethylamines as supporting electrolytes are summarized in Table I. As shown in run 1 (Table I) the electrolysis of **1b** in a mixed solvent of pyridine–H_2O (9:1) using carbon rod electrodes gave a mixture of products **2** and **3** in which the α,β-unsaturated ketone **2** was obtained in 25% yield. Electrolysis of **1b** in methanol using platinum electrodes (run 2) afforded methoxy derivatives **5** and **6** (ca. 5:1) in 78% yield. However, the product-selective electrolysis of **1b** to give the acetate **4** was



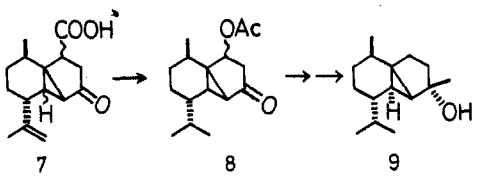
achieved in AcOH–*t*-BuOH (2:1). Properties of the products from **1b** are given in Table II.

It is plausible that the products **2, 4, 5,** and **6** may have been produced on electrolysis of **1b** via carbonium intermediates, owing to two-electron discharges on the anode electrode. In contrast to this, it is considered that the ketone **3** would be derived from a radical intermediate (iii) (Scheme I). The result with respect to the preparation of butenolides by electrolytic decarboxylation of β-carboxy-γ-butyrolactones[6a] demonstrates that the electrolysis in the pyridine–Et_3N–H_2O system gives promise of affording a cation intermediate and we are somewhat surprised at the appearance of **3** in the electrolysis medium. As shown in Scheme I, the electrolysis of **1b** (run 1) would proceed by one-electron discharge to yield a key intermediate (i), which is submitted to further anodic oxidation to provide a cation precursor (ii) for **2**.

Scheme I



The method could be applied successfully to a key step of the conversion to (−)-cubebol (**9**) from (−)-carvone.[7] Thus, electrolysis of **7** in the mixed solvent using platinum electrodes at a constant current of 0.08 A/cm², applied voltage ca. 20 V (1.6–1.7 V vs. SCE), at 10° for 20 hr afforded 72% of the acetate **8**, when the electrolysis was carried out



without using membrane. In this electrolysis condition hydrogenation to the isopropenyl function of **7** occurred synchronously.

The voltammetric oxidation curves of **1b** and **7** in AcOH–*t*-BuOH–Et_3N using smooth platinum electrodes are shown in Figure 1, demonstrating that in the potential range of 1.6–1.7 V vs. SCE anodic oxidation of the substrates **1b** and **7** proceeded favorably rather than that of acetate anion.

Experimental Section

Melting points and boiling points are uncorrected. NMR spectra were determined with a Hitachi R-24 instrument. Ir spectra were

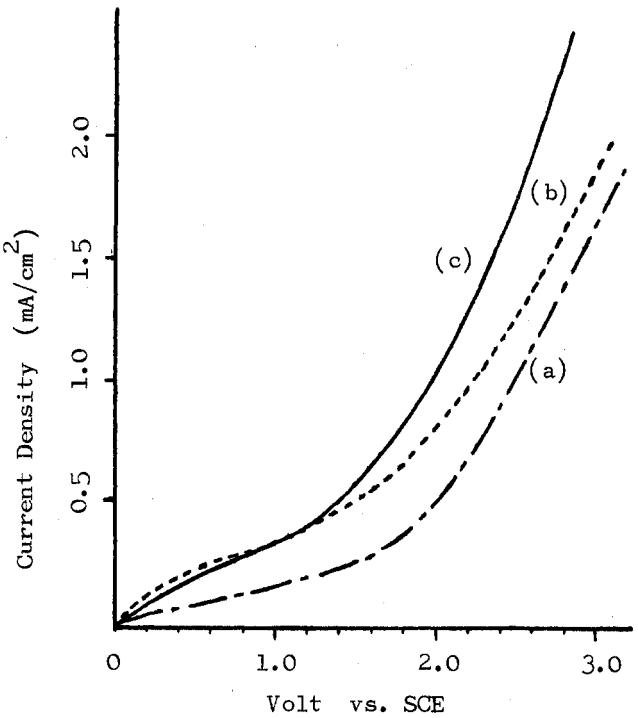


Figure 1. Anodic voltammograms of the acids **1b** and **7** on smooth platinum electrodes in a mixed solvent of AcOH–*t*-BuOH–Et_3N (2:1:0.1) at 15°, sweep rate, 0.05 V/sec: (a) – – – background; (b) - - - - the acid **7** (1.4 *M*); (c) — the acid **1b** (1.1 *M*).

recorded on a Hitachi EPI-S2, with only major absorptions being cited. Mass spectra were obtained on a Hitachi RMS-4 mass spectrometer at 70 eV, with molecular and major fragment ions being cited: *m/e* (rel intensity). Elemental analyses were performed by Mr. Tsutomu Okamoto of our laboratory.

Electrolysis Apparatus. The electrolytic vessel was a water-jacketed beaker, 2.5 cm in diameter and 10 cm high, fitted with a gas lead pipe, a thermometer, a magnetic stirrer, and two smooth platinum (3 cm^2) and/or carbon rod electrodes, being placed parallel to each other 3 mm apart. Current was controlled by manually adjusting the applied voltage as required. The direction of current was changed every 30 sec by means of a commutator.

Ethyl Tricyclo[4.4.0.0^{1,5}]deca-4-one-2-carboxylate (1a). To a stirred solution of 10 ml of dry benzene suspended in 145 mg of NaH (50% mineral oil suspension, washed with anhydrous *n*-hexane before use), 565 mg (2.5 mmol) of the Stobbe half-ester[8] in 5 ml of dry benzene was added dropwise. The mixture was stirred for 1 hr at room temperature and 0.35 ml of oxalyl chloride was added at 5°. The stirring was continued for 1 hr at room temperature and the mixture was filtered under N_2. The residual acid chloride was dissolved in 5 ml of dry benzene. The benzene solution was treated with excess diazomethane at 0°. The mixture was stirred overnight at 0–5°. Removal of the solvent under reduced pressure at 10° and subsequent chromatography over alumina with CH_2Cl_2 gave 570 mg of the diazo ketone, a yellow oil: ir (neat) 2100 (N_2C), 1740 (ester), and 1645 cm^{-1} (diazo ketone); NMR ($CDCl_3$) δ 1.20 (t, J = 6 Hz, 3 H, CH_3), 1.58 (m, 4 H, CH_2), 1.92 (m, 4 H, CH_2), 2.40–2.75 (m, 2 H, CH_2), 3.00–3.30 (m, 1 H, CH), 4.05 (q, J = 6 Hz, 2 H, CH_2), 5.22 (s, 1 H, $COCHN_2$), and 5.50 (m, 1 H, HC=C). Without further purification, the diazo ketone (570 mg, 2.28 mmol) was added to a mixture of 35 ml of benzene and 20 mg of bis(*N*-*n*-propylsalicylideneaminato)copper(II),[9] dried in an oven at 90–100° for 10 min before use, and dissolved in 5 ml of dry benzene with vigorous stirring at 80–81° for 5–6 hr. Then the solvent was removed in a rotoevaporator and the residue was chromatographed over alumina. Elution with 30 ml of *n*-hexane–ether (2:1) monitored by TLC gave 350 mg (62.8%) of **1a**: bp 95° (0.02 mm); ir (neat) 1740 and 1731 cm^{-1} (C=O); NMR (CCl_4) δ 1.10–2.15 (m, 10 H), 1.24 (t, J = 7 Hz, 3 H, CH_3), 2.15–3.20 (m, 3 H), and 4.15 (q, J = 7 Hz, 2 H, CH_2).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.11; H, 8.27.

Hydrolysis of 1a. A mixture of 140 mg (0.658 mmol) of **1a** and 210 mg (3.75 mmol) of KOH in 6 ml of 40% aqueous EtOH was stirred at room temperature for 20 hr. After processing as described in the preparation of **7a**, the crystalline residue (150 mg) was recrystallized from benzene–CH_2Cl_2 (10:1) to give 110 mg (86%) of **1b**: mp 158–159°; ir (Nujol) 3300–3000 (COOH), 1724 (C=O), and 1680 cm^{-1} (COOH); NMR ($CDCl_3$) δ 1.10–2.20 (m, 10 H), 2.20–2.60 (m, 2 H), and 2.80–3.30 (m, 1 H).

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.14; H, 7.22.

Electrolysis of 1b in AcOH–*t*-BuOH–Et_3N (Run 3). The acid **1b** (220 mg, 1.13 mmol) was dissolved in a mixed solution of AcOH (12 ml), *t*-BuOH (6 ml), and Et_3N (40 mg). The mixture was electrolyzed at a constant current of 0.08 A/cm^2 (applied voltage ca. 20 V) at 10° for 20 hr. The solvent was removed in a rotoevaporator and the residue was taken up in benzene–ether (1:1). The organic phase was washed with water and saturated $NaHCO_3$, dried (Na_2SO_4), and concentrated. The residue was chromatographed over silica gel using *n*-hexane–ether (2:1) to give 158 mg (67%) of **4**.

Electrolysis in Pyridine–H_2O (Run 1). A stirred solution of **1b** (100 mg, 0.52 mmol), Et_3N (0.04 ml), and water (1.0 ml) in pyridine (9.0 ml) was electrolyzed using carbon rod electrodes at a constant current of 0.03–0.02 A/cm^2 at 3–5° for 5 hr. The reaction mixture was concentrated on a rotary evaporator. The residue was taken up in benzene–ether (1:1), washed with aqueous 20% tartaric acid, aqueous $NaHCO_3$, and brine, and dried (Na_2SO_4). Removal of the solvent gave a crude oil (55 mg), which showed four spots on TLC (silica gel, *n*-hexane–ether, 1:1) at the R_f values of 0.30, 0.45, 0.65, and 0.73. The two fractions (R_f 0.30 and 0.45) were separated by preparative TLC, and the structures were assigned as **2** (19.2 mg, 25%) and **3** (7.7 mg, 10%), based on their spectral data and elemental analyses. The other fractions (R_f 0.65 and 0.73) gave ca. 3 mg of unknown oils.

Electrolysis in MeOH (Run 2). A solution of 50 mg (0.26 mmol) of **1b** in 8 ml of dry MeOH containing 0.03 ml of Et_2NH was electrolyzed using platinum electrodes at a constant current of 0.07–0.08 A/cm^2 at 5–10° for 2 hr. The reaction mixture was concentrated and extracted with 10 ml of ether–benzene (3:1). The organic phase was washed with aqueous 20% tartaric acid and water and dried (Na_2SO_4). Removal of the solvent gave a neutral material (42 mg) which was chromatographed over silica gel using *n*-hexane–ether (2:1) to give 30 mg of **5** (64%) and 6.6 mg of **6** (14%). Physical constants together with elemental analyses of **2**, **3**, **4**, **5**, and **6** are shown in Table II.

Electrolytic Acetoxylation of 7. The acid **7**, $[\alpha]^{24}D$ +7.7° (*c* 2.92, $CHCl_3$)[7a] (150 mg, 0.61 mmol), was dissolved in a mixed solution of AcOH (6 ml), *t*-BuOH (3 ml), and Et_3N (20 mg). The mixture was electrolyzed at a constant current of 0.25 A (applied voltage ca. 20 V) at 10° for 20 hr. After work-up in a usual manner, there was obtained 115 mg (72%) of **8**: bp 129–130° (0.005 mm); ir (neat) 1735 (C=O), 1370, 1243, 1028, and 910 cm^{-1}; NMR ($CDCl_3$) δ 0.90–1.20 (m, 9 H, 3 CH_3), 2.07 (s, 3 H, CH_3CO), 5.38–5.65 (m, 1 H, HCOAc); mass spectrum *m/e* (rel intensity) 264 (M^+, 1), 222 (5), 204 (32), 189 (18), 176 (21), 162 (55), 161 (80), 147 (38), and 133 (100); $[\alpha]^{24}D$ +7.7° (*c* 1.70, $CHCl_3$).

Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.64; H, 9.20.

Acknowledgment. We gratefully acknowledge financial support from the Ministry of Education, Japan, under the Grant-in-aid for Scientific Research, General Research (B) 047086 (1975).

Registry No.—**1a**, 57065-78-8; **1b**, 57065-79-9; **2**, 57065-80-2; **3**, 769-32-4; **4**, 57065-81-3; **5**, 57065-82-4; **6**, 57065-83-5; **7**, 57065-84-6; **8**, 57065-85-7.

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Reaction of 2-(1,2-Epoxycyclohex-1-yl)cyclohexanone Ketal with Boron Trifluoride Etherate[1]

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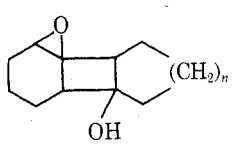
The formation of substituted furans by the action of acids on α,β-epoxy ketones is known,[3,4] and a recent report by Loubinoux and co-workers[5] indicates that in the presence of boron trifluoride etherate β,γ-epoxy alcohols of the type **1** give good yields of furans.



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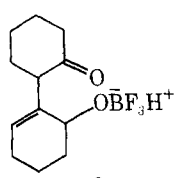
We find that the β,γ-epoxy ketal **2** on treatment with boron trifluoride etherate gives 1,2,3,4,6,7,8,9-octahydrodibenzofuran (**5**) in 43% yield. Scheme I illustrates a possible route, though at this stage it seems difficult to distinguish between the two possible pathways, a and b.

Our result would appear to lend support to the suggestion[5] that epoxy alcohols of the type **1** give rise to furans via ketonic intermediates. Thus, for $n = 2$, the system studied by Loubinoux and co-workers is isomeric with the epoxy ketone **3**, and intermediates **4a** and **4b** are isomeric with their proposed intermediate, **6**.

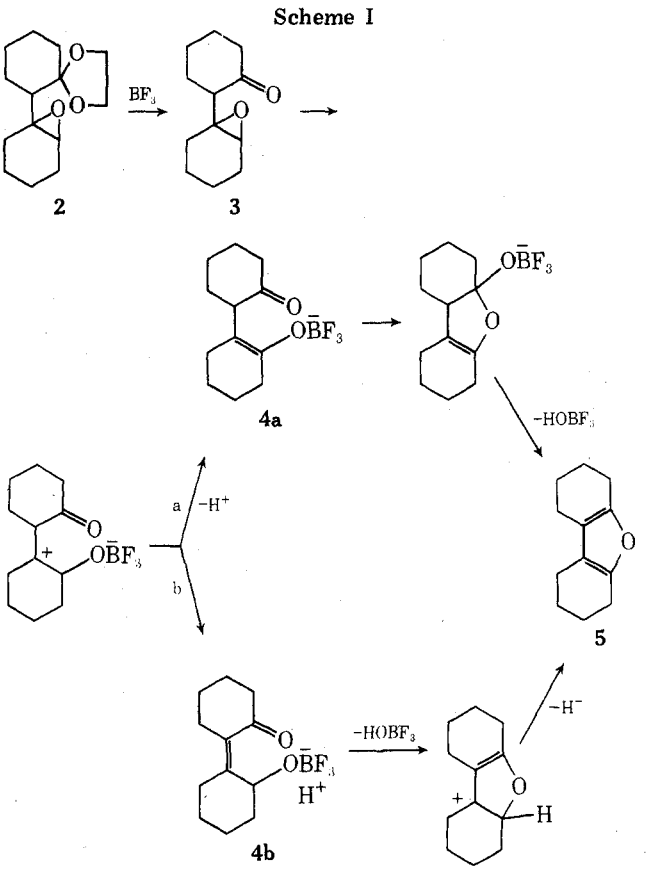


6

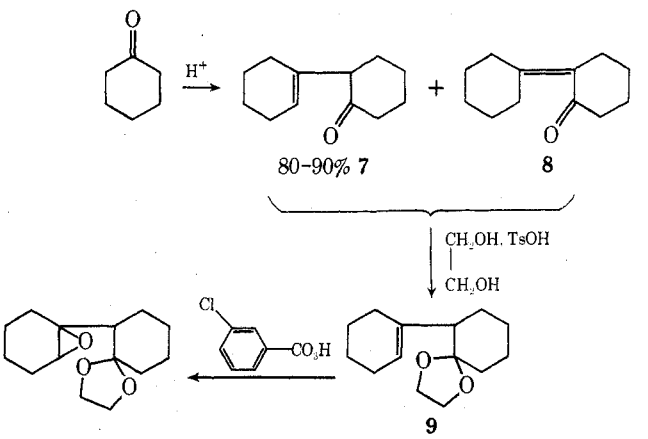
Scheme II outlines the preparation of the title compound.

Self-condensation of cyclohexanone in the presence of 60% H_2SO_4[6] gave 2-(cyclohexen-1-yl)cyclohexanone (**7**), together with a small amount of 2-cyclohexylidenecyclohexanone (**8**). The composition was established by ir and NMR analysis, our results agreeing with those of Wenkert and coworkers.[7] However, VPC failed to reveal the presence of the minor component in the mixture. The many reported investigations[7] of the structure of this condensation product do not appear to include a method for the separation of the isomeric mixture. It has been reported,[8] however, that **7** is the more stable isomer thermally, and thus it seemed possible that **8** might have isomerized to **7** while on the VPC column. Heating the mixture to 140° for varying time

Scheme I



Scheme II



periods did not produce any appreciable change in the isomer ratio as measured by NMR analysis. However, heating with ethylene glycol in benzene in the presence of *p*-toluenesulfonic acid over a period of 7 hr gave the ketal **9**, whose NMR spectrum indicated that it consisted of one isomer only, one olefinic hydrogen being present relative to the four hydrogens from the ethylene glycol residue. This migration of the double bond out of conjugation on ketalization has also been observed in the steroid series.[9,10] [Hydrolysis of **9** in 90% acidified methanol gave 2-(cyclohexen-1-yl)cyclohexanone (**7**).] Ketal **9** reacted smoothly with *m*-chloroperbenzoic acid to give **2**.

Treatment of **2** with boron trifluoride etherate, in either methylene chloride or benzene, gave a dark red oil consisting of four (or five) compounds (TLC), of which the major one was 1,2,3,4,6,7,8,9-octahydrodibenzofuran (**5**). The latter was isolated by dry column chromatography on neutral alumina, followed by distillation, and the structure was established by elemental and spectral analysis.