A New Reaction of a 7,7-Diethoxybicyclo[4.2.0]octan-2-one Derivative. The Formation of the Bicyclo[3.2.1]octane Skeleton

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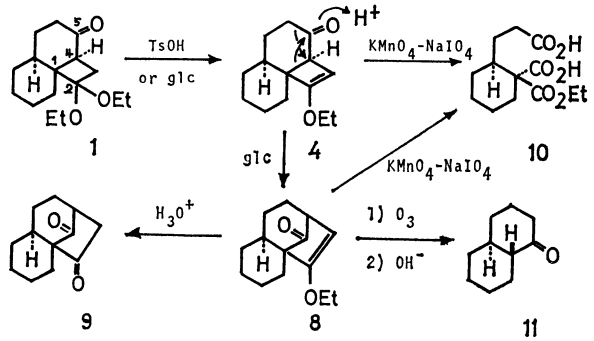
Synopsis. 2,2-Diethoxytricyclo[6.4.0.0^{1,4}]dodecan-5-one was rearranged to 11-ethoxytricyclo[7.2.1.0^{1,6}]dodec-10-en-12-one under GLC conditions (Thermol-3 on Shimalite, 200 °C) in an 87% yield.

A bicyclo[3.2.1]oct-7-en-8-one derivative (**8**) was obtained in one step by an acid-catalyzed rearrangement of a 7,7-diethoxybicyclo[4.2.0]octane derivative (**1**) under GLC conditions. Since compounds of type **1** are readily obtainable through photocycloaddition, and since compounds with the bicyclo[3.2.1]octane skeleton are frequently found among natural products, the present reaction may be of some interest for the synthesis of such compounds as terpenoid.

The irradiation of a solution of 4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone in an excess of 1,1-diethoxyethylene afforded three stereoisomers: 2,2-diethoxytricyclo[6.4.0.0^{1,4}]dodecan-5-one **1** (60%), (**2**) (the C-1, C-4 epimer of **1**, 4.8%), and (**3**) (the C-4 epimer of **1**, 13.6%). The stereostructure of these compounds were determined as follows. On treatment with basic alumina, **3** was completely converted to **1**. The treatment of **1** with a catalytic amount of *p*-toluensulfonic acid afforded an enol ether (**4**) in a quantitative yield, this ether was then ozonized to give ethyl *trans*-decahydro-4-hydroxymethylene-3-oxo-4a-naphthalenecarboxylate (**5**) and *trans*-decahydro-4a-ethoxycarbonyl-3-oxo-4-naphthalenecarboxylic acid (**6**) in 22% and 66% yields respectively. Both **5** and **6** were treated with a refluxing aq alkaline solution to give *trans*-decahydro-3-oxo-4a-naphthalenecarboxylic acid (**7**).[1,2] The stereochemistry of **2** was confirmed by leading it to the *cis*-keto acid[2] in an analogous manner.



Passing the acetal ketone **1** through a column (Thermol-3 on Shimalite[3]) in a stream of helium gave 11-ethoxytricyclo[7.2.1.0^{1,6}]dodec-10-en-12-one (**8**) in an 87% yield. Compound **8** exhibited an IR absorption at 1759 cm^{-1}, and an olefinic structure was evidenced in its IR (1630 cm^{-1}) and NMR (1H, d, δ=4.75) spectra. The hydrolysis of **8** with dil acid afforded a bridged 1,3-diketone (**9**). The degradation of **8** with ozone, followed by an alkaline treatment, gave *trans*-1-decalone (**11**) (86% yield). On the other hand, the oxidation of **8** (and **4**) by the method of Lemieux-von Rudloff[4] afforded a dicarboxylic acid (**10**). Therefore, the structure of the new enol ether is represented by Formula **8**.

The rearrangement **1**→**8** probably proceeds through the bicyclo[4.2.0]oct-7-en-2-one intermediate **4**, since the treatment of **4** under similar GLC conditions afforded **8** in an almost quantitative yield. An analogous skeletal transformation of bicyclo[4.2.0]oct-7-en-2-one using acid washed alumina has been described by Cargill and Crawford.[5]

Experimental

Photocycloaddition of 4,4a,5,6,7,8-Hexahydro-2-(3H)-naphthalenone with 1,1-Diethoxyethylene. A solution of 4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone (1.48 g, 9.3 mmol) and 1,1-diethoxyethylene (16.8 g. 144 mmol) in 60 ml of hexane was irradiated using a 75 W high-pressure Hg lamp (Pyrex filter, −78 °C, 5 h, N_2 bubbling). The subsequent distillation of the product yielded a pale yellow oil (2.54 g, bp 103—122 °C/2 mmHg, 1 mmHg≃133.3 Pa). Three products, **1** (t_R=2.50, relative to the starting enone), **2** (t_R=3.26), and **3** (t_R=4.19), were separated by GLC (DGSP, 200 °C). Adduct **1** solidified on standing and was recrystallized from hexane at −78 °C. Adduct **3** (31 mg) was passed through basic alumina (2 g, benzene) to give **1** (29 mg). Adduct **1** (1.57 g, 60% yield): bp 110—112 °C/3 mmHg: mp 61—63 °C; IR (nujol) 1705, 1058 cm^{-1}; NMR (CCl_4) δ=3.55 (2H, q, J=8 Hz), 3.40 (2H, q, J=8 Hz), 2.62—2.30 (3H, m), 1.20 (3H, t, J=8 Hz), 1.15 (3H, t, J=8 Hz), 2.2—1.0 (13H, m). Found: C, 71.99: H, 9.78%. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84%. Adduct **2** (0.125 g, 4.8%): bp 110—112 °C/3 mmHg; IR (neat) 1705, 1055 cm^{-1}; NMR (CCl_4) δ=3.54 (2H, q, J=8 Hz), 3.49 (2H, q, J=8 Hz), 2.25 (3H, m), 1.20 (6H, t, J=8 Hz), 2.2—1.1 (13H, m). Found: C, 72.07; H, 9.75%. Adduct **3** (0.365 g, 13.6%): bp 120—122 °C/3 mmHg; IR (neat) 1730, 1055 cm^{-1}; NMR (CCl_4) δ=3.35 (2H, q, J=8 Hz), 3.40 (2H, q, J=8 Hz), 2.25 (3H, m), 1.12 (6H, t, J=8 Hz), 2.2—1.0 (13H, m). Found: C, 72.22; H, 9.80%.

Formation of the Enol Ether 4 from 1. A mixture of **1** (0.246 g, 0.923 mmol) and anhyd *p*-TsOH (1 mg) was heated to 120 °C (15 mmHg, 10 min), when the evolution of gas subsided. The subsequent distillation of the residue gave 0.199 g (98%) of **4**: bp 100—102 °C/2 mmHg; IR (neat) 1692, 1630 cm^{-1}; NMR (CCl_4) δ=4.44 (1H, s), 3.90 (2H, q, J=8 Hz), 2.60 (1H, S), 2.42 (1H, S), 2.7—2.2 (2H, b), 1.39 (3H, t, J=8 Hz), 2.2—1.0 (11H, m). Found: C, 76.36; H, 9.15%. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15%.

Oxidative Cleavage of 4 to 7. A solution of **4** (199 mg, 0.905 mmol) in hexane (10 ml) was treated with ozone (−78 °C, 0.5 h). After the excess ozone has been expelled, the solution was diluted with a mixture of MeOH–H_2O (1:1, 20 ml) and stirred for 24 h at r.t. Work up of the product gave an oil (253 mg), which was then chromatographed on silica gel (5 g, benzene) to give 52 mg (22%) of **5**: oil; IR (neat) 1730, 1630, 1590 cm^{-1}; NMR (CCl_4) δ=15.58 (1H, d, J=3 Hz), 9.15 (1H, d, J=3 Hz), 4.17

(2H, q, J=8 Hz), 2.45 (2H, m), 1.27 (3H, t, J=8 Hz), 2.1—1.0 (11H, m), and 163 mg (66%) of **6**: oil; IR (neat) 1730, 1710 cm^{-1}; NMR ($CDCl_3$) δ=12.8 (1H, b), 6.20 and 6.15 (1:4, 2H, each q, J=7 Hz), 3.74 and 3.60 (1:4, 1H, s), 2.48 (2H, m), 2.3—0.8 (11H, m). A solution of **5** (37 mg) in 10% aq KOH was refluxed for 2 h. The solution was acidified with HCl, and the product was taken up into ether. Evaporation of the ether yielded 25.5 mg (89.5%) of the keto acid **7**,[2] mp 116—118 °C, after recrystallization from $CHCl_3$–hexane. Similarly, the keto acid **6** (54 mg) was treated with the KOH solution (reflux, 2 h) to give the same *trans*-keto acid **7** (34 mg, 86%). The *cis*-adduct **2** was converted to the *cis*-keto acid, which was found to be identical (IR, NMR, TLC) with an authentic sample derived from *cis*-9-cyano-2-decalone.[2]

*Rearrangement of **1** (and **4**) to the Keto Enol Ether **8**.* This rearrangement was carried out at 180—220 °C using a Varian A-700 gas chromatograph equipped with a column packed with 15% Thermol-3 coated on Shimalite (3/8″×6 ft). Helium was used as the carrier gas (100 ml/min). In a typical run, an ethereal solution of **1** (330 mg in 1 ml) was used. After the elution of the solvent, the eliminated ethanol was eluted slowly (t_R=2 min) and **4** was eluted as pale yellow oil (t_R=10.5, 237 mg, 87% yield). The products were collected on granular anhyd Na_2SO_4 placed in a short glass tube fitted to the outlet. An analytical sample was obtained by distillation. Bp 100—105 °C/3 mmHg; IR (neat) 1759, 1613 cm^{-1}; NMR (CCl_4) δ=4.75 (1H, d, J=4 Hz, =C–**H**), 3.94 (2H, q, J=8 Hz), 2.77 (1H, m, =C–C–**H**), 1.40 (3H, t, J=8 Hz), 2.3—0.9 (13H, m); MS *m/e* 220 (M^+). Found: C, 76.34; H, 9.16%. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15%.

*Hydrolysis of **8**, Formation of the Diketone **9**.* To a solution of **8** (70 mg) in dioxane–H_2O (2:1, 3 ml), was added 0.1 ml of conc HCl with stirring. White crystals (60 mg, 97%) were immediately precipitated. Recrystallization from ether gave pure **9**: mp 117—118 °C, IR (nujol) 1760, 1720 cm^{-1}; NMR ($CDCl_3$) δ=3.1—2.45 (3H, m), 2.4—1.9 (2H, m), 1.9—0.9 (11H, m). Found: C, 75.12; H, 8.36%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.

*Oxidation of **8** (and **4**) to Dicarboxylic Acid, **10**.* Following the method of Lemieux-von Rudloff,[4] **8** (51 mg, 0.23 mmol) was oxidized with 220 mg (0.125 mmol) of $KMnO_4$ and 486 mg (2.2 mmol) of $NaIO_4$ in *t*-BuOH–H_2O (3:1, 4 ml) to give **10**: mp 161—163 °C; IR (nujol) 1742, 1710 cm^{-1}. Found: C, 57.01; H, 7.40%. Calcd for $C_{13}H_{20}O_6$: C, 57.34; H, 7.40%.

Methyl Ester: Bp 135 °C (bath temp)/2 mmHg; IR (neat) 1735 cm^{-1}; NMR (CCl_4) δ=4.20 (2H, q, J=7 Hz), 3.72 (3H, s), 3.65 (3H, s), 2.28 (2H, t, J=6 Hz), 1.29 (3H, t, J=7 Hz), 2.5—1.0 (11H, m); MS *m/e* 300 (M^+). A similar treatment of **4** (141 mg) with $KMnO_4$ (60 mg)–$NaIO_4$ (1.2 g) gave a dicarboxylic acid which was completely identical with the **10** obtained from **8**.

*Degradation of **8** to **11**.* A solution of **8** (110 mg) in AcOEt (5 ml) was treated successively with an excess of ozone (−78 °C), KI (0.5 g) in MeOH–H_2O (1:1, 5 ml, 2 h), and $Na_2S_2O_3$. The product, obtained in the usual way, was heated in a mixture of aq 10% NaOH (2 ml) and EtOH (2 ml) for 6 h. The ethereal extract boiling at 105 °C/14 mmHg (66 mg) was identical with the authentic **11**.

References

1) The sequence of reactions may be useful for the hydrocarboxylation of α,β-cyclenones.

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