THERMAL CONVERSION OF METHYL 8-VINYL-3-OXO-2-OXABICYCLO[2.2.2]-OCT-5-EN-6-CARBOXYLATES TO TETRAHYDROCOUMARINS AND METHYL BENZOATES

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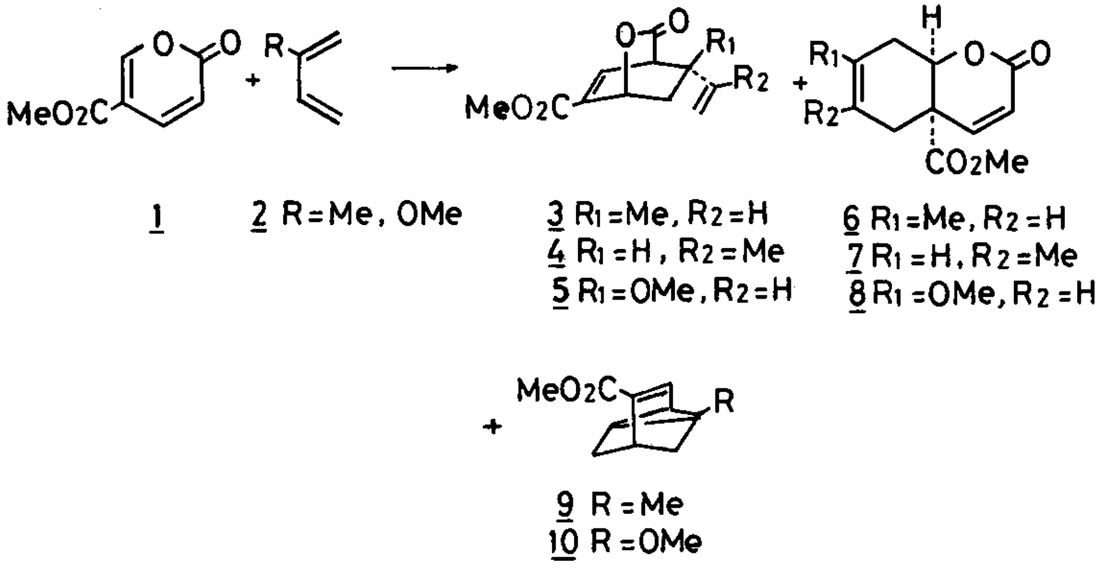
Abstract — Methyl 8-methyl- and 8-methoxy-8-vinyl-3-oxo-2-oxabicyclo[2.2.2]oct-5-en-6-carboxylates (3 and 5), prepared by the Diels-Alder reaction of methyl 2-oxo-2*H*-pyran-5-carboxylate with 2-methyl- and 2-methoxy-1,3-butadienes, were converted into methyl 9-methyl- and 9-methoxy-3-oxo-2-oxabicyclo[4.4.0]deca-4,8-diene-6-carboxylates (tetrahydrocoumarins) by a Cope rearrangement at about 140°C, respectively. On the other hand, 3 and 5 were transformed into methyl 4-isopropyl- and 4-acetylbenzoates *via* the reaction of methyl tricyclo[3.2.1.0^{2,7}]oct-3-en-4-carboxylates at about 257°C in the presence of Pd-C, respectively.

In a previous paper,[1] we reported that the Diels-Alder reaction of methyl 2-oxo-2*H*-pyran-5-carboxylate (1) with 2-methyl- and 2-methoxy-1,3-butadienes afforded three types of the products such as 3-oxo-2-oxabicyclo[2.2.2]octenes (3-5), 3-oxo-2-oxabicyclo[4.4.0]decadienes (tetrahydrocoumarins) (6-8), and tricyclo[3.2.1.0^{2,7}]octenes (9-10) (Scheme 1). However, the combined yields and the ratio between the the products were seriously changed with reaction temperature since



1

2 R = Me, OMe

3 R_1 = Me, R_2 = H
4 R_1 = H, R_2 = Me
5 R_1 = OMe, R_2 = H

6 R_1 = Me, R_2 = H
7 R_1 = H, R_2 = Me
8 R_1 = OMe, R_2 = H

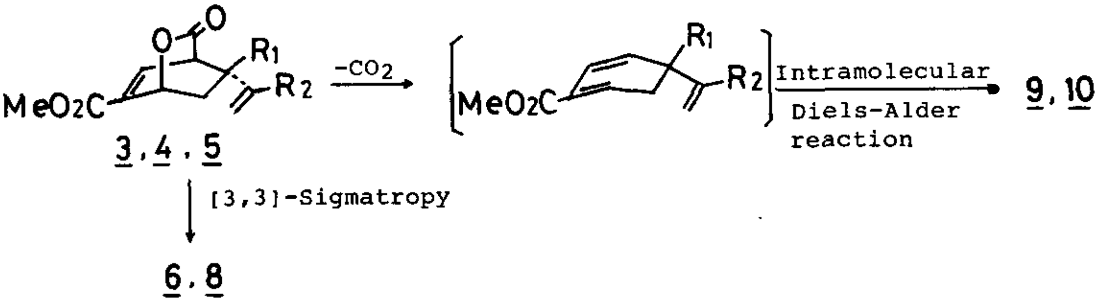
9 R = Me
10 R = OMe

Scheme 1

further conversion of these initial adducts occurred under applied conditions. From the viewpoint of the molecular structure and the thermal conversion, our interests were focused on the transformation of 3-5 into 6-8 by [3,3]-sigmatropic reaction since these compounds involve a strained structure bearing two allyl moieties. Herein, we report the conversion reactions of 3-5 such as intramolecular sigmatropic rearrangement and pericyclic decarboxylation followed by cycloaddition reaction to give 6, 8, 9, and 10 and further conversion of 9 and 10 to methyl benzoates.

RESULTS AND DISCUSSION

A mixture of regioisomers (6) and (7) was prepared by the Diels-Alder reaction of 1 with isoprene,[1,2a,3] but the each single compound has not, hitherto, been obtained. When a m-xylene solution of 3 was heated at ca. 140°C for 4 h, two compounds (6) and (9)[2a] were produced and then separation of this mixture by column chromatography afforded 6 as pure crystals in 21% yield and 9 as colorless oil in 26% yield. Likewise, the reaction of 5 provided 8 in 14% yield, together with 10 in 28% yield. But attempts to obtain the desired tetrahydrocoumarin (7) from 4 were unsuccessful, leading to most of 9 and/or the starting material. A pathway for the formation of 9 from 3 or 4 and of 10 from 5 can be explained on the basis of that for the conversion reaction of methyl 8-vinyl-3-oxo-2-oxabicyclo[2.2.2]oct-5-en-6-carboxylate to the corresponding tricyclo[3.2.1.$0^{2,7}$]octene compound proposed by Imagawa (Scheme 2).[2] On the other hand, the formation of 6 from 3 and of 8 from 5 is considered that it was likely produced through [3,3]-sigmatropic rearrangement. A poor yield or no formation of tetrahydrocoumarin *via* the [3,3]-sigmatropy in 3-5 may be due to a severe ring strain and the steric hindrance of the methyl group in the case of 4 in the transition state, as depicted in Figure 1; the transition state leading to the product must be boat-like form which is generally less favorable than chair-like form, as can be judged from a symmetry-allowed [3,3]-sigmatropic shift.[4] The earlier report demonstrated that the thermal reaction of di-



Scheme 2

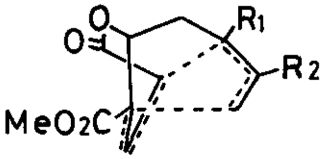


Figure 1

methyl tricyclo[3.2.1.0^{2,7}]oct-3-en-2,4-dicarboxylate over Pd-C gave dimethyl 4-ethylisophthalate.[2b] We similarly treated 9 and 10 with 10% Pd-C in diphenyl ether at ca. 257°C for 4 h and obtained methyl 4-isopropylbenzoate in 32% yield and methyl 4-acetylbenzoate in 27% yield, respectively. Thus, we have observed that methyl 4-substituted benzoates are accessible from methyl 8-vinyl-3-oxo-2-oxabicyclo[2.2.2]oct-5-en-6-carboxylates *via* methyl tricyclo[3.2.1.0^{2,7}]oct-3-en-4-carboxylates.

EXPERIMENTAL SECTION

Melting points are uncorrected. Ir spectra were measured in $CHCl_3$ on a Hitachi 270-30 spectrophotometer. Nmr spectra were recorded on a Hitachi R-1500 spectrometer for ^1H and a Bruker AC 250P spectrometer for ^{13}C in $CDCl_3$ with TMS as an internal standard unless otherwise specified.

Conversion of 3 and 5.

From 3: A solution containing 100 mg (0.45 mmol) of 3 in 20 ml of *m*-xylene was stirred at 139-140°C for 4 h under a nitrogen atmosphere. The solvent was removed in vacuo, and the residue was chromatographed on silica gel with hexane-ethyl acetate (95:5) as an eluent to give 6 (21 mg; 21% yield) and 9[2a] (21 mg; 26% yield), along with the recovered 3 (31 mg). 6: mp 61.5-62.5°C (acetone-hexane); ir 1730 cm^{-1}; ^1H nmr δ=1.69 (3H, d, J=1.2 Hz, $-CH_3$), 1.8-3.0 (4H, m, $-CH_2-$ x2), 3.76 (3H, s, $-CO_2CH_3$), 5.00 (1H, t, J=4.3 Hz, $-\overset{|}{C}H-$), 5.3-5.7 (1H, m, $-CH=\overset{|}{C}-$), 6.03 and 6.93 (each 1H, d, J=10.0 Hz, $-CH=CH-$); ^{13}C nmr δ=22.91, 31.14, 33.67, 45.75, 52.97, 76.01, 117.68, 120.89, 131.20, 149.73, 163.42, 171.84; ms m/z 222 (M^+); Found: m/z 222.0887. Calcd for $C_{12}H_{14}O_4$: M, 222.0892. 9: Colorless oil; ir 1700, 1620 cm^{-1}; ^1H

nmr (CCl_4) δ=0.68 (2H, d, J=11 Hz, methylene-H_{ex} x2), 1.30 (3H, s, CH_3), 1.4-1.9 (4H, m, methylene- and methyne-H), 3.06 (1H, dd, J=8 and 2 Hz, $-\overset{|}{C}H-$), 3.52 (3H, s, $-CO_2CH_3$), 6.76 (1H, dd, J=6 and 2 Hz, $-CH=\overset{|}{C}-$) ; ^{13}C nmr δ=18.12, 25.00, 25.17, 26.18, 28.59, 32.64, 34.37, 51.28, 130.26, 137.23, 165.68; ms m/z 178 (M^+); Found: m/z 178.1004. Calcd for $C_{11}H_{14}O_2$: M, 178.0994. These were almost identical with the reported spectral data.[2a]

From 5: A similar procedure as described above [5 200 mg (0.84 mmol), *m*-xylene 20 ml, 139-140° C, 4 h] gave 8[1] (28 mg; 14% yield) and 10 (45 mg; 28% yield) together with 1 (60 mg). 10: Colorless viscous oil; ir 1700, 1620 cm^{-1}; ^1H nmr δ=0.72 and 1.19 (each 1H, d, J=13 Hz, methylene-H_{ex}), 1.73 and 1.9-2.2 (each 1H and 3H, m, methylene- and methyne-H), 3.2-3.3 (1H, m, $-\overset{|}{C}H-$), 3.33 (3H, s, $-OCH_3$), 3.83 (3H, s, $-CO_2CH_3$), 7.20 (1H, dd, J=5 and 2 Hz, $-CH=\overset{|}{C}-$); ^{13}C nmr δ=24.04, 24.56, 26.38, 27.03, 32.10, 51.33, 56.40, 72.90, 130.99, 135.92, 165.42; ms m/z 194 (M^+); Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.03; H, 7.23.

Conversion of 9 and 10.

From 9: A mixture of 175 mg (0.98 mmol) of 9 and 18 mg of 10% Pd-C in 1.5 g of diphenyl ether was heated at reflux for 4 h under a nitrogen atmosphere. Removal of the Pd-C by filtration followed by column chromatography on silica gel using hexane-benzene (70:30 and 40:60) as an eluent afforded methyl 4-isopropylbenzoate (56 mg; 32% yield); colorless oil; ir 1710, 1600 cm^{-1}; ^1H nmr (CCl_4) δ=1.26 (6H, d, J=8 Hz, $-CH(CH_3)_2$), 2.91 (1H, sept, J=8 Hz, $-CH(CH_3)_2$), 3.82 (3H, s, $-CO_2CH_3$), 7.16 and 7.86 (each 2H, d, J=9 Hz, Ar-H). These were identical with the spectral data of the compound derived from commercially available 4-isopropylbenzoic acid.

From 10: A similar procedure as described above [10 192 mg (1.0 mmol), 10% Pd-C 100 mg, diphenyl ether 2.1 g, reflux, 4 h] afforded 52 mg (27% yield) of methyl 4-acetylbenzoate; mp 95-97°C (aqueous methanol); ir 1730, 1700, 1620, 1580 cm^{-1}; ^1H nmr δ=2.65 (3H, s, $-COCH_3$), 3.96 (3H, s, $-CO_2CH_3$), 7.98 and 8.16 (each 2H, d, J=9 Hz, Ar-H). These were identical with the spectral data of the compound (mp 100-101°C) derived from commercially available 4-acetylbenzoic acid.

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