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A COMBINED 1,2-OXYGEN AND 1,4-CARBONYL GROUP TRANSPOSITION IN TETRALONES VIA HETEROCYCLIC INTERMEDIATES[+,1)]

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The conversions of the oxanorbornadiene **1** to the hydroxy-tetralones **2** and **3** are described. The sequence **1** - - → **3** includes a combined 1,2-oxygen and 1,4-carbonyl group transposition.

Transpositions of the carbonyl group within organic molecules are of considerable interest[1,2)]. Recently we found[1)] an approach to the 1,4-carbonyl group transposition in tetralones which takes advantage of the oxanorbornadiene --→ oxaquadricyclane --→ oxepine-isomerisation studied by H. Prinzbach and coworkers[3)]. We now wish to describe a possibility which allows a combined 1,2-oxygen and 1,4-carbonyl group transposition via the same type of heterocyclic intermediates.

Treatment of the easily available oxanorbornadiene **1**[1)] with acid (conc. hydrochloric acid in methanol, 20 hr under reflux) yields the tetralone **2** (56 %, mp 134-136°C from ether) without migration of functional groups. The synthesis of the rearranged hydroxy-tetralone **3** starts with the photolysis of **1** to the corre-

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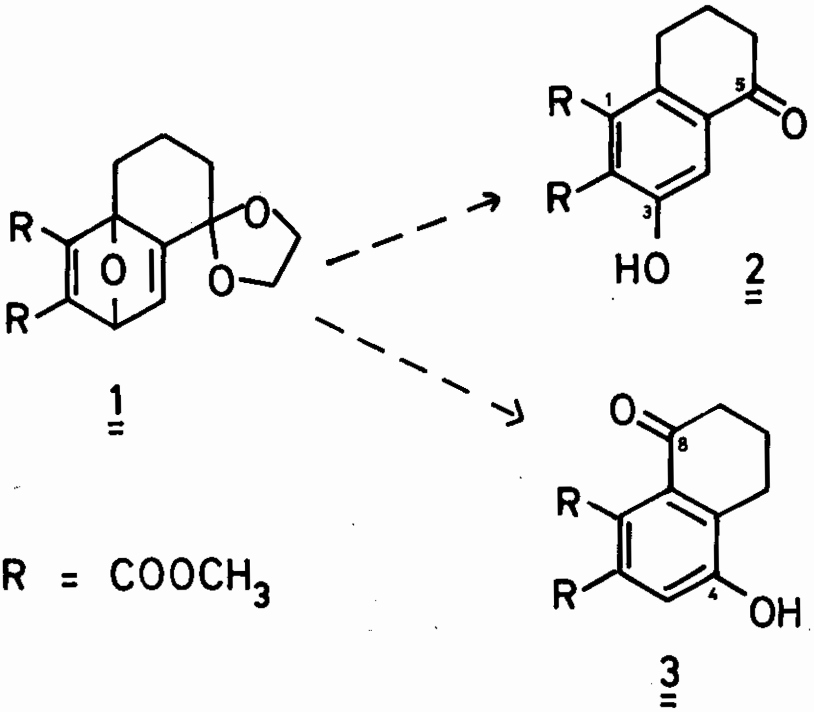
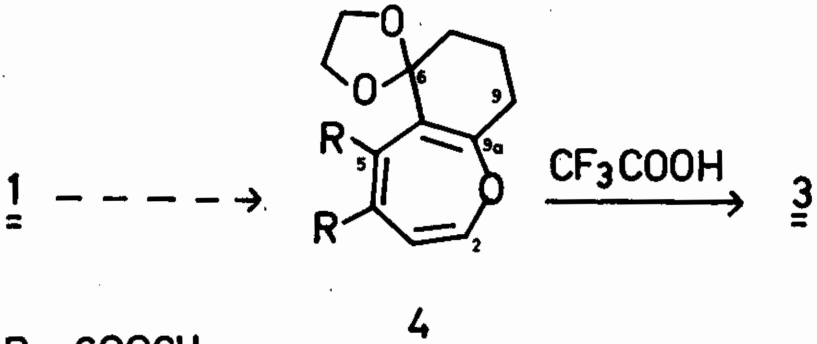
+) Dedicated to Professor Emeritus Tetsuo Nozoe on the occasion of his 77th birthday.



R = COOCH$_3$

sponding oxaquadricyclane and subsequent thermal isomerisation to the oxepine 4 (over all yield 55 %)1). Acid catalysed isomerisation of 4 with trifluoroacetic acid3) leads in 40 % yield to the 4-hydroxy-8-keto-derivative 3 (trifluoroacetic acid: tetrachloromethane 1:10, 2 hr at 25°C, subsequent hydrolysis with



R = COOCH$_3$

sodium hydrogencarbonate solution; mp 203-205°C from ethyl acetate).

2 and **3** differ in the positions of the phenolic hydroxyl group (C-3 in **2**, C-4 in **3**; 1,2-transposition) and of the carbonyl group (C-5 in **2**, C-8 in **3**; 1,4-transposition) as well. The assignment of structure for **2** and **3** is consistent with spectroscopic data (Table 1)[4)]. The ir and ^{1}H-nmr spectra of **2** indicate hydrogen bonding between the phenolic hydroxyl group and one carbomethoxy group. Moreover the uv spectrum of the corresponding alcohol (**2**, CHOH instead of CO on C-5) obtained from **2** and sodium borohydride (methanol, 5 hr at 0°C; mp 75-76°C from ether) is highly similar to that of 3-hydroxy-6-methyl-dimethylphthalate[3)]. On the other hand the same spectra indicate the absence of intramolecular hydrogen bonding in **3**. Thereby other possible isomers are excluded[5)]. **3** is probably formed from **4** by the mechanistic pathway established for other oxepines[3,6)].

Table 1. Spectroscopic data for the compounds **2** - **4**

2: ir (KBr): 1670(CO), 1695(CO_2CH_3), 1745(CO_2CH_3), 3100 cm^{-1}(OH). - uv(C_2H_5OH): $\lambda_{max}(\log\epsilon)$ = 220 (4.36), 257 (4.05), 341 nm (3.66). - ^{1}H-nmr($CDCl_3$): δ = 1.8-2.3 (m,2H,CH_2), 2.5-2.95 (m,4H, 2CH_2), 3.90 (s,3H,CO_2CH_3), 3.92 (s,3H,CO_2CH_3), 7.68 (s,1H,4-H), 10.6 (s,1H,O-H).

3: ir (KBr): 1665(CO), 1725-1745(CO_2CH_3), 3200 cm^{-1}(OH). - uv(C_2H_5OH): λ_{max} (log ϵ)= 234 (4.27), 322 nm (3.20). - ^{1}H-nmr ($CDCl_3$): δ = 1.6-2.35 (m,2H,CH_2), 2.5-2.7(t,2H,CH_2), 2.7-3.1(t, 2H,CH_2), 3.82 (s,3H,CO_2CH_3), 3.97(s,3H,CO_2CH_3), 6.85 (broad,1H, OH), 7.5(s,1H,3-H).

2 (CHOH instead of CO on C-5): ir(KBr): 1680(CO_2CH_3), 1720(CO_2-CH_3), 3110(OH), 3460 cm^{-1}(OH). - uv(C_2H_5OH): λ_{max}(log ε) = 215 (4.41), 250(3.92), 320 nm(3.70). - ^{1}H-nmr($CDCl_3$): δ = 1.5-2.25 (m,5H,2CH_2 + 1 OH), 2.55(t,2H,CH_2), 3.87 (s,3H,CO_2CH_3), 3.90(s,3H,CO_2CH_3), 4.65(t,1H,5-H), 7.15(s,1H,4-H), 10.62(s,1H,OH).

4$^{1)}$: ^{13}C-nmr($CDCl_3$): δ = 18.7(t,J_{CH}=130 Hz,8-C), 29.8(t,J_{CH} = 129 Hz,9-C), 32.9(t,J_{CH} = 129 Hz,7-C), 52.2(q,J_{CH} = 148 Hz, $\underline{C}H_3OOC$), 64.4(t,J_{CH} = 150 Hz,dioxolane ring-C), 108.2(m,6-C), 116.4(dd,J_{CH} = 165 Hz,J_{CCH} = 13 Hz,3-C), 120.9(s,5a-C), 130.4 (d,J_{CCCH} = 7 Hz,5-C), 140.9(d,J_{CCH} = 7 Hz,4-C), 145.6 (dd,J_{CH} = 209 Hz,J_{CCH} = 6 Hz,2-C), 163.3(m,9a-C), 165.4(d,J_{CCCCH} = 4 Hz, $\underline{C}O_2CH_3$ on C-5), 167.8 (d,J_{CCCH}=4 Hz,$\underline{C}O_2CH_3$ on 4-C).

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