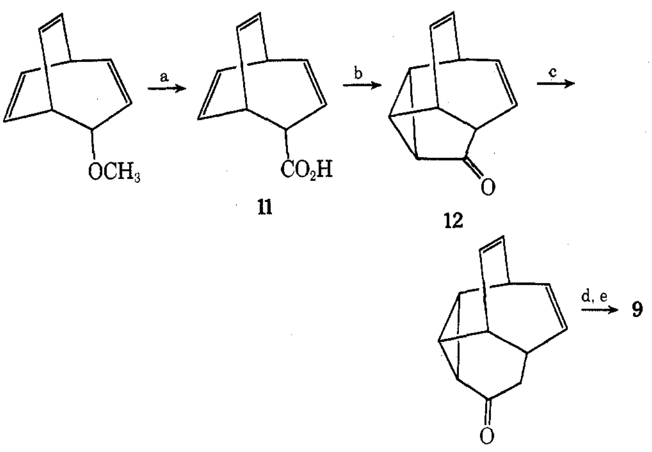
Scheme III[a]



[a] a, Na/K, THF, CO$_2$ (58%); b, (COCl)$_2$, CH$_2$N$_2$, copper bronze, benzene, 80 °C (43% overall); c, LiCHBr$_2$, BuLi[13] (53% overall); d, TsNHNH$_2$, CH$_3$OH (62%); e, LiN(i-Pr)$_2$, THF, room temperature (60%).

possibility that 4 might also equilibrate with 3, but this now appears to be a remote prospect.

Supplementary Material Available. Characterization of compounds **6** and **11**, together with the experimental details for preparation of these intermediates (4 pages). Ordering information is given on any current masthead page.

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(6) Characterization of **4**: NMR (CDCl$_3$) δ 5.8–5.9 (2 H, m), 2.24 (2 H, br s), 1.1–1.5 (4 H, m), 0.7–1.0 (2 H, m); m/e 156. The authors thank Dr. W. Wilber for performing the preparation and identification of **4**.
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(15) We have obtained excellent results using 2–4 mol of LDA for conversion of more typical tosylhydrazones into olefins at 0 °C in THF.[16] In one case, it has been reported that lithium 2,2,6,6-tetramethylpiperidide gives higher yields than LDA.[17] However, we find that LDA is entirely satisfactory for preparation of moderately strained or unstrained olefins.
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(18) Characterization of **9**: NMR (CDCl$_3$) δ 6.86 (1 H, dd, J = 8.2, 6.4 Hz), 6.24 (1 H, dd, J = 8.2, 6.4 Hz), 6.20 (1 H, dd, J = 9.0, 5.9 Hz), 6.06 (1 H, dd, J = 9.0, 6.8 Hz), 5.42 (1 H, dd, J = 9.9, 8.1 Hz), 5.30 (1 H, ddt, J = 9.9, 4.9, ca. 0.6 Hz), 3.15 (1 H, m), 2.71 (2 H, m), 1.4–1.8 (3 H, m); exact mass 156.09366 (calcd 156.09390).

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Reaction of 1,2- and 1,3-Dicarbonyl Compounds with Dimethyl β-Ketoglutarate. I. Synthesis of Methyl 5,6,7,8-Tetrahydro-5-oxocoumarin-$\Delta^{4(3H),\alpha}$-acetate

Summary: Reaction of dimethyl β-ketoglutarate (excess) and 1,3-cyclohexanedione in aqueous buffer (pH 6.8) yielded the product of 1:1 stoichiometry, methyl 5,6,7,8-tetrahydro-5-oxocoumarin-$\Delta^{4(3H),\alpha}$-acetate.

Sir: Reaction of dimethyl β-ketoglutarate **1** with 1,2-dicarbonyl compounds usually proceeds smoothly in aqueous solution (pH 6.8) at room temperature to furnish adducts formed from two molecules of **1** and one molecule of the carbonyl compound. Use of glyoxal (e.g.) yields tetramethyl bicyclo[3.3.0]octane-3,7-dione-2,4,6,8-tetracarboxylate.[1] Other 1,2-dicarbonyl compounds in general give analogous adducts,[1] while in a few cases more complex reaction products have been observed.[2] Cyclic 1,2 diketones yield tetramethyl propellanedione tetracarboxylates.[1,3] The tendency toward 2:1 stoichiometry in this reaction is marked;[1,3] in a few cases, however, 1:1 adducts have been isolated.[4]

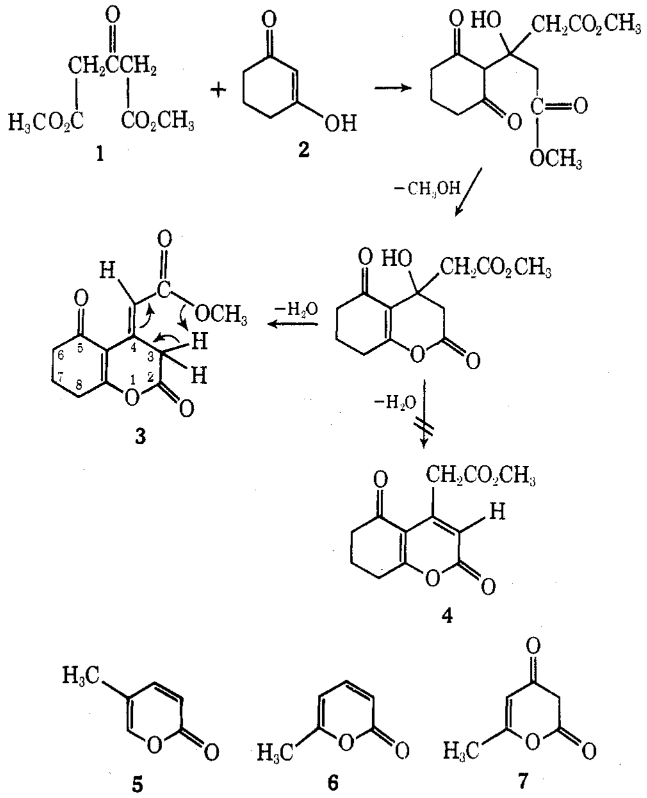
It seemed of interest to examine the analogous reaction between **1** and cyclic 1,3 diketones. We now wish to report on a compound obtained from **1** and 1,3-cyclohexanedione **2**.

When an aqueous solution of **1** (104.4 g, 0.60 mol) and **2** (22.4 g, 0.20 mol) in citrate/phosphate buffer (pH 6.8) was stirred for several days at room temperature, TLC indicated the presence of a single reaction product in addition to starting materials. Extraction with chloroform and concentration to small volume provided a 45% yield of a pure crystalline compound, mp 123–125°, not changed on recrystallization from chloroform. Elemental analysis and high-resolution mass spectrometry indicated that the new compound had the empirical formula $C_{12}H_{12}O_5$. In contrast to the results with 1,2 diketones, it is evidently produced by reaction of **1** and **2** in a 1:1 ratio with loss of one molecule each of water and methanol.

A plausible scheme leading to two alternative structures for $C_{12}H_{12}O_5$ can be easily written (Scheme I). Spectroscopic evidence is compatible with methyl 5,6,7,8-tetrahydro-5-oxocoumarin-$\Delta^{4(3H),\alpha}$-acetate **3** and not the α-pyrone **4**. The ultraviolet spectrum of **3** [λ_{max} 261 nm (log ϵ 4.06)] is different from those of the authentic α-pyrones **5** and **6** (λ_{max} 300[5] and 302[6] nm, respectively) but is similar to that of the ketolactone **7** (λ_{max} 271 nm).[5] In the NMR spectrum of **3**, two triplets representing the protons of C-6 (2 H) and C-8 (2 H) were observed at δ 2.60 and 2.90, respectively. The multiplet at δ 2.15 was assigned to the two protons of C-7. In addition three singlets were observed which were ascribed to the ester function (δ 3.71), the methylene protons of C-3 (3.81), and the vinyl proton (6.03).

Support for the stereochemical assignment of the exocyclic double bond as that depicted in **3** is obtained by close

Scheme I



examination of the mass spectrum. An intense peak (P − 32) was observed in the spectrum and corresponds to the loss of methanol from the parent ion. This process is known to proceed through a six-centered transition state involving a hydrogen atom γ to the ester group, as shown, and can only occur from **3**. The metastable ion for P → P − 32 was observed. Ample precedent for this process is available in the literature;[7] this fragmentation has also been observed repeatedly in the spectra of the tetramethyl propellanedione tetracarboxylate derivatives.[3] Dimedone reacted with **1** in the same fashion as **2** to provide the 7,7-dimethyl derivative of **3** (mp 115–116°C), although the yield of product was somewhat lower.

The obvious possibility for conversion of **3**[8] to α-pyrones, coumarins, and carbostyrils, etc., is at present under investigation in our laboratory; we are also studying analogous reactions of other 1,3-dicarbonyl compounds.

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