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ON THE PUTATIVE FORMATION OF STABLE ENOLS

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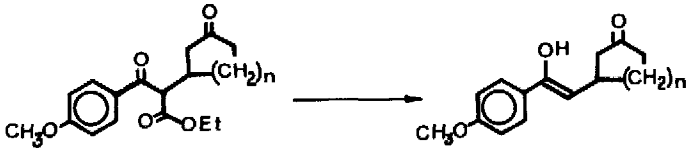
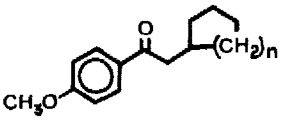
Recently it was reported in this journal[1] that the thermodynamically stable enols 2a and 2b were obtained by hydrochloric acid treatment of diketo esters 1a and 1b and dione 4b. Since neither of the closely related mono ketones 3a or 3b exhibited enolic behavior, it was proposed that interaction of non-bonding electrons of the enolic hydroxyl group with the nearby carbonyl carbon was responsible for the stability of the two enols.



1 a,b **2 a,b**



3 a,b

a, n=1 ; **b**, n=2

However, the suggested structures were suspect for several reasons: (1) the unprecedented nature of the enol stabilization interaction, (2) 1,2-dimesityl-1-propen-1-ol, the cited similar case of a stable simple enol,[2] owes its stability largely to steric factors which are not present in 2a and 2b, and (3) both the cyclopentanone enol 2a and the cyclohexanone enol 2b were reported to have the same carbonyl infrared absorption frequency (1705 cm^{-1}). In fact, the properties (particularly the 1705 cm^{-1} C=O absorption) reported for the two enols are more consistent with carboxylic acid structures 6a and 6b derived by acid-catalyzed aldol condensation of the diones 4a and 4b followed by acid-catalyzed cleavage of the aldols as shown in Figure 1. The loss of the protonated hydroxyl group in the cleavage step would be facile because the attached carbon atom is both tertiary and p-methoxybenzylic.

We have found that the compound from acid treatment of 1b is indeed a carboxylic acid from its solubility in aqueous NaHCO$_3$[3] and its reaction with diazomethane to produce a liquid methyl ester, $\nu_{max}^{CHCl_3}$ 1740 cm^{-1} (shifted 35 cm^{-1} from the $\nu_{C=0}$ of the acid), δ^{CDCl_3} 3.66 (3H, s, OCH$_3$), 3.76 (3H, s, OCH$_3$), and 5.97 p.p.m. (1H, bs, C=CH), m/e 260.1409 (calcd. 260.1412). The structure of the acid was established by reaction of p-anisyl magnesium bromide with 3-oxocyclohexylacetic acid[4] in pyridine solution. The resulting tertiary alcohol 7 was dehydrated with p-TsOH in boiling benzene to produce an acid, m.p. 115-119°, identical (t.l.c., mixed m.p., i.r., ^{1}H.m.r.) with the product of 8% hydrochloric acid treatment of 1b. The position of the conjugated double bond is not known with certainty,[5] but it is likely as shown in 6b from the following experiment which also

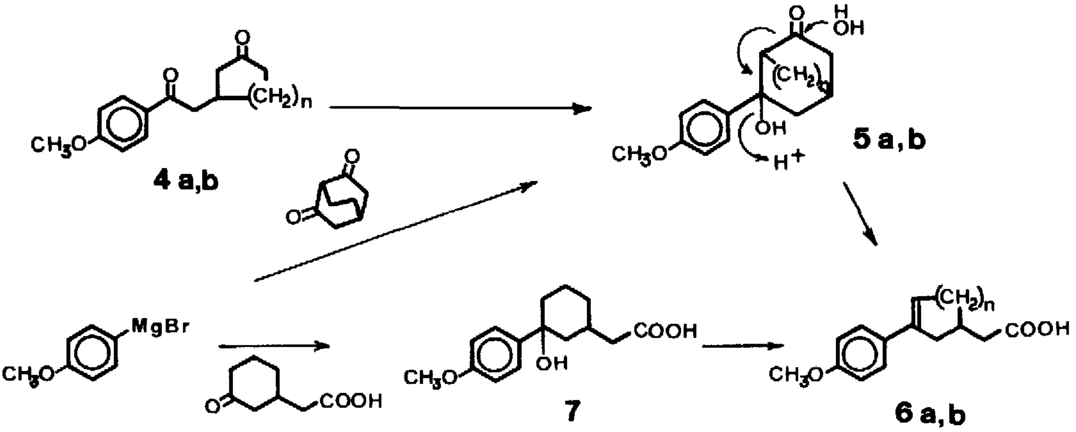


FIGURE 1

provides support for the postulated aldol intermediate 5b. Addition of p-anisyl magnesium bromide to *bicyclo[2.2.2]octane-2,6-dione (prepared in poor yield by the method of Gerlach and Müller*[6]) followed by treatment of the crude product with boiling 8% hydrochloric acid gave the same acid (t.l.c., m.p., mixed m.p., ^{1}H.m.r.), presumably 6b, obtained by both of the methods mentioned earlier. By analogy the compound from hydrochloric acid treatment of 1a is presumably the carboxylic acid 6a.

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REFERENCES AND NOTES

1. V. Dabral, H. Ila, and N. Anand, *Tetrahedron Lett.*, 4681 (1975).
2. *R.C. Fuson, J. Corse, and C.H. McKeever, J. Am. Chem. Soc.*, 62, *3250 (1940).*
3. 1,2-Dimesityl-1-propen-1-ol is not even soluble in aqueous NaOH.[2]
4. P.D. Bartlett and G.F. Woods, *J. Am. Chem. Soc.*, 62, 2935 (1940). The intermediate malonic ester was hydrolyzed with 10% HCl/H$_2$O (instead of base), and the crude acid mixture was distilled (b.p. 149-150°/0.4 torr, bath temp. 220°) to yield the mono acid, m.p. 76-78°.
5. The mass spectrum unfortunately did not exhibit strong peaks for the potentially informative retro Diels-Alder cleavage of the cyclohexene ring. The close spacing of the aliphatic protons in the 100 MHz ^{1}H.m.r. spectrum did not permit a distinction by decoupling, but the relative areas of these protons was in better agreement with 6b than with the other conjugated isomer.
6. H. Gerlach and W. Müller, *Angew. Chem. Int. Ed.*, 11, 1030 (1972).