by a negative carboxethoxyl group on a C₂⁺ carbon atom aiding the fission of the C-H bond and also stabilizing the carbanion.

Paraconic esters have been postulated as intermediates in the Stobbe condensation. The remarkable use of this reaction in synthetic organic chemistry since the discovery of potassium tert-butoxide as a catalyst (also refer Haworth et al.) is probably due to this facile cleavage to itaconic systems (which are the predominant products when this catalyst is used) thus precluding side reactions.

**Experimental**

Methyl γ, γ-pentamethylene paraconate (Ia) (1.0 g.) was treated with potassium tert-butoxide (from 0.30 g. of potassium and 10 ml. of anhydrous tert-butanol) at room temperature (20⁰C) for 15 min. in an inert atmosphere. The reaction mixture was poured into ice-cold water (40 ml.) and then washed with benzene (25 ml.) and ether (25 ml.). The alkaline phase on acidification with 6N-hydrochloric acid yielded β-carbethoxy-β-cyclohexylidene-propionic acid (IIa) (0.85 g.), crystals from ether-light petroleum (40-60⁰C), m.p. 96-97⁰C, eq. wt. 212-8. Found: C, 62.40; H, 7.36%. C₁₁H₁₆O₃ requires eq. wt. 212-2, C, 62.27; H, 7.55%. Alkaline hydrolysis of IIa with 10% sodium hydroxide yielded cyclohexylidene-succinic acid, m.p. 179⁰C.

Dept. of Chemistry, K. RAGHAVAO. Nagpur University, G. BAGAVANT. Nagpur, November 19, 1968.

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**Molecular Orbital Calculations on the Tautomers of Acetylacetone**

The tautomerism of acetylacetone has been extensively studied in the literature. It is well documented that the enol form (I) is generally more stable than the keto form (II), although the relative proportions of the two forms vary with the medium. Even in the vapour phase, acetylacetone exists in the enol form to the extent of 95% at 60⁰C. The heat of tautomerization determined by infrared spectroscopy in the vapour phase is 2.4 kcal/mole.

\[
\begin{align*}
\text{CH₃-CH=CH₂} & \quad \text{CH₃-CH₂=CH₂} \\
(1) & \quad (II)
\end{align*}
\]

Even though the tautomerism of acetylacetone is well understood experimentally, a molecular orbital calculation by Morokuma and co-workers employing the extended Hückel (EHT) method of Hoffmann has shown that the keto form is more stable than the enol form. This result is probably due to an inherent limitation of the EHT method, which does not account for electron repulsions. It was considered worthwhile to calculate the relative stabilities of acetylacetone by employing a more approximate self-consistent molecular orbital method with complete neglect of differential overlap (CNDO/2) proposed by Poppe, Santry and Segal. This method neglects only the less important electron repulsion integrals. These calculations were carried out on IBM 7094 and CDC 6500 computers by assuming the geometry suggested by Ogoshi and Nakamoto for the enol form of acetylacetone.

The total energies of the keto enol forms obtained by the CNDO/2 method were -78.3778 a.u. and -78.3815 a.u. respectively. It is interesting that the CNDO/2 method predicts the stability of the enol form, the energy of stabilization being 0.0037 a.u. or 2.3 kcal. This value for the energy of stabilization is in agreement with the experimental value of Powell and Bernstein. Assuming additivity of bond energies in the keto and enol forms, it can be seen that the energy difference between the two forms is essentially the energy of the intramolecular hydrogen bond in the enol form. It may also be noted that the value 2.3 kcal is in the general range for the dissociation energies of hydrogen bonds.

The present results clearly show the superiority of the CNDO/2 method over the EHT method. The inclusion of electron repulsion terms is therefore very important. Other studies in this laboratory show the importance of the CNDO/2 method in correctly predicting the relative stabilities of the cis- and trans-forms of formic acid. The CNDO/2 method seems to be more effective in predicting the
dissociation energies and proton potential functions of hydrogen bonds. 8-9

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Indian Institute of Technology,
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SYNTHESIS OF 11:12-OXYGENATED COUMESTANS

Compounds containing a 3-phenyl chroman carbon skeleton are abundant in nature and are known to exhibit marked physiological activity. 1 Coumestrol, a 3-aryl coumarin derivative isolated from ladino clover, exhibits considerable oestrogenic activity 2 and many members belonging to this group known as coumestans have recently been isolated mostly from medicinal plants. 3 Certain plants attacked by pathogens are known to produce coumestans 4 as protective agents from further attack and these are known as phytoalexins. Rao and co-workers 5 have shown that a halogen in 7-position of 3-aryl coumarins significantly enhanced their fish toxicity. The present communication deals with the synthesis of 11:12-oxygenated coumestans with a halogen in the main ring in different positions, since a system of this type with a 2' oxygen involved in a ring has an identical side phenyl oxygenation pattern present in Rotenone.

Of the various methods 8-11 available for the synthesis of coumestans, the method due to Wanzlick, 11 involving the oxidative coupling of 4-hydroxy coumarin with catechol using K$_4$Fe(CN)$_6$ and sodium acetate in aqueous acetone medium appears to be suitable in view of the fact, that coumestans with a 11:12-oxygenation pattern required could be obtained directly in good yields in one step. The synthesis of a naturally occurring 7-hydroxy-11:12-dimethoxy coumestan 12 was reported earlier from these laboratories adopting this procedure. This method has now been extended to the synthesis of 6- and 7-substituted coumestans starting from appropriately substituted 4-hydroxy coumarins.

The intermediate 4-hydroxy coumarins required for the synthesis of these coumestans have been prepared by the Boyd-Robertson procedure 13 from the suitable substituted o-hydroxy acetonaphenones.

In general, the yields of the coumestans have been uniformly good and do not seem to depend on the substitution pattern of the 4-hydroxy coumarin.

\[
\begin{align*}
\text{Catechol} & \xrightarrow{\text{oxidative coupling}} \text{K$_4$Fe(CN)$_6$} & \text{R}=	ext{Cl} \text{, Br, NH$_2$-CH$_3$} \\
\text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} & \text{OH} & \text{R} \\
\end{align*}
\]

The compounds synthesised have been listed in Table I with their U.V. spectral data. Table II gives the $\gamma$-C = O absorption of the coumestans along with those of the corresponding 4-hydroxy coumarins. While the $\gamma$-C = O absorption in coumestans is between 1710-1720 cm.$^{-1}$, in the corresponding 4-hydroxy coumarins it is around 1705 cm.$^{-1}$. In 4-hydroxy coumarins (I), there is considerable lowering of the normal lactone carbonyl possibly because of the 4-hydroxy coumarins existing in the dianion (III) state. However, it reverts back to its original position in cases where hydroxyl is involved in ether linkage (II) as the lactone carbonyl is stabilised. Rao and Lalitha have made a similar observation in the case of 3-phenyl 4-hydroxy coumarins. 14 The data presented in Tables I and II are consistent with the known behaviour of coumestans. 15

All the compounds are very sparingly soluble and none of them show appreciable toxicity to fish. The five-membered furan ring involving the 2' and 4' positions does not seem to contribute to the activity.