

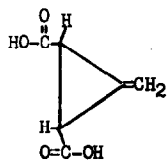
THE OZONATION OF FEIST'S ESTER

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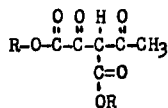
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The structure of Feist's acid was shown conclusively to be I in 1956 after many years of controversy (1,2,3,4,5,6).



I



II

Left unanswered after the structure proof of I had been accomplished was how II, the reported ozonation product of the ethyl ester of I, could have been formed (2). Bottini and Roberts did suggest a possible mechanism to account for the formation of II (6).

Schwan (7) was unable to repeat the ozonation work reported by Goss, et. al. (2) on the ethyl ester of I. She did, however, obtain a compound C₈H₁₀O₄ (mp 68°, positive ferric chloride test) from the methyl ester of I which might have been the methyl ester of II. She showed that Feist's acid derivatives such as trans-1,2-dimethyl-3-methylene cyclopropane (III) did not yield compounds analogous to II (7).

We have ozonized the methyl ester of Feist's acid in methanol

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and methylene chloride at low temperatures and obtained N. M. R. spectra (Varian A-60) on the solutions. The spectra show no absorption bands below 3 ppm. There is, therefore, no II or any other compound containing a $-\overset{|}{\underset{|}{\text{C}}}-\text{CH}_3$ group formed from the ozonation of Feist's ester.

Ozonation of 5 g of the ester in 45 ml of chloroform at -60° , followed by removal of solvent and addition of ether (10 ml) yields about 3.5 g of solid, mp $45-58^\circ$. Numerous fractional recrystallizations from ether and methanol yielded two compounds, A (mp $67-68^\circ$, positive ferric chloride test, IR bands at 1778, 1740, 1675, and 1636 cm^{-1} in CCl_4 , calcd. for $\text{C}_8\text{H}_{10}\text{O}_6$: C, 47.53; H, 4.99, found C, 47.69; H, 4.96) and a minor component, B, (mp $100-102^\circ$, positive ferric chloride test, positive active oxygen test with potassium iodide, IR bands at 1720 cm^{-1} , and 1660 cm^{-1} , anal. C, 45.21, 45.01; H, 4.96, 4.73).

Compound A is obviously the same one found by Schwan and B is probably the same compound obtained by Schwan in one experiment with a reported mp of $91-93^\circ$ (7).

Sufficient amounts of pure A were obtained to establish its structure by use of N. M. R. spectroscopy and degradation studies. Compound B is impure, as witnessed by its analytical data, and insufficient amounts were obtained for a complete structure proof.

The N. M. R. spectrum of A (Varian A-60, CDCl_3 , internal TMS) showed a doublet at 5.1 ppm ($J=7\text{cps}$, relative intensity, 1), a doublet (?) at 4.2 ppm ($J(?) = 3\text{cps}$, relative intensity, 2), a singlet at 3.8 ppm (relative intensity, 6) and a rather confused pattern (relative intensity, approx. 1) partially merging with the 3.8 ppm peak. Part of the pattern appeared to be a doublet at 3.7 ppm with $J=7\text{cps}$. Although this spectrum is reasonably consistent with structure IV, spectra obtained from a Varian HA-100 spectrometer and the use of deuterium

oxide yield more compelling evidence for IV as the structure of A. Figure 1 shows this spectrum.

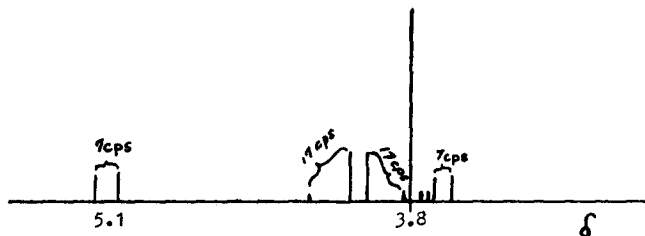
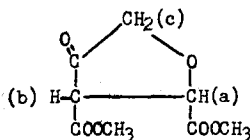


Figure 1

Thus the "doublet" at 4.2 ppm is actually two doublets (AB pattern) and the region between 3.8 and 3.6 ppm is clarified.

Addition of deuterium oxide and obtaining spectra after one, five, and ten minute periods caused the doublet at 3.7 ppm to decrease in intensity and the region around 5.1 ppm to become more complex.

We interpret these results in terms of structure IV, 2,3 dicarbomethoxy-tetrahydro-furan-4-one.



IV

The low field doublet at 5.1 ppm is due to proton (a), the doublet at 3.7 ppm is due to the exchangeable proton (b), the AB pattern is due to the geminal protons (c), and the singlet at 3.8 ppm can be assigned to the carbomethoxy protons. All chemical shifts and coupling constants are consistent with their assignments. It is likely that IV is the trans isomer rather than the cis form.

In addition to the changes already noted when IV is treated with deuterium oxide, a complex pattern was observed around 4.7 ppm (partly

due to water) and the two small peaks at 3.75 ppm increased significantly in intensity (to about $\frac{1}{4}$ that of the carbomethoxy peak). Comparison of the separation between the two small peaks (2.7cps) with the same peaks in the more complex A-60 spectrum (1.8cps separation) show these two absorption bands to be two different chemical shifts.

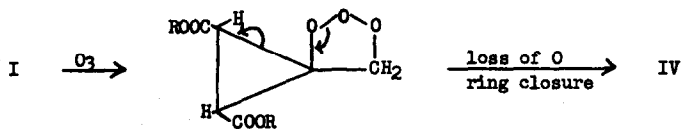
We suggest that the absorption bands at 3.75 ppm are carbomethoxy signals for the enol form of IV, which increases in concentration when the deuterium oxide is added.

The diethyl ester of IV, 2,3 dicarboethoxy-tetrahydro-furan-4-one V, was prepared by Zwicky et. al. (8). Their infrared spectrum showed bands at 1779, 1736, 1672 and 1637 cm^{-1} in CCl_4 . Both the frequencies and relative intensities of these bands are, within experimental error, identical to those found for IV. The procedure of Zwicky et. al. (8) by which V is degraded to VI, 2-carbomethoxy-tetrahydro-furan-4-one was followed and it was found that IV also yields VI, as witnessed by its infrared spectrum which is identical with the literature spectrum.

In contemplating possible modes of formation of IV, two general observations must be considered: 1) methylene cyclopropanes which do not possess electron withdrawing groups yield normal ozonation products (9), and 2) compound IV is obtained without oxidative or reductive workup, that is, one of the three oxygen atoms of ozone has been lost.

The second of these observations is a particularly difficult one to reconcile with normal ozonation mechanisms. It seems likely that initial attack of ozone on I yields VII. For the transformation of VII to IV a possible mechanistic pathway in which relief of the internal strain of the cyclopropyl system via a carbomethoxy stabilized carbanion like intermediate is possible although the fate of the "lost" oxygen atom has not yet been ascertained. With methylene cyclopropanes which

do not contain electron withdrawing groups, intermediates analogous to VII would decompose by the normal Criegee mechanism.



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6. A. T. Bottini and J. D. Roberts, *J. Org. Chem.* **21**, 1169 (1956).
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8. G. Zwicky, P. G. Wasen, and C. H. Engster, *Helv.* **42**, 1177 (1959).
9. Schwan (7) reports $\begin{array}{c} \text{H} \\ | \\ \text{H}_3\text{C} - \text{C} - \text{COCH}_2\text{OH} \\ | \quad \quad | \\ \text{H} \quad \quad \text{COCH}_3 \\ \text{CH}_3 \end{array}$ as one of the most likely

structures for the compound obtained from the ozonation of III in methanol. The author has found a similar compound (cyclopropyl hydrogens in the NMR spectrum) to be formed when the parent compound, methylene cyclopropane, is ozonized in methanol.